Studies of the chemical effects of radiations: investigations, by radioactive tracer methods, of the photochemical decomposition of ketones.

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THESIS

presented in candidature for the degree of

DOCTOR OF PHILOSOPHY

by

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STUDIES OF THE CHEMICAL EFFECTS
OF RADIATIONS.

Investigations, by radioactive tracer methods, of the photochemical decomposition of ketones.

CONTENTS

I THEORETICAL INTRODUCTION

In the last 20 years, a considerable number of publications has appeared concerning the photochemistry of ketones. This interest in the mechanism of the photodecomposition is attributable not only to its intrinsic value, but also to the light it sheds on the properties of certain organic free radicals which may be produced during the process. As in many photochemical reactions, the primary process occurring after absorption of radiation is most generally considered to be a split of the ketone molecule into free radicals; thus in the case of acetone one may envisage the reaction:

$$CH_3COCH_3 \ + \ h\nu \longrightarrow CH_3 + CH_3CO \ \ldots\ldots\ldots\ldots(1)$$

Such a process would require a minimum of some 70-90 kcal. per gm. molecule, since this amount of energy is required to break the carbon-carbon bond in acetone. Acetone begins to absorb light in the ultraviolet at about 3300 Å (Porter and Iddings (50), but absorption reaches its maximum in a continuous region of the spectrum centred around 2800 Å, and extending down to 2200 Å. The energy per einstein of 3300 Å is 88 kcal., so that the above reaction is energetically possible throughout the entire region of absorption, and in particular is very well compatible with the continuous spectrum. However, the spectrum at the long wave end possesses discrete structure, and this banded region extends to 3050 Å, where it gradually merges into the continuum. In this region then, one may reasonably infer the formation of an activated molecule of finite half-life, according to the reaction:

$$CH_3COCH_3 \ + \ h\nu \longrightarrow CH_3COCH_3^{\times} \ \ldots\ldots\ldots(4)$$

The extent to which this reaction contributes to the primary process, and the fate of the excited molecules so produced has become somewhat controversial. Spence and Wild (57,58) contend that such activated molecules may in certain circumstances be deactivated to a second state of lower energy, from which they may in turn revert to normal molecules, or decompose directly into the product molecules - ethane and carbon monoxide.

The exponents of a purely free radical interpretation, notably W. A. Noyes and his collaborators, consider that if reaction (4) occurs to any significant extent, it is followed ultimately either by deactivation to normal molecules, or by a split into free radicals. On this basis all the products of the photolysis are to be attributed to the two radicals methyl and acetyl; in fact there is fairly general agreement that this is the case in the continuum region, and in particular at 2537 Å.

Consideration of the reaction products is quite compatible with this latter interpretation, in certain cases it provides perhaps the only reasonable explanation. Thus Barak and Style's (4) identification of diacetyl in the products at low temperatures is attributable to a recombination between two acetyl radicals, and is strong evidence for their existence during photolysis. Other products normally observed are C_2H_6, CO, and CH_4; these may arise from the reactions:

$$CH_3+CH_3 \rightarrow C_2H_6 \quad .... \; (7)$$

$$CH_3CO \rightarrow CH_3+CO$$

$$CH_3+CH_3COCH_3 \rightarrow CH_4+CH_2COCH_3 \quad ... \; (9)$$

Since in certain cases ethane and carbon monoxide are the sole products in equal proportions, the primary reaction

$$CH_3COCH_3 \rightarrow C_2H_6+CO$$

has been proposed. It cannot be of major importance as a primary process, however, for under suitable conditions the C_2H_6 yield is small compared with that of CH_4, while CO production is still large. The formation of CH_4 is difficult to interprete on any basis other than reaction (9), but this requires the simultaneous formation of the radical CH_2COCH_3. This radical may then combine with methyl,

$$CH_3+CH_2COCH_3 \rightarrow C_2H_5COCH_3$$

yielding methyl-ethyl ketone, and indeed, Allen (2) has identified this product in the products formed at high temperatures. One may also envisage the reactions:

$$CH_2COCH_3+CH_3CO \rightarrow CH_3COCH_2COCH_3$$

$$2(CH_2COCH_3) \rightarrow CH_3COCH_2CH_2COCH_3$$

$$CH_3COCH_3\ \nu \rightarrow CH_3+CH_2CO$$

Very recent work by Ferris and Haynes (23) has proved the formation of ketene at high temperatures, in accord with the last reaction above, but none of the other products has been observed to any significant extent. Rice, Rodowskas and Lewis (55), have, however, identified diacetonyl in the products of the thermal reactions of acetone and methyl radicals at high temperatures.

Quantitative treatments of the photolysis in terms of the above free radical methanism depend very critically on the kinetics assumed for each reaction. Knowledge on such points is inevitably uncertain, its major source is the trial and error method of finding which equations best fit the observed results. Indeed some objection may be raised to free radical treatments in general on this score, for by suitable choice of kinetics they tend to explain too much rather than too little.

Further, it is quite possible that the kinetics of a combination reaction such as that between two methyls may vary with the total pressure in the system, such a reaction may be second order and homogeneous at high pressures, and revert to a first order heterogeneous process as the pressure is lowered. One cannot expect, therefore, complete consistency in the assumed kinetics except over a limited range of pressure, so that proof of the assumed mechanism is even more indefinite.

The present work concerns a more direct method of investigating the radical reactions which may occur during photolysis. Though initially directed elsewhere, my experiments were applied largely to the much discussed case of acetone; it will be convenient at this stage to consider the more relevant evidence on this ketone available from quantitative studies of the products of the direct photolysis.

Kinetic treatment of the photolysis of acetone

In a number of early papers, e.g (30), Noyes and his school proposed a treatment in which radical combination reactions were considered exclusively as wall processes. Thus the rate expression for reaction (7) would be:

$$\frac{d(C_2H_6)}{dt} = \frac{K_7(CH_3)}{(A)}$$

where (A) is the total pressure in the system. This treatment explained most of the observations at low pressures, but it was not entirely satisfactory. In particular, it failed to explain the variation in the ratio of ethane to carbon monoxide in the products with absorbed intensity.

Consideration of a fast growing fund of experimental data has lead to a recent paper by Noyes and Dorfman (45) in which the treatment is based on homogeneous bimolecular combination reactions. This treatment is consistent in its assumptions over a wide range of pressures, and offers an interpretation of nearly all available data on the direct photolysis with some degree of quantitative accuracy. The reactions involved in this treatment are set out below, together with the corresponding rate expression for each reaction.

Reaction	Rate Expression	No.
$CH_3COCH_3 + h\nu \rightarrow CH_3 + CH_3CO$	ϕ I abs.	1.
$aCH_3CO \rightarrow aCH_3 + aCO$	a ϕ I abs.	2.
$CH_3COCH_3 + h\nu \rightarrow 2CH_3 + CO$		3.
$CH_3COCH_3 + h\nu \rightarrow CH_3COCH_3^*$		4.
$CH_3CO \rightarrow CH_3 + CO$	$k_5(CH_3CO)$	5.
$2(COCH_3) \rightarrow CH_3COCOCH_3$	$k_6(CH_3CO_2)^2$	6.
$2(CH_3) \rightarrow C_2H_6$	$k_7(CH_3)^2$	7.
$CH_3CO + CH_3 \rightarrow CH_3COCH_3$	$k_8(CH_3)\ (CH_3CO)$	8.
$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3$	$k_9(CH_3)\ (A)$	9.
$2(CH_3COCH_2) \rightarrow (CH_3COCH_2)_2$	$k_{10}(CH_3COCH_2)^2$	10.
$CH_3 + CH_2COCH_3 \rightarrow CH_3CH_2COCH_3$	$k_{11}(CH_3)(CH_3COCH_2)$	11.
$CH_3CO + CH_2COCH_3 \rightarrow CH_3COCH_2COCH_3$	$k_{12}(CH_3CO)(CH_3COCH_2)$	12.

ϕ, the quantum efficiency of reaction (1) is taken as unity at 2537 Å; at 3130 Å Noyes and Dorfman consider it is temperature dependent, approaching unity above 100°C.

An essential point in the treatment concerns the fate of the acetyl radicals. Various estimates (5,26,30,46,54) of the activation energy for decomposition of acetyl place it as 14-18 kcal. Assuming Rice and Herzfeld's estimate (54) of 70 kcal. for the strength of the C-C bond in acetone, then, on absorption of 3130 Å irradiation, equivalent to 91 kcal.

per einstein, some 20 kcal. excess energy remain to be shared between the acetyl and methyl radicals so formed. Davis (13) shows that some 14 kcal. may be retained by the acetyl radical, so that its spontaneous decomposition is just possible. At 2537 Å, some 43 kcal. excess energy is available, so that spontaneous decomposition of acetyl is more probable at this wavelength. As a result, a fraction "a" of the originally formed acetyl radicals will undergo spontaneous decomposition either immediately, or in a time interval too short to permit the occurence of collisional deactivation. This precess is represented by reaction (2), with the proviso that "a" is dependent on wavelength. Assuming this treatment, Benson and Forbes (6), and Noyes and Dorfman (45) estimate from experimental data that "a" is about .07 at 3130 Å and .22 at 2537 Å.

Those acetyl radicals which survive this initial disruption reach thermal equilibrium with their surroundings, and may in turn decompose according to the thermal reaction (5). Assuming the normal type of unimolecular mechanism for this reaction, Davis (13) estimates from experimental data that its rate becomes independent of pressure above 50mm., and simply proportional to acetyl concentration as set out above.

In terms of the above mechanism, one may attempt a quantitative treatment of observed quantum yields as follows:

Quantum efficiency of acetone decomposition, Φ acetone

If one assigns an activation energy of zero to the back reaction (8), then it will compete favourably with the product forming reactions for removal of methyl and acetyl radicals, thereby lowering Φacetone. This effect will predominate only where the acetyl concentration is comparable to that of methyl, and we must conclude that this is the case at low temperatures where Φacetone is as low as 0.1. At higher temperatures the thermal decomposition of acetyl becomes of increasing importance, and we find that at 100°C and above, Φ acetone = Φ CO = 1. The above value of $\sim$16 kcal. for the activation energy of this decomposition is compatible with this result, for the rate coefficient at 100° would be 240 times as high as at 25°, and one may reasonably infer complete decomposition at the former temperature. Nevertheless, it should be stressed that this result depends entirely on the relative rates of the various reactions which compete for the acetyl radical; it is impossible to assess this degree of decomposition into methyl and carbon monoxide without quantitative knowledge of these rates, and hence of the concentration of the reactants involved. One can say only that the temperature dependance of Φ acetone can be interpreted in the above terms; it could not have been quantitatively predicted, even with the knowledge that E_5 = 16 kcal.

The above discussion relates the temperature dependence of Φ acetone to the rate of equation (5), on the assumption that ϕ is unity throughout. However Noyes and Dorfman conclude from experimental data that ϕ itself is temperature dependent at 3130 Å. To explain this effect, the formation of activated molecules by reaction (4) is invoked. The following mechanism is envisaged:

Reaction	Rate Expression	No.
$CH_3COCH_3 + h\nu \rightarrow CH_3COCH_3^*$	I abs.	(4)
$CH_3COCH_3^* \rightarrow CH_3 + CH_3CO$	$k_{13}(CH_3COCH_3^*)$	(13)
$CH_3COCH_3^* + A \rightarrow 2A$	$k_{14}(CH_3COCH_3^*)(A)$	(14)

Hence the primary quantum yield of radicals "ϕ", will be given by

$$\phi = \frac{1}{1 + k_{14}(A)/k_{13}}$$

Assuming that $E_{14} = 0$, the value $E_{13} = 5$ kcal. is deduced from the experimental observation that $\phi = 1$ at 100°, but falls to .7 at 25°, with an acetone pressure of 100mm. Such a calculation is somewhat speculative, for it is based on assumed absolute values of the rates of reactions (13) and (14). The essential requirement is that $E_{13} - E_{14} =$ 5 kcal; the assumption that $E_{14} = 0$ is by no means proved, though it may be theoretically probable.

Such a scheme interpretes the temperature dependence of ϕ, but it requires a complementary pressure effect where $k_{14}(A)$ is comparable to k_{13}, i.e. at low temperatures. It applies only in the banded region of absorption; at 2537 Å, $\phi = 1$ under all conditions.

Effect of pressure on Φacetone

When the activated molecule effect is negligible, it will be seen that every reaction in the proposed mechanism is independent of pressure, with the single exception of the methane forming reaction, (9). Where ΦCH_4 is low, then Φacetone should be independent of pressure; if ΦCH_4 is appreciable, it (ΦCH_4) will rise with increase of pressure with results which cannot possibly lower Φacetone, though they may increase it.

Experimentally, one finds that Φacetone is indeed pressure independent at 2537 Å at pressures above 50mm. Below this pressure, it begins to rise as the pressure is lowered. Such an effect may be attributed to the increasing predominance of wall reactions, and one is perhaps justified in adopting this value of 50mm. as the limiting pressure below which the above mechanism breaks down, for it will be recalled that it is based entirely on homogeneous reactions. At 3130 Å however, Φ acetone continues to decrease markedly with increase of pressure, right up to 150mm. at 25° (Herr & Noyes), so that some other effect must be operating. It is precisely under these conditions that the above activated molecule mechanism should operate, and its effect would be in accord with these observations. This point does not appear to have been mentioned in the literature, nevertheless it adds confirmation to the proposed activated molecule mechanism at 3130 Å.

Effect of Intensity on Φ acetone

Since the rate of the back reaction (8) is proportional to the product of methyl and acetyl concentration, i.e. it is second order, then as the standing concentration of these radicals is increased with increase of intensity, its probability as a method of radical removal will also increase, relative to the product forming reactions (5) and (11), for both of these are first order with respect to radical concentration. The result will be to lower Φ acetone with increasing intensity. If, however, conditions are such that (5) and (11) are negligible compared to the second order product forming reactions (6) and (7), then Φ should be independent of I abs. It is impossible to assess this effect quantitatively, for a mathematical analysis required a prohibitive amount of data, nevertheless the general trend may be foreseen.

Herr and Noyes find that Φ acetone falls with increase of intensity at 2537 Å, but it is intensity independent at 3130 Å under otherwise similar conditions. Spence and Wild contend that this argues in favour of their activated molecule mechanism (to be discussed later), but the data are unconvincing. Unfortunately Herr and Noyes' work was performed at 50mm., at which pressure wall reactions may begin to contribute to the mechanism, thus rendering the above treatment invalid. It is difficult however, to see why such an effect should predominate any more at one wavelength than another. More recent work by Howland and Noyes (31) was performed at 120mm. and 3130 Å. They found a definite decrease in Φ acetone with increase in intensity, precisely as found at 2537 Å, so that this point of Spence and Wild's argument appears to be refuted.

Quantum yields of CO, C_2H_6 and CH_4

A full mathematical analysis of the above mechanism is scarcely desirable, for its use would require a prohibitive knowledge of rate constants and concentrations. Nevertheless, the general trend of experimentally determinable quantities may be deduced, and in certain limiting conditions quantitative expressions have been derived. The following points are particularly relevant:

(a) Quantum yield of carbon monoxide

It has been pointed out above, that Φ CO = Φ acetone = 1 at temperatures above 100°, under practically all conditions of wavelength, pressure, and intensity. This point is well established, in fact the direct photolysis of acetone at 120° is in use as an actinometric reaction. Φ CO falls with decrease in temperature as would be required, but it is an essential point of the above treatment that $\Phi CO \geqslant a$. This should remain true even where all secondary reactions of radicals are inhibited.

(b) The ratio of ethane to carbon monoxide in the products

This ratio falls with increase of pressure at 25°C at both wavelengths; the effect is most pronounced at low pressures where heterogeneous processes could explain it, but it appears to persist at pressures well above 50mm. at 3130 Å. and less significantly so at 2537 Å. The mechanism set out above cannot explain such effects, so that we are forced to conclude that heterogeneous processes still contribute to the overall mechanism at pressures above 50mm. There is considerable evidence on this point:-

(1) Iredale and Lyons (35) find that diacetyl production is quenched, and the C_2H_6/CO ratio falls, when the photolysis is performed with the addition of 50 cm. of inert gas. This work was carried out at 150mm. of acetone.

(2) Herr and Noyes (30) have shown that calculations of the C_2H_6/CO ratio based exclusively on heterogeneous mechanisms are in reasonable accord with experiment up to pressures of 200mm.

(3) Spence and Wild (59) and Howland and Noyes (32) have shown that the C_2H_6/CO ratio depends, inter alia, on the dimensions of the reaction vessel, again at high pressures (160mm.).

Either or both of two low pressure reactions would explain these results; one is the heterogeneous formation of diacetyl, the other is the pressure dependent decomposition of acetyl. Point (3) above appears to favour the former. It is worthy of note that the persistence of such reactions would also explain the pressure dependence of Φ acetone, without the introduction of the activated molecule mechanism discussed above. It is questionable, however, whether the rather marked difference in behaviour observed at the two wavelengths could be accounted for on this basis.

The above treatment products that the C_2H_6/CO ratio should increase to a limiting maximum with increase in absorbed intensity; Noyes and Dorfman show that such maximum values may be deduced from their estimated values of "a" with results which are in reasonable accord with experiment.

(c) Quantum yield of methane

The formation of methane by reaction (9)

$$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3 \qquad .... (9)$$

has been suggested by Spence and Wild (59), Allen (2) and by Dorfman and Noyes. If reactions (7) and (9) are the sole means of production of ethane and methane respectively, then one obtains:

$$\frac{\Phi\ CH_4}{(\Phi\ C_2H_6)^{1/2}} = \frac{k_9}{k_7^{1/2}} \quad \frac{(A)}{I\ abs.^{1/2}}$$

Dorfman and Noyes (16) show that the constant term $k_9/k_7^{1/2}$ is experimentally independent of intensity at 26° and 122°; the pressure effect was not investigated over a very wide range, but the general agreement was just as good at 3130 Å as at 2537 Å. Trotman, Dickinson and Steacie (68) have investigated this relation at 2537 Å over a large variation in intensity and pressure. Their results are in excellent agreement with the equation as regards intensity, and indicate only a very small drift in the constant term with pressure. Further, Dorfman and Gomer (15) find a similar treatment is in experimental agreement with the methane yields observed in the reaction of photo-chemically produced methyl radicals with dimethylmercury, ethylene oxide, and butane.

Confirmation of this point appears to be excellent, and indeed provides a very strong argument in favour of the free radical treatment. In particular it supports the view that ethane arises from a homogeneous second order reaction, so that the above conclusion that diacetyl formation proceeds hetergeneously under similar conditions is somewhat surprising.

(d) Quantum yield of ethane

In the limiting case where decomposition of acetyl is complete, (i.e. at temperatures above 100°), Noyes and Dorfman have developed an equation for the quantum yield of both methane and ethane, by an extension of the above treatment. Experimental values are in fair agreement with this equation; precise agreement is scarcely to be expected since the equation embodies a number of constants and also terms in Φ^4, so that any small errors in determination of constants would lead to large deviations in Φ.

It appears then that the evidence presented so far is generally in agreement with the reaction scheme set out above. Discrepancies are concerned mainly with the kinetics of reactions of the acetyl radical. There is evidence for the persistence of low pressure reactions of this radical at pressures well above 50mm.; this is contrary to Noyes and Dorfman's assumption, but it does not invalidate the quantitative treatment of other radicals, and in general an overall free radical mechanism appears reasonable at both wavelengths.

Spence and Wild are in agreement with this conclusion at 2537 Å, though differing in their detailed treatment. They propose a very different treatment for the banded region, represented by the following reactions:-

$CH_3COCH_3 + h\nu \longrightarrow CH_3COCH_3^*$ .... S 1

$CH_3COCH_3^* \xrightarrow{10^{-8}\,sec.} CH_3 + CH_3CO$ .... S 2

$CH_3COCH_3^* + A \longrightarrow CH_3COCH_3^{**} + A$ .... S 3

$CH_3COCH_3^{**} \xrightarrow{10^{-2}\,sec.} C_2H_6 + CO$ .... S 4

$CH_3COCH_3^{**} \xrightarrow{Wall} C_2H_6 + CO$ .... S 5

$CH_3COCH_3^{**} \longrightarrow CH_3COCH_3$ .... S 6

$CH_3COCH_3^{**} + CH_3CO \longrightarrow CH_3COCH_3 + CH_3 + CO$ .... S 7

These reactions are founded on the following observations in the banded region, ie. at 3130 Å.:

(1) At constant intensity, both Φ acetone and the ratio C_2H_6/CO decrease with increase of pressure, in a manner more marked than in the continuum. The data suggest that Φ acetone $\rightarrow 1$ as $(A) \rightarrow 0$.

(2) At constant pressure, Φ acetone is independent of I abs., in contrast to its behaviour in the continuum region.

(3) At moderate pressures (160mm) a reduction in the mean dimension of the reaction vessel causes C_2H_6/CO to decrease toward unity.

(4) At high intensities the C_2H_6/CO ratio obtained with continuum light is reduced by the presence of light in the banded region to an extent which is considerably greater than would be expected on a purely additive basis.

(5) The work of Almy et al (3) indicated that the yellow green fluorescence found during acetone photolysis predominently in the banded region, is attributable to a sensitised fluorescence of the diacetyl formed during photolysis, and probably arises from a transference of energy from excited acetone molecules. Consideration of the possible diacetyl concentration leads to the assumption of long lived excited molecules to account for such effects.

In terms of the proposed mechanism, the effect of increased pressure would be to transfer proportionally more activated molecules to the 2nd state. Assuming that deactivation of such molecules in the 2nd state is faster than their dissociation into C_2H_6 & CO, then the net effect of increased pressure would be to lower Φ acetone, and decrease C_2H_6/CO to values nearer unity, in agreement with (1). Such effects are explicable on a purely free radical mechanism, as pointed out above. Since the initial maximum value of C_2H_6/CO at low pressures is higher at 3130 Å than in the continuum (due to lower excess energy of the acetyl radical), then its fall with increase of pressure would be expected to be more pronounced also.

The trend, Φ acetone $\rightarrow$ 1 as (A) $\rightarrow$ 0, is not explained since as (A) $\rightarrow$ 0, the (Spence and Wild) mechanism becomes effectively free radical in nature. Data at low pressures are not conclusive, however.

Unfortunately, a good deal of the data involved is in dispute. Thus the work of Howland and Noyes (31) contradicts (2), at pressures where the Spence and Wild mechanism would indicate an even greater divergence from the continuum results. Further, the data of Herr and Noyes (30) and of Howland and Noyes (32) on the diameter effect yields ratios of C_2H_6/CO which differ markedly from Spence and Wild's observations when due allowance has been made for an apparently mistaken estimate of the mean molecular displacement (Davis,(13)). In any case such diameter effects are explicable on an exclusively free radical interpretation, though the assumption of the wall reaction (S5) in the Spence and Wild mechanism is more acceptable at high pressures.

On any basis, the prediction of mixed light effects presents considerable difficulty, and it is questionable whether the nature of the light used can be determined sufficiently quantitatively to assess additivity of the results. Point (4), therefore, must be accepted with some reserve, though if the effect is genuine it is well explained by Spence and Wild's reaction (S6).

The existence of fluorescence certainly points to the formation of excited molecules. In this respect, however, the results obtained from fluorescence studies are essentially qualitative; there can be little doubt that activated molecules play some part in the mechanism, but the overall energy loss by fluorescence itself is very low. Hunt and Noyes (34) estimate from all previous work that it does not exceed 2% of the absorbed energy, and may well be considerably less.

It appears that the Spence and Wild mechanism does offer an explanation of the above observations; but that most such observations are experimentally in dispute. The remainder may be explained on an exclusively free radical treatment, though perhaps not so concisely. A major objection to such a mechanism is its limited range of applicability; it is most difficult to account for the high quantum yields observed at high temperatures on such a scheme. Spence and Wild contend that the lifetime of the first activated molecules is strongly temperature dependent, so that at 100° and above they dissociate completely into radicals before collisional deactivation can intervene. This necessarilly assumes that the strength of the C - C band in such excited molecules - and therefore in acetone itself - is very close indeed to the energy of one einstein of 3130 Å irradiation, i.e. 91 kcal. Only in this case wouldthe the small additional thermal energy of 1 or 2 kcal. imparted by a rise in temperature, made such a difference to the rate of spontaneous dissociation of such molecules. One cannot be definite about this bond energy; estimates vary from 70 to 90 kcal., but it will be recalled that the treatment of the acetyl decomposition is based on the lowest of these values. The assumption is questionable, to say the least.

Feldman, Burton, Ricci and Davies (21) take an alternative view, and consider that the temperature effect is reflected in the lifetime of the second excited molecules. On this basis the high temperature products would be almost exclusively ethane and carbon monoxide, a situation which is by no means verified experimentally.

Summary of Conclusions

A number of other interpretations of the mechanism have been advanced, differing only in the nature and kinetic treatment of secondary radical reactions. The Noyes and Dorfman treatment has been selected for discussion since it is the most recent and comprehensive; one concludes that the free radical basis of the mechanism is reasonably well borne out by such studies.

The only alternative advanced is that of Spence and Wild, but the evidence in its favour appears to be disputable.

Direct Evidence of Radical Production

Pearson and Purcell (49) have shown from studies of the photolysis in a flow system that the products possess the property of removing mirrors of antimony, tellurium, and lead, in the same manner, and with the same half life as Paneth and his co-workers have found for the methyl radical. These authors also identified methyl-telluride, dimethylmercury, and trimethylarsine in the products, confirming that the radical involved is methyl. Further confirmation comes from the work of Prileshajeva and Terenin (51) and of Glazebrook and Pearson (29) who have also dedected free radicals in the products by the Paneth technique. Glazebrook and Pearson also confirmed the formation of diacetyl at room temperature, and by comparison of the rates of diacetyl formation and mirror removal conclude that methyl and acetyl radicals are produced in substantially equal proportions.

Feldman, Ricci, and Burton (20) have used a flow system with two lead mirrors to investigate the stability of the acetyl radical. At 45° the second mirror is attacked by methyl radicals formed by decomposition of acetyl in the space between the two mirrors; at 100° no such effect was observed. They conclude that acetyl is completely decomposed at 100°, so that all the methyl formed by its decomposition is completely removed by the first mirror. Such a conclusion is entirely compatible with the preceding treatment, but the stability or half life of any such radical is obviously dependent on more factors than temperature alone.

Further evidence for the presence of free radicals is afforded by Taylor and Jungers (65) who found that the polymerization of acetylene is induced by the radicals formed during photolysis of acetone; similarly Danby and Hinshelwood (12) observed an induced polymerization of ethylene. Taylor and Rosenblum (66) have shown that hydrogen reacts with the photolysis products yielding methane, again in accord with the formation of methyl.

Quantitative Estimates

In their studies of the rate of induced polymerization in olefins at 300°, Danby and Hinshelwood (12) conclude that acetone is 70% as effective as acetaldehyde in producing free radicals. In this work the full light of a mercury arc was used, so that it is difficult to estimate primary radical yields from such a result since the radical yield in acetaldehyde rises with increase in wavelength, while in acetone it appears to decrease. The results do show that the primary yield of radicals is of the same order in both cases.

Grahame and Rollefson (25) have extended some earlier work by Akeroyd and Norrish (1) who showed that acetone is able to photosensitize the chain decomposition of acetaldehyde. By comparing the rate of this chain reaction at high temperatures in acetaldehyde alone, with that in acetone-acetaldehyde mixtures, Grahame and Rollefson obtained the following relative values of radical quantum yields:

Wavelength	Acetaldehyde	Acetone
3130 Å	1.00	0.70
2652 "	0.55	0.92

Other work indicates that the absolute value of the radical quantum yield in acetaldehyde is unity at 3130 Å under these conditions, so that the above figures may be taken as an approximate estimate of this quantity for acetone.

It is difficult to obtain quantitative information on radical yields from mirror removal methods, since the yield of metal derivative is too small for accurate analysis, and it is questionable if the method can remove all radicals before secondary reactions take place. Nevertheless, Feldman, Ricci, Burton and Davis (27) have attempted such work, with most surprising results. The reaction was carried out in a flow system at 4mm. pressure, with a long lead mirror immediately adjacent to the irradiated section of the apparatus. The lead alkyl formed was estimated by dithizone titration for lead, and radical yields were estimated on the assumption that the product was entirely $Pb(CH_3)_4$. Analyses for CO and C_2H_6 were also carried out on each run.

With 2537 Å irradiation, it was found that ethane remained a major product, equivalent to 70-90% of the CO yield at all temperatures from 0° to 100°, in spite of the well established fact that the mirrors used were sufficiently long to remove all mirror-active particles. The methyl yield was always less than that of CO, averaging 30-60% of this value even when corrected for small (15%) losses of methyl radicals prior to reaching the mirror. If ethane production were due exclusively to methyl radicals, one would expect it to be completely quenched in these conditions; while at 100° where the acetyl radical is fully decomposed to methyl and CO, the methyl yield should be double that of carbon monoxide.

The authors conclude that only 30% of the reaction proceeds by free radical processes, and interpret their results in terms of the Spence and Wild mechanism. There are objections to the general acceptance of such an interpretation, notably its failure to account for yields of methane at high temperatures. Moreover, even assuming that the mechanism could operate in the continuum region, in direct opposition to all theoretical considerations, it could scarcely account for high yields of ethane by molecular rearrangement at such low pressures. Nevertheless, these results are not to be reconciled with an exclusively radical type of mechanism unless one assumes some kind of poisoning of the lead mirror; in such a way as would favour the production of ethane rather than lead tetramethyl. There is probably quite a large error in the methyl determinations as Davis (13) points out, but one can scarcely question the high yield of ethane. This point appears to defy any reasonable interpretation.

Leighton and Volman (37), and Volman, Leighton, Blacet and Brinton (69) have applied the Paneth technique to the comparison of radical yields at different wavelenghts. Using standard mirrors of tellurium in a flow system at 2mm, they compared the rate of radical production as measured by the rate of mirror removal, with the rate of photolysis, measured by the rate of production of permanent gas; and found the following results:

Wave Lenghth	Relative No. of Free Radicals, for the same rate of Gas Formation.
3160 - 3180 Å	1.06 arbitrary units
2800 "	3.5 " "
2537 "	10.6 " "

A priori, these results would indicate that the radical quantum yield at 3170 Å is only one tenth of its value at 2537 Å. There are, however, several objections to this interpretation:

(1) A distance of 9cm. separated the mirror from the irradiation zone, so that an undetermined fraction, α , of the radicals would form gaseous products before reaching the mirror. Since those radicals formed at

3170 Å would possess less excess energy than those at 2537 Å, it is conceivable that they would have a shorter half life. Thus α would be greater at long wavelengths, and would explain the observed results.

(2) The gas yield is proportional to the rate of photolysis only if one assumes that its quantum yield, Φ gas, is independent of wavelength. There are some indications (Spence and Wild) that this is not so at low pressures, that in fact Φ gas approaches unity at 3130 Å while still remaining low at 2537 Å.

(3) Rates of radical formation were estimated from the reciprocal of the time taken for complete removal of mirrors. Obviously, for most of the duration of a run the mirrors did not quantitatively remove the radicals passing them. One must then make the very questionable assumption that the efficiency of radical removal is independent of the wavelength at which such radicals are formed, and hence of their energy.

In view of the above, the authors' conclusions can scarcely be justified quantitatively.

An alternative method of radical estimation has been applied by Gorin (26,27,28). He performed the photolysis in the presence of iodine vapour, under which conditions the alkyl radicals appear to be quantitatively removed according to one or both of the following reactions:

$$CH_3 + I_2 \longrightarrow CH_3I + I$$

$$CH_3 + I \longrightarrow CH_3I$$

Various estimates of the activation energy of such reactions have been given (Steacie (61)), varying from 0 to 12 kcal. Probably 0 -1 kcal. is reasonable, and is compatible with the low quantum yields in the photolysis of methyl iodide. Hence, even assuming that the normal radical combination reactions have zero activation energy, they could not compete with the iodide forming reactions above, since the concentration of iodine is enormously higher than that of any of the radicals present. Gorin found in fact, that only 0.2mm. of iodine was sufficient to quench nearly all the secondary ethane forming reactions; he therefore concluded that the yield of each radical is quantitatively equivalent to that of its corresponding iodide.

His results were as follows:-

(a) In the unfiltered irradiation of a mercury arc

(1) The quantum yield of methyl iodide, Φ MeI, was found to be unity within experimental error; and independent of acetone pressure from 360 to 616mm., iodine pressure from 1 to 4mm., and temperature from 60 to 80°.

(2) Yields of CO averaged only about 2% of the MeI yield at 80°, but rose to 7% at 100°, and 36% at 130°.

(3) Acetyl iodide was observed, but the yield was not equivalent to that of methyl iodide, varying from 10 to 40% of this value. Φ AcI apparently rose with increase in I_2 pressure, but remained essentially independent of temperature from 60 to 130°.

(b) At 3130 Å

At 90° and high pressures (850 and 1265mm.) of acetone, Φ MeI was found to be about 0.8. Only two experiments were carried out, and yields of CO and acetyl iodide were not reported.

Gorin concluded that the primary process is entirely represented by the reaction

$$CH_3COCH_3 + h\nu \rightarrow CH_3 + CH_3CO$$

at 2537 Å, though perhaps other processes contribute at 3130 Å, to a minor extent.

Since the yield of CO is practically negligible below 100° there can be virtually no decomposition of acetyl into methyl and CO under his conditions, even though Φ AcI is less than Φ MeI. To account for the variation in Φ AcI, a reversible reaction is assumed:

$$CH_3 + I_2 \rightleftharpoons CH_3COI + I$$

This would make Φ AcI proportional to iodine pressure as observed, but such an assumption is improbable from theoretical considerations. Gorin assumes that the balance of the acetyl yield appears as diacetyl, and reports the qualitative detection of diacetyl in support of this. He concludes that the low yields of diacetyl observed at high temperatures in the direct photolysis are not mainly attributable to increased thermal decomposition of acetyl, but rather to the reaction:

$$CH_3 + CH_3CO \rightarrow C_2H_6 + CO$$

Since practically all methyl radicals are removed in the presence of I_2, this reaction could not occur under Gorin's conditions and would leave the acetyl free to take part in other reactions, thus forming diacetyl and acetyl iodide. This reaction has been suggested by other authors e.g. Spence and Wild, and Saunders and Taylor (56), as an integral step in the direct photolysis, and it does provide a very neat explanation of Gorin's results. However, the marked temperature dependence of quantum yields in the direct photolysis between 25° and 100° requires a minimum activation energy of about 19 kcal. for such a reaction; a value which is much more compatible with a number of estimates of the acetyl decomposition, and in particular with the temperature dependence of CO yields in Gorin's work at still higher temperatures. Further, if this reaction is of such major significance as Gorin indicates, then it must also be the main source of ethane production, and must therefore compete favourably with the reaction between two methyl radicals. Yet this latter reaction has only a low activation energy, probably less than 2 or 3 kcal, and must surely be considerably more efficient than the above mechanism, for which we must assume an activation energy of some 19 kcal. Further, there is reason to doubt the validity of Gorin's analysis for acetyl iodide, so that on the whole his conclusions regarding the acetyl mechanism must be seriously questioned.

Nevertheless, Gorin's experiments represent a valuable advance in this field, for they indicate an elegant method of estimating radical yields without interfering with the normal primary processes. A similar investigation in the presence of iodine was carried out by Benson and Forbes (6), who performed the photolysis in a flow system at 12mm. acetone pressure, and with nearly monochromatic 2537 Å light. In spite of very careful control of experimental conditions, their results were not entirely reproducible. This may be due in part to the large number of greased taps in the system, which could absorb small amounts of iodine and acetyl iodide. There results were as follows:

(1) Ethane formation was entirely quenched in the presence of iodine, even though the I_2 pressure was only 1/54 that of acetone.

(2) The yield of CO was reduced in the presence of I_2, but only to 50% to 80% of its normal value.

(3) Methane production was reduced to 14 - 20% of its normal value, equivalent to a quantum yield in the presence of I_2 of approximately 0.015.

(4) They were unable to separate methyl and acetyl iodides by Gorin's method (one vacuum distillation at -30°C), and conclude that his analyses for this product were unreliable. They report no yield of acetyl iodide, though it must have formed to some extent. No diacetyl was found in the presence of iodine at any temperature. It is not possible to draw any

definite conclusions regarding the acetyl mechanism from these results.

(5) By very indirect methods the overall quantum yield of acetone decomposition was found to be unity - within a large experimental error.

The high yields of CO are directly opposed to Gorin's work, even making some allowance for the fact that Gorin's light source was not monochromatic, and suggest that some spontaneous decomposition of acetyl occurs at 2537 Å. Accepting Dorfman and Noyes' estimate of this effect (p.6), one would expect that Φ CO should be at least .07 at 3130 Å, and .22 at 2537 Å. It is possible that heterogeneous decomposition of acetyl contributed in part to Benson and Forbes result that Φ CO = .7 since they worked at 12mm. of acetone, whereas Gorin's investigations were made at very high pressures.

The most striking point in both the iodine investigations is that the results are quantitatively compatible with an exclusively free radical mechanism, as required by most of the indirect considerations pointed out above. The method provides a most convenient means of determining such radical mechanisms, but it still suffers from the inherent difficultues of all photochemical investigations, in that the yields obtained are normally too low for accurate estimation. Thus Gorin obtained yields of the order of 20 x 10^{-6} gm.mole. of methyl iodide, equivalent to about 2 mg of I_2; the separation of such quantities of methyl and acetyl iodides is obviously no small problem. To overcome this, the photolysis may be prolonged, but this may well lead to interference from photochemical decomposition of the products, if they are allowed to build up to any appreciable concentration. Further, prolonged running of the irradiation source raises difficulties in maintaining constant intensity, and measurement of absorbed quanta. Benson and Forbes used a flow system to obviate the first difficulty; the second still remains.

NATURE OF PRESENT INVESTIGATION

The present investigations aim at improving the sensitivity of such determinations with the aid of a radioactive tracer technique. If the photolysis is performed in the presence of radioactive iodine, then the iodide products will also be radioactive, and very readily detected. They may in fact be considerably diluted with their equivalent inactive products in quantities sufficient for reasonable separation, while still displaying sufficient activity for accurate measurement. From such activity measurements on each of the separated products, one may deduce the absolute yield of such products during the photolysis. Such a method should not only improve the sensitivity of determinations, it also enables the separation and measurement of products which are chemically similar, such as methyl and ethyl iodides; a task which is virtually impossible by normal methods on the small yields available.

The photolysis of methyl-ethyl ketone

The work was begun on the basis of Gorin's conclusions, and was applied initially to a study of methyl-ethyl ketone. This ketone offers interesting possibilities, for it may dissociate into either of two pairs of radicals :

$$CH_3COC_2H_5 \begin{array}{l} \nearrow \; CH_3 + C_2H_5CO \quad \ldots\ldots \text{(a)} \\ \\ \searrow \; C_2H_5 + CH_3CO \quad \ldots\ldots \text{(b)} \end{array}$$

There is ample evidence for the formation of radicals during the photolysis, apart from the rather obvious analogy with acetone. Thus Glazebrook and Pearson (29) have dedected radicals with the Paneth technique, and estimate that the rate of mirror removal is 80% as fast as observed in acetone under similar conditions. Barak and Style (4) have found diacetyl in the products at room temperature, indicating the occurrence of reaction (b). Ells and Noyes (18) confirm this, finding that the yield of diacetyl is equivalent to 11% of the CO formed at 2537 Å, while even at 1850 Å its contribution to the total quantum yield is still about 5%.

Perhaps the strongest indirect evidence for radical mechanisms comes from studies of the hydrocarbons produced from methyl-ethyl ketone. If one postulates a primary split directly into product molecules, one would expect only propane and carbon monoxide to be formed, as in reaction (c):

$$CH_3COC_2H_5 + h\nu \longrightarrow C_3H_8 + CO \qquad \ldots\ldots (c).$$

Norrish and Appleyard (47) found not only propane in the products, but also ethane and butane, in approximately equal proportions. Ethylene and methane were also reported. Such results are immediately explicable on a free radical interpretation, since at the temperature in use, 80°, most of the acyl radicals would be largely decomposed into methyl, ethyl and CO. These radicals would then react as follows:

$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad \ldots\ldots (d)$$

$$CH_3 + C_2H_5 \longrightarrow C_3H_8 \qquad \ldots\ldots (e)$$

$$C_2H_5 + C_2H_5 \longrightarrow C_4H_{10} \qquad \ldots\ldots (f)$$

$$C_2H_5 + C_2H_5 \longrightarrow C_2H_6 + C_2H_4 \qquad \ldots\ldots (g)$$

$$CH_3 + CH_3COC_2H_5 \longrightarrow CH_4 + CH_3COC_2H_4 \qquad \ldots\ldots (h)$$

$$C_2H_5 + CH_3COC_2H_5 \longrightarrow C_2H_6 + CH_3COC_2H_4 \qquad \ldots\ldots (j)$$

When reactions (g), (h) and (j) are of little importance, one may reasonably expect equal concentrations of methyl and ethyl radicals. On this basis, Moore and Taylor (42) estimate the relative probabilities reactions (d), (e) and (f) from calculations of relative frequencies of collision, and deduce that the ratio of ethane:propane:butane in the products should be 1: 1.7: 0.83. They reinvestigated the photolysis to check this point, and found the ratio varied from 1: 1.6: 1.15 at 90° to 1: 1.54: 1 at 100° and 1: 0.88: 0.56 at 200°. One would not expect good agreement with their calculation, since it assumes precisely equal activation energies for each of the reactions, and also appears to ignore variations in collision diameters; nevertheless the agreement is reasonable at 90°, and the temperature variation is well explained on the assumption that reactions (h) and (j) have appreciable activation energies.

Ells and Noyes (19) have made an interesting estimate of the relative probabilities of reactions (a) and (b) from a comparison of the yields of carbon monoxide observed from acetone, methyl-ethyl ketone, and diethyl ketone at 25°C. At 3130 Å their results were as follows:

	Acetone	Methyl-ethyl Ketone	Di-ethyl Ketone
Φ CO at 10 mm. pressure	0.095	0.085	0.67
" 10 " "	0.095	0.11	0.98
" 21 " "	0.095	0.12	0.98
" 36 " "	0.095	0.12	1.04

The high value of Φ CO for methyl ketone is attributable to a low degree of stability of the propionyl radical, and indicates that even at 3130 Å, it is formed with sufficient excess energy to decompose spontaneously into ethyl and CO. Assuming that this decomposition is 90% complete in the case of propionyl, and 10% in the case of acetyl (in accord with the value of Φ CO for acetone), also that the quantum efficiency of reaction (a) is x. and of (b) is (1 - x), then Φ CO from methyl-ethyl ketone will be given by:

$$\Phi\ CO = .9x + .1\,(1-x) = .8x + .1$$

Taking a mean value of Φ CO = 0.12, they find x = .025, indicating that reaction (b) accounts for 97% of the overall primary process. One may question the accuracy of this estimate, not only because of the above assumptions, but also because it places considerable weight on the observed values of Φ CO, values which the authors point out are very approximate as they are based on the further approximation that the absorption coefficient of methyl-ethyl ketone is the same as that of acetone. Nevertheless the result is very probably qualitatively true. At shorter wavelengths, the relative probabilities of reactions (a) and (b) would be expected to become more nearly equal, since the excess energy available would tend to over-ride small differences in bond strengths. Ells and Noyes' results at 1850 - 2000 Å accord with this interpretation, for in this region they found that Φ CO in methyl-ethyl ketone was an approximate mean of the corresponding quantities observed in acetone and diethyl ketone.

Gorin (26) has also briefly studied the photolysis in the presence of iodine at 70°, and found results very similar to those obtained with acetone. The yield of uncondensable gases was largely, but not entirely, quenched in the presence of iodine. At 3130 Å the yield of CO was about 4.5% that of alkyl iodide; in unfiltered light this value rose to 7.5%. He did not estimate absolute quantum yields, but he showed that, at equal pressures and with unfiltered light, the yield of alkyl iodide from methyl-ethyl ketone was 10% higher than from acetone. This result is compatible with a quantum yield of about unity, since the absorption coefficients of the two ketones are also in approximately the same ratio. Gorin concludes from the propane yields that some of the primary process must be represented by a direct split into propane and CO; he estimates that this accounts for 6% of the yield at 3130 A, and 3% in unfiltered light. In general, however, most of the photolysis must proceed by free radical mechanisms, though his results were unable to distinguish between reactions (a) and (b).

It would seem that the tracer technique outlined above offers a direct method of elucidating this point, for it should enable independent estimations of methyl and ethyl iodides in the products. A study of methyl ethyl ketone was chosen mainly as a proving ground for the method; it was hoped later to extend it to diethyl ketone with a view to determining the activation energy of decomposition of the propionyl radical. However, the results obtained did not confirm Gorin's conclusions, and the entire investigation was confined to the two ketones, acetone and methyl-ethyl ketone.

SUMMARY

The above considerationsmay be summarised as follows:

Acetone: (1) Considerations of the products of the direct photolysis are practically all explicable on a free radical interpretation, in some cases with quantitative precision.

(2) Certain of the results may also be explained on an activated molecule mechanism, involving the direct formation of products without the intervention of free radicals.

(3) Some evidence has been presented in the banded region of absorption which is explicable only in terms of the direct formation theory, but this evidence is disputed, and has not been confirmed.

(4) Direct tests for free radicals have qualitatively proved their existence during photolysis.

(5) Quantitative determinations of radical yields have been made with two methods, the results of one of which is quantitatively in

accord with free radical mechanisms at all wavelengths. The results of the other method have not been confirmed, but they are directly opposed to radical interpretations, and appear to indicate a direct formation mechanism even in the region of continuous absorption.

(6) Spectroscopic studies, fluorescence data, and certain other pressure dependent results indicate the existence of excited molecules during photolysis, but give no quantitative information on the ultimate fate of such entities.

Methyl-ethyl ketone:

(1) All the evidence available may be explained on a predominently free radical basis, at all wavelengths.

(2) Two primary reactions are suggested for the formation of radicals. The evidence available does not permit a direct evaluation of their relative preponderence, though this has been indirectly assessed under certain conditions.

(3) Practically no evidence is available on the possible contribution of excited molecules to the overall mechanism.

II RADIOCHEMICAL TECHNIQUE

(a) PREPARATION OF RADIOACTIVE IODINE

Choice of Isotope

The 8 day isotope, I^{131}, was selected for the work since it has a convenient half life, and emits β radiation of 0.6 m.e.v., sufficiently energetic for satisfactory measurement with the normal type of β counting apparatus. This isotope is now available in carrier free form from the A.E.R.A. at Harwell, where it is produced by the (n,γ) reaction on Te^{130}. It was found more economical for present purposes to extract the isotope from the products of the slow neutron induced fission reaction on Uranium^{235}:

$$U^{235}(n.f) \rightarrow Te^{131} \xrightarrow[\text{I.T.}]{\text{30 hours}} Te^{131} \xrightarrow[\beta^-]{\text{25 mins.}} - I^{131}$$

A number of other iodine isotopes are also produced, in particular I^{132} and I^{133}, but most of these are readily eliminated since they have comparatively short half lives. I^{132} arises from the reactions:

$$U^{235}(n.f) \rightarrow Sb^{132} \xrightarrow[\beta^-]{\text{5 mins.}} Te^{132} \xrightarrow[\beta^-]{\text{77 hrs.}} I^{132}$$

Since its immediate precurser has a 77 hour half life, some I^{132} always accompanies the iodine products, and in fact the total γ activity of the iodine extract follows the 2.4 hour half life of I^{132} fairly closely for some hours. This energetic γ activity (1.0 and 0.6 m.e.v.) acts as a readily detectable indicator during extraction procedure, and is finally removed by storing overnight, by when it has decayed to negligible proportions.

Iodine^{133} has a half life of 22 hours and emits a strong β (1.3 m.e.v.) and γ (0.55 m.e.v.) radiation. It is formed with a yield initially comparable to that of I^{131}, by the following reactions :

$$U^{235}(n,f,) \rightarrow Sb^{133} \xrightarrow[\beta^-]{10min.} Te^{133} \xrightarrow[\beta^-]{60min.} I^{133}$$

Mixtures of I^{131} with I^{133} (or any other iodine isotope) would be permissible for the present work, since only comparative activity measurements are required. Nevertheless, the presence of two β activities of very different energy and half life introduces awkward corrections for self absorption, and it was deemed desirable to remove this I^{133} activity by storing the irradiated uranium for one week prior to extraction; at the cost of some 50% of the desired I^{131} activity.

Extraction Procedure :

Sufficient iodine activity for about a month's experiments was obtained by the following routine:

(1) 25 gm. of UO_3 were irradiated in the A.E.R.E. pile for one fortnight, stored for one week, and then treated as follows:

(2) The UO_3 was placed in an all glass distillation apparatus, to which was added the required quantity of iodine carrier. Normally some 50 to 100 mg. of I_2 was added as NaI solution, in addition a few mg. of KBr were used as hold back carrier for any small amounts of bromine activity. The mixture was heated with 100cc. of 2N. H_2SO_4 until it had dissolved, when the iodide was oxidised to iodine by dissolved uranyl salts. Some time was allowed to complete exchange as far as possible between the active iodine in its various oxidation states and the carrier, then the iodine was distilled into a KOH solution.

(3) The iodide so extracted was oxidised to elementary I_2 with $NaNO_2$ and dilute H_2SO_4, again adding a little more KBr as hold back carrier. Such mild oxidation oxidises iodide but not bromide. The iodine was extracted with ether, washed, reduced again to iodide with the minimum quantity of Na_2SO_3 solution, and separated from the ether. This cycle of

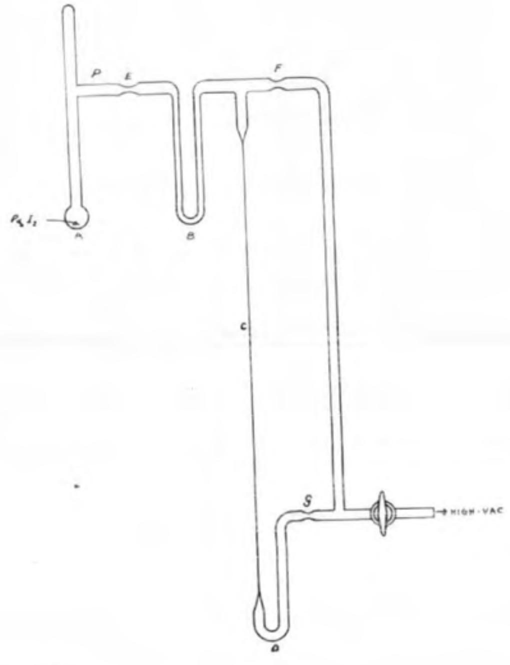


FIGURE I.

oxidation and reduction was twice repeated to improve the purity of the product.

(4) Finally the iodine was precipitated from iodide solution as PdI_2 by treatment with very slightly acidic (HCl) palladous chloride, after prolonged boiling to expel excess sulphite and ether residues.

(5) Continued heating caused the PdI_2 to agglomerate and settle, when it was washed, centrifuged, and ultimately decomposed to elementary iodine in the apparatus sketched in figure I. The PdI_2 was suspended in water, and dropped into "A", which was then sealed off, and the whole system was warmed under high vacuum until all water and gas was removed. Heating "A" to 400°C caused the PdI_2 to decompose into I_2 and Pd. The I_2 was sublimed into "B" at liquid nitrogen temperature through a glass wool plug at "P" to hold back flakes of palladium. The constrictions at "E" and "F" were sealed off, "D" was cooled in liquid nitrogen and finally the I_2 was sublimed into the fine glass capilliary "C", all the while keeping the tap open to the vacuum line. By such means, the iodine could be made to settle as desired in a short length of the capilliary, a procedure which was found well nigh impossible without continued evacuation of the capilliary, owing to persistent clogging. The capilliary was sealed off at each end and removed; while any small amount of I_2 in the trap "D" was collected by sealing off the constriction "G".

(6) The iodine was subdivided by judicious sublimation into short lengths of the capilliary, each of which was sealed off when filled with the desired amount. Amounts were assessed solely from their γ activity relative to that of a small portion initially sealed off and used as a standard. A second small portion containing some 3 mg. of I_2 was also sealed off and used for β specific activity determinations, again after

measuring its γ activity relative to that of the standard. This sample was then broken under NaI solution, its iodine content was estimated by titration with thiosulphate, and the titrated solution was precipitated as silver iodide. Small aliquots of this silver iodide were used for β activity measurements, retaining one such aliquot as a reference standard for subsequent iodine determinations. In this way both the γ and β activity associated with a known amount of iodine could be determined.

Yield

The average yield obtained was about 10mc., or 100μc. per milligram of I_2 at the time of extraction. Only 70% of the iodine originally added as carrier was recovered, the loss is almost certainly in stage (2) above, possibly due to iodate formation. All other stages were found to give nearly 100% yields of iodine, though the transfer of activity in the first oxidation and reduction cycle was by no means so quantitative. In some cases 25% of the γ activity would remain in the ether layer after complete reduction of iodine, suggesting the pressure of active isotopes of other elements. In later extractions 100mg of telluric acid was added to the UO_3 as hold back carrier for possible Te isotopes, resulting in almost complete elimination of such effects.

Purity of Product

The chemical purity of such a product can scarcely be questioned. Its "isotopic" purity was proved by prolonged measurements of half life; in all investigated cases this was found to be 7.9 ± 0.5 days over the maximum period of measurement (about 60 days).

Protection from Irradiation

This was of importance mainly during stages (1) and (2), which were performed in a fume cupboard behind 5cm. lead blocks. Such lead walls were dispensed with for subsequent work, but rubber gloves and fume cupboards were used until the final high vacuum stage, which was performed in the open laboratory. No serious hazard was encountered, as shown by monitoring tests with a radiation rate meter during extraction, and by periodic checks with "pocket" type ionization chambers.

(b) MEASUREMENT OF ACTIVITY

Type of Counter

An end window type Geiger Muller counter was used for β activity measurements. Initial measurements were made with a counter prepared in the laboratory. This counter was of the bell jar type, approximately 2cm. diameter x 6cm. high, with a thin mica window waxed onto the base. It was filled with 1cm. of ethanol and 9cm. of argon, and maintained a reasonable working plateau with a slope of 7% per 100 volts. Most of the later measurements employed a G.E.C. type II counter of similar dimensions, with a window 20mg/cm^2. The counter was housed in the customary "castle" with 4cm lead walls, lined with aluminium, thereby reducing background counts to about 12 per minute.

Electronic equipment was obtained from the Atomic Energy Research Establishment. Pulses from the GM counter were fed into a pre-amplifier type X200, and thence to a scaler type 200 for recording purposes. A type 1007 stabilised high voltage unit was connected to a potentiometer (type 1007) and adjusted to give the desired voltage for the G.M. tube. Normally the counter was run at the centre of its plateau or 100 volts about starting point; it was found that the precise voltage required varied with age of the tube, temperature, and apparently also with duration of use during each day's measurements.

Mounting of Source

All β activity measurements were made on silver iodide sources. These were prepared by evenly depositing a suspension of the silver iodide in acetone on standard silver trays 2cm. diameter, and 200 mg/cm^2 thickness.

The acetone was evaporated off with the aid of a radiant heater, leaving an approximately even layer of AgI in the tray. These trays were mounted in one of 5 standard positions directly below the G.M. counter, on a thick aluminium support. Absolute measurements were never required; accordingly silver trays and aluminium support were made sufficiently thick to obtain a constant "saturation" backscattered radiation rather than attempting to minimise such effects. The topmost position was 2.5cm below the counter window, the radiating area was approximately equal to that of the counter window, and in this normally used position the counter had an efficiency of about 2%

Positioning errors were in general less than those due to statistical deviations in counting rates and were probably less than 1%

γ Activity comparisons were normally required on thin capillaries containing variable amounts of iodine. These were mounted in a glass tube of 1.5mm. wall thickness, at 30 to 60cm. from the counter, and were further screened by an aluminium absorber of 500 mg/cm^2. This completely eliminated β radiation, and reduced variable self absorption effects to practically zero. Portions of the source could be almost entirely screened when required, with the use of 5cm. lead blocks.

Corrections

Apart from the normal procedure of deducting the background counting rate, to arrive at the activities due to the source, the following corrections and precautions were applied:

(1) β activities were measured relative to that of a reference standard, also of silver iodide, as mentioned on page 35 . To correct for variable efficiency effects, and also for the very small decay rate of the I^{131} itself (about 3% per 8 hours), frequent measurements of this standard were interposed between sample measurements at about half hourly intervals.

(2) Self absorption corrections were by far the most important. An empirical correction curve was obtained by plotting on semi logarithimic paper the activity observed from a given source, expressed in counts per minute per gram of silver iodide, against the weight of silver iodide in the tray. Such a graph appeared as a fairly straight line up to 150mg. with a self absorption half thickness of 200mg., or 63.5 mg/cm^2. The amount of AgI normally used was 100 mg. and the correction curve was finally adjusted so that the correction factor for such an amount was unity. Corrections for other quantities varied from $\frac{1}{1.19}$ for 50mg. to $\frac{1}{0.84}$ for 150mg, these being the maximum deviations allowed.

(3) Correction for losses due to the resolving time of the counting circuit were minimised by keeping the counting rate below a maximum of 10,000 counts per minute. This was achieved by using one of the lower positions for the source where necessary. Normally sample and reference standard were measured in the same position; when this was not practicable a predetermined efficiency ratio was used to correct the readings. Small corrections for counting rates up to 10,000cm. were made using the equation:-

$$n_o = n_i(1 + n_i t)$$

where n_0 = true counting rate, corrected for resolving time losses.

n_1 = observed counting rate

t = resolving time of the circuit = 300 μ sec.

Such a correction is equivalent to 0.5% per 1,000 counts per minute, and does not exceed 5% at the maximum rate permitted.

(4) Errors due to statistical variation in counting rate were in general kept below 2% by prolonging the time of counting where necessary. Normally five to ten thousand counts were recorded on each sample; very low activities of the order of the background count rate were counted for one or two hours, but these were not treated as quantitatively reliable.

(c) EXPERIMENTS ON THE VALIDITY OF THE TRACER TECHNIQUE

The proposed procedure for analysing the products of the photolysis may be outlined as follows:

(1) A mixture of 3 ketone at 50mm. pressure, and radioactive iodine at 1mm. pressure is photolysed for the desired time.

(2) Condensible reaction products, CH_3I, C_2H_5I, CH_3COI, C_2H_5COI, excess iodine, and ketone are frozen out in a liquid nitrogen trap during analysis for uncondensible gases.

(3) The iodide products are distilled into a receiver, then diluted with a mixture of known amounts of inactive carrier iodides.

(4) From the above diluted mixture, a pure sample of each iodide is obtained by fractional distillation.

(5) The separated samples are treated with silver nitrate, converting the iodide to silver iodide.

(6) The activity per gram of silver iodide associated with each of the products is measured and compared with a reference standard, thus enabling determination of yield.

Such a determination assumes that the activity associated with any given separated product, e.g., methyl iodide, arises solely from the active methyl iodide formed during photolysis. It is possible that inactive methyl iodide carrier could aquire activity from other sources however, such sources being exchange reactions either (a) with the other active iodides, or (b) with unused active iodine remaining in the products. These reactions may be represented thus:

$$\text{(a)} \quad R_1I + R_2I^* \rightarrow R_1I^* + R_2I$$

$$\text{(b)} \quad R_1I + I_2^* \rightarrow R_1I^* + I_2$$

If type (a) reactions occur at all, they would presumably require the intermediate formation of an iodine atom or i~~r~~on. Previous workers have shown that non-ionizing alkyl halides do not normally undergo thermal exchange at appreciable rates, either with free halogens, or halide ions. Thus Szilard and Chalmers (64) were able to separate concentrated radioactive silver halides from a large bulk of neutron irradiated ethyl iodide; McKay (40) found no exchange between methyl iodide and iodine at 100° in 15 minutes; and Hull, Shiflet, and Lind (33) found similar results with ethyl iodide and iodine. The above determination would involve the presence of ketones however, and such solvents as acetone and alcohol promote exchange considerably. McKay (40) reports complete exchange between methyl iodide and iodine in alcohol at 100° in a few minutes, and numerous workers have observed exchange in sodium iodide-methyl iodide systems in such solvents, the reaction being particularly rapid in dry acetone.

Obviously the validity of the proposed method is very critically dependent on the absence of such exchanges, since quantities of the order of a few microgramms of product are anticipated in the presence of some milligrams of iodine. For this reason a series of experiments was carried out to investigate such effects.

TYPE (a) EXCHANGE REACTIONS

Active ethyl iodide was prepared by reacting diluted radioactive iodine with ethanol in the presence of red phosphorus; the product was dried and fractionally distilled. Mixtures of 3cc. of this active ethyl iodide with similar quantities of other components were made up, allowed to react, and finally separated by fractional distillation in a small fractionating column. This column had the dimensions 20 cm. x 1.6 cm., it was electrically heated, and packed with small glass helices. A reflux ratio of 2:1 was maintained during distillation, but no attempt at accurate control was made, since the boiling points of the components used differed by some 30°. Distillate was collected at 2-4cc. per hour in successive 0.3cc. portions. Trial distillations showed that the separation was satisfactory; about 2cc. of the original 3cc. portions would come over at the corresponding boiling point, and subsequent boiling point determinations on separate fractions confirmed their purity. The separated fractions were prepared for activity determinations firstly by removal of iodine (if present) by washing with aqueous Na_2SO_3. Conversion to silver iodide was effected by warming with alcoholic silver nitrate in a centrifuge tube, followed by centrifugation, warming in water, and finally washing in acetone. Ultimately, weighed samples of the silver iodide were deposited on silver trays for activity measurements.

The results of two typical experiments are set out below:

TABLE I: EXCHANGE EXPERIMENTS ON ALKYL IODIDE-ACETONE MIXTURES

Experiment No.	Activity observed in various fractions, corrected for self absorption, and expressed in counts per minute per gram of silver iodide.		
	Methyl iodide.	Recovered ethyl iodide.	Initial ethyl iodide
(1)	38	2790	2820
	64	2790	2830
		2810	
(2)	26	1780	1750

The sensitivity of these initial experiments was somewhat limited by the low specific activity of the ethyl iodide used. Thus the actual counts observed on methyl iodide specimens were less than 5 cpm. above a background of 20 cpm., and are probably not significant. Even so, they are equivalent to only about 1% of the activity found in the recovered ethyl iodide fractions, and the specific activity of the recovered ethyl iodide is in good agreement with that of the starting material. Subsequent results on actual runs have confirmed this, since in certain cases the activity observed in ethyl iodide fractions was only 10 to 20cpm., compared to some 3000cpm., on similar quantities of methyl iodide specimens.

TYPE (b) EXCHANGE REACTIONS

Several experiments were made on mixtures of active iodine with methyl and ethyl iodides. The active iodine was prepared by decomposing active palladous iodide at atmospheric pressure in a long open test tube, afterwards taking up the iodine in an ether solution. Iodine was obtained as required from this solution, aliquots of which were mixed with methyl and ethyl iodides. After reaction, the iodine was removed by washing with sulphite, and the activity in the alkyl iodide was determined in the usual way.

It was found impossible to recover alkyl iodide from such mixtures in a completely inactive form. The degree of retention of activity varied from one to ten per cent of the active iodine used, equivalent in weight to 10 to 100μg of iodine. The results were not appreciably altered by:

(a) Time of storing the mixture before separation.

(b) Diluting the initial active iodine solution with an excess of inactive iodine.

(c) Substituting alkyl bromide for alkyl iodide.

(d) Repeated washing of the separated alkyl iodide with sulphite, inactive iodine, and then sulphite again.

(e) Exhaustive purification of both alkyl iodide and ether, including pretreatment with inactive iodine to eliminate any unsaturated components.

(f) Use of I^{128} prepared from neutron irradiated iodo benzene, instead of I^{131}.

Particularly in view of (a), (b) and (c), the results cannot be attributated to a true exchange reaction. The retention effect was however very considerably reduced by careful removal of ether from the iodine solution, prior to adding the alkyl iodide. This was achieved by pumping off the ether under vacuum, keeping the iodine tube at -15°. Some (10%) loss of iodine resulted, but on adding alkyl iodide to the residue, it could be recovered from it in a state of almost complete inactivity.

These curious results were attributed finally to the method of preparing the active iodine. Palladous iodide is difficult to handle in small quantities, in that it resists agglomeration and will not easily settle in a centifuge tube. To overcome this, acetone was added as a settling agent, and it appears that some of this acetone remained absorbed on the palladous iodide until the time of its thermal decomposition. Under such conditions, it is possible that the acetone would react with the evolved iodine, forming radioactive products such as iodo acetone or methyl iodide. These products would then be taken up in any organic solvent which may be added subsequently, and would lead to just those results described above. All subsequent preparations have avoided the use of organic reagents at any stage, and the iodine prepared in this way gave perfectly satisfactory results.

Exchange reactions between iodine and alkyl iodides would appear to be negligible, for present purposes. However, mixtures of ketones and iodine will react in the liquid state, by way of the enol form of the ketone, forming products such as iodo acetone. A qualitative experiment showed, indeed, that active iodine in acetone imparts a significant activity to methyl iodide, after standing the mixture for two hours at room temperature. In view of this, it would seem desirable to reduce to a minimum the time during which the reactants remain admixed in the liquid state, and also to remove excess iodine before adding carrier iodides.

Iodine may be easily removed by distilling the products over mercury, but some experiments of Dr. R. W. Durham in this laboratory have shown that mercuric iodide catalyses and in fact initiates exchange reactions quite significantly. It has been found that iodine may also be removed by distilling the products through a glass wool trap at -30°, or by distillation over silver powder. These techniques will be described in later chapters, but it may be stated here that blank experiments in the absence of photolysis have proved the validity of the method beyond any reasonable doubt.

It is of interest that publications have appeared in recent literature in which essentially the same technique of isotope dilution has been used. Thus Williams and Hamill (70) have used active iodine to investigate the radiolysis of hydrocarbons, and Friedman and Libby (24) have used a similar dilution technique in investigations on the chemical form in which "hot" atoms are produced in organic bromides exposed to ionizing radiations.

III PHOTOCHEMICAL TECHNIQUE

(a) PREPARATION OF MATERIALS

(1) Methyl-ethyl ketone

The best quality of this ketone available was ordinary technical grade. An attempt at purification by means of the bisulphite addition compound was made, but it was finally rejected in favour of repeated fractional distillation. The bisulphite compound requires considerable washing to remove absorbed impurities; this washing must be carried out with an organic solvent such as ether or methanol, and since it is virtually impossible to remove the last traces of this wash liquid, the requirements for its purity became almost as stringent as those for the purity of the final product. Further, the fact that this ketone forms an azeotropic mixture with water raises difficulties in the separation of the regenerated ketone.

An initially large quantity of crude ketone was fractionally distilled three times in an all glass fractionating apparatus, using a helix packed column 50cm x 1.8cm, and maintaining a reflux ratio of 10 : 1. The column was maintained at 2° below the temperature of the vapour at the point of removal from the apparatus. Temperatures were read on a standard N.P.L. thermometer introduced by means of a ground joint. The middle third of the distillate was used for subsequent fractions, though after the first distillation practically all the distillate came over at temperatures and pressures in excellent agreement with the figures given by Felsing, Shofner and Garloch (22), equivalent to 79.56°C at 760mm. The final product was dried over $MgSO_4$, subsequently degassed, and vacuum distilled into a reservoir where it was kept permanently under vacuum.

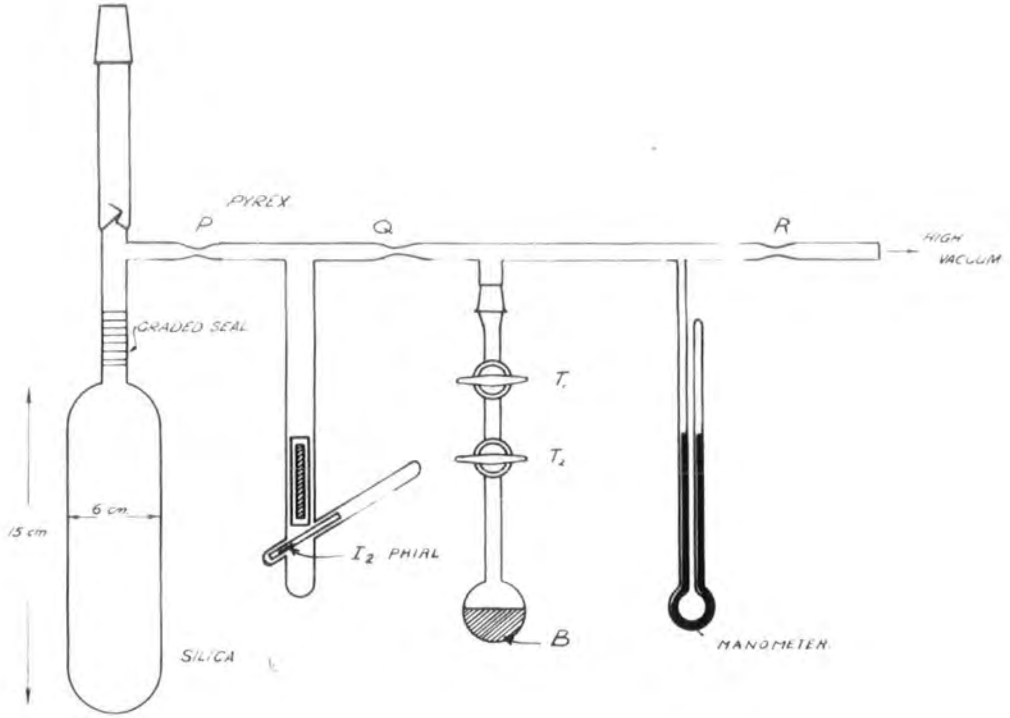

PYREX
P
Q
R
HIGH VACUUM
GRADED SEAL
T_1
T_2
15 cm
6 cm
I_2 PHIAL
B
SILICA
MANOMETER

FIGURE 2.

(2) Alkyl iodides

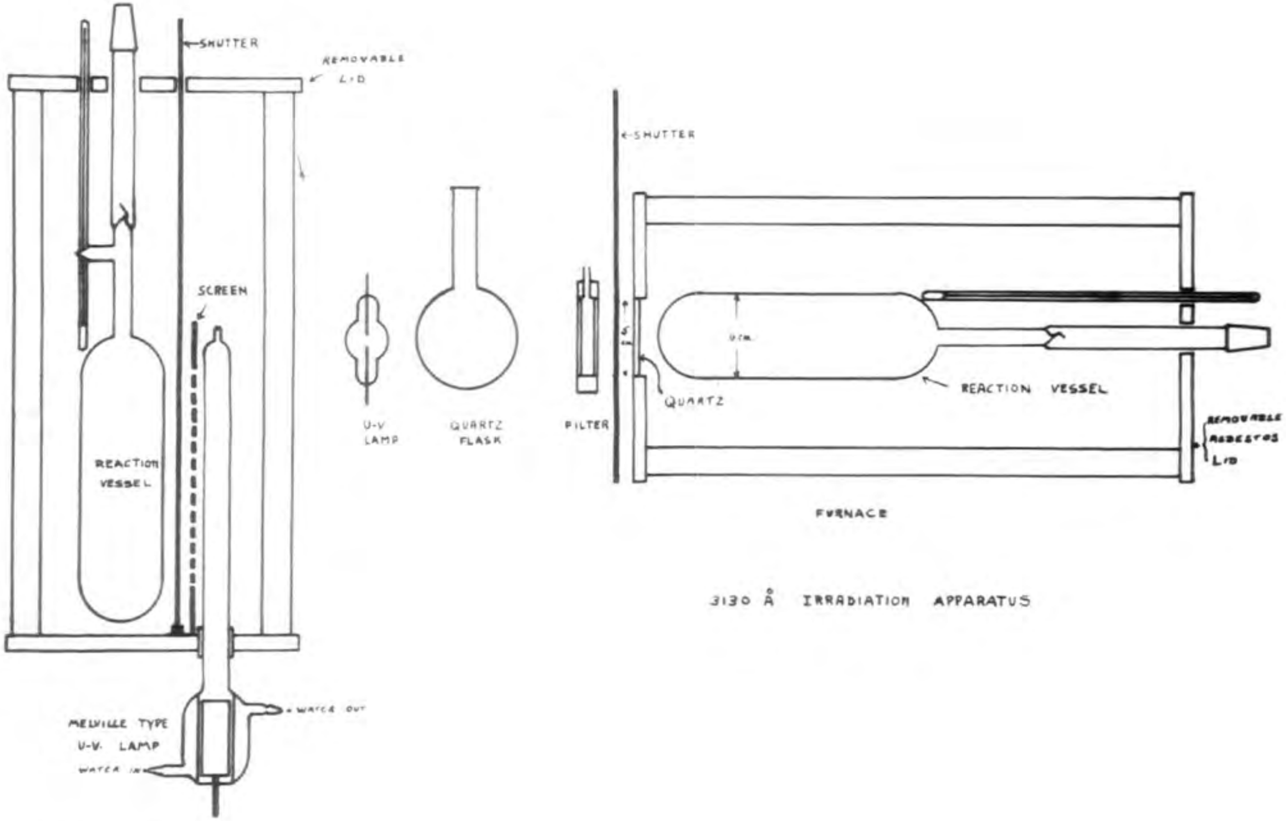
Methyl and ethyl iodides of chemically pure quality were dried over $MgClO_4$, then fractionally distilled in the small column described previously. The resulting clear, clean boiling liquids were stored in light proof glass stoppered bottles.

(b) PHOTOCHEMICAL APPARATUS AND EXPERIMENTAL METHOD

As is perhaps customary in such work, no single apparatus or technique was adopted throughout, rather were modifications made as the work progressed. In this section the initial technique will be discussed, modifications will be described in later sections as they were introduced.

(1) Reaction vessel and method of filling

Figure II represents the apparatus schematically. The quartz reaction vessel of 320cc. volume was connected to the pyrex filling system with a graded seal. The reservoir B contained methyl-ethyl ketone; it was normally kept cooled in dry ice, and was repeatedly degassed before each experiment. Prior to filling operations the system was evacuated and degassed with a two stage mercury diffusion pump giving pressures less than 10^{-5}mm of Hg. The constriction R was then sealed off, and ketone was admitted to the desired pressure, with the reaction vessel immersed in a water bath at 20°. Predetermined volume calibrations enabled estimation of the final pressure of ketone during photolysis from the pressure observed at this stage; the volume of the tubing etc., was kept nearly constant, but any small variations were neglected, since they would represent less than 1% of the total volume. The ketone was then condensed in the base of the reaction vessel by immersing it in liquid nitrogen; the constriction Q was sealed off and iodine was released by breaking the small capillary with the aid of the iron cored plunger. The



2537 Å IRRADIATION APPARATUS.

3130 Å IRRADIATION APPARATUS

FIGURE 3.

iodine then sublimed into the reaction vessel, and was kept as far from the condensed ketone as possible by raising the level of the liquid nitrogen. Finally the constriction P was sealed off, the reaction vessel was wiped clean, and transferred to a preheated furnace in the irradiation apparatus.

(2) Irradiation Apparatus

A diagram of the apparatus is given in figure III. For 2537 Å irradiation, a water cooled, low pressure mercury lamp as described by Melville (47) was used. This was run at 500 volts and 120 m.a. from a 1000 V. transformer, powered directly from the A.C. mains. It was manually controlled at constant current with the aid of a variable resistance in the primary circuit. No attempt at improving the isolation of the 2537 Å line was made, since the makers of the lamp, Messrs. Thermal Syndicate Ltd., quote figures which indicate that 99% of the ultra violet output occurs at the required resonance line. The lamp was set up in the position shown, and by suitable clamps and spring clips the position of the reaction vessel was maintained constant with respect to it. When the shutter was raised, radiation from one limb of the inverted U shaped lamp entered the vessel through a perforated screen, thus reducing the intensity to practical limits. The furnace was electrically heated, and manually controlled to within ± I or 2° during a run.

3130 Å irradiation was obtained from a 125 watt medium pressure "Osira" mercury lamp, run off the A.C. mains with a choke and resistance. This resistance was manually adjusted during irradiation to maintain constant running at 0.80 amp. The lamp consists simply in two electrodes sealed into a spherical silica bulb, containing a drop of mercury. Normally the lamp is supplied with a Woods' glass filter; this absorbs all the visible output, but also a good deal of U-V; it was removed without impairing the

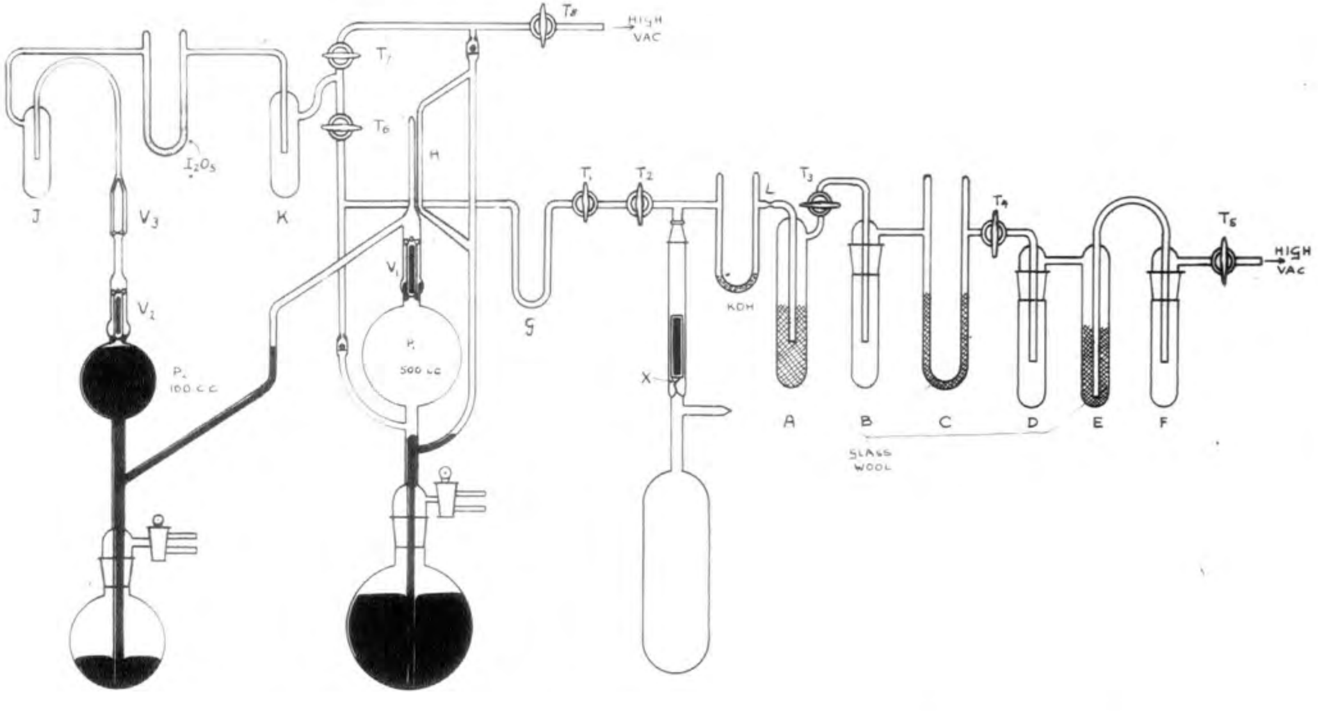

T_8
HIGH VAC
T_7
T_6
H
I_2O_5
J
V_3
K
V_2
P_2 100 c.c.
V_1
P_1 500 c.c.
G
T_1
T_2
X
KOH
L
T_3
T_4
T_5
HIGH VAC
A
B
C
D
E
F
GLASS WOOL

FIGURE 4.

running of the lamp.

The beam of irradiation was roughly collimated with a 250cc. spherical quartz flask, filled with an aqueous filter solution. The filtration system for isolating the 3130 Å line from the extremely polychromatic output of the lamp was as recommended by Bowen (9), using however only half the $NiSO_4$ concentration he advises, after consideration of more recent figures given by Davis and Hunt (14). The system was as follows:

(a) Visible radiation was removed in the quartz collimating flask of mean path length 7.5cm, filled with a solution of A.R. quality $NiSO_4 .6-7 H_2O$ at 90 g./l. and A.R. quality $CoCl_2 .6H_2O$ at 47.6 g./l.

(b) Ultraviolet radiation of wavelengths shorter than 2900 Å was removed in the 1cm quartz walled filter, filled with potassium hydrogen phthalate at 5g./l. This solution was renewed before each run, and fresh stock was made up at frequent intervals, as it showed a tendency to grow mould.

Before irradiation, the furnace was brought up to temperature, and the lamp was run until steady conditions were maintained. The reaction vessel was then placed in position with the shutter closed, half an hour was allowed for its contents to reach furnace temperature, and the shutter was finally opened for the desired period.

(3) Analysis of Products

(a) Gas Analysis

After irradiation, the reaction vessel was removed from the furnace and connected to the analysis system with a greased ground joint, in the position shown in figure IV. Immediately, condensible products were frozen out by cooling the base of the reaction vessel in liquid nitrogen.

The system was then evacuated, and with T_2 closed, the tubing leading to the gas analysis system was thoroughly degassed with the aid of the toepler pump P_1. The break seal X was broken, and uncondensed gases in the reaction vessel were quantitatively collected with some 30 strokes of P_1, and finally compressed into the graduated capillary H for measurement of volume and pressure.

For runs involving ketone alone, a test for quantitative removal of gas was made by warming and refreezing the ketone; in other cases this was not normally attempted for fear of losing alkyl iodides and other products in the process, e.g. by absorption on tap grease. In all cases, however, 30 to 40 strokes of P_1 appeared perfectly adequate.

Having collected these gases, T_1 and T_2 were closed and the measured gas was transferred to the iodine pentoxide tube with 6 strokes of the second toeplar pump, P_2. The I_2O_5 tube was immersed in a glycerol bath electrically heated to 130-160°; at this temperature I_2O_5 quantitatively oxidises CO to CO_2, but leaves H_2, CH_4, and all other hydrocarbons unoxidised (26,67). The trap K and sometimes J were cooled in liquid nitrogen to condense CO_2 as formed, and at hourly intervals the amount of residual gas was measured in H with the aid of pump P_1 again. This process was repeated until two readings of the residual gas agreed. Yields of CO were then estimated from the decrease in total gas after completion of the I_2O_5 reaction; the residue was not analysed, but for present purposes it may be taken as almost entirely methane.

Performance

After some weeks of use and continuous evacuation, the I_2O_5 reacted quantitatively in an hour or two, but in any case where air was admitted to the system - even if followed by immediate re-evacuation - the reaction was most sluggish, requiring possibly 24 hours for completion. Normally the apparatus was kept permanently evacuated and under such conditions it gave entirely satisfactory results. On "blank" experiments, the gas extracted from the hot I_2O_5 tube averaged about 8 x 10^{-10}gm. mole. per hour; whether this was due to thermal decomposition of the I_2O_5 or small leaks from taps was not investigated. This a yield of 1 x 10^{-8}gm. mole. of CO. could be estimated with about 5% accuracy; yields normally obtained on calibration runs (to be described later) averaged 5 x 10^{-6}gm. mole., and were probably subject to less than .1% error. Prolonged (24 hours) exposure of the residual gases to the hot I_2O_5 tube caused no significant decrease in volume, so that the specific nature of the reaction for CO appears to be confirmed. Saunders and Taylor (56) have shown that this method is entirely consistent with others for the estimation of CO.

(b) <u>Iodide Analysis</u>

The reaction vessel was warmed to room temperature, allowing volatile products to distil through the KOH tube, containing about 10 pellets of KOH freshly introduced before each run, and thence through the glass wool trap A, cooled to - 30°C, into B, cooled in liquid nitrogen. The time of distillation was normally one minute longer than that required for complete distillation of the methyl-ethyl ketone. Under these conditions distillation of CH_3I and C_2H_5I is complete, while any traces of HI and probably most of the CH_3COI are absorbed on the KOH. The glass wool trap at - 30° kept back nearly all the unused iodine, but occasionally a little would collect in B. Distillation was stopped by sealing off the constriction L. 0.50cc of methyl iodide, and the same amount of ethyl iodide were placed in D, and degassed; these carriers were then distilled

TABLE II

Activity measurements on product of experiment (13).

Sample of alkyl iodide.	B.P	Wt. of resultant AgI used for activity measurements	Net count rate on AgI sample (counts per minute).	Count rate per gm. AgI (corrected for self absorption).	Count rate of standard "X" *	Specific Activity of sample in standard units per gm. AgI.	Mean specific activity
Ethyl Iodide (1)	72.4°	.1246 gm.	1,148 c.p.m.	10,120 cpm/gm.	12,450 c.p.m.	.814 s.u/gm	
(2)	72.4°	.1100 "	1,080 "	10,180 "	12,600 "	.808 "	
(2)	"	.0870 "	1,000 "	10,920 "	12,600 "	.867 "	
(3)	72.4°	.1235 "	1,083 "	9,750 "	12,300 "	.792 "	.824 s.u/gm.
(3)	"	.1332 "	1,175	9,900	12,450 "	.794	
(4)	72.6°	.1440 "	1,330	10,800	12,450 "	.868	
(4)	"	.0995 "	1,034	10,380	12,600 "	.823	
Methyl Iodide (1)	42.4°	.1625 "	68	525	12,250	.0429	
(1)	"	.2036 "	68	478	11,050	.0433	
(2)	42.5°	.1295 "	65	557	12,500	.0447	.0444 s.u/gm.
(2)	"	.1226 "	56.5	502	11,560	.0434	
(3)	42.7°	.1517	71	565	12,000	.0470	
(3)	"	.1706	64	481	10,600	.0453	

*To obviate large corrections forresolving time losses, standard "X" was measured in a position of lower efficienty than was used for other samples, at a mean rate of 3,800 c.p.m. The figures given in this column were obtained by multiplying the observed count rate by a pre-determined efficiency ratio of 3.35.

into B which was ultimately warmed to -30°C, and its contents were distilled through the second glass wool trap C, also at - 30°, into D at liquid nitrogen temperature. All traces of residual iodine were thereby d/ removed; probably some of the relatively involatile acetyl iodi~~n~~e was also retained. A third glass wool trap E was included in case any iodine still remained in D; in every case however, the product in D was colourless. This product was warmed to room temperature, further diluted with 2.5cc more of each carrier, then fractionated into its components as described above. 2cc. of toluene (B.P.110°) and 0.5cc. of methylene iodide (B.P:180°) were added as hold back carriers for any traces of acetyl iodide (B.P.105°) and iodo acetone (B.P. > 200°) which may have escaped the above treatment. The separated fractions, generally three of each iodide, each of approximately 0.3 to 0.5cc. volume, were finally converted to silver iodide and prepared for activity determination as described in previous sections.

Calculations of yields from activity determinations

The method of estimating absolute yields from activity determinations will be illustrated with the results of an actual run. The following observations were recorded in experiment (13), in the first series of experiments on methyl-ethyl ketone at 3130 Å.

(1) Estimation of specific activity of the iodine

A capillary of active iodine was broken under KI solution.

Iodine content of capillary, determined by titration

against N/200 $Na_2S_2O_3$ .. .. .. 3.00 mg.

Total weight of AgI equivalent to the KI soltn.

determined (a) by gravimetric analysis of two aliquots

(b) by calculation from the known weight of Kl. 3.52 gm.

Weight of resultant AgI sample in counting tray "X", selected as a mean standard from 4 similar samples .. 0.1229 g.

Self absorption correction for this weight of AgI .. 1/0.920

Hence, expressing the counting rate from sample "X" as 1 standard unit (1 s.u.) the specific activity, S, of the original iodine will be given by:

$$S = \frac{1\ \text{s.u.}}{0.92} \times \frac{3.52}{.1229} \times \frac{1}{3.00} \quad \text{s.u/mg. } I_2$$

$$= 10.40 \ \text{s.u./mg. } I_2 = 1.320 \times 10^{6} \ \text{s.u./ equivalent of I.}$$

(2) Activity of separated products

The measurements are set out in table II. From these results, the absolute yields are deduced as follows:

Weight of ethyl iodide carrier used .. 4.542 g. = 6.840g. AgI.

" " methyl " " " .. 3.302 g. = 5.470g. "

Mean specific activity of AgI precipitated from ethyl iodide .. .. =0.824 s.u./g. AgI.

Mean specific activity of AgI precipitated from methyl iodide .. .. =0.0444 s.u./g. AgI.

$$\text{Yield of ethyl iodide} = \frac{0.8244 \times 6.840}{1.320 \times 10^{6}} \quad \text{equivalents.}$$

$$= \underline{4.27 \times 10^{-6} \text{gm.mole. } C_2H_5I}$$

$$\text{Yield of methyl iodide} = \frac{0.0444 \times 5.470}{1.320 \times 10^{6}}$$

$$= \underline{1.84 \times 10 \text{ gm. mole } CH_3I}.$$

An estimate of the accuracy in activity determinations may also be obtained from the data in table II. The degree of reproducibility is probably ± 5% in this instance, though somewhat more inaccurate from methyl iodide counts. In later experiments, iodine of higher specific activity was available, particularly after the availability of the new high power pile at Harwell. This increased the accuracy on all yields, so that the error in activity determination was not more than ± 3 to 4% on nearly all samples.

IV INITIAL STUDIES ON METHYL ETHYL KETONE

This initial work was directed primarily at a determination of the ratio of ethyl to methyl radicals produced during photolysis, and hence the relative preponderence of the two reactions:

$$CH_3COC_2H_5 + h\nu \begin{array}{l} \nearrow \quad CH_3 + C_2H_2CO \qquad\qquad (a) \\ \searrow \quad C_2H_5 + CH_3CO \qquad\qquad (b) \end{array}$$

Determination of quantum yields

Estimates of the quanta absorbed during an experiment were made by measuring the yield of CO produced in separate calibration runs during photolysis of the ketone alone. The assumption was made that Φ CO is unity in the direct photolysis at temperatures over 100°, both at 2537 Å, and 3130 Å. This point has not been investigated in any of the literature so far published, nevertheless it appears very reasonable from the following considerations:

(1) Noyes et al have repeatedly verified that ΦCO tends to unity in the acetone photolysis at temperatures above 100°.

(2) There is no indication of any chain reaction in the photolysis of acetone, methyl ethyl ketone, or di-ethyl ketone at any temperature, so that a value of Φ CO greater than one is most improbable.

(3) The work of Ells and Noyes shows that Φ CO in methyl-ethyl ketone at 3130 Å is slightly above the value observed in acetone at room temperature; in diethyl ketone the value is higher still and approached .7 at 25°. Thus one would expect the trend towards unity to occur at temperatures at least as low as in the acetone photolysis, and probably lower.

On the above assumption, the number of quanta absorbed during an experimental run may be expressed by the equation:

$$E = \text{No. of einsteins absorbed} = M \frac{\left(t_{exp.}\right)\left(I_{o\ exp.}\right)\left(1-10^{-\epsilon cd}\ _{exp.}\right)}{\left(t_{cal}\right)\left(I_{o\ cal.}\right)\left(1-10^{-\epsilon cd}\ _{cal.}\right)}$$

where M = gm.moles. of CO produced in calibration run.

t_{exp} = duration of experimental run.

t_{cal} = " " calibration "

$I_{o\ exp}$ = incident intensity in experimental run.

$I_{o\ cal}$ = " " " calibration "

ϵ = molecular absorption coefficient of the ketone.

c = concentration of ketone in gm.moles./litre.

d = mean path length of irradiation in reaction vessel.

Since iodine does not absorb to any significant extent at wavelengths shorter than 4000 Å, the final term in the above equation can be adjusted to unity by using the same concentration of gas in experimental and calibration runs. This was the general procedure; where necessary corrections for small pressure differences were made with the above equation, using the values $\epsilon = 3.80$ at 3130 Å, and 11.0 at 2537 Å. These values have been derived from figures given by Damon and Daniels (11) for acetone, and by F.O. Rice (53) for acetone and certain other ketones. They are only approximate, but the correction is insensitive to the absolute values of ϵ. In fact, the absorption correction is small; it is less than linearly dependent on pressure under most normal conditions where some 30% of the incident light is absorbed.

Again, by using identical values of I_o, t, and C, in experimental and calibration runs, the no. of einsteins absorbed is given simply by M, and the quantum yield of any product, e.g., MeI, is then y/M where y is the yield of MeI in gm. moles.

TABLE III

Photolysis of Methyl-ethyl ketone/Iodine Mixtures at 2537 Å

Experiment No.	Temperature	Pressure of Ketone Corrected to 100°C.	Pressure of Iodine	Time of Irradiation (minutes)	Yield X 10^7 gm.moles.				EtI/MeI	Φ CO	Φ EtI	Φ MeI
					CO	Residual gas (CH_4)	EtI	MeI				
3	100°C	50mm.	0.8mm.	Nil	N.D.	N.D.	.02	.07				
4	60°	51 "	0.75mm.	2.5	N.D.	N.D.	not absolutely Determined.		2.48			
5	100°	53 "	0	5.0	26.5	2.64				1.0(a)		
6	80°	52	0.80 "	10.0	6.1	1.6	24.3	10.6	2.29	.14	.47	.20
7	100°	52	0.80 "	5.0	4.3	0.4	12.4	4.9	2.51	.17	.48	.19
8	100°	52.5	0	5.0	25.4	2.68				1.0(a)		

N.D. Not Determined (a) assumed.

Initially, no very great interest was attached to absolute values of the quantum yields. It was assumed on the basis of Gorin's work that they would be unity. As the work progressed it became apparent even with the rather rough results available, that this was the most important section of the work, and the technique was altered accordingly.

Experiments at 2537 Å.

The results of these first experiments are set out in table III. Experimentally, they are subject to considerable errors in absolute values of quantum yields, since it was not possible to run the mercury lamp under constant and reproducible conditions.

Every effort was made to reduce the time of contact of iodine and ketone in the liquid phase. It was found impossible to work below 60°, for even at this temperature there was some slight tendency for the ketone and iodine to condense out in small drops on the walls of the reaction vessel. One run at 50° displayed this effect considerably and gave quite anomalous results. This behaviour is surprising since the saturated vapour pressure both of methyl-ethyl ketone (300mm.) and of iodine (2.16mm.) at 50° are well above those used in practice.

Discussion of Results

An approximate estimate of the relative predominance of the primary reactions may be obtained as follows:

Suppose (x + y) gm. moles. of ketone decompose as set out below:

$$(x + y)\ CH_3COC_2H_5 \rightarrow x(CH_3+C_2H_5CO)+y(C_2H_5+CH_3CO)$$

Further, suppose a fraction α of the propionyl radicals decomposes spontaneously:

$$\alpha\, x(C_2H_5CO) \longrightarrow \alpha\, x\, C_2H_5 + \alpha x\, CO$$

Similarly, β of the acetyl radicals decompose:

$$\beta\, y\, (CH_3CO) \longrightarrow \beta\, y\, CH_3 + \beta\, y\, CO$$

Then the total yield of methyl will be $x + \beta y$

and " " " " ethyl " " $y + \alpha x$

" " " " " CO " " $\alpha x + \beta y$

Hence the ratio of ethyl to methyl, equivalent to that of ethyl iodide to methyl iodide in the products, will be given by:

$$R = \frac{\text{yield of ethyl iodide}}{\text{yield of methyl iodide}} = \frac{y + \alpha x}{x + \beta y}$$

Let $A = y/x = \dfrac{\text{probability of reaction (b)}}{\text{probability of reaction (a)}}$

Then $R = (A + \alpha)/(1 + \beta A)$

Also the ratio S, of the yield of CO to that of MeI is given by:

$$S = \frac{CO}{MeI} = \frac{\alpha + \beta A}{1 + \beta A}$$

It is known that the propionyl radical is much less stable than acetyl; as a limiting assumption suppose $\alpha = 1$ and $\beta = 0$; then $R = A + 1$. Taking a mean value of $R = 2.4$ from the observed results, a lower limit of 1.4 for the value of A is obtained. This limiting assumption is obviously invalid, for some at least of the acetyl radicals must decompose at 2537 Å; further S does not equal unity, as would be required. As a better approximation, let us take the estimate of Noyes et al. that $\beta = 0.15$ at 2537 Å, and taking a mean value of $S = 0.78$ from the two observations, then we obtain α .69 and $A = 2.65$. That is, reaction (b) is 2.65 times more predominant than reaction (a) at 2537 Å.

Obviously this estimate is subject to considerable error, and requires an accurate knowledge of α and β for proper estimation.

TABLE IV

Photolysis of Methyl-ethyl ketone/Iodine mixtures at 3130 Å

Experiment No.	Temperature	Ketone pressure (corrected to 100°)	Iodine pressure	Time of Irradiation	Yield X 10^7 gm. moles.				$\frac{EtI}{MeI}$	Φ EtI	Φ MeI	Φ CO
					CO	Residual gas CH_4	EtI	MeI				
9	100°	51mm.	1.0mm.	0			<.1	<.04				
10	100°	52 "	0	45 mins.	77.5	7.5						1.0(a)
11	80°	52 "	1.0	15 "	.18	.21	15.0	.67	22.5	.535	.024	.0067
12	60°	53	1.0	45	.50	.20	46.0	2.00	22.3	.538	.024	.0058
13	100°	53	0.9	45	.67	.02	42.7	1.84	23.1	.502	.023	.0078
14	100°	53	0	45	88.4	19.2						1.0(a)

Possibly this information could be obtained by detailed analysis for acetyl and propionyl iodides, but such an analysis would scarcely be practical. In view of this uncertainty, work at this wavelength was abandoned in favour of the less energetic 3130 Å, where β is probably very low.

A notable point in these results concerns the low values of quantum yields. It will be apparent from the above analysis that the overall quantum efficiency of radical production, ΦR; is given by:

$$\Phi R = \frac{x + y}{E} = \Phi EtI + \Phi MeI - \Phi CO$$

where E = no. of einsteins absorbed.

All previous considerations would indicate that $\Phi R = 1$ at 2537 Å. On the two results available, the observed values of ΦR calculated as above were .53 and .50. The discrepancy appears to be beyond experimental error, but it may be due to the presence of mercury vapour. This would cause increased absorption in calibration runs owing to the excitation of resonance radiation, but in the presence of iodine, mercury would be removed as mercuric iodide, so that there would be no compensating effect in iodine runs.

Experiments at 3130 Å

The results of the first series of experiments at 3130 Å are set out in table IV. Only those experiments are reported in which successive fractions of each iodide exhibited constant specific activity, within a reasonable and non-systematic error. In general three such fractions were taken off at the boiling point of each iodide, and they did not vary in specific activity more than was reasonably attributable to counting errors. This was not always so, however, e.g., in one unreported run the counting rate of the ethyl iodide product rose by some 20% in each of three successive fractions, even though the boiling point of each was nearly constant. The reason for this is not clear, one would suspect the presence of some highly active product of slightly higher boiling point such as acetyl iodide, but it is difficult to see how any such product could have evaded the separation system used in analysis.

Again there is some uncertainty in the quantum yields, for the two calibration runs (10 and (14) differ by 14% in yield of CO, although the lamp was run under conditions as constant as possible. Relative yields are more reliable, though the good agreement between the three observed ratios of ethyl to methyl iodide is to a large extent fortuitous.

Discussion of results

Since the yield of CO is extremely low, the observed EtI/MeI ratio gives a valid measure of the relative probability of reactions (a) and (b). Results show that this ratio is 22:1 in favour of reaction (b):

$$CH_3COC_2H_5 \longrightarrow C_2H_5 + CH_3CO \qquad \ldots\ldots\ldots \text{(b)}$$

Although subject to an undeterminable experimental error, the results indicate that Φ R is significantly below unity, averaging only 0.55. This result is so surprising and contrary to assumptions that a further series of experiments was planned to investigate the point. These experiments will be discussed in the following chapter; there is little to be gained from any further discussion until their results have been presented.

Summary

The results show that reaction (b) predominates over (a) in the primary process at both wavelengths. At 3130 Å, the ratio is 22:1 in favour of (b); at 2537 Å, the ratio falls to approximately 2.6:1.

Observed values of radical yields are considerably below unity, but this may be due to experimental error.

V FURTHER EXPERIMENTS ON METHYL ETHYL KETONE

In view of the low values of quantum yields obtained in previous experiments, the analytical technique was modified with the object of minimising possible sources of loss of alkyl iodides. In addition, a more rigorous purification of the ketone was effected.

Revised method of purification

F. O. Rice (53) has shown during absorption measurements on various ketones that small (·5%) amounts of unsaturated and cyclic compounds may be present even in repeatedly fractionated samples of ketones. These components may have absorption coefficients some 500 times as large as that of the ketone itself, and consequently may interfere with photolytic experiments in spite of their low concentrations. Their presence is often dedected by treating the ketone with neutral $KMnO_4$; if the permanganate is sufficiently dilute, no visible discolouration should occur in 15 minutes at room temperature, but such impurities may cause a significant reduction. Removal of these impurities is no easy process, it would seem to require some chemical step such as bisulphite treatment in addition to repeated fractionation.

A permanganate test on the ketone used in previous experiments was definitely positive; reduction was visible in about one minute, and soon went to completion. Accordingly further purification was carried out along the following lines:

(1) An attempt was made to purify the ketone by means of the sodium iodide addition complex described by Shipsey and Werner (63) for acetone. Well defined crystals were obtained; these could be washed efficiently, but the overall yield of ketone recovered was less than 5%

(2) Several portions of ketone were purified as far as possible with

the bisulphite process. From large quantities of the well washed complex a small sample of ketone was obtained; this was sufficient for one fractional distillation, and the middle third of the distillate was retained for use.

(3) Once fractionated ketone was treated with dry, finely ground $KMnO_4$ in successive portions until no further rapid reaction occurred. The product was freed of residual $KMnO_4$ by vacuum distillation, and was then twice fractionated.

Process (3) yielded a product which was initially entirely negative in $KMnO_4$ reaction. On storing it gradually reverted, and finally displayed a small but constant reaction to the $KMnO_4$ test. The following table presents the results of observations of refractivity and permanganate reaction on the above products, after that from process (3) had attained a constant reaction.

Ketone	N_d20	$KMnO_4$ reaction
Original methyl-ethyl ketone as used in first experiments	1.37871 ± .00005	1 minute
Product of process (2)	1.37897 "	8-10 minutes
Product of process (3)	1.37892 "	8-10 minutes

$KMnO_4$ reaction is expressed as the time required to obtain a visible reduction, on mixing 2cc. of ketone with 10cc. of faintly pink, freshly prepared $KMnO_4$ solution.

It will be seen that processes (2) and (3) yield products which are practically indistinguishable, so that one may place some confidence in their purity. The product of process (3) was used for further experiments. It was dried over $MgSO_4$ without alteration in its optical

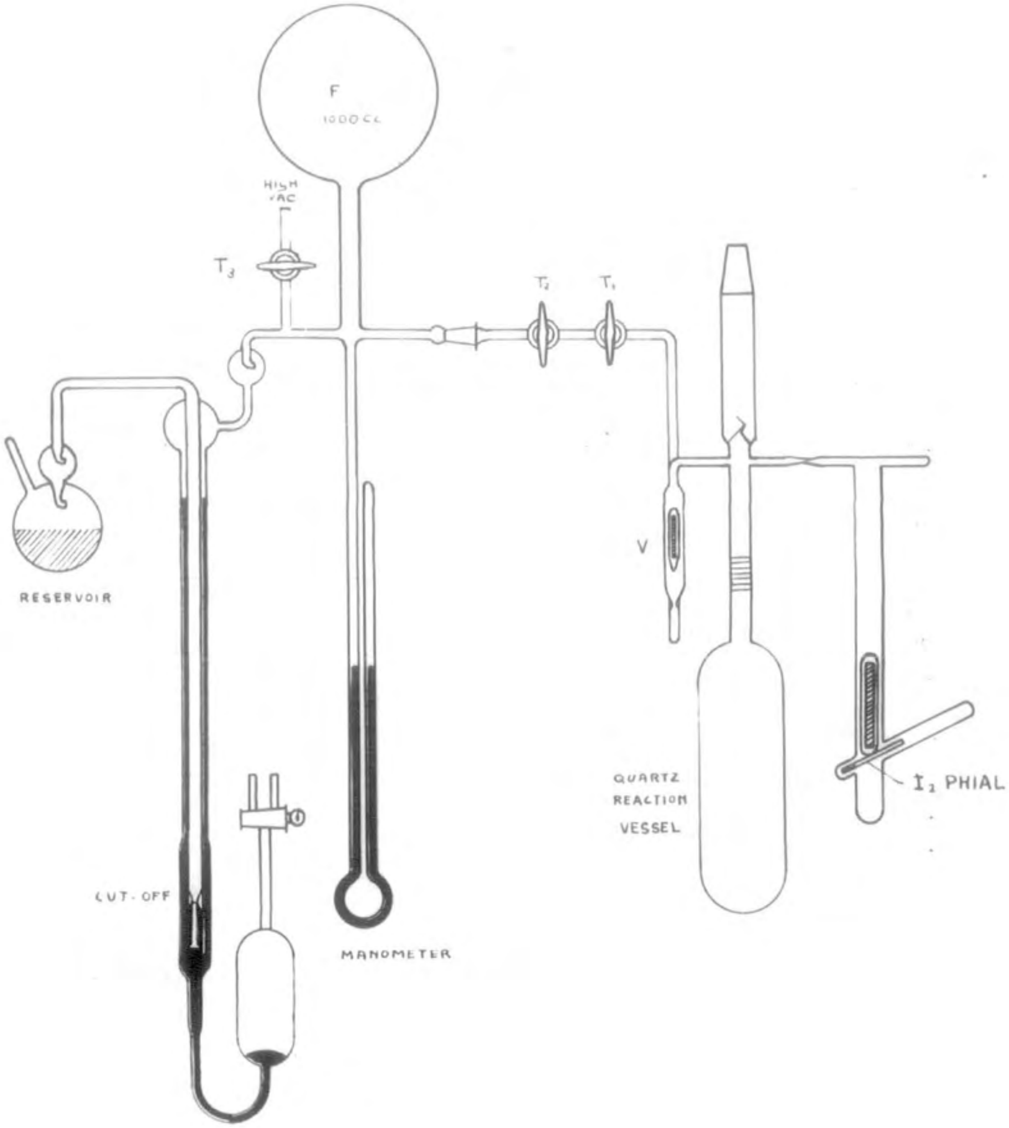

F
1000 CC
HIGH VAC
T3
T2
T1
RESERVOIR
V
QUARTZ REACTION VESSEL
I2 PHIAL
CUT-OFF
MANOMETER

FIGURE 5.

properties or $KMnO_4$ reaction; finally it was degassed and vacuum distilled into a reservoir.

The same process was used for the purification of acetone. The product was slightly more positive in permanganate reaction than was the final methyl ethyl ketone, but this is probably attributable to a genuine difference in reactivity of the pure ketones.

It is worthy of note that Trotman-Dickinson and Steacie (68) have found in some recent experiments on the direct photolysis of acetone that its behaviour is insensitive to its method of purification. They obtained identical results from three samples, two of which were simply distilled, the third was distilled from permanganate.

Method of filling reaction vessel

Since the proposed experiments were to be carried out at 3130 Å, the presence of small traces of mercury vapour should not be objectionable. In view of this, a mercury cut off was used to isolate the ketone reservoir since it enables complete protection from stopcock grease. The filling system shown in figure V was designed to enable mixing the reactants as vapours rather than allowing contact in the liquid state. Iodine was sublimed into the reaction vessel first, then with the well ground valve V firmly closed, the vessel was warmed to 60°, vapourising the iodine. Ketone vapour was then admitted from the volume calibrated ballast flask; finally the reaction vessel was removed, after closing taps T1 and T2; it was then quickly wiped dry and placed in a preheated furnace. The system requires the use of a greased tap to close the reaction vessel, but this was used only in filling operations, and the products were extracted through a break seal as before, thereby reducing contact of the products with tap grease to almost negligible proportions.

Photolysis of acetone/iodine mixtures at 3130 Å

Experiment No.	Series	Temperature	Ketone pressure (corrected to100°)	Iodine pressure	Time of irradiation (minutes)	Intensity of Irradiation			Yield x 10^7 gm moles				Φ CO	Φ MeI	Q † (arbitrary units)
						I_o* (arbitrary units)	I_t* (arbitrary units)	I abs.x 10^{-12} quanta/cc/sec	CO	Residual gas (CH_4)	MeI	CH_3COI			
21	D	100°	61 mm.	1.3	51	2.15		1.15	.124	0.18	3.49	N.D.	.0084	.215	
22	"	120	60	0	43	2.46			15.6	3.8			1.0(a)		1.49
23	E	120	62	0	15	77			41.7	9.0			1.0(a)		3.60
24	"	100	62	0.8	73.5	55.8		8.05	N.D.	N.D.	40.5	N.D.		.270	
25	"	120	61	0	20	58			41.6	9.2			1.0(a)		3.62
26	F	100	64	1.2	Blank - No Photolysis				0.02	0.02	0.005	.1			
27	"	120	63.5	0	29	44			69	13.3			1.0(a)		
28	"	100	64	3.6	88	47.5		10.30	0.5	0.18	37.8	1.1	.0022	.164	
29	G	120	60	0	9	77	57		51.2	8.2			1.0(a)		7.45
30	"	100	61.5	0.45	10	87	63.5	13.8	0.36	0.07	16.9	2.4	.0056	.262	
31	"	120	61	0	10.25	84	61		63.4	9.4			1.0(a)		7.36
32	"	100	61.5	0.45	10	76	55	12.05	0.35	0.04	14.3	N.D.	.0061	.254	
33	H	120	63	0	10	43	31		30.7	7.8			1.0(a)		
34	"	100	62.5	2.43	10	50	36	7.62	0.076	0.05	7.12	8.2	.0013	.200	
35	I	120	198	0	5	71.0	26.3		53.4	16.6			1.0(a)		1.52
36	"	120	198	0	5	60.2	22.1		44.4	14.1			1.0(a)		1.49
37	"	100	199	.92	5	57.8	21.2	18.25	0.05	0.07	4.48	N.D.	.0012	.105	
38	"	100	200	.95	10	55.4	20.5	17.73	0.07	0.06	9.53	13.0	.0008	.115	
39	J	120	16.3	0	20	98	90		29.5	2.6			1.0(a)		
40	"	100	16.3	0.53	19	89.5	82	2.92	0.50	1.1(?)	12.7	.69	.[illegible]20	.490	
41	K	120	16.3	0	20	76	70		24.8	3.0			1.0(a)		
42	"	100	15.5	1.93	21.5	74	68.5	2.44	0.42	0.3	9.53	.53	.017	.390	

* These units are constant only for experiments in the same series

† Q = Yield of CO/ Io.t. (See p. 74)

Irradiation apparatus

~~The apparatus used was essentially the same as previously described,~~ but an attempt was made to measure the output of the lamp during photolysis in addition to maintaining it as constant as possible. Obviously this is not entirely practicable unless the intensity transmitted through the reaction vessel can be measured, and a vessel with plane ends was ordered to enable such measurements to be made. Since its delivery was long delayed, some experiments with the old vessel were carried out. A quartz window was let into the rear of the furnace, so that estimates of the intensity before and after each experiment could be obtained when the reaction vessel was removed. Measurements were made with a selenium photo-cell connected directly to a microammeter. A mean of these readings was taken as a comparative estimate of intensity from one run to another, and such readings are recorded directly as intensity in the tabled results.

A more rigorous filtration system was adopted for isolation of the 3130 Å line, based mainly on the addition of K_2CrO_4 to the original system. K_2CrO_4 has a peak in its transmission curve which corresponds very closely to the desired wavelength, in particular it removes the neighbouring group of lines in the mercury spectrum at 3660 Å, but only at the cost of some considerable loss in transmission of the 3130 Å line itself. The system finally selected is closely in agreement with that recommended by Davis and Hunt (14) and more recently by Kasha (36). Its components were as follows:

(1) $NiSO_4.7H_2O$, c 63.4 g/l. was placed in the 250cc quartz collimating flask.

(2) A 1cm. quartz walled filter of K_2CrO_4 at 0.242g/l. was followed by

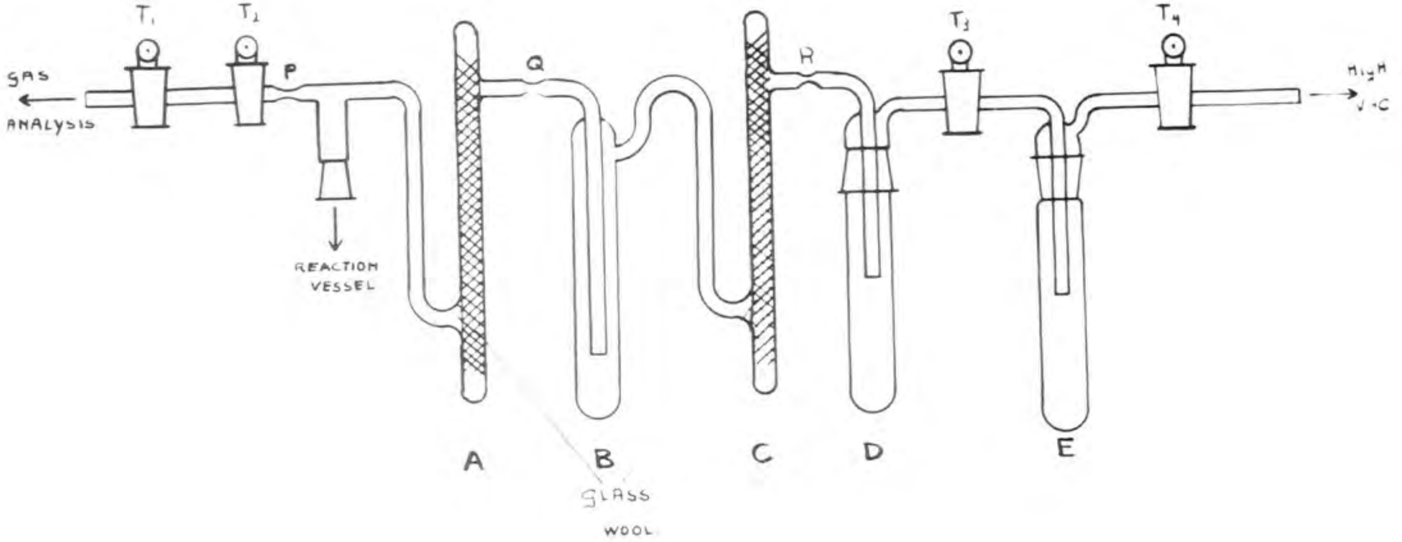

GAS ANALYSIS
T₁
T₂
P
REACTION VESSEL
Q
R
T₃
T₄
HIGH V.C
A
B
GLASS WOOL
C
D
E

FIGURE 6.

(3) A 1.6cm. filter of potassium hydrogen phthalate at 3.16 g/l. with both walls of Chance OX7 glass 2mm. thick. This glass transmits 90% of all wavelengths in the region 2900 Å to 3800 Å, and cuts off very sharply on either side of this region. Consequently it acts as a very convenient filter for removal of visible radiation, and also short wave ultra violet. It is a considerable improvement on the $NiSO_4/CoCl_2$ filter previously used, since this could only act efficiently at the expense of 50-80% loss in transmission of the desired wavelength.

Analysis of products

Gas analyses were made as before, but the iodide analysis system was reduced in size and greased taps were eliminated at the expense of yet more make and break seals. The apparatus is shown in figure VI. As before, the reaction vessel was connected with a greased ground joint. For these and all later experiments, a special grease of a type developed by Dr. L. Tordai in this laboratory was used for this joint. The grease is composed of mannitol, starch, and glycerol in the ratio of 1:2:6. Its tendency to absorb organic vapours is much less marked than that of Apiezon greases, and it may be warmed considerably without seriously affecting its properties. It was used in certain joints mainly on account of its latter property, since it enables the joint to be flamed and degassed more readily.

The procedure in iodide analysis was essentially the same as before. After removal of permanent gases, the constriction P was sealed off, the residual products were twice distilled through glass wool traps at -30° and finally collected in D at -180°. Carriers were degassed, and distilled into D as before. The times of such distillations were only very slightly more than required to effect transfer of the ketone; by these means iodine

TABLE V

Revised Photolysis of Methyl-ethyl ketone/iodine mixtures at 3130 Å

Experiment No.	Series	Ketone	Temperature	Ketone pressure (corrected to 100°)	Iodine pressure	Time of irradiation	Intensity of irradiation (arbitrary units*)	Yield x 10^7 gm. moles.				$\frac{EtI}{MeI}$	Φ EtI	Φ MeI	Φ CO
								CO	Residual gas	EtI	MeI				
15	A	M	101°	48mm.	1.0mm.	45mins.	N.D.	.25	.09	17.3	.91	19.0	N.D.	N.D.	N.D.
16	B	A	120°	60 "	0	45 "	3.34	17.4	8.0						1.0(a)
17	B	M	100°	47 "	1.0 "	110 "	3.16	.067	.06	16.4	.78	21.2	.48	.023	.0019
18	B	A	120°	61 "	0	48	3.20	14.4	8.8						1.0(a)
19	C	A	120°	61 "	0	40	2.84	14.1	7.3						1.0(a)
20	C	M	100	50 "	1.1 "	40 "	2.56	.03	.02	9.0	.4 ± .1	22	.71	.031	.0023

* These units are constant only for experiments in the same series.

M = Methyl-ethyl ketone A = acetone.

was completely removed, and in most - but not all - cases acetyl iodide was also held back. No attempt at removal of HI was made. It cannot be fractionated from methyl iodide with any success, and the use of KOH may involve the loss of other products by absorption. However, there is no reason for its formation in anything more than negligible proportions.

Estimation of quantum yields

As a check on the values of quantum yields obtained in previous experiments, a different scheme was adopted for estimation of these quantities. Calibration runs were made on acetone at 100°C, under which conditions the value of ϕ_{CO} is known to be unity. Available data indicate that the absorption coefficient of methyl ethyl ketone is 1.23 times larger than that of acetone at 3130 Å. Accordingly, the pressure of acetone in calibration runs was increased in the same ratio, so that the same percentage absorption would result. This ratio of 1.23 has been derived after suitable corrections from Rice's (53) studies on ketones in the liquid phase. Due consideration was also given to some measurements on diethyl ketone in the gaseous phase which Dr. Dorfman (17) has kindly made available. These measurements show that the corresponding ratio of ϵ diethyl ketone/ϵ acetone is 1.35. The value adopted for methyl ethyl ketone is an approximation only, it may be subject of ± 5 to 10% error; nevertheless it does provide an independent check on previous determinations of quantum yields.

Results

The results of this brief series of experiments are set out in table V.

Constant specific activity from successive fractions of ethyl iodide was obtained only when the vacuum distillations at -30° were properly adjusted. In one unreported run the ethyl iodide displayed a marked increase in activity in successive fractions; an effect which is almost certainly attributable to acetyl iodide.

Once again, the absolute values of quantum yields are subject to considerable error, owing very largely to the necessity for long runs with the new filtration system, and consequent long term variations in intensity, variations which were difficult to allow for with the technique in use. Nevertheless, the results agree in general with those found initially. The ratio of methyl to ethyl iodide in the products is approximately 21:1, and the overall quantum yields appear to be significantly below unity in spite of the large experimental error.

In view of this, it was decided to reinvestigate the photolysis of acetone, in an attempt to confirm Gorin's results. This work will be discussed in the following chapter.

VI STUDIES OF THE PHOTOLYSIS OF ACETONE

Since all previous work has failed to confirm Gorin's conclusion that the overall quantum efficiency of radical production is nearly unity, it was decided to repeat his work on acetone. At the same time any uncertainties in estimates of quantum yields are largely removed, since Φ CO in the direct photolysis is known to be unity under appropriate conditions.

This chapter deals exclusively with experimental procedure and results, a full discussion of the reasons for these experiments and their interpretation is reserved for the final section.

Preparation of materials

Acetone was purified as described on page 63.

Acetyl iodide was prepared by reacting dry hydrogen iodide with acetyl chloride in the cold (Staudinger (60)). I am indebted to Doctors Carson and Skinner (10) for details of their elegant method of preparing dry hydrogen iodide by refluxing iodine with tetrahydronaphthalene. The crude acetyl iodide was freed from excess acetyl chloride by a preliminary distillation at atmospheric pressure. It was then once fractionated at 4cm. pressure in a small Fenske packed column. About the middle 2/3 of the acetyl iodide distillate was retained, shaken with mercury to free it of iodine, and finally distilled under high vacuum into a reservoir in which it was sealed off. Attached to this reservoir was a system of some 12 receivers, into which portions of the product could be distilled as required for use and sealed off. The product was initially almost colourless, it became slightly yellow due to iodine formation after two months storage. Two determinations of its iodide content yielded results equivalent to 98% of the theoretical value for acetyl iodide.

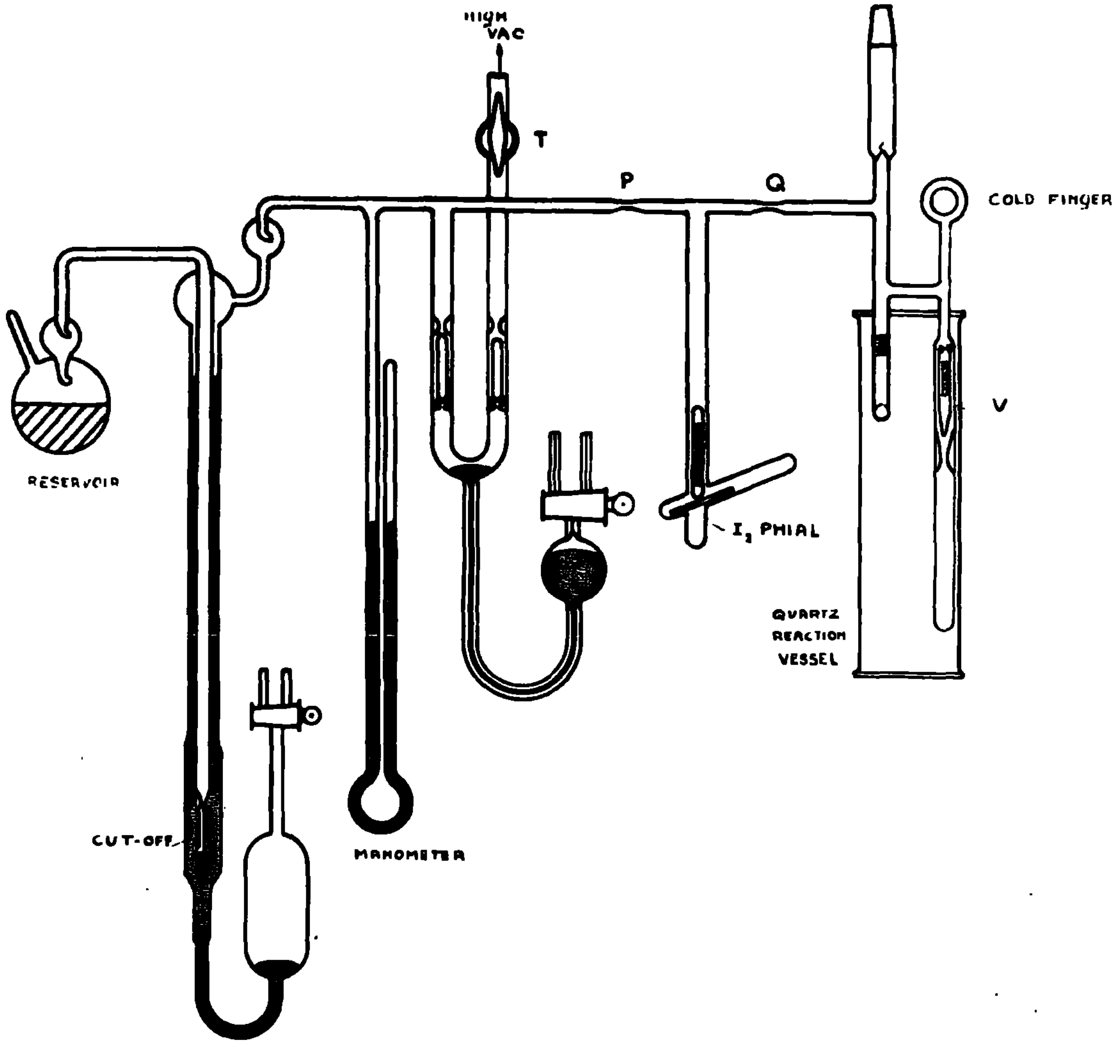

HIGH VAC
T
P
Q
COLD FINGER
RESERVOIR
V
I$_2$ PHIAL
QUARTZ REACTION VESSEL
CUT-OFF
MANOMETER

FIGURE 7.

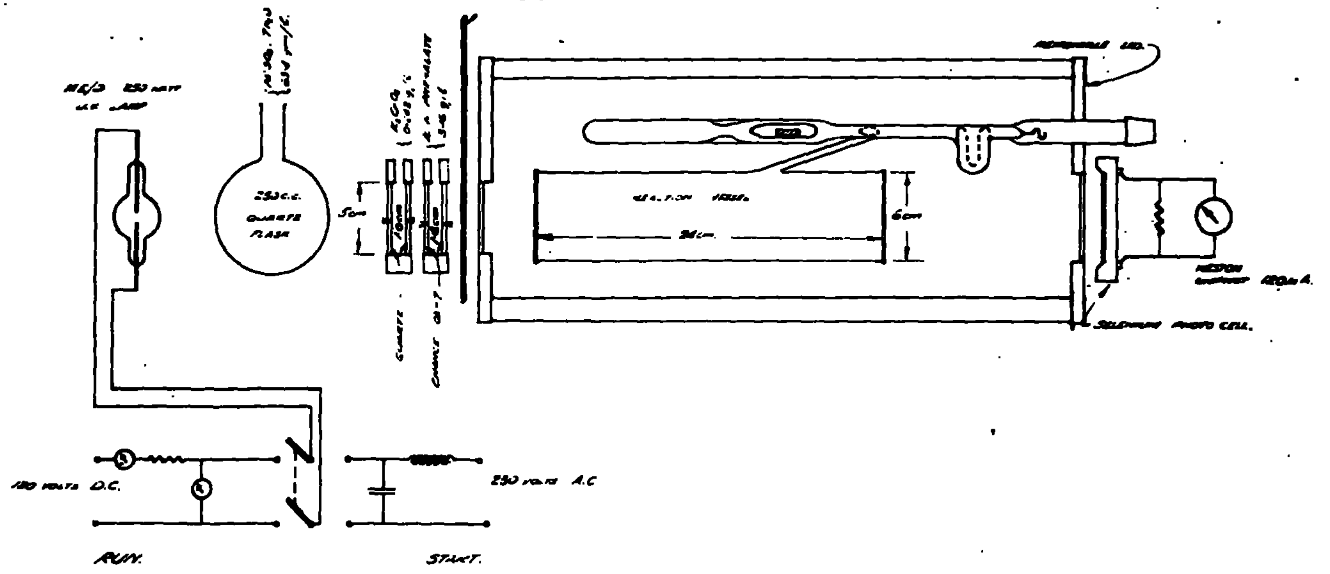
Carbon dioxide was purified from commercially available "dry ice". It was sublimed through a P_2O_5 tube to remove water, then was repeatedly fractionated at -30° into a receiver at -180°; about the middle 80% of the gas was retained at each stage. Finally it was freed from permanent gases by condensation at -180°, followed by prolonged evacuation, and was stored in a 3 litre reservoir sealed with greased taps.

Reaction vessel and method of filling. Fig.VII

All except the first few experiments in this work were carried out with a new cylindrical reaction vessel with plane polished ends. This was filled with reactants by means of the apparatus shown in figure VII. The normal routine was as follows: The reaction vessel was cleaned in chromic acid after each run, then washed and dried by complete evacuation. The vessel was then filled with dry air, and sealed onto the apparatus as shown. The system was evacuated, degassed, and left overnight under vacuum prior to filling operations. These were essentially as used before, with the addition of a second mercury cut off to protect the ketone from any tap grease, and to enable a completely dry product to be obtained. Acetone was admitted to the desired pressure, and condensed in the side-arm below the valve V. Iodine was then sublimed in and condensed in the reaction vessel with the aid of a piece of cotton wool immersed in liquid nitrogen. Finally the vessel was sealed off at Q, warmed to 60° with the ketone section still frozen below the closed valve V, and then placed in the furnace enabling the acetone to mix with the iodine, already largely vapourised.

Irradiation apparatus. Fig.VIII

At 250 watt medium pressure mercury burner type ME/D, as supplied by B.T.H., gave a much higher output of the desired wavelength. The lamp



— 3130Å IRRADIATION APPARATUS. —

FIGURE 8.

was run at 50 volts and 5 amps off a direct current supply. The arc was struck with the A.C. system shown in figure VIII, the lamp was then switched over to the more stable D.C. system for continuous running. The filter system was precisely as previously described.

Transmitted irradiation intensities were measured with a selenium photo cell in the position shown. The cold finger, more clearly depicted in figure VIII, afforded a convenient method of freezing out reactants, and thus measuring I_o, the intensity of irradiation in the absence of absorbing gas. For runs in the presence of iodine, I_o could be measured only on completion of the photolysis, but in all cases the transmitted intensity, I_t, was measured during the photolysis. Slight variations in lamp emission between the times of measuring I_o, and I_t were corrected for on the assumption that the emission is directly proportioned to the total wattage consumed by the lamp, as read on voltage and current meters. In practice, such variations were small, and indeed after the first few runs measurements of I_o were regarded more in the nature of a check than anything else. Since the ketone pressure was always the same as in calibration runs, the ratio I_o/I_t was constant for each series of experiments, and comparisons of I_t were perhaps more reliable than those of I_o.

Analysis of products. Fig.IX

Gas analyses were made as before.

The iodide analysis procedure was modified in an attempt to estimate acetyl iodide. Since this product is in part retained by the previous methods of removal of iodine, it was decided to substitute a silver powder tube for the two fractionations at -30°. The system is shown in figure IX. Condensible products were simply distilled through the silver powder

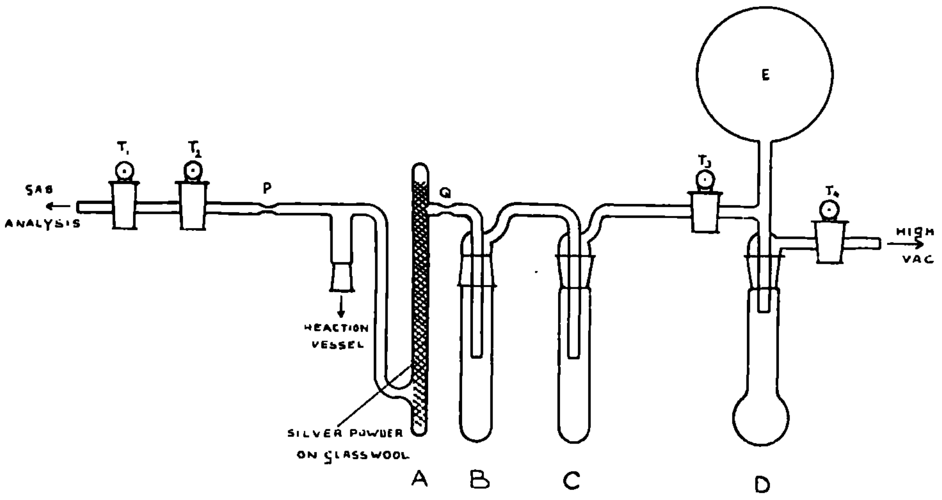

T₁
T₂
GAS ANALYSIS
P
REACTION VESSEL
SILVER POWDER ON GLASSWOOL
Q
E
T₃
T₄
HIGH VAC
A
B
C
D

FIGURE 9.

tube A into B, and were then diluted with a mixture of carriers, including 2 cc. of acetyl iodide. These carriers were degassed in D, and then distilled onto the condensed products in B, after the usual precaution of sealing off the constriction Q. B was then warmed to -10°C, its contents were thoroughly mixed by judicious local warming and shaking, and two thirds of its contents were next distilled into C, still maintaining B at -10°. By means of this rough fractionation, most of the methyl iodide and a large portion of the ethyl iodide were collected in C, while B retained mainly acetyl iodide. Air was admitted, and the two fractions were treated as follows:

The alkyl iodide fraction in C was freed of acetyl iodide by mixing with an equal volume of cold water. Hydrolysis of the acetyl iodide is complete in a few minutes, and provided the mixture is kept cooled, alkyl iodides are not affected. The aqueous layer was mechanically separated, residual alkyl iodides were twice washed, roughly dried with a large quantity of $CaCl_2$, freed of traces of iodine by shaking with silver powder, and finally fractionated into their two components as usual, using a little toluene and methylene iodide as hold back carriers for any less volatile iodides that may be present.

The acetyl iodide fraction in B was distilled in a small helix packed column at 4cm. pressure, with the addition of 1cc. of methylene iodide as hold back carrier. No attempt was made to obtain pure samples of alkyl iodides in this distillation, in any case they were minor components. Four fractions of acetyl iodide were taken off under nearly constant conditions, normally at 30°C and 4cm. pressure. Such fractions were nevertheless not pure; they were treated further by aqueous hydrolysis, washed with inactive ethyl iodide to remove traces of dissolved active alkyl iodides, and were then converted to silver iodide.

It was not entirely practical to separate a mixture of all the carriers in one fractionation; pure samples of acetyl iodide could not be obtained at the high temperatures (105°) required at room temperature owing to decomposition. The above separation appears rather drastic, nevertheless it does not lead to any significant exchange in the short period of aqueous treatment as the following experiment shows:

Experimental verification of the method

3cc. of highly active methyl iodide was mixed with 2.6 of inactive ethyl iodide, 1.6cc of propyl iodide, 0.12cc. of acetone (being the amount normally used in each run), and 2.3cc. of acetyl iodide. The mixture was placed in C, degassed, and then treated as described above. The activity observed in the separated components is shown below:

Component	Total Activity in Component
Initial methyl iodide.	100 arbitrary units.
Recovered methyl "	101.4 " "
" ethyl "	1.6 " "
" propyl "	0.1 " "
" acetyl "	0.7 " "

Within experimental error, the recovered methyl iodide has the same activity as that originally used; furthermore the originally inactive components display in general an almost negligible activity, so that the method appears to be justified. The activity of 1.6 units in the ethyl iodide product is due to imperfect fractionation rather than exchange. Such an effect was noticed in subsequent experiments, it was reduced to almost insignificant proportions by a slight modification in the fractionating column.

Results

Results are set out in the following tables. In general they are treated as before, but certain points require some clarification.

A. Photolysis of acetone iodine mixtures at 3130 Å. Table VI

Intensity of irradiation

It must be stressed that while values of I abs. are expressed in quanta absorbed per cc. per second, the units for I_o and I_t are quite arbitrary, and are in fact the mean currents observed in the photocell. Further, the absolute value of these units was varied from time to time owing to changes in the geometry of the system, the resistance in parallel with the recording microammeter, and other factors. These units are constant however, for all experiments in the same series, and have been used in calculation of quantum yields.

Reproducibility of calibration runs

The quantity Q is a measure of the reproducibility in calibration runs. It is defined as follows:

$$Q = (\text{Yield of CO})/I_o\ (\text{time of irradiation}).$$

Accordingly, Q should be constant for all calibration runs in the same series, subject only to corrections for pressure variations; corrections which in general are negligible except at low pressures where I abs. $\propto I_oP$. However, since the units of I_o are constant only in each series, the constancy of Q is equally limited.

Experimentally, the constancy is verified to within about 3%, so that this may be taken as a reasonable estimate of the accuracy on determination of absorbed quanta. The first three series were performed with the previous reaction vessel and technique, the error here is much larger, and may be as large as ± 20%.

Quantum yields of alkyl iodides

Relative values of ΦMeI are probably correct to within ± 5-10% for all runs after series F. Absolute values are of similar accuracy since they depend only on the well established assumption that ΦCO = 1 in the direct photolysis.

It is not possible to give definite figures for the ethyl iodide yields since the specific activity of ethyl iodide fractions was not constant, tending to decrease somewhat with successive fractions. In general however, the activities observed were very low, and if one takes the final fraction as representative of the yield, then the results indicate that ΦEtI is less than 1% of Φ MeI, and in fact is zero within experimental error.

Absorption measurements

Analysis of the observed values of I_o and I_t for runs with the same pressure of ketone indicate that the percentage absorption of incident radiation is independent of the presence of iodine, as has been assumed. No very high accuracy can be claimed for this result, but it was confirmed by some absorption measurements on iodine alone.

The reaction vessel was filled with iodine equivalent to 2mm. pressure at 100°, and measurements of transmitted intensity were made (a) with the iodine vapourised at 100° and (b) with the iodine condensed in a side arm. Frequent alternations of (a) and (b) failed to show any significant absorption within a 1% experimental error, due mainly to drifts in the emission of the lamp. The percentage absorption by the ketone varied from 10% at 16mm. to 63% at 200mm. so that absorption by iodine is comparatively negligible. This result is in agreement with the

TABLE VII

Photolysis of Acetone/Carbon Dioxide Mixtures at 3130 Å and 120°C.

Experiment No.	Series	Acetone pressure (corrected to 100°)	CO_2 pressure	Time of irradiation (Minutes)	I_o arbitrary units *	I_t arbitrary units*	Yield X 10^7 gm.moles.		% absorption of irradiation.	Φ CO
							CO	Residual gas (CH_4)		
43	L	202mm.	0	5	78	30.7	63.4	14.2	60.7	1.0(a)
44	L	194 "	193mm.	5	78	30.5	56.0	17.6	60.4	.92
45	L	0	195	5	89	89	.01	.05	0±1	
46	M	195	0	5	91	36.7	62.3	20.2	59.7	1.0(a)
46A	M	195	195	5	84.5	34.6	54.7	16.8	59.2	.945

*These units are constant only for experiments in the same series.

observations of Rabinowitch and Wood (52) who have shown that the absorption coefficient of iodine tends to very low values at wavelengths shorter than 4000 Å, though they did not investigate the spectrum beyond this wavelength.

B. Photolysis of acetone-carbon dioxide mixtures at 3130 Å. Table VII

Method of filling

CO_2 was admitted to the reaction vessel to the desired pressure after acetone had been frozen out in the side arm, below the closed ground valve. Subsequently the CO_2 was also condensed and the reaction vessel was sealed off and irradiated in the normal way.

Analysis of gases

Since CO_2 is quantitatively frozen out at -180°, it does not interfere in any way with the normal analysis. Extra care was taken to ensure complete extraction of the products, involving two cycles of thawing and refreezing.

Absorption of irradiation

The results show quite definitely that the CO_2 behaved entirely as an inert gas. Thus:

(a) The CO_2 alone showed no absorption of radiation, and yielded no uncondensable products.

(b) The percentage absorption in acetone was unaltered in the presence of CO_2.

C. Photolysis of acetone-iodine mixtures at 2537 Å. Table VIII

Method of filling

A fresh sample of acetone was distilled into the reservoir shown in figure X. Since it could not be stored behind a mercury seal, an ordinary greased tap was used; the vapour was partially protected from tap grease with a ground valve as shown. In addition the reservoir was kept permanently cooled in dry ice except when required for use. During evacuation and filling operations, the system was protected from mercury vapour with the aid of a gold foil tube and liquid nitrogen trap immediately adjacent to the high vacuum line.

Ketone pressures were read on a mercury manometer but this was normally isolated behind a closed tap, and measurements were made in such a way that gas was always run into the manometer and never out of it. Furthermore, any small amounts of gas that may have escaped this procedure must pass over the gold foil before entering the reaction vessel.

Apart from these precautions, the method of filling was the same as used previously.

Irradiation technique

In principle, the same system was used as described initially for methyl ethyl ketone on page 48.

The lamp was run from a 1000 V. transformer as before, but the primary voltage for the transformer was obtained from a stabilised voltage supply, with a fixed resistance in the primary circuit. Measurements of voltage and current showed that the wattage consumed by the lamp remained constant to better than 1%, in spite of 5-10% individual fluctuations in each variable.

Results of calibration runs indicate that the overall reproducibility was constant to within 5-10%; if one omits experiment 50 the figure becomes nearer 3%, and in particular the reproducibility on low pressure runs was within this estimate.

Accuracy of quantum yields

In view of this degree of reproducibility, and because of the above

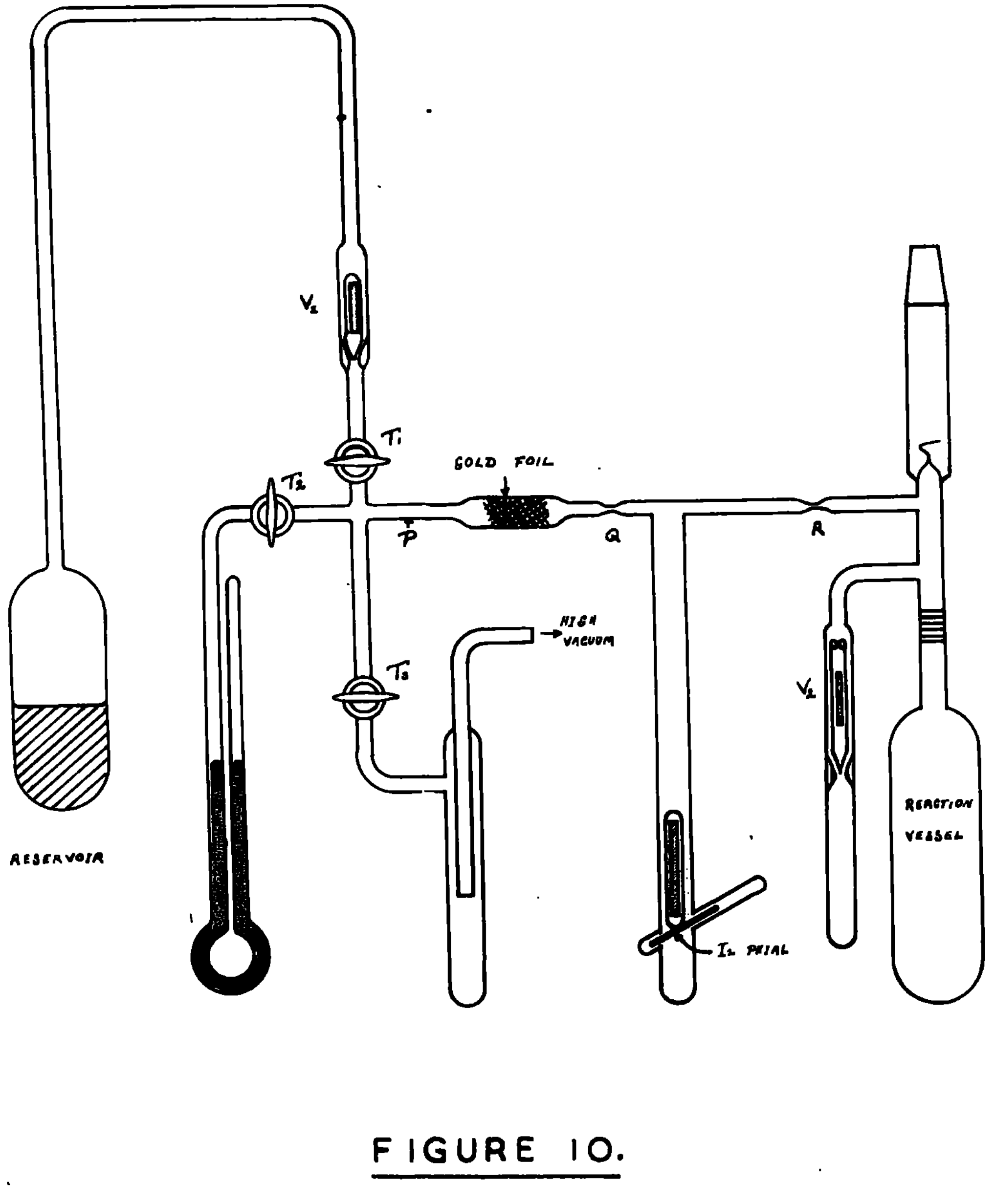

V₁
T₁
T₂
GOLD FOIL
P
Q
R
HIGH VACUUM
T₃
V₂
RESERVOIR
REACTION VESSEL
I₂ PHIAL

FIGURE 10.

precautions it was assumed that mercury vapour was completely eliminated. However, the observed quantum yields at low pressure were very much lower than one would expect. Furthermore, in calibration runs at 200mm. the yield of CO per minute of irradiation was raised by a factor of only 1.8 above the corresponding value at 20mm. Considerations based on published absorption coefficients at 2537 Å would require a factor of 4 rather than 1.8, thus indicating an abnormally high degree of absorption under experimental conditions. This points very strongly to the presence of mercury vapour in spite of the above precautions, so that one is compelled to question the validity of the reported quantum yields. To test this point, the final calibration run (55) was carried out under more rigorous conditions. The gold foil was removed and baked out before replacing. During filling operations, the acetone was condensed immediately after pressure measurement in a side tube, and was distilled from this tube at -40° into the reaction vessel, passing over the gold foil in the process. Nevertheless the yield of CO was not significantly lowered, as can be seen from the table of results.

To reconcile these observations, one has to assume that the most minute traces of mercury vapour will cause a saturation resonance effect. Otherwise, one cannot account for the reproducibility of calibration runs, for it is surely inconceivable that precisely the same amount of mercury should have been introduced in each case.

With considerable misgiving these experiments were abandoned at this point. The true quantum yields of alkyl iodides are almost certainly higher than those reported, yet it would seem to require a very elaborate mercury removal system to obtain genuine readings. At this stage of the work, time did not permit such an undertaking. In any case the main

TABLE IX

Effect of Visible Radiation on the Photolysis of Acetone/Iodine Mixtures at 3130 Å

Experiment No.	Series	Acetone pressure (corrected to 100°)	Iodine pressure	Temperature	Minutes of irradiation			Intensity of ultraviolet		Yield X 10^7 gm. moles.			R	Φ MeI	Φ CO
					Total ultra violet	Total visible	Mixed irradiation	I_o*	I_t *	CO	MeI	CH_3COI			
56	P	198mm.	0	120°	5	0	0	99	39	59.5			1.20		1.0(a)
57	P	200	1.02mm.	100°	5	0	0	115	45.5	.07	7.77	12.2		.109	
58	P	199	0	120°	6	4	4	68	25.5	54.8			1.31		1.0(a)
59	Q	201	0	120°	0	4	0	0	0	.02					
60	Q	200	.56	100°	0	4	0	0	0	.02	.08	.8			
61	R	198	0	120°	6	4	4	62	22	54.0			1.45		1.0(a)
62	R	200	1.24	100°	12	8	8	62	22.6		15.1	2.2		.137	
63	R	200	0	120°	6	0	0	62	22.6	55.8			1.49		1.0(a)

* These units are constant only for experiments in the same series

R = (Yield of CO)/$I_o t$

point of these investigations has been established even on the results available, for they show that the radical quantum yield is at least .65 at 200mm., a value very much higher than at 3130 Å, and possibly unity within experimental error.

D. Effect of visible radiation on the photolysis at 3130 Å. Table IX

Method of filling

Essentially the same system was used as described above for the 2537 Å work. It differs from that used in section A only in the use of greased stopcorks in place of mercury seals.

Irradiation

A collimated beam of visible light was obtained from a 250 watt tungsten lamp and condenser system. Such a source displays a continuous spectrum beginінng at 4000 Å at the short wave end; in particular it gives an intense output in the neighbourhood of 5000 Å. where iodine exhibits maximum absorption. The absolute output was not measured, nor was the absorbed intensity of this visible light, but on the basis of available absorption coefficients one would calculate that some 50-90% of the incident visible radiation would be absorbed by iodine vapour under experimental conditions.

The source was placed at the rear of the irradiation apparatus, 20cm. from the window at the end of the furnace, so that visible light entered the reaction vessel in a direction opposing that of the ultraviolet. Measurements of I_o and I_t were made as usual with the 3130 Å irradiation alone; visible light was then admitted in addition to the ultraviolet for the times specified in table IX, normally 2/3 of the total duration of the run. Finally, visible light was switched off, enabling a final check on I_t and I_o before turning off the mercury arc.

E. Yield of ethane in the presence of iodine

Ethane was not estimated in normal runs, since it is difficult, if not impossible, to separate it quantitatively from methyl iodide by physical means. Further, any such analysis involves thawing the products prior to recondensing at a higher temperature, with consequent losses by absorption on tap grease and formation of iodo ketone compounds in the liquid phase.

At -190°, ethane is ~~most~~ almost quantitatively frozen out; at -140° the ethane yield in two calibration runs (equivalent to about 80% of the CO) was completely extracted by 30 strokes of the toepler pump, while 6 strokes extracted 85% of it. At -130° a sample of pure, repeatedly degassed methyl iodide was found to exert a small but significant vapour pressure, such that approximately 3×10^{-8} gm. mole. of vapour were removed for each 6 strokes of the toepler pump.

Detailed gas analyses were made on two runs in the presence of iodine at different wavelengths. The results of these runs are set out in table X, together with the blank yields of gas extracted from pure methyl iodide under similar conditions. It will be seen that the yield of gas obtained from irradiated acetone-iodine mixtures at -130° is in neither case significantly above that extracted from methyl iodide alone. Since ethane yields, 100 times as large, were at least 80% extracted at even lower temperatures, it may be concluded that the yield of ethane was practically negligible in both cases; and certainly less than 1% of the einsteins absorbed.

The carbon monoxide yields are also worthy of note. The additional total gas extracted after thawing and refreezing the products at -190° was only of the order of 5×10^{-9} gm. mole, so that the normal procedure for CO

TABLE VIII

Photolysis of Acetone/Iodine Mixtures at 2537 Å and Constant Incident Intensity

Experiment No.	Series	Acetone pressure (corrected to 100°)	Iodine pressure	Temperature	Time of irradiation (minutes)	Yield X 10^7 gm.moles.				Φ CO	Φ MeI
						CO	Res.gas (CH_4)	MeI	CH_3COI		
47	N	205mm.	0	120°	5	68.8	11.0			1.0(a)	
48	N	204 "	0	120°	5	71.0	11.6			"	
49	N	208 "	1.90mm	100°	5	10.3	.65	58.7	2.5	.138	.78(?)
50	N	210 "	0	120°	5	85.1	12.2			1.0(a)	
51	O	22.6	0	120°	4	30.7	1.65			"	
52	O	22.0	0	120°	4	32.4	1.42			"	
53	O	21.7	2.0	100°	4	3.87	.26	13.7	.92	.126	.45(?)
54	O	22.4	2.0	100°	4	3.87	.13	13.8	1.23	.126	.45(?)
55	O	21.0	0	120°	4	28.7	.15			1.0(a)	

TABLE X

Ethane and other gas yields in the presence of iodine

Nature of Gas	Gm.moles. x 10^7 extracted from:		
	Photolysed acetone iodine mixtures		De-gassed Methyl Iodide
	3130 Å	2537 Å	
(a) $CO + CH_4$			
Gas extracted at -190°C with 20 strokes of the toepler pump.	0.05	4.00	
Additional gas extracted after thawing and refreezing the products at -190°C.	0.04	0.05	
(b) $C_2H_6 + CH_3I$			
Further gas extracted with 6 strokes of the toepler pump after thawing and refreezing the products at T°C.	0.47	0.35	0.30
T°C.	- 130°	- 135°	- 130°
Additional gas extracted with 6 strokes of the toepler pump after repeated thawing and refreezing at T°C.	0.30	0.10	0.23
Pressure of acetone.	200 mm.	20 mm.	
Pressure of iodine.	.92 mm.	2 mm.	
Quanta absorbed (einsteins x 10^7).	65	31	

analysis appears to be practically quantitative.

F. Yields of acetyl iodide

Experiments have provided abundant qualitative evidence for the formation of acetyl iodide, but by no means were the results reproducible. Yields varied from 5% of the methyl iodide yield to 156% of this quantity, and all attempts at improving these results were unsuccessful. It is perhaps significant that of the three reasonable yields, equivalent to 135%, 156% and 115% of methyl iodide, the first two were obtained at 200mm. and the last at 62mm. of acetone. Thinking that the low yields in other cases might be due to insufficient carrier to bring over the small amounts of relatively involatile acetyl iodide in the reaction vessel, an experiment was performed in which a little toluene was distilled into the condensed products before distillation. Nevertheless the yield of acetyl iodide was practically negligible, and later results on the less volatile methyl ethyl ketone in which acetyl iodide yields were still low, appear to invalidate this contention. No attempt at distilling acetyl iodide carrier into the reaction vessel before removal of iodine was made, since this would almost certainly lead to blank yields and exchange.

It is possible that acetyl iodide is decomposed on the silver powder during distillation from the reaction vessel, but a final run in which iodine was removed by fractional distillation without the use of silver powder gave no higher yields.

Gorin's contention that a large fraction of the acetyl yield appears as diacetyl was qualitatively tested in one experiment at 200mm. of acetone with 4mm. of inactive iodine. Photolysis at 3130 Å was prolonged until about 400 x 10^{-6} einsteins were absorbed, and the product was tested for diacetyl after removal of iodine by fractional distillation. The product was converted to its oxime with hydroxylamine, and was then tested for dimethyl glyoxime by addition of $NiSO_4$. No trace of the red nickel salt appeared, though preliminary tests showed that 4×10^{-6} gm.mole. of diacetyl could be detected by this method under similar conditions. It is estimated that the yield of methyl iodide in this experiment was of the order of 40×10^{-6} gm. mole. so that if any diacetyl were formed, it represented less than 10% of the methyl iodide yield.

It seems reasonable to assume that acetyl iodide is formed during photolysis in quantities equivalent to methyl iodide, but that it is in some manner decomposed during the analytical procedure. The three high yields support this contention; the fact that they were somewhat higher than those of methyl iodide may possibly be attributed to small amounts of iodo acetone.

VII FINAL EXPERIMENTS ON METHYL ETHYL KETONE

It will be recalled that previous experiments on methyl-ethyl ketone have established the ratio of the photolysis products, but that absolute values of quantum yields were determined only very approximately. More recent techniques have proved staisfactorily reproducible, and will also enable a direct experimental check on previous assumptions regarding the quantum yield of CO in the direct photolysis, and the ratio of absorption coefficients. Some experiments were carried out with this object, since a knowledge of the absolute quantum yields of alkyl iodides in this ketone would be interesting to compare with those found for acetone.

The experimental procedure was exactly as described in the previous section, using a freshly prepared sample of methyl-ethyl ketone. The ketone was stored in a reservoir isolated with a stopcock, and the same mercury free filling system was used as in the experiments on the effects of visible light.

Determination of ΦCO

The quantum yield of CO in the direct photolysis of methyl ethyl ketone was determined from comparison of the CO yields observed from this ketone and acetone.

The amount of radiation absorbed during an experiment may be expressed as:

$$E = Kt(I_o - I_t).$$

where E = number of einsteins absorbed.

t = minutes of photolysis.

I_o = intensity of irradiation transmitted through the empty reaction vessel.

I_t = transmitted intensity during photolysis.

K = an experimentally determined constant.

Further,

$$Q = E\,\Phi CO$$

where Q = gm.moles, of CO formed during photolysis.

and ΦCO = quantum yield of CO

Hence,

$$K = E/t(I_o - I_t) = Q/t\Phi CO(I_o - I_t)$$

Denoting the term "$Q/t\ (I_o - I_t)$" by "S", an experimentally determinable quantity, we have:

$$S = K\,\Phi CO.$$

Further, since $\Phi CO = 1$ in the case of acetone, we may determine K from calibration runs on acetone:

$$S \text{ acetone} = S_A = K.$$

Similarly, in the case of methyl-ethyl ketone, we have:

$$S \text{ methyl-ethyl ketone} = S_M = K\,\Phi CO_M$$

where the subscripts "A", and "M" refer to acetone and methyl-ethyl ketone respectively.

Hence,

$$\Phi CO_M = S_M/S_A \qquad \text{..........} \quad (1)$$

This treatment is independent of the units in which I_o and I_t are expressed, so that the use of microammeter readings in the photocell circuit is permissible. It will be valid only if these readings are directly proportional to intensity; but any errors arising from deviations from strict proportionality will be negligible of the ketone pressures are adjusted so that the values of I_o and I_t are similar in both cases.

Absorption of Coefficients

The ratio of absroption coefficients of the two ketones was obtained from the same experiments, using the relation:

$$\frac{\epsilon_A}{\epsilon_M} = \left\{\frac{\text{Log}\,I_o/I_t}{P}\right\}_A \Big/ \left\{\frac{\text{Log}\,I_o/I_t}{P}\right\}_M \quad \text{..........} \; (2)$$

where P = pressure (in mms.)

and ϵ = absorption coefficient of each ketone.

ϵ is defined by:

$$I_t = I_o\, 10^{-\epsilon cd.}$$

where c = concentration in gm.moles./litre.

d = length of absorption vessel.

Again, the treatment is valid irrespective of the units in which I_o and I_t are expressed, but the desirability for similar values in each ketone is even more to be stressed.

Results

The results are set out in table XI. They will be discussed later from a theoretical viewpoint, but the following experimental observations are more relevant to this chapter.

(a) Quantum yield of carbon monoxide in the direct photolysis

The mean value of S_A from experiments 65 & 67 is $2.22 \pm .06$. Combining this with the mean value of $S_M = 2.165$ from experiments 64 & 66 we obtain:

$$\Phi CO_M = 2.165/2.22 = 0.975.$$

This is very close to 1 as has been assumed in previous work, and may be taken as unity within experimental error. This value has been assumed in calculation of quantum yields in both runs.

(b) Absorption coefficients

The quantity $(\mathrm{Log}_e I_o/I_t) / P$ is found to be 0.02465 for methyl-ethyl ketone, and 0.02165 for acetone within a very small margin of error. Hence from equation (2), we have

$$\epsilon_M/\epsilon_A = 1.14$$

It will be recalled that a value of 1.23 was assumed for this quantity in the experiments in chapter V. The effect of this alteration will be to raise the quantum yields calculated in that chapter by 8%, thus obtaining values Φ_{EtI} = 0.52 and 0.78 from the two observations. However, the experimental error in these previous determinations was so large that it is doubtful if this correction is of much quantitative significance.

It is of interest that the absolute values of ϵ_A obtained from these experiments is 2.11. This value was reasonably constant throughout the work, averaging 2.2 ± .3 at 15mm. pressure, 2.2 ±.2 at 61mm., and 2.1 ± .1 at 200mm. This may be taken as a rough check on the efficiency of the filtration system, but no absolute significance can be attached to any such determinations, since the precise value observed depends very critically on the polychromatic nature of the light source. Thus Dr. Dorfman (17) finds large variations of 30% in observed values of I_t/I_o in the course of some measurements on diethyl ketone, determined with different ultraviolet lamps but with the same filtration system.

That the above value is at least of the right order may be seen from the table:

ϵ_A at 3130 Å	Investigator
2.88	Damon and Daniels (11)
3.27	Luckey and Dorfman. (38)
2.11	Present work

It should be stressed that although absolute values of ϵ_A may be greatly in error, the relative values from one ketone to another obtained by the above method are probably correct to within 1 or 2%.

VIII DISCUSSION OF RESULTS

The most striking point in the results obtained on acetone is the large discrepancy between the values of ΦMeI reported by Gorin at 3130 Å, and those observed in this work. Most of Gorin's experiments were concerned with 2537 Å irradiation, or rather the unfiltered output of a mercury arc, but he did report two experiments at 3130 Å and 90°C, in which he found:

(a) At 850mm. of acetone and 1.0mm. of I_2, Φ MeI = 0.85

(b) " 1265 " " " " 0.5 " " " = 0.78.

None of my results were obtained at such high pressures, but at 200mm, the observed value of ΦMeI was .11 under otherwise comparable conditions, and it would be somewhat lower at Gorin's pressures. The discrepancy cannot be due to formation of products other than methyl iodide in my case, since the yields of CO, C_2H_6, and CH_4 were all practically negligible. The discrepancy is so very large that one might well question the validity of the methods described herein.

Validity of results

Practically every step in the work has been verified as far as possible; the radiochemical technique has been shown to be valid as regards absence of exchange and blank yields, and it gives reproducible results from many different samples of radioactive iodine, each of which was necessarily subjected to a separate determination of specific activity. The purity of the ketones is well established, and is confirmed by results of calibration runs. Thus, observed yields of methane are in reasonable agreement with Noyes and Dorfman's equation for ΦCH_4, and the variation of this quantity with pressure and intensity is also in accord with previous investigators' results. Further, the comparison of calibration runs on acetone and methyl-ethyl ketone provides some check on their purity, and the conclusion that ΦCO = 1 in both cases is precisely as required by all previous considerations.

The only impurity which probably was present during photolysis was mercury vapour. Its presence and effects at 2537 Å have been discussed, but such effects could not arise at 3130 Å since light of this wavelength cannot excite resonance radiation in mercury vapour. It is still conceivable that mercury vapour would interfere with the photolysis in other ways, but in a system which is remarkable for absence of chain reactions it is difficult to see how the minute quantities present could cause much effect. In fact, Saunders and Taylor (56), in investigating the effects of mercury vapour on the direct photolysis, reported only second order effects when the mercury vapour pressure was as high as 30mm. The present results in no way bear out any such interference, for in one run in which mercury was definitely present, as evidenced by a visible deposit of mercuric iodide, the results were perfectly consistent with others. Again the final experiments on acetone in the presence of mixed light used a filling system which must have removed all but minute traces of mercury; the results were in good accord with previous experiments.

In view of the above, and in particular of the fact that under certain conditions the alkyl iodide quantum yield in methyl-ethyl ketone did rise to unity, one feels reasonably confident that the results reported are geniune.

Validity of Gorin's results

On this basis, it would seem that the discrepancy might be attributable to Gorin's investigations. A detailed consideration of his technique brought to light a serious point concerning his estimates of quantum yields. He based his estimates of absorbed quanta on calibration runs on acetone alone, choosing, for his 3130 Å work, a temperature of 80° for the direct photolysis. On the basis of Damon and Daniels' results (11), the only ones then available, he assumed a value of ΦCO = .17 and calculated his ΦMeI yeilds accordingly. Damon and Daniels' results were obtained at 56°, 750mm., and with very high absorbed intensities of 3×10^{15} quanta /cc/sec. More recent work, in particular the detailed investigations of Herr and Noyes, indicates that the probable value of ΦCO under Gorin's conditions was .8 ± .15, owing mainly to the fact that ΦCO is markedly temperature dependent and approaches unity at 90-100°C. The effect of other variables would not be very appreciable at this temperature, and in any case Gorin's absorbed intensities must have been of the same order as those used by Herr and Noyes. One cannot evaluate absorbed intensities accurately in Gorin's case, since he did not specify the volume of his reaction vessel; but on the approximate assumption that this volume was 100cc. his reported yeilds are equivalent to I abs. = 5×10^{12} quanta/cc[sec.

Recalculation of Gorin's results on this basis leads to the surprising conclusion that ΦMeI = 4 ± .8, rather than .8 as previously stated. In view of this almost inexplicable result one feels that Gorin's estimates of ΦMeI at 3130 Å are not to be treated as reliable.

Similar considerations apply to his work at 2537 Å, though in this case it is difficult to assess the true value of ΦCO under his conditions. In this instance he performed his calibration runs at 60°, with absorbed intensity of approx. 10^{14} quanta /cc/sec., a value 100 times as high as that used by Herr and Noyes and more nearly equivalent to Damon and Daniel's conditions. The adopted figure of ΦCO = .17 is certainly more

TABLE XI

Photolysis of Methyl-ethyl Ketone/Iodine Mixtures at 3130 Å (Final Series)

Experiment No.	Series	Ketone A acetone M methyl-ethyl ketone	Ketone pressure corrected to 100°	Iodine pressure	Temperature	Time of irradiation (minutes)	I_o arbitrary units *	I_t arbitrary units *	I_o/I_t	$\frac{\log I_o/I_t}{P}$	Yield X 10^7 gm. moles				S	R	EtI/MeI	ϕ EtI	ϕ MeI	ϕ CO
											CO	Res.Gas (CH_4)	EtI	MeI						
64	S	M	88.8mm.	0	120°	5.00	101.2	61.3	1.65	.0247	43.2	15.2			2.17					
65	S	A	111.0	0	120°	5.16	100.2	57.6	1.74	.0216	47.4	11.6			2.16					1.0(a)
66	S	M	89.5	0	120°	5.00	97.0	58.4	1.66	.0246	42.2	14.8			2.18					
67	S	A	100.2	0	120°	5.10	98	59.5	1.65	.0217	44.8	10.3			2.28					1.0(a)
68	S	M	88.8	1.02mm	100°	5.00	93.5	56.5	1.65		.163	.043	34.1	1.72			19.8	.835	.042	.004
69	S	M	88.0	0.99	100°	5.00	93	55	1.68		.8(?)	.15(?)	32.8	1.75			19.0	.818	.044	?
70	T	M	14.8	0	120°	20	102	91	1.12		36.1	6.9				1.195				1.0(a)
71	T	M	15.4	0	120°	21.5	100	89.5	1.12		39.9	7.4				1.21				1.0(a)
72	T	M	14.8	1.00	100°	20	96.6	86.3	1.12		3.33	.21	33.6	3.26			10.3	.975	.095	.096

* These units are constant only for experiments in the same series. S = (Yield of CO)/$t(I_o - I_t)$ in arbitrary units. R = (Yield of CO)/$t.I_o.P$.

reasonable in this instance, though a rough extrapolation of Herr and Noyes' data would indicate a somewhat higher value. It is significant here that Gorin made no attempt to remove mercury vapour under any conditions, storing his acetone behind a mercury cut off. It is possible, but not definitely established, that discrepancies due to absorption variations would vanish in his work, for his acetone pressures were so high as to cause practically complete absorption of radiation in any case. Again the result depends on the size of his reaction vessel.

The difficulty of estimating such small quantities of methyl iodide as Gorin attempted needs no emphasis. His method consisted in separating methyl iodide from acetyl iodide at -30° by distilling off 80% of the acetone in his reaction products into a separate receiver, thereby taking with it practically all the methyl iodide. Excess iodine was removed previously by distillation over mercury. Total iodine in the two fractions was estimated by conversion to elementary iodine, and titration against thiosulphate. It is worthy of note that Gorin also investigated the photolysis of acetaldehyde with the same technique. This work was later repeated by Blacet and Heldman (7) and Blacet and Loeffler (8) with results which differed considerably from Gorin's. The latter investigators found much lower yields of alkyl iodides than those reported by Gorin.

INTERPRETATION OF RESULTS

A. The quantum yield of methyl iodide in acetone at 3130 Å

It will be seen from table VI that ΦMeI is markedly dependent on pressure. At roughly constant I_2 pressure, ΦMeI falls from .5 at 16mm. of acetone to .11 at 200mm; while at constant acetone pressure the yield falls with increase in pressure of iodine.

The latter result could conceivably be explained on the assumption that the photolysis proceeds via a chain mechanism, as is certainly the case in acetaldehyde, and that the action of the iodine is to quench such chains by removing their propogating radicals with an efficiency dependent on iodine pressure.

There is abundant evidence against such an interpretation. Firstly, the fact that the overall quantum yield in the direct photolysis is unity and essentially independent of all variables at temperatures above 100°, could be explained only on the improbable assumption that in all cases a small radical yield is combined with a large chain length in such a manner that their product is always 1. Further, Mitchell and Hinshelwood (43) have shown that small amounts of nitric oxide have no effect on the photolysis at 300°, Leermakers (39) finds no appreciable rise in quantum yields at high temperatures as one might expect from a chain mechanism, and more recently Steacie and Darwent (62) have shown that the results are independent of the nature of the surface of the reaction vessel; e.g. coating it with lead or KCl made no difference. Finally, one could scarcely explain the effect of acetone pressure in the present investigations on such an assumption.

The results may be explained in a much more reasonable manner on the assumption that the primary process at 3130 Å is the formation of an activated molecule which breaks down to radicals with a half life sufficiently long to enable collisional deactivation by iodine and acetone. However, the same activated molecule must be formed at 3130 Å regardless of the presence or absence of iodine, yet in the direct photolysis the quantum yield is independent of pressure. We must conclude that the activated molecule as originally formed is incapable of deactivation by acetone; in fact, this property of deactivating, or in some way reacting with the excited molecule appears to be confined to iodine, whilst at the same time it renders the overall process dependent on acetone pressure. This suggests that the product of the iodine reaction is a second activated species which ultimately breaks down to the reaction products or is deactivated by acetone. The precise nature of this second activated species is difficult to assess; it may be a second electronic state of acetone or a transition complex formed by the addition of iodine. A number of considerations favour a particular form of the latter interpretation, represented by the reaction:

$$CH_3COCH_3^* + I_2 \rightarrow [CH_3COCH_3 \ldots\ldots\ldots I]^* + I$$

Representing this complex by AI^*, the proposed mechanism is set out in full below:

Reaction	Rate Expression	No.
$CH_3COCH_3 + h\nu \rightarrow CH_3COCH_3^*$	I_a	1.
$CH_3COCH_3^* \rightarrow CH_3+CH_3CO$	$k_2(A^*)$	2.
$CH_3COCH_3^* + I_2 \rightarrow AI^* + I$	$K_3(A^*)(I_2)$	3.
$AI^* \rightarrow CH_3I+CH_3CO$	$k_{4a}(AI^*)$	4.a.
$AI^* \rightarrow CH_3+CH_3COI$	$k_{4b}(Al^*)$	4.b.
$AI^* + A \rightarrow 2A + I$	$k_{5a}(AI^*)(A)$	5.a.
$AI^* + I_2 \rightarrow A+I_2+I$	$k_{5b}(AI^*)(I_2)$	5.b.
$CH_3 + I_2 \rightarrow CH_3I+I$	$k_6(CH_3)(I_2)$	6.
$CH_3CO + I_2 \rightarrow CH_3COI+1$	$k_7(CH_3CO)(I_2)$	7.
$CH_3CO \rightarrow CH_3+CO$	$k_8(CH_3CO)$	8.
$I + I + A \rightarrow I_2+A$	$k_9(I)^2(P)$	9.

The numbering of these reactions refers to this discussion only; it is not related to that used for similar reactions on previous pages.

A^* represents the first activated molecule of acetone.

AI^* represents the second activated complex mentioned above.

A represents a normal acetone molecule.

(P) represents the total pressure in the system.

Quantitative treatment

On the basis of this mechanism an expression for Φ MeI may be deduced. It is assumed :

(a) that the quantum efficiency of reaction (1) is unity.

(b) that reaction (6) is quantitative. i.e. that both the yield and rate of formation of methyl radicals is equivalent to that of methyl iodide.

(c) that acetyl radicals are also quantitatively removed from the system,probably according to reaction (7), but not necessarily so. The essential point is that any subsequent reaction of acetyl will not affect Φ MeI except by operation of reaction (8). For example, reactions such as

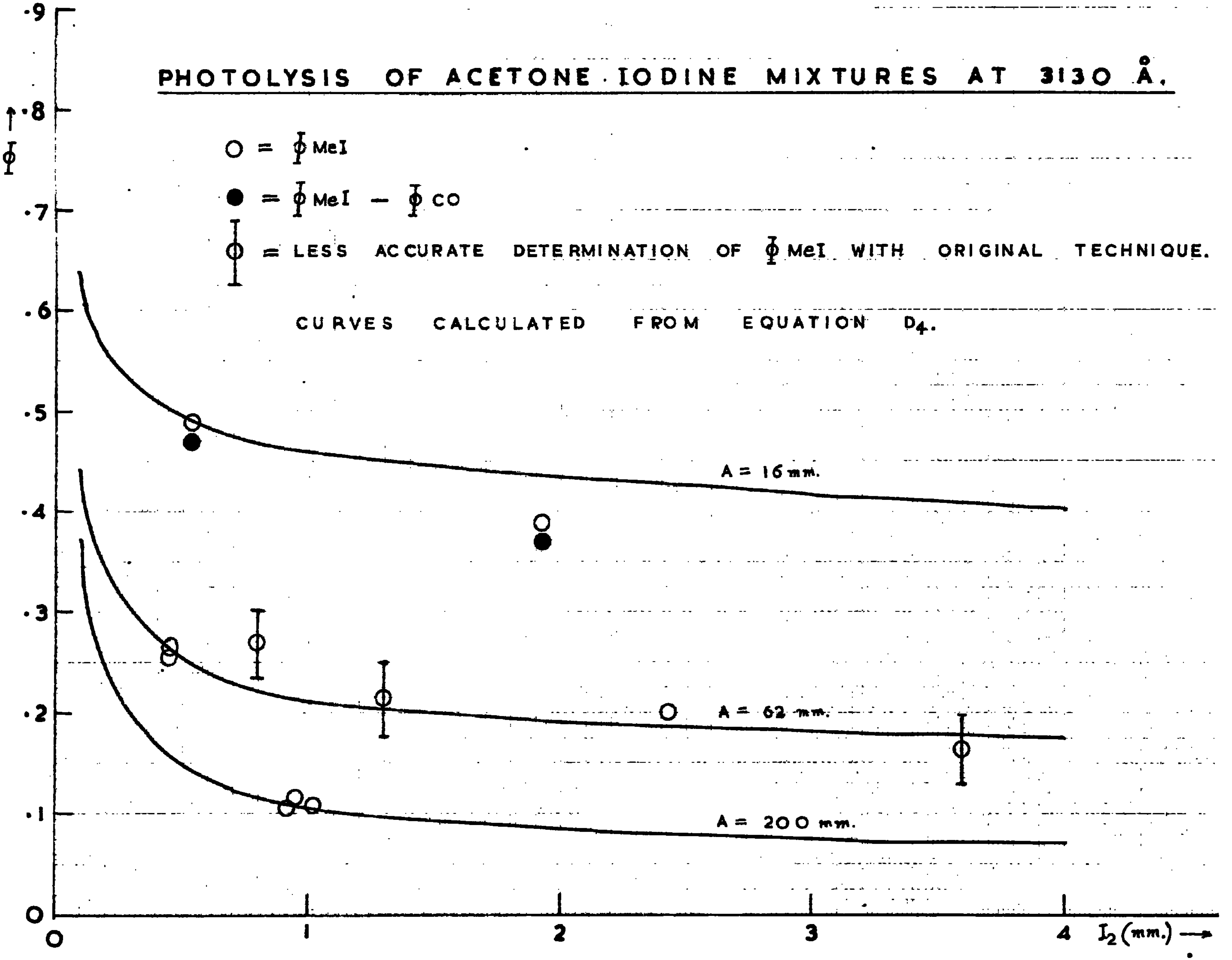
$$CH_3 + CH_3CO \rightarrow CH_3COCH_3$$

are assumed to be negligible, as is of course perfectly reasonable since the methyl concentration is so low.

(d) that the deactivation of AI^* is effected equally efficiently by both acetone and iodine, i.e. $k_{5a} = k_{5b}$, so that the rate expression for this reaction becomes $k_5(P)$.

(e) that as a reasonable approximation reaction (8) may be neglected as a source of methyl radicals, in accord with the experimental fact that the yield of CO was in all cases very small compared to that of methyl iodide.

Assuming further that the standing concentration of A^* and AI^* is constant, we obtain:



PHOTOLYSIS OF ACETONE IODINE MIXTURES AT 3130 Å.

CURVES CALCULATED FROM EQUATION D_4.

$$\frac{d(A^*)}{dt} = Ia - k_2(A^*) - k_3(A^*)(I_2) = 0$$

In view of (b) above, it is immaterial for present purposes whether AI^* follows reaction 4(a) or 4(b); we may replace $k_{4a} + k_{4b}$ by k_4, so that:

$$\frac{d(AI^*)}{dt} = k_3(A^*)(I_2) - k_4(AI^*) - k_5(AI^*)(P) = 0$$

Hence $(A^*) = I_a / \{k_2+k_3(I_2)\}$ D1

and $(AI^*) = I_a k_3(I_2) / \{k_4+k_5(P)\}\{k_2+k_3(I_2)\}$ D2

Now $\frac{d(MeI)}{dt} = \frac{d(CH_3)}{dt} = k_2(A^*)+k_4(AI^*)$

and $\Phi\,MeI = \frac{1}{Ia} \cdot \frac{d(MeI)}{dt}$

$= \{k_2(A^*) + k_4(AI^*)\} / Ia$ D3

Substituting D_1 and D_2 in D_3, and simplifying,

$$\Phi\,MeI = 1 - \frac{1}{\left\{1 + \frac{k_2}{k_3(I_2)}\right\}\left\{1 + \frac{k_4}{k_5(P)}\right\}} \quad \text{....D4}$$

This equation has been applied to the experimental results in such a way as to give the best fit to the most well established points. In this way numerical values of the constants have been evaluated as follows:

$k_2/k_3 = 0.05$mm. ; $k_4/k_5 = 13$mm.

where

(I_2) and (P) are expressed in mms. pressure.

Using these experimentally determined constants, the three smooth curves on the adjoining graph have been obtained from D_4, plotting Φ MeI against iodine pressure for each of the three different pressures of acetone used. It will be seen that the experimental results fit the equation reasonably well, and certainly within experimental error.

A slight discrepancy arises in the low pressure ~~temperature~~ region if correction is made for the yield of CO in this case. It will be recalled that the above treatment neglects reaction (8); if any CO is formed by this process it will be accompanied by an equivalent quantity of methyl iodide in excess of that calculated from equation D4. In fact, equation D4 represents Φ MeI - ΦCO more nearly than ΦMeI alone. Deducting the observed values of ΦCO, the heavily inked points are obtained at low pressures; however the correction is only -4%;and -1 to -2% in other regions. A better fit to these points could be obtained by a slight alteration in the constants, but the general agreement is satisfactory without this refinement.

Again, the iodine pressure dependence appears to be more marked at low acetone pressures than equation D4 would predict. This may well be attributable to assumption (d). If this assumption is removed, the following equation is obtained

$$\Phi \text{ MeI} = 1 - \left\{ \frac{1}{1 + \dfrac{k_2}{k_3(I_2)}} \right\} \left\{ \frac{1}{1 + \dfrac{k_4}{k_{5a}(A) + k_{5b}(I_2)}} \right\} \quad \ldots\text{D5}$$

This equation may be made to fit the results more precisely than D4 if the constants are so chosen that $k_{5b} = 1.8\ k_{5a}$. However the introduction of a third constant is scarcely justified on the basis of the two points available at low pressures, and in fact the effect may not be real.

It is perhaps worthy of note that a much simpler mechanism than that discussed above will also lead to an equation in agreement with the observations. On the assumption that the mechanism involves only one activated molecule, susceptible to deactivation both by iodine and acetone, an equation of the form

$$\Phi \text{ MeI} = 1 \Big/ \left\{1 + K_1(A) + K_2\,(I_2)\right\} \qquad \text{......D6}$$

is obtained. This is in reasonable agreement with the results, though not quite as good as D4; but the treatment is nevertheless invalid since acetone alone is incapable of deactivating the excited molecule.

The effect of CO_2 on the photolysis

It has been pointed out that iodine possesses the property of "deactivating" A^*, while acetone does not. As a further test of the specific nature of this property, some experiments on the effect of CO_2 on the direct photolysis were carried out.

Previous work by Howland and Noyes (32) shows that ΦCO rises in the presence of large pressures of CO_2 at 25° and 3130 Å. Iredale and Lyons (35) found a similar result with the unfiltered output of a mercury arc, but both these results are attributable mainly to increased decomposition of acetyl. It is in fact impossible to decide whether any deactivation process contributes to their results. To eliminate this ambiguity the direct photolysis was studied at 120°, at which temperature acetyl is fully decomposed even in the absence of CO_2. In this case, ΦCO is a direct measure of the overall quantum yield.

The results in table VII (p. 76) show only a very small decrease in ΦCO at 200mm. of acetone when a further 200mm. of CO_2 is added. The observed fall from $\Phi = 1$ to $\Phi = .93$ under such conditions is scarcely comparable to the effect of iodine, at pressures 200 times lower. It is concluded that the marked deactivating property of iodine is not shared by CO_2 or acetone.

Nature of the deactivation reaction

The above mechanism interpretes the specific nature of this property of iodine in terms of a reaction between iodine and A^* which occurs in two stages, involving the intermediate formation of an activated complex of finite half life. The behaviour of this complex is not known with any certainty; it is contended simply that it breaks down in the absence of collisional deactivation into the reaction products methyl iodide and acetyl, or acetyl iodide and methyl. Both of these reactions would be exothermic to the extent of some 24 kcal. if we take the strength of the C - C bond in acetone as 80 kcal, and assume that the iodine atom evolved in formation of the AI^* complex is in its normal $^2P_{1/2}$ state.

Half life considerations

At very high pressures of acetone practically all those activated molecules which reach the AI^* state are ultimately deactivated. In this case equation D4 reduces to

$$\Phi\,\mathrm{MeI} = 1 - \frac{1}{\left\{1 + \dfrac{k_2}{k_3(I_2)}\right\}} \qquad \ldots\ldots D7$$

Introducing the value obtained for k_2/k_3, it will be seen that Φ MeI = 0.5 at 0.05mm. of I_2. Hence at this pressure the initially activated molecule A^* has a 50:50 chance of spontaneous disruption into radicals, or of transformation into AI^*, by collision with I_2. This pressure corresponds to a collision frequency of approx. 0.5×10^8 collisions per second between any one A^* molecule and iodine, assuming a collision diameter of 4.6×10^{-8} cm. both for iodine and A^*; so that the average time between collisions is 2×10^{-8} sec. If every collision with I_2 results in reaction, then this figure is a reasonable estimate of the half life of A^*; if not, then the half life must be somewhat longer.

Certain evidence has been discussed in the introduction (p.7-9) relating to the temperature and pressure dependence of quantum yields in the direct photolysis. It was shown that although any primarily formed activated molecule was not subject to collisional deactivation by acetone at 100°, some degree of deactivation does occur at 25°, indicating a difference of 5 kcal. in activation energies for the spontaneous decomposition of A^*, and its collisional deactivation by acetone. Noyes and Dorfman made the further assumption that the activation energy of the latter reaction is zero, i.e. that it occurs at every collision. From this assumption a half life of very approximately 10^{-10} sec. at 100° may be deduced from their data, but the present investigations show that this assumption is very far from the truth. At 100°, A^* must be able to suffer at least 2000 collisions with acetone without deactivation and probably very many more. Nevertheless, the essential point of their argument remains, for it is shown that activated molecules do play some part in the mechanism, and that under certain conditions their half life is long enough to permit a small degree of deactivation by acetone, in spite of the relatively low efficiency of this process. The small decrease in ΦCO from 1 to .93 in the presence of CO_2 might be explained on the same basis, assuming a slightly higher, but still very low efficiency of deactivation by CO_2.

The half life of the AI^* complex cannot be evaluated with any certainty. If it is deactivated at every collision with acetone, then its half life may be assessed at 10^{-10} sec. but there is no reason for such an assumption, and certain evidence on the effects of visible light indicate the half life is considerably longer.

Alternative interpretations

It has been shown that the above mechanism gives a satisfactory quantitative account of the results, and is not in disagreement with previous investigations on the direct photolysis. However, this does not entirely prove its validity and in the following paragraphs some consideration will be given to certain other interpretations.

(a) A mechanism involving two electronic states of acetone

The mechanism advanced above involves the formation of two activated species of finite half life. The first of these is almost certainly an activated acetone molecule, the second has been assumed to be a complex formed on the addition of iodine. However the above quantitative treatment would follow equally well on the assumption that the second complex is nothing more than a second electronic state of acetone, a state which still retains sufficient energy to dissociate spontaneously into free radicals, but which is susceptible to deactivation by acetone into normal molecules. The kinetics and quantitative treatment of such a mechanism are identical with those used before, and lead to the same form of equation for ΦMeI.

This postulate is in some degree supported by the fluorescence studies of Hunt and Noyes (34), who conclude that at least two excited states of acetone must contribute to the fluorescence; that the half life of one of them may be of the order of 10^{-8} sec (in good agreement with the value obtained above) while the other is considerably longer lived. Furthermore, Luckey, Duncan and Noyes (38) have found definite structure in the blue fluorescence characteristic of acetone, thus proving that the lower level to which the molecule falls after emission of fluorescent radiation is also capable of existence for long enough to give a discrete spectrum. The short wave end of the fluorescence lies at about 26000cm.$^{-1}$, equivalent to 74 kcal. per gm. mole., so that if this fluorescence arises from the second excited molecule indicated above, it would still possess just about enough energy for spontaneous decomposition into radicals.

Such evidence is of rather doubtful validity, for it is not known whether the fluorescence of 26000cm.$^{-1}$ arises from a second level which is 74 kcal. above the ground state, as the above argument assumes; or from a transition from the initially activated state A^*, to a level 74 kcal. below it, in which case radical formation from the second level would be energetically impossible. A point of more importance is that the energy loss by fluorescence itself is practically negligible, and there is no good reason to believe that most or any of the photochemical decomposition occurs by similar paths, though its possibility is certainly indicated.

A major objection to this mechanism concerns the specific nature of the deactivation reaction. If these two electronic levels do exist, they cannot differ in energy by more than about 10 kcal. if the lower one is still to decompose into radicals; for the energy of the first state is 91 kcal. (equivalent to one einstein of 3130 Å radiation) and about 80 kcal. are required to break the C - C bond. Now it is true that the ability of any molecule to remove energy from collision with another is dependent upon its own energy levels as well as those of the activated species; but since the energy transferred in this deactivation is only 10 kcal. it could surely be accommodated in vibrational and rotational levels of practically any molecule with which the excited species collides. Yet the evidence is that neither acetone nor CO_2 can cause such a deactivation, while iodine does so very effectively, and probably at every collision.

One is forced to the conclusion that this mechanism is unable to account satisfactority for this point, and that it must be rejected accordingly.

(b) Modified application of the Spence and Wild mechanism

It will be recalled that Spence and Wild have proposed a mechanism based on two excited states of acetone in which the second state is of much lower energy than the first - and therefore free from the objection pointed out in (a) for present purposes. This second state is assumed to decompose into ethane and carbon monoxide at a rate which competes with its deactivation. It is obviously untenable in its original form in the present work, for the yields of ethane and generally CO are practically negligible. However Feldman, Ricci, Burton, and Davis (21) have attempted to explain Gorin's results on such a basis, assuming that both these normal reactions of the second state are quenched in the presence of iodine by the quantitative reaction:

$$CH_3COCH_3^{**} + I_2 \longrightarrow CH_3I \quad CH_3COI$$

Hence ΦMeI would be unity, as Gorin found.

It is difficult to see how such a reaction could be quantitative at iodine pressures as low as 1/500 that of acetone, since the Spence and Wild mechanism requires that A^{**} is definitely susceptible to deactivation. However the point is difficult to prove experimentally so long as ΦMeI remains at unity.

If one applies this interpretation to the present work, and assumes that the second state A^{**} does exist, but does not dissociate into ethane and CO (to account for the absence of these products) then the fate of this second activated molecule will be decided by a competition between its collisional deactivation, and participation in the above reaction. On this basis the quantum yield of methyl iodide will be given by an equation of the form:

$$\Phi_{\text{MeI}} = 1 - \frac{1}{\left\{1 + \frac{K_1}{(I_2)}\right\}\left\{1 + \frac{K_2(I_2)}{(A)}\right\}} \qquad \text{.......D8}$$

Such an equation does not express the experimental results; e.g. if one attempts to calculate the constants K_1 and K_2 from the two best established points, a negative value for K_2 is obtained. It must be concluded that this mechanism does not operate under the conditions of my investigations. One feels that this weakens very considerably the contention that it operates at 2537 Å as Burton et.al. maintain, and that in fact the results at this wavelength are to be attributed solely to a free radical mechanism.

(c) A mechanism based on atomic iodine reactions

A process that might very well explain the specific character of the deactivating property of iodine is the reaction:

$$A^{*} + I_2 \rightarrow A^{**} + 2I \qquad \text{.......(x)}$$

Since iodine may be dissociated into two normal atoms with absorption of 35 kcal. (or 57 kcal. if one atom is in the excited $^2P_{3/2}$ state, though this is perhaps unnecessary in the neighbouring magnetic field of an acetone molecule), then such a reaction is conceivable for iodine but energetically improbable for acetone and CO_2. The resultant molecule A^{**} would possess some 58 kcal. excess energy; insufficient for spontaneous decomposition into radicals, but enough to enable a further reaction with iodine atoms according to such reactions as :

$$A^{**} \quad + \quad I \quad \rightarrow \quad CH_3I + CH_3CO \qquad ....(y)$$

$$A^{**} \quad + \quad I \quad \rightarrow \quad CH_3 + CH_3COI \qquad ....(z)$$

Such reactions would be exothermic to the extent of some 22 kcal. if the atoms produced in (x) are both normal; if one is excited then (y) would be just energetically possible with the normal atom and again 22 kcal. exothermic with the excited atom.

A weak point of this interpretation is the requirement that A^{**} should have a very long half life; otherwise its chances of collision with iodine atoms would be negligible; though it is difficult to assess iodine atom concentrations in any given conditions. Assuming for the moment that such conditions are obtainable in practice, then the net effect of such a mechanism is the replacement of reaction (4) in the original mechanism by reactions (y) and (z). This leads to the following expression for ΦMeI:

$$\Phi \text{MeI} = 1 - \frac{1}{\left\{1 + \frac{K_1}{(I_2)}\right\}\left\{1 + \frac{K_2(I)}{(P)}\right\}} \qquad ....D9$$

where (I) is the iodine atom concentration.

The iodine atom mechanism involves so many reactions that it is difficult to obtain an expression for (I) which would enable an experimental test of D9. The following approximation may be considered:

Iodine atoms are formed by the reactions:

$$A^{*} + I_2 \rightarrow A^{**} + 2I \qquad \ldots\ldots\ \alpha$$

$$\left.\begin{array}{l} CH_3 + I_2 \rightarrow CH_3I + I \\ CH_3CO + I_2 \rightarrow CH_3COI + I \end{array}\right\} \qquad \ldots\ldots\ \beta$$

and are destroyed by the reactions:

$$A + I + I \rightarrow I_2 + A \qquad \ldots\ldots\ \gamma$$

$$\left.\begin{array}{l} I + A^{**} \rightarrow CH_3I + CH_3CO \\ I + A^{**} \rightarrow CH_3COI + CH_3 \end{array}\right\} \qquad \ldots\ldots\ \delta$$

At the most, reactions δ can remove only half the iodine atoms produced by α ; as a first approximation such δ reactions will be neglected for purposes of estimating (I).

Balancing γ against α , we obtain by a further approximation:

$$(I) = K^{1}\sqrt{\frac{Ia}{(A)}} \qquad \text{where } Ia = \text{absorbed intensity}$$

Further, this dependence on $(Ia)^{1/2}$ remains, without the additional approximation.

Alternatively, if we make the much more improbable assumption that β is the main source of iodine atom production, we obtain:

$$(I) = K^{11}\sqrt{\frac{I_2}{(A)}}$$

Substituting either of these equations in D9 gives an expression for ΦMeI which is not in accord with the results. In particular there is no indication of any intensity dependence, in spite of a five fold variation in Ia. If the mechanism is treated more fully by balancing $\alpha + \beta$ against $\gamma + \delta$ the result is incapable of experimental verification; but the general conclusion is that equation D9 will express the results only if the iodine atom concentration remains constant under all experimental conditions, for in this case, and in this case only, it reverts to the original equation D4. It is most improbable that this requirement could be met in practice, in view of the complexity of the iodine atom mechanism. On the whole, the iodine atom treatment appears untenable.

Effect of visible light on the photolysis

As a qualitative test of the participation of iodine atoms in the mechanism, some experiments were performed in which these atoms were artificially introduced into the system during photolysis, by irradiating it with visible light. The results, set out in table IX (p. 79), have established the following points:

(a) That the visible irradiation in use was alone incapable of photochemical reaction, either on acetone alone or in acetone iodine mixtures. No reaction can occur between iodine atoms and normal acetone molecules.

(b) That addition of visible radiation to the ultraviolet makes no appreciable difference to the results obtained on acetone alone.

(c) That the quantum yield of methyl iodide in the presence of iodine showed a small but probably significant increase from .11 to .137 when the photolysis was performed in the additional presence of visible radiation.

It is concluded that some species is formed during ultraviolet irradiation with a half life sufficiently long to permit some degree of interaction with iodine atoms, in spite of their low concentration. Unfortunately the result is essentially qualitative, for it is extremely difficult to estimate the iodine atom concentration during normal conditions and in the presence of visible irradiation. It could be taken as evidence in favour of (c) above, but in essence it only shows the possibility of atomic iodine reactions if their concentration is made sufficiently high, and the arguments against (c) are too strong to be refuted by this one result.

It is by no means impossible to reconcile this result with the mechanism originally advanced, for iodine atoms may very well react with the AI^* complex according to one or other of the reactions:

$$AI^* + I \rightarrow CH_3 + CH_3CO + I_2$$

$$\text{"} \qquad \text{"} \rightarrow CH_3I + CH_3COI$$

This would require that the AI^{**} complex has a fairly long half life, and is therefore to a certain extent resistant to deactivation by acetone, but one cannot be definite about such points in the absence of knowledge of iodine concentrations. It would be of some interest to investigate the iodine atom effect more quantitatively, but such a study would present considerable practical difficulties.

Conclusions regarding the mechanism

The above discussion makes no pretence of being exhaustive, doubtless there are other interpretations which would lead to the same kinetic equations. Nevertheless, the mechanism as advanced originally appears to be the only one of those considered which can reasonably explain all the evidence of the present investigation; at the same time it is not opposed to the results of previous investigations,as it becomes effective only in the presence of iodine. The evidence for the existence of two excited entities of finite half life appears to be fairly conclusive; if one accepts this, then the proposed equation

D4 is not unduly complicated since it involves only two rate coefficients for each of the excited states.

The precise nature of the 2nd state is not well established; it may be an addition complex of elementary iodine of the type AI_2^* rather than AI^*, but its subsequent reactions and kinetics would be entirely analagous to those discussed above. The evidence available is not adequate to decide between these two possibilities, though the following considerations would perhaps favour the AI^* complex:

(1) The increase in Φ MeI in the presence of iodine atoms is more readily explained on the basis of a reaction with AI^* than with AI_2^*.

(2) Rabinowitch and Wood (71) have shown that recombination of iodine atoms by ternary process occurs with a remarkably high efficency in the presence of benzene and other polyatomic molecules. This suggests the existence of an intermediate addition complex of the type C_6H_6-I^*, with an appreciable half life.

In view of the foregoing, it is concluded that the original mechanism offers the most reasonable interpretation of the results.

(B) The quantum yields of methyl iodide at 2537 Å

Very little can be said on this subject since the results were so unsatisfactory. However they do show a marked increase in quantum yields over those observed at 3130 Å, and the radical quantum yield may well be unity within experimental error. There seems no reason to doubt the conclusions of Gorin and other workers that the primary process at this wavelength is a direct split into radicals.

(C) Yields of uncondensed gases

It has been shown that the yield of ethane is negligible at both wavelengths, in full agreement with earlier work by Gorin and by Benson and Forbes. There can be no reasonable doubt that if methyl radicals do contribute to the mechanism, their combination to form ethane is completely quenched in the presence of iodine even at pressures as low as .5mm. in 200mm. of acetone.

Methane yields were not accurately estimated, but were found to be very low, in general less than the CO yields. Quantum yields of residual gas after removal of CO were in practically every instance less than .01, and generally less than .005, indicating that ΦCH_4 is somewhat lower than this figure.

If is assumed that methane arises solely from the reaction:

$$CH_3 + CO_3COCH_3 \longrightarrow CH_4 + CH_2COCH_3 \qquad \ldots\ldots\ (10)$$

and methyl iodide from the reaction:

$$CH_3 + I_2 \longrightarrow CH_3I + I \qquad \ldots\ldots\ (6)$$

then we obtain:

$$\frac{CH_3I}{CH_4} = \frac{k_6(I_2)}{k_{10}(A)}$$

and if both reactions have the same steric factor, this becomes

$$\frac{CH_3I}{CH_4} = \frac{(A)}{(I_2)} \quad e^{-(E_{10} - E_6)/RT}$$

where E_{10} and E_6 refer to the activation energies of their respective reactions.

The experimental results show that CH_3I / CH_4 is greater than 100 when $(A)/(I_2) = 200$.

Hence $E_{10} - E_6 \quad = \quad 7.4$ kcal.

The value of E_{10} is not known with any certainty. Allen (2) estimates it at 7.1 kcal; Dorfman and Noyes (16) deduce a value of

6.5 kcal. on rather dubious assumptions, while Rice and Herzfeld (54) and Leermakers (39) consider it is of the order of 15 kcal. It is concluded that E_6 is small and may even be zero, in accord with previous assumptions.

It must be pointed out that the above calculation is relevant only to the results at 2537 Å, for the mechanism at 3130 Å is such that methyl iodide arises in part from spontaneous dissociation of AI^*, and does not necessarily proceed through intermediate free radical formation.

Yields of carbon monoxide

The yields of CO are of some interest in relation to the stability of the acetyl radical. The following table summarises the results obtained on acetone:

Conditions	CO / CH_3 I	Φ CO
(a) at 3130 Å		
Acetone pressure 200mm.	.01 .005	.001
" " 62 "	.02 "	.006
" " 16 "	.04 "	.019
(b) at 2537 Å		
Acetone pressure 200mm.	.17	> .14
" " 20 "	.28	> .14

At 3130 Å there appears to be very little decomposition of acetyl, but it is questionable to what extent the acetyl radical contributes to the mechanism. The AI^* complex may break down to methyl iodide and acetyl, or acetyl iodide and methyl; furthermore any acetyl radicals so produced will not possess the same energy as those formed in the direct photolysis, and will therefore decompose to a different extent.

Nevertheless equation D4 shows that at pressures of 200mm. nearly all the methyl iodide in the products arises from methyl radicals formed by decomposition of the initially excited molecule A^*. These must be accompanied by acetyl radicals identical with those produced in the direct photolysis, and results show that only 1% of these radicals break down to CO and CH_3. It was pointed out on page 6 that Noyes and Dorfman's estimates of this degree of spontaneous decomposition of acetyl prior to any thermal reaction place it at 7% at 3130 Å and 22% at 2537 Å. The present work indicates that these estimates are too high, but the wavelength dependence is nevertheless well established.

The rise in CO/MeI with increase in pressure may be correlated with the following effects:

(a) As the pressure is lowered, more acetyl radicals arise from the AI^* complex, with results which are difficult to assess, but which might well lead to a decrease in CO/MeI.

(b) The effect could be explained on the assumption of a heterogeneous decomposition of acetyl on the walls of the reaction vessel.

(c) Most probably, the result is concerned with a pressure dependent deactivation of acetyl radicals. The treatment of Noyes and Dorfman assumes that a certain fraction "a" of these radicals decomposes before thermal equilibrium is attained, followed by a normal thermal decomposition of the unexcited radicals. It would seem reasonable to represent this scheme by the following simplified mechanism, representing the acetyl radicals as originally formed by CH_3CO^* :

$$CH_3CO^{*}CH_3 \rightarrow CH_3 + CO \qquad (a)$$

$$CH_3CO^{*}CH_3 + M \rightarrow CH_3CO + M \qquad (b)$$

followed by the normal thermal decomposition:

$$CH_3CO + M \rightleftharpoons CH_3CO^{**} \rightarrow CH_3 + CO$$

or, in the presence of iodine

$$CH_3CO + I_2 \rightarrow CH_3COI + I$$

On this basis, the percentage of spontaneous decomposition of acetyl would be determined by a competition between (a) and (b), and would therefore increase at low pressures, as observed in the present case. In other words, the fraction "a" in Noyes and Dorfman's treatment should be dependent on pressure as well as wavelength, a conclusion which is surely quite reasonable. One feels thatthis is a more probable explanation than (b), for there is no a priori reason to involve a wall reaction for the decomposition of acetyl.

At 2537 Å the effect is very marked and may well explain the discrepancy between the very small yields of CO reported by Gorin at 1200mm. of acetone and those obtained by Benson and Forbes at 12mm., where values of ΦCO of about .7 were obtained in the presence of iodine.

A similar effect was observed with methyl ethyl ketone; even at 3130 Å the quantum yield of CO rose from .004 at 90mm. to .094 at 15mm. Again this result is probably attributable to factor (c) above. ~~increasing predominance of wall reactions at lower pressures.~~

(D) The photolysis of methyl-ethyl ketone

The quantum efficiency of radical production, ΦR, has been shown on page 59 to be given by:

$$\Phi R = \Phi EtI + \Phi MeI - \Phi CO$$

On this basis, the results of the final series of experiments on methyl ethyl ketone at 3130 Å are summarized below:

Pressure of ketone	Φ EtI	Φ MeI	Φ CO	Φ R
90mm.	.82	.042	.004	.86
15mm.	.975	.094	.094	.97

It appears that the mechanism discussed above is not of much quantitative significance in this case, and activated molecules do not contribute to the mechanism to anything like the same extent. This conclusion is supported by the fact that no fluorescence corresponding to that observed in acetone has been observed in methyl ethyl ketone, though Matheson and Zabor (44), and Padmanabahn (48), have observed the green fluorescence at low temperatures which is characteristic of diacetyl. Further, Ells and Noyes (18) have found no discrete structure in the absorption spectrum of this ketone at 3130 Å, again in contrast to acetone.

Gorin reported the formation of propane from this ketone, even in the presence of iodine. No attempts at propane estimations have been made in this work, but since the CO yields at high pressures were less than 1% of the alkyl iodide yields, any primary reaction of the type

$$CH_3COC_2H_5 \rightarrow C_3H_8 + CO$$

would appear to be negligible.

The primary processes may then be represented by the reactions:

$$CH_3COC_2H_5 \quad h\nu \rightarrow CH_3COC_2H_5^*$$

$$CH_3COC_2H_5^* \nearrow CH_3 + C_2H_5CO \quad \ldots\ldots (a)$$

$$\searrow C_2H_5 + CH_3CO \quad \ldots\ldots (b)$$

It is necessary to invoke the initial formation of an activated ~~molecule followed by a mechanism similar to that discussed above to~~ account for the slight drop in ϕR with increase in ketone pressure; but the half life of this entity is much lower than that formed from acetone, and its inclusion in the mechanism is only of minor importance.

In view of this it is reasonable to treat the yields of iodide as derived solely from radicals. On this basis the results indicate that reaction (b) predominates over (a) in the ratio of 20: 1 at 3130 Å, and very approximately 2.6 : 1 at 2537 Å.

Stability of the propionyl radical

The ratio of CO/MeI in the products, averages 1/10 in all series of experiments at pressures above 50mm., and at 3130 Å. Since any methyl radicals arising from decomposition of acetyl would be accompanied by an equivalent quantity of CO, it is concluded that most of the MeI yield arises from methyl radicals produced in reaction (a). These again must be accompanied by an equivalent quantity of propionyl, and it is concluded that this radical is not as unstable as has been frequently assumed, since under the above conditions its decomposition into ethyl and CO cannot have exceeded 10%. As with acetyl the extent of this decomposition is dependent on the wavelength of the light used in its production, temperature, and also pressure.

SUMMARY

These investigations have been directed to the elucidation of the mechanism of the photochemical decomposition of acetone and methylethyl ketone. Previous work in this field indicates that the mechanism proceeds mainly via the formation of free radicals; in this work an attempt has been made to determine the primary yield of such radicals by combining them with iodine, after the method of Gorin. The method has been improved in sensitivity by the use of a radioactive tracer technique, enabling the separation and measurement of smaller yields than has been possible hitherto. The method consists in performing the photolysis in the presence of radioactive iodine vapour; the products so formed may be diluted with separable quantities of inactive carriers, and ultimately separated and estimated by means of their activity.

The results obtained at 3130 Å show that the quantum yield of methyl iodide in the acetone photolysis is very much lower than unity; it is dependent on the pressure of acetone and iodine while all normal gaseous products are practically absent. It appears that the primary process at this wavelength is the formation of an activated molecule which normally breaks down to free radicals. The function of iodine in the system has been interpreted on a twofold basis; firstly it combines quantitatively with any radicals, as Gorin has shown, and secondly it possesses the remarkably specific property of deactivating the excited molecule. From the pressures at which this deactivation becomes effective, a half life of at least 10^{-8} sec. has been deduced for the excited molecule, a value which is in agreement with certain results of fluorescence studies. Nevertheless pressures of 200mm. of

acetone or CO_2 cause no appreciable deactivation in the direct photolysis, as the results of this and many other investigations have shown.

A mechanism has been advanced to account for the specific nature of this deactivation, and it has been shown to be in quantitive agreement with the observations.

In methyl-ethyl ketone at 3130 Å, the quantum yield of radicals is shown to be nearly unity and only slightly dependent on pressure. It is inferred that the half life of the activated molecules formed in this ketone is much smaller, and the net effect is that the primary process is very largely a split into free radicals. Two such modes of radical formation are possible, their relative predominance has been deduced from the ratio of methyl iodide to ethyl iodide in the products.

Some experiments were carried out at 2537 Å, but the results were not very conclusive as regards absolute values of quantum yields, owing probably to the presence of minute traces of mercury vapour. Nevertheless the yield of methyl iodide is markedly increased at this wavelength, and it is indicated that the primary radical quantum yield may be unity.

The yields of carbon monoxide in the presence of iodine have been considered from the point of view of stability of the acetyl and propionyl radical. It is concluded that when these radicals are produced with 3130 Å irradiation they do not decompose significantly into alkyl radicals and CO, at 100° in the presence of iodine. The extent of this decomposition increases markedly at 2537 Å as has been inferred from previous investigations, and also increases at low pressures, a result which implies that the radicals as originally formed are normally deactivated to thermal energies by a pressure dependent process.

The general conclusion from these investigations is that the normal photochemical mechanism proceeds exclusively by processes which involve the formation of free radicals. Such radicals are produced directly upon absorption of 2537 Å irradiation, but at 3130 Å they arise from the spontaneous decomposition of an activated molecule. The existence of this activated molecule may be inferred from its reaction with iodine, but it appears to be essentially resistant to deactivation by acetone except at high pressures and low temperatures. Accordingly, it would seem that for all practical purposes the net result in the absence of iodine is the formation of radicals with a quantum yield of unity.

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