393. *Primary Photochemical Reactions. Part VIII. The Quantum Yield of the Photolysis of Methyl* n-*Butyl Ketone.*

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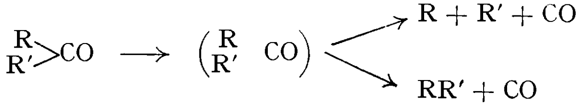
The quantum yields of the photolysis of aldehydes and ketones have been the subject of several researches (Norrish and Kirkbride, J., 1932, 1518; Leighton and Blacet, *J. Amer. Chem. Soc.*, 1932, **54**, 3165; 1933, **55**, 1766; Damon and Daniels, *ibid.*, p. 2363; Norrish, Crone, and Saltmarsh, J., 1934, 1456). The following results have been recorded for temperatures of 100° or lower :

	Wave-length region, Å.				Wave-length region, Å.		
Substance.	3340.	3130.	2536.	Substance.	3340.	3130.	2536.
Formaldehyde	0·7	1·1	0·9	Propaldehyde	—	0·53	1·0
Acetaldehyde	0·75	0·25	0·9	Acetone	—	0·22	0·4

Associated with the decomposition of acetaldehyde there is a marked photopolymerisation, but this was not observed to any appreciable extent in the case of formaldehyde and dry acetone.

All the above substances decompose according to the scheme



$$\begin{matrix}R\\R'\end{matrix}\!>\!CO \longrightarrow \left(\begin{matrix}R\\R'\end{matrix}\ CO\right) \begin{matrix}\nearrow R + R' + CO\\ \searrow RR' + CO\end{matrix}$$

and the quantum yields were usually measured by the volume of carbon monoxide produced. This type of decomposition has been termed Type I. It may also give rise to chain reactions at high temperatures in the case of aldehydes on account of the free hydrogen atoms liberated; Leermakers (*J. Amer. Chem. Soc.*, 1934, **56**, 1537) recorded for acetaldehyde values of 300 or more between 300° and 400°, and Akeroyd and Norrish (unpublished) obtained similar results for formaldehyde.

At low temperatures, however, the quantum yield of decomposition according to Type I tends to be less than unity. The reason for this has been discussed by Norrish, Crone, and Saltmarsh (*loc. cit.*) in the case of acetone. It is clear that it cannot be accounted for by fluorescence, which is restricted to the longer wave-lengths, and it seems probable that in a polyatomic molecule a type of internal deactivation can occur whereby the energy of excitation absorbed by the chromophore may be degraded to heat and distributed throughout the thermal degrees of freedom.

Other authors have held that the low quantum yield may be explained by deactivation due to collisions, but in our opinion such a process is doubtful, especially at low pressures, since it is known that for liquid acetone collisions between an excited and a normal molecule result in association reactions (Bowen and de la Praudière, J., 1934, 1503) without the elimination of carbon monoxide, and Damon and Daniels (*loc. cit.*) found no such association in pure dry gaseous acetone.

With ketones and aldehydes containing larger hydrocarbon chains a new type of decomposition, which we have termed Type II, occurs; *e.g.*, methyl butyl ketone (Norrish and Appleyard, J., 1934, 874) decomposes according to the scheme $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3 \longrightarrow CH_3{\cdot}CH{:}CH_2 + CH_3{\cdot}CO{\cdot}CH_3$. The decomposition of dipropyl ketone and *iso*valeraldehyde (Bamford and Norrish, this vol., p. 1504) and menthone (*idem*, unpublished) is roughly equally divided between Types I and II, and in Type II the fission in the hydrocarbon chain always occurs in the same place. In methyl butyl ketone decomposition is more in favour of Type II, and Norrish and Appleyard (*loc. cit.*) showed the amounts of acetone and propylene to be nearly equivalent. From this it may be concluded that 90% of the reaction follows Type II, and 10% follows Type I to give carbon monoxide and a mixture of paraffins. With more extended irradiation, however, the percentage of ethane and carbon monoxide increases, and it is apparent that a secondary decomposition of acetone is occurring.

On account of the marked tendency in favour of Type II, it was considered of interest to investigate the quantum yield in order both to gain some insight into the mechanism and to obtain a basis of comparison of the two types of primary reaction in aldehydes and ketones.

EXPERIMENTAL.

Methyl butyl ketone has the usual carbonyl absorption band. Photographs taken with a hydrogen lamp through a column 1 m. long in the second order of a 3-m. grating showed that this extends from 3200 to 2500 Å. at 40 mm. pressure, and that it is quite structureless from 760 mm. down to 4 mm. This is in accord with the fact that all attempts to observe fluorescence in the range 4—700 mm. were abortive.

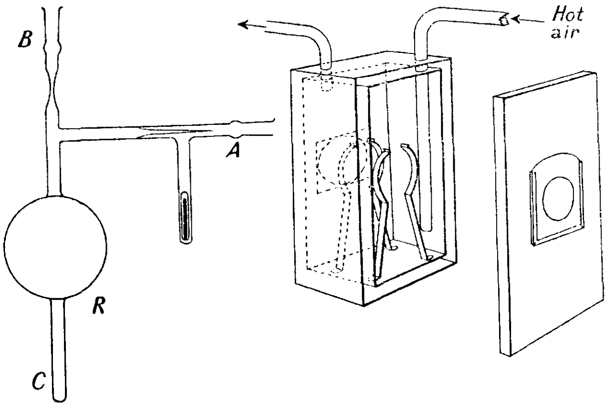
It was decided to use approximately monochromatic light of wave-length 2480—2770 Å. which is situated in the middle of the absorption region. A horizontal mercury lamp of special type was employed as the source of light. It was used in the "end-on" position and was furnished with a plane quartz window so that a sharply defined beam of maximum intensity was obtained. The lamp was run from a battery at constant voltage. The wave-length region mentioned above was isolated by colour filters of nickel chloride and gaseous chlorine contained in plane parallel quartz cells (Bowen, J., 1932, 2236).

A cylindrical quartz reaction vessel of 4 cm. diameter and 5 cm. long with fused-quartz end plates (Fig. 1) was used. The stem *C* containing the liquid was out of the path of the light, so that only the part filled with vapour was exposed. The vessel was furnished with two outlet tubes, *A* and *B*, with ground-glass joints, *A* being closed by a "vacuum Verschluss" and *B* being provided with a constriction for sealing off. The vessel, after careful cleaning and drying under vacuum, was evacuated through *B* by means of a mercury diffusion pump. About 0·5 g. of the purified ketone was then distilled into *C* by cooling with liquid air, and the vessel sealed off at the constriction.

In order to obtain a satisfactory pressure of ketone, the decomposition was carried out at 127°, at which its vapour pressure is atmospheric. For this purpose a double-walled oven with plane parallel quartz windows was constructed to hold the reaction vessel. The oven was heated by means of a stream of hot air from an electric blower. The temperature could easily be maintained constant indefinitely to ± 0·5° by regulating a variable resistance controlling the circuit of the electric heater which warms the air, and also by regulating the quantity of air passing through.

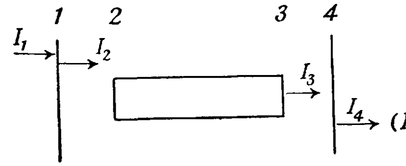
The intensity of the light was measured by means of a Moll thermopile and a Broca galvanometer, the absolute sensitivity of which had been previously determined by means of a standard lamp calibrated by the National Physical Laboratory. A variable potential was included in the galvanometer circuit in order to counteract the zero shift which occurs over long periods (see Griffiths and Norrish, *Proc. Roy. Soc.*, **1931**, *A*, **130**, **591**). The light filter allowed green light to pass through as well as ultra-violet; this visible light is unabsorbed and is without action on the ketone. In order to determine the intensity of the ultra-violet light it was therefore necessary to insert a glass plate which filtered it out and allowed a separate measurement of the intensity of the visible light to be made.

FIG. 1



The whole of the apparatus was mounted on an optical bench, and the light beam, confined by stops and rendered slightly convergent by a quartz lens, was made to pass axially through the quartz cell. After emerging from the cell it was focused by a second quartz lens on to the surface of the Moll thermopile, so that the whole of the light field was collected by the sensitive elements.

FIG. 2.



The thermopile was contained in a highly insulated box with an aperture covered by a quartz cell containing water to admit the light beam. In this way fluctuations due to the proximity of the oven were completely eliminated. The loss in intensity by reflexion and absorption of the water cell, the empty reaction vessel, and the windows of the thermostat were directly determined by measurement. Only the influence of the lens in front of the thermopile could not be determined in this way and had to be calculated. It was estimated with an error of 15%.

The effective absorption was evaluated by the formula

$$I_{\text{abs.}} = \bar{I}_2\sqrt{\frac{I_3}{I_2}}\left(1 - \frac{I_4{}^*}{I_4}\right)\left\{1 + \frac{I_4{}^*}{I_4}R\left[1 + \frac{I_3}{I_2}\left(1 + \frac{1}{(1-R)^2} + \frac{1}{(1-R)^2}\right)\cdot\frac{I_2{}^2}{I_1{}^2}\right]\right\} \qquad (1)$$

in which (see Fig. 2) I_1, I_2, I_3, I_4, and $I_4{}^*$ are the intensities measured respectively when the thermostat and vessel are removed, when the first window of the thermostat is in position, when the empty vessel also is in position, when the thermostat too is in position, and when the vessel is filled; $\bar{I}_2$ differs from I_2 by the correction for the loss on the lens and the water cell in front of the thermopile, and R is the reflecting power of quartz.

By means of the terms containing R, this formula takes into account the part absorbed from the light reflected back from the windows 3 and 4 of the vessel and thermostat. Under our conditions, formula (1) can be written

$$I_{\text{abs.}} = 0{\cdot}85\bar{I}_2(1 - I_4^*/I_4)\{1 + 0{\cdot}12 I_4^*/I_4\} \qquad (1')$$

$0{\cdot}85I_2$ and $0{\cdot}85I_2I_4^*/I_4$ are tabulated respectively as the incident and the transmitted intensity (*i.e.*, falling on and transmitted by the vapour).

The incident intensity was determined before and after each experiment. During irradiation, frequent measurements of the transmitted light were made and so the total quantity of absorbed light energy could be calculated.

After the irradiation, the reaction vessel was removed and attached to a Toepler pump by way of the outlet tube *A*. The contents were frozen in the side tube *C* by liquid air, and the " vacuum Verschluss " was broken. The liquid air was then replaced by a mixture of alcohol and liquid nitrogen at − 110°, and the permanent gases formed in the decomposition were pumped off and analysed. These consisted entirely of propylene, ethane, and carbon monoxide, the last two arising partly from the decomposition of the acetone formed in the primary decomposition of the ketone.

Since 10% of the decomposition occurs according to the equation $C_4H_9{\cdot}CO{\cdot}CH_3 = \frac{1}{3}(C_8H_{18} + C_5H_{12} + C_2H_6) + CO$, and 90% according to the equation $C_4H_9{\cdot}CO{\cdot}CH_3 = C_3H_6 + CH_3{\cdot}CO{\cdot}CH_3$, we can now estimate the quantum yields of the two types of decomposition, due allowance being made for the acetone decomposed, as represented by the carbon monoxide formed in excess of one-ninth of the propylene, and for the fact that the quantum efficiency for the decomposition of acetone at 120° is about 0·5.

The liquid remaining after removal of the permanent gas was slightly brown, showing that some condensation or polymerisation had occurred. In order to estimate the extent of this, the ketone was distilled out of the reaction cell in a vacuum and the non-volatile brown residue was retained in the side arm *C*. This was then cut off, and the weight of the residue accurately determined. It was found that the polymerisation was slight in comparison with the decomposition.

The following results were obtained :

Temperature 127° ; Pressure 760 mm. ; Wave-length region 2480—2770 Å. ; Sensitivity of thermopile–galvanometer system 324 ergs/sec.

	Expt. 1.†	Expt. 2.	Expt. 3.
Incident intensity (galvanometer deflexion, cm.) ($0{\cdot}85\bar{I}_2$)	11·2—22·8	191·1	161·5
Transmitted intensity (galvanometer deflexion, cm.) ($0{\cdot}85\bar{I}_2I_4^*/I_4$)	2·4	99·4	85·6
Time of irradiation (hrs.)	15	12·5	16
Radiation absorbed, × 10^{-7}, ergs	14—40	142	150
Vol. of C_3H_8 at *N.T.P.* (c.c.)	0·31	1·45	2·21
Vol. of C_2H_6 at *N.T.P.* (c.c.)	—	0·17	0·46
Vol. of CO at *N.T.P.* (c.c.)	0·11	0·47	0·56
Weight of solid residue (mg.)	1	3·2	1·5
Quanta absorbed in decomposing $COMe_2$, × 10^{-19}	0·4	1·6	1·6
Quanta absorbed in decomposing COMeBu, × 10^{-19}	1·8—4·8	17·2	18·4
Total mols. of ketone decomposed, × 10^{-19}	0·93	4·36	6·7
Total mols. of ketone polymerised, × 10^{-19}	0·3	0·97	0·45
Quantum yield of decomposition { Type I	0·03—0·02	0·03	0·04
Quantum yield of decomposition { Type II	0·47—0·18	0·22	0·32
Quantum yield of polymerisation	0·17—0·06	0·06	0·03

† Expt. 1 is only approximate. Maximum and minimum values of light absorption and quantum yield are given. The uncertainty arises from the fact that a cobalt sulphate light filter used in this experiment proved to be unstable and gave different transmissions at the beginning and the end of the irradiation. The filter was abandoned and the nickel chloride–chlorine filter was used in Expts. 2 and 3.

DISCUSSION.

The complete diffuseness of the absorption spectrum of methyl butyl ketone and the absence of any fluorescence in the vapour between 700 mm. and 4 mm. show that the primary dissociation takes place in one act. It may further be affirmed that the reaction which we have called Type II is a true primary process which grows in probability as the length of the hydrocarbon chain is increased. This is proved by the complete analogy between the decompositions of methyl butyl ketone, dipropyl ketone, *iso*valeraldehyde, and menthone. In all cases the link between the α and the β carbon atom with reference to the carbonyl group is broken, and this can only occur if a large amount of energy is transferred from the carbonyl group where it is initially absorbed to the αβ link where reaction occurs. The present measurements show that, at a pressure of 1 atm., out of 100 molecules which absorb quanta some 65 lose their energy without reacting, some 27 react according to Type II, 4 react according to Type I, and about 4 become polymerised.

Since there is no fluorescence, the 65% of molecules which lose their excitation energy must be deactivated either by an internal process or by collision. It is possible that at the pressure used both processes play a part, but we are of the opinion that the former is more important, because the absence of structure in the spectrum even at low pressure and under high resolving power shows that the activated state of the carbonyl group is of extremely short duration and less than the period of vibration (10^{-14} sec.). Thus the energy which initially is located there must become extremely rapidly distributed to other parts of the molecule. Such a rapid degradation can only occur by an internal process.

Since the reaction always tends to occur at the same point of the molecule, it suggests that with the ketones and aldehydes containing a long chain, some type of internal resonance exists between the excited carbonyl group, and the C–C link in the αβ position. The quantitative results show that for methyl butyl ketone this resonance leads to chemical decomposition only about once in four times. In the other three cases the state of the molecule is such that it survives this shock, and the energy passes to the other degrees of freedom.

The decomposition according to Type I becomes more probable as the length of the chain is decreased; it also has a very high probability in the case of the cyclic ketones, *cyclo*-heptanone, -hexanone, and -pentanone (Saltmarsh and Norrish, this vol., p. 455), from which cyclic hydrocarbons with unstrained rings can be produced. It is thus apparent that steric factors are largely responsible for the relative probabilities of the two types of decomposition; it is impossible to be more precise until we have a clearer understanding of the mechanics of these polyatomic molecules.

SUMMARY.

The quantum yield of the photodecomposition of methyl butyl ketone has been measured for the wave-length region 248—277 mμ, at 760 mm. pressure. For the reaction (Type I) $C_4H_9{\cdot}CO{\cdot}CH_3 \longrightarrow CO + CH_3 + C_4H_9$, it is about 0·03, and for the reaction (Type II) $C_4H_9{\cdot}CO{\cdot}CH_3 \longrightarrow CH_3{\cdot}CO{\cdot}CH_3 + C_3H_6$, it is about 0·27. For condensation or polymerisation it is about 0·04.

The mechanism of deactivation is considered in the light of the facts that the absorption spectrum is completely diffuse, and that no fluorescence can be detected.

We are indebted to the Royal Society for grants, and to Mr. H. G. Crone for assistance in photographing the absorption spectrum.

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