289. *Primary Photochemical Reactions. Part XII. The Effect of Temperature on the Quantum Yield of the Decomposition of Di-*n*-propyl Ketone in the Vapour Phase and in Solution.*

By C. H. Bamford and R. G. W. Norrish.

The quantum yield of the photolysis of di-*n*-propyl ketone in the gas phase and in paraffinoid solution has been measured for temperatures in the range 0—100°. It has been found that, whereas in the gas phase the quantum yields of Type I and Type II decompositions are practically independent of temperature, yet in solution the quantum yield of Type I is markedly affected by temperature, rising from practically zero at room temperatures to 0·3 at 100°. The quantum yield of Type II in solution is affected by temperature only to a very much smaller extent. The results are explained in terms of the Franck–Rabinowitch principle of primary recombination, and a quantitative treatment is given, based on the simple model of a ketone molecule enclosed by a cage formed by neighbouring solvent molecules. At low temperatures in solution the alkyl and acyl radicals produced by the primary act of Type I mainly recombine, but at higher temperatures stabilisation, and consequently photolysis, occurs through hydrogenation of the radicals, or decomposition of the acyl group. Values of the energies of activation for the hydrogenation and decomposition reactions are calculated as 12·3 kg.-cals. and 17 kg.-cals. respectively. In the case of Type II, no free radicals are produced, and the Franck–Rabinowitch principle does not come into operation.

It has been shown in the previous paper that the primary processes of photolysis of aldehydes and ketones are in general unmodified in solution, but that fundamental secondary processes may intervene which profoundly modify the extent and course of the reactions. Thus, owing to the operation of the principle of primary recombinations, reactions of Type I are completely suppressed in solution at 20°, and only become appreciable at temperatures approaching 100°, when the free radicals can become stabilised by hydrogenation at the expense of the solvent. On the other hand, reactions proceeding with the production of stable molecules, as is the case with Type II, and Type I decompositions with aldehydes, are apparently unaffected by the solvent at all temperatures.

In the present paper we have chosen a ketone, *viz.*, di-*n*-propyl ketone, which in the gas phase decomposes to about equal extents according to reactions of Type I and Type II, and have measured the quantum yields of both processes in the gas phase and in solution over the temperature range 0—100°. Taken in conjunction with the results of the previous paper, the data admit of a remarkably complete interpretation in terms of the principles of primary recombination, and of hydrogenation of radicals. They leave no reasonable doubt of the general correctness of the conclusions at which we have previously arrived on the basis of our earlier work, and at the same time they provide a convincing proof of the importance of the Franck–Rabinowitch principle to the study of reactions in solution.

Experimental.

(1) *The Determination of Quantum Yields for Vapour-phase Photolysis at High Temperatures.*—The apparatus used was similar to that described by Bloch and Norrish (J., **1935**, **1638**). It consisted of a mercury lamp and optical system for supplying a parallel beam of approximately monochromatic light, a quartz reaction vessel, and a thermopile–galvanometer system for measuring light intensities. In principle, the method consists in measuring the transmitted intensity with the reaction vessel empty, and with it filled with ketone vapour at the required temperature. A knowledge of the light losses resulting from reflections and absorptions at the quartz faces of the reaction vessel, etc., enables the effective absorption of the vapour to be calculated, and from this, and a measurement of the volume of gas produced by the decomposition, the quantum yielded was estimated.

The mercury lamp was of the horizontal type, and had a plane quartz window, giving a beam which could easily be focused on the thermopile. It was run from a 110-volt circuit supplied by a battery of storage cells at a constant burner voltage of 75. A filter (see Bowen, J., **1932**, 2236) of nickel chloride solution and gaseous chlorine in separate quartz vessels with plane faces was employed to isolate a spectral region 2480—2770 A. This range of wavelengths is situated approximately in the middle of the carbonyl absorption band.

The reaction vessel was cylindrical and made wholly of quartz. The diameter and length were respectively 4 and 5 cm. The ends were plane, and constructed from fused quartz. Two outlet tubes were attached to the vessel, one carrying a vacuum breaker, and the other a constriction for sealing off. In addition, a third tube served as a reservoir for liquid ketone. When the whole had been very carefully cleaned and dried, a little of the ketone was distilled into this tube in a vacuum and frozen in liquid air. The vessel was then evacuated by a two-stage mercury-diffusion pump backed by a Hyvac pump, and sealed at the constriction. To maintain the reaction cell at the desired temperature, a double-walled air-thermostat, fitted with plane parallel quartz windows, was used. This was heated by blowing in air which had previously passed through an electrically heated Pyrex tube; the temperature could be kept constant to within 0·5° with ease.

A Moll thermopile and Broca galvanometer were employed to measure the intensities. The system was calibrated by means of a standard lamp supplied by the N.P.L., the calibration being frequently checked during the course of the work. A variable potential was included in the circuit to allow for the zero shifts which always occur over long periods. The thermopile was enclosed in a highly insulated box. A quartz cell filled with water covered the aperture of the thermopile, and eliminated disturbing effects due to air currents and fluctuations in the external temperature.

The whole of the apparatus was mounted on an optical bench. Two quartz lenses were used to obtain a slightly convergent light beam, which passed through the filter and reaction cell, and was focused by another quartz lens so that the whole of it fell on and almost covered the sensitive elements of the thermopile.

The filter allowed a certain amount of green light to pass through as well as ultra-violet. This was unabsorbed, and therefore without action on the ketone. Thus it was necessary to make a separate determination of the ultra-violet intensity. This was done by measuring the total intensity, and also the intensity transmitted through a glass plate, which absorbed all the active light. The interposition of this plate, however, introduced losses in the visible light by reflection and absorption; these were estimated by using a second similar plate. The additional fall in intensity produced by this plate was entirely due to the above-named losses, and the correction to be made for changes in the transmitted visible intensity due to the first plate could then be calculated by proportion.

The corrections to be applied for light losses due to reflection and absorption by the quartz windows were determined experimentally as described by Bloch and Norrish. If I_1, I_2, I_3, and I_4 represent ultra-violet intensities at the points represented in Fig. 1, then the effective absorption is given by

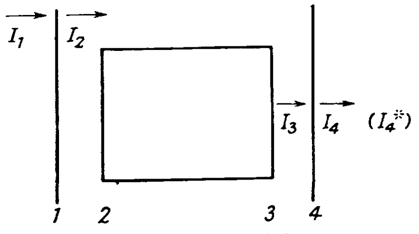
$$I_{\text{abs.}} = I_2\sqrt{\frac{I_3}{I_2}}\left(1 - \frac{I_4^*}{I_4}\right)\left\{1 + \frac{I_4^*}{I_4}R\left[1 + \frac{I_3}{I_2}\left(1 + \frac{1}{(1-R)^2}\right) + \frac{1}{(1-R)^2}\frac{I_2^2}{I_1^2}\right]\right\}$$

where I_4 represents the transmitted intensity with the cell empty, and I_4^* the corresponding intensity with it filled with vapour.

The windows of the thermostat were removable, so that I_1, I_2, I_3, and I_4 could be measured directly. R is the reflecting power of quartz. The terms containing R in the above equation take into account the part absorbed from the light reflected back from the windows 3 and 4 in Fig. 1. This is only a small fraction of the total absorption, and hence it is not necessary to know R accurately.

It will be seen from the above expression that, in order to calculate $I_{\text{abs.}}$, it is necessary to know the absolute value of I_2. To obtain this, the effect of the lens and water cell in front of the thermopile had to be estimated. (Obviously, to evaluate the ratios of intensities which appear in the equation it suffices to determine relative values of the intensities.) By taking measurements with and without the water cell, the effect of the latter was determined, but the correction for the lens could not be found in this way. It was calculated theoretically to within a few units %.

FIG. 1.



1, 4. *Quartz windows of thermostat.*
2, 3. „ „ „ *reaction cell.*

At the conclusion of the run, the reaction cell was connected to a Toepler pump by means of the ground joint on the tube carrying the vacuum breaker. The tube containing the residual ketone was cooled to − 120° in a freezing mixture of liquid nitrogen and alcohol, the breaker broken, and all gaseous products pumped off. Since the volumes obtained were rather small, they were measured by confining the gases above mercury in a previously calibrated volume, and measuring the pressures exerted. These were of the order of 100 mm. and so could be easily determined with sufficient accuracy. The gases were analysed in a Bone and Wheeler apparatus suitable for small quantities. In order to determine the quantum yield of polymerisation, any liquid remaining after removal of the gaseous products was distilled out in a vacuum. The polymer was then left as a non-volatile brown residue in the lower limb of the vessel, and could be estimated by cutting off the tube, weighing, removing the polymer, and reweighing.

(2) *The Quantum Yield at Low Temperatures.*—The determination of the quantum yield at room temperatures presented more difficulty on account of the low vapour pressure, and consequently low absorption, of the ketone. To obtain a reasonable amount of absorption it was necessary to employ an absorption tube 1 m. long, and this raised the difficulty of obtaining an accurately parallel beam of light from an extended source. It was found impossible to avoid the loss of a considerable amount of light by scattering at the walls of the tube, and consequently it was necessary to develop an expression which would correct for such losses, at any rate approximately. This expression is based on measurements of the total intensity entering the tube, and that emerging, when the tube was empty, and on the geometrical properties of the optical system. If $I_{\text{abs.}}$, I_2, and R have the same significance as in the previous equation, we obtain *

$$I_{\text{abs.}} = 0{\cdot}33 I_2(1 - R)^2$$

The set-up and method of investigation were in principle exactly as described previously. The liquid ketone was contained in a side limb of the absorption tube and maintained at 13°, giving a vapour pressure of 5 mm.

* For consider a ray scattered by n reflections inside the tube. Let I'_0 be the incident intensity, I'_1 that immediately after the first reflection, and so on. The distance traversed by the ray between two reflections is approximately l/n, where l is the length of the absorption tube. Then

$$I'_1 = I'_0 e^{-\varepsilon l/n}\,.\,R',$$

where ε is proportional to the extinction coefficient, and R' is the reflection coefficient. Similarly

$$\left.\begin{array}{l} I'_2 = I'_1 e^{-\varepsilon l/n}\,.\,R' = I'_0 e^{-2\varepsilon l/n}\,.\,R'^2 \\ I'_n = I'_0 e^{-\varepsilon l}\,.\,R'^n \end{array}\right\} \quad \ldots\ldots\ldots\ldots \quad (1')$$

The absorbed intensity before the first reflection, $I_1^{\text{abs.}}$, is given by

$$I_1^{\text{abs.}} = I'_0(1 - e^{-\varepsilon l/n})$$

Similarly $$I_2^{\text{abs.}} = I'_1(1 - e^{-\varepsilon l/n}) \text{ and so on} \quad \ldots\ldots\ldots \quad (2')$$

($I_2^{\text{abs.}}$ is the intensity absorbed between the first and the second reflections).

The total absorption is then given from (1′) and (2′) as

$$\begin{aligned} I_{\text{abs.}} &= I_1^{\text{abs.}} + I_2^{\text{abs.}} \ldots\ldots\ldots + I_n^{\text{abs.}} \\ &= I'_0(1 - e^{-\varepsilon l/n})\{1 + R'e^{-\varepsilon l/n} \ldots + R'^{n-1}e^{-\varepsilon l(n-1)/n}\} \quad \ldots\ldots \quad (3') \end{aligned}$$

Thus $$I_{\text{abs.}} = I'_0(1 - e^{-\varepsilon l/n})\left\{\frac{1 - R'^n e^{-\varepsilon l}}{1 - R'e^{-\varepsilon l/n}}\right\} \quad \ldots\ldots\ldots \quad (4')$$

When a pencil is considered, instead of a single ray, an approximate expression for $I_{\text{abs.}}$ is obtained by using the mean value of n in (4′). This may be found experimentally as follows. Let the values of I'_n with the tube empty and when filled with ketone vapour be I'_n and $I'_n{}^*$ respectively. Then by (1′)

$$I'_n/I'_0 = R'^n \quad \ldots\ldots\ldots\ldots \quad (5')$$

(since $\varepsilon = 0$ for the empty tube)

and $$I'_n{}^*/I'_0 = R'^n e^{-\varepsilon l} \quad \ldots\ldots\ldots\ldots \quad (6')$$

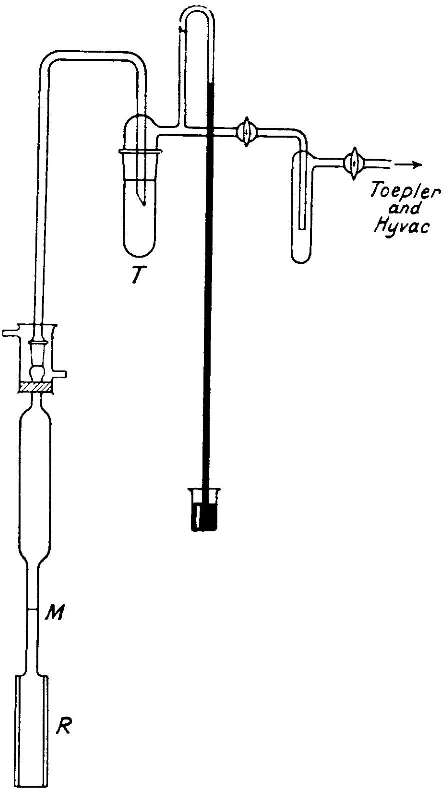
From (5′) and (6′), n and $e^{-\varepsilon l}$ may be found, and substitution of these into (4′) gives $I_{\text{abs.}}$.

In the experiments described above, $I'_n/I'_0 = 0{\cdot}259$, and $I'_n{}^*/I'_0 = 0{\cdot}150$. Thus, taking $R' = 0{\cdot}5$ (the value calculated from Fresnel's equation), $n = 2$ and $e^{-\varepsilon l} = 0{\cdot}58$. Substitution of these values in (4′) gives the equation in the text [since $I'_0 = I_2(1 - R)^2$]. The value of n obtained above from purely optical measurement agrees well with that which would be expected from considerations of the geometry of the systems, and to a certain extent justifies the use of an equation of the form given above.

(3) *Quantum Yields in Solution.*—The reaction cell and system shown in Fig. 2 was employed. The quartz cell *R* was 7 cm. in diameter and 2 cm. long, and had plane faces. It was connected by a water-cooled ground joint to a series of liquid-air traps, leading to a Toepler pump and to a mercury-diffusion pump backed by a Hyvac pump. *R* was filled to the mark *M* with the liquid to be investigated, and the latter was then frozen in the narrow tube, by wrapping the tube in cotton-wool soaked in liquid air. This was repeated several times completely to remove air enclosed in pockets formed below the solid by contraction of the liquid in *R*. The cell was surrounded by the air-thermostat previously described, and was then brought to the desired temperature. If the temperature used was above atmospheric, carbon dioxide was admitted to the apparatus to prevent distillation of liquid to the cool parts of the system. During the early stages of the warming up, and before the irradiation was started, there was considerable frothing, which soon subsided when the liquid had come into equilibrium with its vapour. In order to prevent loss of liquid from the reaction vessel, the tube above *M* was therefore constructed of wide-bore tubing of about 2 cm. diameter.

The optical system was exactly as described previously for the experiments in the vapour phase at high temperatures. Before a run was started, preliminary tests were made on the solvent to ensure its transparency to the wavelengths used. It was found that medicinal paraffin, purified as described in Part XI (p. 1536), possesses a very small but definite absorption. This makes it unsuitable for use in the determination of quantum yields, for, though the light absorbed by the solvent in the presence of the strongly absorbing solute is negligible, it is impossible to determine the light losses at the windows of the reaction cell, as this involves blank experiments with the solvent alone. A satisfactory solvent was found in pure *iso*-octane, kindly supplied by the Anglo-Iranian Oil Company.

FIG. 2.



The experiments were performed in the manner described previously. After irradiation, the traps were cooled to − 80°, and the gaseous products pumped through them, and removed by the Toepler pump. During this process most of the solvent was distilled from *R* to the large trap *T*. In order to remove the gases completely, the traps were allowed to warm to atmospheric temperature; they were then cooled again and any gases disengaged pumped off. This series of events was repeated until no more gas could be obtained. The volumes of products were measured accurately as described before, and the gases were analysed by standard methods.

Since the solutions used gave practically complete absorption, a simplified form of the first equation may be used to calculate the absorption. By putting $I_4^* = 0$, the equation reduces to $I_{\text{abs.}} = \sqrt{I_2 I_3}$.

Results.

(a) *Gas Phase.*—Sensitivity of thermopile–galvanometer system: 655 ergs/sec./cm. for expts. (i) and (ii), 365·5 ergs/sec./cm. for expt. (iii). I_2, I_4, and I_4^* in the following table have the meaning explained previously (p.1545). They represent actual ultra-violet intensities.

Hence, at 100° and 74°, out of 100 molecules of ketone which absorb light, some 36—37 undergo decomposition of Type I, 30—29 that of Type II, and 20 polymerise. The remainder must be deactivated without reaction. Although there is some change in these figures at 15°, and although the results are admittedly less accurate as a result of the greater difficulties of experimentation, it is clear that the quantum yield is *of the same order* at low and at high temperatures.

Experiment.	(i).	(ii).	(iii).
Temperature	100°	74°	15°
Pressure, mm.	260	112	5
I_2, galvanometer deflections, cm.	26·4	26·3	6·65
I_4, ,, ,, ,,	20·0	19·9	1·38
I_4^*, ,, ,, ,,	4·1	9·9	0·80
Time of irradiation, hrs.	15·17	14·5	263·5
Total radiation absorbed, ergs $\times 10^{-7}$	51·9	23·2	70·0
Quanta absorbed $\times 10^{-19}$	6·88	3·08	9·3
Vol. of CO formed, c.c. at *N.T.P.*	0·95	0·41	0·91
,, C_2H_4 ,, ,, ,,	0·74	0·34	1·43
Wt. of solid residue, mg.	2·5	1·2	—
Quantum yield of CO (Type I)	0·37	0·36	0·26
,, ,, C_2H_4 (Type II)	0·29	0·30	0·45
,, ,, polymerisation (based on number of ketone molecules polymerising)	0·20	0·20	—

(b) *Liquid Phase.*—Sensitivity of thermopile–galvanometer system: 655 ergs/sec./cm. I_2 and I_4^* represent actual ultra-violet intensities.

Experiment.	(i).	(ii).	(iii).	(iv).	(v).
Temperature	20·5°	20·5°	68·0°	96·0°	96·0°
I_2, galvo. deflexions, cm.	35·0	31·6	31·5	36·4	37·5
I_4^*, ,, ,,	0·2	0·2	0·2	0·2	0·2
Time of irradiation (hrs.)	17·17	15·75	9·00	17·00	16·37
Radiation absorbed, ergs $\times 10^{-7}$	127·5	106·0	60·5	132·5	144·0
Quanta absorbed $\times 10^{-20}$	1·63	1·40	0·80	1·75	1·91
Vol. of CO, c.c. at *N.T.P.*	0·061	0·070	0·519	1·91	2·11
,, C_2H_4, ,, ,,	1·35	1·27	0·575	1·13	1·21
Quantum yield of CO (γ_{CO}) (Type I)	0·01	0·01	0·175	0·30	0·30
,, ,, C_2H_4 ($\gamma_{C_2H_4}$) (Type II)	0·22	0·25	0·19	0·18	0·17

The results show that $\gamma_{C_2H_4}$ in solution decreases steadily with rise of temperature; the values obtained, when plotted against temperature, lie on a curve which is very nearly a straight line. Further, the values of the yield per hour of ethylene given in the previous paper (p. 1539) also exhibit a practically linear relationship with temperature, the slope of the lines being the same in both cases. Since different wave-length regions were employed in the two sets of experiments, it seemed probable that the relative volumes of the products would be the same for different wave-lengths. This has already been suggested in the previous paper (p. 1540). To test this point, two series of experiments were performed at different temperatures; at each temperature the liquid was irradiated by (*a*) the full light of the hot arc, (*b*) the radiation from a lamp with water-cooled electrodes, in which a high-tension mercury discharge passes through neon at a few mm. pressure. In the former case the most intense lines emitted from the source extend from 2300 A. to longer wave-lengths, and the ketone absorbs all those which fall within the first carbonyl absorption band extending from 2300 to 3100 A. The cold lamp, however, emits practically monochromatic radiation, at least 95% of its output being the mercury resonance line 2536 A. A comparison between the results obtained with the two lamps thus allows an estimate to be made of the effect of wave-length upon the course of the reaction inside the first carbonyl band. The results are tabulated below.

Experiments to determine the effect of change in absorbed wave-length on the course of photolysis.

Vols. of products are given in c.c. of vapour at *N.T.P.* In all cases 10% solutions (by vol.) of the ketone in medicinal paraffin were used.

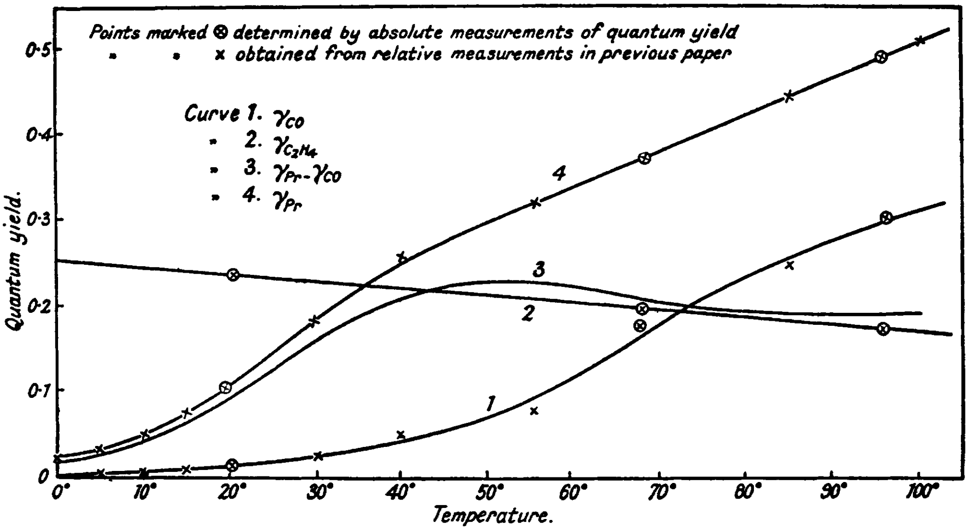
Wave-length.	Temp.	CO.	C_3H_8.	C_2H_4.	Unsaturation (c.c. of olefin).	$\frac{C_3H_8}{CO}$.	$\frac{C_3H_8}{C_2H_4}$.	$\frac{\text{Unsaturation}}{\frac{1}{2}C_3H_8}$.
2536 A.	15°	1·8	11·5	39·7	6·2	6·40	0·29	1·15
Full light of hot arc	15	2·1	14·0	45·2	7·5	6·65	0·31	1·07
2536 A.	95	6·0	9·7	3·6	—	1·62	2·69	—
Full light of hot arc	95	8·0	13·0	4·6	—	1·63	2·81	—

It will be seen that each of the ratios C_3H_8/CO and C_3H_8/C_2H_4 is unaltered by the use of 2536 A. light instead of the full light of the hot arc, and it appears that the course of the reaction is independent of the value of the absorbed quantum. This is true in spite of the slight absorption shown by the paraffin below 2350 A., since, as stated in the preceding paper (p. 1536), the ketone, by reason of its much greater extinction coefficient, absorbs practically all the light. For this reason it is justifiable to combine the quantum-yield measurements described in this paper with the analytical results given in the previous paper. The linear relation between the yield per hour of ethylene and the temperature (referred to on p.1548) was used as a basis for this purpose; a proportionality factor was found which would convert yields per hour into quantum yields. From the figures given on p. 1539 of the previous paper, it is thus possible to obtain a number of values of γ_{CO} and $\gamma_{C_2H_4}$ in addition to those which were determined by direct measurement. In this way the curves of Fig. 3 were constructed. It is to be noted, however, that the results of the previous paper referred to are less accurate than the quantum-yield measurements, and this fact must be borne in mind when seeking a theoretical interpretation of the curves.

DISCUSSION.

It has already been shown that the general form of the curves given in Fig. 3 can be explained in terms of the Franck–Rabinowitch principle. It is desirable, however, to discuss the matter precisely, and this may be done in the following manner. In view of the fact that the primary photochemical act occurs so rapidly, one is concerned in solution with what is virtually a single molecule enclosed by a cage of solvent molecules; it follows that the processes occurring are in general unimolecular, and it is possible to discuss the probabilities of various reactions in terms of the unimolecular velocity coefficients. Such a method of treatment is obviously an idealisation; nevertheless, the extremely low quantum yields for Type I decomposition at ordinary temperatures seem to show that the picture is a fairly true one.

FIG. 3.



The following possibilities are the only ones which confront the dissociated molecule in these circumstances: (*a*) recombination of the radicals to generate dipropyl ketone; (*b*) hydrogenation of the propyl group; (*c*) hydrogenation of the acyl group; (*d*) decomposition of the acyl group. The probability that one of these events, *e.g.*, (*a*), will occur is given by an expression of the form

$$p_a = k_R/(k_H + k'_H + k_R + k_D) = k_R/\Sigma k \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which k_R, k_H, k'_H, and k_D are the unimolecular velocity coefficients for the processes (*a*), (*b*), (*c*), and (*d*) respectively.

The probability of formation of carbon monoxide may now be calculated as follows.

Carbon monoxide may be produced in two ways : (i) From the decomposition of the acyl group according to (*d*) above; the probability of this is $k_D/\Sigma k$. (ii) Acyl groups are liberated from the shell by hydrogenation of the propyl radical, and some of these will later decompose, yielding eventually propane and carbon monoxide; the probability of liberation of the acyl group is $k_H/\Sigma k$, and as an approximation to the probability of its subsequent decomposition we may write $k_D/(k_D + k'_H)$, neglecting possible polymerisation. The probability of the formation of carbon monoxide from a ketone molecule by (ii) is thus

$$(k_H/\Sigma k)\,.\,[k_D/(k_D + k'_H)] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The total probability of carbon monoxide production is the sum of the probabilities for (i) and (ii), and so will be given by

$$p_{CO} = k_D/\Sigma k + k_H k_D/\Sigma k(k_D + k'_H) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The quantum yield of carbon monoxide is proportional to p_{CO} and may be written

$$\gamma_{CO} = \gamma_0 p_{CO}$$

or

$$\gamma_{CO} = \frac{\gamma_0 k_D}{\Sigma k}\left\{1 + \frac{k_H}{k_D + k'_H}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

γ_0 represents the probability that absorption of a quantum will produce a primary dissociation according to Type I; it is therefore the total quantum yield of Type I in the gas phase, it being assumed that in the gas phase no recombination of radicals ($C_3H_7\cdot$ and $C_3H_7\cdot CO\cdot$) occurs. Thus γ_0 is equal to γ_{CO} for the gas-phase photolysis at high temperatures when no diketone is formed, and for the purposes of the present discussion it may be taken as 0·37. The dependence of k_D, k_H, and k'_H upon temperature is expressed by the following equations :

$$\left.\begin{aligned} k_D &= k_d e^{-E/RT} \\ k_H &= k_h e^{-E'/RT} \\ k'_H &= k'_h e^{-E''/RT} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

For simplicity it will be assumed that E' and E'' are approximately equal (see p. 1551). Substitution of (5) into (4) leads to the expression (6) for the variation of γ_{CO} with temperature :

$$\gamma_{CO} = \frac{\gamma_0 k_d e^{-E/RT}}{k_R + (k_h + k'_h)e^{-E'/RT} + k_d e^{-E/RT}}\left\{\frac{k_h e^{-E'/RT}}{k_d e^{-E/RT} + k'_h e^{-E''/RT}} + 1\right\} \quad . \quad . \quad (6)$$

By suitable choice of the k's and E's, the value of $k_h e^{-E/RT}$ can be made large compared to that of $k_d e^{-E/RT}$ at low temperatures, while at high temperatures the reverse will be the case. The variations in the value of the bracketed term in (6) are of minor importance. Taking $k_h \sim k'_h$, its maximum value of approximately 2 is attained at low temperatures when $k_d e^{-E/RT}$ is negligible, and its minimum of 1 at high temperatures when $k_d e^{-E/RT}$ becomes large compared to $k_h e^{-E'/RT}$. At low temperatures, when the total quantum yield of Type I, γ_I, is small, k_R is much larger than any other term, and so (6) becomes approximately

$$\gamma_{CO} = \gamma_0 \cdot 2k_d e^{-E/RT}/k_R$$

As T increases, the other terms in the denominator of (6) become increasingly important, and the bracketed term diminishes. The result is that the slope of the curve begins to diminish, until at sufficiently elevated temperatures (6) shows that γ_{CO} approaches the constant value γ_0 (*i.e.*, its corresponding value in the gas phase), since all other terms may be neglected in comparison with $k_d e^{-E/RT}$. Thus (6) predicts, at any rate qualitatively, the shape of the γ_{CO}–T curve obtained experimentally.

The probability of propane formation may be calculated in a similar manner. As in the case of carbon monoxide, there are two mechanisms by which it may be formed : (i) By hydrogenation of the propyl group. This will necessarily follow the occurrence of any of the processes (*b*), (*c*), (*d*) (p. 1549), if recombination to form hexane is neglected for the moment. It must be noted that process (*d*) would lead to the formation of two propane molecules—one from the hydrogenation of the propyl group originally linked to the acyl, and the other from the hydrogenation of the alkyl produced by decomposition of the acyl radical. Consequently, the probability of propane formation by (i) (recombination of propyl groups being neglected) is

$$(k_{\mathrm{H}} + k'_{\mathrm{H}} + 2k_{\mathrm{D}})/\Sigma k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In order to take into account the formation of hexane, the above must be slightly modified. The probability of hexane formation will be given by:

$$(k_{\mathrm{D}}/\Sigma k) \,.\, k_{\mathrm{P}}/(k_{\mathrm{H}} + k_{\mathrm{P}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The first term represents the probability that two propyls should be inside the shell together, and the second, the further probability of their union; k_{P} refers to the latter reaction. On employing (8), the corrected form of (7) becomes

$$\frac{1}{\Sigma k}\left\{k_{\mathrm{H}} + k'_{\mathrm{H}} + 2k_{\mathrm{D}} - \frac{2k_{\mathrm{D}}k_{\mathrm{P}}}{k_{\mathrm{H}} + k_{\mathrm{P}}}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

(ii) Propane may also be formed from acyl radicals which are liberated and decompose, as described previously (p. 1550). The approximate probability of this will be that given by (2). The total probability that an excited molecule of ketone will yield propane is therefore

$$p_{\mathrm{Pr}} = \frac{1}{\Sigma k}\left\{k_{\mathrm{H}} + k'_{\mathrm{H}} + 2k_{\mathrm{D}} + \frac{k_{\mathrm{D}}k_{\mathrm{H}}}{k_{\mathrm{D}} + k'_{\mathrm{H}}} - \frac{2k_{\mathrm{D}}k_{\mathrm{P}}}{k_{\mathrm{H}} + k_{\mathrm{P}}}\right\} \quad . \quad . \quad (10)$$

From (3) and (10) it follows that the ratio $\gamma_{\mathrm{Pr}}/\gamma_{\mathrm{CO}}$ is given by

$$\frac{\gamma_{\mathrm{Pr}}}{\gamma_{\mathrm{CO}}} = \frac{p_{\mathrm{Pr}}}{p_{\mathrm{CO}}} = \left[2 + \frac{k_{\mathrm{H}} + k'_{\mathrm{H}}}{k_{\mathrm{D}}} + \frac{k_{\mathrm{H}}}{k_{\mathrm{D}} + k'_{\mathrm{H}}} - \frac{2k_{\mathrm{P}}}{k_{\mathrm{H}} + k_{\mathrm{P}}}\right] \Big/ \left[1 + \frac{k_{\mathrm{H}}}{k_{\mathrm{D}} + k'_{\mathrm{H}}}\right] \,.\quad (11)$$

At high temperatures, when $k_{\mathrm{D}} \gg k_{\mathrm{H}}$, (11) reduces to

$$\gamma_{\mathrm{Pr}}/\gamma_{\mathrm{CO}} = 2\{1 - k_{\mathrm{P}}/(k_{\mathrm{H}} + k_{\mathrm{P}})\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

For sufficiently large values of T, k_{H} becomes large compared with k_{P}, and the ratio $\gamma_{\mathrm{Pr}}/\gamma_{\mathrm{CO}}$ approximates to 2. This condition has not been realised experimentally, probably because sufficiently high temperatures have not been employed. Thus at 100°, the highest temperature used, $\gamma_{\mathrm{Pr}}/\gamma_{\mathrm{CO}} = 1{\cdot}6$, so that

$$k_{\mathrm{P}}/(k_{\mathrm{H}} + k_{\mathrm{P}}) = 0{\cdot}2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

(see also p. 1553).

At low temperatures, $k_{\mathrm{D}} \ll k_{\mathrm{H}}$, and also $k_{\mathrm{H}} < k_{\mathrm{P}}$, since the former reaction requires activation; (11) then becomes

$$\frac{\gamma_{\mathrm{Pr}}}{\gamma_{\mathrm{CO}}} = 0{\cdot}5 + \frac{k_{\mathrm{H}} + k'_{\mathrm{H}}}{2k_{\mathrm{D}}} = 0{\cdot}5 + \frac{k_{\mathrm{h}} + k'_{\mathrm{h}}}{2k_{\mathrm{d}}}\, e^{(E-E')/RT} \quad . \quad . \quad . \quad (14)$$

Fig. 4 shows that, in the range 0—20°, the experimental curve connecting $\gamma_{\mathrm{Pr}}/\gamma_{\mathrm{CO}}$ with temperature approximates to that given by

$$\gamma_{\mathrm{Pr}}/\gamma_{\mathrm{CO}} = 0{\cdot}5 + 1{\cdot}65 \times 10^{-3}e^{4{,}700/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

This lends support to the assumptions already made that $E' = E''$ (p. 1550). From (14) and (15),

$$(k_{\mathrm{h}} + k'_{\mathrm{h}})2k_{\mathrm{d}} \sim 1{\cdot}65 \times 10^{-3};\ E - E' = 4{\cdot}7 \text{ kg.-cals.} \quad . \quad . \quad . \quad (16)$$

If it be assumed that k_{h} and k'_{h} are of the same order of magnitude, then $k_{\mathrm{h}}/k_{\mathrm{d}} = 1{\cdot}65 \times 10^{-3}$.

Further information as to the magnitude of the unimolecular constants may be obtained from a comparison of the theoretical and experimental values of the quantity $\gamma_{\mathrm{Pr}} - \gamma_{\mathrm{CO}}$. From equations (3) and (10)

$$\gamma_{\mathrm{Pr}} - \gamma_{\mathrm{CO}} = \gamma_0\{p_{\mathrm{Pr}} - p_{\mathrm{CO}}\} = \frac{\gamma_0 k_{\mathrm{D}}}{\Sigma k}\left\{1 + \frac{k_{\mathrm{H}} + k'_{\mathrm{H}}}{k_{\mathrm{D}}} - \frac{2k_{\mathrm{P}}}{k_{\mathrm{H}} + k_{\mathrm{P}}}\right\} \quad . \quad . \quad (17)$$

At low temperatures, with the same approximations as before, this becomes

$$\gamma_{Pr} - \gamma_{CO} = \gamma_0[(k_h + k'_h)/k_R]e^{-E'/RT} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

FIG. 4.

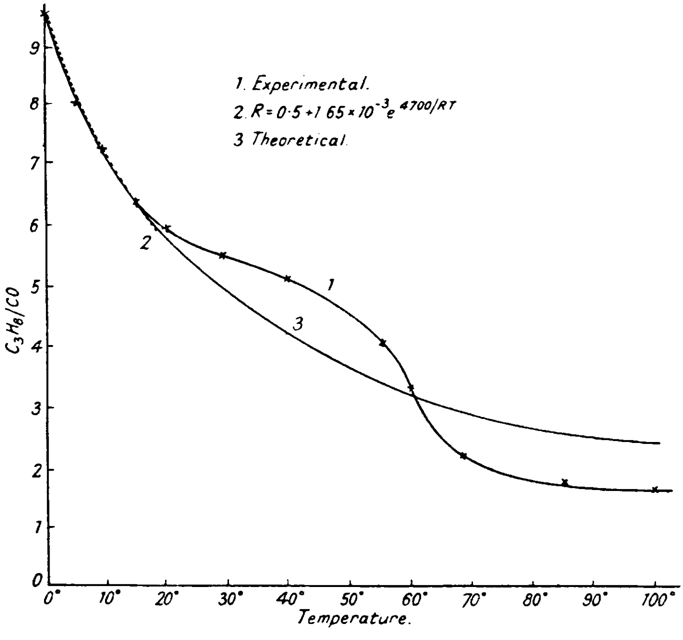


FIG. 5.

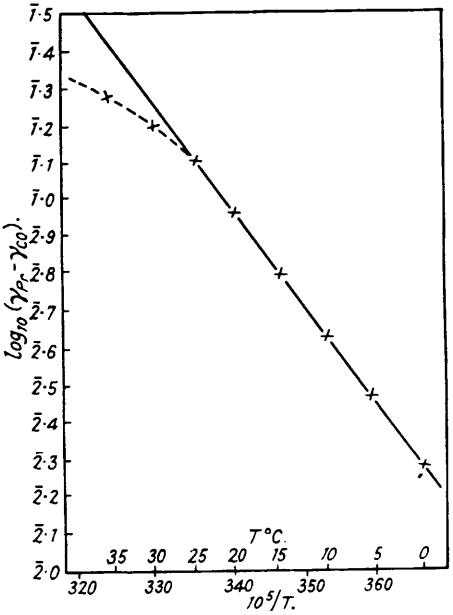


FIG. 6.

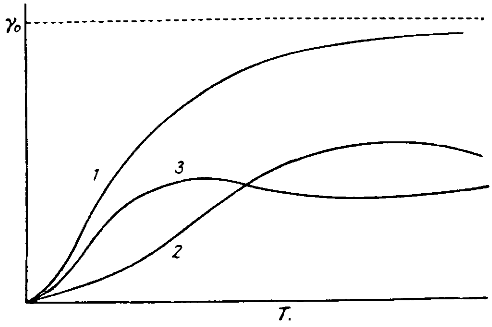


Fig. 5 shows that the experimental curve relating $\gamma_{Pr} - \gamma_{CO}$ to T, over the range 0—25°, is well represented by

$$\gamma_{Pr} - \gamma_{CO} = 5{\cdot}5 \times 10^7e^{-12,300/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Thus $\gamma_0(k_h + k'_h)/k_R = 5{\cdot}5 \times 10^7$, and since $\gamma_0 \sim 0{\cdot}37$, $k_h/k_R \sim 7{\cdot}4 \times 10^7$.

The energy of activation for the hydrogenation reaction is thus 12·3 kg.-cals.; hence that for the decomposition of acyl radicals is, by (16), 12·3 + 4·7 = 17·0 kg.-cals. By using equation (13) and the value for E', it may be calculated that $k_h/k_P(= k_H e^{E'/RT}/k_P) = 5{\cdot}7 \times 10^7$.

Having obtained the ratios of the unimolecular coefficients, we may compare the values of the ratio γ_{Pr}/γ_{CO} given by (11) with those found experimentally. This is done in Fig. 4 : (3) represents the theoretical curve, and although the agreement is only approximate, it is reasonably satisfactory, in view of the approximations and simplifications which have been introduced.

The form of the curves obtained by plotting the positive and negative terms of (17) against temperature is represented by curves (1) and (2) respectively of Fig. 6. Curve (1) rises more rapidly than (2) initially, since it depends mainly on the temperature coefficient of $(k_H + k'_H)$, while (2) depends on that of k_D. The negative term eventually begins to decrease (numerically) and finally becomes zero. The values of $(\gamma_{Pr} - \gamma_{CO})$ are obtained by subtracting the ordinates of (1) and (2), and are thus represented by a curve such as (3). This is of the same form as curve (3), Fig. 3. If the yield of propane continues to increase in a practically linear manner with temperature above 100°, as it does from 50° to 100°, then it follows from the shape of the γ_{CO} curve that curve (3) (Fig. 3) extrapolated above 100° will exhibit an ascending portion, as does the theoretical curve. Although much reliance cannot be placed upon such extrapolation, it seems likely that the agreement between theory and experiment is satisfactory.

The total quantum yield of Type I (γ_I) may be obtained from (17) by omitting the negative term, since the latter represents the reduction in the yield of propane due to combination of propyl groups. Hence

$$\gamma_I = (\gamma_0 k_D/\Sigma k)[1 + (k_H + k'_H)/k_D] \quad . \quad . \quad . \quad . \quad . \quad (20)$$

At high temperatures, when k_D predominates, $\gamma_I = \gamma_0 = \gamma_{CO}$, *i.e.*, (1) γ_0 measures the total quantum yield by Type I since no aldehyde is produced by the hydrogenation of acyl radicals, and (2) the total quantum yield in solution approaches the value for the gas phase.

It remains to consider the magnitudes of the unimolecular coefficients, and to examine the validity of the assumption made about them. The form of the theoretical expressions (6) and (10) makes comparison with experiment difficult except under certain special conditions (*e.g.*, at low temperatures) and over small ranges of temperature. Nevertheless, by taking advantage of such simplifications the values obtained will be of the right order of magnitude, though a high degree of accuracy cannot be claimed. The following values have been calculated.

$$k_h/h_d = 1{\cdot}65 \times 10^{-3},\ k_h/h_R = 7{\cdot}4 \times 10^7,\ k_h/k_P = 5{\cdot}7 \times 10^7$$
$$E = 17{\cdot}0 \text{ kg.-cals.},\ E' = 12{\cdot}3 \text{ kg.-cals.}$$

From these figures, using equation (5), we may then calculate the values of k_H/k_D, k_H/k_R, and k_D/k_R at the various temperatures given below.

Temp.	k_H/k_D.	k_H/k_R.	k_D/k_R.
0°	8·8	$1{\cdot}2 \times 10^{-2}$	$1{\cdot}4 \times 10^{-3}$
100	0·9	5·3	5·9
150	0·4	$4{\cdot}2 \times 10^3$	$1{\cdot}05 \times 10^4$

These figures are consistent with the neglect of k_H and k_D in comparison with k_R at temperatures close to 0°, as was implied, *e.g.*, in the combination of equations (18) and (19). They illustrate the growing importance of k_D with respect to k_H, and the decreasing importance of k_R as compared with k_H and k_D as the temperature rises. In deriving equation (13) it was assumed that, at 100°, $k_D \gg k_H$. The above table shows that this is not the case, and the value of k_P obtained from (13) will thus be only very approximate.

The large value of k_h/k_R is most probably due to the nature of the system under consideration. The k's are kinetic factors which depend on the number of collisions per second between the molecular species concerned. In a system composed of two radicals enclosed by a shell of solvent molecules, collisions between one of the radicals and solvent molecules will be much more frequent than those between the radicals themselves.

CONCLUSION.

The treatment outlined above shows that a quantitative explanation can be obtained of the temperature variation of the quantum yield in solution. It is clear that, although in the gas phase the quantum yields of Types I and II are not affected by temperature to a great extent in the range 0—100°, yet in solution the former is markedly influenced by the secondary factors described above. These may be summarised as follows. Free radicals formed by Type I decomposition are more and more subject to hydrogenation by the solvent, as the temperature approaches 100°. At the same time the acyl radicals become increasingly liable to decomposition. The principle of recombination controls the final quantum yield. At room temperatures the free radicals produced by the primary act mainly recombine, and the quantum yield of Type I is consequently approximately zero.

As the temperature increases, the rapid increase in the probabilities of hydrogenation and decomposition stabilises the primary change, and leads to final photolysis. The correctness of these ideas is strongly supported by the quantitative solution achieved. In addition, probable values for the velocity coefficients may be compared with values already extant in the literature. For instance, taking the value of the C–H bond as 96·5 kg.-cals. (see, *e.g.*, Schmid, *Math. naturw. Anz. ungar. Akad. Wiss.*, 1936, **54**, 769) and that of the H–H link as 101 kg.-cals., and using the value of 17 kg.-cals. found by Geib and Harteck (*Z. physikal. Chem.*, 1934, *A*, **170**, 1) for the energy of activation of the reaction $CH_4 + H\cdot \longrightarrow CH_3\cdot + H_2$, we may calculate a value of 12·5 kg.-cals. as the activation energy of the reaction $CH_3\cdot + H_2 \longrightarrow CH_4 + H\cdot$. This is close to the value (12·3 kg.-cals.) found above for the activation energy of the reaction between methyl groups and paraffinoid molecules. It must be remembered, however, that the former figure (12·5 kg.-cals.) is subject to the uncertainty which is at present attached to the value of the C–H bond.

On the other hand, decomposition of Type II, involving no free radicals, remains, as in the gas phase, largely unaffected by temperature. This in itself confirms the earlier conclusions as to the mechanism of this reaction. It is true that both in the gas phase and in solution there is a decrease in the probability of Type II as the temperature is raised, but this is not more than might be expected from a small change in the relative probabilities of the primary acts associated with Types I and II, as the internal conditions of the molecule are changed by an alteration in the temperature.

The results now presented make it possible to achieve a definite decision as to the nature of the primary acts in Type I. It is clear that hydrocarbon radicals must be eliminated successively, for if decomposition occurred in one act to non-valent $^1\Sigma CO$, no primary recombination would be possible at lower temperatures, nor would the quantum yield be appreciably affected by the solvent. On the other hand, the evidence goes to show that, as the temperature is raised and the probability of thermal decomposition of the acyl radical increases, distinction between the two possibilities becomes more and more academic. It must therefore be concluded quite definitely that, although at the lower temperatures the driving force of the photochemical change is not directly connected with the tendency of the carbonyl group to revert to carbon monoxide, yet at the higher temperatures the decomposition of the acyl group becomes so merged with the primary act that the two are indistinguishable. It is then possible to assume that both free radicals are eliminated at once. Until the conditions for this merging of the two reactions have been achieved it is clear that a molecule like keten cannot decompose. By analogy, it may therefore be assumed that in keten there is an internal photochemical primary act, involving the opening and shutting of the double bond. This is probably the reason why the photopolymerisation of ketene is so predominant.

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