326. *The Photoreactions of Liquid and Dissolved Ketones. Part II.*

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In the preceding paper the hypothesis of two excited levels is advanced to explain the behaviour of ketones in ultra-violet light. The experiments here described relate to the diketone diacetyl, the photodecomposition of which in the vapour state yields carbon monoxide and ethane (Porter, Ramsperger, and Steel, *J. Amer. Chem. Soc.*, 1923, **45**, 1827). The allied substances glyoxal and methylglyoxal photodecompose almost quantitatively in the vapour state into carbon monoxide and solid compounds of high molecular weight (Norrish and Griffiths, J., 1928, 2829; Kirkbride and Norrish, *Trans. Faraday Soc.*, 1931, **27**, 405). We find that solutions of glyoxal and of diacetyl give no gaseous products on illumination with light of wave-lengths between 4360 and 3660 Å.

The experimental details were as indicated in the preceding paper (p. 1503).

25 C.c. of solutions of diacetyl in hexane (made up by weight) were exposed to monochromatic light for various times. Since the solutions were yellow and the product colourless, the concentrations were conveniently estimated with a Pulfrich photometer (Zeiss) illuminated with monochromatic light of 4360 Å. As a white precipitate appears on illumination, which redissolves on stirring, the solutions were agitated with an internal stirrer operated electromagnetically. The reaction velocity was shown to be independent of the stirring rates used. A time–concentration curve was constructed for each exposure up to about 30% change. Preliminary experiments showed that the reaction rate was directly proportional to the light intensity, and hardly affected by bubbling either oxygen or nitrogen through the solutions. The light absorptions were not complete in the cells used, and the quantum efficiencies were calculated from the equation :

$$\frac{a\gamma It}{V} = c - x + \frac{1}{\varepsilon d}\log\left(\frac{1 - 10^{-\epsilon cd}}{1 - 10^{-\epsilon xd}}\right)$$

where γ = quantum efficiency, a = number of molecules of diacetyl in the product molecule (taken as 2, see later), I = number of g.-mol. quanta of incident radiation in time t, V = volume of solution in litres, c and x = concentrations (g.-mols./l.) initially and at time t, respectively, ε = extinction coefficient, and d = thickness of the solution.

Solvent : hexane.

Concn. of diacetyl.	3660 Å.; $\epsilon = 3{\cdot}26$. γ, found.	γ, calc.	4360 Å.; $\epsilon = 17{\cdot}8$. γ, found.	γ, calc.
0·011	0·25	0·25	0·16	0·17
0·027	0·22	0·23	0·16	0·16
0·140	0·13	0·14	0·12	0·12
0·275	0·10	0·09	0·10	0·10

Solvent : ethyl ether.

Concn. of diacetyl.	3660 Å.; $\epsilon = 3{\cdot}87$. γ, found.	γ, calc.	4360 Å.; $\epsilon = 16{\cdot}8$. γ, found.	γ, calc.
0·03	0·9, 1·03	0·91	0·81, 0·85	0·84
0·09	0·82	0·84	0·77	0·80
0·54	0·58	0·54	0·64	0·64

The results are summarised in the tables. The values of γ, calc. for hexane solutions are obtained from the equations :

$$\gamma = 0{\cdot}27/(1 + 7{\cdot}0c) \text{ at 3660 Å.; } \gamma = 0{\cdot}17/(1 + 2{\cdot}8c) \text{ at 4360 Å.}$$

and those for the ether solutions from the equations :

$$\gamma = 0{\cdot}95/(1 + 1{\cdot}4c) \text{ at 3660 Å.; } \gamma = 0{\cdot}85/(1 + 0{\cdot}6c) \text{ at 4360 Å.}$$

The quantum efficiencies shown above diminish as the concentration of the diacetyl is increased. A simple explanation is to be found in the hypotheses advanced in the preceding paper, *viz.*, that the mechanism of reaction is :

$$\mathrm{A} + h\nu \longrightarrow \mathrm{A}^{\times} \xrightarrow{k_1} \mathrm{A}'$$

$$\mathrm{A}^{\times} + \mathrm{A} \xrightarrow{k_2} \text{deactivation}$$

$$\begin{tikzcd}
 & \text{products} \\
\mathrm{A}' + \mathrm{A} \arrow[ur, "k_3"] \arrow[dr, "k_4"'] & \\
 & \text{deactivation.}
\end{tikzcd}$$

The velocity constants of the reactions are shown as k_1, etc. The quantum efficiency should then vary with the concentration according to the equation $\gamma = P/(1 + Kc)$, where $P = k_3/(k_3 + k_4)$, and represents the ratio of probabilities of reaction to reaction + deactivation of the level A′, and $K = k_2/k_1$, which depends inversely on the probability of the change $A^\times \longrightarrow A'$. The figures show that an equation of this type fits the observed values within the experimental error. It will be noticed that both P and K are greater for the wave-length 3660 than for 4360 Å. At the shorter wave-length, therefore, the level A′ has a greater tendency to react, but the change $A^\times \longrightarrow A'$ is slower. This result is capable of explanation by a suitable arrangement of surfaces on a polydimensional potential energy–distance diagram.

Products of the Photoreaction.—The above results show that the photoreaction rate is faster the more dilute the solution. It is peculiarly difficult, therefore, to obtain much of the photoproduct, since in dilute solution the amount is small, while in concentrated solution the rate is small. For this reason, diacetyl itself shows little photochange in light. When dilute solutions in hexane were exposed to sunlight until colourless and evaporated to dryness, the residue amounted to about 20% only of the diacetyl originally present. More concentrated solutions remained coloured after long exposures to sunlight, and on distillation left a very small quantity of a pungent brown liquid. The substance 1 : 4-dihydroxy-1 : 4-dimethyl*cyclo*hexane-2 : 5-dione [Beilstein, (4), Vol. 1, p. 858; Suppl., Vol. 1, p. 434], formed by the double aldol condensation of 2 mols. of diacetyl, is an oil, b. p. 128°/18 mm., and is slightly soluble in hexane. It loses water on heating to give *p*-xyloquinone, a yellow substance of pungent smell. It is possible that this substance is the photoproduct in hexane solutions.

SUMMARY.

The photopolymerisation of diacetyl in solution in light of wave-lengths 4360—3660 Å. has been investigated. The quantum efficiency is greater in more dilute solutions. An explanation based on the existence of two excited levels and on deactivation by normal molecules of diacetyl has been given.

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