325. *The Photoreactions of Liquid and Dissolved Ketones. Part I.*

By Edmund J. Bowen and Emile L. A. E. de la Praudière.

Owing to the difficulty of interpretation of the diffuse absorption spectra of the more complex aldehydes and ketones, a study of the chemical properties of their electronically excited levels is likely to provide useful information. In the vapour state these substances decompose photochemically to give gaseous products by a delay process (predissociation):

$$\mathrm{A} + h\nu \longrightarrow \mathrm{A}^{\times} \xrightarrow{\text{delay} > 10^{-12}\text{ sec.}} \mathrm{A}' \longrightarrow \text{products.}$$

The experiments now described were made upon substances in the liquid or dissolved state, where collisional times were shorter than, or about equal to, the delay in the process $\mathrm{A}^{\times} \longrightarrow \mathrm{A}'$. It is believed that the results show that the excited level $\mathrm{A}^{\times}$ is chemically non-reactive, that the level A′ is the reactive level, and that its dissociation into gaseous products does not occur instantaneously, *i.e.*, that a further reactive level is concerned in the gaseous decomposition.

The arrangement of light sources, filters, and methods of measuring the light absorptions of the liquids have already been described (Bowen, J., 1932, **2236**). The numbers of quanta in the light used were estimated by Leighton and Forbes's uranyl sulphate–oxalic acid method (*J. Amer. Chem. Soc.*, 1930, **52**, 3139). In ultra-violet light, aromatic ketone molecules oxidise alcohols according to the following equation, a pinacol being formed:

$$2\mathrm{COPh_2} + \mathrm{C_2H_5{\cdot}OH} \longrightarrow \mathrm{CPh_2(OH){\cdot}CPh_2{\cdot}OH} + \mathrm{CH_3{\cdot}CHO}$$

(Ciamician and Silber, *Ber.*, 1900, **33**, 1911; 1901, **34**, 1538; 1903, **36**, 1577; Berthoud, *Helv. Chim. Acta*, 1933, **16**, 592; Bäckström, *Z. physikal. Chem.*, 1934, *B*, **25**, 99).

In the presence of oxygen, no pinacol is formed, but the alcohol is oxidised indirectly to aldehyde as before. Aliphatic ketones react bimolecularly with alcohols under similar conditions to give several products, the ketone being reduced to a monohydric alcohol, or condensing with the alcohol (Ciamician and Silber, *Ber.*, 1911, **44**, 1280; Sernagiotto, *Atti R. Accad. Lincei*, 1919, **28**, i, 432). In the absence of alcohol molecules, excited ketone molecules can attack normal ketone molecules to give various products.

Expt. 1. 5 C.c. of molten benzophenone at 100° were exposed to the full light of the mercury lamp for 9 hours. The ultra-violet region was completely absorbed by the liquid. The m. p. (49°) showed no change after the exposure.

Expt. 2. 5 C.c. of molten acetophenone were similarly illuminated for 7 hours, and again there was no change in m. p. (18°).

Expt. 3. 25 C.c. of a *M*/10-solution of benzophenone in hexane were exposed at room temperature for 3½ hours to the full light of the mercury lamp. 0·212 G. of benzpinacol (m. p. 182°) crystallised out. The quantum efficiency was about 0·04. The residual solution was titrated with *M*/50-bromine in carbon tetrachloride, requiring 16 c.c. Titre equivalent to all the hydrogen used in reduction, 30 c.c.

Expt. 4. As before, but with benzene as solvent. Benzpinacol formed as before.

Expt. 5. As before, but with carbon tetrachloride as solvent. No benzpinacol formed.

Expt. 6. 25 C.c. of acetone [purified by the sodium iodide method (Shipsey and Werner, J., 1913, **103**, 1255) and by the sodium bisulphite method, and dried with calcium chloride and with anhydrous copper sulphate; $d_{18^\circ}^{18^\circ}$ 0·79366] were exposed for 2½ hours to filtered ultra-violet light, λ 3135—2800 Å. The liquid after exposure was titrated with *M*/50-bromine dissolved in carbon tetrachloride, a little water being added: titre = 2 c.c. Under these conditions unexposed acetone does not react rapidly with bromine.

Expt. 7. 25 C.c. of a 20% solution of acetone in pure hexane were exposed and afterwards titrated as above: titre = 19·2 c.c.

These experiments show that the photoreactions of benzophenone and of acetone are many times greater in solution than in the pure liquid state. It is possible that the excited molecules extract hydrogen from the hexane or benzene (cf. the photodecomposition of ammonia in hexane solution, L. Farkas, *Z. physikal. Chem.*, 1933, *B*, **23**, 89), but this seems very unlikely. It seems more probable that the effect is to be explained by the hypotheses that the first excited level ($\mathrm{A}^{\times}$) is non-reactive, but is capable of deactivation by collision with normal ketone molecules, and that reaction occurs only when the level $A^{\times}$ passes into the level A′. This explanation also covers the results obtained for diacetyl (Part II, following paper). On this view, the second level A′ cannot be assumed to be an unstable level dissociating instantly into radicals, for no gaseous products are formed when the reaction occurs in the liquid or the dissolved state, in contrast to the results obtained for the vapours of ketones and aldehydes (cf. Damon and Daniels, *J. Amer. Chem. Soc.*, 1933, **55**, 2363; Leighton and Blacet, *ibid.*, p. 1766).

Expt. 8. 25 C.c. of liquid acetaldehyde were exposed for 6 hours to the full light from the mercury lamp. No gas evolution was observed. If the quantum efficiency of dissociation had been 0·5, 500 c.c. of gas should have been obtained.

Expt. 9. 25 C.c. of liquid acetone were exposed in a similar manner. No gas evolution was observed, although 200 c.c. would have been expected if the quantum efficiency of dissociation were 0·2.

Expt. 10. 25 C.c. of 2% and of 0·2% solutions of acetone in carbon tetrachloride were exposed similarly. No gas evolution was observed. In the second solution the concentration is of the same order as that used by other investigators on the gaseous photodecompositions.

Expt. 11. The photoreactions occurring in purified liquid acetone were investigated by density changes. Range of light used 3135—2900 Å. All densities (determined with a pyknometer) are given as $d_{18°}^{15°}$.

	Acetone, *d* 0·79366.				Acetone + 1¼% of water, *d* 0·79766.			
Time of exposure, mins. ...	45	92	183	272	118	238	372	501
Density increase × 10^5	10	10	23	38	10	24	32	43

Assuming that the product is diacetone alcohol, the quantum efficiency of polymerisation is about 0·05.

	Acetone + 2% MeOH, *d* 0·79413.								Acetone + 2% MeOH + 1¼% H_2O, *d* 0·79839.					
Time of exposure, mins.	1	3	7½	23½	92	211	377	466	40	122	144	244	310	394
Density increase × 10^5	25	49	51	54	83	125	145	165	12	33	39	56	71	86

The above data show that while water has a reducing effect on the rate, small amounts of methyl alcohol produce a rapid change of high quantum efficiency, very large changes of density occurring in short exposure times. These results agree with the hypothesis that the reactive level A′ has a relatively long life compared with collisional frequencies in a liquid.

Since diacetone alcohol has been found to decompose photochemically into gaseous products in the vapour state (Damon and Daniels, *loc. cit.*), its behaviour in the liquid state was investigated.

Expt. 12. 25 C.c. of diacetone alcohol exposed to light, 3135—2800 Å.

Time of exposure, mins.	0	70	188	258
d	0·94057	0·94056	0·94049	0·94057

No gaseous products were observed, and the density changes are within the experimental error. The addition of 2% of water did not promote any photochange. The excited level of this substance is therefore very easily deactivated by collision with normal molecules.

These experiments are being continued.

SUMMARY.

The photoreactions of acetone and of benzophenone have been investigated in solution and in the pure liquid state. No gaseous products are liberated, and the reaction is much faster in the former than in the latter state. These results are explained on the hypotheses that the primary excited level of the ketone is non-reactive, and capable of deactivation on collision, and can pass into a second reactive level (which does not dissociate instantly) after a time of the order of 10^{-12} sec.

PHYSICAL CHEMISTRY LABORATORY,
BALLIOL AND TRINITY COLLEGES, OXFORD.

[*Received, July* 14*th*, 1934.]