541. *The Photo-oxidation of Biacetyl in Solution.*

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The phosphorescence intensity of aerated aqueous solutions of biacetyl increases with time of irradiation, due to photochemical consumption of oxygen; in aerated hexane the major product of photolysis of biacetyl is acetic acid.

BIACETYL has the unusual property of exhibiting two types of luminescence in the gas phase[1] and in deoxygenated solutions.[2] The blue fluorescence spectrum emitted with low quantum yield shows an approximate mirror correspondence with the long-wavelength absorption band[3,4] and is not significantly quenched by oxygen. The long-lived green emission, on the other hand, is strongly quenched by oxygen and by aromatic hydrocarbons with low-lying triplet states, whilst the emitting level of biacetyl appears to abstract a hydrogen atom from primary and secondary amines, phenols, aldehydes, and alcohols.[3] This behaviour supports the conclusion that the green luminescence originates from the triplet (biradical) state of biacetyl and is by definition a phosphorescence;[5,6] however, no response of the corresponding $S \longrightarrow T$ absorption band to magnetic perturbation by dissolved oxygen at high pressures is observed[7] and solvent perturbation[8] of the same band is very weak.

The photochemical reactions of biacetyl in solution appear to depend both on the solvent and on the biacetyl concentration. Under irradiation by the Hg 436 mμ line the rate of disappearance of biacetyl in hexane or ether is proportional to the light intensity and is scarcely affected by the presence of oxygen;[9] the photoproduct is believed to be

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[1] *E.g.*, see Noyes, Porter, and Jolley, *Chem. Rev.*, 1956, **56**, 49.

[2] Backstrom and Sandros, *Acta Chem. Scand.*, 1960, **14**, 48.

[3] Backstrom and Sandros, *Acta Chem. Scand.*, 1958, **12**, 823.

[4] Dubois and Stevens, Internat. Symposium on Luminescence, New York, Oct. 1961.

[5] Sidman and McClure, *J. Amer. Chem. Soc.*, 1955, **77**, 646.

[6] Lewis and Kasha, *J. Amer. Chem. Soc.*, 1945, **67**, 994.

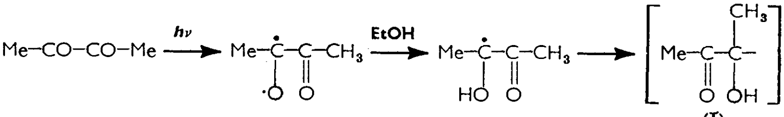
[7] D. F. Evans, personal communication.

[8] Forster, *J. Chem. Phys.*, 1957, **26**, 1761.

[9] Bowen and Horton, *J.*, 1934, 1505.

a cyclic dimer 1,4-dihydroxy-1,4-dimethylcyclohexane-2,5-dione, presumably formed by the interaction of excited and unexcited molecules.

Sunlight decolorises alcoholic solutions of biacetyl[10] to give[11] 3,4-dihydroxy-3,4-dimethylhexane-2,5-dione (I) which could be produced by dimerisation of the radical formed following hydrogen abstraction from this solvent by biacetyl in its biradical (triplet) state:



$$\text{Me–CO–CO–Me} \xrightarrow{h\nu} \text{Me–}\underset{\cdot\text{O}}{\dot{\text{C}}}\text{–}\underset{\text{O}}{\overset{}{\text{C}}}\text{–CH}_3 \xrightarrow{\text{EtOH}} \text{Me–}\underset{\text{HO}}{\dot{\text{C}}}\text{–}\underset{\text{O}}{\text{C}}\text{–CH}_3 \longrightarrow \left[\text{Me–}\underset{\text{O}}{\text{C}}\text{–}\underset{\text{OH}}{\overset{\text{CH}_3}{\text{C}}}\text{–}\right]_2$$

(I)

In aqueous and methanolic solutions the intensity of the long-wavelength absorption band is considerably reduced and is time-dependent;[12] this is attributed to a reaction between solvent and solute with the formation of a colourless product. Acetic acid and acetaldehyde are the photolysis products of biacetyl in aqueous solution,[13] where presumably the overall reaction is a photochemical hydrolysis

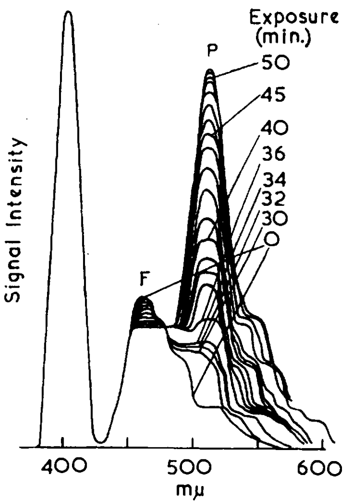


FIG. 1. Spectrophotofluorimeter traces of biacetyl luminescence recorded at time intervals shown for 0·01M-aerated aqueous solution $\lambda_{ex}' = 400$ mμ.

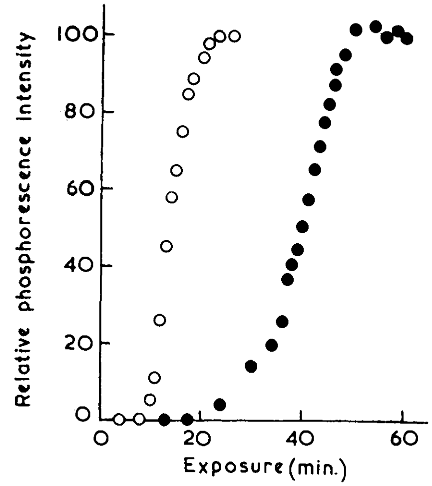


FIG. 2. Plot of relative intensity of biacetyl phosphorescence in aqueous solution against time of exposure. Final intensity is arbitrarily assigned value of 100 in each case. 0·05M- (○) and 0·01M-solutions (●) of biacetyl.

$$\text{Me–CO–CO–Me} + \text{H}_2\text{O} \longrightarrow \text{Me–CHO} + \text{Me–CO}_2\text{H}$$

Although biacetyl is rapidly oxidised to acetic acid by periodic acid[14] and hydrogen peroxide[10,15] in aqueous solution, the former reagent producing 2 mol. of acid, little is known of its photochemical oxidation in solution. This note describes some qualitative observations related to the photo-oxidation of biacetyl in aqueous and cyclohexane solutions which were made during an investigation of the sensitised fluorescence of biacetyl in aerated solvents.

As previously described,[4] an Aminco-Bowman spectrophotofluorimeter was used to

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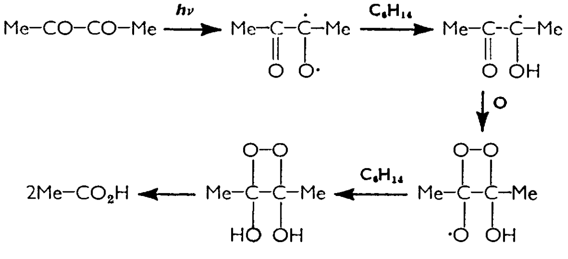
[10] Yamada and Hanai, *J. Soc. Brewing* (*Japan*), 1951, **46**, *J*, 47.
[11] Cohen, *Chem. Weekblad*, 1916, **13**, 590.
[12] Forster, *J. Amer. Chem. Soc.*, 1955, **77**, 1417.
[13] Porter, Ramsperger, and Steel, *J. Amer. Chem. Soc.*, 1923, **45**, 1830.
[14] Clutterbuck and Reuter, *J.*, 1935, 1467; Shriner and Wasmith, *J. Amer. Chem. Soc.*, 1959, **81**, 37.
[15] Matui and Yamada, *J. Agric. Chem. Soc. Japan*, 1939, **15**, 708.

record the biacetyl fluorescence signal as a function of wavelength. To ensure that no photochemical change is promoted by the light used to excite the fluorescence, the signal spectrum of the same solution was recorded two or three times in succession under the same conditions. In aerated solutions of biacetyl in cyclohexane no change in fluorescence signal was observed, but when aerated water was used as solvent it was found that after a few minutes a green luminescence appeared, the intensity of which increased with time of irradiation. Fig. 1 shows experimental recordings. After correction for the wavelength sensitivity of the detecting system (by using a quinine bisulphate standard [16]) the original recorded spectrum F closely resembles the fluorescence spectrum of biacetyl, whereas the time-dependent green luminescence P is almost identical with the published phosphorescence spectrum exhibited by deoxygenated solutions.[2]

The increase in intensity of phosphorescence with time can be attributed to the photochemical consumption of oxygen which quenches this emission. An examination of the fluorescence signal from the $0{\cdot}01$M-solution shows that this decreases by $\sim 20\%$, indicating a simultaneous consumption of biacetyl to the extent of 2×10^{-3}M; since the concentration of dissolved oxygen in air-saturated water is only $2{\cdot}5 \times 10^{-4}$M at 25°, biacetyl must also be consumed in an additional process, such as the photolytic hydrolysis, which does not involve oxygen. The variation of phosphorescence intensity with time shown in Fig. 2 is characteristic of an autocatalytic process, the " induction " period increasing with a decrease in biacetyl concentration. This effect may be artificial in the kinetic sense in that it involves the diffusion of oxygen into the illuminated zone from the rest of the solution, or it may signify the accumulation of some product such as acetaldehyde (from the photolytic hydrolysis) from which the triplet state of biacetyl can readily abstract a hydrogen atom [3] before reacting with an oxygen molecule. It is unlikely that the triplet state abstracts hydrogen from a water molecule since the phosphorescence is not quenched in this solvent. Attempts to identify the photolysis products by vapour-phase chromatography were unsuccessful.

During preliminary investigations of sensitised fluorescence of biacetyl in hydrocarbon solvents it was observed that solutions in aerated n-hexane were completely decolorised after exposure to sunlight for about a week. Although again it was not possible to identify the photolysis products chromatographically, the exposed solutions exhibited no absorption due to biacetyl or acetaldehyde and smelled strongly of acetic acid. Titration against standard alkali led to inconsistent results but did show that $1{\cdot}7 \pm 0{\cdot}3$ moles of acid were produced per mole of biacetyl consumed; the major overall process responsible for biacetyl consumption must therefore be $\mathrm{Me{-}CO{-}CO{-}Me} + O_2 + 2H \longrightarrow 2\mathrm{Me{\cdot}CO_2H}$ which could proceed in the following stages:



The slowness of the reaction may reflect the difficulty of hydrogen abstraction from this solvent.

This work was done while one of us (B. S.; Sheffield University) was a Visiting Research Associate at WPAFB.

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[16] Melhuish, *J. Phys. Chem.*, 1960, **64**, 762.