Phosphorescence of Benzophenone in Fluid Solution

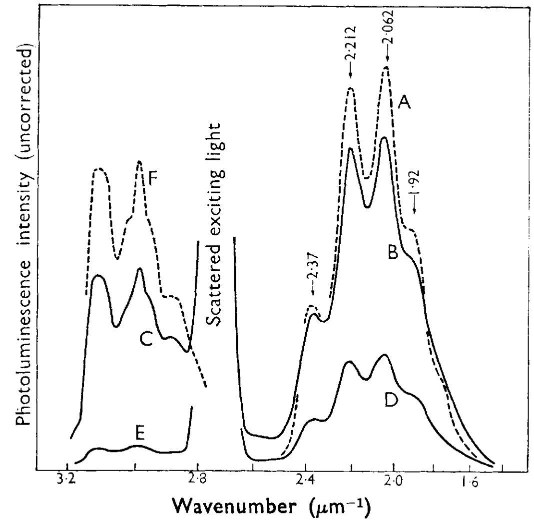
By C. A. PARKER* and THELMA A. JOYCE
(*Admiralty Materials Laboratory, Holton Heath, Poole, Dorset*)

ALTHOUGH the phosphorescence from benzophenone in rigid glasses at 77° K can be readily observed at high quantum efficiency, the only recorded observation of its phosphorescence in fluid solution at room temperature is that of Bäckström and Sandros,[1] who observed a weak blue luminescence when an oxygen-free solution of benzophenone in benzene was irradiated with light of wavelength 366 nm. They found the triplet lifetime in benzene to be $1{\cdot}9 \times 10^{-6}$ sec. at 20° compared with a radiative lifetime of about 10^{-2} sec.[2] In isopropanol the lifetime was reduced to $5{\cdot}7 \times 10^{-8}$ sec.[1] owing to efficient hydrogen abstraction from the solvent by the benzophenone triplet. Beckett and Porter[3] found high quantum efficiencies for the disappearance of benzophenone in isopropanol and other "reactive" solvents, while the value in benzene was less than 0·05.

In de-oxygenated perfluoromethylcyclohexane, where hydrogen abstraction from the solvent† is impossible, we have observed an intense phosphorescence from benzophenone at 20°. The spectrum was overlapped by a much weaker broad band emission attributed to impurity, which disappeared on irradiation while the benzophenone emission became more intense (Figure, A). In a $2{\cdot}0 \times 10^{-4}$ M irradiated solution the phosphorescence was emitted with a quantum efficiency of 0·097 and decayed with a lifetime of 0·71 msec. Assuming triplet-formation efficiency to be unity these results imply a radiative lifetime of 7·3 msec., in agreement with the value (8 msec.) reported by Gilmore and his co-workers.[2]

Addition of naphthalene caused strong quenching of the phosphorescence and a weak delayed fluorescence of naphthalene appeared (see Figure, B and C, which were recorded at a higher rate of light absorption). The delayed fluorescence was shown to be *P*-type[4] by the fact that its intensity varied as the square of the rate of light absorption while the residual phosphorescence of the benzophenone was directly proportional to the rate of light absorption (compare curves D and E with B and C). There is little doubt therefore that the phosphorescence is indeed due to the triplet–singlet radiative transition of the benzophencne. The composite *pseudo* first-order rate constant for its decay in the absence of naphthalene ($2{\cdot}5 \times 10^{3}$ sec.$^{-1}$ in $1{\cdot}9 \times 10^{-3}$ M solution) includes contributions from the rates of radiative decay, intersystem crossing to the ground state, quenching by impurities, and quenching by the ground state of benzophenone. The latter seems to be considerable: it may be the result of hydrogen abstraction from the benzophenone itself, or quenching by an impurity in the benzophenone.

Beckett and Porter[3] attributed the short lifetime of the benzophenone triplet in benzene to rapid radiationless decay. In view of the present results it is of interest to consider whether the rapid decay in benzene is due to impurity quenching or to inefficient hydrogen abstraction from the solvent, followed by rapid reversal, before escape of the radicals from the solvent cage. It may be



FIGURE

Photoluminescence emission spectra in perfluoromethylcyclohexane at 20°. (A) $1{\cdot}9 \times 10^{-3}$ M benzophenone with rate of light absorption of $0{\cdot}56 \times 10^{-6}$ einstein l.$^{-1}$ sec.$^{-1}$ at 366 nm. measured at unit sensitivity; (B and C) as for (A) but with $2{\cdot}4 \times 10^{-5}$ M naphthalene added, a rate of light absorption of 18×10^{-6} einstein l.$^{-1}$ sec.$^{-1}$ and measured at sensitivities 1·3 and 3·7; (D and E) as for (B and C) but with $6{\cdot}0 \times 10^{-6}$ einstein l.$^{-1}$ sec.$^{-1}$; (F) prompt fluorescence of $2{\cdot}4 \times 10^{-3}$ M naphthalene excited by 313 nm. Band width of double silica prism analysing monochromator was 0·023 and 0·037 μm^{-1} at 3·0 and 2·0 μm^{-1}.

---

† The solvent was obtained from Imperial Smelting Corporation (N.S.C.) Ltd., Bristol. A selected batch showing how fluorescence excited by 250 nm. was used without further purification. A discussion of fluorocarbons as solvents for photoluminescence spectrometry will be given elsewhere.

significant that Tsubomura and his co-workers[5] have observed a transient absorption spectrum, attributed to the benzophenone triplet, in trichlorotrifluoroethane. The transient decayed with a lifetime of 2×10^{-5} sec., *i.e.* ten times slower than the triplet decay in benzene but more than 30-times faster than the phosphorescence decay in perfluoromethylcyclohexane.

(*Received, April* 25*th*, 1968; *Com.* 505.)

---

[1] H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, 1960, **14**, 48.
[2] E. H. Gilmore, G. E. Gibson, and D. S. McClure, *J. Chem. Phys.*, 1955, **23**, 399.
[3] A. Beckett and G. Porter, *Trans. Faraday Soc.*, 1963, **59**, 2038.
[4] C. A. Parker, *Adv. Photochem.*, 1964, **2**, 305.
[5] H. Tsubomura, N. Yamamoto, and S. Tanaka, *Chem. Phys. Letters*, 1967, **1**, 309.