The Effect of Solvent upon the Phosphorescence Spectrum of 4-Aminobenzophenone

By R. S. DAVIDSON* and M. SANTHANAM
(*Department of Chemistry, The University, Leicester* LE1 7RH)

Summary The phosphorescence of 4-aminobenzophenone occurs at longer wavelength, and the spectrum has a different shape, in protic solvents compared with aprotic solvents with which it can form hydrogen bonds.

EXCITATION of many compounds, when contained in a rigid matrix, causes phosphorescence. From the wavelength at which this occurs and from its lifetime it is possible to deduce the energy and type of triplet which is emitting. Porter and Suppan[1] have previously reported that 4-aminobenzophenone exhibits phosphorescence having a short lifetime in non-polar solvents whereas in polar solvents it has a long lifetime. This was explained on the basis that in non-polar solvents the reactive n,π^* triplet state of the ketone is populated whereas in polar solvents an unreactive π,π^* triplet (having considerable polar character and therefore termed a charge-transfer triplet) is populated. We now describe emission studies which show that the phosphorescence spectrum of the ketone is dependent on whether the carbonyl group can form hydrogen bonds to the solvent or not.

We have found that 4-aminobenzophenone does not exhibit strong normal phosphorescence in dry hydrocarbon glasses at 77 K. If the hydrocarbon glass contains an aprotic solvent capable of forming hydrogen bonds to the amino-group of the ketone, strong phosphorescence is observed. From our recent studies on the effect of solvent upon the phosphorescence spectra of anilines,[2] we conclude that 4-aminobenzophenone does not phosphoresce in dry hydrocarbon matrices because aggregates are formed. Thus the nature of the lowest excited triplet state of 4-aminobenzophenone in hydrocarbon solvents cannot be ascertained by emission studies.

4-Aminobenzophenone exhibits strong phosphorescence (see Figure) having a long lifetime in matrices formed from polar aprotic solvents, *e.g.* ether or triethylamine. The position at which phosphorescence occurs is dependent upon the polarity of the solvent as is the excitation wavelength for the ketone (Table). Over the whole solvent polarity range, the phosphorescence spectrum displays two maxima, having a constant wavelength difference. So far as we can ascertain, the phosphorescence decay for each of the maxima is

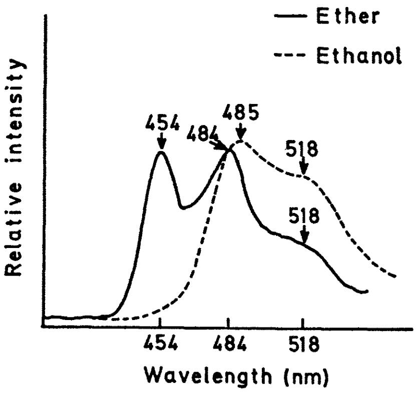

FIGURE. *Phosphorescence spectrum of 4-aminobenzophenone in ether and ethanol at* 77 K (*fluorescence chopped*).

TABLE

Positions of excitation wavelength, fluorescence, and phosphorescence emission of 4-*aminobenzophenone in matrixes of varying polarity at* 77 *K*

Solvent	λ_{excit} (nm)	λ_{fluo} (nm)	λ_{phos} (nm)	Half-life of phosphoresence (ms)
2-Methylheptane	376	478	510 (vw)	
2-Methylheptane + small amount of ether	350		456(s), 485(s), 522(sh)	
Methylcyclohexane	380	474	520 (vw)	
Methylcyclohexane + small amount of n-propylamine	384	450(sh)	492(s), 516(s)	
Methylcyclohexane + small amount of di-n-propylamine	382	454(sh)	482(s), 510(s)	
Methylcyclohexane + small amount of triethylamine	372		473(s), 500(s)	39
Ether	344		454(s), 484(s), 518(sh)	57
2-Methyltetrahydrofuran	352		458(s), 487(s), 521(sh)	
Triethylamine	380		466(s), 494(s)	47
Ethyl acetate	374		463(s), 490(s)	
Ether–isopentane–ethanol (5:5:2)	377	444(sh)	482(s), 506(w)	
Ethanol	380	446(sh)	485(s), 518 (sh)	25
Methylcyclohexane + small amount of ethanol	368	445(sh)	482(s), 510(sh)	43

identical and therefore we believe they emanate from the same excited state.

In protic solvents, the phosphorescence spectrum has a very different shape (see Figure). The emission generally occurs at longer wavelength (see Table) compared with that for aprotic solvents. It also has a long lifetime . If small amounts of protic solvents, *e.g.* alcohols or primary or secondary aliphatic amines are present in matrices formed from aprotic solvents which are not capable of forming hydrogen bonds, the phosphorescence spectrum is typical of that obtained in pure protic solvent. We assume that the previously reported value[3] of 480 nm for the position of maximum phosphorescence in 3-methylpentane matrix is due to the presence of a protic impurity in the solvent.

In agreement with O'Connell,[3] we observed that 4-aminobenzophenone fluoresced in protic solvents (at 77 K), and in hydrocarbons in which it formed aggregates. Fluorescence, if observable, in polar aprotic solvents was always very weak.

We conclude that the intrinsic difference between the phosphorescence spectrum of aminoketone in protic and aprotic solvents is due to either hydrogen bonding of the solvent to the carbonyl group or proton donation to the excited carbonyl group of the ketone.

We thank the S.R.C. for a fellowship (to M.S.) and for a grant to purchase the spectrofluorimeter.

(*Received, June* 18*th*, 1971; *Com.* 1001.)

---

[1] G. Porter and P. Suppan, *Trans. Faraday Soc.*, 1965, **61**, 1664.

[2] R. S. Davidson and M. Santhanam, *J. Chem. Soc.* (*B*), 1971, 1151.

[3] E. J. O'Connell, jun., *Chem. Comm.*, 1969, 571.