BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (11), 2283—3384 (1978)

Excitation Wavelength Dependence of Quinoline Phosphorescence Lifetime†

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(Received April 19, 1978)

Synopsis. The quinoline phosphorescence lifetime in several rigid media at 77 K has been found to be dependent on excitation wavelength. The change of lifetime is especially remarkable in hydroxylic solvents. This observation has been attributed to the inhomogeneous broadening of spectral lines caused by the distribution of solvent environments around quinoline molecules.

The quinoline phosphorescence lifetime has been shown to be solvent dependent with the ones observed in hydrocarbons being shorter than in hydroxylic solvents.[1,2] These results were interpreted by Lim and Yu[1] as due to the solvent effect on the second order perturbation including spin-orbit coupling and vibronic interaction among the excited singlet and triplet states. This was supported from the polarization measurement where the phosphorescence is found to be more in-plane polarized in hydrocarbon than in hydroxylic solvents outside the 0,0 band. In order to examine such a solvent effect more in detail, the measurement of quinoline phosphorescence lifetime in several solvents has been conducted with the excitation wavelength varied across the first absorption band.

The results of lifetime measurements are listed in Table 1 and also shown in Fig. 1. It is clearly seen that the quinoline phosphorescence lifetime observed in hydroxylic solvents is markedly dependent upon the excitation wavelength whereas those measured in hydrocarbon solvents show only slight dependence. The lifetimes observed in hydroxylic and hydrocarbon solvents by excitation at the long wavelength edge (red edge) of the first absorption band are very similar except for the one in ethyl alcohol excited at 317.5 nm which is shorter than those for other solvents. Itoh and Azumi[3] observed a slight but significant spectral shift of quinoline phosphorescence in EPA by red edge excitation. In the present work as shown in Fig. 2, the phosphorescence spectra measured in ethyl alcohol show very little change in spectral profile and peak position with excitation outside the red edge region, except for a slight change in relative peak height which is barely observable under the experimental conditions (apparent 0,0 peak was observed at 314.5 nm in phosphorescence excitation spectrum). In consideration of these observations, it is not unlikely that the considerable change of phosphorescence lifetime observed by the red edge excitation is caused by the same sort of effect they observed, though the origin of such red edge effect has not been consistently interpreted for all molecules studied so far.[3,4]

Johnson and Levin[5] reported the excitation wavelength dependent phosphorescence lifetime of benzene and naphthalene in nonpolar rigid media and attributed such observations mainly to the change in the radiationless transition rate caused by the presence of a distribution of local environment for the solute molecules which shows up as an inhomogeneous line

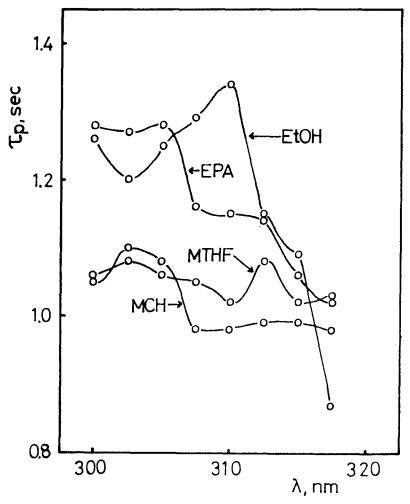

Fig. 1. Excitation wavelength dependence of the phosphorescence lifetime of quinoline at 77 K. Solvents used are indicated by arrows.

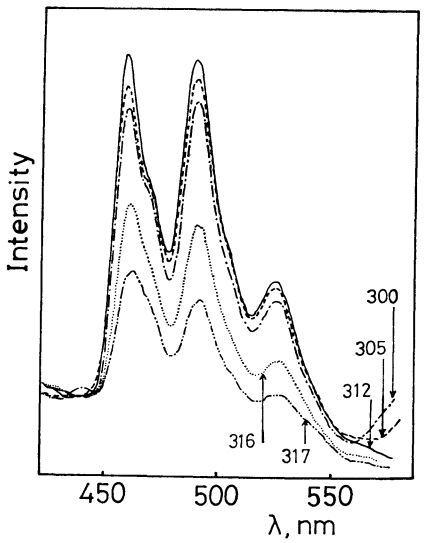

Fig. 2. Phosphorescence spectra of quinoline in ethyl alcohol excited at different wavelength region. Excitation wavelength in nm is given by following the arrows.

† Issued as NRCC No. 16903.

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Table 1. Phosphorescence lifetimes of quinoline as a function of excitation wavelength[a)]

Excitation wavelength (nm)	Phosphorescence lifetime (s)			
	EtOH	EPA	MTHF	MCH
275	—	1.24±0.07	—	1.05±0.09
300	1.26±0.04	1.28±0.11	1.06±0.05	1.05±0.04
302.5	1.20±0.04	1.27±0.08	1.08±0.04	1.10±0.07
305	1.25±0.05	1.28±0.06	1.06±0.06	1.08±0.06
307.5	1.29±0.06	1.16±0.08	1.05±0.05	0.98±0.08
310	1.34±0.08	1.15±0.09	1.02±0.08	0.98±0.06
312.5	1.15±0.10	1.14±0.10	1.08±0.04	0.99±0.05
315	1.09±0.06	1.06±0.12	1.02±0.11	0.99±0.05
317.5	0.87±0.03	1.02±0.12	1.03±0.11	0.98±0.08

a) Solvents: EtOH: ethyl alcohol; EPA: ethanol-isopentane-diethyl ether, 2 : 5 : 5; MTHF: 2-methyltetrahydrofuran; MCH: methylcyclohexane.

broadening of the molecule. While the effect of solvent perturbation on the radiationless transition rate has been observed recently in anthracenes in the low temperature region,[6] it is not clear as to what extent this effect might have on both the radiative and the radiationless transition rate of the quinoline molecule. The greater change in lifetime observed in hydroxylic solvents appears to indicate the enhancement of inhomogeneous line broadening in hydroxylic solvents, though the effect of using a narrower bandwidth can not be entirely discounted. It is also worth noting that in a recent study of diphenylanthracence fluorescence in EtOH low temperature glass,[7] the fluorescence band shift with the excitation wavelength has been attributed to the effect caused by the inhomogeneous line broadening.

Thus, in view of these results, it is concluded that the excitation wavelength dependence of quinoline phosphorescence lifetime observed in this study is most likely due to the solvent induced inhomogeneous line broadening effect on both the radiative and the radiationless relaxation processes of the lowest triplet state.

Experimental

Quinoline used for the measurement of phosphorescence lifetime and spectrum was laboratory reagent (BDH Chemicals) and guaranteed reagent (Tokyo Kasei) respectively and these were further purified by successive vacuum distillation. Spectrograde ethyl alcohol was used as received for the measurement of phosphorescence spectrum and the other solvent used for the lifetime measurement were treated with activated charcoal to remove luminescent impurities. Quinoline solutions of 10^{-3} M concentration were all degassed and sealed in the supracil tubes. The phosphorescence lifetime was calculated from the oscilloscope trace obtained by using a xenon flash lamp excitation source of 5 microsecond duration which was coupled with a 1/4 meter B & L monochromator. Both the entrance and the exit slit widths were set at 1.0 mm (bandwidth of 7.4 nm) for measurement in EtOH and EPA solvents and 1.5 mm (bandwidth of 11.1 nm) for those measured in methylcyclohexane and 2-methyltetrahydrofuran. A Corning 3-73 filter was used in front of the photomultiplier to eliminate scattered light. Phosphorescence spectra were measured using a fluorescence spectrometer Hitachi MPF-2A with the spectral resolution set at 10 nm.

The authors are grateful to Professor T. Azumi for the reprints on subjects relevant to this study.

References

1) E. C. Lim and J. M. H. Yu, *J. Chem. Phys.*, **47**, 3270 (1967).
2) M. F. Anton and W. R. Moomaw, *J. Chem. Phys.*, **66**, 1808 (1977).
3) K. Itoh and T. Azumi, *J. Chem. Phys.*, **62**, 3431 (1975).
4) W. C. Galley and R. M. Purkey, *Proc. Natl. Acad. Sci. U. S. A.*, **67**, 1116 (1970); W. Klopffer, *Chem. Phys. Lett.*, **11**, 482 (1971); P. R. Callis and R. W. Wilson, *ibid.*, **13**, 417 (1972); O. S. Khalil, C. J. Seliskar, and S. P. McGlynn, *J. Chem. Phys.*, **58**, 1607 (1973).
5) P. M. Johnson and D. Levin, *Mol. Photochem.*, **6**, 263 (1974).
6) I. F. Hung and B. R. Henry, *Chem. Phys.*, **27**, 263 (1978).
7) G. Flatscher, K. Fritz, and J. Friedrich, *Z. Naturforsch., Teil A*, **31**, 1220 (1976).