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Short Communication

Primary photophysical processes in benzene-d_6

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Introduction

Considerable attention has been directed to the examination of isotope effects on primary photochemical processes for benzene in both the solid and gaseous phases but the effect of complete deuteration on the primary decay processes of the excited $^1B_{2u}$ state in fluid solutions has not been extensively studied.

Here we present details of the variation with temperature of the fluorescence and triplet yields, fluorescence lifetime, and, by inference, the internal conversion yield of C_6D_6 in dilute methylcyclohexane solution. Comparison with the results for benzene-h_6[1] allows some assignment of the processes affected by deuteration.

Experimental

Fluorescence quantum yields were measured with a fully self-correcting spectrofluorophosphorimeter[1] and fluorescence lifetimes were determined using either a pulse sampling[2] or single photon technique[3].

Triplet yield measurements were made by the butene-2 isomerization technique described previously[1].

Results

The fluorescence quantum yield at 24° C for benzene-d_6 in methylcyclohexane was measured relative to the value of 0.052 for benzene-h_6 reported by Cundall and Pereira[4]. The yield of 0.042 at 24° C is lower than that for benzene-h_6 and is in the reverse order to that noted by Berlman[5] and Sandros[6]. Several different samples of solute and solvent gave identical results ($\pm 10\%$) for C_6D_6 and C_6H_6 in cyclohexane. The shape of the fluorescence spectrum was not affected by temperature over the range examined. Variation of the fluorescence quantum yield and lifetime with temperature is shown in Fig. 1. Our value of 30 ns for the fluorescence lifetime of the excited singlet monomer, τ_M, at 25°C is to be compared with those of Berlman[5] (26.6 ns) and Helman[7] (32 ns) for cyclohexane solutions of benzene-d_6. At the concentrations and temperatures used excimers have no effect on the photophysical behaviour.

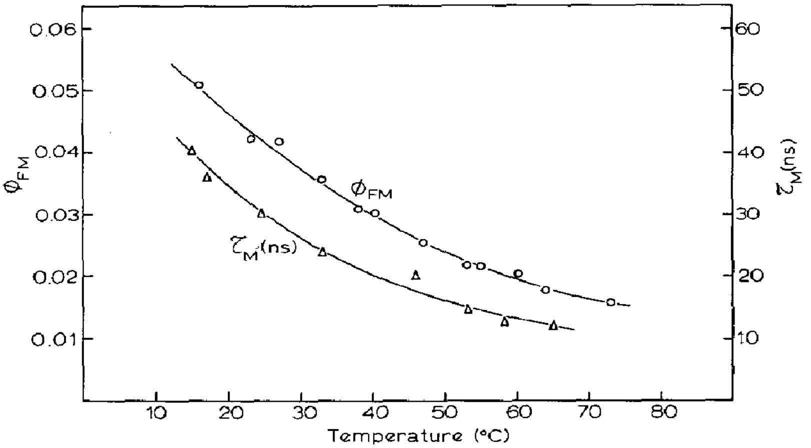

Fig. 1. Effect of temperature on the fluorescence yield (Φ_{FM}) and fluorescence lifetime τ_M of benzene-d_6 in methylcyclohexane solution ($10^{-2}M$).

TABLE 1

TRIPLET YIELD MEASUREMENTS ON BENZENE-d_6 ($10^{-2}M$) IN METHYLCYCLOHEXANE AT DIFFERENT TEMPERATURES

Temp. (°C)	*cis*-butene-2 (*M*)	Φ_{ISOM}	$\Phi_{TRIPLET}$	Φ_{ICM}
27	0.170	0.124 (7)	0.249	0.713
28	0.171	0.122 (3)	0.244	0.717
33	0.164	0.108 (4)	0.217	0.749
42	0.160	0.088 (4)	0.177	0.794
52	0.168	0.075 (5)	0.151	0.830
63	0.193	0.060 (5)	0.121	0.862

Triplet yields (Table 1) were determined from the measured isomerization yields when sufficient *cis*-butene-2 (≥ 0.1 *M*) was present to scavenge practically all the quenchable benzene triplet species generated. A branching ratio, which is the probability of the olefin triplet relaxing to the *trans* isomeric form, of 0.5 was used in the calculation of Φ_T.

The quantum yield deficit, $1-(\Phi_{FM}+\Phi_T)$, is given as the internal conversion yield, Φ_{ICM}.

Butene-2 had no effect on the fluorescence of deuterated benzene at the concentrations used.

Discussion

The radiative $S_1 \rightarrow S_0$ transition

The radiative rate constants k_{FM} calculated from Φ_{FM} and τ_M data for methylcyclohexane solutions is $1.35(5) \times 10^6$ s^{-1} at 24°C and the value increases slightly with rise in temperature as shown in Table 2. k_{FM} for benzene-h_6 under the same conditions is 1.73×10^6 s^{-1} and shows some increase with temperature. The very slight temperature dependence can arise from the effect of vibrations on the electronic transition moment integral predicted by Strickler and Berg's equation[10] for the probability of fluorescence. Values of higher order terms in this equation are increased by molecular vibrations and assume importance for the nominally forbidden $^1A_{1g}$–$^1B_{2u}$ transition in benzene.

TABLE 2

S_1 DECAY RATE PARAMETERS FOR BENZENE-d_6 (10^{-2} M) IN METHYLCYCLOHEXANE

Temp. (°C)	k_{FM} ($\times 10^{-6}$) (s^{-1})	k_{ISCM} ($\times 10^{-6}$) (s^{-1})	k_{ICM} ($\times 10^{-6}$) (s^{-1})
25	1.37	8.67	23.3
30	1.40	8.75	27.7
35	1.42	8.80	32.5
40	1.43	8.97	37.9
45	1.43	9.18	44.3
50	1.45	9.56	51.5
55	1.43	9.72	58.8
60	1.45	9.85	65.6
65	1.45	9.83	73.5

The intrinsic radiative transition rate constant in a medium of unit refractive index should be calculated by the equation $k_{FM} = k^o_{FM}\, n^2$ [11]. The refractive index of methylcyclohexane at 287 nm, the wavelength of maximum fluorescence intensity for C_6D_6 in this solvent, was estimated by the Selmeier–Drude equation and constants derived by Lauer[12]. At 25°C an intrinsic radiative lifetime τ^o_r ($1/k^o_{FM}$) of 1584 ns, calculated from the value of τ_r in methylcyclohexane, is about 25% greater than the corresponding value of τ^o_r for benzene-h_6 (1270 ns) which is independent on solvent[6].

Low pressure vapour studies [13, 14] on emission from the zeroth level of S_1 give intrinsic radiative lifetimes of C_6D_6 and C_6H_6 of 565 ns and 455 ns respectively. The difference of 25% appears to show that the *relative* effect of deuteration on k^o_{FM} is independent of phase.

The apparent increase of τ^o_r for both C_6H_6 and C_6D_6 in going from gas to liquid phases show that either perturbations of excited states by the close proximity of other molecules in the liquid state occurs and the cause of this effect is not explained by an n^2 relationship or that the latter is invalid. Further examination of this problem is required.

Studies on the gas, liquid and crystal phase of benzene-h_6 and benzene-d_6 show[15–19] that deuterium substitution reduces the energy separation of all the vibrational levels, the most significant effect involving C–H or C–D stretching modes. Changes in the transition probability are, however, primarily caused by changes in the nature of the electronic states[20, 21]. There is evidence[22] of a slight decrease in oscillator strength for the O–O band, and for all other bands also, in C_6D_6 compared with C_6H_6 at room temperature. The decrease in intensity of the O–O band shows that C_6D_6 has higher electronic purity than C_6H_6. The reasons for the change in the electronic make-up of the S_1 state, which explains the increase in the intrinsic radiative lifetime of C_6D_6, are not clear.

Intersystem crossing

The triplet yield for C_6D_6 in methycyclohexane is slightly higher than for C_6H_6 in cyclohexane at room temperature[1]; the difference of about 10% may be a solvent effect. In cyclohexane the C_6D_6 triplet yield is fractionally smaller than that for C_6H_6 and for both cyclohexane and methylcyclohexane no isotope effect on the triplet yields like that found in the gas phase occurs[9].

The intersystem crossing rate constants k_{ISCM} calculated from $\Phi_{\mathrm{T}}/\tau_{\mathrm{M}}$ in methylcyclohexane are presented in Table 2. k_{ISCM} for benzene-d$_6$ shows a temperature dependence similar to benzene-h$_6$. This has been explained[23], using group theory, as arising from two alternative intersystem crossing processes: (i) a temperature independent $S_1 \rightarrow T_1$ step, and (ii), a temperature dependent $S_1 \rightarrow T_2$ transition. The smaller temperature dependence for intersystem crossing of the $^1B_{2u}$ state of C_6D_6 compared with C_6H_6 is consistent with a lowering of the vibrational energy levels in the excited states of the deuterated molecule[24, 25].

Data on the $T_1 \rightarrow S_0$ process in the solid or glassy phase is obtained from the phosphorescence lifetime. This is affected by crystal site, solvent and temperature and it is well established that τ_p for C_6H_6 is less than for C_6D_6. It has been concluded [27–29] that the rate constant for the radiative $T_1 \rightarrow S_0$ transition is independent of deuterium substitution and an isotope effect on the radiationless $T_1 \rightarrow S_0$ process is dominant in affecting the phosphorescence lifetime due to changes in the anharmonicities and Franck–Condon overlap between the states[27].

It is surprising that a similar effect is not seen in our data on the influence of deuteration on the radiationless intersystem crossing of S_1. It is significant that Johnson and Ziegler[30] have recently shown that the radiationless $T_1 \rightarrow S_0$ process is insensitive to deuteration and it is proposed that, unlike earlier interpretations, radiative process is substantially affected by changes in vibronic coupling.

It appears from this work with C_6D_6, and other simple aromatic molecules[1, 23, 31], that the only factors which seriously affect the S_1 to triplet conversion and probably $T_1 \rightarrow S_0$ also, are substituents or solvents which introduce mixed character into the electronic levels of the aromatic ring and increase vibronic coupling.

Internal conversion

The quantum deficit, Φ_{IC}, is assigned in the absence of contrary evidence, to a single radiationless $S_1 \rightarrow S_0$ decay process. The yields of chemical products reported for photolysis of benzene under our conditions are low in comparison with Φ_{IC}, and assignment in the manner proposed has been found satisfactory in benzene-h_6[1]. The temperature dependence of the rate constant k_{ICM} (Φ_{IC}/τ_M) follows an Arrhenius relationship with an activation energy of 0.25 eV and pre-exponential factor of 4.1×10^{11} s^{-1}. Comparable values are 0.28 eV due to Helman[7] calculated from lifetime measurements, and (0.292 eV and 2×10^{12} s^{-1}) obtained by Sandros[6] using Helman's lifetime data with measured triplet yields. Results in our laboratory for benzene-h_6 in methylcyclohexane yield an A factor of 4.6×10^{11} s^{-1} and $E_{ICM} = 0.25$ eV and other measurements in cyclohexane have given 8×10^{12} s^{-1} and 0.32 eV for internal conversion[2].

It has been reported that there is no change in the S_0–S_1 energy gap in benzene on deuteration but more recent work[23, 32, 33] indicates an increase of 200 cm^{-1} in the energy separation, a result confirmed by our own observations.

Of the various theories proposed to explain the nature of radiationless $S_1 \rightarrow S_0$ decay the recent suggestion of Callomon *et al.*[34] provides an acceptable, though incomplete, model. We consider that the (σ, π^*) state involved is a singlet rather than triplet, in view of the high pre-exponential factor for a spin forbidden process, and since triplet state formation has not been detected by either the butene-2 or biacetyl techniques. The effect of deuteration on energy of the possible (σ, π^*) state is unknown but shifting the relative energies of S_0 and S_1 states may affect crossover efficiency.

Conclusions

In contrast to the behaviour in gas and solid phase systems the effect of deuteration on the primary decay processes in solutions of benzene is only slight. The major deactivation route at room temperature and above is a radiationless $S_1 \rightarrow S_0$ internal conversion which may be slightly more efficient in C_6D_6 than C_6H_6.

1 R. B. Cundall and D. A. Robinson, *J. Chem. Soc., Faraday Trans. II*, 68 (1972) 1145.
2 R. B. Cundall and D. A. Robinson, *J. Chem. Soc., Faraday Trans. II*, 68 (1972) 1133.
3 J. R. Lockwood and T. F. Palmer, personal communication.
4 R. B. Cundall and L. C. Pereira, *J. Chem. Soc., Faraday Trans. II*, 68 (1972) 1152.
5 I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York, 1965.
6 K. Sandros, *Acta Chem. Scand.*, 25 (1971) 3651.
7 W. P. Helman, *J. Chem. Phys.*, 51 (1969) 354.
8 E. M. Anderson and G. B. Kistiakowsky, *J. Chem. Phys.*, 51 (1969) 182.
9 K. Dunnicliff, *Ph. D. Thesis*, University of Nottingham, 1971.
10 S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, 37 (1962) 814.
11 J. B. Birks and D. J. Dyson, *Proc. Roy. Soc.*, A275 (1963) 135.
12 J. L. Lauer, *J. Chem. Phys.*, 16 (1948) 612.
13 A. Abramson, K. G. Spears and S. A. Rice, *J. Chem. Phys.*, 56 (1972) 2291.
14 K. G. Spears and S. A. Rice, *J. Chem. Phys.*, 55 (1971) 5561.
15 F. M. Garforth, C. K. Ingold and H. G. Poole, *J. Chem. Soc.*, (1948) 491.
16 E. R. Bernstein, S. D. Colson, D. S. Tinti and G. W. Robinson, *J. Chem. Phys.*, 48 (1968) 4632.

17 G. Nonnenmacher and R. Mecke, *Spectrochim. Acta*, 17 (1961) 1049.
18 F. Langenbucher and R. Mecke, *Spectrochim. Acta*, 21 (1965) 1287.
19 A. R. Gee and G. W. Robinson, *J. Chem. Phys.*, 46 (1967) 4847.
20 J. Petruska, *J. Chem. Phys.*, 34 (1961) 1120.
21 P. E. Stevenson, *J. Chem. Educ.*, 41 (1964) 234.
22 A. Trombetti and C. Zauli, *J. Chem. Soc. (B)*, (1968) 1574.
23 R. B. Cundall, L. C. Pereira and D. A. Robinson, *J. Chem. Soc., Faraday Trans. II*, 69 (1973) in press.
24 D. M. Burland, G. Castro and G. W. Robinson, *J. Chem. Phys.*, 52 (1970) 4100.
25 G. W. King and E. H. Pinnington, *J. Mol. Spectros.*, 15 (1963) 394.
26 P. Sigal, *J. Chem. Phys.*, 46 (1967) 1043.
27 J. W. Rabelais, H. J. Maria and S. P. McGlynn, *J. Chem. Phys.*, 51 (1969) 2259.
28 T. E. Martin and A. H. Kalanter in C. Lim (ed.), *Int. Conf. Mol. Luminescence, Chicago*, Benjamin, New York, 1969, p. 437.
29 G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, 38 (1963) 1187.
30 P. M. Johnson and L. Ziegler, *J. Chem. Phys.*, 56 (1972) 2169.
31 R. B. Cundall and L. C. Pereira, *Chem. Phys. Lett.*, in press.
32 G. C. Nieman and G. W. Robinson, *J. Chem. Phys.*, 39 (1963) 1298.
33 S. D. Colson and G. W. Robinson, *J. Chem. Phys.*, 48 (1968) 2550.
34 J. H. Callomon, J. E. Parkin and R. Lopez-Delgado, *Chem. Phys. Lett.*, 13 (1972) 125.