Short Communication

Radiative decay of substituted benzenes: correlation with simple theory

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A recent publication[1] relates the rate constant for radiative decay (k_R) of the first excited singlet state of the series of methyl-substituted benzenes to the values of the extinction coefficient for the reverse transition (absorption) expected on the basis of the simple treatment given by Petruska[2] and Murrell[3]. Although the authors[1] state, correctly, that in point group D_{6h} (benzene and hexa-substituted benzenes) the $^1A_{1g}$–$^1B_{2u}$ symmetry forbidden transition is made partially allowed by perturbations of E_{2g} symmetry, it should be noted that these perturbations are due to *vibrations* in the molecule, and are not connected with substituent effects. The influence of substitution upon the extinction coefficient for and position of the absorption band in benzenes is considered by Petruska and Murrell to be due to a second-order inductive mixing of the ground and excited states with other states. The possible states which mix with the $^1A_{1g}$ and $^1B_{2u}$ states are shown in Table 1, together with the relative values of extinction coefficients expected on the basis of simple symmetry considerations. Since the $^1A_{1g}$–$^1E_{1u}$ transition is the only symmetry allowed π–π^* transition in benzene, the most important second-order interaction which determines the oscillator strength of the transition in substituted benzenes corresponding to the $^1A_{1g}$–$^1E_{1u}$ transition in benzene is that which mixes the $^1B_{2u}$ and $^1E_{1u}$ states (marked* in Table 1). Murrell has shown that experimental values of extinction coefficients correlate with expected values quite well for a variety of substituent groups[3].

Neglecting vibrational effects, the rate constant for radiative decay of the excited singlet states of the same molecules, on the basis of the Strickler–Berg[4] equation (1), might also be expected to correlate with the effect of substituent pattern in Table 1, although it must be noted in this case that the average frequency of fluorescence emission appears in the equation.

$$k_R = 2.88 \times 10^{-9} \; n^2 <\nu_f^{-3}>_{av}^{-1} \int \frac{\varepsilon}{\nu} \, d\bar{\nu} \tag{1}$$

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If $<\nu_f^{-3}>_{av}^{-1}$ varies markedly from molecule to molecule, comparison of k_R values with simple theory must allow for the distortion of k_R values (as compared with ε values) by the frequency term. In the earlier paper this fact was not considered. Table 2 shows experimental values of $<\nu_f^{-3}>_{av}^{-1}$ obtained for a variety of substituted benzenes in the vapour phase, from which it can be seen that there is some variation in this quantity between molecules. As stated above, Reiser and Leyshon[1]

TABLE 1

B^a VALUES FOR INTERACTION BETWEEN ELECTRONIC STATES OF BENZENE[b]

Substitution	Interaction with A_{1g} state				Interaction with B_{2u} state			
	A_{1g}	B_{1u}	E_{1u}	E_{2g}	A_{2g}	B_{2u}	$E_{1u}{}^*$	E_{2g}
1	1	1	1	1	1	1	1	1
1, 2	4	0	3	1	0	4	1	3
1, 3	4	4	1	1	4	4	1	1
1, 4	4	0	0	4	0	4	4	0
1, 2, 3	9	1	4	0	1	9	0	4
1, 2, 4	9	1	1	3	1	9	3	1
1, 3, 5	9	9	0	0	9	9	0	0
1, 2, 4, 5	16	0	0	4	0	16	4	0

[a] The B value is a measure of the mixing of the particular states shown introduced by the second-order inductive effect of the substituent. On this simple basis the B values in column* would be a measure of the relative values of the extinction coefficients for the S_0–S_1, transition in each case.
[b] Taken from ref. 3.

compared the variation in k_R with that expected on the basis of Table 1. These authors considered the unit B value in Table 1 to be given by the difference between the k_R values for benzene and toluene, since the theory neglects vibrational effects. Alternatively, one could equate the k_R value for the monosubstituted compound with unit B value, and consider deviations in the k_R value for benzene from zero to be a measure of the involvement of vibrational effects in the substituted compounds. Figure 1 shows that this leads to a slightly different matching of prediction with experiment than that shown by Reiser and Leyshon. Figure 1 also shows that corrections to predicted k_R values for $<\nu_f^{-3}>_{av}^{-1}$ variations are slight.

Considering the known importance of vibrational effects in determining the radiative rate constant for benzene, the apparent success of this very simple treatment in predicting the rate constants for methyl-substituted benzenes is perhaps surprising. The effect has also been remarked upon in a recent article on alkyl-substituted benzenes in condensed phases[1]. Data processed in a similar fashion for other simply substituted benzenes in the vapour phase are shown in Fig. 2. Although it is apparent in the (CH_3)-benzenes, the (F)-benzenes and the (CF_3)-benzenes that the 1,4-disubstituted molecule has a larger k_R value than the mono-, 1,2- and 1,3-substituted compounds, as would be expected on the basis of the treatment above, it is evident that agreement is much poorer than that observed in the liquid phase. For mixed substituents, little or no correlation is observable. In view of the

TABLE 2

VALUES OF $<\nu_f^{-3}>_{av}^{-1}$ FOR FLUORESCENCE EMISSION OF SUBSTITUTED BENZENES

Substituents	Positions	Pressure (Torr)	$<\nu_f^{-3}>_{av}^{-1}$ $(\times\ 10^{-13}\ cm^{-3})$	
F	1	20	4.45	(a)
F,F	1, 2	20	4.54	(a)
F,F	1, 3	23	4.49	(a)
F,F	1, 4	20	4.20	(a)
F,CH₃	1, 2	13	4.36	(a)
F,CH₃	1, 3	12	4.35	(a)
F,CH₃	1, 4	12	4.16	(a)
F,CF₃	1, 2	12	4.02	(a)
F,CF₃	1, 3	12	4.15	(a)
CF₃	1	18	4.50	(a)
CF₃,CF₃	1, 3	15	4.57	(a)
CF₃,CF₃	1, 4	15	4.50	(a)
CH₃	1	20	4.34	(a)
CH₃,CH₃	1, 2	liq	4.04	(b)
CH₃,CH₃	1, 3	liq	4.01	(b)
CH₃,CH₃	1, 4	liq	3.95	(b)
CH₃,CH₃,CH₃	1, 2, 4	liq	3.95	(b)
CH₃,CH₃,CH₃	1, 3, 5	liq	3.86	(b)
CH₃	1	liq	4.20	(b)
—	—	liq	4.31	(b)
		20	4.47	(a)

(a) = Calculated from uncorrected gas phase emission spectra taken on Farrand Mk.1 spectro-fluorimeter by Mr. R. G. Brown.

(b) = Calculated from wavelength-corrected emission spectra in cyclohexane solution from Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York, 1965.
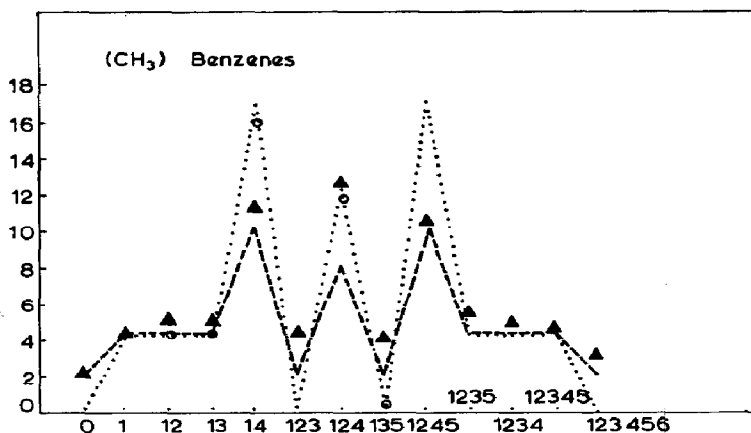

Fig. 1. Correlation of radiative rate constant with theory for methyl benzenes in solution. ▲, Experimental, from ref. 1; O, predicted as k_R (toluene) $\times$ B $\times$ $[<\nu_f^{-3}>^{-1}_{benzene}]/[<\nu_f^{-3}>^{-1}_{compound}]$. B values from Table 1, $<\nu_f^{-3}>^{-1}$ values from Table 2, k_R (toluene) values from ref. 1. ...., Predicted from B $\times$ k_R (toluene); ————————, predicted from B $\times$ $[k_R$ (toluene)$-k_R$ (benzene)].
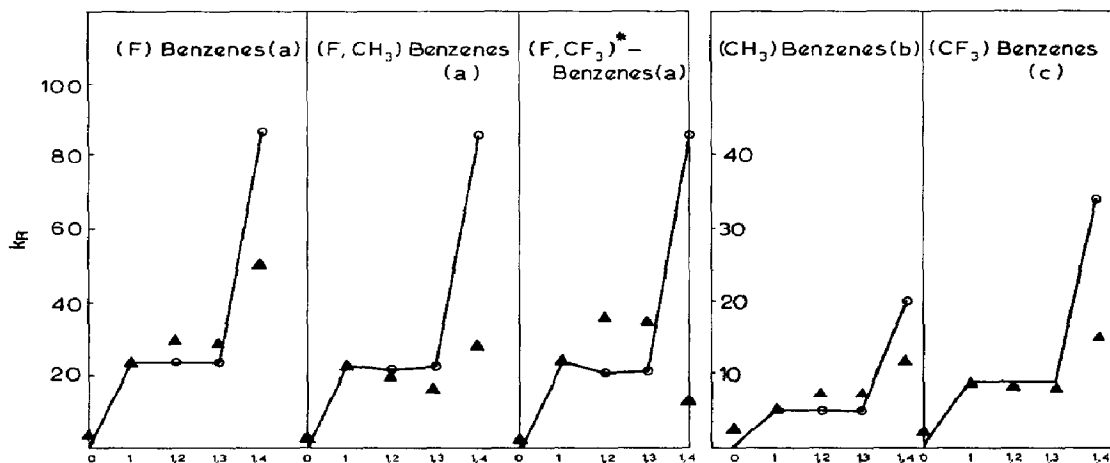
Fig. 2. Rate constants for radiative decay of substituted benzenes in vapour phase. ▲, Experimental; data from those collated in D. Phillips, *J. Photochem.*, 1 (1972) 97. O, Predicted from: (a) k_R (fluorobenzene) = 1; (b) k_R (toluene) = 1; (c) k_R (trifluoromethylbenzene) = 1. *Quantum yield data for 1,4-isomer from Kh. Al-Ani, personal communication; decay time from M. G. Rockley, unpublished work.

total neglect of vibrational interactions and the extreme simplicity of the theoretical treatment, however, this is hardly surprising.

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