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Radiative and Nonradiative Transitions in Solution. First Excited Singlet State of Benzene and Its Methyl Derivatives

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Abstract: Intersystem crossing quantum yield data, along with measured singlet lifetimes and literature values for the fluorescence quantum yields, are used to evaluate rate constants for deactivation of the first excited singlet state of benzene and 11 of its methyl derivatives in cyclohexane solution at room temperature. A qualitative dependence of the intersystem crossing rate constants on the symmetry of methyl substitution is observed and mechanisms involving intersystem crossing via the second triplet state are discussed. Nonradiative decay by routes not involving intersystem crossing is found to be an important process for all of these compounds except *p*-xylene.

Recently Reiser and Leyshon,[2] in a study of the fluorescence quantum yields (Φ_f) of the methylbenzenes in degassed cyclohexane solution at room temperature, demonstrated that variations of the radiative rate constant (k_f) with methyl substitution were related to the symmetry of the substitution. Except for hexa- and pentamethylbenzene, the total nonradiative decay rates (k_{nr}) of benzene and its derivatives were found to be quite similar. These authors suggested that the lack of significant variation of k_{nr} might indicate that the rate constants for intersystem crossing (k_{isc}) and internal conversion (k_d) were relatively insensitive to methyl substitution. Because the limited intersystem crossing[3,4] and singlet lifetime[5] data available indicated that substantial variations in k_{isc} might occur among the methylbenzenes, we undertook a systematic determination of the intersystem crossing rate constants of benzene and its methyl derivatives.

Results

The determination of the intersystem crossing quantum yields is described in the accompanying paper.[6] Fluorescence quantum yields were taken from the literature and refer to dilute cyclohexane solution at room temperature. Values of the internal conversion quantum yields (Φ_d) were calculated from eq 1.

$$\Phi_d = 1 - (\Phi_f + \Phi_{isc}) \qquad (1)$$

The singlet lifetimes (τ_f^0) were determined directly from the fluorescence decay. These lifetimes are generally in reasonable agreement with those reported by Berlman in cyclohexane[5] and Morrison in hexane[7] solution. Our values are lower than those reported by Cundall[8,9,10] in methylcyclohexane solution.

Experimental values of τ_f^0 were used to calculate rate constants according to eq 2. The use of this equation implicitly assumes that complete vibrational relaxation occurs

$$k_x = \Phi_x/\tau_f^0 \qquad (2)$$

prior to decay of S_1 under our excitation conditions (λ >240 nm). Several studies support the validity of this assumption. The fluorescence quantum yields of benzene and several of its methyl derivatives have been shown to be inde-

Table I. Fluorescence Lifetime Data for the Methylbenzenes in Degassed Solution at Room Temperature

Compd	τ_f°(this work), nsec	τ_f(lit.), nsec		
	Cyclohexane soln	Cyclohexane[a] soln	Hexane[7] soln	Methylcyclohexane soln
Benzene	28 ± 2	29 28[b] 34[8]	33.6	30[8]
Toluene	34 ± 2	34	35.2	40[9]
o-Xylene	32 ± 2	32.2	38.2	47.2[10]
m-Xylene	31 ± 2	30.8	32.7	
p-Xylene	30 ± 2	30	33.3	
1,2,3-Trimethylbenzene	35 ± 2			
1,2,4-Trimethylbenzene	28 ± 2	27.2		
1,3,5-Trimethylbenzene	36.5 ± 2	36.5	38.5	
1,2,4,5-Tetramethylbenzene	26.5 ± 2		28.6	
1,2,3,5-Tetramethylbenzene	31 ± 2		27.9	
1,2,3,4-Tetramethylbenzene	27 ± 2		33.8	
Pentamethylbenzene	15 ± 1		15.7	

[a] Data of ref 5 except as noted. [b] W. P. Helman, *J. Chem. Phys.*, 51, 354 (1969).

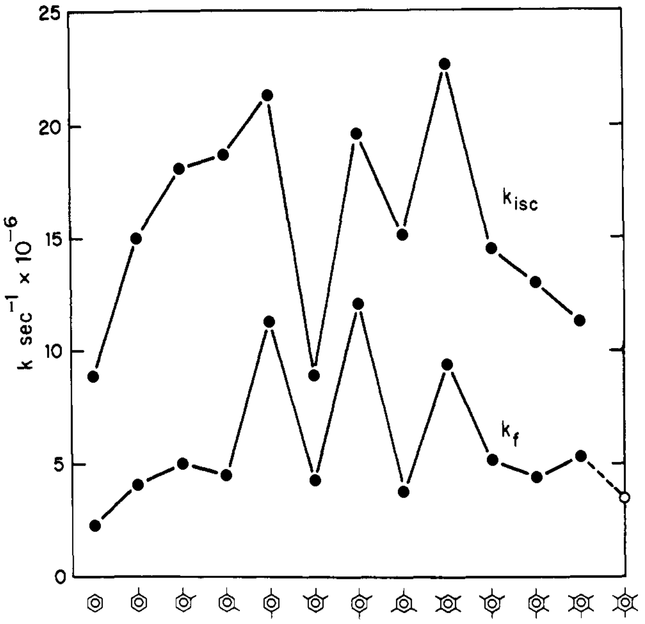

Figure 1. Variation of k_f and k_{isc} among the methylbenzenes.

pendent of excitation wavelength in solution throughout the region of interest.[11,12] In addition, the quantum yield for formation of benzvalene from excited benzene[13] and the quantum yields for photoisomerization of the xylenes[14] are found to be constant for wavelengths greater than 230 nm.

The results are summarized in Tables I and II and the rate data are schematically displayed in Figure 1.

Discussion

The ground state of benzene has symmetry $^1A_{1g}$ and the first excited singlet is $^1B_{2u}$. The $^1A_{1g} \rightarrow {}^1B_{2u}$ ($S_0 \rightarrow S_1$) transition is forbidden and derives its intensity from the allowed $^1A_{1g} \rightarrow {}^1E_{1u}$ transition via $^1B_{2u}$-$^1E_{1u}$ vibronic coupling. The 0-0 band is present in solution, due largely to solvent-solute interactions which mix $^1E_{1u}$ character into S_1, but is quite weak.[15-17] According to Petruska,[18] methyl substitution of the benzene nucleus has two effects on the $S_0 \rightarrow S_1$ transition. The first is to enhance the $^1B_{2u}$-$^1E_{1u}$ vibronic coupling, resulting in a general increase in the "vibronic" intensity of the $S_0 \rightarrow S_1$ transition with increasing methyl substitution. The second effect depends on the symmetry of the methyl substitution rather than the number of substituents and is due principally to second-order inductive perturbations which mix $^1E_{1u}$ character into S_1.[19] This gives rise to a new "allowed" or "electronic" intensity which possesses a prominent 0-0 band in absorption. The second effect is predicted to be unimportant for mesitylene, 1,2,3-trimethylbenzene, and hexamethylbenzene and to be most important for *p*-xylene, 1,2,4-trimethylbenzene, and 1,2,4,5-tetramethylbenzene. The total intensity of the $S_0 \rightarrow S_1$ transition for a given methylbenzene may thus be approximated as the sum of a "vibronic" intensity and an "electronic" intensity. Differences between methylbenzenes possessing an equal number of methyl substituents are therefore attributed principally to differences in their electronic intensity.

Values of k_f calculated using our lifetimes for the methylbenzenes confirm the earlier estimates made by Reiser and Leyshon.[2] As was noted by these authors, the substitution-dependent changes in k_f correlate reasonably well with the corresponding changes in absorption oscillator strength. Thus, the compounds which exhibit the largest k_f value (*p*-

Table II. Quantum Yield and Rate Data for the Methylbenzenes in Degassed Cyclohexane Solution

Compd	Φ_f[a]	Φ_{isc}[6]	Φ_d[b]	k_f,[c] sec^{-1} × 10^{-6}	k_{isc},[c,d] sec^{-1} × 10^{-6}	k_d,[c] sec^{-1} × 10^{-6}
Benzene	0.063 0.058 0.06[8] 0.061[15]	0.25 ± 0.02	0.69	2.2	8.9	25
Toluene	0.14	0.51 ± 0.03	0.35	4.1	15	10
o-Xylene	0.16	0.58 ± 0.03	0.26	5.0	18	8.1
m-Xylene	0.14	0.58 ± 0.03	0.28	4.5	19	9.0
p-Xylene	0.34 0.33	0.64 ± 0.03	(0.02)	11	21	(0.7)
1,2,3-Trimethylbenzene	0.15	0.31 ± 0.02	0.54	4.3	8.9	15
1,2,4-Trimethylbenzene	0.34	0.55 ± 0.03	0.11	12	20	3.9
Mesitylene	0.14	0.55 ± 0.03	0.31	3.8	15	8.5
1,2,4,5-Tetramethylbenzene	0.25	0.60 ± 0.03	0.15	9.4	23	5.7
1,2,3,5-Tetramethylbenzene	0.16	0.44 ± 0.02	0.40	5.2	14	13
1,2,3,4-Tetramethylbenzene	0.12	0.35 ± 0.02	0.53	4.4	13	20
Pentamethylbenzene	0.08	0.17 ± 0.01	0.75	5.3	11	50
Hexamethylbenzene	0.015			3.3[a]		

[a] Data from ref 2 except as noted. [b] Calculated from eq 1. [c] Calculated from eq 2. [d] ±15%.

xylene, 1,2,4-trimethylbenzene, and 1,2,4,5-tetramethylbenzene) are also the compounds which possess the largest "electronic" contribution to the absorption intensity. Such a correlation between k_f and the absorption oscillator strength is not uncommon and is anticipated by the Strickler-Berg equation.[20]

As can be seen from the values of Φ_d in Table II, nonradiative decay via pathways other than intersystem crossing is an important process for all of the compounds studied here except *p*-xylene.[21] The processes which contribute to Φ_d are not well understood despite extensive investigation.[9,10,13,14,22-27] For the benzene derivatives which have been studied, k_d, in contrast to k_f and k_{isc}, is highly temperature dependent[9,10,22,27] and may be dominated by activated crossing to σ-π^* states[28] or to isomeric potential surfaces.[25,26,29] In any event, yields of stable products are quite small[13,14,23-26] and the net result is internal conversion from S_1 to S_0. Since k_d represents the rate constant for a temperature-dependent process, we hesitate to ascribe any significance to the relative values of k_d at room temperature in the absence of data at other temperatures. It is interesting to note, however, that room-temperature values of k_d are smallest for those methylbenzenes with the largest values of k_f and k_{isc}.

According to the present theory of nonradiative transitions, the rate constant for intersystem crossing from S_1 of benzene may be described by eq 3, where β represents the

$$k_{isc} = (2\pi/\hbar)\beta^2\rho(E) \qquad (3)$$

interaction (either spin-orbit or vibronic-spin-orbit) between the initial ($^1B_{2u}$) and final states and $\rho(E)$ represents the density of directly coupled final states.[30-33] Since T_1 ($^3B_{1u}$) lies about 8600 cm^{-1} below S_1 and T_2 ($^3E_{1u}$) about 1700 cm^{-1} below S_1 in the gas phase,[34] intersystem crossing from S_1 of benzene (which persists in the "isolated" molecule even at very low pressures)[34] may potentially occur either directly to T_1 or via T_2. The interaction (β) responsible for the $S_1 \rightsquigarrow T_1$ transition should be direct $^1B_{2u}$-$^3B_{1u}$ spin-orbit coupling, which is symmetry allowed in first order. Direct $^1B_{2u}$-$^3E_{1u}$ spin-orbit coupling is forbidden, requiring that second-order interactions, principally vibronic-spin-orbit, be responsible for the $S_1 \rightsquigarrow T_2$ transition.[35,36] Although the small S_1-T_2 energy gap may give rise to relatively large Franck-Condon factors between the $^1B_{2u}$ and $^3E_{1u}$ states, it also implies that the vibrational levels of T_2 will be coarsely spaced in the vicinity of the lower levels of S_1. Thus, barring accidental resonances of levels of S_1 and T_2, the density of directly coupled final states responsible for irreversible intersystem crossing in the "isolated" benzene molecule will derive from T_1[36] and the role of T_2 should be minimal in the gas phase.

Intersystem crossing of benzene in solution is not well understood. In condensed media, intersystem crossing to T_2 might play an important role since collisions with solvent molecules may serve not only to promote the transition (especially if it is at all activated), but also to render it irreversible as a result of rapid vibrational relaxation in T_2. Thus, the transition can reasonably be expected to occur to either T_1 or T_2 or perhaps competitively to both.

Any discussion of the variations of k_{isc} with methyl substitution must also recognize that in solution intersystem crossing to either T_1 or T_2 may be responsible for the observed differences. Reasonable sources of variation of k_{isc} would therefore include substitution-dependent changes in the S_1-T_1 energy gap, the occurrence of temperature-dependent processes such as activated crossing to T_2, substitution-dependent effects on the interaction coupling S_1 and T_1, and substitution-dependent effects on the interaction coupling S_1 and T_2.

The most striking result to emerge from our data is shown graphically in Figure 1. Apparently there is a substantial correlation between substituent effects on k_f and k_{isc}. Since we and others have attributed the marked effect of substituent positions on k_f to increased mixing of $^1E_{1u}$ character into S_1, we should examine the effect that this will have on the intersystem crossing rates. The most obvious effect would be to increase the contribution of $^1E_{1u}$-$^3E_{1u}$ spin-orbit coupling to β for the $S_1 \rightsquigarrow T_2$ transition.[37] If the Franck-Condon factors are indeed large for the $S_1 \rightsquigarrow T_2$ transition of benzene itself (vide supra), changes in them resulting from methyl substitution may be less important. The high values of k_{isc} for *p*-xylene, 1,2,4-trimethylbenzene, and 1,2,4,5-tetramethylbenzene would then be the consequence of high rates of crossing to T_2.

Even if we accept this conclusion with its qualitative theoretical base, it does not teach us much about intersystem crossing in benzene. Note in Figure 1 that if the values of k_{isc} for the three "fast" compounds were all close to 15 × 10^6 sec^{-1} we would be inclined to say that there is very little effect of methyl substituents on k_{isc}. This would have been compatible with the notion that crossing to T_2 is unimportant and that the analysis of Robinson,[36] summarized above, for benzene in the vapor phase holds for benzene and all of its methyl derivatives. Although the present results are compatible with the notion that very little of the T_2 state is produced with any but the three "fast" compounds, the nature of the results is such that this conclusion is at best suggestive. Development of a discriminating method for measuring the yields of T_2 states of the compounds would clarify the issue.

Other factors which might be expected to affect the intersystem crossing rates do not seem to predict the observed pattern of results. The S_1-T_1 energy gaps calculated for the methylbenzenes using singlet energies taken from absorption data and triplet energies from phosphorescence data (77 °K)[38] are remarkably insensitive to methyl substitution. Since these values are probably representative of the energy gap in cyclohexane solution at room temperature, simple differences in the S_1-T_1 energy gap are inadequate to explain the variations we observe in k_{isc} with methyl substitution.

The rate constant for the direct $S_1 \rightsquigarrow T_1$ transition in the methylbenzenes should be dominated by the $^1B_{2u}$-$^3B_{1u}$[19] spin-orbit interaction. The most likely source of substitution-dependent variations in this interaction would be via the Franck-Condon factors for the transition. Although the relative constancy of the S_1-T_1 energy gap does not necessarily eliminate the possibility that changes in the Franck-Condon factors or the number of directly coupled final states may be related in some manner to the symmetry of methyl substitution, gas-phase values of k_{isc},[38] which should reflect predominantly the $S_1 \rightsquigarrow T_1$ transition, are much less sensitive to methyl substitution than the corresponding solution values. Thus, we might expect the rate of direct $S_1 \rightsquigarrow T_1$ intersystem crossing in solution to be relatively unaffected by methyl substitution.

As in the case of anthracene,[39] intersystem crossing to T_2 of the methylbenzenes might be an activated process in solution. The value of k_{isc} for benzene has been shown to be slightly temperature dependent in methylcyclohexane solution;[22] however, the values for toluene[9] and *o*-xylene[10] are temperature independent under the same conditions. Although the experimental data are quite limited, calculations[38] indicate that T_2 remains below S_1 in energy throughout the methylbenzenes, suggesting (by analogy to substituted anthracenes having T_2 lower than S_1[39,40]) that temperature effects on k_{isc} will be small when present.

The failure of an overall correlation of k_f with k_{isc} emphasizes the qualitative nature of our discussion and the lack of experimental data for factors such as changes in the S_1–T_2 energy gap and the precise role of competing intersystem crossing pathways. However, despite the potential complexity of intersystem crossing in the methylbenzenes, substitution-dependent utilization of the S_1–T_2 pathway does appear to provide a reasonable rationale for the observed variations of k_{isc}.

Experimental Section

The purification of materials, the determination of the intersystem crossing yields, and the degassing procedure are detailed in the accompanying paper.[6] Fluorescence lifetimes of degassed samples of the methylbenzenes (OD 2.2 cm^{-1} at 254 nm) were determined with a TRW Model 31A nanosecond spectral source (D_2 lamp) with decay time computer coupled to a Tektronix Type 556 dual-beam oscilloscope. No significant differences were observed for similarly degassed solutions prepared such that the aromatic had an absorbance of 1.0 cm^{-1} at 254 nm. All measurements were performed at room temperature (24 ± 1°).

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