

Activation Energies for the Singlet Excited State Processes of Substituted Benzenes: para, meta, and ortho Isomers of Methylbenzonitrile and Methylanisole in Acetonitrile

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The photochemistry and photophysics of organic substrates upon excitation in fluid solution is controlled, almost without exception, by the reactivity of the first excited singlet state (S_1). As shown in Scheme 1, the competitive processes and their associated quantum yields are: k_f (Φ_f), k_{isc} (Φ_{isc}), k_{ic} (Φ_{ic}), and k_r (Φ_r). The reaction process, k_r , often results in the formation of a reactive intermediate, RI, that may return to S_0 (k_{icr}) or proceed to observable products (k_p).

Ermolaev's rule¹ for S_1 of aromatic compounds, which have been fundamental in the development of organic photochemistry, states that $(\Phi_f + \Phi_{isc}) = 1$. This rule applies reasonably well to polycyclic aromatics: naphthalene ($\Phi_f = 0.19$, $\Phi_{isc} = 0.75$),² anthracene (0.30, 0.71),² and phenanthrene (0.13, 0.85).² However, it fails completely for benzene and many of its derivatives: benzene (0.06, 0.25),² toluene (0.14, 0.51),² and *ortho*-xylene (0.16, 0.58).² The reason for this "quantum yield deficiency" is well-established; some combination of k_{ic} and k_r contributes to the decay of S_1 . In fact, many experimental results for substituted benzenes demonstrate that RI is a prefulvene biradical formed by meta bonding (A, Scheme 1).³ These results are supported by calculations for benzene itself, indicating that a barrier exists between S_1 and a conical intersection that leads to A.⁴ Therefore, eq 1, where Φ_d is the quantum yield for the sum of $(k_r + k_{ic}) = k_d$, must be used. Nevertheless, estimations of Φ_{isc} for substituted benzenes using Ermolaev's rule have recently been reported.⁵

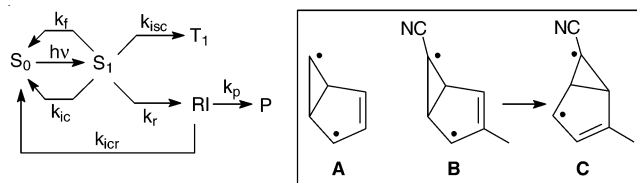
$$\Phi_f + \Phi_{isc} + \Phi_d = 1 \quad (1)$$

The effect of temperature on the rate constants of excited state processes has received far less attention than it merits. However, recently Lewis and co-workers have shown that quantum yield and fluorescence measurements over a broad range of temperatures provide a powerful tool for understanding the details of excited-state processes for substituted styrenes.⁶ The basic idea is that the total rate constant of decay (k_t) of S_1 is given by eq 2, with $k_d = k_r + k_{ic}$ and using the reasonable assumption that the photophysical processes k_f and k_{isc} have no temperature dependence. Therefore, the Arrhenius parameters A and E_a refer to k_d , equal to k_r if $k_r \gg k_{ic}$. This last assumption is reasonable if the S_1 to S_0 energy gap is large, leading to unfavorable Franck–Condon overlap and small values of k_{ic} . The reaction process k_r can itself result in internal conversion if the geometric changes that lead to RI do not prevent return to S_0 (k_{icr}). The values of k_t can be conveniently obtained using fluorescence decay as a way of monitoring $[S_1]$ as a function of time.

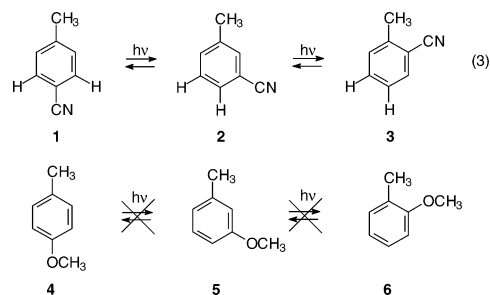
$$\begin{aligned} k_t &= k_f + k_{isc} + k_{ic} + k_r = k_f + k_{isc} + k_d \\ &= (k_f + k_{isc}) + A \exp(-E_a/RT) \end{aligned} \quad (2)$$

Recently, we have published a series of articles on the phototransposition reactions (ortho, meta, para) in acetonitrile of a range

Scheme 1. Reaction Pathways of S_1 and RIs Exemplified by the Prefulvene Biradicals, A, B, and C



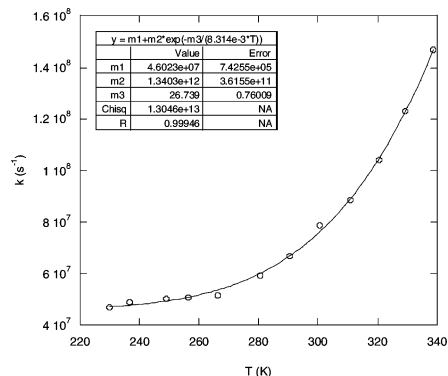
of substituted benzenes.⁷ An example is shown in eq 3 for the methylbenzonitriles. As shown by deuterium labeling and as the equation indicates, the nitrile-substituted carbon is the active one. Therefore, the critical RI from the para isomer is the prefulvene biradical B (Scheme 1), which rearranges to C, providing a pathway to the meta isomer. In fact, products derived from C have been obtained from irradiations of both **1** and **2** in 2,2,2-trifluoroethanol. Moreover, this phototransposition reaction has been shown to occur from S_1 . Therefore, these reactions are ideal candidates for a study of temperature effects. We now report an analysis for literature results for benzene, toluene, and *ortho*-xylene⁸ and for new results for the methylbenzonitriles (**1**, **2**, **3**) and the methylanisoles (**4**, **5**, **6**), chosen because they do not undergo the phototransposition reaction of eq 3. Are the anisole isomers unreactive relative to the benzonitriles because a larger kinetic barrier separates S_1 from the corresponding substituted prefulvene or do larger barriers exist on the surface that allow the prefulvenes to rearrange (B to C for the methylbenzonitriles, Scheme 1)? This question can be answered by variable temperature studies of fluorescence of the two sets of substrates which probe only the first possibility and not the second.



Rate constants of decay ($k_t = 1/\tau_s$) for compounds **1**–**6** were obtained from the lifetimes (τ_s) of the exponential decays of fluorescence (nanosecond single photon counting) over the temperature range of -45 to $+65$ °C in acetonitrile. A plot of the data according to eq 2 for **1** is shown in Figure 1, along with a nonlinear least-squares fit. Plots for **2** and **3** are shown in the Supporting Information (Figure S1 and S2). Similar plots were made from literature data for benzene, toluene, and *ortho*-xylene in hydrocarbon solvents.^{8,9} The Arrhenius parameters are given in Table 1,

Table 1. Arrhenius Parameters, Rate Constants (25 °C), and Quantum Yields for Reactions of S₁

compd	A/10 ¹¹ s ⁻¹	E _a /kJ mol ⁻¹ = m3	(k _f + k _{isc})/10 ⁷ s ⁻¹ = m1	k _d /10 ⁷ s ⁻¹	Φ _d	k _f /10 ⁷ s ⁻¹	k _t /10 ⁷ s ⁻¹	Φ _f	k _{isc} /10 ⁷ s ⁻¹	Φ _{isc}	Φ _{prod}
benzene	5.0 ± 3.9	23.8 ± 2.3	0.35 ± 0.51	3.2	0.69	3.6	0.22	0.06	0.89	0.25	0.02
toluene	4.3 ± 2.4	27.0 ± 1.5	1.6 ± 0.1	1.0	0.34	2.9	0.41	0.14	1.5	0.52	
<i>o</i> -xylene	2.1 ± 1.8	25.4 ± 2.6	1.5 ± 0.1	0.70	0.26	3.1	0.50	0.16	1.8	0.58	0.01
1	13.4 ± 0.4	26.7 ± 0.8	4.6 ± 0.1	2.7	0.29	9.3	1.5	0.16		(0.55)	0.025
2	10.0 ± 0.4	25.4 ± 1.1	8.0 ± 0.4	3.3	0.28	12	2.6	0.22		(0.40)	0.003
3	0.21 ± 0.15	19.5 ± 2.1	9.4 ± 0.1	0.8	0.08	10	2.2	0.22		(0.65)	

**Figure 1.** Arrhenius plot for the rate constant of decay (k_t) of S₁ for **1** versus T .

along with values for ($k_f + k_{isc}$), the intercept at 0 K of the plots and k_d , calculated at 25 °C.

For the alkylbenzene derivatives, both Φ_f and Φ_{isc} values have been determined previously,¹⁰ and therefore k_t (25 °C) can be divided into each of its component processes, k_f , k_{isc} , and k_d , using eq 1 and $k_x = \Phi_x k_t$. These values are given in Table 1. The values of ($k_f + k_{isc}$) obtained from these quantum yield measurements (1.1 , 1.9 , and $2.3 \times 10^{-7} \text{ s}^{-1}$ for benzene, toluene, and *ortho*-xylene, respectively) agree quite well with those from the Arrhenius plots (0.35 ± 0.51 , 1.6 ± 0.1 , and $1.5 \pm 0.1 \times 10^{-7} \text{ s}^{-1}$, respectively)¹¹ especially considering the long extrapolation necessary for the latter. The k_d values can also be calculated at 25 °C from the Arrhenius parameters and then summed into ($k_f + k_{isc}$) to give k_t . These k_t values (3.6 , 2.6 , and $2.2 \times 10^7 \text{ s}^{-1}$ for benzene, toluene, and *ortho*-xylene, respectively) also agree remarkably well with those obtained from independent fluorescence lifetime measurements (3.6 , 2.9 , and $3.1 \times 10^7 \text{ s}^{-1}$). This comparison of using either nonlinear fits to the Arrhenius equation or directly measured quantum yields for determining rate constants for the reactions of S₁ gives us considerable confidence that the Arrhenius plot method is reliable.

An examination of the rate constants in Table 1 reveals that all substrates have k_t values considerably higher than ($k_f + k_{isc}$) values. As expected, Ermolaev's rule does not apply but eq 1 does. In fact, Φ_d values, obtained from eq 1 for the alkyl benzenes and from k_d/k_t values for compounds **1–3** in Table 1, indicate that, in all cases, $k_d = (k_{isc} + k_f)$ is a significant contributor to the decay of S₁. The agreement between $[k_d/(k_f + k_{isc} + k_d)] = 9.3/7.3$, $12/11.3$, and $10/10.2$ for **1**, **2**, and **3**, respectively, obtained from fluorescence decay for k_t and from the Arrhenius plots for ($k_f + k_{isc} + k_d$) is again excellent.¹²

The question then arises as to the partitioning of k_d between k_{isc} and k_f . Literature data for anisole ($\Phi_f = 0.24$, $\Phi_{isc} = 0.64$)² and fluorobenzene ($\Phi_f = 0.11$, $\Phi_{isc} = 0.80$)² indicate that k_{isc} is only a minor contributor to the decay of S₁ for these two chromophores. Moreover, neither the methylanisoles (**4–6**) nor the methylfluorobenzenes undergo phototransposition reactions.⁷ As well, the

fluorescence data for the anisoles were quite different from the toluonitriles as the k_t values decreased only slightly with temperature; the averages over the entire temperature range were 14 ± 2 , 13 ± 2 , and $15 \pm 2 \times 10^{-7} \text{ s}^{-1}$, for **4**, **5**, and **6**, respectively. These observations provide strong circumstantial evidence that if E_a is large enough to prevent k_f from contributing to k_t , then $k_t \approx k_f + k_{isc}$. Therefore, the quantum yield deficiency for substituted benzenes may only be significant for those that decay efficiently through k_f to RI, i.e., $k_f \gg k_{isc}$ and $\Phi_d \approx \Phi_f$.

Finally, the quantum yields of product formation Φ_{prod} are quite small for substituted benzenes. Values are given in Table 1 for benzene (benzvalene formation),¹³ *ortho*-xylene (formation of *meta*-xylene),¹⁴ **1** (formation of **2** and **3**),⁷ and **2** (formation of **1** and **3**).⁷ These values are all significantly lower than Φ_d . Therefore, the formation of RI, in agreement with calculations,⁴ is a major pathway for internal conversion by k_{isc} (Scheme 1). In conclusion, the effect of temperature on fluorescence is a valuable tool for probing the reactivity of S₁ of substituted benzenes.

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Supporting Information Available: Arrhenius plots for compounds **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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