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# A New Method for the Determination of Intersystem Crossing Quantum Yields.[1] Application to Benzene and Its Methyl Derivatives

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**Abstract:** A method for the determination of intersystem crossing quantum yields which is particularly useful for benzene derivatives is described. The experimental procedure involves measurement of relative fluorescence intensities of the aromatic compound and relative yields of triplet sensitized reaction in solutions with varying concentrations of a heavy atom fluorescence quencher such as xenon. Intersystem crossing quantum yields are reported for benzene and 11 of its methyl derivatives in cyclohexane solution at room temperature and the values obtained are compared, where possible, with literature values. Discrepancies between values reported here and those determined by direct "triplet counting" techniques suggest that there may be important energy wasting processes in the triplet sensitized isomerization of olefins by some benzene derivatives.

Despite their importance in developing an understanding of excited state decay processes, very few reliable intersystem crossing quantum yields ($\Phi_{isc}$) have been reported for benzene derivatives in solution. This is due in large part to the high energy of the benzene singlet, the short lifetime and poor spectral characteristics of the benzene triplet, and the lack of a simple, generally applicable method for the determination of $\Phi_{isc}$. Thus, although a large number of procedures for the determination of $\Phi_{isc}$ are available,[3-13] only a few of these methods have been applied to benzene derivatives. In this respect, the difficulties encountered in extending the method of Wilkinson and coworkers[5] to benzene derivatives are typical. This elegant technique utilizes heavy atom additives to enhance intersystem crossing in the aromatic compound under investigation. The intersystem crossing yield of the aromatic may be obtained from an analysis of the decrease in fluorescence intensities and the increase in flash spectroscopic triplet-triplet absorption intensities of the aromatic with increasing concentration of the heavy atom additive. This method is not applicable to benzene derivatives because they typically do not exhibit triplet-triplet absorption under conventional flash spectroscopic conditions.[14]

The method of Lamola and Hammond[3] (sensitized piperylene isomerization) has been applied to toluene by Morrison.[15] Competitive absorption by the diene (with subsequent singlet isomerization of the diene) and the efficient quenching of toluene singlets by the diene require that large corrections be applied to the experimental data. The magnitude of these corrections seriously limits the accuracy and utility of this method.

Berenfel'd and Krongauz[16] have used the sensitized isomerization of *trans*-stilbene to determine the triplet yields of a number of benzene derivatives. Their reported triplet yields are generally quite small and are probably unreliable estimates of $\Phi_{isc}$. Since the triplet lifetimes of benzene derivatives are of the order of microseconds in dilute solution[6,17] and, at least in the cases of benzene[17,18] and *o*-xylene,[19] decrease with increasing concentration,[18] the experimental concentrations of *trans*-stilbene (2-3 × $10^{-4}$ *M*) are probably inadequate to intercept all of the sensitizer triplets. Furthermore, at the high concentrations of aromatic (0.3-0.5 *M*) employed, excimer effects on the triplet yield[17-19] may be quite significant.

Cundall[4] and later others[17] have utilized the sensitized isomerization of simple olefins to determine benzene intersystem crossing yields. The method is based on the assumption that the sum of limiting quantum yields for isomerization of the olefin ($\Phi_{c\to t}$ and $\Phi_{t\to c}$ at high concentrations of olefin) is equal to $\Phi_{isc}$. The assumption that bimolecular processes not leading to excitation of the olefin are unimportant relative to energy transfer[20] while apparently valid for benzene, must be made with caution when the method is applied to a wide variety of benzene derivatives (vide infra). In general, however, the method may suffer from experimental difficulties in addition to uncertain kinetic assumptions. For example, literature values of $\Phi_{c\to t}$ for the toluene-sensitized isomerization of simple olefins in solution at room temperature range from 0.14 to 0.24 and values of the ratio $\Phi_{t\to c}/\Phi_{c\to t}$ range from 0.95 to 1.15.[15,17,21,22]

Sandros[6] has developed a method for determining $\Phi_{isc}$ from phosphorescence data which gives reasonable results for a variety of compounds including benzene derivatives. Since the method requires a sensitive experimental procedure and an elaborate kinetic analysis to correct for the effects of singlet energy transfer to biacetyl, it has seen only limited use.

Recently, we developed a new method designed primarily for the determination of intersystem crossing quantum yields of substituted benzenes in solution.[1] In this paper, we describe our method in greater detail and report additional values of $\Phi_{\text{isc}}$ determined by this method. In the accompanying paper,[23] we use these values of $\Phi_{\text{isc}}$ and the corresponding fluorescence lifetimes to calculate intersystem crossing rates for the methylbenzenes and discuss the nature of the processes deactivating the first excited singlet state of these compounds in solution.

## Procedure and Results

Relative fluorescence intensities of the hydrocarbons (A) were measured: (1) in the absence of any quencher ($F^0$), (2) in the presence of *cis*-2-pentene (C) at 0.05 *M* concentration ($F'$), and (3) in a series of solutions under varying pressures of xenon ($F$). The yields of *trans*-2-pentene (T) were measured in the solutions containing C as the only additive ($Y_{\text{T}}'$) and in the samples containing both C and xenon ($Y_{\text{T}}$).

The data were analyzed assuming the following mechanism for fluorescence quenching (H = xenon). The predicted relationship between concentration of C and its fluorescence quenching effect with no added H is given by eq 12. The predicted effect on fluorescence intensity of adding H to solutions which also contain C is shown in eq 13.

$$A_0 \xrightarrow{h\nu} A^{*(1)} \tag{1}$$

$$A^{*(1)} \xrightarrow{k_2} A_0 + h\nu' \tag{2}$$

$$A^{*(1)} \xrightarrow{k_3} A_0 \tag{3}$$

$$A^{*(1)} + C \xrightarrow{k_4} A_0 + C \tag{4}$$

$$A^{*(1)} \xrightarrow{k_5} A^{*(3)} \tag{5}$$

$$A^{*(1)} + H \xrightarrow{k_6} A^{*(3)} + H \tag{6}$$

$$A^{*(3)} \xrightarrow{k_7} A_0 \tag{7}$$

$$A^{*(3)} + C \xrightarrow{k_8} A_0 + C^{*(3)} \tag{8}$$

$$A^{*(3)} + C \xrightarrow{k_9} A_0 + C \tag{9}$$

$$C^{*(3)} \xrightarrow{k_{10}} C \tag{10}$$

$$C^{*(3)} \xrightarrow{k_{11}} T \tag{11}$$

$$F^0/F' = \tau_f^{\,0}/\tau_f' = 1 + k_4\tau_f^{\,0}[C] \tag{12}$$

$$F'/F = \tau_f'/\tau_f = 1 + k_6\tau_f'[H] \tag{13}$$

The solutions in which the relative rates of isomerization of C were measured were subjected to identical light doses. Under these conditions the increase in the yield of T because of the enhancement of the triplet yield by addition of H is given by eq 14, where the terms in square brackets are explicitly included to emphasize their cancellation in the present method.

$$Y_{\text{T}}/Y_{\text{T}}' = \frac{(k_5 + k_6[H])\tau_f\left[\dfrac{k_8[C]}{k_7 + k_8[C] + k_9[C]}\,\dfrac{k_{11}}{k_{10} + k_{11}}\right]}{k_5\tau_f'\left[\dfrac{k_8[C]}{k_7 + k_8[C] + k_9[C]}\,\dfrac{k_{11}}{k_{10} + k_{11}}\right]} \tag{14}$$

Equations 12–14 can be combined to give eq 15. Values of $\Phi_{\text{isc}}$ for benzene and 11 of its methyl derivatives in cyclohexane solution at room temperature have been measured by the method described above. Concentrations of the methylbenzenes ranged from 0.008 to 0.02 *M*. The data obtained thus represent monomer triplet yields, since excimer interactions are unimportant at these concentrations.[24] Figures 1 and 2 show plots of $(F^0/F')(F'/F - 1)$ vs. $(Y_{\text{T}}F'/Y_{\text{T}}'F) - 1$. The slopes give values of $\Phi_{\text{isc}}$ and are listed in Table I along with values reported in the literature for the same compounds.

$$\left(\frac{F^0}{F'}\right)\left(\frac{F'}{F} - 1\right) = \Phi_{\text{isc}}\left(\frac{Y_{\text{T}}}{Y_{\text{T}}'}\frac{F'}{F} - 1\right) \tag{15}$$

An important advantage of the present method over previous methods employing sensitized isomerization[3,4] is that neither the efficiency of energy transfer nor the triplet counter decay ratio need be known. In addition, only relative measurements with the same sensitizer are required and actinometry is unnecessary if all samples are irradiated under identical conditions. Unlike the Wilkinson method,[5] this method is not limited by the lifetime or spectral characteristics of the aromatic triplet state as long as this state can be intercepted by a triplet counter.

We were unable to detect isomerization of *cis*-2-pentene in experiments with hexamethylbenzene as sensitizer ($\Phi_{c\to t} \ll 0.005$). Since the triplet energy of hexamethylbenzene is slightly lower than that of pentamethylbenzene at 77°K (78.4[25] vs. 79.5[26] kcal/mol), this failure might be attributable to a change in energetics. A very short hexamethylbenzene triplet lifetime at room temperature, a very low intersystem crossing yield, and/or the presence of efficient energy wasting steps would also account for the failure to sensitize the isomerization of *cis*-2-pentene.

## Discussion

As was noted in the introduction and as can be seen from the data in Table I, there are few literature values of $\Phi_{\text{isc}}$ with which to compare the results of this study. Our value of $\Phi_{\text{isc}}$ for benzene agrees well with those reported by Sandros[6] and by Cundall[27] and others.[17,28] However, our value of 0.51 for toluene is somewhat larger than values determined by the Cundall technique, 0.42[17] and 0.48.[21] Similarly our value of 0.64 for *p*-xylene is higher than the value of 0.57 obtained from the sensitized isomerization of *trans*-2-octene.[17] Finally our value of 0.58 for *o*-xylene is substantially higher than the value of 0.34 reported by Cundall.[29] In this regard, the good agreement of our values for toluene and *p*-xylene with those reported by Sandros (0.53 and 0.63, respectively)[6] is significant since it demonstrates a similar discrepancy between values of $\Phi_{\text{isc}}$ measured in solution by biacetyl and olefin sensitization techniques.[30]

Our method is characterized by two important assumptions which, if incorrect, may lead to errors in measured values of $\Phi_{\text{isc}}$. The first of these is that singlet quenching by *cis*-2-pentene does not result (either directly or indirectly) in isomerization of the olefin. The precise nature of the singlet quenching by *cis*-2-pentene is uncertain. Cundall[4] reports that "pure olefins, free from dienes and oxidation

**Table I.** Intersystem Crossing Yields for the Methylbenzenes in Degassed Cyclohexane Solution at Room Temperature

| | | | | $\Phi_{isc}$(lit.) | |
|---|---|---|---|---|---|
| Compd (A) | $[A_0], M \times 10^2$ | $F^0/F'^a$ | $\Phi_{isc}$ (this work) | Sandros method[6] | Cundall method |
| Benzene | 1.08 | 1.10 | 0.25 ± 0.02 | 0.25 | 0.25,[28] 0.23,[27] 0.24 [27,b] |
| Toluene | 1.09 | 1.08 | 0.51 ± 0.03 | 0.53 | 0.42,[17,b] 0.48 [21,b] |
| *o*-Xylene | 1.25 | 1.03 | 0.58 ± 0.03 | | 0.34[29,b] |
| *m*-Xylene | 1.47 | 1.00 | 0.58 ± 0.03 | | |
| *p*-Xylene | 1.11 | 1.04 | 0.64 ± 0.03 | 0.63 | 0.57[17,b] |
| 1,2,3-Trimethylbenzene | 1.52 | 1.00 | 0.31 ± 0.02 | | |
| 1,2,4-Trimethylbenzene | 0.84 | 1.00 | 0.55 ± 0.03 | | |
| Mesitylene | 2.27 | 1.00 | 0.55 ± 0.03 | | |
| 1,2,4,5-Tetramethylbenzene | 1.24 | 1.00 | 0.60 ± 0.03 | | |
| 1,2,3,5-Tetramethylbenzene | 2.02 | 1.00 | 0.44 ± 0.02 | | |
| 1,2,3,4-Tetramethylbenzene | 1.69 | 1.00 | 0.35 ± 0.02 | | |
| Pentamethylbenzene | 0.87 | 1.00 | 0.17 ± 0.01 | | |

[a] Initial *cis*-2-pentene concentration 0.05 *M*. [b] In methylcyclohexane solution.

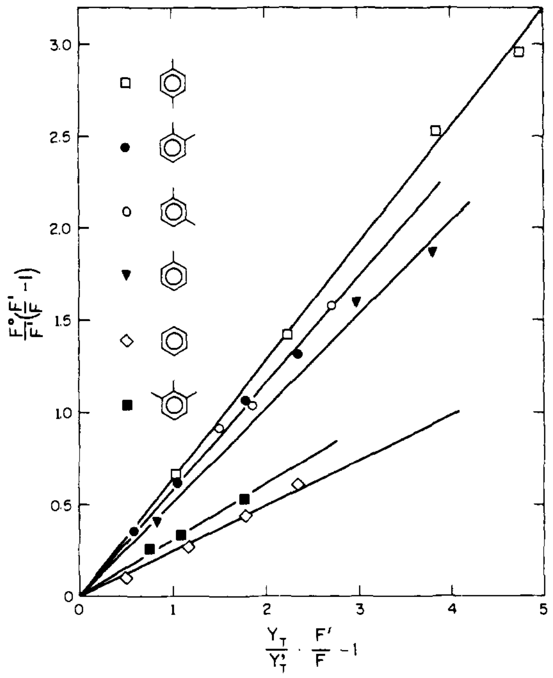

**Figure 1.** Plots of eq 15 for *p*-xylene (□), *o*-xylene (●), *m*-xylene (○), toluene (▼), benzene (◇), and 1,2,3-trimethylbenzene (■).

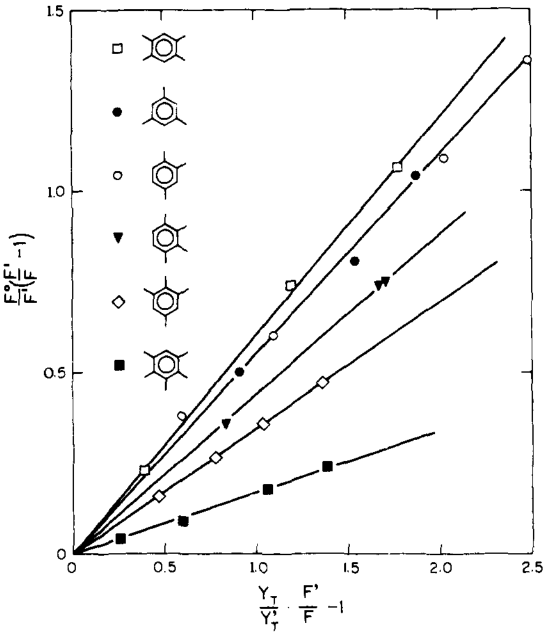

**Figure 2.** Plots of eq 15 for durene (□), mesitylene (●), 1,2,4-trimethylbenzene (○), 1,2,3,4-tetramethylbenzene (▼), 1,2,3,5-tetramethylbenzene (◇), and pentamethylbenzene (■).

products", quench the fluorescence of benzene and toluene with rate constants of the order of $10^5$ $M^{-1}$ sec$^{-1}$. Morrison,[22] however, obtained a rate of $1.5 \times 10^7$ $M^{-1}$ sec$^{-1}$ for the quenching of toluene fluorescence by *trans*-2-heptene. Hentz and Thibault[17] report a value of $5.4 \times 10^7$ $M^{-1}$ sec$^{-1}$ for the quenching of benzene fluorescence by *trans*-2-octene. We have also observed quenching rate constants of similar magnitude. Values of $k_q$ for quenching of benzene and toluene fluorescence by *cis*-2-pentene in degassed isooctane solution are $4 \times 10^7$ and $3 \times 10^7$ $M^{-1}$ sec$^{-1}$, respectively.[31] Somewhat larger values of $k_q$ for degassed cyclohexane solution may be calculated from the data in Table I. The absence of significant amounts of diene impurities (<0.01% by GLC) and the efficiency of the process (an impurity with $k_q = 10^{10}$ $M^{-1}$ sec$^{-1}$ would have to be present to the extent of 0.6 mol % in order to quench benzene fluorescence at the observed rate) argue for a process involving pentene rather than impurities. Actually, it is of little consequence whether impurities are involved as long as the impurity quenching does not ultimately lead to olefin isomerization.

As shown in Table I, only benzene, toluene, *o*-xylene, and *p*-xylene exhibit measurable singlet quenching by *cis*-2-pentene at the olefin concentration used in this study. Since the terms $F^0/F'$ are not large, singlet quenching would have to result in efficient isomerization of the olefin in order to significantly affect the validity of the $\Phi_{isc}$ values for these compounds. The strongest support for our assumption that isomerization does *not* accompany quenching comes from the study of the photochemistry of 6-phenyl-2-hexene by Morrison.[15] Although this compound exhibits efficient intramolecular quenching of the aromatic singlet, isomerization of the olefinic unit upon direct irradiation at 254 nm is very inefficient. Since intramolecular cyclization is quite efficient in this system, Morrison and others have associated bimolecular singlet quenching with processes other than olefin isomerization, e.g., adduct formation.[15,32-34] It is important to note that Hentz and Thibault have employed assumptions similar to ours in correcting for the effects of singlet quenching by olefins in their application of the Cundall method. Thus the difference between their values of $\Phi_{isc}$ and ours must be due to other factors.

The second important assumption is that quenching by xenon is limited to enhancing singlet-to-triplet intersystem crossing in the aromatic (eq 6). Other possible processes involving quenching by xenon which could affect the accuracy of our results are shown in eq 16–19. These processes were

$$A^{*(3)} + H \xrightarrow{k_{16}} A_0 + H \tag{16}$$

$$C^{*(3)} + H \xrightarrow{k_{17}} C + H \tag{17}$$

$$C^{*(3)} + H \xrightarrow{k_{18}} T + H \tag{18}$$

$$A^{*(1)} + H \xrightarrow{k_{19}} A_0 + H \tag{19}$$

not included in the derivation of eq 15 for several reasons. Even if energy transfer does not occur on every collision, interception by "triplet counters" must provide a fast trapping process for $A^{*(3)}$ (eq 8 and 9). In the presence of reasonably high concentrations of C, quenching of aromatic triplets by xenon (eq 16) is unlikely to be competitive since the available data indicate that the triplet decay rates of aromatics are relatively unaffected by xenon in solution.[5] Although the lifetimes of simple olefin triplets are not known with any certainty, they must be quite short in fluid solution and quenching of pentene triplets by xenon (eq 17 and 18) should be unimportant. Since the processes in eq 16 and 17 predict upward curvature and that in eq 18 downward curvature with increasing xenon concentration in plots of eq 15, the absence of significant curvature in such plots (Figures 1 and 2) provides experimental evidence against their importance. The process represented by eq 19 is the most difficult to rule out experimentally. Inclusion of eq 19 in the kinetic derivation gives eq 20, from which it is apparent that

$$\left(\frac{F^0}{F'}\right)\left(\frac{F'}{F} - 1\right) = \left(1 + \frac{k_{19}}{k_6}\right)\Phi_{\mathrm{isc}}\left(\frac{Y_T}{Y_T'}\frac{F'}{F} - 1\right) \tag{20}$$

values of $\Phi_{\mathrm{isc}}$ obtained from the slopes in Figures 1 and 2 are potentially too large by the factor $(1 + k_{19}/k_6)$. We expect that this quenching pathway might become important when the heavy atom is incorporated into a chemically reactive molecule. However, Wilkinson and coworkers have presented compelling evidence for the unimportance of $k_{19}$ relative to $k_6$ with xenon[5] and bromobenzene[35] as heavy atom fluorescence quenchers for a large number of aromatic hydrocarbons.

Since the assumptions upon which our method is based seem reasonable, we suggest that the lower values of $\Phi_{\mathrm{isc}}$ obtained using the Cundall technique (vide supra) may result from invalid kinetic assumptions. There is evidence to indicate that phenyl triplets may not transfer excitation to simple olefins at a diffusion controlled rate, perhaps as a result of the similarity of their triplet energies.[17] In Table II we list triplet lifetimes for benzene, toluene, and *p*-xylene determined by Sandros in dilute cyclohexane solution from biacetyl quenching data[6] and for benzene in dilute methylcyclohexane solution calculated by Hentz and Thibault.[17] The values for $k_8\tau_T$ are also taken from the data of Hentz and Thibault. As can be seen, calculated values of $k_8$ for transfer to *trans*-2-octene are in the range of $10^8$–$10^9$ $M^{-1}$ sec$^{-1}$ and, even allowing for substantial error in $\tau_T$, are well below the diffusion controlled limit of ca. $9 \times 10^9$ $M^{-1}$ sec$^{-1}$ for methylcyclohexane. Rates for transfer from benzene to the 2-butenes are similar to those for *trans*-2-octene and are lower than those for transfer to low-energy acceptors such as 3,5-cycloheptadienone and *trans*-stilbene.[17] If, then, triplet energy transfer to olefins occurs at rates below that of diffusion, it is not unreasonable to expect that otherwise inefficient processes which do not lead to excitation of the olefin (eq 9) may be able to compete with energy transfer.[20] We suggest that this may indeed be the explanation for the observed discrepancy in $\Phi_{\mathrm{isc}}$ values since, unlike the Cundall technique, our method is not affected by the efficiency of the transfer step. The Sandros technique should also avoid this complication since triplet energy transfer to biacetyl is highly exothermic and inefficient processes not leading to biacetyl excitation should be unable to compete with energy transfer. Although the good agreement of $\Phi_{\mathrm{isc}}$ values (Table I) suggests that such processes may be relatively unimportant for benzene, the lower values for toluene, *p*-xylene, and *o*-xylene determined by the Cundall technique imply that processes represented by eq 9 may be quite important with substituted benzenes and that the basic assumptions of the Cundall technique may not be generally valid in solution for these compounds. It is also quite possible that the degree of inefficiency of the transfer may depend on the olefin employed as the triplet counter, since this would explain the scatter in values of $\Phi_{\mathrm{isc}}$ and $\Phi_{c\to t}$ for toluene obtained with different olefins. An extreme example of this may be *o*-xylene; we have obtained a value of 0.51 for the sum of initial quantum yields for sensitized isomerization of the 2-pentenes ($\Phi_{c\to t} + \Phi_{t\to c}$),[36] significantly larger than the sum of 0.34 for the isomerization of the 2-butenes reported by Cundall.[19] A thorough comparison of $\Phi_{\mathrm{isc}}$ values for the methylbenzenes in solution employing both the Sandros and the Cundall techniques or perhaps direct spectroscopic measurements of overall olefin quenching rates ($k_8 + k_9$) would be quite helpful in resolving these questions.

Table II. Quenching of Triplets of Benzene Derivatives by Simple Olefins in Solution at Room Temperature

| Compd | $\tau_T$,[a] μsec | $k_8\tau_T$,[c] $M^{-1}$ | $k_8$, $M^{-1}$ sec$^{-1}$ × $10^{-9}$ |
|---|---|---|---|
| Benzene | 2, 1.0[b] | 1600 | 0.8–1.6 |
| Toluene | 3.3 | 2460 | 0.74 |
| *p*-Xylene | 5 | 620 | 0.12 |

[a] Determined by Sandros from biacetyl quenching data in cyclohexane assuming $k_q$(biacetyl) = $5 \times 10^9$ $M^{-1}$ sec$^{-1}$ except as noted.[6] [b] Calculated by Hentz and Thibault for infinite dilution in methylcyclohexane solution.[17] [c] Data of Hentz and Thibault for 0.05 $M$ sensitizer in methylcyclohexane solution.[17]

## Extensions of the Method

In this paper we have presented a general method for the determination of intersystem crossing quantum yields which combines features of several previously reported methods. Unlike other procedures, it may be simply and accurately applied to the study of benzene and its derivatives.

The method may be extended in a variety of ways. For example, the determination of relative fluorescence intensities might be replaced by determination of relative yields of a singlet photoproduct. In fact, any process which is characteristic of the singlet state may be used as the "singlet counter", and any process which is characteristic of the triplet state may serve as the "triplet counter". One important limitation of the method is that it is applicable only to systems which are susceptible to heavy-atom enhancement of intersystem crossing. In general, this restricts the method to aromatic hydrocarbons and their derivatives. For these systems, however, the method is limited only by the availability of an appropriate triplet counter. Although other heavy-atom additives may be used, the chemical inertness of xenon makes it the heavy atom of choice. If care is taken to measure the relative fluorescence and isomerization yields at the same temperature, the method may be used to investigate the temperature dependence of $\Phi_{\mathrm{isc}}$. In addition, it should also be possible to apply the principles discussed here to the study of photochemical and photophysical processes in the gas phase. Care must be taken, however, to ensure that the experimental fluorescence quenching and triplet yield ratios represent the desired quantities (rather than reflecting effects due to impurities or pressure dependent processes).[38]

This study underscores the potential importance of heavy-atom enhancement of intersystem crossing as a photochemical tool. Interesting possibilities include the use of intersystem crossing enhancement to elucidate the mechanisms of photochemical reactions in bichromophoric systems and other systems in which the multiplicity of the reacting state is not clearly defined. Several studies of the latter type have been conducted.[39-43]

Because the method does not require completely efficient energy transfer to the triplet counter, it is especially suited for the study of short-lived triplet states. For example, the method might be applied to a quantification of the role of upper triplet states in the photochemistry and photophysics of compounds in which these states exhibit finite lifetimes and can be selectively intercepted by triplet counters.

An additional application of the method is suggested by eq 20. If the intersystem crossing yield of the aromatic is measured using xenon or is otherwise independently known, H may be replaced by a general singlet quencher and the fraction of singlet quenching events which produce aromatic triplet states $[k_6/(k_6 + k_{19})]$ determined using eq 20. We are currently investigating these and other applications of the general method.

## Experimental Section

**Materials.** Cyclohexane (Matheson Coleman and Bell (MCB), Spectroquality) was purified by the method of Murray and Keller,[44] followed by careful distillation through an 80-cm spinning-band column to remove saturated impurities which interfered with the analysis of the pentenes. *n*-Pentane (Phillips, 99%) was purified by the method of Murray and Keller,[44] followed by distillation from lithium aluminum hydride. *cis*-2-Pentene (Phillips, 99.9%) and *trans*-2-pentene (Chemical Samples Co. (CS), 99.9%) were distilled from lithium aluminum hydride and stored at <0° until use. No diene (e.g., 1,3-pentadiene) impurities (<0.01%) could be detected by gas chromatography (GLC). Xenon (Airco analyzed reagent grade) was used as received; the lot analysis supplied indicated 12 ppm krypton as the only impurity detectable by mass spectrometry. Benzene (MCB, Spectroquality) was purified by the photochlorination technique[45] and distilled from sodium prior to use. Mesitylene (Aldrich Gold Label, 99+%) was distilled from sodium. The other methylbenzenes were used as received: compound (supplier, stated purity); toluene (Harleco, Fluorimetric Grade); *o*-xylene (James Hinton (JH), 99.85%); *m*-xylene (JH, 99.7%); *p*-xylene (CS, 99.6%); 1,2,3-trimethylbenzene (CS, 99.5%); 1,2,4-trimethylbenzene (CS, 99.6%); 1,2,4,5-tetramethylbenzene (Aldrich, zone refined, 99.9%); 1,2,3,5-tetramethylbenzene (CS, 99.5%); 1,2,3,4-tetramethylbenzene (CS, 99%); pentamethylbenzene (Aldrich, 99%); hexamethylbenzene (Aldrich, 99+%).

**Apparatus.** Absorption spectra were determined with a Cary Model 14 spectrophotometer. Relative fluorescence intensities were determined with a Hitachi Perkin-Elmer MPF-3 fluorescence spectrophotometer. GLC analyses were performed with a Hewlett-Packard Model 700 gas chromatograph (flame-ionization detector); peak integrals were measured by means of a Hewlett-Packard Model 3307B electronic integrator.

**Procedure for Determination of $\Phi_{isc}$.[46]** A cyclohexane stock solution of the aromatic sensitizer with an optical density of about 11 $cm^{-1}$ at 254 nm[47] was prepared (solution I). The value of $\epsilon_{254}$ was either taken from the data of Berlman[48] or determined experimentally. A 2.00-ml aliquot of solution I was diluted to 10.0 ml with cyclohexane (solution II). A 5.00-ml aliquot of solution I, 5.0 $\mu$l of *n*-pentane (internal standard), and 5.0 $\mu$l of *cis*-2-pentene were diluted to 25.0 ml with cyclohexane (solution III). A set of matched 13-mm quartz tubes (tubes A–H) with graded glass seals, Pyrex constrictions, grease seals, and ground glass joints was used for each determination. Aliquots (4.0 ml) of solution II were added by syringe to tubes A and B; aliquots (4.0 ml) of solution III were similarly added to tubes C–H. The remaining portion of solution III served as the blank for the GLC analysis. The tubes were degassed on a mercury-free vacuum line by two freeze–pump–thaw cycles at $2 \times 10^{-4}$ Torr and two cycles with an oil diffusion pump at $<5 \times 10^{-6}$ Torr. The xenon flask was connected to the vacuum line via a short glass tube of known volume (2.5 ml) between two stopcocks. After the fourth pumping cycle, the tubes and the xenon flask were isolated from the remainder of the vacuum line. By alternately opening and closing stopcocks to the xenon bulb, any number of 2.5-ml aliquots of xenon could be distilled into a selected tube. In this manner, increasing amounts of xenon were added to tubes E–H. All eight tubes were then sealed without being reopened to the vacuum line.

All measurements were carried out at room temperature (24 ± 1°). The solutions were allowed to equilibrate for several hours in the dark, and relative fluorescence spectra (254-nm excitation) were recorded. $F^0$, $F'$, and $F$ were obtained from peak intensities for tubes A–B, C–D, and E–H, respectively. Tubes C–H were then irradiated simultaneously at 254 nm in a merry-go-round apparatus.[49] Light intensities were monitored by potassium ferrioxalate actinometry; the quantum yield for ferrous ion production at 254 nm was taken to be 1.25.[50] Conversions of *cis*-2-pentene to *trans*-2-pentene were low (<5%) in all cases. *trans*-2-Pentene analyses were performed by GLC on a tandem column consisting of 7 in. × ⅛ in. of 10% UCW-98, 22 ft × ⅛ in. of 25% $\beta,\beta'$-oxydipropionitrile ($\beta\beta'$), and 15 ft × ⅛ in. of 25% $\beta\beta'$ plus 5% $AgNO_3$, all on Chromosorb W, operated at room temperature. Peak areas of *trans*-2-pentene relative to *n*-pentane gave $Y_T'$ (tubes C–D) and $Y_T$ (tubes E–H). Data were treated graphically according to eq 15 to obtain $\Phi_{isc}$. Several measurements of each parameter were averaged and the average values were treated graphically according to eq 15 to obtain $\Phi_{isc}$. The standard deviation of the slopes of lines plotted in this fashion indicated a precision of 2–4%. Considering the preaveraging of the data, the actual experimental uncertainty in $\Phi_{isc}$ values is estimated to be 5–8%, as indicated in Table I.

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## References and Notes

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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 ($\Phi_f$) 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 ($\Phi_d$) were calculated from eq 1.

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

The singlet lifetimes ($\tau_f^0$) 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 $\tau_f^0$ were used to calculate rate constants according to eq 2. The use of this equation implicitly assumes that complete vibrational relaxation occurs

$$k_x = \Phi_x/\tau_f^0 \tag{2}$$

prior to decay of $S_1$ under our excitation conditions ($\lambda$ >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-