# Excimer Effects on the Triplet State of *o*-Xylene

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THE formation of excimers by the first excited singlet state of simple aromatic molecules has been established by fluorescence measurements.[1-3] Triplet excimers appear to have been observed directly by the low-temperature phosphorescence of halogenated benzene crystals and glasses.[4] We present evidence that triplet excimers may be largely responsible for the unusually short lifetimes of some aromatic triplet molecules.

Some of the earlier attempts to detect triplet benzene and toluene in the liquid phase have used the sensitized phosphorescence of biacetyl. Lipsky[5] observed triplet–triplet transfer in $10^{-2}$M benzene solutions in cyclohexane, but Dubois and Wilkinson[6] failed to find transfer from benzene under virtually identical conditions in hexane. van Loben Sels and Dubois[7] have detected triplet–triplet transfer only at high concentrations of benzene; with toluene they found no direct sensitization of biacetyl phosphorescence. The participation of both singlet and triplet excimers was considered. Lisovskaya, Zakharova, and Kaplan[8] have found that in dilute solution transfer from triplet benzene and toluene is observed only if the biacetyl concentration is sufficiently low to prevent substantial quenching of the aromatic singlet. Evidence for the triplet state of liquid benzene has been obtained by the sensitization effect on *cis–trans* isomerization reactions.[9,10] There is some disagreement over the lifetime of the triplet inferred from them but the results from the sensitized isomerization of but-2-ene indicate that the lifetime is very short, *ca.* $10^{-8}$ sec.[10]

We have studied the effect of *o*-xylene concentration on the quantum yield of *trans*-isomer, $\phi_{t\text{-but}}$, by the sensitized isomerization of *cis*-but-2-ene in methyl cyclohexane solutions and undiluted *o*-xylene irradiated at 2537 Å and 60°. The but-2-ene method is advantageous for two main reasons; (i) it does not absorb light itself at 2537 Å, and (ii) it can only be excited by energy transfer from the aromatic triplet.

If the quenching rate constant of the triplet aromatic by but-2-ene is taken as $4 \times 10^9$ M$^{-1}$ sec.$^{-1}$,[1,11] from plots of $[\phi_{t\text{-but}}]^{-1}$ *vs.* [*cis*-but-2-ene]$^{-1}$ we can estimate lifetimes for the *o*-xylene triplet under different conditions (Table). The considerable decrease in estimated lifetimes, which are probably only reliable within 10%, with increasing *o*-xylene concentration is consistent with rapid deactivation of the triplet by an excimer route. Full kinetic treatment requires more data, but it seems that intersystem crossing from the triplet excimer is extremely fast. The rate constant for this process must be greater than $0{\cdot}8 \times 10^8$ sec.$^{-1}$. The rate constant for self quenching of the *o*-xylene triplet is *ca.* 1—2 $\times 10^7$ M$^{-1}$ sec.$^{-1}$. It is not yet possible to give a precise value for the lifetime of the monomeric triplet but a value of greater than $10^{-6}$ sec. is consistent with the results. Low concentrations of impurities such as olefins or hydrocarbon oxidation products in the the solvent may be acting as triplet quenchers, owing to the high energy of the *o*-xylene triplet (3·5 ev). The possibility of some form of chemical interaction[12] between the solvent and the *o*-xylene which leads to deactivation cannot be ignored.

| *o*-Xylene concentration (M) | Estimated triplet life (nsec.) |
|---|---|
| 8·0 | 13 |
| 3·0 | 17 |
| 0·48 | 130 |
| 0·01 | *ca.* 900* |

* The decrease in $\phi_{trans}$ occurred below $10^{-3}$ M *cis*-but-2-ene; practical difficulties limited the data which could be obtained

If it is assumed that the *cis* and *trans* isomers of but-2-ene are produced with equal probability from the triplet but-2-ene, then the *o*-xylene triplet yield $\phi_T$, is *ca.* 0·28 at all concentrations. Since an increase in the *o*-xylene concentration and a rise in the temperature both reduce the fluorescence yield, $\phi_F$, of 0·15 in dilute solution at 20°,[3] this can be taken as the maximum value possible in the range studied. The sum $\phi_F + \phi_T$ is clearly less than unity and some form of internal conversion process of the excited singlet state must occur. This is not accounted for by irreversible isomerizations or reactions of *o*-xylene since these yields are small[13] in comparison with the quantum yield deficit (*ca*0·5) under consideration.

The short lifetime of the triplet excimer may be due to a spin-relaxation process which can be represented

$$\begin{tikzcd}[column sep=small] {}^3A + A \arrow[r, phantom, "\rightleftharpoons"] & {}^3(A_2) \arrow[r, leftrightarrow] & {}^3(A^+A^-) \arrow[r, leftrightarrow] & {[{}^2A^+; {}^2A^-]} \arrow[d, "\text{``double'' doublet}"] \\ & \text{excimer} & & A + A \end{tikzcd}$$

The spin-forbidden character of the triplet–ground transition is reduced by the charge-transfer character of the excimer. This gives the complex some double doublet character; a state from which singlet formation is not forbidden.

(*Received, November* 29*th*, 1968; *Com.* 1632.)

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