Temperature Dependence of the Primary Processes in the Photolysis of Diphenylacetylene in Solution

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SEVERAL workers[1,2] have studied the temperature dependence of the quantum yield of fluorescence of systems in which the corresponding $S_1 \rightarrow S_0$ (first excited singlet to ground state) radiationless transition is thought to be insignificant. Lim[3] has shown that the temperature dependence of the quantum yield of fluorescence of 9- and 9,10-substituted anthracenes observed by Bowen is due to the large activation energy for the $S_1 \rightarrow T$ (lowest excited singlet to triplet) intersystem crossing. The triplet state concerned is thought to be the second which is higher in energy than S_1. We have investigated the temperature dependence of the quantum yield of fluorescence of diphenylacetylene in hexane both in the presence and absence of dissolved oxygen, a system in which the $S_1 \rightarrow S_0$ radiationless transition is significant.

Solutions of diphenylacetylene in hexane were contained in quartz fluorimeter cells with an attached quartz-Pyrex graded seal. Solutions were used open to the atmosphere or deoxygenated by repeated freeze–thaw cycles on a conventional high-vacuum pumping system. Fluorescence was measured on an Aminco 4–8202B spectrophotofluorometer, and the temperature was controlled by an Aminco 4–81485P thermo-electric cooler.

In a previous communication[4] we showed that when a solution of diphenylacetylene in hexane was photolysed in the absence of oxygen the intersystem crossing process $S_1 \rightarrow T$ was insignificant and that the only reactions taking place were:—

$$D + h\nu \rightarrow {}^1D$$

$$^1D \rightarrow D + h\nu^1 \qquad (1)$$

$$^1D \rightarrow D \qquad (2)$$

Since the fluorescence quantum yield in the absence of oxygen (ϕ_{F^0}) was of the order of 3×10^{-3} at room temperature, reaction (2), the radiationless internal conversion was the major mode of deactivation of ^1D. The first-order rate constants for reactions (1) and (2) are related to ϕ_{F^0} by the expression:—

$$(1/\phi_{F^0} - 1) = k_2/k_1 \qquad (3)$$

If k_2 is the only temperature-dependent process then expression (3) may be written

$$(1/\phi_{F^0} - 1) = A_2 \exp\,(-E_2/\boldsymbol{R}T)/k_1 \qquad (4)$$

where A_2 and E_2 are the pre-exponential factor and activation energy for process (2). E_2 and A_2/k_1 were calculated from the graph A of the Figure and k_1 from the absorption spectrum of diphenylacetylene. The results may be expressed:—

$$k_1 = 5{\cdot}01 \times 10^8 \text{ sec.}^{-1};\ k_2 = 10^{13{\cdot}4} \exp\,(-3{,}177/\boldsymbol{R}T)$$

When solutions were open to the atmosphere, the quantum yield of fluorescence in the presence of oxygen (ϕ_F) was reduced to around $2{\cdot}8 \times 10^{-3}$. We have shown[4] that the effect of oxygen is to bring about intersystem crossing by a process of the type:—

$$^1D + {}^3O_2 \rightarrow {}^3D + {}^1O_2 \qquad (5)$$

The quantum yield of triplet formation[4] is $3{\cdot}3 \times 10^{-2}$, thus reaction (5) proceeds largely at the expense of reaction (2).

The inclusion of reaction (5) leads to an expression:—

$$(1/\phi_F - 1) = (k_2 + k_5[O_2])/k_1 \qquad (6)$$

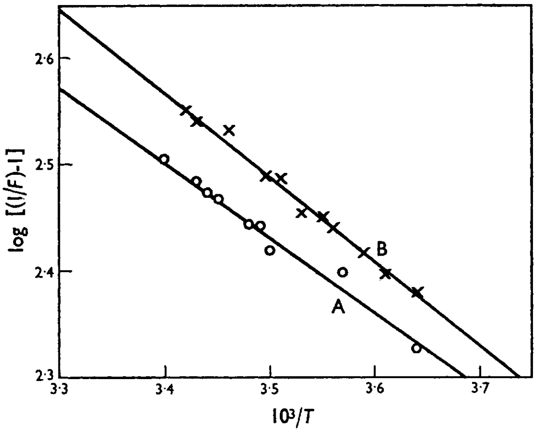
Combining equations (3) and (6) leads to

$$\{[(1/\phi_F - 1)/(1\phi_{F^0} - 1)] - 1\} = (A_5/A_2)[O_2] \exp\,\{-(E_5 - E_2)/\boldsymbol{R}T\}$$

and a graph of

$\log\,\{[(1/\phi_F - 1)/(1/\phi_{F^0} - 1)] - 1\}$ against $1/T$ gave a value for $E_5 - E_2$ of 0·73 kcal. mole^{-1} from which E_1 equals 3·91 kcal. mole^{-1}.

Since the slopes of the lines in the Figure were so critical, they were calculated by a least-squares analysis using a computer.



FIGURE

Graph of log [(1/quantum yield of fluorescence) −1] *against* 10^3/T *for diphenylacetylene in hexane. Curve* A *in absence of oxygen; Curve* B *in presence of oxygen;* [*diphenylacetylene*] = 2×10^{-5} M

Lim[3] has obtained a value of 2·4 kcal. for the intersystem crossing in the 9-methylanthracene system in which the triplet state concerned is thought to be of higher energy than the singlet state. Our value of E_5 does not seem an unreasonable one, therefore, for the activation energy for the formation of the ($^3D \cdots {}^1O_2$) complex which we suggested[4] as an intermediate in the photo-oxidation of diphenylacetylene. The results do not suggest which of the two possible singlet states of oxygen ($^1\Sigma_g^+$ or $^1\Delta_g$) are involved since the participation of either would make reaction (5) exothermic assuming no vibrational excitation.

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