Solvent Effect on Photochemical Interaction of Excited Anthracene with Carbon Tetrachloride

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The solvent effect on the fluorescence quenching of anthracene by carbon tetrachloride and photoreaction ensuing from the same system has been investigated. Both quenching and photoreaction proceed via the intermediacy of a weak reversible exciplex formed between excited singlet anthracene and ground state carbon tetrachloride. Quenching is maximum in polar solvents. Among the solvents of comparable polarity quenching seems to be controlled by the viscosity of the medium. A kinetic study of the photoreaction reveals that the photoreaction is controlled by the polarity of the medium, the reaction rate increasing with polarity. The photoreaction is quenched efficiently by free radical quenchers like 2, 6-di-t-butyl-4-hydroxytoluene suggesting a free radical pathway. A mechanistic scheme has been proposed to delineate the steps involved in the course of the photoreaction.

The discovery of exciplex formation by Weller has tempted many authors to invoke exciplex intermediacy in explaining the mechanisms of several photoreactions. The photoreaction of anthracene and carbon tetrachloride is one such reaction in which exciplex can be the intermediate. The reaction was studied by Bowen and Rohatgi. The product identified was 9-chloro-10-trichloromethyl-9, 10-dihydroanthracene. The reaction occurred through the formation of radicals CCl₄ and I as shown in Scheme 1.

\[ \text{H} \quad \text{Cl} \quad \text{I} \]

\[ \text{H} \quad \text{Cl} \quad \text{I} \]

\[ \text{I}^* + \text{CCl}_4 \rightarrow \text{I}^*(\text{ACl}_4)^* \quad 0.6 \]

\[ \text{I}^*(\text{ACl}_4)^* \rightarrow \text{I}^*(\text{ACl}_4) \rightarrow \text{I}^* + \text{CCl}_4 \]

\[ \text{I}^*(\text{ACl}_4)^* \rightarrow \text{ACl} + \text{CCl}_4 \rightarrow \text{Products} \]

Scheme 1

Recently Ware and Lewis studied the fluorescence quenching of anthracene by carbon tetrachloride in cyclohexane as a function of excitation wavelength. The fact that exciting wavelength has a bearing on the magnitude of quenching was attributed to charge transfer complex formation in the ground state. However during the present study we found no evidence for complexation in the ground state. Very recently it has been reported that excitation of anthracene in the presence of chlorohydrocarbons leads to aperiodic and periodic oscillations in emission intensity of the excitation wavelength is around 270 nm. However, no such oscillations could be noted if the irradiation was carried out with 365 nm light.

These observations coupled with the fact that a rapid photoreaction also occurs, besides fluorescence quenching necessitated the present investigation.

Materials and Methods

Anthracene was purified by co-distillation with ethylene glycol. Carbon tetrachloride and the solvents were purified according to standard methods recommended in the literature. The instrument used and the methods were as described earlier. Irradiations were done at 365 nm with 3.5 ml of solutions in 1 cm cell at 30°C. Light intensity measurements were done by the method of Hatchard and Parker.

Results and Discussion

Fluorescence quenching — Carbon tetrachloride efficiently quenches the fluorescence of anthracene and the quenching follows the linear Stern-Volmer relation \[ F_0/F = 1 + k_q \tau \] where \( F_0 \) and \( F \) refer to fluorescence intensities of anthracene in absence and presence of carbon tetrachloride, \( k_q \) is the bimolecular quenching rate constant and \( \tau \) is the lifetime of the excited singlet anthracene. The plots of \( F_0/F \) versus \([\text{CCl}_4]\) were linear in all the solvents employed. The slope of the plots gave values of \( k_q \). Taking \( \tau \) from the literature \( k_q \) was evaluated (Table I).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( k_q \times 10^9 \text{ M}^{-1} \text{sec}^{-1} )</th>
<th>( k_d \times 10^9 )</th>
<th>Viscosity (cp)</th>
<th>Dielectric constant</th>
<th>Z value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>1.28</td>
<td>5.8</td>
<td>0.21</td>
<td>0.31</td>
<td>1.88</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.95</td>
<td>4.9</td>
<td>0.19</td>
<td>0.90</td>
<td>2.02</td>
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<tr>
<td>Benzene</td>
<td>1.50</td>
<td>4.8</td>
<td>1.40</td>
<td>0.65</td>
<td>2.00</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>25.34</td>
<td>4.2</td>
<td>6.03</td>
<td>0.35</td>
<td>37.50</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>8.5</td>
<td>6.0</td>
<td>1.40</td>
<td>2.86</td>
<td>19.92</td>
</tr>
<tr>
<td>Methanol</td>
<td>21.0</td>
<td>5.7</td>
<td>3.70</td>
<td>0.55</td>
<td>32.70</td>
</tr>
</tbody>
</table>
TABLE 2 — $k_q/k_{diff}$ RATIOS IN VARIOUS SOLVENTS

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$k_q \times 10^{-2}$</th>
<th>$k_{diff} \times 10^{-3}$</th>
<th>$k_q/k_{diff} \times 10^8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.40</td>
<td>16.0</td>
<td>8.90</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.19</td>
<td>11.0</td>
<td>1.73</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>1.40</td>
<td>4.5</td>
<td>31.60</td>
</tr>
<tr>
<td>Methanol</td>
<td>3.70</td>
<td>18.0</td>
<td>20.54</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>6.23</td>
<td>29.0</td>
<td>20.79</td>
</tr>
</tbody>
</table>

The low value of $k_q$ in comparison with $k_{diff}$ is indicative of reversibility associated with exciplex formation. The low efficiency of exciplex formation may be another contributing factor for the low $k_q/k_{diff}$ ratios (Table 2). In the present system, the hydrocarbon plays the role of an electron donor; anthracene due to its neutral character cannot act as a strong donor like amine and consequently exciplex formation is reversible as in the case of pyrene-amine system.

In the case of nonpolar solvents $k_q/k_{diff}$ is a very small quantity indicating extreme reversibility. In the case of polar solvents $k_q/k_{diff}$ although is not equal to one, has a fairly large value. The reason for this is attributed to the following facts. (i) A polar solvent stabilises the exciplex and its ion-pair structure and causes backward process ineffective. (ii) Further it may promote the dissociation of the exciplex into solvated ions. In effect $k_q/k_{diff}$ is made as close to unity as possible in the case of polar solvents. Therefore in the case of weak complexes polarity must outweigh to some extent the viscosity effect at least in the case of polar solvents.

Photoreaction of anthracene with carbon tetrachloride — The fluorescence intensity as well as the absorbance of anthracene decreased with time of irradiation in the presence of $CCl_4$, on irradiation with 365 nm source. The absorption spectral pattern remained the same without any isobestic point. When the irradiation was discontinued till the complete disappearance of anthracene, there was no increase in absorbance and the absorption characteristic of anthracene structure was lost. These facts collectively imply that the product does not have anthracenic structure. This is in accordance with the earlier observation of Bowen and Rohatgi who identified the product as 9-chloro-10-trichloromethyl-9,10-dihydroanthracene.

The kinetics of the photoreaction was followed spectrophotometrically by measuring the optical density on irradiation for different time periods. The decrease in optical density was plotted against the time of irradiation (Fig. 1). From the initial slope of the plot the initial rate and hence the quantum yield of the reaction was calculated. It was found that the initial quantum yield increased with increase in concentration of carbon tetrachloride (Table 3) but was independent of anthracene concentration and light intensity. Further the plots of $1/q$ versus $1/[CCl_4]$ were linear in all the solvents (Fig. 2).

The kinetics was investigated in solvents of varying degree of polarity and viscosity. The variation of reaction rate with solvent is depicted in Fig. 3. The initial quantum yields of the photoreactions in
different solvents under identical conditions are given in Table 4.

The initial quantum yield was higher in polar solvents and lower in nonpolar solvents (Table 4). The trend was very similar to fluorescence quenching. Among solvents of equal polarity the reaction rate decreased as the viscosity of the medium increased. However, neither the viscosity taken individually could account for the observed trend. Among the nonpolar solvents the rate was higher in aromatic solvents and solvents which could enter into weak complex formation with carbon tetrachloride than in aliphatic inert solvents like hexane and cyclohexane. This may be due to the fact that these solvents enter into weak complexation through $n-p$ interaction. This weak complex may attack the excited hydrocarbons much more efficiently than free $\text{CCl}_4$ to form the exciplex which gives rise to the product. The higher rate in polar solvents may be ascribed to the fact that the efficiency of the exciplex formation increases with polarity of the medium due to change transfer nature of the exciplex. Further the transfer is facilitated in polar solvents leading to charge separation and subsequent radical formation as the essential act for adduct formation. The fact that the reaction proceeds through the radicals is supported by the following facts.

(i) The quantum yield of the photoreaction is reduced by the addition of radical quenchers like benzophenone. Even a low concentration of the quencher ($\sim 10^{-3} M$) is sufficient to quench the reaction much efficiently as seen from Table 5.

(ii) If the reaction is carried out in the presence of a saturated potassium iodide solution, the spectrum characteristic of anthracene structure is lost and a broad band at 355 nm, the intensity of which increases with time of irradiation appears. The spectral pattern is identical with that of $I_2$. No such band could be observed in the absence of either anthracene or $\text{CCl}_4$ or KI. The formation of $I_2$ can be explained as follows.

Based on the above discussions, Scheme 2 has been proposed to explain the observed kinetic data.
In Scheme 2 \( \alpha \) is the fraction of ion-pair yielding the adduct. If the exciplex is assumed to have considerable charge transfer character so that the adduct is formed directly from the exciplex, then

\[
{^1A^* + CCl_4 \xrightarrow{\alpha} \text{Exciplex} \xrightarrow{\text{adduct}}}
\]

where

\[
K_a = \frac{K_4 (K_5 + K_6)}{(K_{-4} + K_5 + K_6)}
\]

According to Scheme 2.

\[
\frac{1}{q} = \frac{(K_1 + K_2 + K_3)(K_{-4} + K_5 + K_6)}{(K_5 + K_6) K_a [CCl_4]} + \frac{1}{\alpha}
\]

The plot of \( 1/q \) versus \( 1/[CCl_4] \) should be linear. This is found to be so in all the solvents thus justifying the mechanistic Scheme 2.

In Scheme 2 \( k_a \) is supposed to be a constant consisting of \( K_4, K_5, K_6, \) and \( K_4 \). Assuming \( K_4 \) to be purely controlled by viscosity, \( K_5, K_6 \) and \( K_4 \) are quantities dependent upon viscosity as well as polarity. It is true that \( K_4 \) will be much influenced by polarity rather than viscosity. \( K_4 \) is the rate constant of radiationless relaxation and it is not possible to make any specific guess regarding its solvent sensitivity. A quantitative discussion of solvent effect can thus be meaningfully made only if the actual values of \( K_4, K_5, K_6 \) and \( K_{-4} \) are available. In the absence of any such data the conclusions given here are valid only for solvents with extreme properties with respect to viscosity and dielectric constant and in solvent media having intermediate characteristics cannot be satisfactorily explained. Further since the exciplex is nonemissive it is not possible to obtain direct results on the nature of the exciplex. However, the criteria used in this discussion are capable of explaining the behaviour in most solvents of extreme nature and as such can bear the deductive burdens implied in the discussion in this paper. The same observation holds good with respect to reactivity also.

It is seen from Scheme 2 that \( 1:1 \)--adduct results straight away from the exciplex. It may be necessary to speculate the manner in which the formation occurs. The exciplex possesses ion pair structure (\( A^+ \ldots CCl_4^- \)). Removal of \( \text{Cl}^- \) to \( A^+ \) will lead to the production of a neutral radical pair \( ACl_4 ... CCl_4^- \). The first chlorine attacks 9-position of anthracene and subsequently CCl_4 radical attacks 10-position. Oxidation of \( I^- \) suggests that \( I^- \) can interact with exciplex attacking \( A^+ \) thereby \( I^- \) is oxidised to iodine. There is yet another way by which the adduct formation can occur. The radical pair may dissociate and the dissociated radicals can recombine to give the adduct.

The substituent effect on the kinetics of the above photoreaction also suggests that the exciplex in the present system is weak and the hydrocarbon acts as an electron donor in the formation of exciplex.

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References