

Short Communication

Photoreduction of anthracene by diethylhydroxylamine

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(Received May 2, 1986; in revised form June 16, 1986)

Excited aromatic hydrocarbons can be photoreduced by amines to give the corresponding dihydro derivatives [1]. This process, which can produce free radicals [1, 2], is generally considered to take place through the formation of charge transfer intermediates [1] whose participation is in general indirectly deduced from the dependence of the quenching rate constant on the solvent polarity, and the ionization potential and electron affinities of donors and quenchers. Hydroxylamines are a special class of amines since they can participate both in the formation of charge transfer complexes and in free-radical-type hydrogen transfer processes, because of the lability of the hydroxylic hydrogen [3]. In order to evaluate the mechanism of quenching of excited aromatic compounds by hydroxylamines, we have carried out a study of the interaction between several excited anthracene derivatives and diethylhydroxylamine (DEHA). The results obtained indicate that under conditions which do not favour charge transfer structures DEHA can still react efficiently with excited aromatic compounds via pathways involving a hydrogen-atom transfer process.

1. Experimental details

Quenching experiments were carried out by measuring the decrease in fluorescence yields as a function of the added amines, using a Perkin-Elmer LS-5 spectrofluorometer. Anthracene consumption was monitored by following the decrease in absorbance. No change was observed in the shape of the anthracene absorption band. Actinometry was performed by photobleaching anthracene in the presence of excess carbon tetrachloride [4]. 9,10-Dihydroanthracene production was followed by estimating it with a Sigma-3 gas chromatograph employing a capillary column. Light of wavelength 366 nm from a medium pressure mercury lamp was employed in the experiments. All results were obtained at room temperature (20 ± 2 °C).

The amines employed were Aldrich products of the highest purity available. They were vacuum distilled prior to use.

2. Results and discussion

Fluorescence quenching of several anthracene derivatives by DEHA, triethylamine (TEA) and diethylamine (DEA) was carried out in benzene.

TABLE 1
Quenching rate constants in benzene

<i>Anthracene derivative</i>	<i>Quenching rate constant ($\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)</i>		
	<i>DEHA</i>	<i>DEA</i>	<i>TEA</i>
9-Cyanoanthracene	1.6	3.2	4.2
Anthracene	0.6	1.0	1.8
9-Methylanthracene	0.32	0.22	1.6
9,10-Dimethylanthracene	0.14	0.060	0.064

The data obtained are given in Table 1. These data show that the reactivity of the amine decreases when the electron affinity of the aromatic compound decreases. Nevertheless, the changes are much larger for TEA and DEA than for DEHA. In particular, comparison of the results obtained employing DEA and DEHA shows that with 9-cyanoanthracene DEA reacts twice as fast as DEHA while the opposite is true when 9,10-dimethylanthracene is employed. Similar differences are also observed when DEHA and TEA are compared. These results might indicate that charge transfer structures are more important for the amines than for DEHA. In order to assess this point further, we have measured the rates of quenching of anthracene singlets by DEA and DEHA in several solvents. The results obtained are given in Table 2, together with the π^* , α and β indexes of the solvents employed [5].

These data show that the values of $k_{\text{DEA}}/k_{\text{DEHA}}$ change by a factor of nearly 20 between water-ethanol and diethyl ether. Furthermore, they

TABLE 2
Effect of solvent on quenching of anthracene

<i>Solvent</i>	π^*	α	β	$k_{\text{DEA}}/k_{\text{DEHA}}$
Diethyl ether	0.27	0.0	0.47	8.7
<i>N,N</i> -Dimethylformamide	0.88	0.0	0.69	6.5
Ethyl acetate	0.55	0.0	0.45	6.5
Acetonitrile	0.75	0.19	0.31	4.3
Dimethyl sulphoxide	1.0	0.0	0.76	4.0
Dichloromethane	0.82	0.30	0	3.8
Acetone	0.71	0.06	0.48	3.6
Methylformamide				3.4
Chlorobenzene	0.71	0.0	0.07	2.0
Cyclohexene	0.0	0.0	0.0	1.8
Benzene	0.59	0.0	0.1	1.7
Ethanol	0.54	0.83	0.77	1.1
Isopropanol	0.48	0.76	0.95	1.0
Water-ethanol (1:1)				0.45
Water	1.09	1.17	0.18	

show that large values of $k_{\text{DEA}}/k_{\text{DEHA}}$ seem to be favoured when both π^* and β are large. However, small π^* and large α correspond to low values of $k_{\text{DEA}}/k_{\text{DEHA}}$. Since (i) the π^* scale is an index of solvent dipolarity/polarizability, (ii) the α scale describes the ability of the solvent to donate a proton in a solvent-to-solute hydrogen bond and (iii) the β scale provides a measure of the solvent ability to accept a proton [5], the observed trends are compatible with an increase in importance of structures in DEA arising from electron transfer from the nitrogen lone pair to the aromatics. This is further supported by the fact that quenching of anthracene in water by DEHA takes place with a rate constant of $5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, a value similar to those obtained in benzene ($6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and acetonitrile ($6.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). Furthermore, the fact that quenching of anthracene by DEHA is slower in diethyl ether ($2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) than in benzene ($6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), in spite of the larger π^* value of the former solvent, emphasizes the role that the availability of the hydroxylic hydrogen plays in the quenching by DEHA. Evidence for the dependence of the rate of quenching by DEHA on the hydroxylic hydrogen is also given by the fact that ethylation of DEHA gives a compound (triethylhydroxylamine) that is practically unable to quench anthracene in benzene ($k < 0.16 \times 10^8$).

Efficient photobleaching of anthracene by DEHA is observed in all the solvents considered. If the photobleaching efficiency γ is defined as the number of anthracene molecules consumed per quenching event, its value can be obtained from the equation

$$\gamma = \frac{\phi_{\text{bleaching}}}{\phi_{\text{quenching}}} \quad (1)$$

where

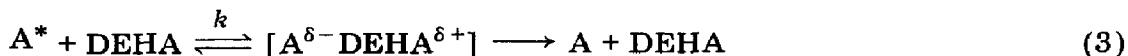
$$\phi_{\text{quenching}} = \frac{K_{sv}Q}{1 + K_{sv}Q} \quad (2)$$

K_{sv} is the Stern-Volmer slope obtained from measurements of fluorescence quenching.

By applying these equations to the photobleaching of anthracene by DEHA, the following values of γ were obtained: 0.15 ± 0.02 in methanol (DEHA from 1.7×10^{-2} to $13.6 \times 10^{-2} \text{ M}$), 0.28 ± 0.04 in acetonitrile (DEHA from 1.7×10^{-2} to $13.6 \times 10^{-2} \text{ M}$) and 0.90 ± 0.10 in benzene (DEHA from 0.17×10^{-2} to $13.6 \times 10^{-2} \text{ M}$). The fact that the γ obtained are independent of DEHA concentration over a wide concentration range shows conclusively that photobleaching of anthracene in the presence of DEHA is an excited singlet process.

Photobleaching of anthracene produces 9,10-dihydroanthracene. Nearly 0.5 molecules of this compound are formed by each molecule of anthracene consumed, regardless of the DEHA concentration.

All the above-mentioned results can be interpreted by the following reaction scheme.



Reaction (4) is the rate-limiting step; only a moderate charge separation is required in the $A^{\delta-}\text{DEHA}^{\delta+}$ intermediate for this step to occur. In this mechanism, processes (5), (6) and (7) can represent "cage" processes or could involve uncaged free radicals. The fact that in the presence of oxygen the production of dihydroanthracene is considerably reduced without significant changes in the anthracene photobleaching yield favours this last possibility.

The observed increase in photobleaching yield obtained when the polarity of the solvent decreases is similar to that found for other photo-processes mediated by charge transfer complexes [6] and is generally explained in terms of competition between the proton transfer (process (4) in our system) and ion pair stabilization followed by back electron transfer to produce the parent reactants in their ground state. With the present system, it is interesting to note that in benzene the anthracene photobleaching yield is near unity; showing that process (4), mediated by a charge transfer complex or representing a free-radical-type process directly involving transfer of a hydrogen atom, dominates the interaction between the excited anthracene and DEHA.

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