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THE AMINE ASSISTED PHOTO-DEHALOGENATION OF HALO-AROMATIC HYDROCARBONS

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Summary: The rate constants for quenching the triplet states of 4-chlorobiphenyl, 1-chloronaphthalene and 1-methylnaphthalene have been determined by use of the technique of laser flash photolysis. Evidence in favour of the quenching occurring by a charge transfer process, is presented.

The irradiation of many halo-aromatic compounds in hydrogen donating solvents leads to homolysis of the aryl-halogen bond [1]. The aryl radicals so formed, subsequently abstract hydrogen from the solvent to give the related aromatic hydrocarbon.

$$\mathrm{Ar{-}Hal} \xrightarrow{h\nu} \mathrm{\dot{A}r} + \mathrm{\dot{H}al} \xrightarrow[\text{solvent}]{\text{H-donating}} \mathrm{ArH} + \mathrm{H{-}Hal}$$

The rate of dechlorination of many chloroaromatics is enhanced by the use of polar solvents containing a tertiary amine, e.g. acetonitrile containing triethylamine [2,3]. A suggested mechanism for this process involves the excited chloroaromatic acting as an electron acceptor.

$$\begin{tikzcd}
 & \mathrm{ArCl^{*}} + \mathrm{Et_3N} \arrow[r] & {[(\mathrm{ArCl})^{\overline{\cdot}}(\mathrm{Et_3N})^{+\cdot}]^{*}} \arrow[d] \\
\mathrm{ArH} + \mathrm{HCl} + \mathrm{CH_2{=}CHNEt_2} & & \mathrm{Ar^{\cdot}} + \mathrm{Cl^{-}} + \mathrm{Et_3N^{+\cdot}} \arrow[ll]
\end{tikzcd}$$

Arguments presented in support of the occurrence of a charge transfer process include (a) the enhancement in the rate of dechlorination caused by increasing the solvent polarity [3,4] and (b) the finding that tertiary amines quench the fluorescence of many chloroaromatics and in some cases exciplex fluorescence can be observed [3,5]. Although, as yet, no one has any direct evidence for the intermediacy of radical ions, their formation appears to have been validated by the finding that the use of solvent mixtures containing deuterium oxide leads to the incorporation of deuterium into the products [4]. Until recently it had been tacitly assumed that the excited singlet state of the chloroaromatics is the only reactive state. However, it has now been claimed [6,7] that the reactions can involve both the excited singlet and triplet state on the basis of the Stern-Volmer constant for fluorescence quenching, being less than the value for the slope of the line obtained by plotting the reciprocal of the quantum yield for reaction versus the reciprocal of the amine concentration. Thus the case for quenching the triplet state of chloroaromatics by amines has only been established by indirect means.

We now report the rate constants for quenching triplet 4-chlorobiphenyl and 1-chloronaphthalene by several amines and these are shown in the Table, together with those for quenching triplet 1-methylnaphthalene. The rate constants were obtained by utilising the technique of nanosecond laser flash photolysis [8]. Measurements were made of the lifetimes of the various hydrocarbons in the presence of known amounts of amine. Rate constants were evaluated using the equation :

$$\frac{1}{\tau} = \frac{1}{\tau_o} + k_q^T\,[\text{Amine}]$$

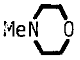
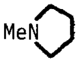
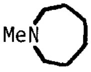
where τ = triplet lifetime in the presence of amine at a concentration [Amine].

τ_o = triplet lifetime in the absence of amine.

and k_q^T = bimolecular rate constant for triplet quenching.

TABLE

Rate Constants for Quenching Triplet Aromatic Hydrocarbons by Amines in Acetonitrile Solution (k_q^T) and Stern-Volmer Constants for Quenching the Fluorescence of Chloroaromatics by Amines in Acetonitrile solution (K_{sv})$^{(a)}$

	4-Chlorobiphenyl		1-Methyl-naphthalene	1-Chloronaphthalene	
	k_q^T (M^{-1} s^{-1})	K_{sv} (M^{-1})	k_q^T (M^{-1} s^{-1})	k_q^T (M^{-1} s^{-1})	K_{sv} (M^{-1})
	1.4 ± 0.20 x 10^7	9.46 ± 0.48	2.18 ± 0.20 x 10^7	2.75 ± 2.0 x 10^6	15.65 ± 0.47
	2.62 ± 0.10 x 10^7	15.54 ± 0.82	9.4 ± 0.40 x 10^7	2.48 ± 0.55 x 10^7	24.68 ± 0.41
Et_3N	5.45 ± 0.55 x 10^7	24.30 ± 1.16	1.08 ± 0.14 x 10^8	6.15 ± 0.75 x 10^7	35.47 ± 0.77
	9.13 ± 0.80 x 10^7	17.66 ± 0.82	8.6 ± 0.70 x 10^7	7.23 ± 0.65 x 10^7	30.37 ± 0.16
	9.84 ± 0.90 x 10^7	29.87 ± 0.91	1.59 ± 1.20 x 10^8	1.74 ± 0.90 x 10^8	46.0 ± 1.34

(a) K_{sv} for quenching of singlet 1-methylnaphthalene not determined.

For the cyclic amines, the order of reactivity for the three hydrocarbons is N-methylazacycloheptane > N-methylazacyclopentane > N-methylazacyclohexane > N-methyl-4-oxa-azacyclohexane. The reactivity of triethylamine appears to be similar to that of N-methylazacyclopentane. The question arises as to the mechanism of quenching and whether this order of reactivity gives any clue as to the nature of the mechanism. Quenching via energy transfer seems unlikely since the triplet energies of the hydrocarbons should lie below those of the amines. It was found that the quenching of the triplet states by the amines is much greater in acetonitrile than in cyclohexane. This solvent effect suggests the occurrence of a charge transfer process. However, all attempts to verify the production of radical ions using laser flash photolysis failed. Further evidence in support of the charge transfer quenching mechanism comes from the finding that the order of reactivity of the cyclic amines towards excited singlet states of the chloroaromatics is the same as that towards the triplet states. The Stern-Volmer constants for quenching the fluorescence are shown in the Table. The only anomaly is triethylamine which, for fluorescence quenching, is more reactive than N-methylazacyclopentane. This may reflect a difference in the conformation for the complex which gives rise to fluorescence quenching to that which causes triplet quenching. Since it is well established that the quenching of excited singlet states of aromatic hydrocarbons by amines occurs via a charge transfer process [9], it seems from the similarity in order of reactivity for fluorescence and triplet quenching, that triplet quenching also occurs via a charge transfer process. Unfortunately a comprehensive range of ionisation and oxidation potentials for the amines is not available. However, the ionisation potential for N-methyl-4-oxa-azacyclohexane is considerably higher than that of N-methylazacyclohexane[10] and not surprisingly it is the less efficient quencher. Chlorine dioxide oxidises tertiary amines via a one electron process and it was found that N-t-butylazacyclopentane is more reactive than N-methylazacyclohexane [11]. The Table shows that the N-methylazacyclopentane is a better quencher than the N-methylazacyclohexane.

This work shows that the triplet states of aromatic hydrocarbons are quenched by tertiary amines. In the case of the chloroaromatics this does not provide unequivocal proof that dechlorination occurs from the triplet state. However, from a consideration of the rate constant for quenching triplet 4-chlorobiphenyl it can be calculated that ~50% of the triplets are quenched at an amine concentration of 2×10^{-4} M and ~90% quenched at a 10^{-3} M amine concentration. At this latter concentration very little fluorescence quenching occurs. Since dechlorination occurs at amine concentrations in the range of 10^{-3} to

10^{-4} M it appears reasonable to invoke reaction occurring via the triplet state. To get 50% quenching of the excited singlet states an amine concentration of 4.5 x 10^{-2} M is required. Thus at high amine concentrations some excited singlet state quenching will occur and nearly total triplet quenching. Since the Stern-Volmer plots of the reciprocal of the quantum yield of reaction versus the reciprocal of the amine concentration are linear over a wide range of amine concentrations it must be, in the light of the rate constant data presented in this paper, that the reactions occur via the excited singlet and triplet states [7].

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