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Mechanistic Aspects of the Triethylamine Assisted Photo-induced Dehalogenation of Halogeno-aromatic Compounds

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Summary. Criteria for the intervention of radical ions in the photoreactions of aromatic halides with triethylamine is given and where appropriate evidence for the intermediary of such species is presented.

It has been shown that the photo-induced dechlorination of 1-chloronaphthalene,[1] chlorinated biphenyls[2,3] chlorinated terphenyls[4] and bromoquinolines[5] is accelerated by the addition of triethylamine. It has been suggested that the acceleration is due to the amine reacting with the excited singlet state of the halocarbon to give a radical anion which breaks down to give an aryl radical and a chlorine anion.

$$Et_3N + ArCl_{S_1} \rightarrow Et_3\overset{+\cdot}{N} + (ArCl)^{\overset{-}{\cdot}}$$

$$(ArCl)^{\overset{-}{\cdot}} \rightarrow Ar\cdot + Cl^-$$

$$Cl^- + Et_3\overset{+\cdot}{N} \rightarrow HCl + Et_2N\dot{C}HMe$$

$$Ar\cdot + Et_3N \rightarrow ArH + Et_2N\dot{C}HMe$$

We now present evidence which defines conditions under which this electron transfer mechanism operates.

When methanol solutions of 4-bromoanisole, 1,4-dibromobenzene and 4-bromobenzonitrile containing triethylamine (0.02M) were photolysed, dehalogenation to give the appropriate aromatic hydrocarbon occurred but the presence of amine did not acclerate the reaction. Acceleration was observed for 1-chloronaphthalene, 1-bromonaphthalene. Since the reactivity of triethylamine may be reduced by hydrogen bonding to methanol, a comparison was made of the accelerating effect of added triethylamine in three solvents of widely differing solvating character. To favour the bimolecular reaction with the amine, the concentration of the amine was raised to 2.8×10^{-2}M. The results are shown in Table 1 and these demonstrate that the accelerating effect of added triethylamine is far more pronounced in acetonitrile than in methanol or cyclohexane.[6] This result is what one would expect if the amine reacts with the hydrocarbon via an electron transfer process.[7] From Table 1, one can also see that the accelerating effect of the amine is more marked for chloro-compounds than it is for bromo compounds. Two reasons can be found to account for this observation. Dehalogenation of bromo compounds is less energy demanding than that of chloro-compounds. For the bromo-compounds in Table 1 the reaction is probably exogonic. Thus homolysis of the carbon-bromine bond will compete effectively with the reaction with triethylamine i.e. $k_1\,[ArBr^*] > k_2\,[ArBr^*]\,[Et_3N]$

$$ArBr \xrightarrow[k_1]{h\nu} Ar\cdot + Br\cdot$$

$$ArBr + Et_3N \xrightarrow[k_2]{h\nu} (ArBr)^{\overset{-}{\cdot}} + (Et_3N)^{+\cdot}$$

Since the homolytic cleavage of chloro-compounds is energetically less favourable[8], the rate constant k_3

$$\mathrm{ArCl} \xrightarrow[k_3]{h\nu} \mathrm{Ar}^{\bullet} + \mathrm{Cl}^{\bullet}$$

should be less than k_1 and therefore make reaction with triethylamine more competitive. A second factor is that, because of the heavy atom effect the lifetimes of the excited states of bromo-aromatics are shorter than those of the corresponding chloro-compounds. Consequently, bromo-compounds are less likely to undergo bimolecular reactions than their corresponding chloro-compounds.

TABLE 1

Substrate	Product	Comparative Rate of product formation Acetonitrile	Methanol	Cyclohexane
1-Chloronaphthalene	Naphthalene	34.5	4.1	1.0
1-Bromonaphthalene	Naphthalene	12.4	4.3	1.0
4-Chlorobiphenyl	Biphenyl	32.0	11.5	1.0
4-Bromobiphenyl	Biphenyl	6.9	4.6	1.0
4-Chloroanisole	Anisole	3.0	1.0	1.0
4-Bromoanisole	Anisole	1.9	1.4	1.0
4-Chlorobenzonitrile	Benzonitrile	11.7	2.8	1.0

The results in Table 1 also show that on going from benzenoid to naphthalene and biphenyl compounds the accelerating effect of triethylamine becomes more marked. This may be due to the lower reduction potential of the naphthyl and biphenyl compounds compared with the benzenoid compounds which will favour the electron transfer process.[9] Furthermore the dehalogenation of the naphthyl and biphenyl compounds will be less exogonic than the benzenoid compounds and therefore the bimolecular reaction with the amine will have more chance to compete with the homolysis reaction.

Previous work on chlorinated biphenyls has shown that added triethylamine only markedly enhances the rate of dechlorination of unreactive compounds.[2] From the results shown in Table 1 we can say that in general the accelerating effect of triethylamine increases as the unassisted reaction becomes less exogonic and also if polar aprotic solvents are utilised. The latter observation is in accord with triethylamine undergoing an electron transfer reaction with the halogeno aromatics in such solvents.

Another way of ascertaining whether radical ions are intermediates in the amine assisted dehalogenation reactions is to carry out the reactions using an acetonitrile-deuterium oxide solvent mixture. If the radical anions are sufficiently long lived

(i.e. $k_4\ [\mathrm{ArHal}^{\cdot -}] < k_5\ [\mathrm{D_2O}]\ [\mathrm{ArHal}^{\cdot -}]$

$$(\mathrm{ArHal})^{\cdot -} \xrightarrow{k_4} \mathrm{Ar}^{\bullet} + \mathrm{Hal}^{-}$$

$$(\mathrm{ArHal})^{\cdot -} + \mathrm{D_2O} \xrightarrow{k_5} (\mathrm{ArHalD})^{\bullet}$$

$$(\mathrm{ArHalD})^{\bullet} \rightarrow \mathrm{ArD} + \mathrm{Hal}^{\bullet}$$

the deuterium incorporation should be observed.[10]

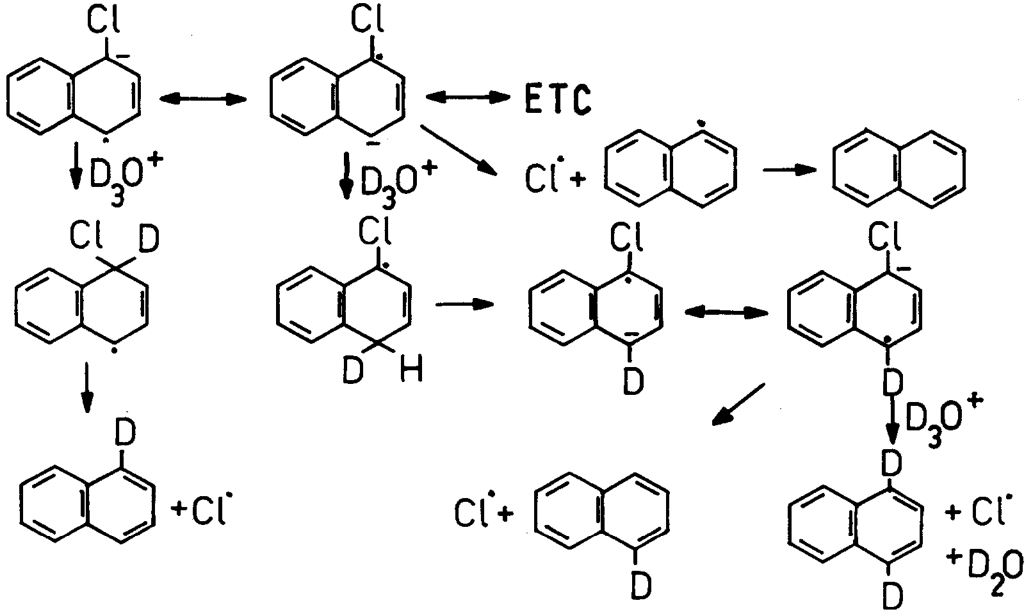
When 4-chloroanisole, 4-bromoanisole, 4-chlorobenzonitrile, 4-bromobenzonitrile and 1,4-dichlorobenzene were photolysed in acetonitrile containing deuterium oxide and triethylamine (MeCN : D_2O, 5 : 1 v/v) no deuterium incorporation was detected in either the unreacted starting material or the dehalogenated product. Irradiation of 1-chloronaphthalene, 1-bromonaphthalene, 9-chloroanthracene, 9-bromoanthracene, 4-chlorobiphenyl, and 4-bromobiphenyl and bromopyrene under similar conditions led to deuterium incorporation and the results are shown in Table 2.

TABLE 2

DEUTERIUM INCORPORATION INTO PRODUCT

COMPOUND	n=0	n=1	n=2	n=3	n=4	n=5
$C_{10}H_{8-n}D_n$						
1-Chloronaphthalene	1.0	0.35	0.085	0.066	0.038	
1-Bromonaphthalene	1.0	1.16	0.605	0.243	0.103	
Naphthalene	1.0	0.29	0.054	0.054	0.015	
$C_{12}H_{10-n}D_n$						
4-Chlorobiphenyl	1.0	0.66	0.346	0.622	0.45	0.088
4-Bromobiphenyl	1.0	0.238	0.039	0.011	0.002	0.002
$C_{14}H_{10-n}D_n$						
9-Chloroanthracene	1.0	0.13				
9-Bromoanthracene	1.0	0.425				
$C_{16}H_{10-n}D_n$						
1-Bromopyrene	1.0	0.356				

Deuterium incorporation may however arise by two processes: (i) as outlined above and (ii) by photo-induced electron transfer reactions of the dehalogenated product with the amine.[11] Irradiation of naphthalene under similar conditions but with the irradiation period doubled led to the production of labelled naphthalene. Although the concentration of naphthalene in this control reaction is higher than that produced in the dehalogenation reactions, there is less deuterium incorporation than in the dehalogenation reactions; this is also true of biphenyl, anthracene and pyrene. Thus one can say the observed deuterium incorporation in the dehalogenation reactions is due, at least in part, to the interception of radical anions by deuterium oxide.



Since no deuterium incorporation into the haloaromatics occurred it appears that the back electron transfer

$$(Et_3N)^{+\bullet} + (ArHal)^{\bar{\bullet}} \rightarrow Et_3N + ArHal$$

does not occur. This probably reflects the ease with which $(ArHal)^{\bar{\bullet}}$ expels Hal^-.

The deuterium incorporation studies show that the halogenated polycyclic aromatics which do not readily photolyse undergo photo-induced electron transfer reactions with triethylamine. It is anticipated that reactive halogenated aromatics e.g. 2,4-dichlorobiphenyl will not show effect to any marked degree. The lack of deuterium incorporation into the halogenated benzenoid compounds is probably a manifestation of the ease with which the radical anions of these species break up to give halide ions[12] and also the electron transfer reaction with triethylamine is less important with these compounds since dehalogenation is exogonic.

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