Electron Transfer on Photolysis of 1-Chloronaphthalene in Alkane Solvents[†]

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Photoreduction of 1-chloronaphthalene to naphthalene is stimulated in the presence of electron donors such as triethylamine and 1,3-cyclohexadiene. These reactions are demonstrated by fluorescence measurements to involve the $^1\pi,\pi^*$ state of chloronaphthalene. In the absence of such compounds, 1-chloronaphthalene itself acts as a donor molecule, and excimers are involved.

Photolysis of 1-chloronaphthalene in solvents liable to hydrogen abstraction affords naphthalene and binaphthyls.[1] The distribution of these products varies widely with the experimental conditions; the observation that the efficiency of photolysis increases greatly in the presence of triethylamine (a known electron donor[2]) suggests a mechanism involving electron transfer to chloronaphthalene (eq 1, X = Et_3N) to be more likely than a simple C–Cl bond fission (eq 2).

$$C_{10}H_7Cl^* + X \rightarrow C_{10}H_7\cdot + Cl^- + X\cdot^+ \quad (1)$$

$$C_{10}H_7Cl^* \rightarrow C_{10}H_7\cdot + Cl\cdot \quad (2)$$

In this paper, we attempt to substantiate the above suggestion.

The mechanism under consideration is shown in full as Scheme I; it involves the radical anion of 1-chloronaphthalene as a central intermediate. Radical anions of haloaromatic compounds are known to expel halide ion and hence lead to reduction products.[3]

Scheme I

$$C_{10}H_7Cl \xrightarrow{h\nu} C_{10}H_7Cl^*$$

$$X + C_{10}H_7Cl^* \rightarrow C_{10}H_7Cl\cdot^- + X\cdot^+$$

$$C_{10}H_7Cl\cdot^- \rightarrow C_{10}H_7\cdot + Cl^-$$

$$C_{10}H_7\cdot + RH \rightarrow C_{10}H_8 + R\cdot$$

Reactions in the Presence of Triethylamine (TEA). In the photolysis of 1-chloronaphthalene, the presence of varying amounts of TEA greatly enhanced both naphthalene production and the quantum yield for decomposition: ϕ ([TEA] = 0) = 0.002; ϕ ([TEA] = 0.01 M) = 0.015. A plot of $[TEA]^{-1}$ vs. ϕ^0/ϕ is linear. The almost exclusive production of naphthalene at the higher TEA concentrations argues strongly against the simple homolysis of eq 2 on the grounds that the ratio of hydrogen abstraction to arylation[4] should be independent of [TEA] if both kinds of product derive from the same naphthyl radical. (However, this argument would be invalid if TEA not only enhanced the production of naphthyl radicals, but also scavenged them efficiently, thus making them unavailable for arylation.)

Correspondingly, the fluorescence of 1-chloronaphthalene (λ_{max} 335 nm)[5] is quenched upon addition of TEA and simultaneously a broad emission characteristic of an exciplex (λ_{max} 435 nm in isooctane) is observed (cf. ref 6). Triethylamine (up to 0.2 M) is without effect on the absorption spectrum of 1-chloronaphthalene in isooctane. It is thus likely that the amine-stimulated photoreduction derives from the singlet state of 1-chloronaphthalene, since it is improbable that TEA would simultaneously act upon excited 1-chloronaphthalene both to quench fluorescence and to enhance the reactivity of a reactive triplet. A similar conclusion has been reached for the TEA-assisted photoreduction of 4-chlorobiphenyl.[7] In addition, we have found that there is a complete parallel between the relative efficiency of an added substance for quenching the fluorescence of 1-chloronaphthalene and the efficacy of the same substance in promoting photoreduction; see Tables III and IV.

The effect of oxygen upon the reactivity of the 1-chloronaphthalene–TEA system is likewise consistent with the intervention of an exciplex. Degassed solutions react about three times as fast as aerated ones; these findings can be explained not in terms of a triplet reactive state, as we proposed previously,[1] but instead in terms of an exciplex intermediate, for Caldwell[8] has shown that oxygen is a quencher for exciplexes, albeit an inefficient one. Dimethyl acetylenedicarboxylate (DMA) quenches exciplexes much more efficiently,[8] and we find that this substance is an efficient quencher of both the photoreaction and the 1-chloronaphthalene–TEA exciplex emission. DMA also quenches the fluorescence of uncomplexed 1-chloronaphthalene at a comparable rate, perhaps demonstrating the establishment of a very rapid equilibrium between the exciplex and its components. When both TEA and DMA are present at high concentrations, the Stern-Volmer plots become curved; absorption spectroscopy indicates ground state complexation between DMA and TEA, causing quenching to be more efficient than would be expected if quenching resulted only from diffusion from the bulk of the solution.

The effect of solvent polarity supports the involvement of the exciplex intermediate. A polar solvent should be more effective at dissociating the radical cation–radical anion pair, thus allowing them to diffuse into the bulk of the solution. This will reduce the probability of back electron transfer, and enhance the likelihood of successful reaction. Both the direct and amine assisted reactions are speeded up when the solvent is an acetonitrile solution of an alkane, rather than a pure alkane. Likewise, no TEA–1-chloronaphthalene exciplex emission is seen in acetonitrile, though quenching of the fluorescence of uncomplexed 1-chloronaphthalene is still observed.

Direct Photolysis of 1-Chloronaphthalene. We have argued that in the TEA-assisted reaction, C–Cl bond cleavage is brought about by electron transfer from the amine to chloronaphthalene, followed by expulsion of chloride ion to leave a naphthyl radical. In the direct photolysis, we have to suggest a method for chlorine removal and to explain the substantial increase in biaryl formation. One mechanistic possibility might be that in the absence of the added electron donor, a second molecule of 1-chloronaphthalene may be able so to act (eq 1, X = $C_{10}H_7Cl$). Biaryls could then result from the attack of $C_{10}H_7Cl\cdot^+$ upon another aromatic species, as occurs in the anodic oxidation of aryl substrates.[9] Such a proposal implies excimer formation. This is known for other

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Table I. Concentration Dependence of Chloronaphthalene Photodegradation[a]

$C_{10}H_7Cl$, M	ϕ_{rel}
3.2×10^{-2}	1.00
3.2×10^{-3}	0.75
3.2×10^{-4}	0.57
3.2×10^{-5}	0.13

[a] In 3-methylpentane, irradiated at 254 nm.

Table II. Effect of Added 4-Chlorobiphenyl on the Efficiency of 1-Chloronaphthalene Photolysis[a]

$C_{12}H_9Cl$, M	ϕ_{rel}
0	1.0
1×10^{-6}	2.8
1×10^{-5}	7.6
1×10^{-4}	2.4
1×10^{-3}	0.8

[a] In 3-methylpentane, 1-chloronaphthalene concentration was 2.9×10^{-3} M.

Table III. Effect of Added Substances on the Photoreactivity of 1-Chloronaphthalene

Added substance	(M)	$C_{10}H_7Cl$, M	Reactivity ratio[a]
TEA	(0.01)	1.0×10^{-3}	7.5[b]
TEA (0.01 M) and DMA	(0.02)	1.2×10^{-3}	1.1[b,c]
Acetonitrile and TEA	(0.01)	1.2×10^{-3}	2.2[d]
Acetonitrile		2.9×10^{-3}	2.5[d]
1,3-Cyclohexadiene	(0.07)	2.0×10^{-3}	23.0[e]
1,4-Cyclohexadiene	(0.59)	2.0×10^{-3}	2.2[e]
Cyclohexene	(1.0)	2.0×10^{-3}	1.2[e]

[a] Ratio of the rate of disappearance of 1-chloronaphthalene with the added substance compared with control reactions. [b] Solvent was isooctane. [c] Comparing solution with both addends with that containing neither. [d] In this experiment, the comparison was between acetonitrile containing 1 M cyclohexane and pure cyclohexane. [e] Solvent was hexane.

Table IV. Effect of Added Substances on the Fluorescence of 1-Chloronaphthalene[a]

Added substance	$k_q\tau$	k_q[b]	Exciplex
TEA	26	3.5×10^9	Yes[c]
DMA	59	7.9×10^9	No
TEA (10^{-2} M) + DMA[d]	52	6.9×10^9	
1,3-Cyclohexadiene	16	2.1×10^9	No
1,4-Cyclohexadiene	0.22	2.9×10^7	No
Cyclohexene	0.05	7×10^6	No
TMD[e]	400[f]	5×10^{10}	No
1,3-Pentadiene	1.3	1.7×10^8	No

[a] Solvent was isooctane. [b] $\tau_0 = 7.5$ ns (ref 14). [c] λ_{max} 435 nm. [d] TEA concentration constant; DMA concentration varied. [e] Tetramethylazetine dioxide. [f] Based on only four data points in the Stern–Volmer plot.

simple naphthalene derivatives,[10] and is supported in the present work by the following evidence.

1. Concentrated solutions of 1-chloronaphthalene exhibit excimer emission at low temperatures. Thus at −59 °C a 0.059 M solution of 1-chloronaphthalene displayed two emission bands of approximately equal intensity, λ_{max} 335 and 410 nm, upon excitation at 290 nm. Correction for the monomer emission spectrum revealed the broad band characteristic of excimer emission over the range 350–500 nm with a maximum at 410 nm.

2. The quantum yield for 1-chloronaphthalene reactivity rises with increasing substrate concentration (Table I).

3. The efficiency of photolysis is also raised in the presence of 4-chlorobiphenyl as a foreign, but nonabsorbing aromatic compound (Table II). At very low concentrations of 4-chlorobiphenyl, almost all the light is absorbed by 1-chloronaphthalene (absorption spectrum), and no photoreduction of 4-chlorobiphenyl is observed. Even so, 4-chlorobiphenyl enhances the reactivity of 1-chloronaphthalene under these conditions, and we postulate that electron transfer to excited 1-chloronaphthalene is occurring (eq 1, X = $C_{12}H_9Cl$). Consistent with this view, 4-chlorobiphenyl quenches the fluorescence of 1-chloronaphthalene, despite its higher singlet energy. At high 4-chlorobiphenyl concentrations, the added substrate absorbs much of the light, and the photoreactivity of 1-chloronaphthalene drops again.

4. The binaphthyl fraction of the photolysis mixture is a complex mixture containing species with zero, one, and two chlorine atoms. This is consistent with arylation involving at least in part the radical cation (rather than the alternative hypothesis that the lack of arylation in the TEA-assisted reaction involves only scavenging by TEA) on the following grounds. Simple radical coupling leads only to unchlorinated binaphthyl, while arylation by a naphthyl radical affords biaryls containing zero or one chlorine, depending upon whether preformed naphthalene or unreacted 1-chloronaphthalene was substituted. Furthermore, in the reactions assisted by 4-chlorobiphenyl, biaryls containing both biphenylyl and naphthyl residues were observed. Although many other reactions besides attack on an arene are presumably open to the radical cation, we have no evidence for them. Electron transfer from some reaction component to restore chloronaphthalene is chemically undetectable, and while the observation of 1-naphthol and 1-methoxynaphthalene in solvents containing water or methanol might be construed as involving capture of a nucleophile by the radical cation, numerous other pathways can be devised to reach these products.

The above observations and the self-quenching of 1-chloronaphthalene fluorescence suggest that, like the amine-assisted reaction, the direct photolysis involves electron transfer to a singlet excited state. It is not known whether the reaction is suppressed completely at very low concentration when bimolecular processes will be improbably slow, or whether another mechanism is possible. We had hoped to test this point using dilute solutions in the presence of tetramethylazetine *N*,*N*-dioxide, which is reported to quench triplet, but not singlet, excited states.[11] Unfortunately, the compound proved to be an efficient quencher of 1-chloronaphthalene fluorescence, so this was not possible.

Reactions in the Presence of Alkenes. We previously reported that 1,3-cyclohexadiene and 1,3-pentadiene enhanced the photoreactivity of 1-chloronaphthalene in methanolic solutions, and suggested that this involved some kind of complexation between the diene and the aryl halide.[1] Repetition of these experiments in alkane solvents produces a much more dramatic increase in reactivity. Like the amine-stimulated reactions, the diene-assisted photolyses lead predominantly to photoreduction, suggesting that aryl radicals are now the main intermediates derived from 1-chloronaphthalene. A reaction corresponding to eq 1, X = diene, is proposed on the basis of the following evidence.

1. The fluorescence of 1-chloronaphthalene is quenched by 1,3-cyclohexadiene at a rate similar to that reported for quenching naphthalene and 1-methylnaphthalene with the

same quencher.[12] However, no exciplex emission could be observed, even at low temperatures (cf. ref 13).

2. From photolyses of 1-chloronaphthalene assisted by 1,3-cyclohexadiene in methanolic solution, small quantities of the methanol adducts of cyclohexadiene are obtained. Such adducts can be rationalized as arising by attack of methanol on the radical cation of cyclohexadiene.

3. 1,4-Cyclohexadiene and cyclohexene are also effective at increasing the reactivity of 1-chloronaphthalene, but much less so than the conjugated diene. The order of effectiveness is 1,3-cyclohexadiene > 1,4-cyclohexadiene > cyclohexene, which is also the order of efficiency of quenching chloronaphthalene fluorescence.

Conclusions

The above observations are consistent with the operation of a mechanism such as that given in Scheme I. The photoreduction product naphthalene arises by expulsion of the chloride ion from the radical anion of 1-chloronaphthalene. Electron donor molecules such as cyclohexadiene or TEA increase the production of these radical anions and hence enhance photoreduction at the expense of arylation, which involves the radical cation of chloronaphthalene. These reactions take place from the singlet state of 1-chloronaphthalene as evidenced by the effect of the added substances in quenching the fluorescence and the parallel between the effectiveness of the compounds in enhancing reactivity and quenching fluorescence.

As mentioned in our previous paper, this study is part of an effort to determine whether photolysis is likely to be important as a mechanism for the natural degradation of halogenated aromatic pollutants. Further studies are planned into the mechanisms of photodegradation of chlorinated naphthalenes and biphenyls in aqueous, as well as organic, media.

Experimental Section

Procedures for photolysis and gas chromatographic analysis were described in detail previously.[1] Photolyses were normally carried out in sealed Pyrex glass ampules using illumination of maximum intensity at 300 nm, following evacuation of the ampules by freeze-pump-thaw cycles. For studying the effect of changing a reaction parameter, a merry-go-round was used to ensure equal illumination of the samples. In some cases noted in the tables, light of 254-nm wavelength was used, and quartz ampules were employed. Photochemical results are given in Tables I-III.

Product Analyses. Quantum yields for disappearance of 1-chloronaphthalene ($\approx 10^{-3}$ M) varied with solvent, but in alkanes were 0.001-0.002 at 300 nm based on ferrioxalate actinometry. Typical distributions of products were naphthalene 50-70% and binaphthyls 30-50% at these initial concentrations, with >95% material balance in the early stages of the reactions. In the presence of high (0.1 M) concentrations of TEA or 1,3-cyclohexadiene, naphthalene became the almost exclusive (90-98%) product.

Fluorescence experiments at room temperature were carried out using a Hitachi Perkin-Elmer Model MPF 2A fluorescence spectrophotometer. Isooctane (BDH spectroscopic grade) was used throughout as solvent. At least six data points covering at least a tenfold range in concentration were obtained for all the quenching studies, which are reported in Table IV. For work at low temperature, a Farrand Optical Co. Mark I spectrofluorometer was used; its low temperature cell holder was designed in our laboratory, and permitted temperature measurement by means of a thermocouple which protruded into the solution.

Photolysis of 1-Chloronaphthalene with 1,3-Cyclohexadiene in Methanolic Solution. A solution containing 1-chloronaphthalene (10^{-2} M) and 1,3-cyclohexadiene (10^{-2} M) in methanol was photolyzed at 300 nm for 20 days. Water was added, and the organic materials extracted into ether. The concentrated extract was analyzed by gas chromatography on columns of 3% SE-30 and 3% OV 225 each on Chromosorb W, and at two temperatures on each column. Small peaks corresponding in retention time to those of 3-methoxycyclohexene and 4-methoxycyclohexene were observed in each case. These amounted to only ~2% of the total product; however, no attempt was made to optimize their yield. The authentic materials were made by the action of methyl iodide upon the sodium salts of the corresponding alcohols, using dimethyl sulfoxide as solvent.

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Registry No.—1-Chloronaphthalene, 90-13-1; TEA, 121-44-8; DMA, 762-42-5; acetonitrile, 75-05-8; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1; cyclohexene, 110-83-8; 1,3-pentadiene, 504-60-9.

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