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Photochemistry of Naphthylmethyl Halides. Direct and Sensitized Paths to Homolytic and Heterolytic Carbon–Halogen Bond Cleavage[1]

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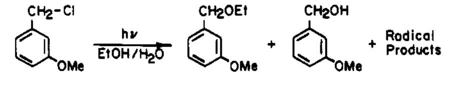
Photolysis of the 1-(halomethyl)naphthalenes (X = Cl, Br, I) in methanol and in cyclohexane solution was investigated. Direct and sensitized irradiation leads to carbon–halogen bond cleavage. In methanol solution direct irradiation leads to products of carbon–halogen bond heterolysis, i.e., (methoxymethyl)naphthalene, as well as products derived from bond homolysis. In cyclohexane only homolysis products are observed. The mechanism of the photoreactions was probed by laser spectroscopy, sensitization, and quenching techniques. The results indicate that bond cleavage occurs from excited singlet states but not from the lowest triplet state. Also, an exciplex between sensitizers and the (halomethyl)naphthalene also undergoes carbon–halogen bond cleavage.

The photochemistry of the heteroatomic benzylic bond has been the subject of investigation and mechanistic speculation for over 20 years. One of the intriguing discoveries is that partitioning between homolytic cleavage to give radicals and heterolytic cleavage to give ions is closely balanced. The balance can be tipped by changing the solvent and leaving group (X, eq 1), and, most surprisingly, by the way that energy is supplied to the bond.

$$\mathrm{ArCH_2{-}X} \xrightarrow[\substack{\text{sensitized}\\ \text{photolysis}}]{\text{direct or}} (\mathrm{ArCH_2{\bullet}} + \mathrm{X{\bullet}}) \text{ and/or } (\mathrm{ArCH_2^+} + \mathrm{X^-}) \qquad (1)$$

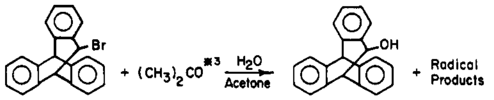
A wide range of benzylic systems have been studied. The first series examined in depth was the benzyl acetates[2] (X = OAc). Since then sulfonium salts[3] (X = $(CH_3)_2S^+$-BF_4^-), ammonium salts[4] (X = $(CH_3)_3N^+Cl^-$), phosphonium salts[5] (X = $(C_6H_5)_3P^+Cl^-$), and a group of homobenzylic systems have also been investigated. However, the most thoroughly studied examples are benzyl halides (X = Cl, Br), and these compounds set the pattern that is followed by the other benzylic systems.[6]

In the gas phase,[7] or in hydrocarbon glasses at 77 K,[8] direct irradiation of benzyl chloride gives the benzyl radical and a chlorine atom. In a study directed primarily toward an investigation of benzyl acetates Zimmerman and Sandel[2] observed that direct irradiation of 3-methoxybenzyl chloride in an ethanol–water solution gives the appropriate alcohol, the ether, and lesser amounts of free-radical products, eq 2. The solvolytic products were taken as evidence for the formation of an intermediate 3-methoxybenzyl cation. However, the nature of the state, and the sequence of reactions leading to the cation was left unspecified by these authors.



(2)

The investigation of 2-bromohomotriptycene by Cristol and Schloemer[9] revealed, through the use of deuterium labeling, the clear participation of cationic intermediates in the acetone-sensitized photochemical hydrolysis, eq 3.



(3)

In a first attempt to rationalize these results these authors suggested that the photosolvolysis originates from a vibrationally excited ground state rather than an electronically excited state.

The first report on the photolysis of benzyl chloride in ethanol claimed that it was solvolytically stable.[4] This was quickly contradicted by Kuz'min and co-workers[10] who observed that direct irradiation of a range of chloromethyl and bromomethyl derivatives of aromatic hydrocarbons, including benzyl chloride, in alcohol–water solution led to the corresponding carbinols in high yield. The lack of quenching of these reactions by dissolved oxygen led these authors to conclude that photosolvolysis proceeds by direct heterolytic bond cleavage from the excited singlet state.

In contrast, Cristol and Greenwald[11] reported that direct irradiation of benzyl chloride in methanol gave no benzyl methyl ether (the expected heterolytic cleavage product) but only products derived from benzyl radicals and chlorine atoms. However, they report that sensitization of benzyl chloride with acetone or acetophenone in methanol resulted in exclusive formation of the anticipated solvolysis product. These results imply that the excited singlet state of benzyl chloride cleaves homolytically and that some state formed from reaction with the triplet sensitizer leads to heterolytic cleavage of the carbon–chlorine bond.

Hyömäki and Koskikallio[12] studied the direct irradiation of benzyl chloride in methanol–water mixtures. They observed formation of both the alcohol and ether products characteristic of heterolytic cleavage and the radical coupling products characteristic of homolytic cleavage of the carbon–chlorine bond. On the basis of the changes in the relative amounts of these products with solvent composition, these authors suggested that the initial photochemical reaction is homolytic cleavage from the excited singlet state followed by a competition between in-cage electron transfer to form ions and hydrogen atom abstraction to give radicals, eq 4. A similar proposal had

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(1) Some of these results have appeared in a preliminary form: Slocum, G. H.; Kaufmann, K.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 3068.

(2) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, *85*, 915.

(3) Maycock, A. L.; Berchtold, G. A. *J. Org. Chem.* **1970**, *35*, 2532.

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(5) Griffin, C. E.; Kaufman, M. O. *Tetrahedran Lett.* **1965**, 773.

(6) Cristol, S. J.; Bindel, T. H. *Org. Photochem.* **1983**, *6*, 327.

(7) Ichimura, T.; Moi, Y. *J. Chem. Phys.* **1972**, *57*, 1677. Boyrakecken, F.; Nicholas, J. E. *J. Chem. Soc. B.* **1970**, 691.

(8) Calvert, J. G.; Pitts, J. N., Jr. "Photochemistry"; Wiley: New York, 1966; p 528.

(9) Cristol, S. J.; Schloemer, G. C. *J. Am. Chem. Soc.* **1972**, *94*, 5916.

(10) Ivanov, V. B.; Ivanov, V. L.; Kuz'min *Zh. Org. Khim.* **1973**, *9*, 340; *J. Org. Chem. USSR* **1973**, *9*, 345.

(11) Cristol, S. J.; Greenwald, B. E. *Tetrahedron Lett.* **1976**, 2105.

(12) Hyömäki, J.; Koskikallio, J. *Acta Chem. Scand. Ser. A* **1977**, *A31*, 321.

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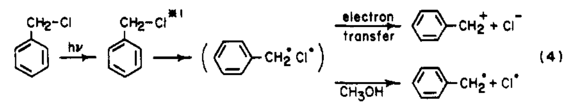
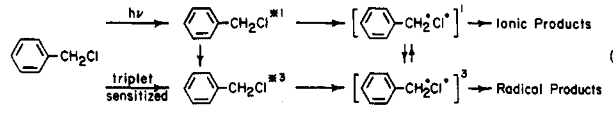


(4)

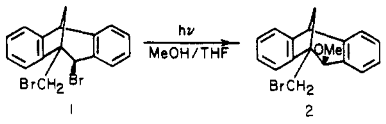
been made earlier by Kropp[13,14] to account for the photochemistry of some aliphatic iodides in methanol solution.

McKenna and co-workers[15] also irradiated benzyl chloride in methanol. In their hands, direct photolysis gave products characteristic of both ionic and free-radical pathways in yields quite similar to those reported independently by Hyömäki and Koskikallio,[12] but in contrast to the complete absence of ionic products reported by Cristol and Greenwald.[11] Acetone-sensitized photolysis also gave both radical and ionic products, but in a different ratio than the direct irradiation. These authors also examined photolysis of the corresponding bromide and iodide and obtained comparable results. These findings, and the similarity noted to their earlier work on the photochemistry of ammonium salts,[16] encouraged McKenna and coworkers to suggest that both the singlet and triplet excited states of benzyl chloride undergo exclusive homolytic cleavage, that the triplet radical pair can intersystem cross to the singlet radical pair, and that the singlet radical pair is either in equilibrium with the ions formed by electron transfer or is one contributor to a resonance hybrid that includes both the ions and the singlet radical pair, eq 5.



(5)

Cristol and his students have pursued the investigation of the photochemistry of the heteroatomic benzylic bond with a variety of compounds including benzyl chloride. Photolysis of dibromide 1, either exo or endo, in a methanol–THF solution gave principally the exo ether 2, eq 6.[17]



1 2 (6)

However, attempts to sensitize this reaction with acetone or acetophenone gave mainly products believed to be characteristic of benzylic carbon–bromine bond homolysis. The authors note that his pattern is precisely the opposite of their results with benzyl chloride in methanol.

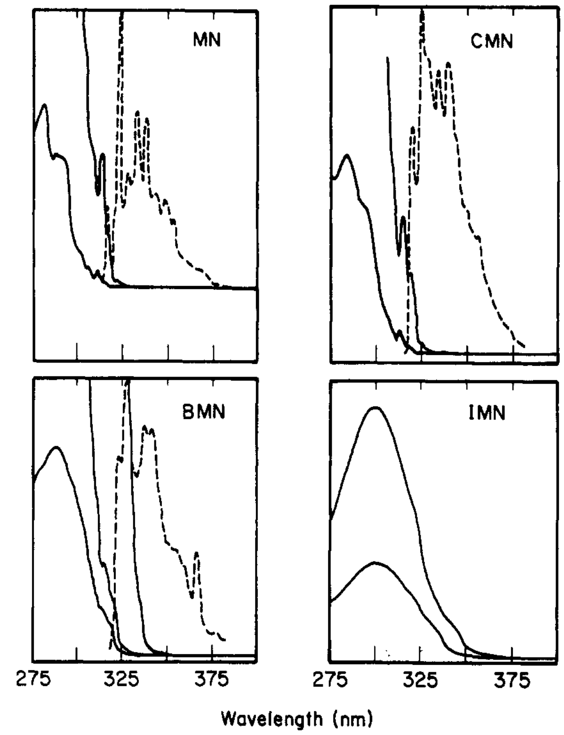
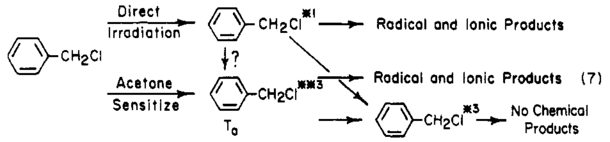


Figure 1. Absorption (solid line) of methylnaphthalene derivatives in cyclohexane solution at room temperature. Fluorescence (broken line) of methylnaphthalene derivatives at 77 K in a methylcyclohexane glass.

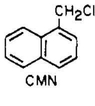
Cristol and Bindel[18] have carried out an intensive investigation of the photochemical transformations of benzyl chloride and some of its derivatives in *tert*-butyl alcohol. They report that the products obtained in both the direct and acetone-sensitized irradiations are the same, but that they are formed in different proportions. Sensitization favors free-radical products. Furthermore, a detailed analysis of the sensitized reaction using a combination of several quenching techniques revealed that the state responsible for formation of ionic products in the sensitized reaction has a much shorter lifetime than the lowest triplet state of benzyl chloride. These authors conclude that an unspecified, short-lived upper triplet state (T_2) is formed in the sensitized reaction, and perhaps from intersystem crossing from the singlet, and that this state is primarily responsible for the formation of ionic intermediates, eq 7.

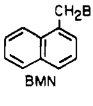


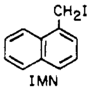
(7)

Finally, in a very recent study of the dynamics of methylnaphthyl radical formation from photolysis of 1-(halomethyl)naphthalene in hexane, Rentzepis and coworkers[19] suggest that homolytic cleavage of the carbon–halogen bond occurs in the singlet manifold exclusively from an upper excited singlet state (S_2).

It is against this backdrop of mechanistic postulates that we began an investigation of the photochemistry of the 1-(halomethyl)naphthalenes. In this study we have employed a combination of spectroscopic, product, sensitization, and quenching experiments to deduce and support yet another mechanistic possibility.


CMN


BMN


IMN

Results

We have investigated the photochemistry of three compounds, 1-(chloromethyl)naphthalene (CMN), 1-(bromomethyl)naphthalene (BMN), and 1-(iodomethyl)naphthalene (IMN). In general, we probed the direct

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[17] Cristol, S. J.; Stull, D. P.; McEntee, T. E., Jr. *J. Org. Chem.* **1978**, *43*, 1756.

[18] Cristol, S. J.; Bindel, T. H. *J. Org. Chem.* **1980**, *45*, 951. Cristol, S. J.; Bindel, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 7287.

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Table I. Spectroscopic and Thermodynamic Data for Some Substituted Naphthalenes

	ϕ_f[a] (rel)	τ,[b] ns	FWHM,[c] nm	Stokes shift,[d] cm^{-1}	E_s, kcal/mol	E_t, kcal/mol
MN	1	67	10	~0	90.2	59.6
CMN	0.015	0.49[e]	10	159	90.0	
BMN	0.0083	(0.50)	11	311	89.3	
IMN		(<0.1)	<18		≥82	
MMN	f		10	150	90.7	60.6

[a] Fluorescence quantum yield relative to 1-methylnaphthalene (0.25) in cyclohexane solution at room temperature. [b] Fluorescence lifetime in cyclohexane solution. Values in parentheses are estimates from the fluorescence yields. [c] Full width of half maximum of the ^1L_B absorption band. [d] The Stokes shift was measured by comparing the absorption spectrum at room temperature to the fluorescence emission at 77 K in hydrocarbon media. Thus these values should be used only for internal comparison. [e] Huppert, D.; Rand, S. D.; Reynolds, A. H.; Rentzepis, P. M. *J. Chem. Phys.* **1982**, *77*, 1214. [f] Not determined.

irradiation and the sensitized photolysis in both methanol and cyclohexane solution using a variety of experimental techniques.

Absorption and Emission Spectroscopy of the (Halomethyl)naphthalenes. The absorption spectra of the (halomethyl)naphthalenes and 1-methylnaphthalene in cyclohexane are displayed in Figure 1. It is clear that substitution of the halogen atom causes an apparent red shift in the lowest energy (^1L_b) band. The magnitude of this shift increases according to the series Cl < Br < I. For CMN and BMN the bandwidth of the absorption is essentially unchanged by the halogen. However, for IMN the absorption band broadens considerably and shows a long asymmetric tail.

The fluorescence spectra of CMN, BMN, and methylnaphthalene (MN) in methylcyclohexane at 77 K are also shown in Figure 1. IMN does not fluoresce at room temperature or at 77 K. The relative fluorescence quantum yields for CMN and BMN in cyclohexane are contained in Table I. Similar results were reported while this work was in progress by Joussot-Dubien and co-workers[20] except that very weak fluorescence from IMN was claimed.

We are unable to identify conclusively phosphorescence from any of the (halomethyl)naphthalenes when they are irradiated at 77 K in EPA or methylcyclohexane glasses. However, we are able to show that the triplets of CMN and BMN are formed by irradiation at room temperature.

The triplet–triplet absorption spectra of many naphthalene derivatives have a band at ca. 420 nm.[21] Laser flash photolysis of 1-methylnaphthalene in deoxygenated methanol generates the triplet which appears with a ca. 50 ns risetime (the lifetime of the singlet) and decays with a half-time of several microseconds. The lifetime of this triplet is apparently controlled by a combination of impurity (residual oxygen) quenching and by triplet–triplet annihilation. Similar irradiation of the (halomethyl)naphthalenes reveals a triplet–triplet absorption for both CMN and BMN (vide infra) but none for IMN. The intensity of the triplet–triplet absorptions of CMN and BMN is ca. 10% of that observed for methylnaphthalene. If similar extinction coefficients are assumed, this finding implies that the intersystem crossing efficiencies of CMN and BMN are ca. 10% of that of the hydrocarbon.

The risetimes of the triplet–triplet absorption spectra for CMN and BMN are faster than the ca. 13 ns our laser system can resolve. The fluorescence decay similarly shows a lifetime too short to resolve with the 2 ns resolution available. Estimation of the lifetimes of excited singlet CMN and BMN from the fluorescence yields (Table I) by comparison with methylnaphthalene and calculating radiative rates from the absorption spectra (Figure 1) indicates subnanosecond lifetimes for both compounds. A recent report by Rentzepis[22] on the fluorescence decay of CMN monitored by picosecond techniques put its lifetime at 0.49 ns.

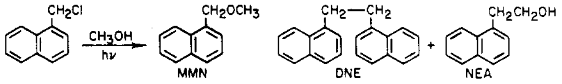
The lifetimes of CMN and BMN triplets in deoxygenated methanol are 180 ± 12 ns and 174 ± 15 ns, respectively, and both triplets decay following a simple first-order rate law.

These spectroscopic results reveal a great deal about the lowest singlet and triplet excited states of the (halomethyl)naphthalenes. The typical "mirror image" relationship between the absorption and fluorescence spectra of CMN and BMN, and the invariance of the Stokes shift imply that the lowest singlet state is dominated by the ^1L_b contribution of the naphthalene chromophore.[23] However, unlike methylnaphthalene, the sums of the fluorescence and intersystem crossing yields of CMN and BMN are far less than unity. This finding suggests that at least part of the observed photochemistry of these compounds (vide infra) originates with the lowest excited singlet state.

The singlet excited state of IMN is qualitatively different from those of the two other (halomethyl)naphthalenes. In particular, the absence of fluorescence and the changes in the absorption of the ground state both point to a dissociative state. Our inability to detect the absorption of triplet IMN is also consistent with this interpretation.

Direct Irradiation of the (Halomethyl)naphthalenes. The observed photochemistry of the (halomethyl)naphthalenes depends on the nature of the halogen, the solvent, and, in part, on whether the energy is supplied by direct irradiation or by photosensitization. In this section the results of product, spectroscopic, and quenching experiments on the direct irradiation of these compounds are presented.

(A) Products. Irradiation of CMN at 254 nm (or at 266 nm with a pulsed laser) in deoxygenated methanol leads to the formation of three primary products. These are 1-(methoxymethyl)naphthalene (MMN), dinaphthylethane (DNE) and 2-(1-naphthyl)ethyl alcohol (NEA), eq 8. We



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associate MMN with the heterolytic cleavage of CMN to generate the naphthylmethyl cation, and DNE and NEA with the homolytic cleavage of CMN to generate the naphthylmethyl radical and a chlorine atom. The chemical

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(20) Davidson, R. S.; Bonneau, R.; Joussot-Dubien, J.; Trethewey, K. R. *Chem. Phys. Lett.* **1980**, *74*, 318.

(21) Birks J. "Photophysics of Aromatic Molecules"; Wiley: New York, 1970; p 256.

(22) Huppert, D.; Rand, S. D.; Reynolds, A. H.; Rentzepis, P. M. *J. Chem. Phys.* **1982**, *77*, 1214.

(23) Berlman, I. "Handbook of Fluorescence Spectra of Aromatic Molecules"; Academic Press: New York, 1971; p 332.

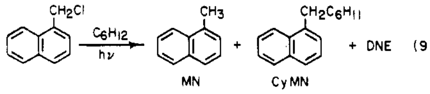
Table II. Direct Irradiation of 1-(Halomethyl)naphthalenes

XMN	solvent	dissolved gas	MMN[a]	DNE	MN	NEA	NA	CyMN
CMN	CH_3OH	Ar	0.11 (46)[f]	0.04 (15)	~0.01[c]	0.12 (49)	*c*	*c*
CMN	CH_3OH	O_2	0.11	*d*	*d*	0.033	(0.27)[b]	*c*
CMN	C_6H_{12}	Ar	*c*	0.055	0.033	*c*	*c*	0.15
CMN	C_6H_{12}	O_2	*c*	*d*	0.014	*c*	(0.81)	0.055
BMN	CH_3OH	Ar	0.18 (88)	0.018 (12)	*d*	*d*	*c*	*c*
BMN	CH_3OH	O_2	(0.16)	*d*	*d*	*d*	(0.05)	*c*
BMN	C_6H_{12}	Ar	*c*	trace[e]	*d*	*c*	*c*	*d*
BMN	C_6H_{12}	O_2	*c*	*d*	*d*	*c*	(0.25)	*d*
IMN	CH_3OH	Ar	0.094	trace[e]	*d*	*d*	*c*	*c*
IMN	CH_3OH	O_2	0.098	*d*	*d*	*d*	(0.40)	*c*
IMN	C_6H_{12}	Ar	*c*	trace[e]	*d*	*c*	*c*	*d*
IMN	C_6H_{12}	O_2	*c*	*d*	*d*	*c*	(0.47)	*d*

[a] MMN = 1-(methoxymethyl)naphthalene; DNE = di-(1-naphthyl)ethane; MN = 1-methylnaphthalene; NEA = naphthylethyl alcohol; NA = 1-naphthaldehyde; CyMN = 1-(cyclohexylmethyl)naphthalene. [b] Quantum yields of naphthaldehyde formation are less reliable than the others reported because even at low conversion the aldehyde absorbs a significant fraction of the exciting light. [c] The product is not expected. [d] None detected. [e] A gas chromatogram shows a peak with appropriate retention time but in an amount too small to quantitate or characterize further. [f] Quantum yield at low conversion (chemical yield).

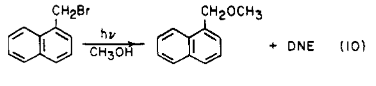
and quantum yields for these processes are displayed in Table II.

Irradiation of CMN in deoxygenated cyclohexane solution gives methylnaphthalene, (cyclohexylmethyl)-naphthalene, and DNE, eq 9. The quantum yields for this reaction are also contained in Table II. These products are consistent with photochemical homolysis of the carbon–chlorine bond of CMN followed by combination and disproportionation of the expected radicals.



Photolysis of CMN in solutions containing dissolved oxygen provides further insight into the nature and origin of the intermediates. In oxygen-saturated cyclohexane, direct irradiation of CMN gives methylnaphthalene and (cyclohexylmethyl)naphthalene in much reduced yield, and the major product is 1-naphthaldehyde. This aldehyde is presumed to result from the trapping of naphthylmethyl radical by oxygen and subsequent rearrangement of the peroxide. In oxygen-saturated methanol, irradiation of CMN still gives (methoxymethyl)naphthalene, the cation trapping product, in virtually undiminished yield, but the amounts of DNE and NEA, the radical products, are much reduced, and naphthaldehyde is again a major product. Quantum yields for these reactions are displayed in Table II. These data reveal that the precursor to the cationic products cannot be trapped with oxygen.

Irradiation of BMN at 337 nm in deoxygenated methanol gives results largely analogous to those from CMN. The primary products of this reaction are MMN and DNE, eq 10. No NEA is detected. This is a reasonable consequence of the difference in reactivity of bromine and chlorine atoms towards hydrogen atom abstraction from methanol. The quantum yield of MMN formation from BMN is independent of the BMN concentration. Irradiation of BMN in deaerated cyclohexane gives very slow formation of DNE.



The effect of oxygen on the photochemistry of BMN is exactly analogous to that of CMN. In oxygen-saturated methanol the yield of DNE is reduced while the yield of MMN is essentially unchanged. In oxygen-saturated cyclohexane, the rate of reaction is greatly increased and naphthaldehyde is the major product. It is important to note that irradiation of BMN at 337 nm generates the lowest singlet (S_1, ^1L_B) not S_2 (see Figure 1). In cyclohexane solution this leads to efficient homolytic carbon–bromine bond cleavage that is clearly not originating from S_2. Irradiation of BMN in methanol solution at 254 nm (absorption into S_2) does not change the products.

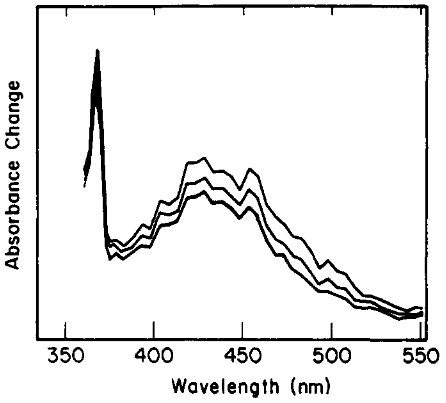


Figure 2. Transient spectra obtained from irradiation of CMN in deoxygenated cyclohexane with a 266-nm laser pulse. The sharp peak with a maximum at 370 nm is identified as naphthylmethyl radical and the broad absorbance with a maximum at ca. 422 nm is CMN triplet.

Similarly, photolysis of IMN in deoxygenated methanol gives MMN. However, in this case, the quantum yield of reaction is somewhat dependent on the IMN concentration.[1,24] In cyclohexane, the IMN reaction is slow and leads to DNE, but saturation with oxygen causes an increase in rate and the formation of naphthaldehyde. Oxygen saturation of the methanol solution does not cause a measurable reduction of the MMN yield. These data also are summarized in Table II.

(B) Transient Spectroscopy. Pulsed irradiation of the (halomethyl)naphthalenes with a nitrogen or quadrupled Nd-YAG laser permits observation of several reactive intermediates. The identity and chemical properties of these intermediates depend upon the identity of the halogen and the reaction solvent.

Irradiation of CMN in deoxygenated cyclohexane with a ca. 20 ns pulse from the YAG laser gives the spectra shown in Figure 2. Two transient products are observed

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[24] The preliminary account of this phenomenon[1] reported a doubling of the quantum yield over a ca. 10-fold IMN concentration range. Reinvestigation of the concentration dependence using improved actinometry (see experimental section) has reduced the magnitude of this effect to a ca. 10% increase over a similar concentration range.

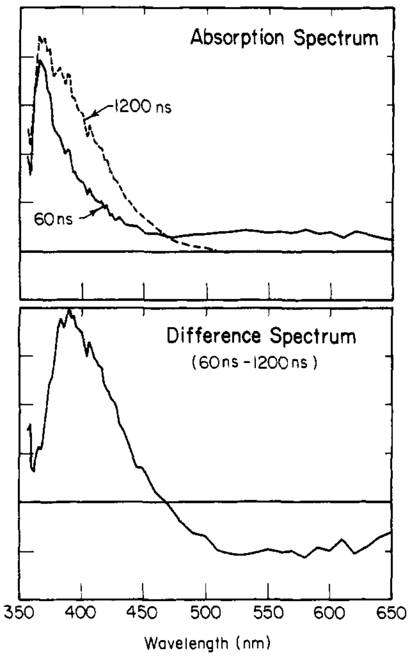

Figure 3. Transient spectra obtained from irradiation of IMN in methanol mesitylene with a 337-nm laser pulse. The absorptions at 60 ns (top) show naphthylenemethyl radical and the iodine atom–mesitylene charge-transfer complex absorption (λ_{max} 560 nm). The bottom spectrum is the difference between the transient spectra recorded at 60 and 1200 ns and shows the growth of $I_2^{-}\cdot$ and decay of the charge-transfer absorption.

to rise within the lifetime of the laser pulse. The first has an absorption maximum at ca. 370 nm and a decay time of several microseconds. The lifetime of this transient is shortened to ca. 1 μs when the cyclohexane solution is saturated with oxygen. This transient product is formed also by photolysis of CMN in methanol. This same transient product is formed also by the photolysis of BMN or IMN in cyclohexane or methanol. Inclusion of the triplet quencher tetramethyldiazetidine dioxide[25] (TMDD) in the methanol solution (it is insoluble in cyclohexane) has little effect on the lifetime of this transient.

The second transient product from photolysis of CMN absorbs with an apparent maximum at 422 nm and decays following first-order kinetics. The lifetime of this product also is shortened by oxygen, and in addition, it is quenched by TMDD in methanol. This same transient product is also formed when CMN is used to quench the triplet of benzophenone or thioxanthane in methanol solution.

On the basis of these findings we assign the 370 nm absorbing transient to the naphthylmethyl radical. The absorption spectrum of this species was recorded first by Porter and Strachan,[26] and we have generated it independently by the photolysis of 1-(naphthyl)diazomethane in hydrocarbon solution.[27] Homolytic cleavage of the carbon–chlorine bond in CMN should generate a chlorine atom as well as the observed radical. We cannot detect the chlorine atom, presumably due to its very rapid hydrogen atom abstraction reaction, but we can easily observe the bromine and iodine atoms by their characteristic charge-transfer absorptions[28] with benzene or mesitylene following photolysis of BMN or IMN in methanol or cyclohexane containing these hydrocarbons.

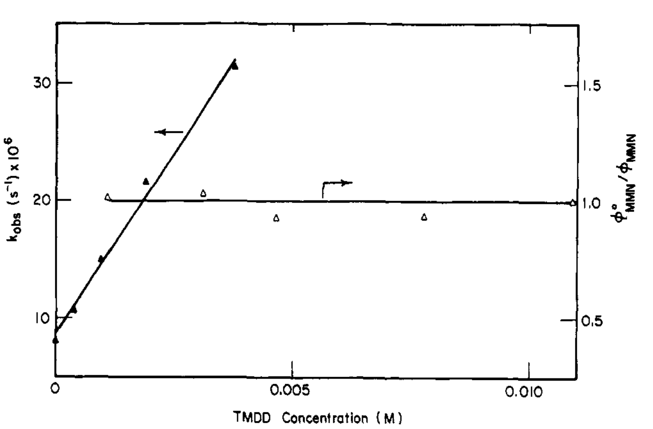

Figure 4. Quenching of the BNM triplet by TMDD (▲, left axis) and MMN formation (△, right axis) in methanol solution.

The other shorter-lived transient species formed from photolysis of CMN absorbs at 422 nm and is assigned to triplet CMN based on its behavior with TMDD, the similarity of its spectrum and with the triplet–triplet absorption spectra of other naphthalene derivitives, and its formation by triplet sensitization. Similarly, irradiation of BMN gives a transient with an apparent absorption maximum at 426 nm that likewise is assigned to triplet BMN. Irradiation of IMN does not give a detectable transient that can be assigned to triplet IMN. This implies either that triplet IMN is not formed or that it has a very short lifetime.

A third transient product grows into the absorption spectrum obtained from photolysis of BMN or IMN in methanol, but it is not observed in cyclohexane solution. In the case of IMN (Figure 3), this product has a broad absorption with a maximum at ca. 390 nm. For BMN a similar band, but with a maximum at 380 nm, is obtained. In both cases, these bands grow into the spectrum with a half-time of ca. 500 ns, which is approximately the same as the decay times observed for the iodine and bromine atoms.

Grossweiner and Matheson[29] studied the flash photolysis of aqueous alkali halide solutions. They observed unstable species that were assigned to the dihalide radical ions ($X_2^{-}\cdot$). Despite some controversy in the intervening period, deViolet, Bonneau, and Joussot-Dubien[30] later confirmed the identity of $I_2^{-}\cdot$ and also observed it in methanol. In these studies the dihalide radical ions are believed to be formed by the reaction of halogen atom with halide ion. The absorption spectra of these ions are quite similar to those of the secondary products obtained in the photolysis of BMN or IMN in methanol. Moreover, it is certain that both the halogen atom and ion are present in solution. For these reasons, we assign these secondary transients observed in the photolysis of BMN or IMN to the dihalide radical ions.

The rate of reaction of the iodine atom formed from photolysis of IMN depends on the concentration of IMN.[1] This is not unexpected since formation and reaction of iodine atom–alkyl iodide charge-transfer complexes has been previously observed.[31] In this case, reaction of the initial "outer" complex to form an "inner" complex and

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(25) Ullman, E. F.; Singh, P. *J. Am. Chem. Soc.* **1972**, *94*, 5077. Ullman, E. F.; Singh, P. *Ibid.* **1976**, *98*, 3018.

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(29) Grossweiner, L. I.; Matheson, M. S. *J. Chem. Phys.* **1957**, *61*, 1089.

(30) deViolet, P. F.; Bonneau, R.; Joussot-Dubien, *J. Chem. Phys. Lett.* **1973**, *19*, 251. deViolet, P. F.; Bonneau, R.; Joussot-Dubien, J. *Mol. Photochem.* **1973**, *5*, 61.

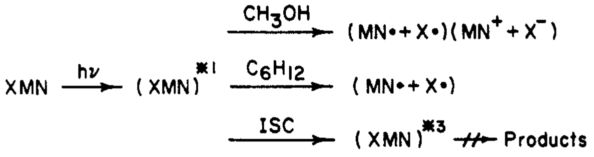
(31) Brühlmann, U.; Büchler, H.; Marchetti, F.; Bühler, R. E. *Chem. Phys. Lett.* **1973**, *21*, 412. Büchler, H.; Brühlmann, U.; Bühler, R. E. *Chem. Phys.* **1977**, *19*, 43. Strong, R. L.; Venditti, F., Jr. *Chem. Phys. Lett.* **1977**, *46*, 546.

Table III. Thermodynamic and Kinetic Data for Sensitizers

	THX[a]	CHY	1-AN	DBC	BEN	Py
E_s, kcal/mol[b]	70.0	79.2	(73)[f]	77.9	59.0	77.0
E_t, kcal/mol	65.5	57.3	56.5	55.5	54.3	48.1
E_{red}, V[c]	-1.97	-2.65	-2.16	(-2.66)[f]	-1.47	-2.38
E_{ox}, V		1.22		*d*		0.87
K_{sv}(CMN/MeOH), M^{-1}	5.3	41.2	*e*	11.2	*e*	88
K_{sv}(BMN/MeOH), M^{-1}	*d*	95.7	*e*	(9)[f]	*e*	554
k_q^t(CMN/MeOH), $M^{-1}\ s^{-1}$	6.1×10^9	2.3×10^8	7.8×10^7	3.6×10^6	*d*	*d*
k_q^t(BMN/MeOH), $M^{-1}\ s^{-1}$	6.2×10^9	4.0×10^9	2.0×10^9	7.9×10^8	3.0×10^7	*d*
k_q^t(BMN/C_6H_{14}), $M^{-1}\ s^{-1}$	*d*	2.0×10^9	*d*	4.7×10^8	*d*	*d*

[a] THX = thioxathanthone; CHY = chrysene; 1-AN = 1-acetylnaphthalene; DBC = 2,8-dibromochrysene; BEN = benzil; Py = pyrene. [b] Singlet and triplet energies were determined from the fluorescence and phosphorescence, respectively, or have been previously reported: Murov, S. "Handbook of Photochemistry"; Dekker: New York, 1973. [c] Oxidation and reduction potentials are referenced to a Ag/Ag$^+$ (0.01 M) electrode. [d] Not determined. [e] Too slow to measure or no fluorescence. [f] Values in parentheses may contain significant error.

Scheme I



solvolysis of the latter gives $I_2^{-}\cdot$ and accounts for the concentration dependence of the iodine atom lifetime.

(C) Triplet Quenching. The chemical and spectroscopic results presented thus far indicate that there are at least two excited states formed on irradiation of CMN and BMN. These are the first formed singlet and the lowest triplet. Classically, the chemical behavior of these states can be differentiated by utilization of a specific quencher of the latter. This is difficult to accomplish in the present series because the relatively low-energy triplet of substituted naphthalenes ($E_T \sim 59$ kcal/mol) combined with their high-energy singlet states ($E_S \sim 90$ kcal/mol) and intense absorption bands limits the choice of possible quenchers. Nevertheless, we have found that TMDD can be used to quench the lowest triplet state of BMN.

Figure 4 contains a plot of the reciprocal lifetime of triplet BMN against the concentration of TMDD in methanol solution. The triplet lifetime is obtained by monitoring the decay of the triplet–triplet absorption following pulsed irradiation at 337 nm with the nitrogen laser. The slope of this line in Figure 4 gives a quenching rate constant (k_q) of $6.2 \times 10^9\ M^{-1}\ s^{-1}$. Thus, as expected, TMDD is an effective triplet quencher in this system.

Also shown on Figure 4 is a Stern–Volmer plot of the quantum yields of MMN formation from irradiation of BMN in methanol in the presence of increasing concentrations of TMDD. It is apparent from these data that, although TMDD does quench triplet BMN, it has no effect on the yield of ether.

These results indicate that the lowest triplet state of BMN, and presumably CMN as well, does not participate significantly in the chemical reactions of these (halomethyl)naphthalenes. This finding is entirely consistent with a similar conclusion reached by Cristol and Bindel[18] from a study of the quenching of the sensitized photolysis of benzyl chloride. The results of the direct irradiation of the (halomethyl)naphthalenes are summarized in Scheme I.

Singlet- and Triplet-Sensitized Reactions. A second general approach to the discrimination of chemical reactions originating from singlet and triplet excited states is sensitization. Typically, a sensitizer is chosen so that its excited singlet state is short-lived, or of insufficient energy, so that transfer to form the excited singlet of the substrate is improbable. The triplet state of the sensitizer, on the other hand, should be relatively long-lived and of high enough energy to transfer to the substrate. In these circumstances it is customarily assumed that triplet–triplet energy transfer occurs from the sensitizer to form the triplet state of the substrate. Chemical reactions observed under these conditions are typically associated with the triplet excited state of the substrate.

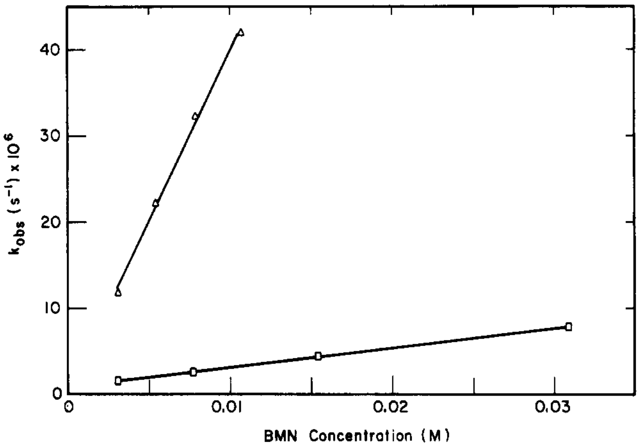


Figure 5. Quenching of the chyrsene triplet by CMN (□) and BMN (△) by decay of the triplet–triplet absorption in methanol solution.

(A) Spectroscopic Properties of Sensitizers. In order to interpret the outcome of a sensitization experiment it is necessary to determine what state is being quenched and at what rate. We have employed the group of sensitizers shown in Table III, and, to the extent possible, probed their interactions with the (halomethyl)naphthalenes.

The highest energy triplet sensitizer employed in this study is thioxanthone (THX). The singlet lifetime of THX in methanol is reported to be 2.4 ns.[32] CMN quenches the fluorescence of THX in methanol, Stern–Volmer analysis of these data gives a quenching constant (K_{sv}) of 5.3 M^{-1}. Similarly, we measured the rate constant for CMN and BMN quenching of triplet sensitizers (k_q^t) by monitoring their lifetimes by triplet–triplet absorption following pulsed laser irradiation (Figure 5). These results, are displayed in Table III.

The singlet energies of all of the sensitizers used are well below those of CMN and BMN (Table I). However, in those cases where significant fluorescence of the sensitizer can be detected, both these compounds do quench this emission. Thus, some interaction other than simple energy transfer must be occurring between the excited singlet

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Table IV. Sensitized Irradiation of 1-(Halomethyl)naphthalenes in Methanol-Benzene Solution

[XMN], M	sensitizer	X_s[a]	X_T	ϕ_{MMN}	ϕ_{CyMN}[b]	DNE/MMN	NEA/MMN
CMN, 1.1×10^{-2}	THX	0.055	0.94	0.19	0.14	0.25	0.5
CMN, 4.5×10^{-2}	pyrene	0.80	[c]	0.025	0.016	0.2	0.2
CMN, 5.0×10^{-3}	CHY	0.18	0.80	0.06	[e]	0.03	[e]
CMN, 5.0×10^{-2}	DBC	0.35	0.47	0.11	0.07	<0.02	[e]
CMN, 2.1×10^{-2}	ACN	[e]	0.98	0.18	0.13	<0.02	[e]
BMN, 4.6×10^{-3}	THX	(0.12)	0.87	0.21	[d]	0.05	[d]
BMN, 6.2×10^{-3}	pyrene	0.77	[c]	0.16	[d]	0.10	[d]
BMN, 5.0×10^{-3}	CHY	0.32	0.68	0.12	[d]	<0.03	[d]
BMN, 5.0×10^{-3}	DBC	(0.05)	(0.94)	0.14	[d]	<0.02	[d]
BMN, 6.1×10^{-3}	ACN	[e]	0.99	0.24	[d]	<0.02	[d]
BMN, 1.0×10^{-2}	benzil	[e]	0.89	0.017	[d]	<0.02	[d]

[a] X_s (X_T) is the fraction of the singlet (triplet) sensitizer quenched by XMN. [b] Determined in cyclohexane solution. [c] Neither BMN nor CMN are expected to quench the low energy triplet of pyrene. [d] Product not expected. [e] None detected.

sensitizer and the (halomethyl)naphthalene. A likely possibility is exciplex formation, but no new emission is observed from cyclohexane solutions of BMN and pyrene.

The triplet energies of many of the sensitizers used in this study are below the lowest triplets of CMN and BMN (based on methylnaphthalene and (methoxymethyl)-naphthalene phosphorescence). In these cases, the rate constants for triplet quenching (Table III) decrease as the energy of the sensitizer declines, and, for those examples studied, do not show a very marked solvent dependence.

(B) Products. It has been noted previously for the benzyl halides that direct and sensitized photolysis give similar products.[18] This appears to be true also for the (halomethyl)naphthalenes. The products obtained from the sensitized irradiation of CMN and BMN in deoxygenated methanol containing 20% benzene (to improve the solubility of some sensitizers) are reported in Table IV.

The data in Table IV reveal that thioxanthone sensitization of CMN gives the same set of products as does direct irradiation. However, the ratio of homolytic to heterolytic bond cleavage is slightly smaller in the sensitized experiment. In this case the interaction is primarily between triplet THX and CMN. As expected, including 1.5×10^{-2} M TMDD as a quencher in sensitization experiments (TMDD does not significantly quench sensitizer fluorescence) reduces the quantum yield of the sensitized reaction. It is important to note that the energy of triplet THX is above that of triplet CMN and also somewhat greater than the bond energy of the carbon–chlorine bond.[33]

When a lower energy triplet sensitizer is used, for example ACN, the dominance of the heterolytic cleavage products increases. In this case, the triplet energy of the sensitizer is below both CMN triplet and the carbon–chlorine bond strength. However, sensitization in cyclohexane solution does lead to homolytic bond cleavage as evidenced by the formation of (cyclohexylmethyl)-naphthalene. BMN gives largely analogous results except that the products of homolytic cleavage are less in evidence.

Sensitization of CMN in deoxygenated methanol–benzene by pyrene also leads to both homolytic and heterolytic cleavage products. In this case, however, it is the excited singlet state of the sensitizer that is being quenched. The energy of this state is below that of singlet CMN but above that for homolytic carbon–chlorine bond cleavage. Homolytic cleavage is the exclusive path in cyclohexane solution with this sensitizer. In methanol for the other sensitizers shown in Table IV, it is generally observed that if the energy of the (predominantly) quenched state is above that required for homolytic bond cleavage, then this route is observed. In cyclohexane solution it appears that homolytic cleavage of CMN is more likely even with relatively low energy sensitizers.

Discussion

The results of the direct and sensitized irradiation of the (halomethyl)naphthalenes do not fit entirely within any of the schemes proposed previously for the benzyl halides. It is clear that there are at least two states responsible for chemical reaction. Among the possibilities that must be considered are S_2, S_1, T_2, T_1, and a series of exciplexes with excited sensitizers. Our findings permit some choices to be made and provide some insight into the properties of the reactive states.

Rentzepis[19] has observed that in nonpolar solvents S_2 is an origin for the homolytic cleavage of the carbon–halogen bond in CMN and BMN. We also have obtained products characteristic of carbon–halogen bond cleavage by irradiation of compounds into the S_2 transition (254 or 266 nm). However, we obtain a virtually identical product mixture from irradiation of BMN at 337 nm. At this wavelength BMN is raised only to S_1, and this state, or some state derived from S_1, therefore must also be capable of initiating carbon–halogen bond cleavage.

The excited states that can be derived from S_1 are in the triplet manifold. The spectroscopic evidence indicates that for CMN and BMN S_1 is almost totally dominated by the naphthalene ^1L_b state. There is no evidence in these cases for a singlet state with an important charge-transfer component from the carbon–halogen bond. This is significant since such a singlet state might have a triplet counterpart whose energy is located somewhere between T_1 of naphthalene (ca. 60 kcal/mol) and T_2 of naphthalene (ca. 88 kcal/mol).[34] The absence of a charge-transfer state in the singlet manifold makes it less likely that one will play an important role in the triplet. Thus, the triplet states that can be reached from S_1 are T_2 and T_1. The quenching and sensitization experiments seem to eliminate any important role for these states in the chemistry of the (halomethyl)naphthalenes.

The inclusion of TMDD in methanol solutions of BMN causes quenching of the lowest triplet of the bromide without significantly affecting the chemical outcome of the direct irradiation. This finding clearly eliminates a role for T_1 of BMN in its direct irradiation and presumably also for that of the analogous state in CMN photolysis. However, triplet sensitizers do initiate reactions of BMN and

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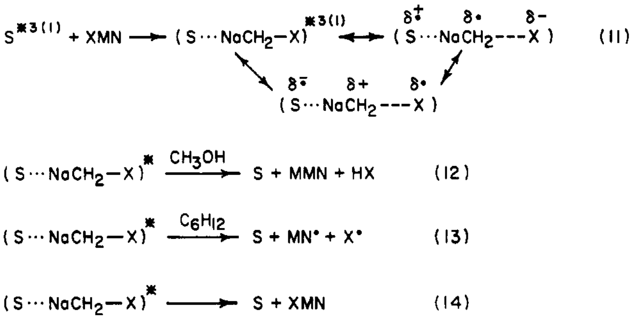
[33] The carbon–halogen bond strengths of benzyl chloride, bromide, and iodide are 69, 55, and 45 kcal/mol, respectively. Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: London, 1970.

[34] Reference 21, p 284.

Scheme II



$$S^{*3(1)} + XMN \longrightarrow (S\cdots NaCH_2{-}X)^{*3(1)} \longleftrightarrow (\overset{\delta\dot{+}}{S}\cdots \overset{\delta\cdot}{NaCH_2}{-}{-}{-}\overset{\delta-}{X}) \quad (11)$$

$$(\overset{\delta\dot{-}}{S}\cdots \overset{\delta+}{NaCH_2}{-}{-}{-}\overset{\delta\cdot}{X})$$

$$(S\cdots NaCH_2{-}X)^{*} \xrightarrow{CH_3OH} S + MMN + HX \quad (12)$$

$$(S\cdots NaCH_2{-}X)^{*} \xrightarrow{C_6H_{12}} S + MN^{\bullet} + X^{\bullet} \quad (13)$$

$$(S\cdots NaCH_2{-}X)^{*} \longrightarrow S + XMN \quad (14)$$

CMN that appear to be quite similar to those obtained by their direct irradiation.

It has been suggested for benzyl chloride that sensitization gives a reactive upper triplet state.[18] However, many of the sensitizers that we find to be effective have energies somewhat below T_1 of naphthalene. This makes reaching the naphthalene T_2 in these cases absolutely out of the question. Moreover, there is no evidence for a triplet state with energy between T_1 and T_2 that might be populated directly by these sensitizers or that could be in thermal equilibrium with T_1. Also, singlet sensitizers with energy well below S_1 are effective at initiating these reactions. In this case, reaching an upper, reactive triplet would require a very special energy transfer to give this state of the (halomethyl)naphthalene, which has an energy greater than 60 kcal/mol, while the other partner, pyrene, has a triplet energy of 48 kcal/mol. This seems unlikely. Instead, we suggest that both the triplet and singlet sensitization reactions originate directly from an exciplex of the (halomethyl)naphthalene and the sensitizer.

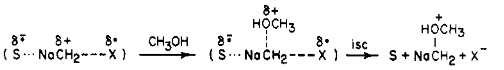
The formation and reaction of exciplexes from alkyl halides and various sensitizers has been suggested previously.[35-37] The evidence in these cases points to an exciplex with a relatively small degree of charge resonance, the predominant direction of which appears to depend on the specific nature of the sensitizer. The results suggest that a similar weakly bound, nonemissive exciplex is formed by the (halomethyl)naphthalenes, and, by implication, for the benzyl halides as well.

Inspection of the data in Table III shows that the rate of quenching of the triplet sensitizers by CMN and BMN follows more closely the triplet energies than the redox properties of the sensitizers. Also, in the cases examined, there is only a small dependence of solvent polarity on the rate constants for quenching. These observations imply that these exciplexes are not highly polar and that energy transfer to the lowest, unreactive, naphthalene triplet is an important consequence of exciplex formation.

A further point in support of the exciplex hypothesis is the formation of homolysis products in cyclohexane solution from sensitizers whose triplet energies are below the carbon–halogen bond strength. This implies the operation of an activated process which requires a relatively long-lived state. It is reasonable, if we eliminate a role for T_1, that the exciplex serves as this state.

These conclusions are summarized in Scheme I for the direct irradiation, and in Scheme II for the sensitized processes. In the direct irradiation, bond cleavage occurs from S_1 or S_2 (whichever is reached by irradiation) both homolytically and (in methanol) heterolytically. Our findings do not distinguish between a single excited state giving both types of cleavage simultaneously (similar to the proposal of Walling[38]) from initial homolysis followed by electron transfer to generate ions.[14,15] However, if it is the latter route, then electron transfer must occur within the solvent cage very rapidly since the findings show that oxygen does not significantly inhibit MMN formation.

The sensitized path (Scheme II) requires initial formation of an exciplex, eq 11. This exciplex can react with methanol, eq 12, to give predominantly MMN. The specific details of the nature of the reaction between the exciplex and the alcohol are not revealed. However, it is clear that, for example, solvation followed by intersystem crossing and relaxation overcomes the spin prohibition implied by a triplet sensitizer giving spin-paired ionic products, eq 15. The exciplex can also dissociate homolytically in nonpolar solvents, eq 13, or it may simply relax to the lowest energy locally excited triplet state. Finally, radiationless deactivation of the exciplex simply regenerates the reagents. Incorporation of a similar short-lived exciplex in the reaction sequence proposed by Bindel and Cristol[18] is entirely consistent with their findings for benzyl chloride and eliminates the need for postulation of reaction from an upper triplet state.



$$(\overset{\delta\dot{-}}{S}\cdots \overset{\delta+}{NaCH_2}{-}{-}{-}\overset{\delta\cdot}{X}) \xrightarrow{CH_3OH} (\overset{\delta\dot{-}}{S}\cdots Na\overset{\overset{\delta+}{HOCH_3}}{\overset{\vdots}{C}}H_2{-}{-}{-}\overset{\delta\cdot}{X}) \xrightarrow{isc} S + Na\overset{\overset{+}{HOCH_3}}{\overset{|}{C}}H_2 + X^{-} \quad (15)$$

In sum, the direct and sensitized photolysis of the (halomethyl)naphthalenes reveals three modes of heterolytic bond cleavage. The first originates from a singlet excited state, and may be direct or may proceed through a radical pair that undergoes very rapid electron transfer. The second is through an exciplex of the halide with a singlet or triplet sensitizer. Finally, the third mode operates apparently only for concentrated solutions of IMN. In this case a complex of this halide with atomic iodine in methanol can give ether. Carbon–halogen bond homolysis occurs from all three halides by direct and sensitized irradiation. There are apparently two modes for homolysis. The first is from the locally excited singlet state, and the second is from an exciplex. There appears to be a propensity for these exciplexes to cleave heterolytically in methanol and homolytically in cyclohexane.

Experimental Section

General Procedures. Fluorescence emission and excitation spectra were obtained using a Farrand Mark I spectrofluorometer. In general solutions of the (halomethyl)naphthalenes to be used for emission spectroscopy were prepared so that the absorbance at the exciting wavelength was ca. 0.2.

Analytical gas chromatography was performed by using a Varian instrument equipped with a Hewlett Packard 3390A recording integrator. Care must be exercised in the interpretation of the gas chromatographic results since injection of methanol solutions of the (halomethyl)naphthalenes leads to some thermal formation of MMN. To avoid this difficulty the photoproducts were extracted from the methanol solution before analysis by adding 3 mL of hexane to 1 mL of photolysis solution and then 1 mL of water was added to this combination. The mixture was separated and the hexane layer dried with anhydrous $MgSO_4$. Control experiments showed quantitative extraction of all photoproducts except NEA, which is not formed thermally and was analyzed in the unextracted methanol solutions.

Three different gas chromatography columns were used for the different analyses: a 1-M 2.5% QF-1, a 1-M 2% OV-101, and a 2-M 10% QF-1 all on chromasorb WHP in $^1/_4$-in. glass columns.

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[35] Harriman, A.; Rockett, B. W.; Poyner, W. R. *J. Chem. Soc. Perkin Trans. 2* **1974**, 485. Harriman, A.; Rockett, B. W. *Ibid.* **1974**, 1235.

[36] Hirayama, S.; Foster, R. J.; Mellor, J. M.; Whitling, P. H.; Grant, K. R.; Phillips, D. *Eur. Polym. J.* **1978**, *14*, 679.

[37] Khwaja, H. A.; Semeluk, G. P.; Unger, I. *Can. J. Chem.* **1982**, *60*, 1767.

[38] Walling, C.; Waits, H. P.; Milovanovic, J.; Pappiadnnou, G. G. *J. Am. Chem. Soc.* **1970**, *92*, 4927.

The first column was used in the analysis of MMN, CMN, CYMN, and naphthaldehyde. For these analyses *n*-tetradecane and eicosane were used as internal standards, the injector temperature was at 230 °C, and the He carrier gas flow was 35 mL/min with a column temperature of 130 °C. The second column operated at 130 °C with a carrier flow of 35 mL/min and was used in analyses of BMN, IMN, and MMN again using *n*-tetradecane and eicosane as internal standards. This column was also used for analysis of DNE when operated at 230 °C with di-*n*-tetradecyl ether as internal standard. The third column was used at 160 °C to analyze NEA and naphthaldehyde. Calibration and control experiments showed that these techniques gave accurate analysis of the concentrations with standard errors of ±10%.

Quantum yields of reaction were determined by ferrioxalate actinometry using the method described by Calvert and Pitts.[39] For CNM a merry-go-round apparatus was constructed inside a Rayonet photoreactor equipped with low-pressure Hg resonance lamps (irradiation at 254 nm). For BNM and IMN the quantum yields were determined by irradiation at 337 nm using the nitrogen laser and a series of beam splitters. The beam splitters were calibrated with ferrioxalate and both the ferrioxalate and (halomethyl)naphthalene quantum yields were shown to be independent of laser power. However, the ferrioxalate actinometer was found to be not linear beyond a total light dose of 1.1×10^{-7} einstein/mL. This nonlinearity resulted in the overestimation of the INM photosolvolysis quantum yield concentration dependence previously reported.[1]

Materials. Tetramethyldiazetidine dioxide (TMDD) was prepared by the procedure of Ullman and Singh:[25] mp 190–192 °C (lit.[25] mp 190 °C). 2,8-Dibromochrysene was prepared by the procedure of Funke and Miller:[40] mp 276–280 °C (lit.[40] mp 275 °C). CNM was purchased from Aldrich and purified by recrystallization from pentane/ether: mp 33–33.5 °C (lit.[41] mp 32 °C). BNM was prepared by adaptation of the procedure described by Olah et al.[42] mp (hexane) 54–56 °C (lit.[42] mp 56 °C). (1-Naphthyl)diazoethane was prepared by the procedure of Nakaya et al.[43] and was stored over ice. MMN was prepared from CNM according to the procedure of Sharp and Patrick.[44] NEA was synthesized by addition of ethylene oxide to 1-naphthylmagnesium bromide according to the procedure of Wilds[45] mp 60–62 °C (lit.[45] mp 62 °C). DNE was obtained from coupling of BNM as described by Copeland et al.[46] mp 160–162 °C (lit.[46] mp 161–162 °C).

(Iodomethyl)naphthalene (IMN). The complete procedure for the preparation of this compound had to be run under safe lights. Exposure to ordinary room light leads to fairly rapid decomposition of the product. 1-(Bromomethyl)naphthalene (1.1 g, 5.0 mmol) was stirred with NaI (1.1 g, 7.5 mmol) in 50 mL of acetone for 4 h. The NABr that precipitated was removed by filtration and the solution evaporated to dryness on a rotary evaporator. The residue was dissolved in 100 mL of warm hexane and filtered to remove excess NaI. The hexane solution was washed with 25 mL of 10% aqueous Na_2SO_3 and dried for 1 h with anhydrous $MgSO_4$. The solution was filtered and cooled to −20 °C overnight. The crystals that precipitated were collected by filtration. Recrystallization was accomplished by dissolving the crude (iodomethyl)naphthalene in warm hexane, washing the solution with 10% aqueous Na_2SO_3, drying it with anhydrous $MgSO_4$, filtering, and then cooling to −20 °C overnight. Failure to wash the hexane solution with aqueous Na_2SO_3 during recrystallization led to decomposition of the recovered crystals. The recrystallized IMN (0.5 g, 35%) was stable if kept at −20 °C in the dark: mp 92–93 °C; UV (cyclohexane) max 300 (9400), 225 (42 000); NMR (CCl_4) δ 4.8 (s, 2), 7.5 (m, 7). Anal. Calcd. for $C_{11}H_9I$: C, 49.28; H, 3.38; I, 47.34. Found: C, 49.45; H, 3.45; I, 47.13.

(Cyclohexylmethyl)naphthalene (CYMN). CMN (1 g, 5.7 mmol) was dissolved in 50 mL of cyclohexane. The solution was placed in quartz tubes fitted with stopcocks and each tube was purged with argon for 4 min. The solutions were irradiated by using a low-pressure Hg lamp (254 nm) for 4 h. During this time a light brown film deposited on the walls of the tube so the solution was transferred to clean tubes, purged again, and irradiated four additional hours. The resulting dark yellow solution was evaporated on a rotary evaporator and the residue dissolved in 5 mL of hexane. This solution was chromatographed on silica gel, eluting with hexane, to give, after evaporation, a clear, colorless oil (0.3 g, 20%). Analysis of this oil by gas chromatography gave one peak accounting for ca. 95% of the integrated peak area and three smaller peaks: NMR (CCl_4) δ 1.1 (m, 11), 1.7 (m, 5), 2.9 (d, 2), 7.1–7.8 (m, 9); mass spectrum (10 eV), *m/e* (rel intensity) 224 (70), 142 (100), 141 (50), 83 (10); exact mass calcd for $C_{17}H_{20}$, 224.1565; found, 224.1565.

Procedures. Several standard photochemical techniques were employed in the sensitization, quenching, and transient spectroscopic investigation of the (halomethyl)naphthalenes. A typical example of each is presented.

Quenching of Chyrsene Fluorescence by CMN. The fluorescence spectrum of an argon-purged solution of chyrsene in methanol was recorded. The fluorescence intensity was compared to the intensity obtained from identical chrysene solutions containing various concentrations of CMN ranging from 6.7×10^{-3} M to 8.9×10^{-1} M. The ratio of I° (no CMN) to I was plotted against the CNM concentration and revealed a linear relationship. The slope of this line, calculated by nonlinear least squares gives K_{sv} (Table III).

Quenching of the Chrysene Triplet by CMN. The nitrogen laser configured as previously described was used. A solution of chrysene (1×10^{-3} M) in methanol was deoxygenated by purging with argon. Pulsed irradiation of this solution gave a transient whose spectrum was recorded 1.5 μs after irradiation. The spectrum obtained had an absorption maximum of 560 nm and decayed by mixed-order kinetics with a lifetime of several hundred microseconds. This transient is identified as triplet chrysene by comparison with spectral data reported previously.[47] The lifetime of triplet chrysene in the presence of CMN is much shorter than in its absence and, at CMN concentrations greater than 3×10^{-3} M the decay of chrysene triplet follows first-order kinetics. The decay rate of this transient was determined in solutions containing CMN between 3.1×10^{-3} M and 3.1×10^{-2} M. When this decay rate is plotted against CMN concentration a straight line is obtained. The slope of this line, calculated by nonlinear least squares, gives k_q^t (Table III).

Quenching of BMN with TMDD. A series of solutions of BMN (1.0×10^{-2} M) in deoxygenated methanol containing TMDD ($0–1.1 \times 10^{-2}$ M) were prepared. The solutions were irradiated with the nitrogen laser using a 50:50 beam splitter to less than 10% conversion. Relative quantum yields (ϕ_0/ϕ) were calculated by analysis of MMN formation by gas chromatography and corrected for the absorbance of TMDD at 337 nm. The results are shown in Figure 4.

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Registry No. MN, 90-12-0; CMN, 86-52-2; BMN, 3163-27-7; IMN, 24471-54-3; MMN, 5903-23-1; THX, 492-22-8; CHY, 218-01-9; 1-AN, 941-98-0; DBC, 50637-63-3; BEN, 134-81-6; Py, 129-00-0; DNE, 15374-45-5; NEA, 773-99-9; NA, 66-77-3; CyMN, 64833-56-3; CH_3OH, 67-56-1; C_6H_{12}, 110-82-7; O_2, 7782-44-7; Ar, 7440-37-1; mesitylene, 108-67-8.

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