J. Am. Chem. Soc. **1984**, *106*, 1951-1957

Photodissociation of Haloaromatics: Detection, Kinetics, and Mechanism of Arylmethyl Radical Formation

E. F. Hilinski, D. Huppert,[†] D. F. Kelley,[‡] S. V. Milton, and P. M. Rentzepis*

Contribution from Bell Laboratories, Murray Hill, New Jersey 07974.

Received October 3, 1983

Abstract: The photodissociation of 1- and 2-(halomethyl)naphthalenes in room-temperature hexane solution was studied by means of picosecond emission and absorption spectroscopy. Excitation of the (halomethyl)naphthalenes at 266 or 299 nm into the $S_2(\pi,\pi^*)$ state caused the molecules to undergo carbon–halogen bond homolysis. Emission from the 1- and 2-naphthylmethyl radicals was observed when a 355-nm, 25-ps pulse was directed into the sample at times ranging from 0 ps to 40 ns after the arrival of the first photolysis pulse. A broad absorption in the spectral region between 325 and 395 nm was observed for the 1-naphthylmethyl radical with a maximum near 365 nm and for the 2-naphthylmethyl radical with a maximum near 380 nm which appeared within the laser pulse width and persisted for times longer than 500 ps after excitation. A mechanism incorporating the experimental data is proposed for the photodissociation of (halomethyl)naphthalenes which is quite generally applicable to haloaromatic compounds. Excitation of the $S_2(\pi,\pi^*)$ state results in energy dissipation through two channels: (1) internal conversion to $S_1(\pi,\pi^*)$ followed by fluorescence to S_0 and (2) intersystem crossing to an upper triplet state which is itself, or crosses to, a dissociative (σ,σ^*) triplet state that leads to homolysis of the carbon–halogen bond. The branching ratio of channel 2 to channel 1 was found to be ~6:1 for 2-(chloromethyl)naphthalene in hexane at room temperature.

Photoexcitation of several halogen-substituted aromatic compounds is known to induce carbon–halogen (C–X) bond homolysis and to generate the corresponding aryl radical and halogen atom. These types of radicals play prominent roles as reactive intermediates in organic chemistry. Although aryl-substituted radicals have been identified in a variety of reactions and postulated as intermediates in others, the detailed mechanism of their formation via photoinduced C–X bond cleavage, including the excited state from which dissociation occurs, has not been well established. The photochemistry of haloaromatics recently has been studied in an effort to elucidate the photodissociation mechanism of these compounds.

A variety of experimental technqiues have been employed. In the early studies of room-temperature fluorescence and low-temperature phosphorescence, Ermolaev and Svitashev[1] demonstrated the range of fluorescence (ϕ_f) and phosphorescence (ϕ_p) quantum yields exhibited by the series of aryl halides consisting of 1-iodonaphthalene ($\phi_f < 0.0005$, $\phi_p = 0.38$), 1-bromonaphthalene ($\phi_f = 0.001$, $\phi_p = 0.27$), and 1-chloronaphthalene ($\phi_f = 0.3$, $\phi_p = 0.058$).

Using pulse radiolysis techniques, Grieser and Thomas[2] measured the triplet-state lifetimes of several aryl halides. Temperature-dependent lifetimes were found for 1-iodonaphthalene, 2-iodonaphthalene, and 4-iodobiphenyl in toluene and were correlated to the following Arrhenius expression, $\ln (1/\tau) = -E_a/RT + \ln A$. They proposed that the temperature dependence may result from a crossing of the phosphorescent triplet-state surface to a dissociative triplet (σ,σ^*) level. Wilkinson[3] and Levy et al.[4] have proposed that excited-state energy dissipation proceeds from the triplet state or possibly even directly from an excited singlet state that ultimately results in carbon–halogen bond dissociation.

Bersohn and co-workers[5] studied gas-phase photodissociation processes of haloaromatics in a molecular beam. The lifetimes of iodobenzene, 1-iodonaphthalene, and 2-iodonaphthalene were found to be ~1 ps. The analogous aryl bromides exhibited excited-state lifetimes that were approximately two orders of magnitude longer than the corresponding aryl iodides. Bersohn and co-workers[5] concluded that photodissociation proceeds via intersystem crossing to a triplet state localized in the carbon–halogen bond according to the scheme

$$S_0 \rightarrow S_2(\pi,\pi^*) \rightarrow S_1(\pi,\pi^*) \rightarrow T(\sigma,\sigma^*) \rightarrow \text{fragments}$$

It is possible, of course, that predissociation occurs via intersystem crossing directly from $S_2(\pi,\pi^*)$ to $T(\sigma,\sigma^*)$ in view of the ultrafast observed dissociation rate.

Table I. Room-Temperature Fluorescence Lifetimes, τ_f, of Several Haloaromatics Excited at Wavelength λ in Hexane[13]

sample	λ, nm	τ_f, ps
4,4′-dibromobiphenyl	265	30
4-bromobiphenyl	265	35
1-bromonaphthalene	265	75
1-bromo-4-methylnaphthalene	265	80
1-bromo-2-methylnaphthalene	265	72
2-bromonaphthalene	265	150
1-(chloromethyl)naphthalene	265	490
2-(bromomethyl)naphthalene	265	*a*
1-chloronaphthalene	265	2400
2-chloronaphthalene (zone refined >99%)	265	3300
2-chloronaphthalene	265	3500
9-bromoanthracene	355	100
9,10-dibromoanthracene	355	1300
2-iodoanthracene	265	14
9-iodoanthracene	265	35
2-iodoanthracene	355	17
9-iodoanthracene	355	55

[a] Not detected.

Previously, fluorescence lifetimes and emission and transient absorption spectra were measured which provided a means for monitoring the energy flow from the Frank-Condon photoselected state. Picosecond spectroscopic studies were performed by Struve and co-workers[6] and Huppert et al.[7] The time-resolved emission studies of several halogen-substituted aromatics (see Table I), in hydrocarbon solvent at room temperature, revealed that the fluorescence lifetimes were several orders of magnitude shorter than expected from absorption coefficient calculations. For 1-bromonaphthalene, 1-bromo-2-methylnaphthalene, 1-bromo-4-

---

[†] Permanent Address: Department of Chemistry, Tel Aviv University, Ramat Aviv 69978, Tel Aviv, Israel.

[‡] Present Address: Department of Chemistry, University of California, Los Angeles, CA.

(1) Ermolaev, V. L.; Svitashev, K. K. *Opt. Spectrosc.* **1959**, *7*, 399.

(2) Grieser, F.; Thomas, J. K. *J. Chem. Phys.* **1980**, *73*, 2115.

(3) Wilkinson, F. *J. Phys. Chem.* **1962**, 66, 2564.

(4) Levy, A.; Meyerstein, D.; Ottolenghi, M. *J. Phys. Chem.* **1973**, 77, 3044.

(5) (a) Freedman, A.; Yang, S. C.; Kawasaki, M.; Bersohn, R. *J. Chem. Phys.* **1980**, *72*, 1028. (b) Kawasaki, S. J. Lee; Bersohn, R. *J. Chem. Phys.* **1977**, *66*, 2647. (c) Dzvonik, M.; Yang, S.; Bersohn, R. *J. Chem. Phys.* **1974**, *61*, 4408.

(6) Pineault, R. L.; Morgante, C. G.; Struve, W. S. *J. Photochem.* **1981**, *17*, 435.

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

0002-7863/84/1506-1951$01.50/0

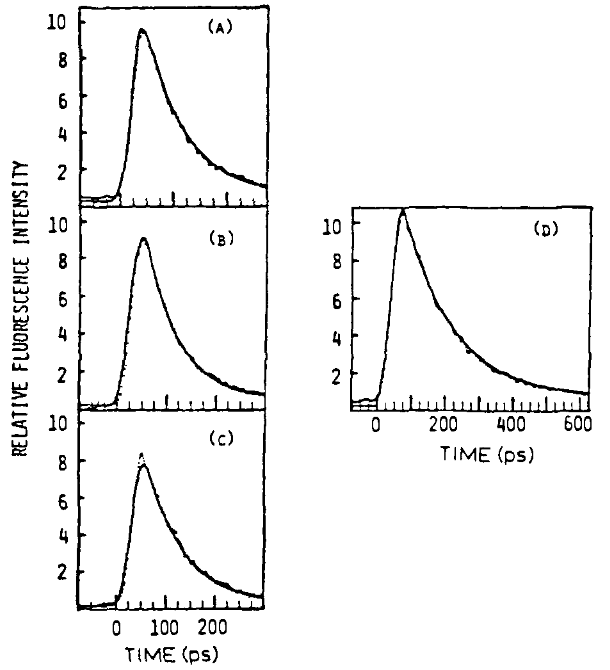


Figure 1. Relative fluorescence intensity vs. time for (A) 1-bromonaphthalene, (B) 1-bromo-2-methylnaphthalene, (C) 1-bromo-4-methylnaphthalene, and (D) 2-bromonaphthalene in hexane excited at 266 nm with a 25-ps pulse at room temperature and monitored at wavelengths between 310 and 550 nm. Fluorescence lifetimes are 75, 72, 80, and 150 ps, respectively.[13]

methylnaphthalene, and 2-bromonaphthalene in hexane excited with a 266-nm picosecond pulse, fluorescence lifetimes of 75, 72, 80, and 150 ps, respectively, were measured. These kinetics are shown in Figure 1. The quenching of $S_1 \rightarrow S_0$ emission was attributed to heavy-atom enhanced intersystem crossing to the triplet manifold.

Transient absorption spectra of several haloaromatics recorded by Huppert et al.[7] explicitly demonstrated the identity of the states involved in the quenching of emission induced by 266-nm excitation. The transient absorption spectra of photoexcited 1-bromonaphthalene are reproduced in Figure 2. The decay of the singlet-state absorption spectrum (Figure 2a) and the growth of the triplet-state population manifested by the absorption near 425 nm agree very well with the decay characteristics of the $S_1 \rightarrow S_0$ fluorescence lifetime. The fluorescence decay lifetime for 1-bromonaphthalene was found to be 75 ps, which is essentially the same as the decay of the singlet-state absorption and population growth rate of the lowest triplet-state absorption of 1-bromonaphthalene. Therefore, in these molecules, intersystem crossing is an important channel involved in excited-state energy dissipation. Similar behavior was observed for other haloaromatics and (halomethyl)aromatics. Although these experiments identified and measured the excited states through which the excited-state energy dissipates, the radical species were not observed, and their formation rate was inferred, but not directly measured.

Kelley et al.[8] recently have employed a two-pulse laser-induced fluorescence experiment which made the identification of the radical and measurement of its formation and decay kinetics possible. In this experiment, either 1-(chloromethyl)naphthalene or 1-(bromomethyl)naphthalene was excited at 266 nm with a 25-ps laser pulse to induce dissociation. To monitor the radicals by means of picosecond emission spectroscopy, a second laser pulse which was delayed relative to the first was directed into the sample and excited the radical at 355 nm. The fact that identical emission spectra from both 1-(bromomethyl)naphthalene and 1-(chloromethyl)naphthalene were obtained when the sample was excited at 355 nm and that the emission was at wavelengths expected for the 1-naphthylmethyl radical[9,10] led to the spectral assignment of the transient fluorescence to the naphthylmethyl radical.

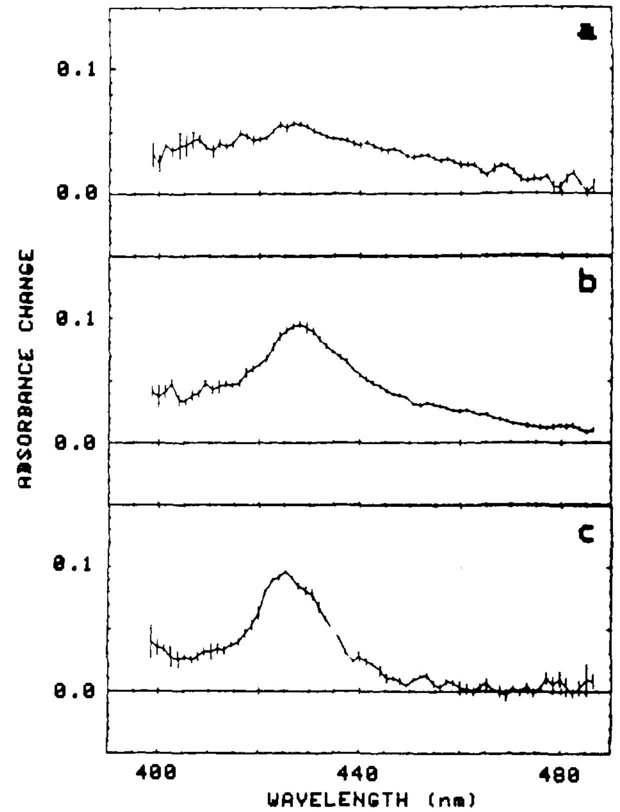


Figure 2. Difference absorption spectra recorded at (a) 25, (b) 100, and (c) 500 ps after excitation of 1-bromonaphthalene in hexane at room temperature with a 266-nm, 25-ps laser pulse.[13]

Further experimental data presented for the dissociation of several haloaromatics suggest that the mechanism proposeed in this paper may find a wide application to all of these types of molecules. In addition, we have been able to observe the transient absorption spectra of the radicals in solution and estimate the quantum yields and rates of their formation.

Experimental Section

Two experimental systems were employed for recording the results discussed.

(1) Emission spectra and formation and decay lifetimes were obtained by means of the picosecond spectroscopy system described previously by Barbara et al.[11] It is based on a Nd^{3+}/YAG laser system operated in a manner similar to the study described by Huppert et al.[7] for the identification of the emission of haloaromatics and lately by Kelley et al.[8] for the detection of radicals. The emission spectra were recorded by a vidicon which was attached to the exit slit of a 1/4-m polychromator. The lifetimes were measured by a streak camera and SIT vidicon system capable of a resolution of ~6 ps. Laser pulses (266 nm and 355 nm) were generated from the 1064-nm fundamental by directing laser pulses of appropriate wavelength(s) through harmonic-generating crystals. Laser pulses (299 nm) were generated by stimulated Raman scattering induced by focusing a 266-nm pulse into a cell containing hydrogen, at a pressure of ~100 psi, which results in a 4155-cm^{-1} shift.

(2) Difference absorption spectra of the transients were obtained by the system described fully by Reynolds et al.[12] The samples were excited by the 266-nm fourth harmonic of an amplified 1064-nm Nd^{3+}/YAG pulse. The spectra were recorded and digitized by means of a two-dimensional vidicon OMA attached to a 1/4-m polychromator. The spectra obtained with and without excitation were stored for processing,

---

(8) Kelley, D. F.; Milton, S. V.; Huppert, D.; Rentzepis, P. M. *J. Phys. Chem.* **1983**, *87*, 1842.

(9) Porter, G.; Strachan, E. *Trans. Faraday Soc.* **1958**, *54*, 1595.

(10) Slocum, G. H.; Kaufmann, K.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 4625.

(11) Barbara, P. F.; Brus, L. E.; Rentzepis, P. M. *Chem. Phys. Lett.* **1980**, *69*, 447.

(12) Reynolds, A. H.; Rand, S. D.; Rentzepis, P. M. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2292.

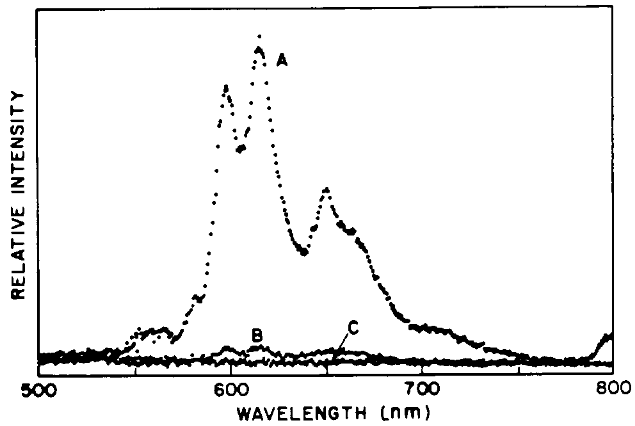


Figure 3. Emission spectrum of the 1-naphthylmethyl radical generated by photolysis of 1-(chloromethyl)naphthalene: (A) produced by excitation of the same solution with a 266-nm pulse followed 320 ps later by a 355-nm pulse; (B) produced with only the 266-nm pulse; (C) produced with only the 355-nm pulse.

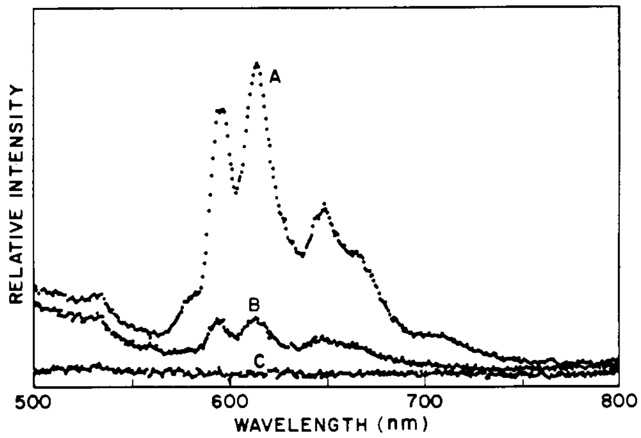


Figure 4. Same as Figure 3, but for 1-(bromomethyl)naphthalene.

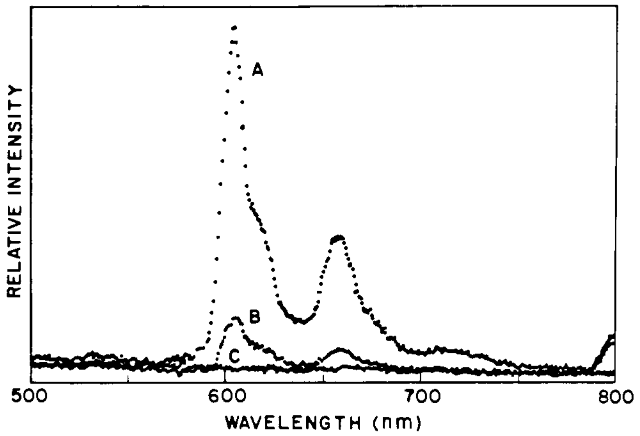


Figure 5. Emission spectrum of the 2-naphthylmethyl radical generated by photolysis of 2-(bromomethyl)naphthalene: (A) produced by excitation of the same solution with a 266-nm pulse followed 320 ps later by a 355-nm pulse; (B) produced with only the 266-nm pulse; (C) produced with only the 355-nm pulse.

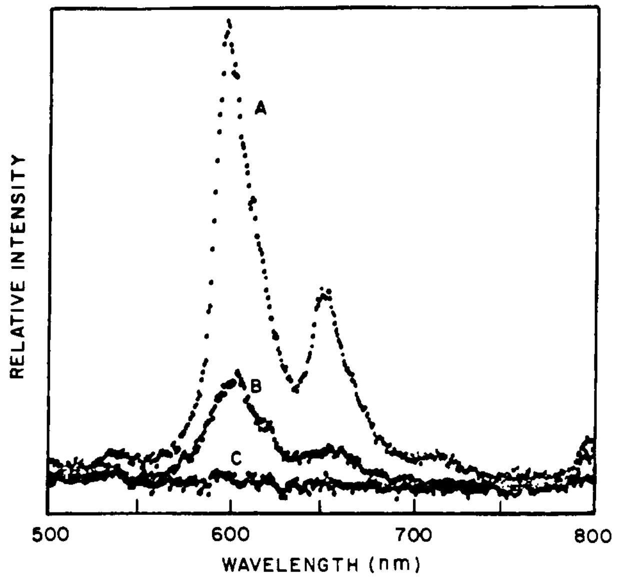


Figure 6. Emission spectrum of the 2-naphthylmethyl radical generated by excitation of 2-(chloromethyl)naphthalene with (A) a 299-nm, 25-ps laser pulse followed 500 ps later by a 355-nm, 25-ps laser pulse, (B) a 299-nm pulse alone, and (C) a 355-nm pulse alone.

analysis, and plotting by a Data General Eclipse minicomputer. Difference absorption spectra covering the wavelength range from 320 to 840 nm may be obtained at selected times after excitation by varying the arrival time of the excitation pulse relative to the probing continuum pulse. The delay times reported in this paper were selected because they cover the time constant of formation and decay of the singlet state and of radical formation. Excited-state absorption of the compounds studied and the ground-state absorptions of the radicals that were observed are within the wavelength range investigated.

Steady-state absorption and emission spectra were recorded by a Cary 15 and a Perkin-Elmer Hitachi spectrometer; respectively. To ascertain that the mechanism for dissociation we propose is valid, we have studied the dynamics of several haloaromatics including 1-(chloromethyl)-naphthalene, 2-(chloromethyl)naphthalene, (1-bromomethyl)-naphthalene, 2-(bromomethyl)naphthalene, and 1-(chloromethyl)-2-methylnaphthalene. All were purchased from Aldrich Chemical Co., except 1-(bromomethyl)naphthalene which was synthesized by Dr. Rena Arad Yellin. These compounds were purified, when necessary, by passage through a Florisil column eluted with hexane.

The solvent used was hexane (MCB, omnisolv extra low UV cutoff), purified to the extent that no fluorescence was recorded under our experimental conditions.

Results

Photoexcitation of the (halomethyl)naphthalenes with a 266-nm pulse induces the emission spectra and kinetics previously presented by Huppert et al.[7] Simultaneous excitation of the (halomethyl)naphthalenes at 266 nm and 355 nm was found to induce an intense orange emission. This emission from samples of 1-(chloromethyl)- and 1-(bromomethyl)naphthalene is shown in Figures 3A and 4A. These emission spectra are superimposable and exhibit two prominent bands located near 600 nm and a rather well-defined vibrational progression with ~600-cm^{-1} spacings.

Figures 5A and 6A, which are also identical with each other but distinctly different from Figures 3A and 4A, show the emissions emanating from 2-(bromomethyl)- and 2-(chloromethyl)naphthalene, respectively, after consecutive excitations with two laser pulses of different wavelengths. The band positions and vibrational progression spacings for 2-(halomethyl)-naphthalenes are practically the same as those observed for the 1-(halomethyl)naphthalenes. However, the relative band intensities differ drastically. The effect of varying the relative excitation times of the 266- and 355-nm pulses on the emission spectra is shown in Figures 3, 4, and 5. The spectra depicted in Figures 3A, 4A, and 5A were generated by initial excitation of the sample at 266 nm, followed 320 ps later by excitation at 355 nm. The spectra depicted in Figures 3B, 4B, and 5B resulted from excitation at 266 nm alone, while those shown in Figures 3C, 4C, and 5C resulted from excitation by only the 355-nm pulse. It is evident after examining these figures that the 355-nm excitation alone (Figures 3C, 4C, and 5C) fails to induce any detectable emission. Excitation at 266 nm alone results in rather weak spectra in contrast to consecutive 266- and 355-nm excitations which induced intense orange spectra that we assign to naphthylmethyl radicals in both cases. Excitation of 2-(chloromethyl)naphthalene, first at 299 nm with a 25-ps pulse followed by a 355-nm 25-ps pulse,

---

(13) Taken from ref 7.

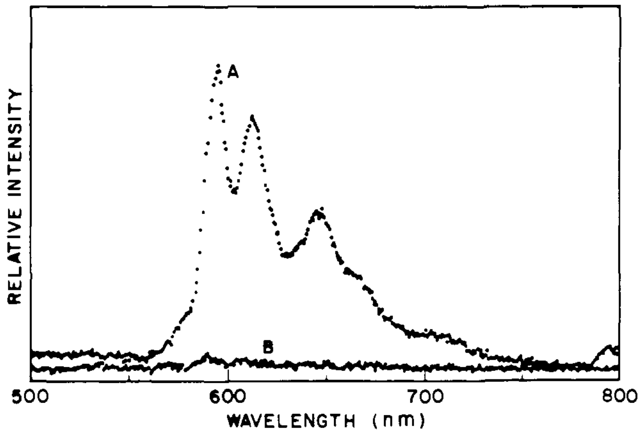


Figure 7. Emission spectra obtained for 1-(chloromethyl)-2-methylnaphthalene with (A) 355-nm excitation at 150 ps after 266-nm excitation and (B) 266-nm excitation only.

induces the same emission spectrum and intensity, within experimental error, as in the case of 266-nm excitation followed by 355-nm excitation (Figure 6). Results of variations in the delay time between the 266-nm and 355-nm pulses led us to believe that within the range of 10 ps to 40 ns the emission shape is independent of the time interval elapsed between the 266-nm excitation of the sample and the subsequent excitation of the radical at 355 nm. A decrease in emission intensity observed for spectra observed for 355-nm excitation at 40 ns after 266-nm excitation relative to other delay times is due to reduced 355-nm pulse energy resulting from the multiple reflections used to delay the 355-nm pulse relative to the 266-nm pulse, and also possibly to radical disappearance through reaction.

The photodissociation of 1-(chloromethyl)-2-methylnaphthalene was studied under identical conditions in order to establish that we can distinguish experimentally by our methods intermediates and radicals which are quite similar but not identical. As seen in Figure 7, the 1-(2-methylnaphthyl)methyl radical exhibits features similar to those of the 1- and 2-naphthylmethyl radicals. However, there is a highly evident change in the relative peak intensities of the 1-(2-methylnaphthyl)methyl radical which fall between the 1- and 2-naphthylmethyl radicals.

Lifetimes of the 1- and 2-naphthylmethyl radical emission in hexane at room temperature were measured with the streak camera to be 13 ± 3 ns and are shown in Figure 8. Extrapolation from the delay data indicates that the lifetime of the ground-state radical is longer than 40 ns under these experimental conditions.

To examine energy dissipation processes in the S_1 and S_2 states, we recorded the steady-state fluorescence spectra of 2-(chloromethyl)naphthalene and 2-chloronaphthalene after direct steady-state excitation to the S_1 and S_2 states. We observed that excitation of these two haloaromatics to the S_1 state at ~320 nm induced fluorescence spectra, emission intensities, and decay lifetimes which were very comparable. Excitation at 266 nm to the S_2 state, however, showed distinct changes in the observed fluorescence which, of course, also originates from the S_1 state. The fluorescence spectra (Figures 9A,B and 10) show maxima at ~350 nm. The ratio of emission intensities of the 2-chloronaphthalene vs. 2-(chloromethyl)naphthalene is found to be ~6. The excitation spectra in the range of 220 to 350 nm monitored at the emission wavelength of 360 nm for these two compounds are shown in Figure 9C,D. The fluorescence emitted from the S_1 states of 2-chloronaphthalene and 2-(chloromethyl)naphthalene, after excitation with a 266-nm picosecond pulse, is shown in Figure 10. The emission intensity ratio of 2-chloronaphthalene to 2-(chloromethyl)naphthalene is ~6 under both pulsed and steady-state modes of excitation. As will be further discussed, we believe that the decrease in the 2-(chloromethyl)naphthalene $S_1 \rightarrow S_0$ emission is the result of dissociation that occurs via the S_2 state.

Difference absorption spectra of the two isomeric naphthylmethyl radicals resulting from photodissociation of the corresponding (halomethyl)naphthalenes in hexane at 295 K have been recorded for times between 0 and 500 ps after excitation.

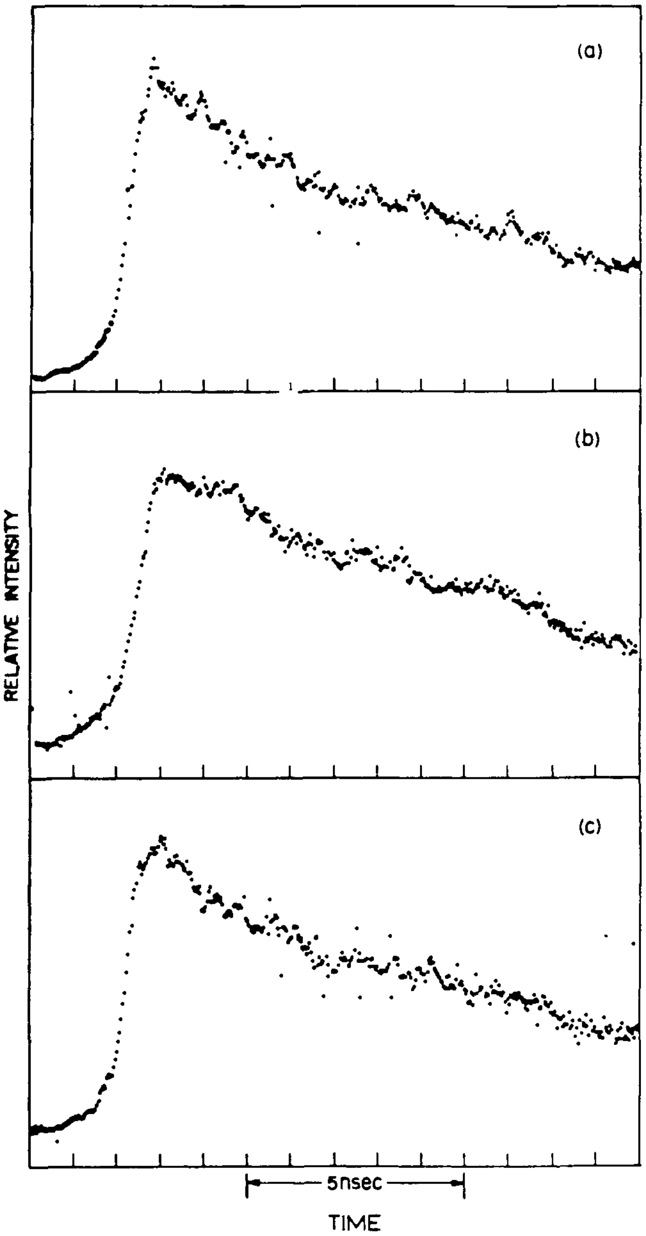


Figure 8. Time-resolved emission of the 1- and 2-naphthylmethyl radicals observed for wavelengths longer than 570 nm. 1-Naphthylmethyl emission induced by 355-nm excitation at (a) 60 ps and (b) 320 ps after 266-nm excitation of 1-(chloromethyl)naphthalene. (c) 2-Naphthylmethyl emission induced by 355-nm excitation at 60 ps after 266-nm excitation of 2-(bromomethyl)naphthalene. Note the 1- and 2-naphthylmethyl radicals exhibit similar fluorescence lifetimes of ~13 ns.

Transient absorption spectra of the 1-naphthylmethyl radical generated by excitation of 1-(bromomethyl)- and 1-(chloromethyl)naphthalene at 266-nm with a 25-ps, ~0.7-mJ laser pulse are shown in Figure 11a,b, respectively. Both series of spectra are identical in appearance and exhibit a broad absorption with a maximum near 365 nm. These spectra assigned to the 1-naphthylmethyl radical agree with the absorption spectrum previously reported by Porter et al.[9] and Schuster and co-workers.[10] For samples of 1-(bromomethyl)- and 1-(chloromethyl)-naphthalene in hexane, we observe that the radical spectrum appears immediately after excitation and maintains the same shape and intensity for times longer than 500 ps which is in good agreement with the immediate fluorescence formation and decay monitored by our picosecond emission system.

For samples of 2-(bromomethyl)- and 2-(chloromethyl)-naphthalene, the absorption spectra presented in the form of ΔA

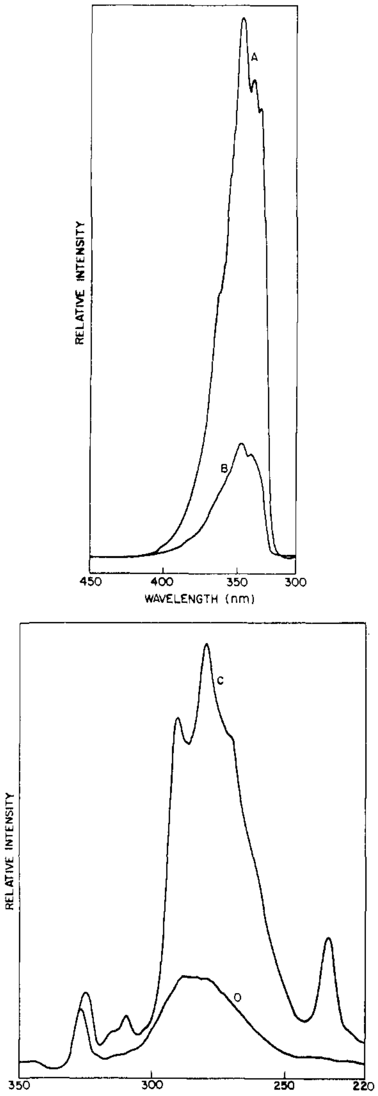


Figure 9. Steady-state emission spectra for excitation at 266 nm recorded with a Perkin-Elmer fluorimeter of (A) 2-chloronaphthalene and (B) 2-(chloromethyl)naphthalene. $S_1 \leftarrow S_0$ transition (300–330 nm) and $S_2 \leftarrow S_0$ transition (250–300 nm) of the steady-state excitation spectra of (C) 2-chloronaphthalene and (D) 2-(chloromethyl)naphthalene with fluorescence collected at 360 nm.

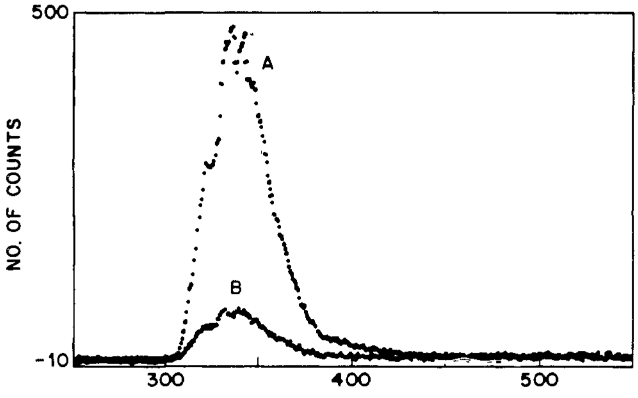


Figure 10. Emission spectra in the 300–400-nm region measured with a spectrometer–vidicon system for excitation of (A) 2-chloronaphthalene and (B) 2-(chloromethyl)naphthalene with a 25-ps fwhm, 266-nm laser pulse.

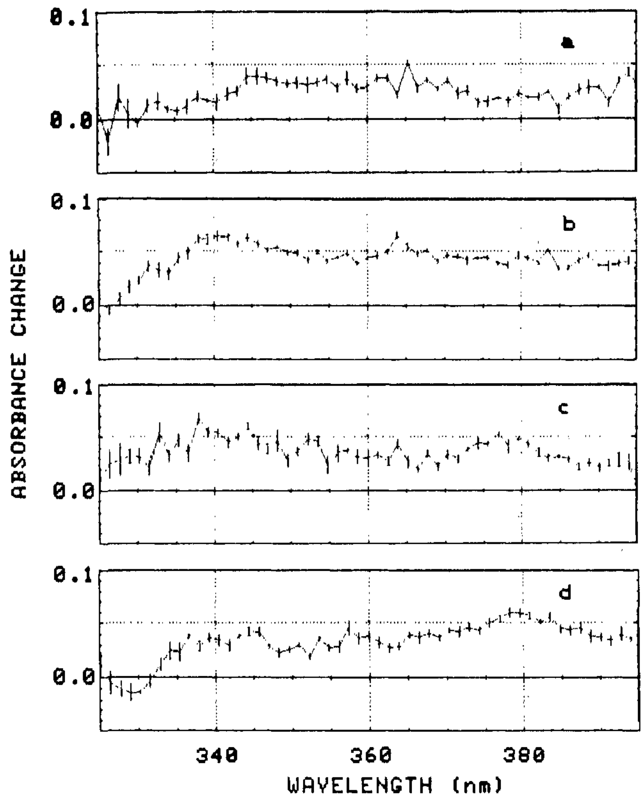


Figure 11. Difference absorption spectra recorded at 50 ps after 266-nm excitation of (a) 1-(bromomethyl)naphthalene, (b) 1-(chloromethyl)naphthalene, (c) 2-(bromomethyl)naphthalene, and (d) 2-(chloromethyl)naphthalene in hexane with a 25-ps laser pulse.

vs. λ and recorded at several delay times (Figures 11c,d) are identical in appearance featuring a broad absorption with a maximum near 380 nm that appears within the time duration of the 266-nm excitation pulse and persists for times longer than 500 ps. We assign these transient absorption spectra to the 2-naphthylmethyl radical. As expected, the spectra depicted in Figure 11c,d are different from those shown in Figure 11a,b. Unfortunately, the vibrational bands in the room-temperature absorption spectra are very broad and are not sufficiently resolved to permit comparison with the emission spectra.

Discussion

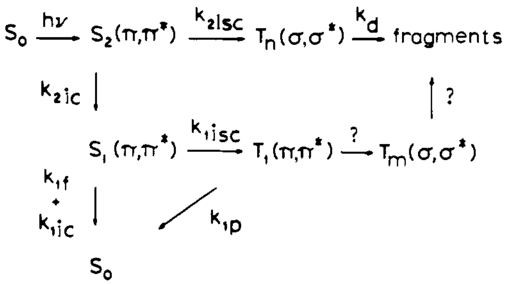
The dissociation mechanism of haloaromatics, specifically of halonaphthalenes and (halomethyl)naphthalenes, is found to be dependent on both the electronic state of excitation and on the substitution on the ring.

Excitation of the halonaphthalenes with 266 nm (ν = 37 594 cm^{-1}) populates the $S_2(\pi,\pi^*)$ state ($\nu_0 \approx$ 32 700 cm^{-1}) with ~5000 cm^{-1} of excess vibrational energy. Several channels of energy dissipation are available from this excited state. One possibility is direct radiative relaxation, that is, emission from the excited vibronic level to the ground state. Because of the high density of states expected for such large molecules, vibronic coupling to other excited states within the singlet manifold, particularly S_1, is expected to be very efficient; therefore, nonradiative decay from vibrationally excited S_2 to S_1 is expected to occur faster than $S_2 \rightarrow S_0$ emission. This assumption is confirmed by the absence of unrelaxed fluorescence from the photoselected state.

A second possible channel which appears to be very efficient for the haloaryls studied here is internal conversion from ν_n of S_2 to ν_0 of S_1. This ultrafast process is manifested by emission at room temperature from only the $\nu = 0$ state of S_1 observed for intact, excited haloaryl molecules.

A third process available for deactivation of the excited molecule is intersystem crossing (ISC). ISC may occur after internal conversion from ν_n of S_2 to ν_0 of S_1 so that T_1 of the haloaromatic is populated as is observed for 2-bromonaphthalene (see Figure 2). ISC is also feasible directly from S_2 to some higher energy T_n state or T_1 if the ISC rate is competitive with the internal conversion rate.

Scheme I



Finally, dissociation from an excited state within the singlet or triplet manifold, excluding, of course, such associative states as the $S_1(\pi,\pi^*)$, $S_2(\pi,\pi^*)$, and $T_1(\pi,\pi^*)$ states, would provide an effective means for excited-state energy dissipation.

Excitation of 1-chloro- and 1-bromonapthalene in solution at room temperature to a vibrationally excited level of the $S_2(\pi,\pi^*)$ state by a 266-nm picosecond pulse was found to result in rapid internal conversion to ν_0 of the $S_1(\pi,\pi^*)$ lowest excited singlet state which relaxes further radiatively to the ground state and nonradiatively by intersystem crossing to the $T_1(\pi,\pi^*)$ state. The lifetime of the $S_1 \rightarrow S_0$ emission was previously shown to be 2400 and 75 ps for 1-chloro- and 1-bromonaphthalene, respectively.[7] The lifetime of the triplet state was measured to be longer than 500 ps for both. In contrast, 1-(chloromethyl)- and 1-(bromomethyl)naphthalene excited under identical conditions as the 1-chloro- and 1-bromonaphthalenes to the $S_2(\pi,\pi^*)$ state with ~ 5000 cm^{-1} of excess energy display a different mode of relaxation manifested by the following: (a) the internal conversion to the $S_1(\pi,\pi^*)$ state is highly diminished; (b) new induced fluorescence appears immediately upon simultaneous excitation with 266- and 355-nm pulses that has a maximum near 600 nm (Figure 3–5) which decays with a 13 ± 3 ns emission lifetime; and (c) a broad transient absorption band centered near 370 nm is observed after excitation at 266 nm. The transient absorption and emission spectra resulting from excitation of the 1-(chloromethyl)- and 1-(bromomethyl)naphthalenes are identical with each other as are those resulting from the 2-(chloromethyl)- and 2-(bromomethyl)naphthalenes. However, as made clear by Figures 3–6 and 11, the spectra generated from the 1-(halomethyl)naphthalenes are distinctly different from those generated from the 2-(halomethyl)naphthalenes. This supports the proposal that these spectra correspond to the respective naphthylmethyl radicals. Therefore, the energy dissipation mechanism from the $S_2(\pi,\pi^*)$ state of the (halomethyl)naphthalenes is characterized by two channels—one that directly populates an upper triplet state which either may be dissociative itself or crosses to a dissociative level resulting in fragmentation and a second that leads to internal conversion to S_1 which decays radiatively to S_0 and nonradiatively by ISC to T_1. The decay channels from S_1 are the same in both halonaphthalenes and (halomethyl)naphthalenes. The fact that the $S_1 \rightarrow S_0$ fluorescence, induced by excitation to S_2, is $\sim$6 times more intense for halonaphthalenes than for (halomethyl)naphthalenes provides further supporting evidence for the proposed branched-channel mechanism for the relaxation of the (halomethyl)naphthalenes from S_2.

The amount of excess vibrational energy that the molecule possesses in the S_2 state does not appear to be an important factor governing the mechanism of energy dissipation. When 2-(chloromethyl)naphthalene was excited at 299 nm ($\nu = 33\,445$ cm^{-1}) to S_2 with only $\sim$750 cm^{-1} of excess vibrational energy, the same emission intensity, within experimental error, was observed for the photochemically generated 2-naphthylmethyl radical (see Figure 6) as with 266-nm excitation.

This mechanism is in agreement with the data of Bersohn who found that, in the gas phase, the rate of dissociation of haloaromatics from the S_2 state increased from chloro to bromo to iodo substituents because of the spin-orbit effect.[5] In the mechanism shown in Scheme I, the rates and therefore efficiency of the conversion and fragmentation are strongly dependent upon the identity of the halogen. This mechanism is further validated by Grieser and Thomas[2] who have shown that dissociation from the first excited singlet state is not efficient.

Quantum Yields. Utilizing our experimental data for the $S_1 \rightarrow S_0$ risetimes and the fluorescence intensities, we can estimate the intersystem crossing rates from the photoselected $S_2(\pi,\pi^*)$ state to the T_n state. The quantum yield ϕ of the $S_1 \rightarrow S_0$ fluorescence when excitation is performed into S_2 is given by

$$\phi_F \approx \frac{k_{1f}}{\sum k_{1i}} \frac{k_{2ic}}{\sum k_{2j}} \tag{1}$$

k_{1f} is the pure radiative rate from S_1 to S_0 and k_{2ic} the internal conversion rate from S_2 to S_1. $\sum k_{2j} \approx k_{2isc} + k_{2ic}$, $\sum k_{1i} \approx k_{1f} + k_{1ic} + k_{1isc}$ where ic refers to internal conversion and isc to intersystem crossing from either S_1 or S_2 designated by the subscript 1 or 2, respectively.

The fluorescence quantum yield ($S_1 \rightarrow S_0$) for 2-(chloromethyl)naphthalene and 2-chloronaphthalene is approximately the same when the S_1 state is selectively excited. When excited to S_2, $S_2 \rightarrow S_1$ internal conversion is found to occur in less than 10 ps, as indicated by a fluorescence risetime of <10 ps for both compounds. However, excitation to S_2 of 2-chloronaphthalene induces a fluorescence which is sixfold more intense than that of 2-(chloromethyl)naphthalene, and therefore the second term of eq 1 is six times larger for 2-chloronaphthalene than the corresponding term for 2-(chloromethyl)naphthalene. The ratio (R) of the fluorescence quantum yield for 2-chloro- and 2-(chloromethyl)naphthalene may be expressed as

$$R = \frac{\phi'}{\phi} = 6 = \frac{k_{2ic}'/\sum k_{2j}'}{k_{2ic}/\sum k_{2j}} \tag{2}$$

where the primed and unprimed values correspond to 2-chloronaphthalene and 2-(chloromethyl)naphthalene, respectively.

The internal conversion rate is most strongly influenced by the ring system which most significantly contributes to the vibronic coupling matrix elements and density of states. Since the ring skeleton is the same in both cases, 2-chloro- and 2-(chloromethyl)naphthalene, the internal conversion rates are assumed to be similar; therefore $k_{ic} = k_{ic}'$ and $R = (k_{2ic}' + k_{2isc}')/(k_{2ic} + k_{2isc})$. Considering the experimental data presented, we deduce that $k_{2isc}' < k_{2ic}'$ and $k_{2isc} > k_{2ic}$ and, therefore, that $R = k_{2isc}/k_{2ic} = 6$. In addition, we estimate that $k_{2ic} = 1/\tau_{2ic} > 10^{11}$ s^{-1}. Hence, $k_{2isc} > 6 \times 10^{11}$ s^{-1}.

The effect of the spin-orbit coupling elements, if calculated by the Z number only does not completely account for the observed chloro or bromo isc rates, although it is the predominant factor. The fact that substitution of the methyl group drastically enhances the dissociation rate of (halomethyl)arenes was shown previously by Huppert el al.,[7] Kelley et al.,[8] and Bersohn.[5] It is envisioned that dissociation is enhanced by the halomethyl substituent more than when the halogen is directly attached to the ring because excitation to the $S_2(\pi,\pi^*)$ state couples better with the C–C bond of the methyl rather than the C–Cl to promote crossing to the dissociative $T(\sigma,\sigma^*)$ state. Localization of the energy in the methyl group would result in immediate dissociation as is well established by the high rates ($k > 10^{12}$ s^{-1}) for methyl halides[5] and the high quantum yield for radical formation by photolysis of these halides. The fact that dissociation is not as efficient from the lower singlet state as from the S_2 state, although the intersystem crossing rate is fast, suggests that the dissociative level does not cross the lowest vibrational levels of the T_1 state or at least it is coupled much more weakly than with the upper triplet states. These data also provide a rather complete description of the spectroscopic states and kinetics of all states of the parent and radical species involved in the dissociation process of haloaromatics. In addition this dual channel mechanism which is based on these data and is consistent with previously published work should be generally applicable to haloaromatics and other substituted aromatic molecules.

Registry No. 1-Naphthylmethyl radical, 7419-60-5; 2-naphthylmethyl radical, 7419-61-6; 4,4′-dibromobiphenyl, 92-86-4; 4-bromobiphenyl, 92-66-0; 1-bromonaphthalene, 90-11-9; 1-bromo-4-methylnaphthalene, 6627-78-7; 1-bromo-2-methylnaphthalene, 2586-62-1; 2-bromonaphthalene, 580-13-2; 1-(chloromethyl)naphthalene, 86-52-2; 2-(bromomethyl)naphthalene, 939-26-4; 1-chloronaphthalene, 90-13-1; 2-chloronaphthalene, 91-58-7; 9-bromoanthracene, 1564-64-3; 9,10-dibromoanthracene, 523-27-3; 2-iodoanthracene, 22362-94-3; 9-iodoanthracene, 22362-86-3; 1-(bromomethyl)naphthalene, 3163-27-7; 2-(chloromethyl)naphthalene, 2506-41-4; 1-(chloromethyl)-2-methylnaphthalene, 6626-23-9.

Preceding Chemical Reaction Mechanisms in Homogeneous Electron Transfer Reactions. Mediated Electrochemical Reduction of Highly Reactive Benzylic Halides

Claude P. Andrieux,[1a] Andreas Merz,*[1b] Jean-Michel Saveant,*[1a] and Robert Tomahogh[1b]

Contribution from the Institut für Organische Chemie der Universität Regensburg, Universitätsstrasse 31, D-8400 Regensburg, West Germany, and the Laboratoire d'Electrochimie de l'Université de Paris 7-2, place Jussieu, 75 251 Paris Cedex 05, France.

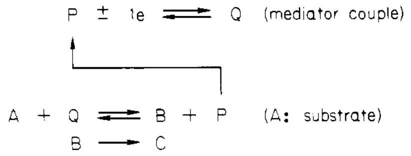
Received October 17, 1983

Abstract: The reduction of 9-chloro-9-[α-(9-fluorenylidene)benzyl]fluorene and 9-chloro-9-mesitylfluorene in acetonitrile can be homogeneously catalyzed by ferrocenes and organic reversible couples at potentials up to 2 V ahead of the direct electrochemical process leading to the corresponding persistent radicals, whereas the carbanions are obtained in the uncatalyzed reduction. In this very positive potential range, the catalytic efficiency does not depend upon the concentration and standard potential of the catalyst, suggesting the occurrence of a predissociation mechanism in which the primary step is the uphill formation of the carbocations which are then rapidly reduced into the radicals by the catalyst. The validity of this mechanism was proved by a detailed analysis of the kinetics as a function of the substrate and chloride ion concentration and the standard potential of the catalyst. This also led to the determination of the rate constants of the various steps. The occurrence of such a mechanism underscores the possible importance of predissociation steps in the reduction of aliphatic halides similar to S_N1 processes in nucleophilic substitution reactions.

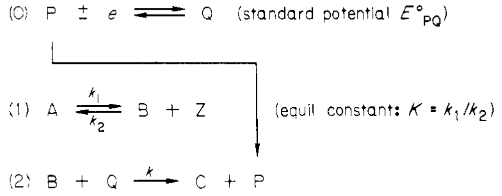
Kinetic studies of homogeneous electron transfer reactions generally involve one redox couple, both members of which are chemically stable, and a second reactant which may give rise to a chemically stable or unstable species on reduction or oxidation. The electrochemical analogues of these reaction schemes are simple electrode electron transfer reactions in the first case and "EC" (electrochemical–chemical) mechanisms in the second. One way of investigating homogeneous electron transfer reactions or reactions triggered by a prior electron transfer step is to use electrochemical techniques indirectly. The electron transfer reagent (mediator) is generated at the electrode surface under controlled potential conditions. It then transfers (or abstracts) one electron to (or from) the substrate, the reduction (or oxidation) product of which being either chemically stable or able to undergo a further chemical reaction. It is then observed that the current corresponding to the generation of the electron transfer reagent is increased by the addition of the substrate according to the reaction sequence in Scheme I.

The catalytic enhancement of the reduction (or oxidation) current of P is a function of the overall kinetics of the homogeneous reactions.[2] Means are thus provided for determining the rate constants of these reactions and/or the standard potential of the substrate couple A/B. Experimental investigation of several reactions have demonstrated the practical applicability of this approach. Illustrative examples have concerned the reductive cleavage of aryl halides,[3] of aryl sulfides,[4] and triarylhalogermane[5] as well as electron transfer induced conformational changes of bianthrone.[6] When the homogeneous electron transfer step is an outer-sphere reaction giving rise to "redox catalysis" as opposed to "chemical catalysis",[2] the essential reason why reduction (or oxidation) occurs in a potential region where the direct electrochemical process would be inefficient pertains to the three-dimensional distribution of the electron exchanging particles as opposed to the surface character of the electrochemical process.

Scheme I



Scheme II



In direct electrochemistry, reaction schemes involving dissociation of the substrate prior to electron transfer

$$A \rightleftarrows B + Z$$
$$B \pm 1e \rightleftarrows C$$

---

(1) (a) Universite de Paris 7. (b) Universität Regensburg.

(2) (a) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Electroanal. Chem.* **1978**, *87*, 39. (b) *Ibid.* **1978**, *87*, 55. (c) *Ibid.* **1978**, *88*, 43. (d) *Ibid.* **1980**, *113*, 1. (e) *Ibid.* **1980**, *113*, 19.

(3) (a) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 3431. (b) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; M'Halla, F.; Savéant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 3806.

(4) Griggio, L. *J. Electroanal. Chem.* **1982**, *140*, 155.

(5) Dabosi, G.; Martineau, M.; Simonet, J. *J. Electroanal. Chem.* **1982**, *139*, 211.

(6) (a) Evans, D. H.; Xie, N. *J. Electroanal. Chem.* **1982**, *133*, 367. (b) Evans, D. H.; Xie, N. *J. Am. Chem. Soc.* **1983**, *105*, 315.

0002-7863/84/1506-1957$01.50/0