- (21) Nibbering, N. M. M.; De Boer, Th. J.; Hofman, H. J. Recl. Trav. Chim. Pays-Bas 1965, 84, 481.
- (22) McEwen, K. L. J. Chem. Phys. 1960, 32, 1801.
- (23) Robin, M. B. Higher Excited States of Polyatomic Molecules; Academic Press: London, 1974, (Vol. 1), 1975 (Vol. 2), 1985 (Vol. 3).
  - (24) Roszak, S.; Kaufman, J. J. J. Chem. Phys. 1991, 94, 6030.
     (25) Sholeen, C. M.; Herm, R. R. J. Chem. Phys. 1976, 65, 5398.
- (25) Shoteen, C. M., Herni, R. K. J. Chem. Phys. 1970, 05, 5556. (26) Lobo, R. F. M.; Moutinho, A. M. C.; Lacmann, K.; Los, J. J. Chem.

Phys. 1991, 95, 166.

- M. J. Chem. Phys. 1975, 63, 3425.
  - (29) McKee, M. L. J. Am. Chem. Soc. 1986, 108, 5784.
  - (30) McKee, M. L. J. Phys. Chem. 1986, 90, 2335.
- (31) Larrieu, C.; Dargelos, A.; Chaillet, M. Chem. Phys. Lett. 1982, 91, 465.
- (32) Lahmani, F.; Lardeux, C.; Lavollee, M. J. Chem. Phys. 1980, 73, 1187.
  - (33) Lahmani, F.; Lardeux, C.; Solgadi, D. J. Chem. Phys. 1980, 73, 4433.

# Mechanism of the Formation of Transient Aromatic Radical Cations in Alcohols: Laser Flash Photolysis and Pulse Radiolysis Studies<sup>†</sup>

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A product of the reaction of  $SF_6$  with a solvated electron in an alcohol (presumably  $SF_5^{\circ}$ ) reacts with an aromatic solute molecule such as anthracene, perylene, naphthalene, or hexamethylbenzene to form aromatic radical cations. This reaction depends on both the ionization potential of the aromatic solute molecule and the polarity of the solvent. The rates of these reactions are (except for naphthalene) in the range of  $(1-10) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The reaction of the aromatic molecule (except for naphthalene) with  $SF_5^{\circ}$  appears to have two pathways, one of which leads to the radical cation and a second that forms an undetermined product.

#### Introduction

Transient aromatic radical cations, AH\*+, have been observed in nonpolar<sup>1</sup> and polar<sup>2</sup> solvents upon laser excitation at room temperature. The generation of AH<sup>•+</sup> is rapid and exhibits a biphotonic character<sup>1,2</sup> from the consecutive two-photon ionization. In pulse radiolysis studies, AH<sup>•+</sup> was observed in cyclohexane,<sup>2</sup> benzonitrile,<sup>3</sup> and dichloromethane<sup>4</sup> solutions and the formation of AH<sup>++</sup> was interpreted to result from charge transfer from the solvent radical cation to the aromatic molecule. Aromatic radical cations can also be produced by excitation of the charge-transfer donor-acceptor complex.<sup>5</sup> Recently, we have carried out laser flash photolysis and pulse radiolysis studies on solutions of several aromatic molecules in alcohols. As in other solvents, two-photon ionization of aromatic molecules was observed in laser flash photolysis, yielding prompt aromatic radical cations. However, in alcohol solutions saturated with the widely-used electron scavenger  $SF_6$ , an unusual slow formation of aromatic radical cation on a microsecond time scale was observed in both laser flash photolysis and pulse radiolysis. This slow formation reveals a novel mechanism for the creation of aromatic radical cations in alcohols and provides a convenient method to generate the aromatic radical cations and to study their reaction kinetics in liquid alcohols. Here we report the experimental results and discuss the reaction mechanism of this formation of aromatic radical cations in alcohol solutions.

#### **Experimental Section**

**Materials.** Aromatic compounds were obtained in the highest purity available from Aldrich and used as received. Methanol and 2-propanol were Burdick & Jackson high-purity grade. Argon and oxygen gases (UHP grade) were from Scott Speciality Gases, and SF<sub>6</sub> (99.99%) was from Matheson Gas Products. The alcohols were saturated with these gases by bubbling at 1-atm pressure. Typical concentrations for saturation at 1 atm are >0.01 M. For example, the solubility of SF<sub>6</sub> in methanol is 0.022 M and in ethanol is 0.066 M,<sup>6</sup> and the solubility of oxygen in methanol or 2-propanol is 0.010 M.<sup>7</sup> In some cases, different concentrations of the gaseous solute were obtained by mixing, in the absence of a vapor phase, two solutions containing the same concentration of the aromatic molecule and saturated with different gases. These operations were done using a syringe technique.

Laser Flash Photolysis. The excitation lasers used in this experiment were a Lumonics HyperEx-400 and a Questek 2440 excimer laser. The pulse width is  $\sim 20$  ns (FWHM), and the maximum output power is  $\sim 100 \text{ mJ/pulse}$  or  $\sim 5 \text{ MW}$  (for both 248 and 308 nm). The incident laser integration in the reaction cell was  $\sim 60 \text{ (mJ/pulse)/cm}^2$  or  $\sim 3 \text{ MW/cm}^2$ . The transient optical absorption was measured by a kinetic spectrophotometer, the major components of which were a pulsed 75-W Xe-arc lamp, a SPEX Minimate monochromator, and a Hamamatsu R1913 photomultiplier. The conductivity signal produced by photoionization was measured in a kinetic dc conductivity experimental setup that has been described previously.<sup>8,9</sup> A Tektronix digitizing signal analyzer, DSA 601, with a sampling rate of up to 1 GHz, was used to record transient signals. The data acquisition was controlled by a National Instrument's LABVIEW program installed on a Macintosh IIx computer. For most experiments, 8-16 data acquisition cycles were taken and averaged to increase the signal-to-noise ratio. Each data acquisition cycle includes baseline correction, emission subtraction, and Xe lamp fluctuation elimination. The concentrations of anthracene were adjusted to have an optical density at the laser excitation wavelength of 0.8-1.0 in a 1-cm cell. To avoid the depletion of starting materials and accumulation of possible photolysis products, the spectra were taken using a sample flow system. During the measurement of absorption, glass color filters (Corning Glass Works) were used to avoid the second harmonic absorptions. The slits on the monochromator were adjusted to be less than 0.03 mm to obtain resolution of better than  $\pm 1$  nm.

**Pulse Radiolysis.** Pulses of 20-MeV electrons were obtained from the Argonne National Laboratory (Chemistry Division) linear accelerator. The pulse duration used was 4 ns (FWHM), and doses per pulse ranged from 2 to 8 krad. Samples were irradiated in cells with suprasil windows, having an optical path

 <sup>(27)</sup> Fluendy, M. A. D.; Lunt, S. Mol. Phys. 1983, 49, 1007.
 (28) Gillispie, G. D.; Khan, A. U.; Wahl, A. U.; Hosteny, R. P.; Krauss,

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Figure 1. (A) Transient absorption spectra observed in  $5 \times 10^{-4}$  M anthracene in methanol solution saturated with SF<sub>6</sub> in 308-nm laser flash photolysis. (B) Time profile of transient absorption, measured at 716 nm. The solid line is the pseudo-first-order fit. The dependence of these pseudo-first-order rate constants on anthracene concentration is shown in the insert.

length of 2 cm, with the analyzing light beam passing through the cell in a direction opposite to that of the electron beam. The system for measurement of transient absorptivity consisted of a 75-W Xe lamp that was pulsed during the observation period, an optical system to transport the light to an interference filter (9-10-nm bandwidth) at the desired wavelength, a photodiode (CD-10) as a detector, and a Tektronix 7912 digitizer. Data from the digitizer were averaged by a computer.

#### **Results and Discussion**

Transient absorption spectra observed in 308-nm laser flash photolysis of  $5 \times 10^{-4}$  M anthracene in SF<sub>6</sub>-saturated methanol are shown in Figure 1A. The time profile of the 716-nm band is shown in Figure 1B. At early times, the spectrum has two maxima, at 600 and 716 nm (see spectrum recorded at 20 ns in Figure 1A). From previous work,<sup>10</sup> the 600-nm band is assigned to the excited singlet state of anthracene. The 716-nm species decays rapidly at early times (see the initial spike in Figure 1B). At later times, the 716-nm absorbance increases and reaches a maximum at approximately 2  $\mu$ s. In 2-propanol solutions, similar results were obtained and the absorption maximum is slightly shifted to 718 nm.

The absorption bands with maxima at 716 nm in methanol and 718 nm in 2-propanol obtained at early time are assigned to anthracene radical cation  $(An^{+})$  formed by direct two-photon ionization:

$$An \xrightarrow{2h\nu} An^{*+} + e_{sol}^{-}$$
(1)

$$e^{-} \xrightarrow{\text{ROH}} e_{\text{sol}}^{-}$$
 (2)

Here ROH is the alcohol and  $e_{sol}^-$  is the solvated electron (An<sup>++</sup> will also be solvated by the polar solvent; for simplification, An<sup>++</sup> will be used in this paper to designate both the unsolvated and solvated cations of anthracene). The initially formed An<sup>++</sup> will



Figure 2. Absorption spectra and time profile of transients observed in pulse radiolysis of  $SF_6$ -saturated 2-propanol solution containing  $5 \times 10^{-4}$  M anthracene. The radiation dose was 1.8 krad/pulse.

decay rapidly by geminate ion-pair recombination followed by slow bulk recombination of free ions (second-order reaction) and reaction with anthracene to form anthracene dimer radical cations (pseudo-first-order reaction).<sup>3</sup>

The assignment of the species responsible for the peak at 720 nm in the 20-ns spectrum in Figure 1A to anthracene radical cations is consistent with the peak positions in previous experiments. In liquid alkanes, we have observed the absorption of An<sup>\*+</sup> at 730 nm by two-photon ionization.<sup>1</sup> In *s*-BuCl glass by  $\gamma$ -radiolysis, Shida has reported a maximum of 726 nm for An<sup>\*+</sup>.<sup>11</sup> Yamamoto et al. observed An<sup>\*+</sup> with a maximum at 724 nm in liquid dichloromethane by pulse radiolysis.<sup>4</sup> Delaire et al. observed An<sup>\*+</sup> at 720 nm in acetonitrile by laser flash photolysis.<sup>2</sup> In these cases, the observed blue shift in polar solvents compared with nonpolar solvents can be explained by the solvation of ions.

Both the early and late spectral peaks at 720 nm were observed to be scavenged by triethylamine, which is an efficient agent for capturing positive charge via electron or proton transfer. A similar slow formation in SF<sub>6</sub>-saturated alcohols was also observed in our pulse radiolysis experiments. The absorption spectra and time profiles observed in pulse radiolysis of SF<sub>6</sub>-saturated 2-propanol or methanol solution containing anthracene, hexamethylbenzene (HMB), and perylene (Pe) are shown in Figures 2–4. In all these cases, the slow formation can be fitted with first-order kinetics.

The slowly forming species observed in both laser flash photolysis and pulse radiolysis is assigned to aromatic radical cations  $AH^{+}$ . (This notation is not intended to specify the location of the unpaired electron). Their generation is proposed to result from one-electron oxidation of aromatic molecules by oxidizing species generated through dissociation of  $SF_6^-$ :

$$SF_6 + e_{sol} \rightarrow SF_6^{\bullet-}$$
 (3)

$$SF_6^{-} \rightarrow SF_5^{-} + F^-$$
 (4)

$$SF_5^* + AH \rightarrow SF_5^{*-} + AH^{*+}$$
 (5)

The electrons in reaction 3 are produced by the two-photon ionization of solute in laser flash photolysis (reaction 1) and by the ionization of the solvent in pulse radiolysis:

$$ROH \rightarrow ROH^{++} + e^{-}$$
 (6)

The lack of initial spike in the pulse radiolysis results is due to the absence of appreciable direct ionization of the aromatic molecule. It also implies that there is no substantial charge transfer from ROH<sup>\*+</sup> to the aromatic solutes at early times, which is reasonable because ROH<sup>\*+</sup> radical cations are generally acknowledged to be short-lived due to rapid proton transfer to the solvent. In addition to the reactions shown, AH<sup>\*+</sup> reacts by recombination with negative ions and possibly by reaction with impurities. The solid lines in Figure 4B represent the least-squares fits of the data using first-order formation and second-order decay kinetics where the first-order rate constant, the second-order rate constant, and the maximum absorption if there were no decay were fit. The decay is much slower than the formation, so it has little effect on the derived formation constant; approximately the same value of the formation constant would be obtained if a first-order



Figure 3. (A) Absorption spectra of transients observed in pulse radiolysis of methanol solution containing 0.01 M hexamethylbenzene saturated with SF<sub>6</sub>. The radiation dose was 7.6 krad/pulse. (B) Time profile of transient absorption at 500 nm. Two different concentrations of HMB were tested.

formation, first-order decay mechanism were used. The decay is predominantly second order due to the recombination of ions, but first-order processes (e.g., reaction of AH<sup>\*+</sup> with impurities) may also contribute, and thus, the fitted second-order constant has neither chemical nor numerical significance.

In other solvents, similar reactions of  $SF_5^*$  have been observed. Asmus and Fendler have shown that the  $SF_5^*$  radical in water oxidizes the solvent to form the OH radical and  $H_3O^+$ , <sup>12</sup> and Bansal and Fessenden<sup>13</sup> have observed the oxidation of phenol and hydroquinone by  $SF_5^*$  in water and the oxidation of  $Br^-$  by  $SF_5^*$  in methanol. The reported gas-phase electron affinity (EA) of  $SF_5^*$  is 2.8 eV.<sup>14</sup>

In this mechanism, the pseudo-first-order formation constant for  $AH^{*+}$ ,  $k_f$ , is  $k_5[AH]$ . To test the mechanism, the following three tests were carried out.

(1) Since reaction 5 creates charged species from neutral species, an increase in the conductivity of the solution should result and this is observed. Direct-current conductivity measurements in solutions saturated with SF<sub>6</sub>, argon, and  $O_2$  were carried out by laser flash photolysis. The time profiles of conductivity signals in 2-propanol solution are shown in Figure 5B. Consistent with the optical measurements (shown in Figure 5A), the conductivity signal increases slowly after an initial sharp spike in SF<sub>6</sub>-saturated solution. Figure 6 shows the laser intensity dependence of the initial spike and the final maximum of the conductivity signals. The observed curvature indicates that a multiphoton process is responsible for both the fast and slow signals. In argon- and  $O_2$ -saturated solutions, only fast buildup and slow decay of signals was observed in both optical and conductivity experiments.

(2) If AH<sup>\*+</sup> is formed by reaction 5, the formation should be a pseudo-first-order reaction and the pseudo-first-order rate of formation,  $k_{\rm f}$ , should depend on the aromatic molecule concentration. The dependence of  $k_{\rm f}$  on anthracene concentration is plotted in the insert of Figure 1B for a methanol solution. This measurement was carried out using laser flash photolysis. A straight line is obtained from which the bimolecular rate constant of reaction 5 is derived as  $8 \times 10^9 \,{\rm M}^{-1} \,{\rm s}^{-1}$ . The same bimolecular



Figure 4. (A) Absorption spectra of transients observed in pulse radiolysis of 2-propanol solution containing  $2 \times 10^{-4}$  M perylene saturated with SF<sub>6</sub>. The dose was 2.3 krad/pulse. Absorbances at different times are normalized to demonstrate that only perylene radical cation is being observed in this wavelength region. Open square, 0.15  $\mu$ s, ×4.65; open circle, 0.34  $\mu$ s, ×2.22; filled triangle, 2  $\mu$ s, × 1.03; cross, 4.3  $\mu$ s. (B) Time profiles of transient absorption at 540 nm observed with two different concentrations of perylene. The solid lines are the fittings to the kinetics of first-order formation and second-order decay.

rate constant was obtained from similar pulse radiolysis experiments on anthracene in 2-propanol. In the case of perylene (Figure 3B) and HMB (Figure 4B), a similar dependence of  $k_f$  on the aromatic molecule concentration was also observed. A summary of these observations is given in the last two columns of Table I.

(3) Since in most cases [AH]  $\gg$  [SF<sub>5</sub><sup>•</sup>],  $k_f$  will mainly depend on [AH] (however, an exception is discussed below for naphthalene solutions). Variation of [SF<sub>6</sub>] should only influence the total yield of  $[AH^{*+}]$  but not  $k_f$ . The variation in yield will depend on how much the reaction of SF<sub>6</sub> with the electron interferes with the recombination of the geminate ions. The independence of  $k_{\rm f}$  on SF<sub>6</sub> was tested in flash photolysis of methanol solution containing anthracene. The time profiles under different conditions are shown on Figure 7. When  $[SF_6]$  was reduced to 50% (keeping the solution oxygen free),  $k_{\rm f}$  was unchanged but the maximum of [An<sup>•+</sup>] was reduced by approximately 10%. Oxygen was found to reduce the secondary formation of radical cations. In 50% SF<sub>6</sub> + 50% O<sub>2</sub> solution, the maximum of An<sup>•+</sup> was reduced to 36% and  $k_{\rm f}$  was doubled. This is interpreted as scavenging of the oxidizing radicals by oxygen. In oxygen-saturated solution, no secondary formation of An\*+ was found. The effect of variation of  $[SF_6]$  was also tested in the perylene solution by pulse radiolysis; no effect on the kinetics was found.

For naphthalene in methanol,  $k_f$  was found *not* to depend on [naphthalene]. Significant naphthalene radical cation absorbance could be obtained only at relatively high [naphthalene], i.e., 0.005–0.01 M. In this case, the rate-determining step for SF<sub>5</sub><sup>•</sup> disappearance must be some other reaction (perhaps a reaction with the solvent). This is supported by the fact that the transient absorbance approximately doubles in going from 0.005 to 0.01 M naphthalene. This behavior is contrary to that observed for

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TABLE I: G Values and Rate Constants Derived from the Formation of Aromatic Radical Cations in the Pulse Radiolysis of SF<sub>6</sub>-Saturated 2-Propanol and Methanol Solutions<sup>a</sup>

solute	IP, eV	λ <sub>max</sub> , nm	$\mathbf{M}^{-1} \mathbf{cm}^{-1}$	G, per 100 eV		$10^{-9}(k_5 + k_{11}), M^{-1} s^{-1}$	
				2-propanol	methanol	2-propanol	methanol
pervlene	7.0	540	$3.5 \times 10^{4b}$	1.74		4	
anthracene	7.5	720	$1.2 \times 10^{-4c}$	1.72		8	81
hexamethylbenzene	7.9	500	$2.33 \times 10^{3 d}$	0.56	4.26	2	1.7
naphthalene	8.1	690	$2.70 \times 10^{3}$ e	<0.1	0.44 <sup>ƒ</sup>		

<sup>a</sup>G value is the measured yield of radical cations in number per 100 eV of absorbed radiation energy. IP is the gas-phase ionization potential of the aromatic molecule from ref 15.  $\lambda_{max}$  is the measured maximum of the transient absorption spectrum of solute radical cations.  $\epsilon$  is the molar extinction coefficient of the solute radical cations from the literature. Where no number is entered for G or the rate constant, the measurements have not been carried out. <sup>b</sup> From ref 19. The measurement was carried out in acetonitrile solution by laser flash photolysis. <sup>c</sup> From ref 20. The measurement was carried out in 1,2-dichloroethane solution by pulse radiolysis. A similar result ( $\epsilon_{710mm} = 1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) was obtained in laser flash photolysis of methanol solution by Borovkova and co-workers.<sup>21</sup> <sup>d</sup> Shida has reported  $\epsilon_{498nm} = 3100 \text{ M}^{-1} \text{ cm}^{-1}$  for HMB<sup>+\*</sup> in Freon matrices at 77 K (ref 11, p 47). The width at half-amplitude of the absorption band obtained in our pulse radiolysis is 33% wider than that obtained at low temperature by Shida. Using to the same oscillator strength of the absorption band in these two cases, we obtain  $\epsilon_{500nm} = 2.33 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  for HMB<sup>+\*</sup> in 2-propanol. <sup>e</sup> From ref 22. The measurement was carried out in methanol solution by laser flash photolysis. A similar result ( $\epsilon_{685nm} = 2.97 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) was obtained at room temperature by Gschwind and Haselbach.<sup>23</sup> <sup>f</sup> This value was obtained at 0.01 M naphthalene; the value is approximately proportional to [N]. <sup>e</sup> Measured by laser flash photolysis.



Figure 5. (A) Time profiles of transient absorption observed in 2propanol solution containing  $5 \times 10^{-4}$  M anthracene saturated with argon, O<sub>2</sub>, and SF<sub>6</sub>. (B) Time profiles of transient dc-conductivity signals observed in the same conditions. The signals in both cases have been normalized to have the same maximum value during the laser pulse for easy comparison.



Figure 6. Dependence of conductivity signal on laser beam intensities observed in SF<sub>6</sub>-saturated 2-propanol solution containing  $5 \times 10^{-4}$  M anthracene in laser flash photolysis. The solid line is the least-squares fit of the signal at 800 ns and is of the form  $3.5 \times 10^{-5}$  [laser power]<sup>1.63</sup>.



Figure 7. Dependence of the time profiles of the 716-nm transient absorption observed in SF<sub>6</sub>- and O<sub>2</sub>-saturated methanol solutions containing  $5 \times 10^{-4}$  M anthracene and for  $5 \times 10^{-4}$  M anthracene solutions made up by mixing equal volumes of the appropriate solutions saturated with Ar, SF<sub>6</sub>, and O<sub>2</sub>. Measurements were made using laser flash photolysis at 308 nm.

the other aromatic solutes in 2-propanol or methanol, where the transient absorbance depended only weakly on the concentration of the aromatic molecule.

The experiments discussed above indicate that the mechanism given by reactions 3-5 provides a reasonable explanation of the experimental results.

In pulse radiolysis, Yamamoto and co-workers<sup>4</sup> have observed a similar slow formation of radical cations of anthracene by adding  $Ph_2IPF_6$  or  $Ph_2IAsF_6$  (Ph = phenyl) to dichloromethane solutions. They interpreted this slow formation of aromatic radical cations as the result of charge transfer from  $CH_2Cl^+$ , which was created from oxidation of  $CH_2Cl^+$  by  $Ph_2IPF_6$  or  $Ph_2IAsF_6$ . We suggest that oxidation of anthracene by  $Ph_2IPF_5^+$ , which is formed by scavenging electron and subsequent ejection of an  $F^-$ , is a possible alternative mechanism.

Because of the relatively large ratio of  $[^{3}AH]/[AH^{++}]$ , which exists in general because of the two-photon nature of the ionization and intersystem crossing from AH in the laser photolysis experiments, the possibility of involvement of the excited triplet state of the aromatic molecules, <sup>3</sup>AH, in the slow formation of AH<sup>++</sup> was tested and was ruled out for the following reasons: (a) In the laser flash photolysis of anthracene in methanol, the first-order formation rate of An<sup>++</sup> is 10 times faster than the first-order decay rate we observe for <sup>3</sup>An, and the decay rate of <sup>3</sup>An does not depend on anthracene concentration. (b) In the pulse radiolysis experiments reported here, the <sup>3</sup>AH produced from geminate ion-pair recombination is significantly smaller than the high concentration of AH<sup>++</sup> observed. (c) The reaction of transient oxidizing species with <sup>3</sup>AH would be a bimolecular reaction, and the formation rate of AH<sup>++</sup> should depend on the radiation dose or the number of photons absorbed per unit volume. This is not observed. Therefore, a reaction between an oxidizing species and a ground-state aromatic molecule is indicated.

Enough information to make an estimate of the energetic feasibility of reaction 5 is available. Using anthracene as an example, we present two possible schemes below to explain the results:

### SCHEME I

$$\mathbf{RX}^{\bullet} + \mathbf{An} \rightarrow \mathbf{RX}^{-} + \mathbf{An}^{\bullet+}$$
(7)

where  $RX^{\bullet}$  is an oxidizing radical such as  $SF_5^{\bullet}$ . The enthalpy change of this reaction can be approximated by

$$\Delta H = IP_{An} - EA_{RX} + \Delta H_{sol} + \Delta H_{sol}^{-}$$
(8)

where  $IP_{An}$  is the ionization potential of anthracene,  $EA_{RX^*}$  is the electron affinity of RX<sup>\*</sup>, and  $\Delta H_{sol}^+$  and  $\Delta H_{sol}^-$  are the energies released by solvation of An<sup>\*+</sup> and RX<sup>-</sup> (the normal convention of a negative value meaning energy is released is used). The gas-phase ionization potential of anthracene is 7.5 eV.<sup>15</sup> The Gibbs solvation free energy of An<sup>\*+</sup> ( $\Delta G_{solv}^+$ ) in acetonitrile is obtained by Parker<sup>16</sup> as -1.94 eV. Neglecting the enetropy effect, one can use  $\Delta H_{sol}^+ = -1.94$  eV. If SF<sub>5</sub><sup>\*</sup> is the oxidizing species (EA = 2.8 eV), for energetic feasibility ( $\Delta H \leq 0$ ), we must have  $\Delta H_{sol}^- \leq 2.76$  eV. Such a value for the solvation energy of SF<sub>5</sub><sup>-</sup> seems reasonable because the solvation energy will increase with decreasing ionic radius and we assume the diameter of SF<sub>5</sub><sup>\*-</sup> is smaller than that of An<sup>\*+</sup>.

## SCHEME II

$$\mathbf{RX}^* + \mathbf{An} \rightarrow \mathbf{R} + \mathbf{An}^{*+} + \mathbf{X}^- \tag{9}$$

This scheme suggests simultaneous electron transfer and dissociation. The enthalpy change of this reaction can be written as

$$\Delta H = IP_{An} + BE_{RX} - EA_X + \Delta H_{sol}^+ + \Delta H_{sol}^- \quad (10)$$

where BE<sub>RX</sub> is the bond energy of R-X and EA<sub>X</sub> is the electron affinity of X. The bond energy of a free radical is usually smaller than that of the corresponding molecule. We can assume that the bond energies of  ${}^{\circ}SF_{4}$ -F are less than 2 eV. The reported value of electron affinity of F is 3.4 eV.<sup>14</sup> Therefore, the solvation energy of F<sup>-</sup> must be  $\leq 4.2$  eV to obtain  $\Delta H \leq 0$ . This value is close to the reported solvation enthalpy of F<sup>-</sup> in water (-4.93 eV<sup>17</sup>).

Either of the two schemes can explain reasonably well the anthracene results. The solvation energies for the cation radicals of perylene and HMB are not available in alcohols. Because it is larger, Pe<sup>++</sup> probably has a less negative  $\Delta H_{sol}^+$  than An<sup>++</sup>; similarly HMB<sup>++</sup> would be expected to have a more negative  $\Delta H_{sol}^+$  than An<sup>++</sup>. The ionization potentials of perylene (7.0 eV) and HMB (7.9 eV) are within ±0.5 eV of that of anthracene. The energetic feasibility of reaction 5 for perylene and HMB can also be reasonably explained by the same schemes.

From eqs 8 and 10, it is clear that the energetic feasibility of reaction 5 will strongly depend on the ionization potentials of the aromatic molecules, the electron affinities of the oxidizers, and the polarities of the solvents (which influence the solvation energies). The G values of  $AH^{*+}$  will depend on the degree of exothermicity if the reaction of  $SF_5^*$  with the aromatic molecule has two outcomes, one not leading to  $AH^{*+}$  as shown in reaction 11a, or if there is a significant competing pathway (not involving the aromatic solute) for the disappearance of RX<sup>\*</sup>, as shown in eq 11b.

$$SF_5 + AH \rightarrow product$$
 (11a)

$$SF_5 + alcohol \rightarrow product$$
 (11b)

Table I shows G values obtained in the pulse radiolysis of aromatic molecules of different ionization potentials in 2-propanol and the rate constant  $k_5 + k_{11a}$  for the formation of the aromatic radical cation. The G values are clearly higher for solutes where the excess energy is greater, i.e., lower ionization potentials.<sup>18</sup> The experimental results for perylene, anthracene, and hexamethylbenzene show no significant dependence of  $AH^{*+}$  yield on [AH]; the experimentally observed changes in  $G(AH^{*+})$  for the three aromatic molecules can therefore be explained by a branching described by reactions 5 and 11a. However, for naphthalene, a significant concentration dependence is observed; therefore, the disappearance of SF<sub>5</sub><sup>\*</sup> by reactions not involving AH (reaction 11b) apparently becomes dominant.

The results for hexamethylbenzene show that the yield from reaction 5 depends strongly on the polarity of the solvent. There is approximately 8 times more HMB<sup>\*+</sup> formed in methanol (dielectric constant of  $32.66^{24}$ ) than in 2-propanol (dielectric constant of  $19.92^{24}$ ) (see Table I). While the yield of SF<sub>5</sub><sup>\*</sup> may not be exactly the same in methanol and 2-propanol, nowhere near a factor of 8 difference is expected. Similarly, in laser flash photolysis, we observed the absorbance at 720 nm due to An<sup>++</sup> to be twice as large in methanol as in 2-propanol. This dependence on solvent polarity is consistent with the charge-formation mechanism given by reactions 3–5 and the energetics as described by eqs 8 and 10.

#### Summary

Generation of transient aromatic radical cations through one-electron oxidation of aromatic molecules was observed in SF<sub>6</sub>-saturated 2-propanol and methanol solutions by laser flash photolysis and pulse radiolysis. The oxidizing species is suggested to be SF<sub>5</sub><sup>•</sup>, which is formed by dissociation of SF<sub>6</sub><sup>-.</sup>. The efficiency of the oxidation of aromatic molecules depends strongly on the ionization potentials of the aromatic molecules and the polarities of the solvents. The yield of transient oxidizer also depends on the initial yield of electrons, i.e., the efficiency of the initial photoionization of the aromatic molecules. SF<sub>5</sub><sup>•</sup> appears to react with the aromatic molecule via two different pathways, one of which forms the cation radical and the other of which leads to different, as yet unidentified, products.

The study of these dependences will reveal more details of primary and secondary processes initiated by the UV radiation or ionizing radiation in the condensed phase. The formation of long-lived aromatic radical cations in alcohols by laser flash photolysis and pulse radiolysis also provides a convenient method to generate the aromatic radical cations and to study their kinetics in the liquid phase at room temperature. A systematic investigation of the formation of aromatic radical cations by laser flash photolysis and pulse radiolysis with different aromatic molecules and different electron scavengers in different solvents is continuing in this laboratory. These studies will make it possible to delineate the energy dependence of these reactions and to assign the role of the solvent in the reactions.

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**Registry No.** SF<sub>6</sub>, 2551-62-4; perylene, 198-55-0; anthracene, 120-12-7; hexamethylbenzene, 87-85-4; naphthalene, 91-20-3; 2-propanol, 67-63-0; methanol, 67-56-1; argon, 7440-37-1; oxygen, 7782-44-7.

#### **References and Notes**

(1) Liu, A.; Sauer, M. C., Jr.; Loffredo, D.; Trifunac, A. D. J. Photochem. Photobiol. A 1992, 67, 197.

(2) Delaire, J. A.; Castella, M.; Faure, J.; Vanderauwera, P.; De Schryver, F. C. Nouv. J. Chim. 1984, 231.

(3) Kira, A.; Arai, S.; Imamura, M. J. Phys. Chem. 1972, 76, 1119.
(4) Yamamoto, Y.; Ma, X.-H.; Hayashi, K. J. Phys. Chem. 1987, 91, 5343.

(5) (a) Masnovi, J. M.; Seddon, E. A.; Kochi, J. K. Can. J. Chem. 1984,
62, 2552. (b) Masnovi, J. M.; Kochi, J. K. J. Am. Chem. Soc. 1985, 107,
7880. (c) Masnovi, J. M.; Kochi, J. K.; Hilinski, E. F.; Rentzepis, P. M. J.
Am. Chem. Soc. 1986, 108, 1126.

(6) Rzad, S. J.; Fendler, J. H. J. Chem. Phys. 1970, 52, 5395.

(7) Battino, R.; Rettich, T. R.; Tominaga, Ť. J. Phys. Chem. Ref. Data 1983, 12, 163.

(8) Sauer, M. C., Jr.; Schmidt, K. H.; Liu, A. J. Phys. Chem. 1987, 91, 4836.

(9) Schmidt, K. H.; Sauer, M. C., Jr.; Lu, Y.; Liu, A. J. Phys. Chem. 1990, 94, 244.

(10) Bebelaar, D. Chem. Phys. 1974, 3, 206.

(11) Shida, T. Electronic Absorption Spectra of Radical Ions; Elsevier: New York, 1988.

 (12) Asmus, K.-D.; Fendler, J. H. J. Phys. Chem. 1968, 72, 4285.
 (13) Bansal, K. M.; Fessenden, R. W. J. Phys. Chem. 1976, 80, 1743. (14) Hatano, A., Matuoka, S., Chapter Eds. CRC Handbook of Radiation Chemistry; Tabata, Y., Ed.; CRC: Boca Raton, FL, 1990; pp 190-202.

(15) Ionization Potential and Appearance Potential Measurements, 1971-1981; Report NSRDS-NBS 71; U. S. Government Printing Office: Washington, DC.

(16) Parker, V. D. J. Am. Chem. Soc. 1976, 98, 98.

(17) Friedman, H. L.; Krishnan, C. V. Water. A Comprehensive Treatise. In Aqueous Solutions of Simple Electrolytes; Franks, F., Ed.; Plenum: New York-London, 1973; p 56.

(18) Because G values vary by a factor of nearly 20, this trend is clear even with the uncertainty in the values of the extinction coefficients of the aromatic

radical cations. The extinction coefficients were estimated from values in the literature. We assumed that the oscillator strength was approximately constant for a particular cation in the different solvents, and thus the maximum absorption coefficient in our solutions could be estimated using the widths of the absorption band.

(19) Mataga, N.; Asahi, T.; Kanda, Y.; Okada, T. Chem. Phys. 1988, 127, 246

(20) Wang, Y.; Tria, J. J.; Dorfman, L. M. J. Phys. Chem. 1979, 83 (15), 1946.

(21) Borovkova, V. A.; Kirynkhin, Yu. I.; Sinitsyna, Z. A.; Romashow, L. V.; Bagdasar'yan, Kh. S. High Energy Chem. 1984, 88 (15), 192.
 (22) Kirynkhin, Yu. I.; Borovkova, V. A.; Sinitsyna, Z. A.; Bagdasar'yan,

Kh. S. High Energy Chem. 1979, 13 (6), 428.

 (23) Gschwind, R.; Haselbach, E. Helv. Chim. Acta 1979, 62 (4), 941.
 (24) Reichardt, C. Solvent and Solvent Effects in Organic Chemistry; VCH: Weinheim, 1988; Table A-1.

## Comparative Behavior of the Autocatalytic $MnO_4^-/H_2C_2O_4$ Reaction in Open and Closed Systems

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If the rate equation of a chemical reaction can be expressed in terms of a single variable, the steady-state conditions in a CSTR can be predicted from the batch kinetics. This does not require detailed knowledge of the reaction mechanism. However, if the reaction comprises several elementary steps, deduction is not possible since the rate depends on several independent concentrations. Experimentally useful predictions can nevertheless be made in certain situations. For example, the presence of an isosbestic point in the UV/visible spectrum of a reaction mixture is frequently indicative of a single-variable process. The permanganate-oxalic acid reaction is a convenient system for testing the method since it exhibits an isosbestic point in batch and its shows bistability in a CSTR for a limited range of oxalic acid concentrations. By using the rate data for two different oxalic acid concentrations, one can predict that bistability will be exhibited for one but not the other. The prediction is confirmed by experiments using a CSTR.

#### Introduction

In order to design new bistable chemical systems, we evaluated autocatalytic behavior from batch kinetics. This approach has the merit of speed and simplicity. However, to find out whether a particular system will exhibit bistability in a continuous stirred tank reactor (CSTR), appropriate calculations are required<sup>1,2</sup> on the simplifying assumption that the course of the reaction can be defined in terms of a single differential equation, which only depends on a single variable. A simple graphical method can be employed to deduce the steady-state curve and the multiplicity of a reaction in a CSTR starting from batch kinetics.

However, if there are several elementary steps, the rate of the reaction will normally depend on several concentrations, and the graphical method is no longer applicable. In this case, bistability cannot be predicted reliably.<sup>3</sup>

We show here that, in some experimental situations, useful predictions can be made even though the reaction mechanism is not known in detail. In the case of the autocatalytic reduction of the  $MnO_4^-$  ion by oxalic acid, multiplicity in a CSTR can be predicted from batch experiments.

### Noyes-Epstein Single-Variable Graphical Method<sup>4</sup>

The single differential equation defining the behavior in a CSTR is

$$d[A]/dt = (1/\tau)([A]_0 - [A]) - v_C$$
(1)

This equation includes two terms: (1) the flux term, which is a linear function of the concentration [A] of reactant A, and (2) the chemical term  $v_{\rm C}$ , which is the algebraic sum of the rates of all chemical processes involving species A in the CSTR.  $\tau$  is the residence time in the CSTR and  $[A]_0$  the concentration of reactant A in the input. Steady states are reached when the flux term exactly counterbalances the chemical term.<sup>5</sup> This gives

dA/dt = 0(2)

The chemical rate  $v_{\rm C}$  is thus expressed as a sole function of [A] and is the same in both types of reactor. It is plotted as a function of the residual reactant  $[A]_0 - [A]$ . The flux straight line,  $v_F =$  $(1/\tau)([A]_0 - [A])$ , is traced on the same diagram.  $(1/\tau)$  is the slope. The steady states (progress and residence time) are indicated by the intersections. If the acceleration of an autocatalytic reaction is sufficiently marked, the rate curve is concave, and it will intersect the flux line at three points for certain values of residence time. This zone corresponds to the residence time domain where bistability will be observed. It is bounded by the tangents (dotted lines 2 and 4 in Figure 1) to the curve passing through the origin.<sup>6,7</sup> At low residence times, the intersections define the flux branch, and at high residence times, it defines the thermodynamic branch.8

Although rapid and convenient, this graphical method has limited applicability. For multistep reactions, the chemical rate will be a function of several independent concentrations. Thus

$$v_{\rm C} = v(X_1, \dots X_n) \tag{3}$$

where  $X_i$  are the concentrations of species involved in the reaction mechanism. The rates are not the same in the two types of reactor (CSTR and batch). We show, however, that the observation of an isosbestic point (or linearly related spectra<sup>9</sup>) enables reduction of the number of independent variables to approximate a single variable situation.<sup>10-1</sup>

#### **Reduction of the Number of Variables**

In a CSTR, the course of a reaction involving various elementary steps is defined by a series of n differential equations of the type

$$dX_i/dt = f_i(X_i) + v_{Ci}(X_1,...X_n)$$
(4)