(8) Even at a lower temperature, benzeneseleninic acid proved to be unstable when mixed with aqueous hydrogen peroxide (ref 4). This precludes synthesis of a catalyst based on polystyrene functionalized by the –Se(O)(OH) groups matching the stability of the catalysts described herein.

(9) D. Pressman and D. H. Brown, *J. Am. Chem. Soc.*, **65**, 540 (1943).

(10) "Handbook of Chemistry", 57th ed., R. C. Weast, Ed., CRC Press, Cleveland, Ohio, 1975, p D-150.

(11) The biphase system consists of insoluble arsonated polystyrene beads and of an organic solvent miscible with aqueous hydrogen peroxide.

(12) C. R. Harrison and P. Hodge, *J. Chem. Soc., Perkin Trans. 1*, 605 (1976).

(13) H. O. House, "Modern Synthetic Reactions", 2nd ed., W. A. Benjamin, Menlo Park, Calif., 1972, Chapter 6.

(14) G. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.*, 1958 (1957).

(15) The presence of allyl arsonates as intermediates is supported by the facts that: (a) trialkyl arsenates were found to exchange alcohols rapidly at temperatures ≥60 °C (P. J. White, M. J. Kaus, J. O. Edwards, and P. H. Rieger, *J. Chem. Soc., Chem. Commun.*, 429 (1976)); (b) in a methanol-toluenearsonic acid mixture, a rapid exchange is observed in ^{1}H NMR between methyl ester and free methanol at temperatures ≥60 °C; and (c) a reaction of an excess of benzyl alcohol with benzenearsonic acid at 80 °C followed by a vacuum evaporation of the unreacted alcohol results in quantitative formation of dibenzyl benzenearsonate. The possibility for asymmetric epoxidation in the presence of asymmetric bidentate ligands is being investigated.

(16) K. B. Sharpless and R. C. Michaelson, *J. Am. Chem. Soc.*, **95**, 6136 (1973); T. Itoh, K. Kaneda, and S. Teranishi, *J. Chem. Soc., Chem. Commun.*, 421 (1976); T. Itoh, K. Jitsukawa, K. Kaneda, and S. Teranishi, *J. Am. Chem. Soc.*, **101**, 159 (1979).

(17) E. G. Sander and W. P. Jencks, *J. Am. Chem. Soc.*, **90**, 6154 (1968).

(18) Y. Sawaki and Y. Ogata, *Bull. Chem. Soc. Jpn.*, **38**, 2103 (1965).

(19) H. Kwart and D. M. Hoffman, *J. Org. Chem.*, **31**, 419 (1966).

(20) K. D. Bingham, G. D. Meakins, and G. H. Whitman, *J. Chem. Soc., Chem. Commun.*, 445 (1966).

(21) K. B. Sharpless, J. M. Towsend, and D. R. Williams, *J. Am. Chem. Soc.*, **94**, 295 (1972).

Studies of the Reactions of Molecular Fluorine with Methane, Acetylene, Ethylene, Allene, and Other Small Hydrocarbons in Matrices at Low Temperatures

R. H. Hauge, S. Gransden, J. L-F. Wang,[†] and J. L. Margrave*

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001.

Received May 3, 1979

Abstract: Reactions of molecular fluorine with small hydrocarbons were studied in fluorine and argon–fluorine matrices. Certain hydrocarbons (methane, acetylene, benzene, ethane, etc.) could be condensed into a pure fluorine matrix without reaction. Ethylene and allene could also be condensed in fluorine without reaction, but did react when exposed to light in the wavelength region from 1 to 4 μ. The ethylene reaction produced either 1,2-*gauche*- and *trans*-difluoroethane or vinyl fluoride and hydrogen fluoride. Propylene, butadiene, and cyclohexene reacted (spontaneously) with molecular fluorine in low-temperature matrices.

Introduction

Fluorine is known to react explosively with hydrocarbons in the gas phase via a free radical chain mechanism.[1] As a result, molecular complexes and reaction intermediates of the fluorine molecule with hydrocarbons are difficult to study; however, they can be investigated at low temperatures in solid matrices of fluorine or mixtures of fluorine and argon. In low-temperature solids, reaction will occur primarily between nearest-neighbor molecules. In dilute matrices, where only one fluorine molecule is likely to be a nearest neighbor, reactions of a single fluorine molecule may be studied. Preliminary reports of our results have been published.[2,3]

Experimental Section

We have studied the reactions of small saturated and unsaturated hydrocarbons, e.g., CH_4, C_2H_4, C_2H_2, C_2H_6, and C_6H_6, with fluorine in pure fluorine matrices as well as in matrices of fluorine and argon.[2,3] A schematic of the equipment is shown in Figure 1. The reactants were not mixed until they condensed at the cold surface; condensations were carried out for a period of 1 h at a matrix gas rate of ~2 mmol/h on a polished copper surface held at 15 K. Spectra were taken with a Beckman I.R.-9 spectrometer. Fluorine (98%) was obtained from Linde. High-purity fluorine was obtained from the Chemical Engineering Division, Argonne National Laboratory. An attempt was also made to observe UV–vis–near IR spectra of an F_2–ethylene complex. The matrix was formed on a sapphire window and transmission spectra were taken with a Cary 14 spectrometer.

Results

Typical spectra for hydrocarbons isolated in a fluorine matrix are shown in Figure 2 and the observed bands listed in Table I. One sees from comparison of observed frequencies to gas-phase values that a fluorine matrix is a very nonperturbing matrix.

A list of the hydrocarbons studied and their behavior is given in Table II. It was found that the alkenes either reacted with F_2 during the trapping process or they could be caused to react by exposure to near-infrared radiation from the spectrometer light source after trapping. Neither the alkanes nor alkynes gave any indication of reaction when isolated in a fluorine matrix or as a result of prolonged exposure to the spectrometer light source. This was also the case for benzene. Reactions of the alkenes yielded a mixture of products with the major species resulting either from F_2 addition to the double bond or HF elimination with formation of monofluoro product. Thus, for ethylene, the major products are 1,2-difluoroethane and vinyl fluoride.

The reaction of ethylene with F_2 has been studied extensively and measured frequencies of the product species are given in Table III. Figures 3 and 4 illustrate the photolytic reaction of ethylene in a pure fluorine matrix and a mixed fluorine/argon matrix. The major difference between the two matrices appears to be in the relative amounts of 1,2-difluoroethane and vinyl fluoride formed. The F_2/Ar matrix enhances the formation of vinyl fluoride. The 1,2-difluoroethane is produced as both the trans and gauche isomers. Their identification is based on previously assigned argon matrix spectra.[5] As also observed

---

[†] Inorganic Materials Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, Calif. 94720.

0002-7863/79/1501-6950$01.00/0

Table I. Fundamental Frequencies (cm^{-1}) in F_2 Matrix

	F_2 matrix	gas phase	approximate type of mode
CH_4	3040	3019	CH_4 deg stretch
	1309	1306	CH_4 deg stretch
C_2H_6	2956	2954.0	CH_3 sym stretch
	2897	2895.6	
	1376	1379.2	CH_3 sym deform
	2989	2995.5	CH_3 deg stretch
	1469	1472.2	CH_3 deg deform
	820.5	821.5	CH_3 rock
C_2H_4	957	949	CH_2 wag
	3110	3106	CH_2 anti stretch
	858	826	CH_2 rock
	2998	2989	CH_2 sym stretch
	1443	1444	CH_2 scissors
C_2H_2	3292	3295	CH stretch
	3271	3282	
	736	730	CCH deform

Table II. Molecules Trapped in a Pure Fluorine Matrix at 15 K

molecule	reacted during trapping	photolyzed by $\lambda > 1\ \mu$	IP, eV
ethylene	no	yes	10.50
allene	no	yes	10.16
propylene	yes		9.73
butadiene	yes		9.06
cyclohexene	yes		8.72
acetylene	no	no	11.41
propyne	no	no	10.36
methane	no	no	12.7
ethane	no	no	11.53
cyclopropane	no	no	10.09
benzene	no	no	9.24

Table III. Observed Bands from Ethylene and Fluorine Reaction (cm^{-1})

$C_2H_4F_2$				unassigned	C_2H_3F	
gauche		trans				
matrix		matrix		matrix	matrix	
F_2	Ar[a]	F_2	Ar[a]	F_2	F_2	Ar
891	891	1046	1048			877
1066	1070			864	910	909
1094	1096			1063	924	926
				1074	1127	1121
					1651	1653

[a] Taken from ref 2.

by ref 5, the less stable trans isomer will readily convert to the gauche form when the matrix is warmed to 30 K.

Figure 4A,B also indicates that photolysis causes the disappearance of a band located 7 cm^{-1} higher than the 950-cm^{-1} band. The 950-cm^{-1} band coincides with the measured value for the ν_7 mode of ethylene in an argon matrix. This would suggest that interaction of F_2 with ethylene has caused a shift similar to the +11.5-cm^{-1} shift of the chlorine-ethylene adduct.[6] The remarkable difference in reactivity between ethylene and acetylene is illustrated in Figure 5.

Rates of reaction in the presence of radiation were measured with different filters and are given in Table IV. It is evident that wavelengths greater than 1 μ can cause reaction of ethylene with fluorine. We have examined the region above 1 μ but did not observe any absorption features due to a fluorine-ethylene adduct. However, it would be very difficult to detect a very broad, weak absorption. In order to determine if simple matrix heating by the spectrometer light source was, in part, responsible for the reaction, we increased the temperature of the matrix in steps up to 30 K and found no dependence on temperature.

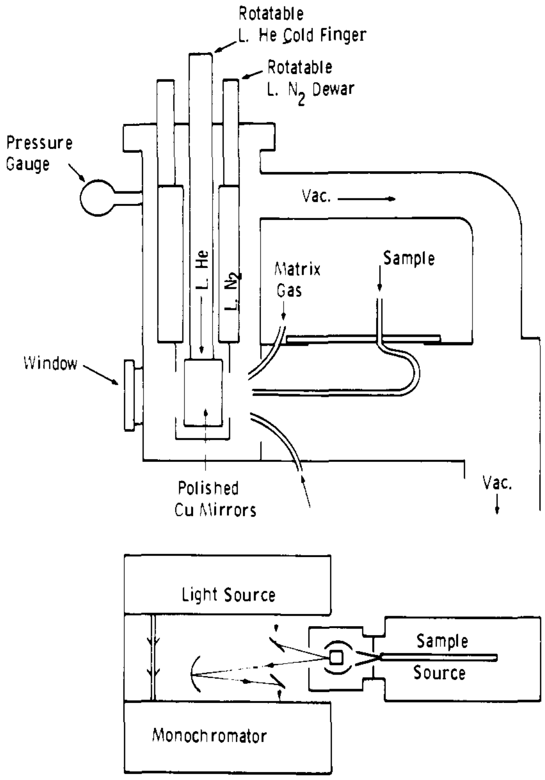


Figure 1. Schematic of matrix trapping apparatus.

Table IV. Photolytic Reaction of Ethylene in Solid Fluorine (15 K)[a]

filter	transmission limits, μm	transmission	measured rate	normalized rate
none (0.6 A)	0.2–40	1.00	0.21	0.21
none (0.4 A)	0.2–40	0.54[b]	0.11	0.21
silicon	1.1–40	0.51	0.12	0.23
IR (no. 2540)	1–4.2	0.89	0.17	0.19
red (no. 241)	0.61–3.4	0.64	0.11	0.17
yellow (no. 3484)	0.53–3.4	0.80	0.14	0.18
quartz	0.18–4.2	0.77	0.13	0.17

[a] Photolysis is due to light from the Nernst glower of a Beckman I.R.-9 spectrometer. The Nernst glower was kept at 0.6 A for all filter studies. [b] Radiation intensity at 2.7 μ was measured as 54% of that emitted with the Nernst glower current set at 0.6 A.

Rates of reaction for C_2H_4 and C_2D_4 with F_2 are shown in Figure 6. The rate for C_2H_4 was seen to be approximately 14 times as fast as that of C_2D_4.

Finally, a brief study of the rate of photolytic fluorination of allene indicates that it reacts with F_2 at least 1.5 times as fast as ethylene in the presence of infrared radiation.

Discussion

Table II shows that only the two alkenes with the highest ionization potentials can be trapped in a fluorine matrix without reaction. In fact, more sensitive EPR measurements[4] have suggested that some reaction of ethylene with fluorine does occur during the trapping process. The other alkenes apparently require very little activation energy for reaction with molecular fluorine since the reactions are occurring on a cold matrix surface. One might correlate this increased reactivity with their lower ionization potentials; however, the lack of reaction by cyclopropane and benzene indicates that a lower

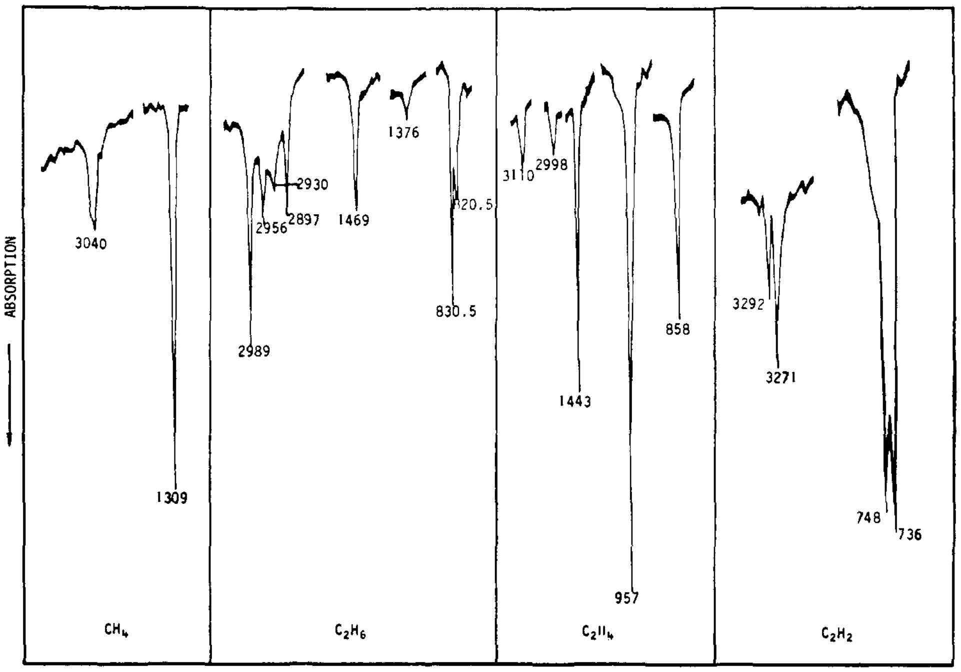


Figure 2. Infrared spectra of CH_4, C_2H_6, C_2H_4, and C_2H_2 trapped in a fluorine matrix.

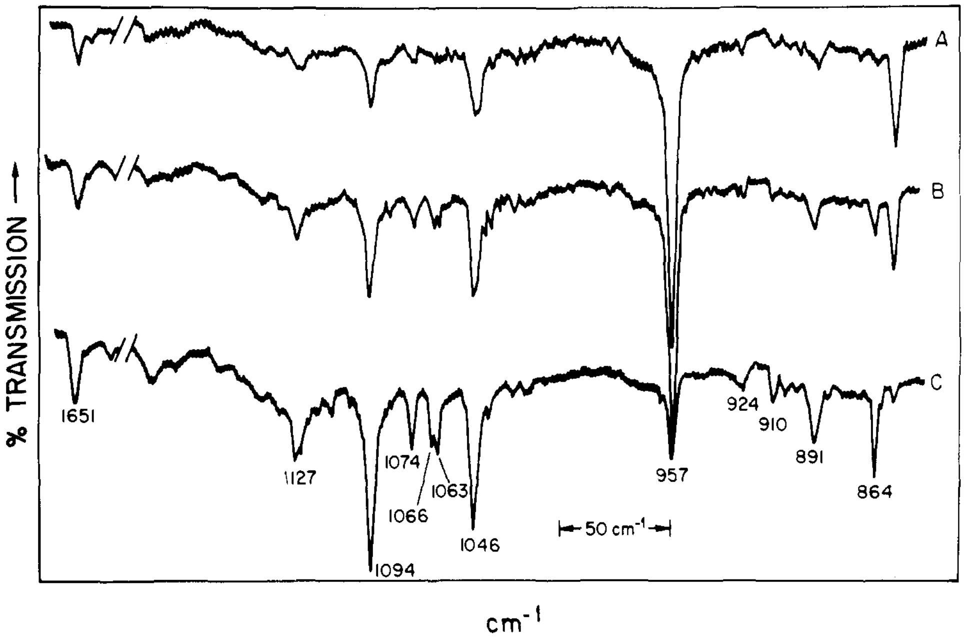


Figure 3. Spectra of ethylene in a pure fluorine matrix: (A) after 22 min exposure to spectrometer glower (0.6 A); (B) after 103 min; (C) after 498 min.

ionization potential is not the only factor involved in predicting the likelihood of spontaneous reaction with molecular fluorine at low temperatures. The ability of alkenes to form stable charge-transfer complexes with halogens probably contributes significantly to their increased reactivity.

The nature of the absorption which leads to photolysis of the complex is uncertain. Possibilities include excitation of a perturbed fluorine molecule or perhaps an overtone of the perturbed ethylene. The large deuterium isotope effect on the reaction rate suggests that excitation of carbon-hydrogen vibrational modes plays a major role in the transition.

A very weak absorption in the 1-4-μ wavelength region could produce the observed rates of photolysis. For instance, the average number of photons/cm^2·s incident on the matrix for a 1-4-μ window was measured for a Corning no. 2540 filter as approximately 2×10^{18}. The number of ethylene molecules present per cm^2 is approximately 1×10^{18}. Thus, if the percent absorption were 10^{-3} and the quantum efficiency were unity, most of the ethylene would react within a period of 10 min. Since the photolysis occurs over a period of hours, it is apparent that a very broad, weak absorption could indeed cause photolysis.

The increased yield of vinyl fluoride in the dilute F_2/Ar matrices can be explained in a number of ways. If the reaction is visualized as proceeding through a hot 1,2-difluoroethane intermediate, one can explain the different amounts of vinyl fluoride formed as due to the different quenching rates for pure fluorine and fluorine-argon matrices. A pure fluorine matrix should be a better quencher because of the presence of an F_2 internal vibration. The increased quenching rate would decrease the probability of hot 1,2-difluoroethane decomposing into vinyl fluoride.[7] The presence of both gauche and trans

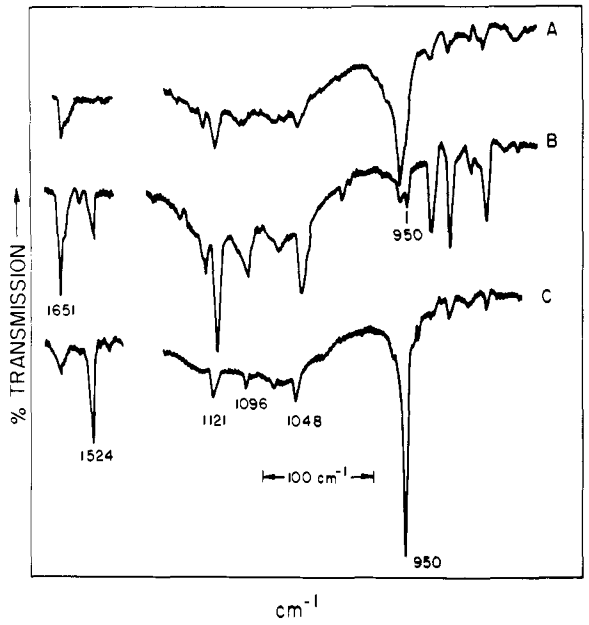


Figure 4. Spectra of ethylene in a mixed F_2/Ar matrix: (A) initial scan after trapping ethylene in a 1/10 F_2Ar matrix; (B) after prolonged exposure to spectrometer light source; (C) scan of ethylene in a 1/50 F_2/Ar matrix after prolonged exposure to spectrometer light source.

forms when the ethylene-F_2 adduct is quenched from the hot state is consistent with previous studies in which 1,2-difluoroethane was heated prior to trapping in an argon matrix.[5]

The effect of quenching would be the same if the reaction proceeded with the first fluorine undergoing addition to the double bond producing a hot 1-fluoroethyl radical in the presence of the second fluorine atom. Radical recombination to form the difluoroethane would have no activation energy whereas fluorine atom attack on a carbon-hydrogen bond would require some activation energy. Thus, rapid quenching would lead to increased 1,2-difluoroethane formation.

Either of the above mechanisms requires a difference in quenching rates for the fluorine and argon-fluorine matrices. An alternate explanation could be based on a F_2 concentration effect where a 1:1 (F_2-C_2H_4) adduct reacts to form vinyl fluoride while a 2:1 (F_2-C_2H_4-F_2) adduct reacts to form difluoroethane. This seems less likely since the relative amounts of vinyl fluoride and difluoroethane remained approximately the same when the F_2/Ar ratio was changed as indicated in Figure 4B,C.

Conclusions

Studies of the reactions of various hydrocarbons in pure fluorine matrices or mixed fluorine-argon matrices provide information on the reactivity of molecular fluorine at low temperatures. Some molecules, such as the alkanes and alkynes, require photodissociation of molecular fluorine into atoms for reaction to occur. There is a small activation energy barrier for reaction of ethylene and allene with molecular fluorine, but they do react extensively upon photoexcitation of the fluorine-alkene complex. Other alkenes were observed to react, even at very low temperatures, without photoexcitation. Within the alkene group, reactivity appears related to their ionization potentials. For ethylene, the reaction appears to proceed primarily through fluorine addition to the double bond, as previously suggested by Miller for halogenated alkenes,[8] with additional reaction to produce vinyl fluoride and hydrogen fluoride occurring when the energy of the initial reaction cannot be dissipated through internal and lattice vibrations.

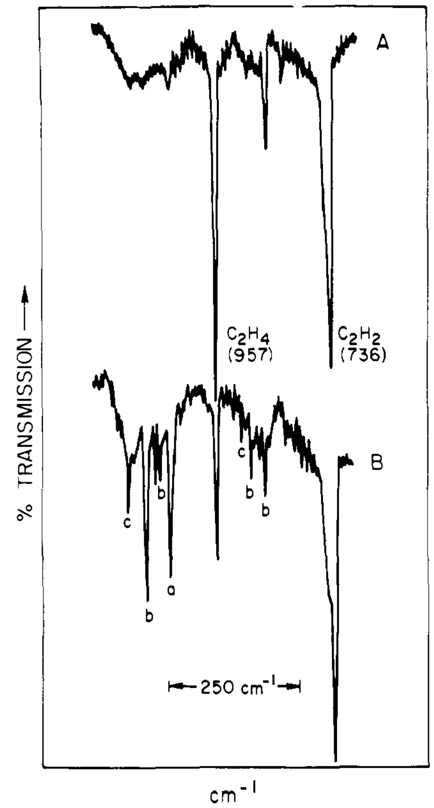


Figure 5. Spectra of C_2H_4 and C_2H_2 in a pure fluorine matrix at ~15 K before (A) and after (B) 8 h of exposure to light from a Nernst glower (0.6 A) through a Corning infrared filter no. 2540 (transmission 1-4.2 μ). Background interference bands are due to a silicon window used during scans (a, *trans*-1,2-difluoroethane; b, *gauche*-1,2-difluoroethane; c, vinyl fluoride).

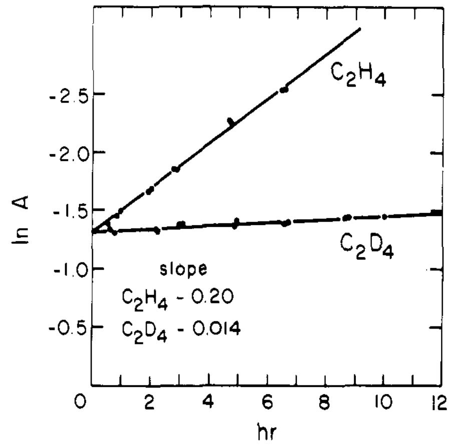


Figure 6. Plot of ln (absorbance) vs. time of photolysis for C_2H_4 and C_2D_4 in the same fluorine matrix. Bands at 950 and 723 cm^{-1} were used to monitor C_2H_4 and C_2D_4, respectively. Photolysis is due to light from the Beckman I.R.-9 Nernst glower operating at 0.6 A.

Acknowledgments. The authors thank Raymond Lim and Steve Ashburn for their assistance in these studies. We also thank Robert Grow and Gerald Johnson for assistance in obtaining high-purity fluorine. This work was supported by the Robert A. Welch Foundation, the National Science Foundation, and the U.S. Army Research Office, Durham, N.C. Liquid helium for this work was available in part through a grant of the U.S. Navy to Rice University.

References and Notes

(1) R. B. Badachhape, R. H. Hauge, R. J. Lagow, and J. L. Margrave in "Kirk-Othmer Encyclopedia of Chemical Technology", Wiley-Interscience, New York, 1979.

(2) R. H. Hauge, S. Gransden, J. Wang, and J. L. Margrave, *Ber. Bunsenges. Phys. Chem.*, **82**, 104 (1978).

(3) R. H. Hauge, J. Wang, and J. L. Margrave, presented at the First Winter Fluorine Conference, St. Petersburg, Fla., Jan 1972.

(4) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Phys. Chem.*, **74**, 2083 (1970).

(5) P. Huber-Wälchli and Hs. H. Günthard, *Chem. Phys. Lett.*, **30**, 347 (1975).

(6) L. Fredin and Bengt Nelander, *J. Mol. Struct.*, **16**, 205 (1973).

(7) S. W. Benson and G. Haugen, *J. Phys. Chem.*, **69**, 3898 (1965).

(8) W. T. Miller, Jr., J. O. Stoffer, G. Fuller, and A. C. Currie, *J. Am. Chem. Soc.*, **86**, 51 (1964).

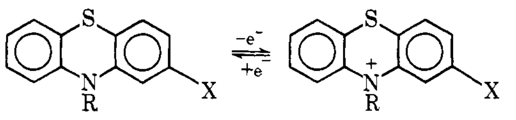
On the Electron Transfer from Ascorbic Acid to Various Phenothiazine Radicals[1]

E. Pelizzetti,[2a] D. Meisel,*[2b] W. A. Mulac,[2b] and P. Neta[2c]

Contribution from the Istituto di Chimica Analitica,
Universita di Torino, 10125 Torino, Italy, Chemistry Division,
Argonne National Laboratory, Argonne, Illinois 60439, and Radiation Laboratory,
University of Notre Dame, Notre Dame, Indiana 46556. *Received March 22, 1979*

Abstract: The reaction of electron transfer from ascorbic acid to *N*-alkylphenothiazine radical cations was studied in the pH range 0–7.2. The radical cations were produced by oxidation with Br_2^- or Cl_2^- using the pulse radiolysis technique. The radical cations are reduced by the deprotonated form of ascorbic acid in the pH range 2.2–7.2. The product of this reaction has a spectrum which is identical with that of the ascorbate radical. It is concluded that, if a charge-transfer complex is formed upon the reaction of ascorbic acid with the phenothiazine radical cations, its lifetime is shorter than 7×10^{-8} s. It is suggested that even at high acidities no long lived complex is formed and it is proposed that at very low pH the thermodynamically stable species in this reaction is the phenothiazine radical cation rather than the ascorbic acid radical. It is shown experimentally that at 1 M HCl the ascorbic acid radical oxidizes *N*-alkylphenothiazine to give the radical cation of the latter in reverse to the direction of the electron transfer at higher pH.

There is currently considerable interest in the thermal and photoinduced electron transfer reactions of *N*-alkylphenothiazines and their radical cations.



	R	X
phenothiazine	H	H
N-methylphenothiazine	CH_3	H
promazine (PMZ)	$(CH_2)_3N(CH_3)_2$	H
chlorpromazine (ClPMZ)	$(CH_2)_3N(CH_3)_2$	Cl
promethazine (PMTZ)	$CH_2CH(CH_3)N(CH_3)_2$	H

The intensive interest in this group of compounds stems primarily from three different aspects, all related to their low ionization potentials.[3] (a) The effective use of *N*-alkyl derivatives in psychiatric therapy[4] (especially ClPMZ) is often attributed to their redox reactivity. Furthermore, much of the interest in the photochemical redox behavior of some of these tranquilizer drugs is stimulated by the observation that treatment with, e.g., ClPMZ causes photosensitization of skin and eye tissues.[7] (b) Due to the ease of their one-electron oxidation, the possible use of some phenothiazine derivatives (often phenothiazine or *N*-methylphenothiazine) as photo redox sensitizers is considered in solar energy conversion systems.[5] Furthermore, the diamino derivative of phenothiazine-thionine, in conjunction with Fe(II), constitutes one of the most studied systems for photogalvanic effects.[6] (c) The one-electron oxidation of the *N*-alkyl derivatives by various metal inorganic complexes is often a simple outer sphere electron transfer process. This fact was recently utilized to evaluate the parameters involved in the electron transfer between $Fe_{aq}^{3/2+}$, $Fe(CN)_6^{3/4-}$, and $Np^{6/5+}$ and several *N*-alkylphenothiazine derivatives, as well as the electron exchange between these derivatives,[8] in light of the Marcus theory for electron-transfer reactions.

In spite of this simple behavior of outer sphere electron-transfer processes, electron donor-acceptor complexes between phenothiazines and various acceptors have been observed in several cases. Thus, spectral evidence for EDA complexes between phenothiazine or ClPMZ and tetracyanobenzene, tetracyanoethylene, trinitrobenzene, and several quinone derivatives was presented by Dwivedi et al.[9] Charge-transfer complexes between acetylcholine or serotonin or hydroxydopamine with ClPMZ or its radical cation were reported.[10] The reduction of the chlorpromazine radical cation by ascorbic acid in 0.25–1.00 M HCl was recently studied by Klein and Toppen.[11] In this system again kinetic evidence was suggested to indicate the formation of an EDA complex between the radical cation and the ascorbate anion prior to the electron-transfer act. On the other hand, the reduction of many inorganic complexes by ascorbic acid was recently shown to follow the Marcus theory correlations of outer sphere electron-transfer reaction.[12]

In the present study we utilize the pulse radiolysis technique to investigate the electron transfer reaction between ascorbic acid (H_2A) and several *N*-alkylphenothiazine radicals over a wide range of pH. Over much of this range (pH 2.5–7.2) the rate of reaction is too rapid to be followed by the previously used stopped-flow technique. In view of the results of Klein and Toppen,[11] we hoped to observe the absorption spectrum of the EDA complex. However, this expectation did not materialize. Furthermore, evidence will be presented that at high acidity the phenothiazines are oxidized by ascorbic acid radicals.

Experimental Section

Materials and Procedure. The *N*-alkylphenothiazines (denoted collectively as PTZ) were obtained from Rhone-Poulenc and their purity was checked as previously described.[8a] The ascorbic acid (Sigma) was purified by recrystallization. All other materials were

0002-7863/79/1501-6954$01.00/0