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Low Temperature Free Radical Addition Reactions in Solid Argon: $F + C_2H_4$, an EPR Study

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Ultraviolet laser photolysis of dilute mixtures of F_2 and C_2H_4 in solid argon form a 2-fluoroethyl radical by addition of translationally 'hot' as well as thermal F atoms to ethene; at $T > 20$ K the major channel is the thermal reaction, which converts up to 25% of ethene to 2-fluoroethyl radical.

In a recent publication,[1] we reported the formation of methyl radicals following 337 nm laser photolysis of dilute mixtures of F_2 and CH_4 in a solid Ar matrix in the temperature range 13–20 K by an EPR technique. There are two important channels of CH_3 formation:

(1) Translationally hot F atoms abstract an H atom from CH_4 following dissociation of a F_2 molecule forming $HF + CH_3$ during the photolysis period.

(2) Thermalised fluorine atoms trapped in the argon lattice react with CH_4 on a time scale of 10^3 s after the photolysis period at 20 K.

The thermal barrier to the $F + CH_4$ reaction is significantly higher than the barriers to diffusion of F atoms in the argon lattice and to the $F + CH_3$ reaction. As a result, the methyl radical concentration can either increase during the dark period due to the thermal $F + CH_4$ reaction (above 16 K) or decrease due to $F + CH_3$ reactions forming the stable product CH_3F (below 16 K). Thus, reactions of 'hot' and thermal F atoms can be directly separated and detailed analysis of the photochemical mechanisms can be suggested.

Besides H atom abstraction, another common reaction mechanism of halogens with simple hydrocarbons is addition to C=C double bonds of alkenes. In this communication we wish to report preliminary experimental findings for the reaction of F atoms with ethene (C_2H_4), in which either of the two reaction mechanisms is possible.

The experimental techniques are similar to those used in our previous study.[1] Dilute mixtures of F_2/Ar and C_2H_4/Ar are deposited through separate gas inlets onto the surface of a sapphire rod cooled to 14 K. In this series of experiments the final relative concentrations in the deposited sample were $Ar:F_2:C_2H_4 = 1000:1:1$ and the total quantity of Ar on the rod was 2×10^{20} cm^{-2} corresponding to a sample thickness of about 100 microns. Deposition time was typically 1.5 h. After deposition, the sample was lowered into the EPR cavity and photolysed with the 337 nm output of a N_2 laser for several minutes (typical photolysis intensity 10^{18} cm^{-2} s^{-1}, F_2 absorption cross-section $\sigma = 1.05 \times 10^{-20}$ cm^2). The relative concentrations of radicals were determined by double integration of the spectrum. Their absolute values were found using internal DPPH standard immersed into the sapphire rod. The quantum yield of radical is evaluated as the ratio of amounts of absorbed photons and radicals formed.

The EPR spectrum of the intermediate product shown in Figure 1 is in good agreement with that of 2-fluoroethyl radical observed previously in cancrinite at 77 K.[2] The overall shape of the spectrum is due to anisotropic g factor and hyperfine splittings on F, two inequivalent α and two equivalent β protons. The better spectrum resolution in Ar allows us to determine the hyperfine constants more accurately than that in ref. 2, where α protons were accepted to be equivalent. The parameters determined from computer

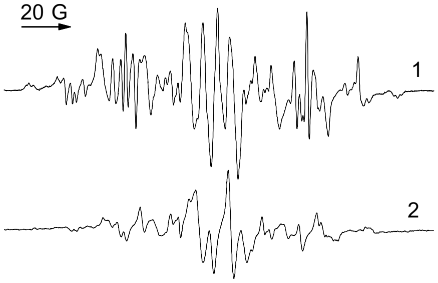

Figure 1 EPR spectrum of $\dot{C}H_2CH_2F$ radical formed under UV photolysis and subsequent dark reaction in Ar:F_2:C_2H_4 = 1000:1:1 mixture recorded at ~4.2 K (1) and 30 K (2).

simulation taking into account forbidden transitions ($m_F = \pm 1$) are given in Table 1. The principal axis of *g* and *hf* tensors do not coincide leading to different shapes for the lowest and highest field components.[3] The line broadening observed on heating the samples to 25–30 K is caused by incomplete averaging of the inequivalent protons as a result of slow rotation about the C–C bond.[4,5] The estimated frequency of this rotation at 30 K is $\sim 10^7$ s^{-1}.

Table 1 The fitted spin Hamiltonian parameters for the C_2H_4F radical.

	hf tensor/G[b]			
g tensor[a]	Splitting form	A_{xx}	A_{yy}	A_{zz}
$g_{xx} = 2.0037$	F	6.0	12.5	39.2
$g_{yy} = 2.0037$	α-H	30.0	29.3	35.2
$g_{zz} = 2.0030$	α′-H	38.8	38.1	44.0
	β-H	24.7	21.8	21.9

[a] ±0.0004. [b] ±0.5 G.

Another possible product of reaction $F + C_2H_4$ is vinyl radical. Its spectrum is expected to be shifted by ~ 6 G in Ar[6] with respect to that of $\dot{C}H_2CH_2F$. Although the experiments were carried out at several different concentrations and photolysis temperatures, no evidence of additional lines characterised by such a *g* shift was obtained.

In three series of experiments, the sample was photolysed continuously at 14, 20 and 26 K. Radical quantum yields were determined from the initial slope of the growth curves and the limiting concentration of radicals. We found that the quantum yield is directly proportional to the initial concentration of C_2H_4, and that it is strongly temperature dependent. In Ar:C_2H_4:F_2 = 1000:1:1 samples the quantum yield is $3\text{–}5 \times 10^{-3}$ at 14 K, but increases by an order of magnitude at 26 K. Extensive photolysis converts as much as 15–25% of the C_2H_4 molecule to 2-fluoroethyl radical at low temperatures.

After the end of the photolysis, we observed slow dark reactions caused by thermal diffusion of F atoms, yielding the same radical product. The kinetic curve of this reaction at 20 K is shown in Figure 2. The duration of the dark reaction is $\sim 10^3\text{–}10^4$ s, the same order of magnitude as observed in our previous experiments with CH_4 under similar conditions.

In one series of experiments the sample was photolysed at 14 K for 20 min. The initial radical yield was small, but grew by more than a factor of five upon slow warming to 32 K over the course of a few hours. A representative plot of this behaviour is given in Figure 3. Note that most of the radicals are formed over the temperature range 20–25 K, and that the final concentration of radicals is only about one-third smaller than for photolysis of a similar sample for the same period at 26 K.

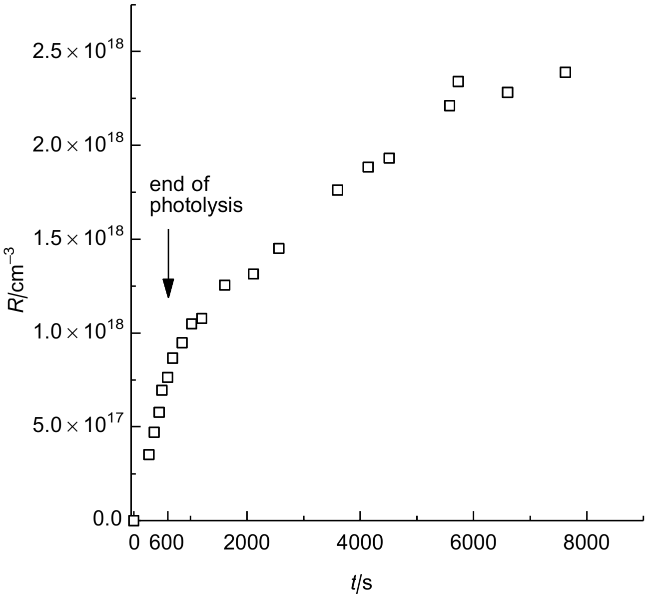

Figure 2 Kinetics of radical accumulation under photolysis and dark reaction at 20 K (Ar:F_2:C_2H_4 = 1000:1:1).

It has been known for more than 20 years that thermal F atoms exhibit an unusually high activated mobility in rare gas solids above 20 K.[7] Apkarian and co-workers have obtained evidence for an exceptionally long-range migration of 'hot' F atoms in crystalline Ar following photodissociation.[8] They have also observed thermally stimulated recombination of F atoms upon warming from 20 to 25 K due to an increase in their diffusion coefficient. The reaction lasts about 1 min at temperatures near 25 K and Ar/F ratios near 2000.

Based on these data on the translation of both types of F atoms we propose the following mechanism of $\dot{C}H_2CH_2F$ radical formation. It can be divided into two main parts. The first involves reactions of translationally hot F atoms generated by photodissociation of F_2 on a short time scale,

$$F_2 \xrightarrow{h\nu} F^* + F^* \qquad \text{(photodissociation)} \qquad (1)$$

$$F^* \longrightarrow F \qquad \text{(thermalisation)} \qquad (2)$$

$$F^* + C_2H_4 \longrightarrow \dot{C}H_2CH_2F \qquad \text{(addition reaction)} \qquad (3)$$

The second part (at $T > 20$ K) involves recombination of thermalised F atoms with each other or reaction with ethene and fluoroethyl radicals:

$$F + F \longrightarrow F_2 \qquad \text{(recombination)} \qquad (4)$$

$$F + C_2H_4 \longrightarrow \dot{C}H_2CH_2F \qquad \text{(addition reaction)} \qquad (5)$$

Within this mechanism reaction (3) determines the quantum yield of radicals at 14 K since translation mobility of thermalized F atoms is frozen.[1,8] The increase in radical yield with temperature above 20 K results from additional contribution of reaction (5). We apply the proposed scheme for treatment of the kinetic curves shown in Figures 2 and 3. It gives $k_4 \sim 5 \times 10^{-23}$ cm^3 s^{-1} and activation energy to F atom diffusion about 1.1–1.2 kcal mol^{-1}, in a satisfactory agreement with those obtained in our previous work[1] and data[8] (see Figure 3). The rate constant of radical formation k_5 is approximately one order of magnitude less than k_4. Nevertheless, k_5 exceeds the rate constant of CH_3 radical formation (from $F + CH_4$) under similar conditions by more than two orders of magnitude. This difference is probably due to the smaller barrier to addition to the double C=C bond as compared to that of H atom abstraction. It is possible that the rate constant of the addition reaction is limited by steric hindrance. It is well-known that analogous reactions in the gas phase possess small pre-exponential factors.[9]

The main result of this communication is the fact that 'hot' and thermal F atoms are able to participate in addition solid-state reaction and the contribution of the latter is more

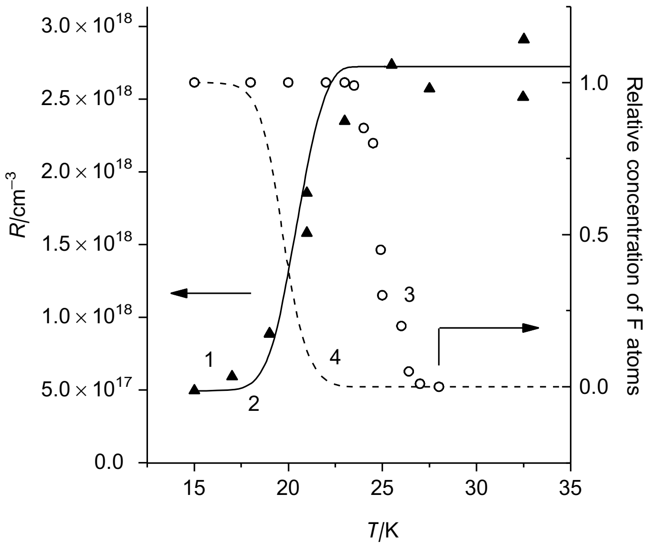

Figure 3 $\dot{C}H_2CH_2F$ radical growth curve upon warming of sample photolysed at 14 K ($Ar{:}F_2{:}C_2H_4 = 1000{:}1{:}1$, heating rate ~ 0.2 K min^{-1}). (1) Experimentally determined radical concentrations (solid triangles). (2) Calculated curve for $\dot{C}H_2CH_2F$ using kinetic scheme (see text). (3) Experimental data from ref. 8 for F atom recombination (open circles). (4) Calculated curve for F atom recombination. The temperature shift between the data[8] and our calculated curve can be attributed partially to the higher heating rate in that experiment (0.5 K min^{-1}).

pronounced than that in the abstraction reaction. A complete analysis of the $Ar/F_2/C_2H_4$ reaction kinetics can only be carried out when parallel studies are completed using infrared spectroscopy to determine the concentrations of C_2H_4, CH_2FCH_2F and possibly the 2-fluoroethyl radical itself. These studies will be carried out in the near future and reported separately.

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References

1 E. Ya. Misochko, V. A. Benderskii, A. U. Goldschleger and A. V. Akimov, *Mendeleev Commun.*, 1995, 198.
2 P. Raghunathan and S. K. Sur, *J. Phys. Chem.*, 1983, **87**, 3383.
3 R. Lefevre and J. Maruani, *J. Chem. Phys.*, 1965, **42**, 1480.
4 C. A. McDowell and K. Shimokoshi, *J. Chem. Phys.*, 1974, **60**, 1619.
5 K. S. Chen, P. J. Krusic, P. Meakin and J. K. Kochl, *J. Phys. Chem.*, 1974, **78**, 2014.
6 P. H. Kasai, *J. Am. Chem. Soc.*, 1972, **94**, 5950.
7 M. E. Jacox, in *Chemistry and Physics of Matrix-isolated Species*, eds. L. Andrews and M. Moskovits, Elsevier, 1989, p. 75.
8 J. Feld, H. Kunttu and V. A. Apkarian, *J. Chem. Phys.*, 1990, **93**, 1009.
9 W. E. Jones and E. G. Skolnik, *Chem. Rev.*, 1976, **76**, 563.

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