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Reactions of Thermalized Fluorine Atoms with CH_4 and CH_3, Trapped in an Argon Matrix at 13–20 K

Eugenii Ya. Misochko,* Viktor A. Benderskii, Albert U. Goldschleger and Alexander V. Akimov

Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 095 938 2156

Accumulation and conversion of CH_3 radicals upon F_2 photolysis in ternary mixtures $Ar{:}F_2{:}CH_4$ has been studied with EPR spectroscopy; the CH_3 radical formation during photolysis period is caused by the reaction of 'hot' F atoms with CH_4. At $T > 18$ K the thermally activated reaction of 'cold' F atoms with CH_4 was also detected; the activation energy of diffusion-controlled recombination of the F atoms falls short of that of F + CH_4 reaction.

Although in several papers[1,2] it has been intimated that F atoms possess an appreciable translation mobility in rare gas matrices, which allows them to react with the trapped partners, up to now these reactions have not been systematically studied. Similar reactions involving 'hot' atoms were also assumed to be ineffective due a to small thermalization length L as compared to the average spacing between reactants in the matrix. However, recent papers by Apkarian's group[3,4] demonstrated that the thermalization length is 50–100 Å for ~1 eV F atoms. The thermal diffusion barrier of the atoms was 1.1–1.3 kcal mol^{-1}, and their recombination at 25 K lasts only ~50 s at initial concentration ~10^{19} cm^{-3}. The long-range migration and diffusion of the thermalized atoms make possible two channels of reaction. In the present paper it is shown that thermalized fluorine atoms react with CH_4 molecules and CH_3 radicals in solid argon at mole ratios $< 10^{-3}$, when the average spacing between reactants is > 50 Å.

The experiments were carried out in a flow helium cryostat with moveable helium shaft.[5] The solid ternary $Ar{:}CH_4{:}F_2$ = 500:1:X (X = 0.25–2.5) mixtures were prepared by simultaneous condensation of the pre-mixed gas samples (Ar/F_2) and (Ar/CH_4) onto a cold sapphire rod kept at ~13 K. F atoms were generated by F_2 photolysis with a N_2 laser (λ 337 nm). F_2 photodissociation gives 'hot' F atoms with an excess energy $E = (h\nu - D)/2 \approx 0.5$ eV. According to the data in ref. 3, 0.5 eV F atoms escape from the parent cage in an Ar crystal with quantum yield $_0 \approx 1$.

Concentration of methyl radicals during the photolysis period and subsequent dark reaction was measured by EPR. The spectrometer sensitivity, along with the small line width, yielded a resolution of 10^{11} radicals in a sample. The typical number of radicals in kinetic measurements was 10^{12}–10^{14}.

The EPR spectrum of CH_3 is illustrated in Fig. 1. The FWHM of components with different values of projection of total spin of the three equivalent protons $\Delta H(m_I)$ varies from 0.3–0.6 G. This dependence is caused by the incomplete averaging of the g tensor and the tensor of hyperfine

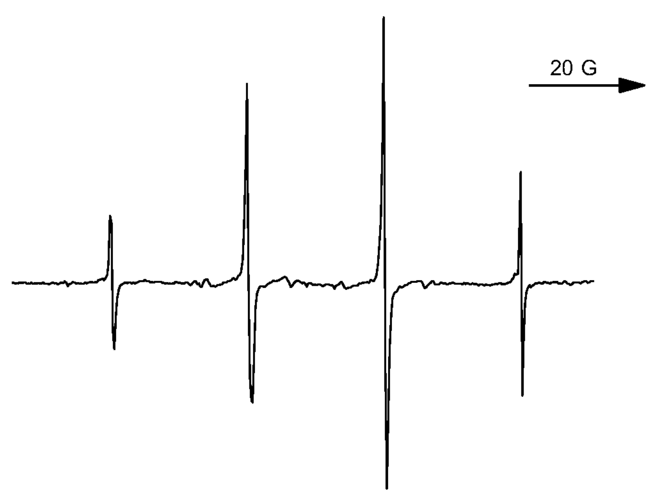

Fig. 1 EPR spectrum of CH_3 radicals formed under photolysis of $Ar/CH_3/F_2$ = 500:1:1 samples.

interactions due to the slow rotation of the radical. The correlation time $\tau_c \sim 10^{-7}$ s at 16 K was estimated within the context of the Fraenkel–Freed[6,7] theory for the anisotropy parameters $g/g = 10^{-3}$, $A = 5$ G. A similar value for τ_c was found from homogeneous saturation curves of HFS components at intensities of the microwave field ~ 0.1 G.

The number of radicals is linear with time in the course of photolysis. The quantum yield, Φ_R, is proportional to the mole fraction of CH_4 (see Fig. 2) and independent of temperature at 13–20 K. The characteristic time of CH_3 conversion is $\sim 10^3$ s. dR/dt changes its sign with increase in temperature: R decreases at $T < 17$ K and increases at $T > 18$ K (see Fig. 3). Such an extraordinary temperature behaviour of kinetic curves unambiguously justifies the competition of accumulation and depletion of radicals in reactions with the thermalized F_t atoms:

$$F_t + CH_4 \rightarrow CH_3 + HF \quad (1)$$

$$F_t + CH_3 \rightarrow CH_3F \quad (2)$$

Reaction (2) is dominant at 13–17 K, decreasing R, whereas above 18 K the rate of reaction (1) exceeds that of reaction (2). Since change in R is, at most, a factor of 2 in 10^3 s, the initial accumulation of radicals during a 100 s photolysis period is caused only by reaction of 'hot' fluorine atoms (F_h) with CH_4:

$$F_h + CH_4 \rightarrow CH_3 + HF \quad (3)$$

The low rate of reaction (1) in comparison with that of reaction (2) at 13–16 K supports this conclusion. The measured quantum yield of radicals in reaction (3) can be described as:

$$_R =_0 \frac{\sigma_t LX}{1 + \sigma_t LX} +' zX \quad (4)$$

where the first term is due to the long-range migration of F atoms, formed by photodissociation of the isolated F_2 molecules [σ_t is the cross-section of reaction (3)]. The second term arises from the contribution of pairs of reactants (photolysis quantum yield $'$). The probability of formation of such a pair equals zX under the random distribution of reactants (z is the coordination number, $z = 12$ for the fcc-lattice of solid argon). Formation of radicals in complexes competes with the cage reaction yielding CH_3F and HF, which according to ref. 2 is the main channel of F atom conversion in ternary mixtures at $T < 20$ K. In binary CH_4/F_2 mixtures Φ_{CH_3} was 0.5.[5] At $\Phi_0 \approx 1$ the first channel would dominate if $\Phi_R/X > 6$, but the experimental value ($_R = 1.1 \pm 0.2$) do not allow us to make such a conclusion.

To complete the set of reactions of 'cold' F atoms the bimolecular recombination is worth considering:

$$F_t + F_t \rightarrow F_2 \quad (5)$$

This process is absent at low temperatures since the yield of radicals is almost independent of the time delay between photolysis and subsequent warming to 24 K. The CH_3 concentration increased by 6–8 times after warming up. This result is in agreement with the previous data,[4] according to which diffusion and recombination of F_t atoms were not detected on a time scale of $\sim 10^3$ s. At $T > 20$ K most F_t atoms recombine in reaction (5), while some of them are involved in reaction (1). The fraction of F_t atoms participating in reaction (1) is proportional to T, testifying to a sharper temperature dependence of k_1 as compared with k_5. The depletion of the radicals at $T < 18$ K can be assigned to geminate recombination of closely spaced CH_3 and F formed under photolysis of complexes. The F–CH_3 spacing L_g in these pairs falls far short of the average spacing in the mixture. The remaining radicals ($\sim 50\%$) correspond to long distance pairs.

We assumed that high-temperature kinetics (curve for $T = 19.5$ K in Fig. 3) is governed by the diffusion-controlled recombination of F_t atoms in reaction (5), homogeneously reacting with CH_4 molecules and CH_3 radicals [reactions (1) and (2), respectively]. Within slow ($k_2 \ll k_5$) and diffusion-controlled ($k_2 = k_5/2$) radical recombination approximations we obtained $k_5 \sim 10^{-22}$ cm^3 s^{-1}, this being in agreement with the previous data,[4] and $k_1 \sim 10^{-25}$–10^{-26} cm^3 s^{-1} [k_1, k_2 and k_5 are the rate constants of reactions (1), (2) and (5), respectively]. Since $k_1/k_5 \sim 10^{-3}$–10^{-4}, the barrier of reaction (1) would be 1.5–1.8 kcal mol^{-1}, which exceeds the value in the gas phase by 1.2 kcal mol^{-1}.[8] A detailed analysis of the kinetics of reactions (1), (2) and (5) will be presented later.

The main result of this work is the detection of hydrogen abstraction from methane molecules by thermalized F atoms. The rate constant is four orders of magnitude smaller than the diffusion limit at 20 K.

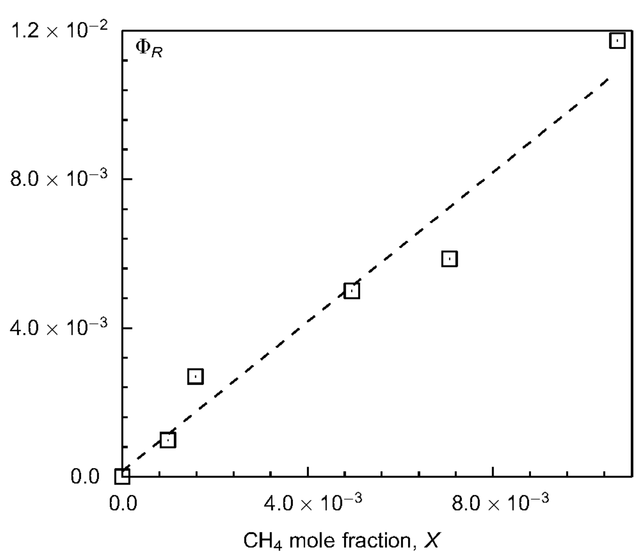

Fig. 2 CH_4 mole fraction dependence of CH_3 quantum yield. Temperature of photolysis 13 K. $Ar/F_2 = 300:1$.

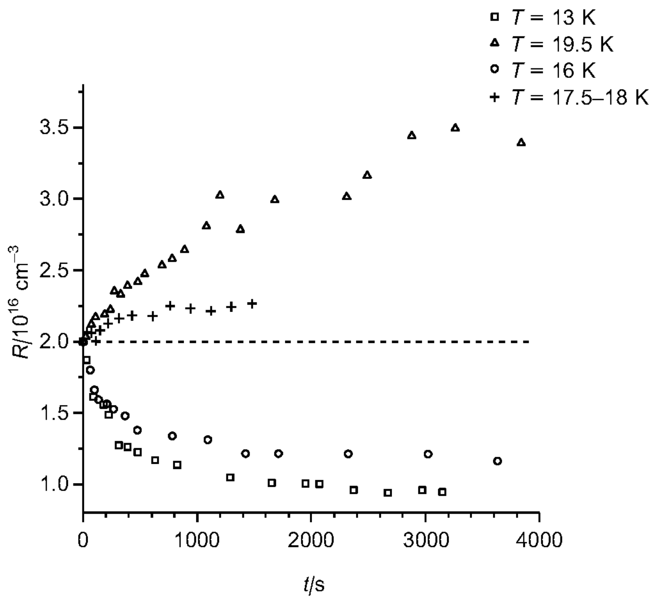

Fig. 3 The variation of CH_3 concentration in the course of the dark reaction in $Ar/CH_4/F_2 = 500:2:1$ at different temperatures.

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