The Formation of Pairs of Widely Spaced Methyl Radicals following Fluorine Photolysis in Solid Methane at 10–15 K

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Quantum yields of CH_3 radicals ($Y_R = 0.95\pm0.2$) and $CH_3F\cdots HF$ complexes ($Y_0 = 0.6\pm0.1$), formed by UV photolysis in CH_4–F_2 solid mixtures (70:1), have been measured using EPR and IR spectroscopy. Since $\frac{1}{2}Y_R + Y_0 \cong 1$, fluorine atoms do not recombine in a cage; approximately half of them are involved in formation of the complexes while the rest gives CH_3 radical pairs. The fraction of pairs with an inter-radical spacing > 20 Å is 0.1–0.15.

The quantum yield of $CH_3F\cdots HF$ complexes $Y_0 = 0.6 \pm 0.1$ has been measured previously in studies of fluorine photolysis in solid methane–fluorine mixtures (with a relative concentration of F_2, $C \leqslant 10^{-2}$).[1] The complexes form in a cage reaction of two F atoms with one of the nearest CH_4 molecules. The destiny of the rest $(1 - Y_0)$ of the atoms remained unknown. They can either recombine or give radical pairs $CH_3\cdots CH_3$. Formation of such a pair is the first step of the previously[1] observed free radical chain reaction in an equimolar mixture of reactants. In this work we determine, for the first time in studies of solid state low temperature reactions, the probabilities of these methods of F atom conversion measuring the quantum yield of the CH_3 radicals formed by photolysis in CH_4–F_2 mixtures. Moreover, we are able to estimate the fraction of the radical pairs, produced by the long range migration of F atoms, escaping from a cage.

The EPR spectra of the CH_3 radical were previously observed in UV-irradiated solid triple mixtures CH_4:F_2:Ar at 4.2 K by Cochran *et al.*[2] IR spectra of this radical in similar mixtures were reported by M. Jacox,[3] G. Johnson and L. Andrews.[4] They established that fluorine atoms, formed by F_2 photolysis in the solid mixture[2,4] as well as those formed in a gas phase and then embedded into the sample,[3] can abstract a hydrogen from CH_4. Nevertheless, quantum yields of the products were not measured.

All experiments were carried out in a home-made cryostat with a moving helium shaft, similar to that described in ref. 5. Samples were prepared by simultaneous deposition of separate effusive beams of reactants onto a flat sapphire rod kept at 10 K. After deposition the rod with the sample was lowered down the microwave cavity. The technique of preparation of solid binary samples, which allows minimisation of the probability of spontaneous reaction upon deposition, was described in ref. 1. The temperature of the sample was monitored with the thermocouple mounted on the top of the rod and with the internal EPR standard attached to the rod near the sample. The temperature dependence of the EPR signal intensity of this standard obeys Curie's law. In a special experiment we checked that the temperatures of the ends of rod differed at most by 1 K. The radical concentration was determined by comparing the intensities of integrated EPR spectra of the sample and the internal standard. The sensitivity of measurements was better than $\sim 10^{11}$ radicals in the sample. A pulsed N_2-laser (λ 337 nm, $\sigma_{F_2} = 1.05 \times 10^{-20}$ cm^2) was used for photolysis. In this work we studied binary mixtures CH_4:F_2 = 70:1. The methane content in the samples varied from 2 to 8 × 10^{19} molecules.

The CH_3 concentration after deposition and before photolysis did not exceed 10^{-6} mol %. Photolysis yielded an intensive EPR spectrum shown in Fig. 1(*a*). It consists of four uniformly spaced hyperfine lines (the line spacing ~22.8 G agrees well with that of CH_3 in solid Ar[6,7]). The intensity ratio of lines is close to that expected 1:3:3:1. The line width being 4 G after deposition increases to ~5 G at high concentration of the radicals. The shape of the spectrum has only a weak dependence on temperature (in the interval 10–15 K) and concentration of radicals (up to 10^{-3} mol%). The kinetics of accumulation of CH_3 radicals is shown in Fig. 2. The quantum yield of the radicals, determined from the initial slope of the curve [equation (1)],

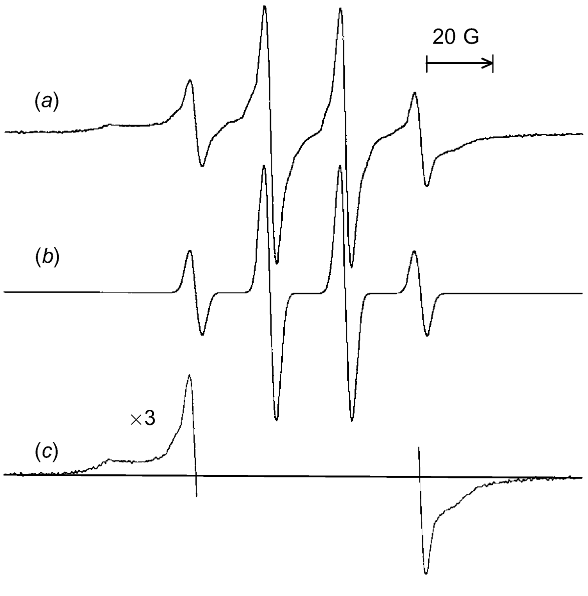

Fig. 1 EPR spectrum of methyl radicals formed by photolysis in mixtures CH_4:F_2 = 70:1 at 10 K: (*a*) total spectrum; (*b*) spectrum of distant radicals found by subtraction of background from spectrum (*a*); (*c*) the side bands of the lowest and highest field components, assigned to pairs with the minimal inter-radical spacing.

$$Y_R = \frac{1}{I}\left(\frac{dN}{dt}\right) \qquad (1)$$

is 0.95 ± 0.2 ($I = \sigma N_{F_2} I_0$, I_0 is the intensity of light, N_{F_2} is the number of F_2 molecules in the sample, dN/dt is the rate of accumulation of radicals).

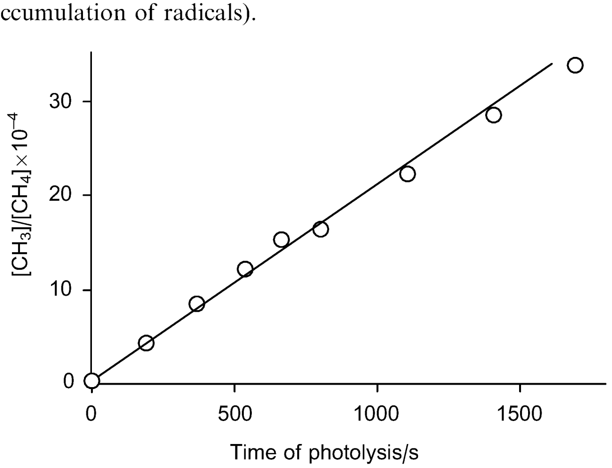

Fig. 2 Kinetics of accumulation of radicals upon photolysis of binary mixture CH_4:F_2 = 70:1 at 10 K. The initial number of methane molecules in the sample N_0 was 3 × 10^{19}. The intensity of laser light I_0 was 2 × 10^{15} cm^{-2} s^{-1}.

When this result is compared with the previously measured Y_0, it is apparent that equation (2) holds:

$$\frac{1}{2} Y_R + Y_0 \cong 1 \qquad (2)$$

Thus the main channels of conversion of F atoms are:
(*a*) *Cage reaction with one* CH_4 *molecule*:

$$[F + CH_4 + F] \xrightarrow{Y_0} [CH_3F \cdots HF], \qquad (3)$$

(*b*) *Formation of a radical pair* $CH_3 \cdots CH_3$:

$$[CH_4 + F \cdots F + CH_4] \xrightarrow{\frac{1}{2}Y_R} [HF + CH_3 \cdots CH_3 + HF] \qquad (4)$$

The overall probability of the other methods of conversion of F atoms, *i.e.* cage recombination and stabilisation, does not exceed the total accuracy of the IR and EPR experiments (< 0.3). This result differs essentially from that obtained in studies of Cl atom reactions in solid hydrocarbons.[8] The main processes following the Cl_2 photodissociation are recombination and a cage reaction similar to reaction (3) (probabilities 0.6–0.7 and 0.25–0.3, respectively) whereas the quantum yield of the stabilised alkyl radicals does not exceed 0.1.

It can be seen from the shape of the integrated spectrum (Fig. 3) that it consists of a well resolved 1:3:3:1 quartet and a line with unresolved hyperfine structure and the same width of the envelope as the quartet. The resolved quartet is assigned to the radical pairs in which splitting between parallel and perpendicular resonant fields is less then the line half-width ($H_{\|} - H_{\perp} \leqslant H_{1/2} \approx 4$ G). Since $H_{\|} - H_{\perp}$ is determined by electron dipole–dipole interactions depending on the inter-radical spacing R in a pair ($H_{\|} - H_{\perp} = 3\mu_0/R^3$),[9] this condition corresponds to $R \geqslant 20$ Å. The structureless background is assigned to $CH_3 \cdots CH_3$ pairs with shorter spacings, because the EPR spectrum of the fluorinated methyl radical (the only possible secondary radical in the studied system) is far beyond the envelope. The shortest spacing R_{min} determines the displacement of the side bands with respect to the lowest and highest field lines $m_I = \pm\frac{3}{2}$ by μ_0/R^3_{min} and $-2\mu_0/R^3_{min}$, respectively [Fig. 1(*c*)]. The value found for R_{min} is 9 Å. This corresponds to the reaction of F atoms with methane molecules from the nearest environment of the dissociated F_2 molecule. The fraction of pairs with $R \geqslant 20$ Å is 0.1–0.15. The absence of the resolved structure of the background points to the fact that the R distribution of pairs is continuous in the range 9 Å $\leqslant R \leqslant 15$ Å.

The results obtained demonstrate that some of the "hot" F atoms, formed by photodissociation of a F_2 molecule with energy $E = (h\nu - D)/2 \cong 0.5$ eV ($h\nu$ is the photon energy, D is the dissociation bond energy of F_2), react outside the parent cage. Previously Alimi *et al.*[10] showed that in solid Ar approximately half of the fluorine atoms with energy ~ 0.3 eV escapes from a cage and migrates over ~ 30 Å before stabilization in the lattice. In the system studied the long range migration proceeds through the ensemble of molecules with which the "hot" atom can react. This result is at variance with the traditional concept of solid state low temperature chemical reactions, which generally proceed inside a cage. In particular the long range migration of the "hot" F atoms leads to peculiarities of stabilisation of the atoms in noble gas crystals[11] and causes the high quantum yield of secondary product (CH_2F_2 molecules) in a chain reaction in equimolar mixtures of methane and fluorine.[1]

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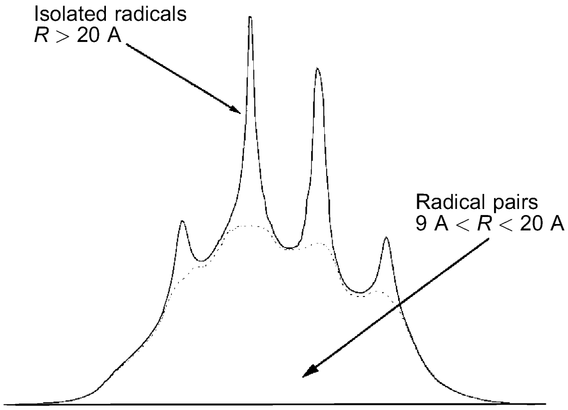

Fig. 3 The integrated EPR spectra of CH_3 radicals.

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