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ScienceDirect
Mendeleev Commun., 1994, **4(2)**, 71–73

Mendeleev
Communications

Chain Crossing upon Solid State Methane Photofluorination at 16 K

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Photolysis of solid equimolar mixtures of CH_4 and F_2 at 16 K leads to formation of spatially isolated CH_3F, CH_2F_2 and HF, whereas in methane-diluted mixtures ($[CH_4]:[F_2] = 60:1$) cage formation of $CH_3F\cdots HF$ complexes prevails; the observed quadratic relation between CH_2F_2 concentration and exposure dose and high quantum yield of the secondary product (per CH_3F molecule formed) means that CH_2F_2 molecules are formed from CH_3F, generated by the growth of previous chains.

Recent studies showed that solid state chain reactions take place at extra low temperatures.[1,2] The central problem in the attainment of long chains and a high conversion degree in these reactions is the preparation of reactant packing suitable for chain growth in the absence of transitional diffusion. The recrystallization technique of preparing mixed C_2H_4:Cl_2 crystals with alternating reactant packing is described elsewhere.[3,4] *trans*-$C_2H_4Cl_2$ was formed during quasi one-dimensional chain

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growth. The conversion degree was close to 100% and initial chain length *v* was about 300 units. However, reactant mixtures formed under cryogenic conditions are normally disordered. As was shown with photochlorination of hydrocarbons, the conditions for chain growth in these mixtures are determined by the statistics of reactant mixing. The chain length is limited by hindered rotation of alkyl radicals and *v* does not exceed 3–7 links.[5,6] In order to study chain growth in mixtures with a random three-dimensional reactant arrangement over the lattice sites, we chose the reaction of methane chain photofluorination in CH_4–F_2 mixtures. Elementary reactions of chain growth, reactions (1) and (2), have low barriers ($\leqslant$ 1 kcal mol^{-1}) in the gas phase. The high reactivity of F atoms at cryogenic temperatures was previously shown by studying photolized matrix-isolated complexes $F_2 \cdots CH_4$. Methane photofluorination was previously studied in argon-diluted systems.[7]

$$F + CH_4 \longrightarrow CH_3 + HF \qquad (1)$$

$$CH_3 + F_2 \longrightarrow CH_3F + F \qquad (2)$$

It is impossible to prepare solid binary samples *via* condensation from a gaseous mixture of reactants at room temperature because of spontaneous collisional reaction. In practice, this goal can be accomplished by condensation of separate molecular jets, crossed in a collision-free region near the cold substrate. Sublimation energies of CH_4 and F_2, 2.28 and 2.46 kcal mol^{-1}, respectively, taken from their phase diagrams below the triple point, are small and approximately equal. This suggests the formation of a solid solution with random reactant arrangement over the lattice sites during the deposition. In this paper we present the first results of a study on photochemical conversion in solid CH_4–F_2 mixtures, obtained with IR spectroscopy.

The techniques of sample preparation and kinetic IR measurements were described earlier.[4] A copper substrate with high thermal conductivity was used instead of a dielectric one and a reflection scheme for recording the IR spectrum was employed. Methane and fluorine films were prepared *via* simultaneous condensation of separate gas beams onto a 12 K substrate at 10^{-6} Torr. The beams were pre-cooled to $\approx$90 K and crossed only near the substrate. The copper substrate was protected from F_2 by condensation of $\approx$100 molecules of methane on its surface. The condensation rate was $\approx 5 \times 10^{15}$ $cm^{-2} s^{-1}$. The thickness of films varied from 1–50 μm. A pulsed N_2-laser [$\lambda = 337$ nm, repetition frequency 1 kHz, F_2 absorption cross-section $\sigma = 1.05 \times 10^{-20}$ cm^2] was used for photolysis. Methane consumption and accumulation of reaction products were monitored by measurement of the intensities of the corresponding IR bands.

Several calibration experiments were carried out (see ref. 4 for details) to measure the characteristic frequencies and intensities of the IR bands in mixtures containing different amounts of reactants and fluoromethanes. In 1:1 mixtures of CH_4 and F_2 the ν_3 band of CH_4 (3006 cm^{-1}) is close to that measured in the Ar matrix,[7] while its integral intensity, 33 km mol^{-1}, corresponds to that measured in the gas phase.[8] The frequencies of the C–F stretching vibrations of fluoromethanes ($\nu_2 = 1011$ cm^{-1} for CH_3F, $\nu_3 = 1045$ cm^{-1} for CH_2F_2 and $\nu_2 = 1130$ cm^{-1} for CH_3F) in the methane matrix are red-shifted by $\approx$25–40 cm^{-1},[9] and their intensities are 1.2–1.4 times higher than those in the gas phase, being 120, 245 and 630 km mol^{-1} for CH_3F, CH_2F_2 and CHF_3, respectively.

Fluorine photolysis in ternary mixtures ($Ar{:}CH_4{:}F_2 = 70{:}1{:}1$) leads to the appearance of intense absorption bands at 1003 and 3775 cm^{-1}, which were previously observed[7] and assigned to C–F and H–F vibrations of molecules in the hydrogen-bonded complex $H_3CF \cdots HF$, formed in the cage reaction of CH_4 with two F atoms. Photolysis of binary mixtures ($CH_4{:}F_2 = 60{:}1$) gives the same products as the photolysis of triple mixtures with a quantum yield of CH_3F formation Y_0 equal to 0.6 ± 0.1. A broad, unassigned band at 950 cm^{-1}, which does not appear in the triple mixtures, was observed in this case. This band was also detected during the photolysis of equimolar mixtures. Heating of photolized samples to $\approx$30 K leads to an increase in the intensity of the band at 1004 cm^{-1} (by $\approx$1.2 times), and to the disappearance of the band at 950 cm^{-1}. The band 950 cm^{-1} was not previously detected; it is tentatively assigned to the attachment radical CH_4F.

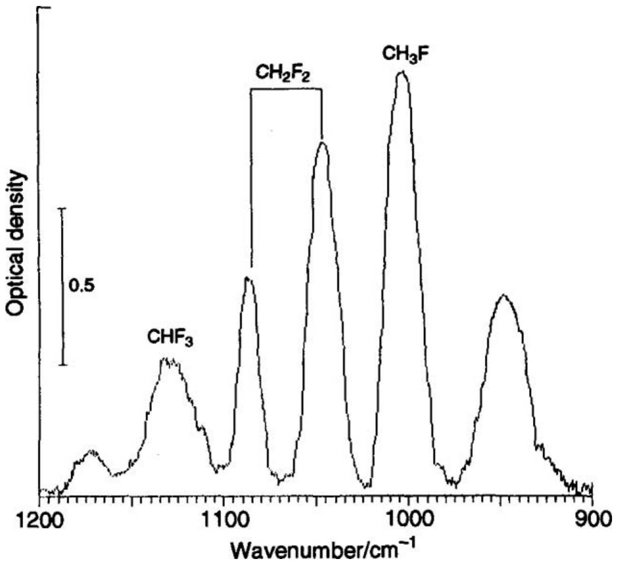

Fig. 1 IR absorption spectra of an equimolar mixture in the C–F vibration region of fluoromethanes after 15 min photolysis at 16 K ($I_0 = 2 \times 10^{15}$ $cm^{-2} s^{-1}$, $N_{0F} = 1.1 \times 10^{19}$ cm^{-2}).

The photolysis of equimolar mixtures $CH_4{:}F_2$ features a high quantum yield of methane consumption $Y_M = 3.7 \pm 0.5$. Absorption at 1011 cm^{-1}, assigned to the formation of hydrogen bond-free CH_3F, grows in the initial stage. The CH_3F concentration (C_1) is proportional to the exposure dose $D = I_0t$ in the photolysis intensity operating region 10^{14}–5×10^{15} cm^2. The quantum yield of CH_3F accumulation, $Y_{FM} = 3.4 \pm 0.5$, is close to Y_M and also exceeds unity. The average values of Y_M and Y_{FM} are independent of the film thickness and photolysis intensity. The values of Y_M and Y_{FM} testify to the chain mechanism of conversion.

Absorption bands, assigned to CH_2F_2 and CHF_3, appear in the spectra with a growing band at 1011 cm^{-1} (see Fig. 1). The CH_2F_2 accumulation is such that the relative CH_2F_2 concentration depends quadratically on the exposure dose, so that equation (3) holds,

$$C_2 = KC_1^2 \qquad (3)$$

where $C_1 = N_1/N_{0F}$, $C_2 = N_2/N_{0F}$, N_1 and N_2 are the number of CH_3F and CH_2F_2 molecules, respectively; N_{0F} is the initial amount of F_2 in mixture and $K = 4.5$ (see Fig. 2).

The quadratic relationship between C_2 and D means that the CH_2F_2 molecule is formed as a result of two independent photolysis events. This rules out the formation of CH_2F_2 as a result of the growth of a single chain, when the products of the reaction (2) combine with the CH_2F radical, reactions (4) and (5).

$$F + CH_3F \longrightarrow CH_2F + HF \qquad (4)$$

$$CH_2F + F_2 \longrightarrow CH_2F_2 + F \qquad (5)$$

The reaction of the excited CH_3F molecule with F_2 should not be considered for the same reason.

For the relation (3) to be valid, fluorine atoms participating in reaction (4) should be created upon absorption of the second photon in some region near the previously-formed CH_3F

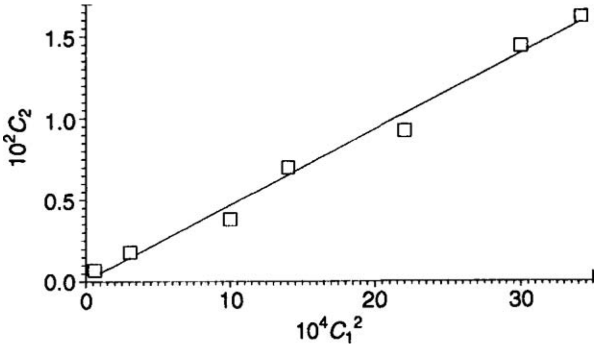

Fig. 2 C_1^2 dependence of relative CH_2F_2 concentration (C_2), formed during photolysis of equimolar CH_4:F_2 mixtures.

molecule. These F atoms can be produced either (*a*) by direct photolysis, or (*b*) by subsequent chain growth. If there are n F_2 molecules in the neighbourhood of the CH_3F molecule, the quantum yield of CH_3F conversion to CH_2F_2 can be expressed in equation (6).

$$Y_2 = \frac{1}{I_0C_1\sigma}\frac{dC_2}{dt} \approx \frac{30}{n} \qquad (6)$$

If the F atom formed in reaction (5) participates in reaction (1) rather than (4), then $Y_2 < 1$ and $n > 30$, so that the neighbourhood contains at least four coordination spheres for the CH_3F molecule. This estimate shows that the mechanism (*a*) above is realized only through the long-range migration of hot fluorine atoms to CH_3F molecules. For $n < 30$, the quantum yield $Y_2 > 1$. This is possible if a chain from the secondary product appears which follows the trace of the previous chain. The length of this chain should be greater than $30/n$.

All mechanisms listed for CH_2F_2 formation imply that an active particle in a growing chain (fluorine atom) crosses the line of CH_3F molecules formed upon the growth of previous chains. Which of the above-described ways of chain crossing predominates will depend on the spatial distribution of CH_3F and the relative probability of reactions (1) and (4). The mixed scenario seems to be the most probable: once several chain links have grown, a crossing occurs; after that, the chain grows along the trace of the previous one, after which it grows through reactions (1) and (2). The detailed analysis of conversion kinetics by means of computer simulations of chain growth and crossings in a three-dimensional lattice, taking into account different mechanisms of hot F atom migration, will be reported separately.

The authors wish to thank the Russian Fund of Fundamental Research (grant no. 93–03–5930) for the financial support of this work, and Mr. B. Nizamov for help in the experiments.

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Received: Moscow, 14th September 1993
Cambridge, 11th January 1994; Com. 3/05647C