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Low-temperature addition of molecular fluorine to unsaturated perfluorohydrocarbons

S. R. Allayarov,^a* I. M. Barkalov,^a L. M. Ivanova,^b and I. P. Kim^a

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

^bUral Industrial Association «Galogen», 610020 Perm', Russian Federation

Calorimetry and ESR spectroscopy were used to study the low-temperature fluorination (77-300 K) of unsaturated perfluorohydrocarbons. In the solid phase at 77-100 K (glassy or crystalline state) fluorination does not occur. On transition from glassy systems to the overcooled liquid state formation of molecular complexes in which fluorine is attached to the >C=C< bond becomes possible. These complexes are stabilized on crystallization of the system; with a further increase in temperature, efficient addition of molecular fluorine takes place in the crystal phase. However, the addition of fluorine by some chain or carbene mechanism must not be ruled out for such systems. Thus, in the case of hexafluoropropylene trimer, the addition proceeds as a chain reaction producing long-living free radicals at the initial stage.

Key words: unsaturated perfluorohydrocarbons; low-temperature fluorination; calorimetry; ESR study.

The interaction of fluorine with perfluorinated olefins can proceed according to the following substantially different mechanisms.

1. Molecular addition

 $>C=C + F_2 \longrightarrow >C-C$

2. Chain-like addition

 $>c=c + F \longrightarrow c - c + F$ $\rightarrow c - c + F_2 \rightarrow c - c + F$

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$$C = C + F \longrightarrow CF + :C <$$

$$:C + F_2 \longrightarrow CF_2$$

$$:C + F_2 \longrightarrow CF_2 + F$$

These paths lead to different sets of final products, which suggests different energetics of each of the processes. The heat effects that should accompany the possible paths can be assessed. The following heat values (ΔH) were used for the assessments: rupture of C-F bond, 124.5 kcal mol⁻¹;¹ dissociation of F₂ molecule into atoms, 37 kcal mol⁻¹;² rupture of C-C bond (in hexafluoroethane), 96 kcal mol⁻¹;³ rupture of >C=C< bond (in tetrafluoroethylene), 76 kcal mol⁻¹.⁴ The heat effects of the two former addition paths are close to 115 kcal mol⁻¹ which is in a satisfactory agreement with the value of ~107 kcal mol⁻¹ assessed in ref.⁵.

Carbene formation (the third reaction path) proceeds with a substantially different heat effect. This value is assessed to be about 174 kcal mol⁻¹ (with respect to one mol of fluorine) which is much greater than the exothermic effects in the former two transformations. As a consequence, calorimetric measurements can provide information on the contribution of each path of fluorine addition to the fluorination process as a whole. In addition, reactions that proceed according to the three paths are accompanied by formation of different radical intermediates whose lifetimes can vary significantly. Therefore, ESR spectroscopy can also be very informative for studying the mechanism of fluorination.

Here we report the results of calorimetric and ESR studies of the addition of molecular fluorine to unsaturated perfluorohydrocarbons at low temperatures.

Experimental

Tetrafluorethylene (TFE), hexafluoropropylene (HFP), the dimer and the trimer of hexafluoropropylene (DHFP and

THFP, respectively), perfluorobenzene, and perfluoro-*p*-xylene were used in the study. All the compounds contained no less than 99 % of the main compound. A weighed specimen of a perfluorohydrocarbon (*ca.* 10^{-3} mol) was placed into a calorimetric quartz tube and degassed to 10^{-3} Torr using a vacuum pump. Then the tube was cooled to 77 K, filled with gaseous fluorine (*ca.* 10^{-5} mol), and sealed by means of a vacuum valve. The tube thus prepared was left to thaw in a calorimetric unit, and the heat effects produced by the phase transitions and the fluorination reactions were monitored.

ESR spectra were recorded using an ESR-211 radiospectrometer. Samples were placed into a thermostat, kept for 8-10min at a desired temperature, and then rapidly cooled to 77 K. All the ESR spectra were taken at this temperature.

Results and Discussion

As the first step, the calorimetric analysis of the phase changes of THFP was carried out in a temperature range of 77–200 K. On rapid freezing to 77 K the whole of THFP adopts a glassy state. In the course of thawing in the calorimeter, its transition from the glassy state to the overcooled liquid state can be observed at $T_{\rm g} \sim 150$ K as a typically steep, step-like change in heat capacity followed by another transition to the thermodynamically stable liquid state which takes place without crystallization and, hence, without melting of the sample (Fig. 1, 1).

Fluorine does not react with glassy THFP at 77 K. On heating the sample in the calorimeter, no heat is released when the system passes to the overcooled liquid state. With a further increase in temperature a region of heat evolution is observed which is associated with the addition of fluorine (Fig. 1, 2). The integral heat evolution corresponding to this peak is not high (~1.6 cal g⁻¹) and already ceases at ~200 K.

Simultaneously, the dynamics of the formation of paramagnetic sites were monitored under identical experimental conditions during thawing of the THFP- F_2 mixture in an ampule placed into the resonator of the



Fig. 1. Calorimetric thawing curves of THFP (1) and THFP+ F_2 (1 mol. %) (2) samples.



Fig. 2. Temperature dependence of the concentration of free radicals in the THFP+ F_2 (3 mol. %) system.

ESR radiospectrometer. The dependence thus obtained is shown in Fig. 2. The onset of the formation of free radicals occurs at ~115 K. There appears a poorly resolved doublet ESR spectrum, which can be assigned to a radical resulting from the addition of a fluorine atom to the double bond of THFP; this process has been described earlier.^{6,7}

$$(F_3C)_2C=C(C_2F_5)CF(CF_3)_2 + F \longrightarrow (F_3C)_2CFC(C_2F_5)CF(CF_3)_2$$

Free radicals of this type are incapable of recombination even in the neat liquid state at ~293 K, and they have an infinite lifetime. Their concentration remains practically constant up to 200 K, and it is only at higher temperatures that it rises sharply to reach $1.4 \cdot 10^{19} \text{ g}^{-1}$ at ~293 K (see Fig. 2).

Thus, virtually no formation of radicals takes place in the temperature range where heat evolution is observed. It seems reasonable to attribute this heat evolution to the addition of fluorine to the double bond. The addition is likely to proceed via molecular complexes formed in the solution. As the temperature increases, the steady-state concentration of such complexes decreases and hence the rate of this addition decreases as well.

At more elevated temperatures (≥ 200 K) there begins the addition of atomic fluorine to give type 1 radicals at the first stage of a chain reaction. These radicals are of low reactivity and can react only with fluorine. However, under these conditions the chain reaction cannot go on due to the depletion of fluorine and thus stops after the formation of radical 1.

From the ESR measurements it can be calculated that the formation of type 1 radicals consumes $1.7 \cdot 10^{-5}$ mol of fluorine. Since the starting amount of fluorine was $3.5 \cdot 10^{-5}$ mol, the low-temperature addition of fluorine must consume $1.8 \cdot 10^{-5}$ mol of fluorine, with heat evolution of 2 cal (see Fig. 1). On the basis of these data, the specific heat of molecular addition of fluorine to the



Fig. 3. Calorimetric thawing curves of DHFP (1) and DHFP+ F_2 (1 mol. %) (2) samples.

double bond of THFP can be calculated. The value thus obtained $(\Delta H \sim 111 \text{ kcal mol}^{-1})$ is in good agreement with the results of calculations and with the literature data cited above.

Thus, the following picture of the low-temperature fluorination of THFP begins to emerge. Virtually no fluorination of glassy THFP takes place. With increasing temperature, upon the transition of the system to the overcooled liquid state, the dissolution of gaseous fluorine in the liquid and the formation of molecular complexes become possible; molecular addition of fluorine to THFP is likely to proceed through these complexes. Naturally, as the temperature rises, the solubility of fluorine in the liquid and hence the concentration of molecular complexes decrease. This is why only about half of the starting amount of fluorine is consumed in the molecular addition. The chain addition of atomic fluorine under the conditions studied does not proceed beyond the first step, which affords only type 1 radicals. This reaction consumes the rest of fluorine. It should be noted that a similar picture is also observed for the fluorination of THFP under more severe conditions.⁶

More complex phase transitions occur in the case of DHFP. On rapid freezing to 77 K, the whole of DHFP adopts the glassy state. When the resulting sample is left to thaw in the calorimeter, a transition from the glassy state to the overcooled liquid state is observed at ~100 K. This is followed by the crystallization of the sample at ~125 K with heat evolution and subsequent melting at 160 K (Fig. 3).

Fluorine does not react with DHFP at 77 K. No heat evolution is observed on heating DHFP in the calorimeter as the system passes to the overcooled liquid state. On further warming the crystallization of the system takes place, followed by heat evolution associated with the addition of fluorine. Heat evolution is also observed after the melting of the system (see Fig. 3). Fluctuations in the fluorination rate reflect the heterogeneous nature of the process.



Fig. 4. Temperature dependence of the concentration of radicals R^1 (1) and R^2 (2) in the DHFP+F₂ (4.5 mol. %) system.

Fig. 4 presents the temperature dependence of paramagnetic centers in the course of low-temperature fluorination of DHFP. Crystallization of DHFP leads to the formation of paramagnetic centers. Two doublets with 18.1 mT and 5.28 mT splittings are observed in the ESR spectrum recorded at 77 K. As the temperature rises, the accumulation of radicals passes through a maximum. The decrease in their concentration above 215 K may be associated with the decay of the first type of radicals. The doublet ESR spectrum of such radicals having 18.1 mT splitting and 21.6 mT half-height width was previously attributed to the perfluoroalkyl radicals with one α -atom of fluorine.⁷ Their formation is due to the addition of a fluorine atom to the double bond of DHFP.

$$(F_3C)_2CFCF=CFCF_3 + F \longrightarrow (F_3C)_2CFCFCF_2CF_3$$

B¹

These radicals are incapable of recombining at low temperatures. The concentration of R^1 radicals reaches a maximum at 215 K (Fig. 4, *I*) and their decay is probably associated with the addition of fluorine atoms.

The concentration of radicals displaying a doublet spectrum with 5.28 mT splitting remains constant at temperatures above 215 K (Fig. 4, 2). The ESR spectrum of this radical is similar to that of the R^2 radicals formed on fluorination of THFP as the result of secondary transformations, where traces (~0.03 %) of a DHFP isomer may be involved.

Similarly to the case of THFP, the appearance of radicals upon fluorination of DHFP is observed at higher temperatures than those at which heat evolution is registered by the calorimetric curves of fluorination. After the transition of DHFP to the overcooled liquid state, the formation of the DHFP— F_2 molecular complex becomes possible. However, in contrast to THFP, these eomplexes do not decompose at elevated temperatures, but rather stabilize due to the crystallization of the system. Further warming leads to the molecular addition of fluorine to the double bond of DHFP with concomitant heat evolution that is recorded by the calorimeter.

The amount of heat evolved on fluorination of DHFP is over an order of magnitude above that registered in the course of fluorination of THFP under similar conditions. On the other hand, the concentration of radicals in a sample of DHFP is almost three orders of magnitude below that registered for THFP. Therefore, a possible contribution of the carbene and chain mechanisms in the process of DHFP fluorination must not be ruled out.

Thus, the dissolution of fluorine in an overcooled liquid brings about the formation of a molecular complex. Naturally, the concentration of such complexes decreases with the increase in temperature. However, as the system crystallizes, the complexes become more stabilized, which provides for more efficient addition of molecular fluorine to the >C=C< bond. In fact, when crystalline perfluorobenzene is warmed up in a calorimeter in the presence of fluorine, a minor heat evolution is observed at 170—180 K which is likely to be associated with the addition of fluorine from the surface of the polycrystals. On further heating of the sample, only melting of perfluorobenzene is observed at 269 K.

On the other hand, in the case of perfluoro-*p*-xylene, just as in the case of DHFP, no heat evolution is observed on the transition of the system to the overcooled liquid state (~150 K). Then, following the crystallization of the system, intensive heat evolution takes place on further warming. This heat evolution, associated with fluorination, ceases after melting (mp ~220 K). The total heat evolved is much higher in this case than for the fluorination of crystalline perfluorobenzene.

On cooling to 77 K, TFE and HFP become crystalline (mp = 142 K and 115 K, respectively). If they are re-melted in the presence of fluorine, spontaneous fluorination occurs at 84 K, followed by explosion. Therefore, the kinetics of their fluorination could not be studied.

Thus, steady warming of the solidified unsaturated perfluorohydrocarbons from 77 K to 200-300 K under gaseous fluorine results first in the dissolution of F_2 in the former (as the system passes to the liquid state or to an overcooled liquid state). Then there follows the formation of molecular complexes, and it is via these complexes that the addition of molecular fluorine to the double bond takes place. With a further increase in the temperature, the solubility of fluorine diminishes, and so does the concentration of the complexes. However, in some of the systems crystallization can stabilize the molecular complexes, which enhances fluorination efficiency. At higher temperatures chain-like fluorination occurs. It can be arrested at the stage of the formation of «sluggish» radicals. In some cases the carbene mechanism of addition cannot be ruled out.

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