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# Low-temperature Fluorination of Perfluoro-2,4-dimethyl-3-ethylpent-2-ene

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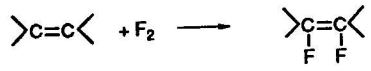
Calorimetric and EPR investigations of the low temperature (77–300 K) fluorination of unsaturated perfluorocarbons have shown that, in glassy systems, the formation of molecular complexes of fluorine with a C=C bond is possible during the transition to the supercooled liquid state; chain addition of fluorine to the title compound stops at the first stage, after formation of stable, long-lived radicals.

Fluorine addition to a C=C bond of perfluorinated alkenes can occur by several completely different mechanisms [eqns. (1)–(3)].

These paths lead to different final products and, respectively, to different energy profiles for the resultant thermal effects. For example, for C—F bond cleavage $\Delta H = 124.5$ kcal mol$^{-1}$,[1] for dissociation of a fluorine molecule into atoms $\Delta H = 37$ kcal mol$^{-1}$,[2] for cleavage of a C—C bond (in hexafluoroethane) $\Delta H = 96$ kcal mol$^{-1}$,[3] and for cleavage of a C=C bond (in tetrafluoroethylene) $\Delta H = 76$ kcal mol$^{-1}$.[4]† The thermal effect of reactions (1) and (2) is $\simeq 115$ kcal mol$^{-1}$, in satisfactory agreement with estimates given in ref. 5 of $\simeq 107$ kcal mol$^{-1}$.

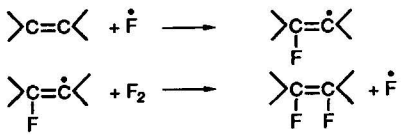
A considerably different thermal effect should arise in the case of carbene formation [reaction (3)]. Estimates give a value for the thermal effect as high as $\simeq 174$ kcal mol$^{-1}$ (per mole of fluorine) that significantly exceeds the exothermicity of the first two conversion paths. Hence, calorimetric measurements

*Molecular addition*



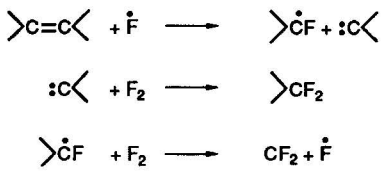
(1)

*Chain addition*



(2)

*Carbene formation*



(3)

would provide information on the contribution of one or other of these fluorine addition paths to a general picture of the fluorination. Since different mechanisms of fluorine addition lead to different radical intermediates, whose lifetimes may differ significantly,[6] an EPR analysis might also elicit information about this mechanism. Calorimetric and EPR investigations of the process of low-temperature addition of molecular fluorine to perfluoro-2,4-dimethyl-3-ethylpent-2-ene **1** (a trimer of hexafluoropropylene) were thus carried out.

We first carried out a calorimetric analysis of the phase state of THFP in the range 77–200 K. On fast freezing down to 77 K, **1** passes completely to a glassy state. On heating such a sample in a calorimeter, there is a transition region from the glassy state to a supercooled liquid, $T_g \simeq 150$ K (a characteristic change of heat capacity, or a 'step'), which then passes to a thermodynamically stable liquid without crystallization and, consequently, melting of the sample [Fig. 1(*a*)].

Fluorine does not interact with **1** in the glassy state at 77 K. On heating the sample in the calorimeter, no heat release is observed when the system passes to a supercooled liquid. After a further temperature rise in the system a region of heat release connected with fluorine addition is observed [Fig. 1(*b*)]. The integral heat release at this peak is not large ($\simeq 1.6$ cal $g^{-1}$) and it stops completely at $\simeq 200$ K.

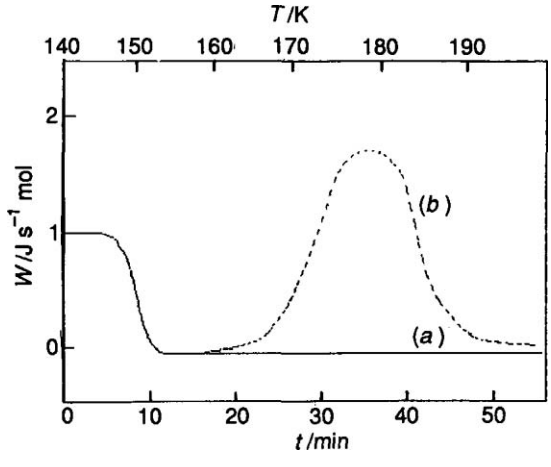



**Fig. 1** Calorimetric curves obtained on heating samples of (*a*) **1** and (*b*) **1** + $F_2$ (1 mol %)

† 1 cal = 4.184 J.

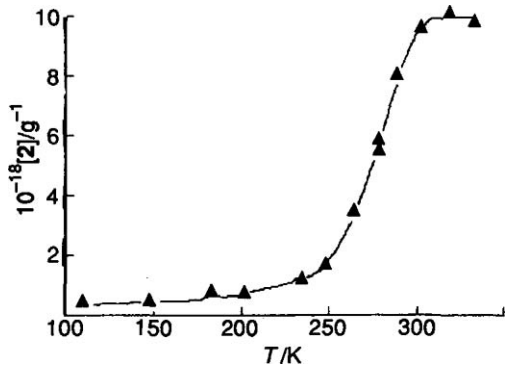



**Fig. 2** Concentration of radicals **2** *vs.* temperature for a sample of THFP + $F_2$ (3 mol %)

Simultaneously, under the same experimental conditions, while defreezing the **1** + $F_2$ system in an ampoule placed in an EPR spectrometer resonator, we followed the dynamics of the formation of paramagnetic centres. The experiment was carried out in the following way: a sample for EPR measurements was placed in a thermostat and held for 8–10 min at the required temperature. Then it was quickly cooled down to 77 K, all the EPR measurements being carried out at this temperature. Thus, the dependence represented in Fig. 2 was obtained. It can be seen that at ~115 K the formation of radicals **2** begins. A poorly resolved doublet appears in the EPR spectrum, assigned to the radical formed on addition of a fluorine atom to the double bond of a molecule of **1**, as described previously[6,7] [eqn. (4); Fig. 3].

Radicals of this type cannot mutually recombine, even in the liquid state at room temperature, and live for an infinitely long time. Up to 200 K the concentration of these radicals is practically unchanged and only at higher temperatures is there

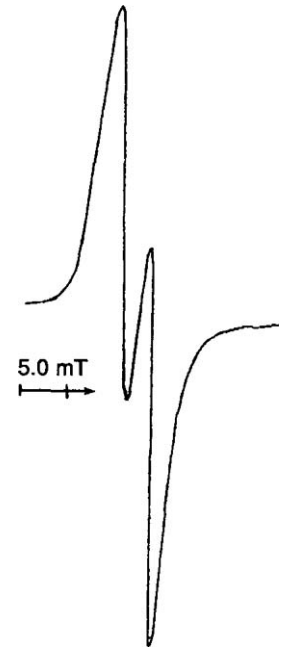
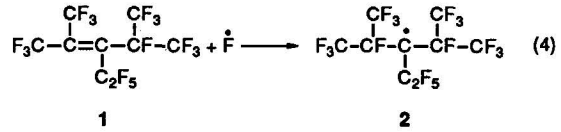



**Fig. 3** EPR spectrum of radicals **2** formed on fluorination of **1**; registration temperature 77 K



(4)

**1** **2**

a sharp increase in their concentration (Fig. 2). Their concentration reaches $1.4 \times 10^{19}$ g$^{-1}$ at room temperature.

Thus, in the temperature range where the heat release is observed, practically no radical formation takes place in the system under study. This was naturally thought to be due to addition of molecular fluorine to the double bond. Such an addition is assumed to occur in molecular complexes arising in solution. With an increase in temperature the steady state concentration of such complexes in the solution falls, hence, the rate of such addition also decreases.

At higher temperatures (> 200 K), addition of atomic fluorine and formation of the radicals of type **2** takes place as a result of the first stage of the chain reaction. This stable radical can interact only with fluorine. However, the chain reaction does not develop under these conditions and terminates with the formation of radicals **2**, as all the fluorine is already consumed.

Let us now give some quantitative estimates. As the EPR data show, in order to form a measured quantity of radicals **1**, $1.7 \times 10^{-5}$ mol of fluorine was consumed. All in all, $3.5 \times 10^{-5}$ mol was used for this experiment, hence, $1.8 \times 10^{-5}$ mol fluorine was used in the low-temperature molecular fluorine addition, 1.6 cal being evolved here (Fig. 1). The enthalpy change for molecular addition of fluorine to the double bond of **1** is $\Delta H \simeq 111$ kcal mol$^{-1}$, which is in good agreement with the calculated and literature data given above.

A picture of the low-temperature fluorination of **1** has thus emerged. For glassy **1**, fluorination is practically absent. At higher temperatures, together with a transition of the system to a supercooled liquid state, dissolution of the gaseous fluorine becomes possible, in addition to the formation of molecular complexes that are assumed to account for the addition of molecular fluorine to **1**. With a temperature increase, the solubility of fluorine in the liquid naturally decreases and, accordingly, lowers the concentration of the molecular complexes. This is why only half the initial quantity of fluorine is used in the molecular addition. The chain addition of atomic fluorine under the experimental conditions stops at the first stage of the formation of radicals **2**. This reaction consumes the remaining part of the initial fluorine. No indication of addition occurring by the carbene mechanism was found in the temperature range studied. It should be noted that the same situation was also observed under more rigorous conditions of fluorination of **1**.[6]

## References

1 C. Lifshitz and F. A. Long, *J. Phys. Chem.*, 1965, **69**, 3746.
2 J. Berkowitz, W. A. Chupka, P. M. Guyon, J. H. Holloway and R. Spohr, *J. Chem. Phys.*, 1971, **54**, 5165.
3 J. W. Coomber and E. Whittel, *Trans. Faraday Soc.*, 1967, **63**, 1394.
4 K. F. Zmbov, O. M. Uy and J. L. Margrave, *J. Am. Chem. Soc.*, 1968, **90**, 5090.
5 S. P. Halasz, F. Kluge and T. Marini, *Chem. Ber.*, 1973, **106**, 2950.
6 K. V. Sherer, T. Ono and K. Yamaguchi, *J. Am. Chem. Soc.*, 1985, **107**, 718.
7 S. R. Allayarov, I. V. Sumina, I. M. Barkalov, Yu. L. Bakhmutov and M. K. Asamov, *Izv. Vus. Khim. Tekhnol.*, 1989, **32**, 26 (in Russian).

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