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Mendeleev Commun., 1994, **4(5)**, 190–191
Mendeleev Communications

Biradical Intermediates in Tetrafluoroethylene Dissociation and Difluorocarbene Recombination

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Tetrafluoroethylene pyrolysis has been studied under the strictly homogeneous conditions of a free-piston monopulse adiabatic compression set-up, and biradical intermediate $\dot{C}F_2$–$\dot{C}F_2$ is shown to precede CF_2 formation. The rate constant for biradical decomposition into two CF_2 species is estimated to be $k_4 = 10^{13.5\pm0.1}\exp(-201 \pm 8 \text{ kJ mol}^{-1}/RT)\ \text{s}^{-1}$. Based on the detailed equilibrium principle CF_2 recombination is proposed to take place through biradical formation.

CF_2 reactions are well known to play a significant role in the thermal conversion of a number of organofluorine compounds. To illustrate this, pyrolytic synthesis of tetrafluoroethylene (TFE) is a good example.[1]

$$CHF_2Cl \rightarrow HCl + CF_2 \quad (1)$$

$$2CF_2 \rightarrow C_2F_4 \quad (2)$$

However, α-elimination such as reaction (1) is not the only method of CF_2 formation. For example, at elevated temperatures reaction (2) becomes reversible; this has been reliably established using spectral techniques under both shock-tube[2] and pulse adiabatic compression[3] TFE pyrolysis.

$$C_2F_4 \rightarrow 2CF_2 \quad (-2)$$

The goal of the present study is to determine whether reactions (2) and (−2) are elementary ones. The answer is of importance since if reaction (−2) is not a one-step reaction then according to the detailed equilibrium principle CF_2 recombination (2) is not an elementary reaction either.

Adiabatic compression was applied to TFE diluted with purified argon using the free-piston monopulse set-up described earlier[4] together with kinetic spectroscopy and mathematical simulation procedures. The main results are presented in Fig. 1, and the mixture under study and experimental conditions are characterized in the legend. In Fig. 1, point size corresponds to measurement errors while zero on the time axis indicates the moment of maximum pressure.

It is worthwhile noting first that neither the parent substances nor the final reaction products absorb in the UV and visible areas. It is seen from Fig. 1 that during the heating pulse an intermediate is formed before CF_2 (CF_2 does not absorb[5] at 250 nm). The intermediate was demonstrated[6]

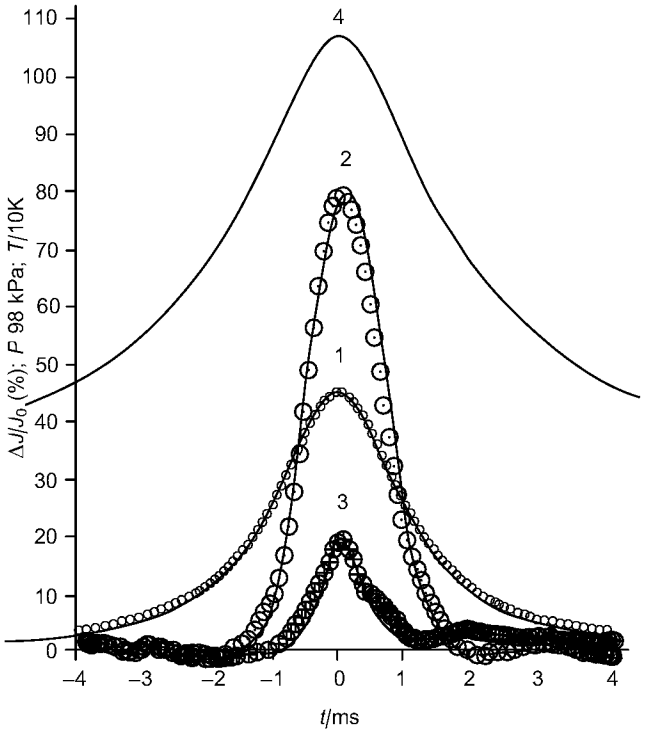

Fig. 1 The pressure (1), absorbance at 250 nm (2) and at 271 nm (3) and computed temperature (4) *versus* time under adiabatic compression pyrolysis of 5 vol.% of an C_2F_4/Ar mixture; measurements (points) and results of calculations (full lines). Extinction values for CF_2 and $\dot{C}F_2$–$\dot{C}F_2$ were used in the calculations as 8×10^5 and 2×10^6 cm^2 mol^{-1}, respectively. Initial pressure, 99.2 kPa; initial temperature, 297 K; maximum compression ratio, 13.

to be a $\dot{C}F_2$–$\dot{C}F_2$ biradical, the reversible formation of which was concluded to be the first step in TFE thermal cyclodimerization, reactions (3) and (−3).

$$CF_2{=}CF_2 \rightleftarrows \dot{C}F_2{-}\dot{C}F_2 \qquad (3), (-3)$$

The absorbance curves of $\dot{C}F_2$–$\dot{C}F_2$ (at 250 nm) and CF_2 (at 271 nm) are seen in Fig. 1 to be non-symmetric relative to the maximum compression point. Under adiabatic compression conditions this implies that the concentrations of both radicals are not in equilibrium during the compression/expansion pulse except for maximum absorbance points. The mathematical simulation of the process has allowed the correction of the rate constants for reactions (3) and (−3) estimated earlier in ref. 6.

$$\lg k_3 = (6.4 \pm 0.15) - (96 \pm 8\,\mathrm{kJ\,mol^{-1}}/2.3RT)$$
$$\lg k_{-3} = (4.5 \pm 0.1) - (12.5 \pm 2\,\mathrm{kJ\,mol^{-1}}/2.3RT)$$

The question arises as to whether a reversible process occurs, reactions (4) and (−4):

$$\dot{C}F_2{-}\dot{C}F_2 \rightleftarrows 2CF_2 \qquad (4), (-4)$$

Supposing the inequality for the corresponding reaction enthalpies $H_4 < H_{-2}$ to be sufficiently evident leads to the view that the most probable mechanism for CF_2 formation includes successive elementary reactions (3) and (−3) and (4) and (−4) while the rate constant for the reaction (−2) is determined as

$$k_{-2} = K_{3,-3}k_4 \qquad (5)$$

where $K_{3,-3}$ is the equilibrium rate constant, and according to ref. 2,

$$\lg k_{-2} = (15.45 \pm 0.2) - (284 \pm 8\,\mathrm{kJ\,mol^{-1}}/2.3RT).$$

Using the above expressions for k_3, k_{-3}, k_{-2} and (5) yields:

$$\lg k_4 = (13.55 \pm 0.3) - (201 \pm 19\,\mathrm{kJ\,mol^{-1}}/2.3RT).$$

A more correct estimation for k_4 has been obtained through direct processing of the CF_2 absorbance curve (at 271 nm) as:

$$k_4 = 10^{13.5\pm0.1} \exp(-201 \pm 8\,\mathrm{kJ\,mol^{-1}}/RT)\ \mathrm{s^{-1}}$$

Thus, an important qualitative inference may be stated: intermediates of one kind (biradicals) can convert into intermediates of another kind (carbenes) under thermal pyrolysis conditions. Since, according to the detailed equilibrium principle the corresponding reverse process must take place, one can conclude that TFE dissociation and CF_2 recombination are not elementary reactions and occur through $\dot{C}F_2$–$\dot{C}F_2$ biradical formation.

Further studies will aim to elucidate to what extent biradical and carbene formation prevails in the course of carbene recombination and biradical dissociation, respectively.

The financial support of the Russian Foundation for Fundamental Researches (grant no. 93-03-18123) is gratefully acknowledged.

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Received: Moscow, 14th March 1994
Cambridge, 17th May 1994; Com. 4/01754D