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1,2-Biradicals as Intermediates in the Cyclodimerization of Tetrafluoroethylene

Nikolai N. Buravtsev,* Yuly A. Kolbanovskii and Anatoly A. Ovsyannikov

A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 117912 Moscow, Russian Federation. Fax: +7 095 230 2224

Using kinetic spectroscopy under strictly homogeneous pyrolysis at temperatures above 800 K, tetrafluoroethylene is shown to convert directly into a 1,2-biradical, the extinction of the latter being estimated to be 2×10^6 cm^2 mol^{-1} at 250 nm. The significance of the biradical is ascertained in the cyclodimerization mechanism and rate constants for elementary reactions are estimated.

One-step 2+2 cycloaddition of tetrafluoroethylene (TFE) is known to be forbidden by orbital-symmetry rules.[1] Two cyclodimerization pathways have been suggested, biradical and ionic. Judging by the absence of a noticeable influence of solvents preference was given to the biradical scheme, and reaction (1):

$$2\,C_2F_4 \longrightarrow \text{cyclo-}C_4F_8 \qquad (1)$$

is now believed to include two stages, reactions (2) and (3).

$$2\,C_2F_4 \longrightarrow \dot{C}F_2{-}CF_2{-}CF_2{-}\dot{C}F_2 \qquad (2)$$

$$\dot{C}F_2{-}CF_2{-}CF_2{-}\dot{C}F_2 \longrightarrow \text{cyclo-}C_4F_8 \qquad (3)$$

The purpose of our study is to investigate the detailed mechanism of these reactions.†

Our earlier macrokinetic study[3] has shown octafluorocyclobutane to be the only stable reaction product, the rate constant for reaction (1) being estimated as:

$$k_1 = 10^{12.4\pm0.2} \exp\left(-\frac{131 \pm 5\,\text{kJ mol}^{-1}}{RT}\right) \text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$$

Since neither initial nor final substance absorbs at wavelengths above 225 nm, the absorbance presented in Figs. 1–4 is due to an intermediate which appears during the heating of TFE in the course of adiabatic compression of the latter (at temperatures 800–1090 K the absorbance of CF_2 was not noticed[4]).

Is this intermediate really a 1,4-biradical which is the result of reaction (2) above? To clarify the nature of the intermediate it is useful to consider the absorbance curve in Fig. 1. This is practically symmetric relative to the zero point on the time axis.‡ The similar symmetric curves for absorbance (or species concentrations) can be strictly proved to correspond to an equilibrium reversible process, *i.e.* at every point on the curve the composition of the compressed gas is in thermodynamic equilibrium (the temperature *vs.* time curves are symmetric relative to the zero point under adiabatic compression/expansion conditions). This implies that the reaction system includes a backward reaction (−2), the rate of which is much higher than that of reaction (3). Mathematical simulation has yielded the thermal effect of the formation of the intermediate observed and showed that simulation of the curves in Figs. 1–4 using only bimolecular (2) and monomolecular (−2) reactions is impossible for any reasonable values of the Arrhenius parameters and extinctions. The authors have therefore concluded that the absorption observed is due to transient species other than 1,4-biradicals.

Other possible intermediates are unstable versions of TFE,

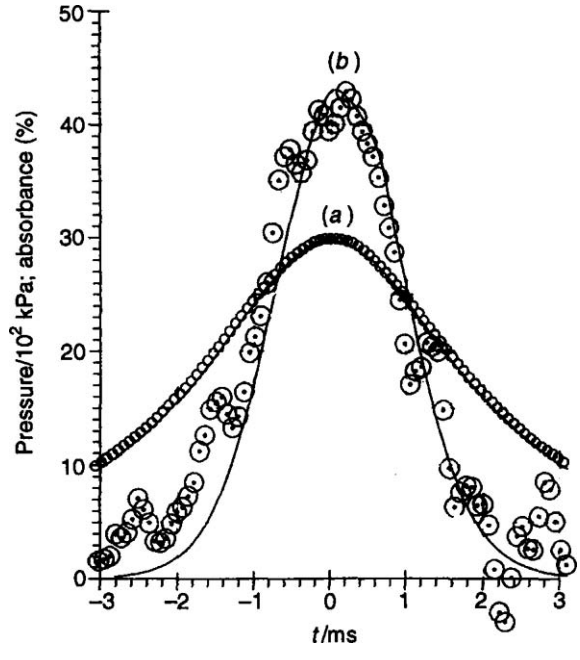

Fig. 1 Adiabatic compression pyrolysis of 1 vol. % C_2F_4 in argon. Measurements (. . . .) and results of calculations (——) for the pressure (*a*) and for the absorbance at 250 nm (*b*); $T_{max} = 1090$ K.

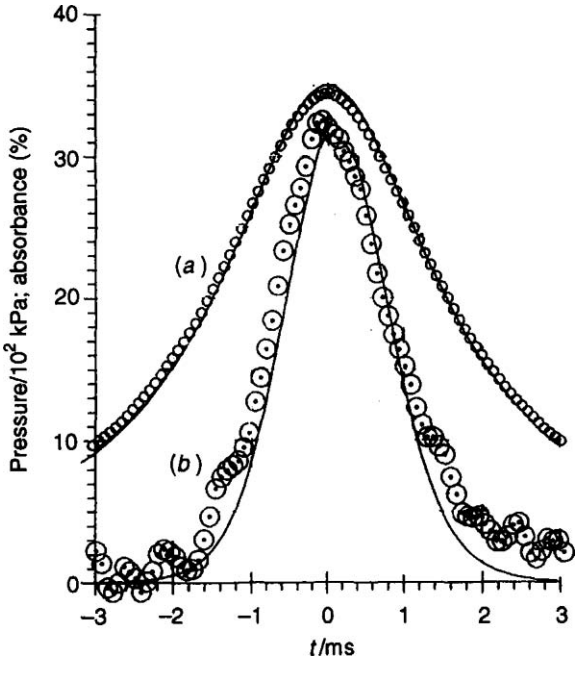

Fig. 2 As Fig. 1, except for 10 vol. % C_2F_4 in argon; $T_{max} = 870$ K.

† *Experimental.* The adiabatic compression of argon-diluted C_2F_4 (1%, 5% and 10% by vol.) was applied using the free-piston adiabatic compression set-up described earlier in this journal[2] together with kinetic spectroscopy and mathematical simulation procedures. Experimental conditions are reported here in the Figure legends. Measurements are presented in the Figures as points whose sizes correspond to the measurement errors. Full lines depict the results of calculations taking into account reactions (3)–(5).

‡ In the adiabatic compression method the time and the piston coordinate are convenient for counting off the maximum compression point, *i.e.* from the time at which the piston stops.

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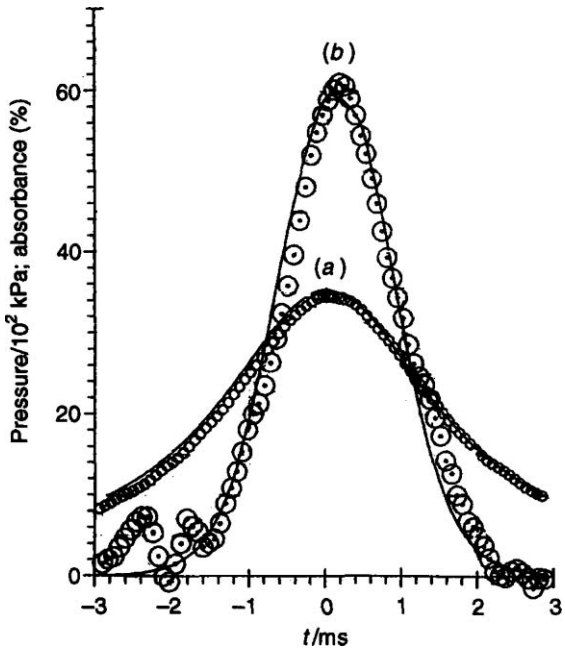

Fig. 3 As Fig. 1, except for 5 vol. % C_2F_4 in argon; T_{max} = 980 K.

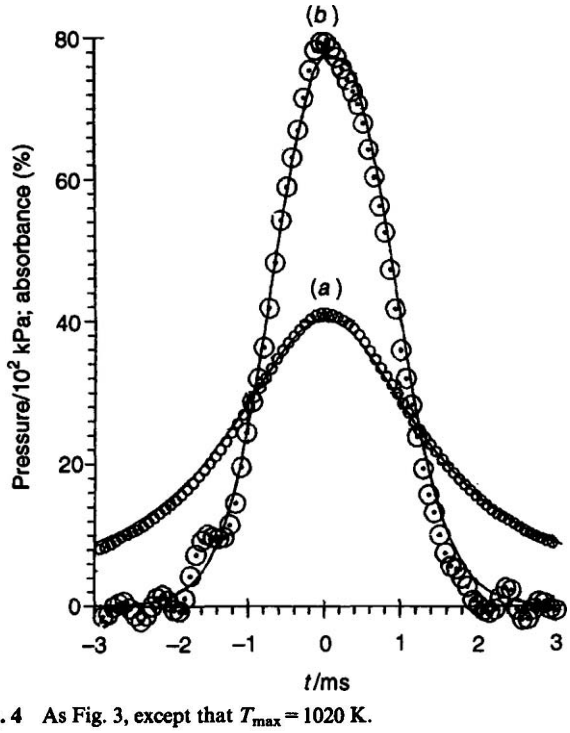

Fig. 4 As Fig. 3, except that T_{max} = 1020 K.

trifluoromethylfluorocarbene :CF–CF_3 and 1,2-biradical $\dot{C}F_2-\dot{C}F_2$.

An absorption at 250 nm was observed in ref. 4 following adiabatic compression of xenon-diluted TFE at maximum pulse temperatures 800–900 K (compression pulse width *ca.* 2 ms). The absorption was proved to be not due to :CF_2 and was explained in ref. 4 by carbene :CF–CF_3 formation as a consequence of the 1,2-shift of fluorine in C_2F_4. The absorption spectrum of :CF–CF_3 which was studied recently in ref. 5 is characterized by a rather wide band in the UV and is 2–3 times less intense than the visible band (maximum absorptions at 235 nm and 465 nm, respectively). Carbene :CF–CF_3 has been identified recently by both absorption bands using kinetic spectroscopy of $C_2F_5SiF_3$ adiabatic compression pyrolysis.[2] However, in the present study the authors have not observed any absorption at 465 nm at temperatures 800 to 1090 K even with initial 10% TFE content in argon.

The above experimental and simulation data make it clear that the only possible intermediate in the system considered is 1,2-biradical $\dot{C}F_2-\dot{C}F_2$ resulting from π-bond disclosure in TFE, the forward reaction (4).

$$C_2F_4 \rightleftharpoons \dot{C}F_2-\dot{C}F_2 \qquad (4)$$

We managed to estimate the equilibrium constant K_4 for reaction (4) to be:

$$K_4 = 10^{2.45\pm0.1} \exp\left(-\frac{92 \pm 3\ \text{kJ mol}^{-1}}{RT}\right)$$

as well as Arrhenius parameters for the reactions (4) and (−4) (see Table 1) and $\dot{C}F_2-\dot{C}F_2$ extinction at 250 nm as $\kappa = 2 \times 10^6$ $\text{mol}^{-1}\ \text{cm}^2$.

Reactions (4) are only the first steps in TFE cyclodimerization. Further reactions of the 1,2-biradical may be as follows,[§] reactions (5)–(7).

$$\dot{C}F_2-\dot{C}F_2 + C_2F_4 \rightleftharpoons \dot{C}F_2-CF_2-CF_2-\dot{C}F_2 \qquad (5)$$

$$2\ \dot{C}F_2-\dot{C}F_2 \rightleftharpoons \dot{C}F_2-CF_2-CF_2-\dot{C}F_2 \qquad (6)$$

$$2\ \dot{C}F_2-\dot{C}F_2 \longrightarrow \text{cyclo-}C_4F_8 \qquad (7)$$

Estimating the rates of processes (5)–(7) rates allows us to reject reactions (6) and (7). Consider the following ratios α_1 and α_2.

$$\alpha_1 = \frac{W_5}{W_6} = \frac{[\dot{C}F_2-\dot{C}F_2][C_2F_4]k_5}{[\dot{C}F_2-\dot{C}F_2]^2 k_6} = \frac{k_5[C_2F_4]}{k_6[\dot{C}F_2-\dot{C}F_2]}$$

$$\alpha_2 = \frac{W_5}{W_7} = \frac{[\dot{C}F_2-\dot{C}F_2][C_2F_4]k_5}{[\dot{C}F_2-\dot{C}F_2]^2 k_7} = \frac{k_5[C_2F_4]}{k_7[\dot{C}F_2-\dot{C}F_2]}$$

According to ref. 6 $k_5/k_6 \geqslant 10^{-1}$ (and naturally $k_5/k_7 \geqslant 10^{-1}$). Using the above estimate for K_4 yields $[C_2F_4]/[\dot{C}F_2-\dot{C}F_2] \geq 10^2$. Therefore, $\alpha_{1,2} \geqslant 10^1$ and the relative contributions from reactions (6) and (7) may be rejected; this is confirmed by other estimates. If we suppose that reactions (5) and (6) are not essential, then $W_1 = W_7 = k_7(K_4^2[C_2F_4]^2)$ and E_1 would be equal to $E_7 + 2\Delta H_4$ only when $E_7 = -53$ kJ mol^{-1}, since $E_1 = 131$ kJ mol^{-1} and $2\Delta H_4 = 184$ kJ mol^{-1}. However, such an estimate for E_7 is evidently absurd.

Finally, we can suggest the cyclodimerization mechanism to be as presented in Table 1. Using Arrhenius parameters from Table 1 simulates all the measurements in Figs. 1–4.

Thus, the previously suggested reaction (2) is not an elementary stage in cyclodimerization, which proceeds through reactions (3)–(5).

Table 1 Reactions proposed in the cyclodimerization mechanism.

No.	Reaction	lg A^a	E/kJ mol^{-1}
(4)	$C_2F_4 \longrightarrow \dot{C}F_2-\dot{C}F_2$	6.9±0.1	105±5
(−4)	$\dot{C}F_2-\dot{C}F_2 \longrightarrow C_2F_4$	4.4±0.1	13±2
(5)	$\dot{C}F_2-\dot{C}F_2 + C_2F_4 \longrightarrow \dot{C}F_2-CF_2-CF_2-\dot{C}F_2$		
(−5)	$\dot{C}F_2-CF_2-CF_2-\dot{C}F_2 \longrightarrow \dot{C}F_2-\dot{C}F_2 + C_2F_4$		
(3)	$\dot{C}F_2-CF_2-CF_2-\dot{C}F_2 \longrightarrow$ cyclo-C_4F_8		

[a] For monomolecular reactions A is expressed in s^{-1}

[§] Under the conditions of the present study cycloreversion reactions effectively do not occur.

Revealing the disclosure of the double bond in TFE and the role of the 1,2-biradical in the strictly homogeneous thermal cyclodimerization poses two main questions. First, is this disclosure inherent to other perfluoroolefines? Second, will the formation of 1,2-biradicals be revealed in the course of cyclodimerization studies?

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