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Adiabatic compression in studies on the kinetics and mechanism of reactions involving fluorine-containing carbenes

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ABSTRACT. The physicochemical principles of adiabatic compression and its characteristics and potentialities in studies on the kinetics and mechanism of thermal gas-phase reactions are examined. The results of studying reactions involving fluorine-containing carbenes are presented. Information is given on the high-temperature tautomerism of tetrafluoroethylene–trifluoromethylfluorocarbene, which has been detected and studied using kinetic spectroscopy during adiabatic compression. The set of experimental data on the pyrolysis and gas-phase isomerisation of perfluoroolefins has been interpreted using the concept of tautomeric changes involving the 1,2-shift of a fluorine atom in olefins.

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I. Introduction

The method of adiabatic compression is not very widely known to chemists. Therefore, we considered one of the aims of the present review to be a demonstration of the characteristics and potentialities of this method for studying the kinetics and mechanism of thermal gas-phase reactions. All the examples that we will use to illustrate the potentialities of adiabatic compression relate to reactions of organofluorine compounds and primarily to reactions involving the formation and conversion of fluoroolefins.

This choice can be substantiated from different viewpoints. Firstly, reactions involving carbenes are highly characteristic for this region of chemistry; secondly, it was in this direction that a number of basic results were obtained using adiabatic compression; and thirdly, we took into account the considerable significance of thermal (pyrolytic) processes in the present-day technology for obtaining monomers for fluorinated rubbers and fluoroplastics. The latter circumstance makes the task of establishing a detailed mechanism of pyrolysis that is directed at the preparation of fluorinated monomers an urgent one for the development of scientific principles in optimising their production.

II. Adiabatic compression in physicochemical studies

The term "adiabatic" in thermodynamics relates to processes for which $dQ = 0$ in the equation of the First Law of Thermodynamics. For this condition to be maintained, the compression of gas must be sufficiently rapid that heat exchange between the gas and the wall of the vessel can be neglected. There are two possible ways of bringing about such a compression: one—with specific times less than the characteristic time for transmitting a sound distances of the order of the linear dimensions of the compressed volume of gas; the second is a slower compression, when the ratio of these times is given by a number greater than unity. In the first of these cases, shock waves develop in the gas and the process is represented by the Hugoniot adiabatic equation, in the second case shock waves do not develop and the process is given by Poisson's adiabatic equation. In units for the adiabatic compression of gases using a piston, its rate of movement is several times less than the speed of sound and, in accordance with Poisson's adiabatic equation, the pressure and temperature of an ideal gas on compression change according to the principle $p = p_0\varepsilon^\gamma$ and $T = T_0\varepsilon^{\gamma-1}$, where $\gamma = C_p/C_V$, the adiabatic factor; C_p and C_V are the specific heats at constant pressure and constant volume respectively; ε is the geometric compression ratio ($\varepsilon = V_0/V$, where V_0 and V are the initial and current values of the volume of gas). With such a compression the entropy of the system does not change and therefore it is sometimes called isentropic compression, taking into account the adiabatic process represented by Poisson's adiabatic equation. In order that the reader can form some idea about the values of the parameters reached in isentropic compression, we shall give one example that illustrates the potentialities of this method. If a monoatomic inert gas is at a temperature $T = 500$ K and pressure $p_0 = 2$ atm. before compression, with a compression ratio $\varepsilon = 50$ the parameters $T_{max} = 6700$ K and $p_{max} = 1320$ atm will be reached in it (the index "max" indicates that the value of the parameter relates to the moment of attaining the maximum compression ratio). No single apparatus could withstand such a combination of pressure and temperature if their duration was not about 10^{-4} s. Heat losses to the wall can hardly take place during this time, and so the compression proves to be adiabatic, the walls of the reactor are not heated up, and the apparatus is not destroyed. Thus, a new region of combinations of high values of p and T parameters is opened up for chemical studies. There are virtually no kinetic data (and sometimes also no thermodynamic data) for this region, and it is extremely important from both a purely scientific and a practical viewpoint to obtain these data.

When chemical reactions are studied using this method, attempts are made in all cases to maintain conditions in which

heat exchange between the gas and the wall can be neglected. However, in far from every case is it possible to ignore the evolution (or absorption) of heat produced by the chemical reaction itself. This does not result in a change in fundamental approach of the method but it must be taken into account in calculations. This will be discussed below.

Two principal features of the method should be apparent from what has been stated: the possibility of studying a gas-phase reaction with a previously known elimination of the effect from the vessel walls and the fact that all of the gas parameters vary with time. Since the temperature is included in these parameters, the adiabatic compression method can be classed as anisothermal. We shall consider these questions in more detail.

In studying the kinetics and mechanism of homogeneous gaseous reactions, problems relating to the effect of the surface of the reaction vessel and in particular its quantitative determination are among the most complex.[1] We consider this point because at the present time the role of the surface has been established in a whole range of processes when they are carried out both under steady-state conditions and in flow reactors of different types.[2-11]

Adiabatic compression can essentially reduce the effect of heterogeneous factors to a negligible level. The lack of isothermal conditions in adiabatic compression led, particularly at the beginning, to difficulties in processing the results. Therefore, in the first stage of studies on reaction kinetics using this method, so-called overall single-stage reactions were mainly studied and approximation methods were used to determine kinetic parameters.[12-17] At the present time reliable computer methods have been developed to calculate kinetic parameters from the experimental data obtained from adiabatic compression. We should note that, in principle, anisothermal methods are more informative than isothermal ones and their advantage can be effectively realised using computers.

We shall consider below approaches to the calculations of kinetic parameters from experimental data obtained on adiabatic compression units. First of all we can demonstrate that adiabatic compression actually ensures that gas reactions take place homogeneously. An obvious condition for homogeneity in the diffusion transfer of a substance[19-21] is that the marked inequality $L_{dif} \ll L_{reac}$, where L_{dif} is the diffusion length and L_{reac} is the characteristic dimension of the reaction volume, should be fulfilled. Let us choose Xe as the gas diluent, a temperature of 1600 K, and an adiabatic factor for the mixture of $\gamma = 1.6$. Such parameters are attained in a gas with standard properties when the compression ratio is 17, which corresponds to a density of the medium 17 times higher and a coefficient of diffusion 17 times lower than at atmospheric pressure. Taking into account the fact that the coefficient of self-diffusion of xenon at a pressure p_{atm} and 1600 K is 1 $cm^2\ s^{-1}$,[18] and the characteristic duration of these parameters during adiabatic compression is about 10^{-3} s, we deduce that the diffusion length will be of the order of 10^{-2} cm, whereas the characteristic dimension of the reaction volume for a compression ratio of 17 in units for studying the kinetics of chemical reactions by this method is usually of the order of 1 cm. Thus, the marked inequality referred to above is fulfilled.[19-21]

Figure 1 depicts the basic diagram of a unit for studying chemical reactions by means of adiabatic compression. The details of the experimental procedure and techniques are reported in detail in a book.[22]

We should say a few words about the treatment of experimental results. All experiments can provisionally be divided into two large groups. In one of them "normal" data—the composition of the products before and after the compression pulse—will occur; in the other group are data from experiments in which (optical) measurements are taken directly during the compression–expansion cycle. We shall only refer here to experiments of the first group. For greater clarity the simplest example can be considered without losing a common approach.

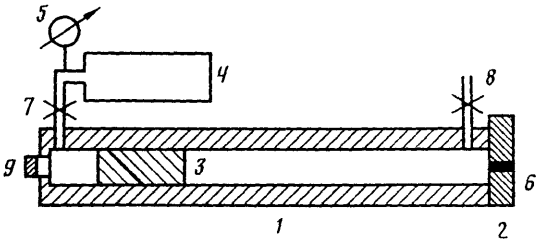


Figure 1. Basic diagram of the adiabatic compression unit:[22] *1*, cylinder; *2*, flange; *3*, piston; *4*, driving gas receiver; *5*, manometer; *6*, pressure gauge; *7*, valve for driving gas; *8*, valve for admission of operating mixture and withdrawal of samples for analysis; *9*, inertial valve.

Let the reaction under study be written in the form:

$$A + Xe \rightarrow \sum_{i=1}^{n} b_i B_i + Xe,$$
$$i = 1, 2 \ldots n,$$

where b_i are stoichiometric coefficients; n is the number of products, including unreacted substance A; B_i are reaction products. The kinetic equation may be written in the form:

$$\dot{N}_A = -kN_A (N_{Xe}/Sx),$$

where N_A and N_{Xe} are the numbers of moles of A and Xe respectively, k is the rate constant, S is the square of the cross section of the (cylinder) piston, x is the piston coordinate. It is assumed that the Arrhenius equation is satisfied, namely:

$$k = k_0 \exp(-E/RT).$$

Thus, in the kinetic equation, not only N_A proves to be a function of time as is usually the case but also the rate constant (since $T = T(t)$, where t is the time) and in addition the volume of the system $V = Sx$, since x also depends on time. Therefore, it is necessary to introduce equations which determine the dependences on time of both the piston coordinate and the temperature.

The piston coordinate can be found by interpreting the equation of its movement:

$$m\ddot{x} = S(p - p_d),$$

where m is the mass of the piston, p is the pressure of compressible gas, p_d is the pressure of driving gas. In this equation the frictional forces acting on the piston when it is moving in the cylinder are not taken into account since the experimental data show that the movement of the piston is wholly determined

by the pressure, and the frictional forces have virtually no effect on the movement of the piston. As is well-known, the relationship between pressure and temperature of a gas is given by the equation of state. In relatively simple cases (up to a compression ratio of about 17 for xenon) the equation of state of an ideal gas can be used. When a high compression is used in kinetic experiments, a virial equation of state must be used. Since the details of the calculation are naturally not covered here, we shall turn our attention to the dependence of temperature on time—the third value necessary to calculate the kinetic parameters. The calculation of temperature can be made in accordance with the equation of the conservation of energy:

$$N_\Sigma C_V^{mx}\dot{T} = q_V\dot{N}_A - Sp\dot{x},$$

where C_V^{mx} is the specific heat of the mixture at constant volume, q_V is the heat effect of the reaction at constant volume, and N_Σ is the total number of moles of the components of the gas mixture.

Thus we obtained a system of three differential equations for all three quantities that are dependent on time: the number of moles of reacting substance, the volume, and the temperature of the working mixture.

Such a simple situation is naturally exceptional. In practice it is necessary to deal with complex reactions, when there are more kinetic equations (according to the number of components) and the dependence of the specific heat of the mixture and the heat effect of the reaction on temperature must be taken into account. With high compression it is also necessary to include the dependences of the virial coefficients on temperature. However, an experiment to resolve these systems of differential equations in a study of the kinetics and mechanism of chemical reactions by means of adiabatic compression showed that the majority of the difficulties in this case were of a technical nature, the operating time expended was comparatively short, and the results were completely reliable. It is difficult now to point to another method used to study homogeneous gas reactions at high temperatures and pressures which is as effective as adiabatic compression.

Studies on high adiabatic compression of gases using a piston were started in the USSR Academy of Sciences on the initiative and under the direction of Khariton in the 1930's in Leningrad. Reinov and Klyazer participated in the studies. After the Second World War research was resumed by Ryabinin, Markevich, and their co-workers at the Institute of Chemical Physics of the USSR Academy of Sciences. Further details about this and references to the literature of those years are given by Kolbanovskii and Markevich.[23]

III. High-temperature carbene reactions involving fluorine-containing molecules

1. Early ideas about the mechanism of formation of lower perfluoroolefins during pyrolysis

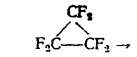
Attempts to construct a consistent scheme for the mechanism of formation of C_2F_4, C_3F_6, and C_4F_8 during pyrolysis were undertaken right from the beginning when this area of chemistry was being developed.

The question concerning the formation of tetrafluoroethylene (TFE) by pyrolysis of CHF_2Cl (Cl-22) was perhaps one of the first to be elucidated. It was shown that the decomposition of Cl-22 leads to the formation of difluorocarbene (DFC), and the subsequent recombination of two molecules of the latter gives tetrafluoroethylene:

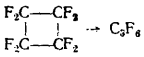
$$CHF_2Cl \rightarrow CF_2 + HCl, \quad (1)$$

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

However, even for the next member of the perfluoroolefin series—hexafluoropropylene (HFP)—elucidation of the kinetics and mechanism of formation proved to be a complex task. The usual method for obtaining HFP is the pyrolysis of TFE. In the opinion of different authors[24,25] two reactions were responsible for the formation of HFP by pyrolysis of TFE:

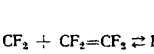


$$\rightarrow C_3F_6, \quad (3)$$

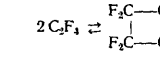


$$\rightarrow C_3F_6 + CF_2. \quad (4)$$

In this case both of the small rings are actually formed during pyrolysis according to the reactions:[26–36]

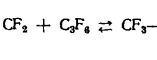


$$CF_2 + CF_2{=}CF_2 \rightleftarrows F_2C{-}CF_2, \quad (5)$$

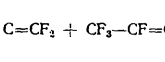


$$2\,C_2F_4 \rightleftarrows . \quad (6)$$

Traditional ideas concerning the formation of the different isomers of C_4F_8 are also based on a similar approach:



$$CF_2 + C_3F_6 \rightleftarrows CF_3{-}FC< , \quad (7)$$



$$\rightarrow (CF_3)_2C{=}CF_2 + CF_3{-}CF{=}CF{-}CF_3 + CF_2{=}CF{-}CF_2{-}CF_3. \quad (8)$$

Let us analyse the basis of these conclusions. Cycloaddition reactions (5) and (7) are well-known for dihalocarbenes as is the cyclodimerisation of TFE. But these reactions do not give fluoroolefins directly, and therefore the conclusion about the mechanism of formation of perfluoroolefins was based on the results of the pyrolysis of perfluorocyclopropane and perfluorocyclobutane—in both the first and second cases HFP was found in the products. However, no real kinetic analysis of these experiments was carried out at that time. As regards reaction (8), there were no reliable data on the pyrolysis of perfluoromethylcyclopropane in the literature.

Let us now consider how the problem of determining the kinetics and mechanism of formation and the reactions of fluoroolefins at high temperatures was resolved.

2. Evidence for the incorrect nature of the early ideas about the mechanism of formation of perfluoroolefins by pyrolysis

We obtained the first evidence of this type without any special experiments at all. It was sufficient to analyse the results of one study[37] by means of comparative selectivities; it transpired that HFP is not a primary product of the pyrolysis of perfluorocyclopropane and hence reaction (3) does not take place. It follows from the same analysis that the only reaction in which this three-membered ring participates is reaction (5) in reverse. Only in this case TFE will be the sole primary stable product of the pyrolysis of perfluorocyclopropane.

Following this, doubts arose as to the possibility of the analogous reaction (8), about which there were no reliable experimental data, taking place. Therefore, an experimental study of the pyrolysis of perfluoromethylcyclopropane was undertaken using adiabatic compression. We shall only report here the qualitative results of this study carried out by Grigor'ev, German, Chepik, and the present author;† only TFE and HFP are found amongst the primary stable decomposition products and there are no compounds with the formula C_4F_8. This means that only reaction (7) in reverse takes place while reaction (8) does not occur at all.

Thus, only reaction (4) remained from the originally proposed mechanism for the formation of perfluoroolefins with composition C_3 and C_4. In order to determine the possible role of reaction (4) in the formation of HFP by pyrolysis of TFE, we undertook a study of the kinetics of the decomposition of octafluorocyclobutane by means of adiabatic compression. We shall report here only the principal results of this study.[38] It was established that the decomposition of perfluorocyclobutane is a first-order kinetic reaction with a rate constant of $10^{15.9\pm1.0}\exp(-322 \pm 19 \text{ kJ mol}^{-1}/RT)$. It was shown by the method of comparative selectivities that the sole primary stable product is TFE. It was found that the order of reaction for formation of HFP with respect to the initial compound was equal to 3/2, which is also not consistent with a scheme involving reaction (4)‡—formation of HFP is evidently first order with respect to the initial compound for this reaction.

Thus, it was shown during the initial studies that not a single one of the previously proposed reactions for formation of HFP and C_4F_8 occurs during pyrolysis and the mechanism of pyrolytic reactions involving lower perfluoroolefins had to be completely re-examined. It was established in this case in particular that perfluorocyclopropane and its derivatives do not undergo isomerisation reactions with ring-opening and decomposition to an olefin and CF_2 is the only route of their thermal reactions.

Thus, it was necessary not only to develop new, more thorough methods for the experimental study of the mechanism of high-temperature reactions involving carbenes but also to formulate a new hypothesis about such processes, since it was clear that a model for the mechanism which was based on any combination of previously proposed stages was not consistent with experiment.

3. Experimental detection of the high-temperature tautomerism $C_2F_4 \rightleftarrows CF_3 \simeq CF$:

We should mention initially that only for the convenience of presentation we will not start this section with an analysis of the literature data relating to the present subject and also with data on the "traditional" study of the kinetics of the pyrolysis of perfluoroolefins using adiabatic compression. These findings will be presented below.

Since it had transpired that not all of the data from studying the mechanism of pyrolysis that were solely based on an analysis of the final stable products could be successfully used, a spectroscopic method of studying the mechanism of pyrolysis was incorporated within the adiabatic compression technique. This method and the main results obtained from it are reported in a study[40] which we will mainly rely on in our review.

The following elements were incorporated into the adiabatic compression unit described in Section II. Windows made of optical quartz for spectroscopic probing of the compressed gas directly during a pulse were positioned at a distance of 9 mm from the closed end (see Fig. 1). The unit was provided with all the necessary equipment for evacuation of the working volume. The whole unit was rigidly fixed in a horizontal position on a main wall. Parallel to a line joining the centres of the quartz windows was positioned an optical bench. A light source (DRSh-500 lamp) and the necessary quartz optical equipment were fixed on it. A wide-aperture SDL-1 spectrometer with an FEU-39 and a double-beam storage S1-13 oscilloscope with a screen on which was recorded the optical signal and the signal from a piezoelectric pressure gauge were used. The data given below were obtained using a mixture of 5 vol. % C_2F_4 + 95 vol. % Ar.

It was necessary first of all to obtain spectroscopic purity in the adiabatic compression unit. There were certain misgivings about the possibility of aerosols being formed when the piston moved in the cylinder. It was therefore necessary to ensure that absorption of light by scattering on aerosol particles was excluded. This was tested in different regions of the ultraviolet and visible spectrum. It can be seen in Fig. 2 that the compression of specially purified argon does not alter the amplitude of the optical signal.

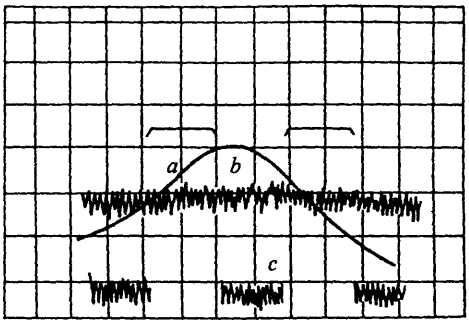


Figure 2. Oscillogram of the compression–expansion cycle of specially purified argon:[40] *a*, signal from piezoelectric pressure gauge; *b*, optical signal at λ = 248.3 nm.

After this it was necessary to ensure that the traces of triethylamine added to TFE in order to prevent it polymerising spontaneously did not contribute to the absorption of light. In order to do this, a comparison of the optical signal was made in two parallel experiments, in one of which TFE was not specially purified and in the other triethylamine was removed by careful freezing out at −60 °C. Within the limits of experimental error no difference was found between the oscillograms of these two experiments.

At high temperatures TFE is known to undergo reversible dissociation to two difluorocarbenes:

$$C_2F_4 \rightleftarrows 2CF_2. \quad (9)$$

†Presented at the anniversary session of the Scientific Council of the Institute of Petrochemical Synthesis, USSR Academy of Sciences, in November 1987.

‡A similar conclusion was reached by Preses et al.,[39] who studied the laser-initiated decomposition of cyclo-C_4F_8.

Amongst the studies investigating reaction (9) we should mention that of Schug and Wagner,[41] in which the values of the equilibrium constant and rate constant of the forward and reverse reaction of (9) were verified again using kinetic spectroscopy in shock waves at 1200–1600 K. The values of the kinetic constants found in this study[41] were used in our study.[40] However, when the first set of data from adiabatic compression was obtained it was found that with the values of the extinction coefficient of CF_2 given in the literature, the optical absorption at the maximum (Fig. 3), being attributed to CF_2, corresponded to concentrations of it that were much higher than that at equilibrium. Since there could be no notions of an excess equilibrium at the moment of maximum absorption during these experiments (on the contrary, it could be shown that the concentration of CF_2 at this point must be the equilibrium concentration) the conviction grew that during compression another component in addition to CF_2 appeared in the system, absorbing light in this region of wavelength. It could also be proved that this component was unstable and that its appearance was the result of a reversible process, since at the end of the compression–expansion pulse the absorption of light disappeared and the original transmission was restored. The result of resolving a direct kinetic problem was used as an addition argument. In this case a calculated curve of optical absorption during a pulse was obtained on the basis of literature data on the kinetics of reaction (9) with known values of the extinction coefficient. This curve was considerably different from the experimental one not only in amplitude, which has already been discussed, but also the characteristic time of the process: 1.8–1.9 ms instead of ~ 3 ms.

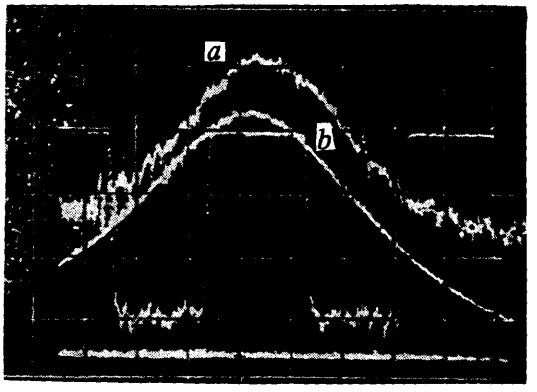


Figure 3. Oscillogram of the adiabatic compression–expansion cycle of a mixture of 5 vol. % C_2F_4 + 95 vol. % specially purified argon:[40] *a*, signal from piezoelectric pressure gauge; *b*, optical signal at λ = 248.3 nm; timescale: 1 square = 5×10^{-4} s.

Two experiments[40] provided definite clarification of the situation. Firstly, absorption of light was detected at a wavelength of 250 nm, where CF_2 does not absorb (taking into account the possible broadening of the lines and slit width). This experiment was based on the data of another study,[42] in which the electronic absorption spectrum of CF_2 was given. Secondly, there is an absorption at a wavelength of 271 nm, where it transpired that only CF_2 absorbs (Fig. 4). It can be clearly seen in Fig. 4 that the characteristic time of the signal actually constitutes about 2 ms, in exact agreement with the kinetic calculations for CF_2.

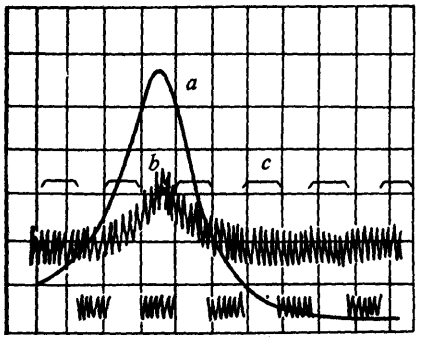


Figure 4. Oscillogram of the compression–expansion cycle of the same mixture (see Fig. 3); λ = 271.37 nm, 1 square = 10^{-3} s.

We should also mention that in all our experiments[40] absorption occurred starting at a temperature of about 820–850 K, although the absorption due to CF_2 at that point was far beyond the sensitivity limits of the spectrometer. Thus, the absorption of light by the carbene $CF_3–CF$:, not recorded previously by any direct methods, was detected in a region of light absorption typical for carbenes at a wavelength of 240–270 nm during the pulsed heating of C_2F_4 in argon. We should emphasise that the process is completely reversible and that the chemical conversion of C_2F_4 to other stable products under the conditions of our study[40] is at a level of about 2% (octafluorocyclobutane, which does not absorb at all in this region of the spectrum, is mainly formed).

It was not difficult to establish from the kinetic absorption curve that the process studied is kinetically first order. This means that trifluoromethylfluorocarbene is formed through a unimolecular reaction involving the 1,2-shift of a fluorine atom. In our opinion, this phenomenon is of basic significance for this area of chemistry and we are attempting to show here not only what conclusions folllow from it for an understanding of a whole series of experimental data but also the predictive power of the concept of olefin–carbene tautomerism in fluoroolefins.

Before going to the next section, it should be mentioned that Kushina et al.[43] had previously interpreted the formation of benzotrifluoride together with fluorobenzene in the combined pyrolysis of tetrafluoroethylene and cyclopentadiene as the result of the formation of $CF_3–CF$: from C_2F_4 and had proposed that this carbene must play an important role in the formation of HFP in the pyrolysis of TFE. Lipkind et al.,[44] by examining the data on the combined pyrolysis of C_2F_4 and C_3F_6 with cyclopentadiene and indene, also suggested that the carbenes CF_3CF and $(CF_3)_2C$ might possibly participate in these processes.

4. Kinetics and mechanism of the pyrolysis of TFE and HFP

In Sections III.1 and III.2 it was shown that the previously held ideas about the mechanism of the high-temperature reactions of TFE and HFP could not be consistent with experiment and it was

necessary to develop a new theory concerning the mechanism of these processes. In this connection let us consider the experimental data obtained using adiabatic compression and a kinetic analysis of the mechanism for pyrolysis of TFE and HFP. In interpreting the experimental results it is assumed that all changes in the number of carbon atoms in perfluoroolefins result from carbene reactions, with the carbenes formed either by decomposition of the olefin at the double bond or by tautomeric changes, namely, through a 1,2-shift of a fluorine atom.

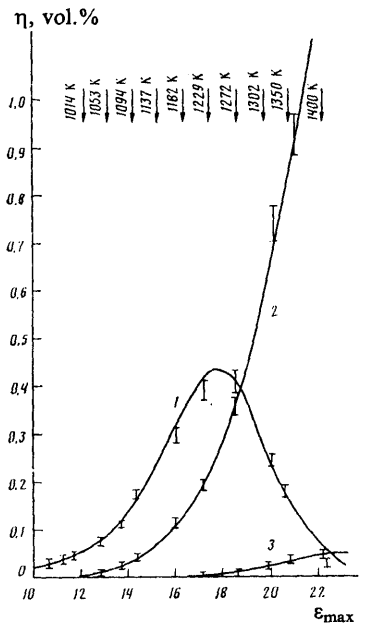


Figure 5. Pyrolysis of 5 vol. % C_2F_4 in specially purified argon by adiabatic compression;[22] T (deg K)—maximum temperature in one compression–expansion cycle; ε_{max}—maximum compression ratio; η—content in mixture after experiment in vol. % of: *1*, cyclo-C_4F_8; *2*, C_3F_6; *3*, C_4 fraction; points—experiment; lines—calculation.

The experimental data of Buravtsev et al.[45] on the pyrolysis of TFE and HFP using adiabatic compression are displayed in Figures 5 and 6. The experimental conditions are indicated in the captions. In Table 1, which is derived from the data collected and obtained by Grigor'ev,[46] are represented the fundamental stages which constitute in totality the mechanism for formation of HFP by pyrolysis of TFE. The values of the rate constants, some of which it was possible to determine for the first time using adiabatic compression, are also given.

An interesting detail was discovered in a computer calculation of the current concentration values of all components of the mixture during a single compression–expansion cycle. It transpired that the concentration of perfluorocyclopropane during pyrolysis was several orders less than the concentration of carbenes in all the systems of practical interest.

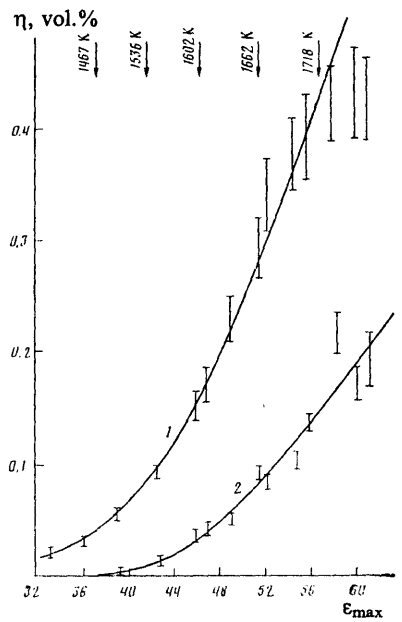


Figure 6. Pyrolysis of 4.65 vol. % C_3F_6 in specially purified argon by adiabatic compression[46] (see Fig. 5 for notation); *1*, C_2F_4; *2*, C_4 fraction.

Table 1. Arrhenius parameters of the fundamental reactions in the initial stages of the pyrolysis of $k = AT^n \exp(-E/RT)$ of TFE.[46]

Sample No.	Reaction	log A	E, kcal mol^{-1}	n
1	$2C_2F_4 \rightarrow$ cyclo-C_4F_8	12.1	30.3	0
2	cyclo-$C_4F_8 \rightarrow 2C_2F_4$	16.1	75.6	0
3	$C_2F_4 \rightarrow 2CF_2$	15.5	68.1	0
4	$2CF_2 \rightarrow C_2F_4$	8.7	1.2	1
5	$C_2F_4+CF_2 \rightarrow$ cyclo-C_3F_6	9.8	7.5	0
6	cyclo-$C_3F_6 \rightarrow CF_2+C_2F_4$	13.3	38.6	0
7	$C_2F_4 \rightarrow CF_3CF$	6.0*	18.0	0
8	$CF_3CF \rightarrow C_2F_4$	4.5*	0.6	0
9	$CF_3CF+CF_2 \rightarrow C_3F_6$	6.7*	1.2	0
10	$C_3F_6 \rightarrow CF_2+CF_3CF$	16.6	90.3	1

*Provisional value.

It is clear that only the stages of initial pyrolysis are given in Table 1, where secondary products, in particular perfluorobutenes of different structures, have not yet been formed. The processes relating to the formation and decomposition of C_4 perfluoroolefins require a separate treatment. As regards the pyrolysis of HFP, it is clear from the data given in Fig. 6 that the only stable primary product in this case is TFE. The reaction in which TFE is formed

by the pyrolysis of HFP is also given in Table 1 [reaction (9)] together with the calculated values of the pre-exponential factor and the energy of activation of the rate constant. The comment made above regarding the kinetics and mechanism of the formation and decomposition of C_4 perfluoroolefins is also valid with respect to the pyrolysis of HFP.

5. Pyrolysis and isomerisation of perfluorobutenes in the gas phase

In all of the data discussed in this review there is specific information on the formation of C_4F_8 compounds, but with two exceptions we will refrain from interpreting it. Let us recall these two cases. Firstly, from the data on the pyrolysis of perfluoromethylcyclopropane, amongst whose primary products there were no C_4 compounds, we could not regard it as an unstable intermediate during the formation of perfluoroolefins $C_2 \rightarrow C_3 \rightarrow C_4$. Secondly, there could be no doubt that the cyclic compound C_4F_8 — octafluorocyclobutane — is readily formed by cyclodimerisation of TFE but does not undergo isomerisation with ring-opening. Thus, it remained unclear how the principal minor products — C_4 perfluorocarbons with an open ring — are formed and how they behave during high-temperature pyrolysis. It should be mentioned that before studies using adiabatic compression were started, there was no information on this question in the literature familiar to us.

Let us consider first the data of German et al.[47] on the pyrolysis and isomerisation of perfluorobutenes of normal structure, obtained by means of adiabatic compression. In the pyrolysis of a mixture of 1.3 vol. % perfluorobut-2-ene (PFB-2) and argon the following was established. Even before the start of other reactions at a maximum temperature during the pulse of about 1100 K *cis-trans*-isomerisation becomes appreciable. When the temperature is increased further to 1200 K the *cis*/*trans* ratio remains almost constant at 0.35. Only TFE and HFP in the molar ratio 1 : 2 are recorded as stable primary products for low degrees of conversion of PFB-2. It must be admitted that for German et al.[47] this result was unexpected. In fact, after studying the pyrolysis of TFE and HFP, where it was found that their decomposition occurs by a carbene mechanism, it was natural to expect similar behaviour for the next members of the homologous series of perfluoroolefins, especially for PFB-2. In such a case only TFE should be amongst the stable primary pyrolysis products. In order for TFE and HFP to be in the stable primary pyrolysis product in the ratio 1 : 2, it was necessary in some way to eliminate from PBF-2 one CF_2 group, which does not exist in this molecule. The experimental data would readily demonstrate if decomposition were preceded by the isomerisation of PFB-2 to PFB-1. The decomposition of PFB-1 at its double bond must result in the formation of two carbenes:

$$CF_2=CF-CF_2-CF_3 \rightarrow CF_2 + CF-CF_2-CF_3.$$

The subsequent recombination of difluorocarbene and 1,2-shift of a fluorine atom in perfluoroethylfluorocarbene would give TFE and HFP in the observed ratio. However, PFB-1 was not found amongst the pyrolysis products of PFB-2. It was therefore necessary to make a second assumption: the isomerisation of PFB-2 to PFB-1 occurs more slowly than the decomposition of PFB-1. In other words, PFB-1 is considerably less stable at high temperatures than its isomer.

The data on the pyrolysis of PFB-1 that were obtained in the same study[47] confirmed both of these assumptions. In fact, when PFB-1 is pyrolysed, the stable primary products are TFE and HFP in the ratio 1 : 2 and the thermal stability of PFB-1 is markedly lower than for PFB-2. At 1174 K, when PFB-2 is completely stable, the degree of conversion of PFB-1 reaches 6%. It is important to mention that small quantities of PFB-2 are also found in this instance. This suggests that there is isomerisation on the double bond under the strictly homogeneous conditions of adiabatic compression. Previously there had been no information about this reaction. In addition, we should mention one further interesting feature of the pyrolysis of PFB-2. At high temperatures (about 1500 K) decomposition on the double bond proceeds more rapidly than isomerisation — TFE starts to predominate in the reaction products. In the pyrolysis of PFB-2 formation of its structural isomer — perfluoroisobutylene (PFI) — was only recorded at very high degrees of conversion and only in trace amounts, while in the pyrolysis of PFB-1 it was not detected at all. It must be concluded that the structural isomerisation of butenes does not occur during homogeneous pyrolysis.

Let us now consider the mechanism for the isomerisation of perfluorobutenes on the double bond. We shall also take into account here the strictly homogeneous reaction conditions and its kinetic first order. Using the concept of tautomeric changes in perfluoroolefins through the 1,2-shift of a fluorine atom, the following scheme can be proposed:

$$CF_3=CF-CF_2-CF_3 \rightleftarrows CF_3-C-CF_2-CF_3 \rightleftarrows CF_3-CF=CF-CF_3.$$

However, it is necessary here to make a reservation which in our opinion is very important. According to quantum-chemical calculations,[48] bis(trifluoromethyl)carbene $(CF_3)_2C$: has a triplet ground state which is separated from an excited singlet by 17.8 kcal mol^{-1}. It may be assumed that other carbenes which do not have fluorine atoms on the carbene carbon atom will also have a triplet ground state. But in that case the type of isomerisation depicted above is spin-forbidden unless we are dealing with the formation of a carbene in an electronically excited (singlet) state by a 1,2-shift. An alternative approach is isomerisation via a 1,3-shift. At the present time it appears to us premature to make a definite choice. For simple molecules, for example triatomic ones, spin-forbidden reactions are in fact known to occur via the formation of species in electronically excited states, as takes place, in particular, in the decomposition of nitrous oxide. There are up to now no data on reactions involving complex molecules of this type.

Let us now turn to the question of the mechanism for formation of PFI in the pyrolysis of perfluoroolefins. We recall (this has already been mentioned above) that in the decomposition of perfluoromethylcyclopropane no compounds with the formula C_4F_8 are formed. The simplest assumption of all is that PFI is formed by recombination of two carbenes:

$$CF_2 + (CF_3)_2C: \rightarrow CF_2=C(CF_3)_2.$$

However, the formation of bis(trifluoromethyl)carbene in the ground state by a 1,2-shift of a fluorine atom in HFP is spin-forbidden, according to Dixon.[48] Moreover, recombination of triplet $(CF_3)_2C$ with difluorocarbene, which has a singlet ground state, is also forbidden. Consequently, only a singlet electronically excited carbene must be obtained for the formation of PFI by this means through a 1,2-shift. In our opinion, this problem merits an additional special study. At the same time there is no prohibition for the formation of PFB-1, for example, in a recombination reaction

$$CF_2 + CF-CF_2-CF_3 \rightarrow CF_2=CF-CF_2-CF_3$$

since the carbene $CF-CF_2-CF_3$ which is formed by another 1,2-shift of a fluorine atom in HFP has a singlet ground state and such a shift is not spin-forbidden. It cannot be excluded that the formation of large quantities of PFI, which often occurs on pyrolysis in tubular reactors, is due to reactions on the wall of the tube, especially if there are deposits of carbon on it. Coking of the walls in metal tubes during pyrolysis is a familiar phenomenon and even in an earlier study[49] it was noted that reactions for the formation of bis(trifluoromethyl)carbene from HFP occur on activated carbon. Formation of the corresponding thioketone was accounted for exactly in this way:

$$CF_3-CF=CF_2 \rightarrow (CF_3)_2C:$$
$$S + (CF_3)_2C: \rightarrow (CF_3)_2C=S.$$

IV. Conclusion

It is evident from what has been stated above that high-temperature reactions of perfluoroolefins, having extensive practical application, have also proved interesting from the point of view of theoretical organic chemistry. We attempt here to arrive at some results. Since this article is both about "carbenes" and "method", our conclusion will touch upon both topics.

Let us start with method. The concentration of the tautomeric form of TFE in the temperature range 800–1000 K as found by Kolbanovskii et al.[40] reaches an equilibrium value after about 10^{-3} s. In adiabatic expansion such temperatures are reached at a compression ratio of 10, and hence the concentration of TFE increases relative to its initial value (under normal conditions) by a factor of 10. The equilibrium concentration of trifluoromethylfluorocarbene correspondingly increases by a factor of 10. With normal procedures for conducting the reaction, heating the gas to 1000 K leads a reduction in its density by approximately a factor of 3. Thus, the concentration of the tautomeric form of TFE using adiabatic compression when other conditions are the same is as a result one and a half decimal orders higher than it would be in conventional experiments at atmospheric pressure§ (in which it could hardly be detected and in fact has not been). It should be noted that in this respect the shock tube method is also considerably inferior to adiabatic compression. As regards the other advantages of adiabatic compression, they are described in sufficient detail in Section II.

Let us now turn to the "carbene" aspect of this review. We shall start with one important qualitative rule. The known processes for pyrolysis of hydrocarbons are usually aimed at obtaining products with a lower molecular weight than the initial starting material. A classic example of this type of process is the pyrolysis of gasoline to obtain ethylene. With perfluoroolefins everything is reversed; in the pyrolysis of C_1 (Cl-22), C_2F_4 is obtained, and in the pyrolysis of the latter, C_3F_6 is obtained. The mechanism of the pyrolysis of hydrocarbons consists of a set of radical chain reactions, as was established earlier by Rice. At the same time the synthetic processes for perfluoroolefins have a non-chain carbene mechanism. It is interesting to note that when it is necessary to account for certain high-temperature processes involving an increase in carbon chain in the chemistry of hydrocarbons, ideas about a carbene reaction mechanism also have to be included. Judging by recent studies, the formation of carbon black from acetylene occurs in precisely this manner.[50] It cannot be stated that high-temperature radical processes are untypical for perfluoroolefins. At high temperatures (usually above 1500 K) even after short pulses ($\sim 10^{-3}$ s), products such as C_2F_6 or C_4F_6 which result from radical reactions are formed from perfluoroolefins. However, even under these conditions, when free-radical reactions take place, chains do not develop.

Some comments should now be made regarding the tautomeric changes of perfluoroolefins. As was mentioned above, if the conversion of C_2F_4 to its tautomeric form is postulated, it is on the basis of indirect data (the final stable reaction products). As regards the reverse conversion of carbene to olefin, we cannot ignore two other studies,[51,52] in which not only was the IR spectrum of $(CF_3)_2C$: obtained for the first time (the carbene was obtained by photolysis of bis(trifluoromethyl)diazirine in an argon matrix at 12 K) but also some of its chemical reactions were studied. We only want to mention here the fact that at a temperature above 40 K this carbene disappeared and C_3F_6 appeared. This was the first direct observation of a reverse (carbene–olefin) change involving the 1,2-shift of a fluorine atom. The occurrence of this reaction at 40 K indicates that the reverse fluorine shift is a reaction which has virtually no energy barrier. There is no reason to suppose that for the other perfluorocarbene— CF_3CF:—there would be a different situation (or, at least, substantially different). At the same time, according to quantum-chemical calculations,[53] for fluoroethylene $CFH=CH_2$ the 1,2-shift of a fluorine atom requires an energy of activation both in the olefin and in the carbene.

In concluding our review of the reactions involving a 1,2-shift of a fluorine atom, we should like to draw the attention of the reader to a study that has been familiar for quite some time.[53] In this study the pyrolysis of trifluoroethylene gave the butene $CF_3-CH=CH-CF_3$ as the main product. When the concept of a 1,2-shift of a fluorine atom is applied, this result has a natural and perhaps the only reasonable explanation, if the following scheme is assumed:

$$CF_2=CHF \rightleftarrows CF_3-CH:,$$
$$2CF_3-CH: \rightarrow CF_3-CH=CH-CF_3.$$

There is no doubt that at the present time by no means everything has yet been clarified with regard to carbene reactions in the high-temperature conversions of organofluorine compounds. It is possible to identify such problems as the reasons for the low values of the recombination coefficients of C_2 and C_3 perfluorocarbenes (it is unclear whether they reduce solely to steric factors or whether there are other more fundamental causes), the possibility of forming electronically excited carbenes when the transition reactions to the ground state are spin-forbidden (this question is closely related to the mechanism for formation of PFI), and certain others. However, on the whole, it can be stated that by using adiabatic compression in studying high-temperature carbene reactions it was possible to obtain a series of new experimental results which did not simply supply facts but also served as a basis for developing the concept of tautomeric changes in fluorinated olefins.

§Dilution of C_2F_4 with an inert gas is necessary in any method for studying its tautomeric changes— otherwise the concentration of TFE will decrease sharply because of its cyclodimerisation.

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