THE PULSED HOMOGENEOUS LASER PYROLYSIS: DETERMINATION OF ARRHENIUS PARAMETERS OF CHClF_2 DESTRUCTION BASING ON THE MODEL OF PHYSICAL AND CHEMICAL PROCESSES

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The Pulsed Homogeneous Laser Pyrolysis (PHLP) of CHClF_2 initiated by IOP(20) radiation of TEA- CO_2 laser was carried out in the presence of SF_6 sensitizer with the mixture components ratio 1:1 under partial pressure of the reactant equal to 1 Torr and 2 Torr.

To describe PHLP process in the afterpulse period we suggested a kinetic model of CHClF_2 thermal destruction accounting for the inhomogeneity of laser heating of the reaction mixture and its further cooling by the heat conduction mechanism. Applying the standard mathematical procedure for matching the experimental results of the degree of reactant destruction, and the numeric computations of this value made according to the suggested model, the Arrhenius parameters of the reaction of CHClF_2 mono-molecular conversion in the temperature range of 1000–1200 K were unambiguously determined. The values were obtained for the activation energy $E_a = 52.8 \pm 0.3$ kcal/mol, and the pre-exponential factor $A = (2.5 \pm 1) \cdot 10^{12} \text{ s}^{-1}$.

INTRODUCTION

The Pulsed Homogeneous Laser Pyrolysis (PHLP) technique enables one to study the gas-phase chemical processes at high temperatures (1000 K plus) and without the catalytic effect of the reaction vessel walls.^{1,2}

The gas thermalization time under pulse irradiation corresponds to V-T, R relaxation time of the multiphoton-excited sensitizer molecules and under the pressure of several torr is *ca.* 10 μs .²

It is known^{3,4} that if the irradiated area is only a small part of the reaction vessel, the main mechanism of cooling would be the adiabatic expansion. Computation of cooling due to shock waves requires creation of complex gas dynamic models that are illustrations of physical processes rather than a tool of kinetic analysis.

To assess the reaction rate constant of thermal destruction of the studied reactant under PHLP a technique of "chemical thermometer" is applied that does not require precise determination of temperature distribution in time and over reactor space.

Also, the course of the studied process is compared to the course, under the same conditions, of a close-type well-studied pyrolysis reaction with the known activation energy and pre-exponential factor values.²⁻⁴ The method error depends on the differences in the activation energy (E_a) and pre-exponential factor (A) of these two processes. The reference reaction is not always easy to select, since there is an additional restriction of the complete mutual inertness of both the initial substances and the conversion products for both reactions.

The CHClF_2 thermal destruction was thoroughly studied under normal conditions in pyrolysis furnaces.⁵⁻⁷ Conversion mechanism was determined:

The reaction (3) plays an important role only under deep conversion of freon-22 and under HCl excess. At low degrees of conversion difluorocarbene completely recombines with tetrafluoroethylene (TFE) formation. In⁵⁻⁷ the following values of the Arrhenius parameters were obtained for the first step of destruction process (1):

$$E_a = 55.8 \text{ kcal/mol}, \quad A = 10^{13.84} \text{ s}^{-1} \quad 5$$

$$E_a = 55.0 \text{ kcal/mol}, \quad A = 10^{13.2} \text{ s}^{-1} \quad 6$$

$$E_a = 55.8 \text{ kcal/mol}, \quad A = 10^{12.6} \text{ s}^{-1} \quad 7$$

The Pulsed Homogeneous Laser Pyrolysis of freon-22 was carried out in the works^{1,8,9} The TFE was found to be the main destruction product. No special kinetic studies were carried out in the mentioned works. It seems interesting to use the CHClF_2 single-channel destruction reaction with well-defined mechanism and kinetic data as the model reaction for probation of the method suggested in the present paper for determination of the activation energy and the pre-exponential factor of reaction (1) under PHLP.

In the absence of the internal reference it is necessary to have information on the spatial and time distribution of temperature over reaction volume. The problem is greatly simplified if laser radiation fills the major part of the cell. In this case the shock waves do not cause any significant temperature changes, and heat conduction is the dominant cooling mechanism.^{10,11} Under initially uniform heating of gas the problem can be reduced to analytical calculation of gas cylinder cooling. Such calculation was made in¹¹ where the ozone PHLP was studied. The activation energy of O_3 destruction reaction was assessed by the slope (tangent) of the experimental curve, O_3 conversion degree ($\Delta C/C_0$) vs. maximum initial gas temperature (T_{VTR}), in the semilogarithmic coordinates $\ln(\Delta C/C_0) - 1/T_{\text{VTR}}$. The pre-exponential factor was determined from the correspondence of $\Delta C/C_0$ values obtained experimentally and those computed by the kinetic equation of O_3 thermal destruction process basing on the "homogeneously-heated-reaction-mix-cooling" model. It should be noted that solving this problem in the analytical form it is practically impossible to account for the relationship of the mix components heat capacity, C_{V_k} , and gas heat

conduction, λ , with temperature. This, generally speaking, is incorrect because at those considerable heating levels occurring under laser action, C_{V_k} changes 1.5–2-fold, and λ – 6–7-fold. To account for these relationships the numeric methods are required.

Moreover, a really existing inhomogeneity of laser beam cross-section intensity leads to spatial distribution of IR-radiation energy absorbed by the gas mix (E_{abs}) and, primordially, to inhomogeneous heating of different areas of the internal reaction cell space. The further temperature variation with time for these areas can be determined through monitoring of heat flows between them and accounting for $C_{V_k}[T(t)]$ and $\lambda[T(t)]$ changes. Such calculation was made in ¹⁰, where cyclobutanone PHLP was studied under TEA- CO_2 laser action. The value of $\Delta C/C_0$ was computed in the afterpulse period as a sum of independent conversion degrees $(\Delta C/C_0)_{V_i}$ for each elementary volume V_i within the cell, assuming parameters E_a and A as the preset ones. The experimental and computed data were in good agreement.

The stationary longitudinal and transverse temperature profiles of SF_6 and $\text{C}_2\text{H}_5\text{Cl}$ under CW- CO_2 laser irradiation were calculated in ¹². Also, that paper presented a calculation of chloroethane conversion degree as a function of laser radiation energy for two values of E_a : 57.4 and 65.0 kcal/mol. The authors of ¹² found that the experimental data are in better agreement with the value 57.4 kcal/mol generally accepted in the literature.

The goal of the present study was development of a method for determination of the primary elementary reaction rate constant for a reactant conversion process exemplified by CHClF_2 under pulsed homogeneous laser IR heating, via the afterpulse temperature and concentration fields modelling that enables unambiguous determination of Arrhenius parameters of the studied reaction basing on the experimental data.

THE HEAT CONDUCTION MODEL

The model we have suggested accounts for temperature variation with time due to heat flows and changes of concentration fields under these conditions. For that purpose the entire internal volume of the cell was presented as the sum of elementary volumes, V_i , and each was assigned, according to its spatial location, the initial gas temperature, $T_0(V_i)$, upon completion of V-T, R relaxation process of SF_6 . It was assumed that in the elementary volumes directly adjoining the reactor walls the temperature was constant throughout the entire process period and equalled to 298 K. For concentration calculations the density gradient was determined basing on that the rate of pressure equalization is considerably higher than that of temperature equalization.¹³ In each elementary volume V_i , the reactant concentration $C(V_i)$, and temperature are related by the equation of the ideal gas state:

$$P(V_i) = R * C(V_i) * T(V_i) \quad (4)$$

Since it can be assumed that the pressure at any moment of time t is constant over the volume $dp/dv = 0$, then $C(V_i) = \varphi(t)/T(V_i)$, where the function

$$\varphi(t) = C_0 * V_{\text{total}}/V_i \sum_{V_i} 1/T(V_i) \quad (5)$$

is obtained from the condition of substance quantity conservation in the entire volume

$$\sum_{V_i} [C(V_i) * V_i] = C_0 * V_{\text{total}} \quad (6)$$

and the ideal gas Eq. (4).

Chemical conversion of the reactant was studied in the selected short time intervals, Δt , and small volumes, V_i , isothermally and described by the general kinetic equation with the rate constant expressed in the Arrhenius form $k = A * \exp[-E_a/RT(V_i)]$. Then, for a relatively short time interval Δt the quantity of the reacted substance can be written as:

$$\Delta C(V_i) = C(V_i) * A * \exp[-E_a/RT(V_i)] * \Delta t \quad (7)$$

under condition of independent course of chemical conversion in each elementary volume.

The heat flow between the adjacent volume elements due to temperature gradient was determined for a time period Δt by the formula:

$$Q(V_i V_j) = \lambda * \{[T(V_i) + T(V_j)]/2\} * S_{ij} * [T(V_i) - T(V_j)] * \Delta t/L_j \quad (8)$$

where S_{ij} is the area of the boundary between subvolumes V_i and V_j ; L_j is the length of the j -th subvolume in the direction of the heat flow from V_j to V_i ; λ is the heat conduction factor. The total heat quantity, Q , transferred to the volume V_i was obtained by summing up those of the adjacent volumes, V_j . The temperature variation within the time interval Δt would be

$$\Delta T(V_i) = Q/\sum_k C(V_i)_k * C_{V_k}[T(V_i)] \quad (9)$$

where $C(V_i)_k$ is the concentration of the k -th component, and $C_{V_k}[T(V_i)]$ is its heat capacity. Temperature relationships of the components, heat capacities were calculated basing on the statistical data, and the heat conduction of mix—by the standard method.¹⁴ This calculation procedure for the time period Δt was performed for all elementary volumes resulting in the new temperature and concentration fields obtained. Then, the calculation was repeated by sequential time intervals Δt throughout the entire cooling process. Summing-up the quantity of reacted substance $\Delta C(V_i)$ of all elementary volumes and over all time intervals we obtained the total conversion degree for one laser pulse. Since conversion degrees in each volume V_i over a time period Δt are very small $\Delta C(V_i) \leq 10^{-4}\%$, and the total reactant destruction degree in one pulse normally does not exceed few per cent, the concentration variation conditioned by the chemical reaction was not accounted for in the concentration field calculations.

Let us note that in the earlier work¹⁰ calculation was based on the prerequisites similar to those that we used. The paper,¹⁰ however, did not account for the concentration gradients. This, as was shown by preliminary estimations¹¹ at quite real temperature difference *ca.* 600° brings about underestimation of the reactant concentration in the “hot” region *ca.* 50%, and in the “cold” one—almost its doubling.

EXPERIMENTAL

Pulsed heating was done by TEA- CO_2 laser ($\text{CO}_2:\text{N}_2:\text{He}:\text{D}_2$ in ratio 1:1:4:1) zeroed in on the IOP(20) line, $\tau_{\text{pulse}} = 150$ ns. The laser output beam of $-(2 \times 1.6)$ cm^2 was diaphragmed with the 1.5-cm-diameter iris diaphragm to separate its most homogeneous part. A sodium chloride plate was placed in the way of the laser beam to reflect *ca.* 1% of its energy onto the calorimeter to monitor the laser output energy. The laser pulse output energy spread was never above 3% in the 100 experiment series. When required, the beam was attenuated by introduction of calibrated wedges and then channelled through a cylindrical stainless steel cell (length $L = 7.2$ cm; internal diameter $d = 1.5$ cm) having barium fluoride windows. Then the beam entered the second calorimetric sensor measuring the value of the IR-radiation incident energy (E_0) when the cell was empty, and the transient energy E_L when the L -long cell contained a reaction mix. The laser beam energy distribution over the cell cross-section was measured with 1×1 mm orifice diaphragm moved by the micrometer screw vertically and horizontally over the whole beam cross-section. According to this procedure the entire internal cell volume was approximated by the set of 149 equal elementary volumes (V_i) each having the cross-section $S(V_i) = 1$ mm^2 ; that corresponds to the diaphragm orifice size. Thus, the output laser beam energy (E_0) distribution over the cell cross-section was represented by the set of $E_0(V_i)$ values of all 149 elementary volumes. Axial inhomogeneity of the laser beam in the reaction mix containing cell was neglected, since the IR-radiation energy absorbed by gas never exceeded 10% of E_0 in all experiments. The ratio of the energy flow $E_0(V_i)$ falling onto the selected elementary volume of $S(V_i)$ area to $[E_0(V_i)]$ averaged by all values is 1.84 in the cell center, and up to 0.54 at the edges.

We have carried out a series of experiments in one of the central elementary volumes for each of the studied mixes to determine the relationship between the absorption cross-section $\text{SF}_6(\sigma_{\text{eff}})$ and the incident energy $E_0(V_i)$; the total energy E_0 was varied in the range $0.4 \div 0.85$ J. The $\text{SF}_6:\text{CHClF}_2$ mix in the ratio 1:1 under total pressure 2 and 4 torr was used. In the main experimental series with the mixes of the mentioned composition the samples were irradiated with the same levels of E_0 energy. Upon irradiation the cell contents were analyzed with the "Khrom-5" chromatograph in a column with "POROPAK-T." The TFE was found to be the main (over 99.9%) product of freon-22's PHLP. The reactant conversion degrees, $\Delta C/C_0$, ranged in one pulse from 1×10^{-2} to 6%, as a function of the laser output energy E_0 .

RESULTS AND DISCUSSION

1. Absorbed Energy Determination and Temperature Computations

It is known,² that for SF_6 at laser radiation energy densities (ϕ) from 1×10^{-4} to 3 J/cm^2 , the mean number of absorbed IR photons with energy $\hbar\omega$ has the relation $[n] \sim \phi^{2/3}$. Since the sensitizer-absorbed energy, $E_{\text{abs}} = \hbar\omega \cdot [n]$, and $\phi = E_0/S$, it may be expected that $E_{\text{abs}} \sim E_0^{2/3}$.

For one of the central elementary volumes, V_i , the experimental data of the absorbed energy relation $E_{\text{abs}}(V_i) = E_0(V_i) - E_L(V_i)$ were processed in the form of a function of the incident energy $E_0(V_i)$ according to the equation:

$$\ln[E_{\text{abs}}(V_i)] = A + B * \ln[E_0(V_i)] \quad (10)$$

by the least squares method. The power exponent (B) values obtained were 0.66 ± 0.02 for mix total pressure of 2 torr, and 0.55 ± 0.02 for 4 torr, this is in good agreement with expected exponential relation E_{abs} vs. E_0 for SF_6 . At that, the absorption cross-section, σ_{eff} , defined as $\sigma_{\text{eff}} = E_{\text{abs}}(V_i)/\phi(V_i)$, where $\phi(V_i) = E_0(V_i)/S(V_i)$, slightly decreases with increasing $E_0(V_i)$ and is $3 * 10^{-19} - 5 * 10^{-19} \text{ cm}^2$ (see Figure 1). These data on SF_6 multiphoton absorption cross-section are in good agreement with the generally accepted,² and enable one to calculate, using the set of $E_0(V_i)$ values, the absorbed energy $E_{\text{abs}}(V_i)$ in each elementary volume V_i . The total IR energy $E_{\text{abs}}(V_i)$ absorbed in the system for each mixture at different E_0 values was determined by summing up all elementary volumes. The corresponding to this energy initial equilibrium gas temperature (T_{VTR}) from which pyrolysis process starts was calculated in the approximation of complete thermalization of E_{abs} energy by the expression:

$$E_{\text{abs}} = \int_{298}^{T_{\text{VTR}}} \sum_k C_k * C_{V_k}(T) * dT \quad (11)$$

where C_k is the k -th component concentration, $C_{V_k}(T)$ is the k -th component heat capacity.

Thus introduced T_{VTR} temperature does not account for the actually existing inhomogeneity of laser heating of a gas; this parameter, however, enables comparison of the PHLP experimental results for mixtures of different composition and different E_{abs} values.

Figure 1 Effective cross-section of multiphoton absorption of SF_6 mixed with CHClF_2 (1:1) vs. the laser radiation energy density. (○)—experimental data at $P = 2$ Torr; (—)—the result of the experimental data processing in the form of exponential relation (10) by the least squares method.

Figure 2 Semilogarithmic relation of CHClF_2 conversion degree and $1/T_{VTR}$ parameter. ($\circ$)—PHLP experimental data at $P = 2$ Torr; ($\triangle$)—PHLP experimental data at $P = 4$ Torr; (—)—computation based on the suggested model; (---)—computation based on the homogeneous heating model. $E_\alpha = 52.5$ kcal/mol, $A = 2 \cdot 10^{12} \text{ s}^{-1}$.

It is assumed in the suggested PHLP model that chemical conversions occur in the completely thermalized system. Under pressure of 10 Torr and above in the gas system the characteristic times of V-T/R equilibrium settlement are almost one order less than the characteristic times of the reaction. In the region of low pressure (*ca.* 1 torr and below) under SF_6 molecules multiphoton excitation (MPE) up to $[n] = 12\text{--}16$ quanta per molecule there occurs on the one hand a considerable, compared to “weak” excitation, increase of V-T/R relaxation rate,¹⁵ and on the other, even greater increase of the rate of V-V’ exchange between the polyatomic molecules is expected.[†] Therefore, at the initial stage of collision relaxation there may occur a brief excess of the “vibration temperature” over the translatory-rotational one. Under conditions of our experiment [$1 \text{ Torr} < P_{\text{total}} < 10 \text{ Torr}$] this “break-away” of vibration temperature is apparently so brief (in the order of few microseconds) that it can be considered that the main conversion of the reactant (CF_2HCl) occurred under conditions of complete thermalization of IR irradiation energy absorbed by the sensitizer, i.e. at temperature close to $T_{V-T/R}$ values (11), which under our experimental conditions is preserved for over 100 microseconds in the process of the afterpulse gas cooling (see Figure 3). A proof of that assumption is on the one hand a good agreement between our experimentally obtained values of E_α and A under CF_2HCl PHLP and the literature data, and on the other hand the results of ⁹

[†] Regrettably, there are no quantitative data in literature on the rates of V-V’ exchange between the MFE molecules of SF_6 and CF_2HCl .

Figure 3 Time evolution of the reactant's radial temperature (a) and concentration (b) profiles in the afterpulse period. (a) 1 - $t = 10 \mu s$; 2 - $t = 200 \mu s$; 3 - $t = 500 \mu s$; 4 - $t = 1 ms$; 5 - $t = 2 ms$; 6 - $t = 5 ms$. (b) 1 - $t = 10 \mu s$; 2 - $t = 5 ms$. Mixture pressure 2 Torr, $E_0 = 0.63 J$.

confirming that in the absence of threshold effects, related to SiF_4 electron excitation or SF_6 MPD, the detected CF_2HCl destruction in the presence of sensitizers (SiF_4 , SF_6) occurs in the thermalized systems. The work⁹ studied the kinetics of real-time $:CF_2$ radical formation with high-sensitivity afterpulse LiF diagnostics. It was found that LiF signal appeared with $\sim 10 \mu s$ delay relative to the initiation pulse. This delay time, according to authors of,⁹ is in good correlation with the termination of thermalization process of SF_6 (1 Torr) + CF_2HCl (1 Torr) mixture. We have obtained similar results in the UV-detection of $:CF_2$ radical ($\lambda = 248,3 nm$) formed under C_3F_6O PHLP (SF_6 sensitizer, 2 Torr total pressure):

The signal of $:CF_2$ absorption was observed in a thermalized system with a delay of 8–10 μs relative to the initiating laser pulse.

As has been mentioned, in the systems with pressure about 10 Torr and above, the times of the vibration temperature "break-away" from the equilibrium $T_{V\text{-}TR}$ would be so short that the contribution of the nonequilibrium mode reactant destruction to the overall destruction degree would be negligible.

Figure 2 shows in symbols the experimental data of difluorochloromethane destruction under PHLP in the coordinates $\ln(\Delta C/C_0) - I/T_{VTR}$. In the case of homogeneous heating of the mixture, as shown in ¹¹, the slope of the straight line—plotted in the mentioned coordinates for the set of experimental data—to the I/T_{VTR} axis corresponds to E_α/R value of the reactant destruction reaction. For the data shown in Figure 2 it would correspond to $E_\alpha = 48$ kcal/mol of CHClF_2 destruction reaction. It was noted in ¹⁰, however, that for the inhomogeneous heating this method yields 5–10% underestimated values of the activation energy of monomolecular destruction reaction. Therefore, according to the above model, E_α was determined with a detailed account of contribution of all zones with different initial temperature $T_0(V_i)$ to the reactant destruction total degree ($\Delta C/C_0$). To calculate the total conversion degree of CHClF_2 ($\Delta C/C_0$) after a laser pulse in each of 149 elementary volumes (V_i parallelepipeds sized $[1 * 1 * 72]$ mm) of the set describing the reaction volume of the cell, an $E_{\text{abs}}(V_i)$ magnitude was calculated by the IR-beam-spatial-energy-distribution net of $E_o(V_i)$ values and the corresponding absorption cross-section values of SF_6 -mixtures with the reactant:

$$E_{\text{abs}}(V_i) = \sigma_{\text{eff}} * \phi(V_i) \quad (12)$$

The initial equilibrium temperature in each elementary volume $T_o(V_i)$ was found similarly to T_{VTR} parameter by the expression:¹¹

$$E_{\text{abs}}(V_i) = \int_{298}^{T_o(V_i)} \sum_k C_k * C_{v_k}(T) * dT \quad (11')$$

Thus found initial temperature distribution of the cell reaction volume was then introduced into the above heat conduction model for numeric calculations of the concentration and temperature fields time variation, as well as for determination of the reactant destruction degree. Also, cooling at the edge windows of the cell was not accounted for, since their area comprised less than 10% of the total cell area and, as has been shown by the preliminary assessment, produced no significant effect on the cooling process and reactant destruction in general.

The calculated temperature and concentration fields are shown in Figure 3. The time pitch Δt , and the finite summation time t_{max} were 10 and 500 μs , respectively, and did not limit the calculation accuracy. The CHClF_2 destruction degrees were computed for the activation energy range of 35–70 kcal/mol and the pre-exponential factor 10^{10} – 10^{14} s^{-1} . These values exceed the range of possible E_α and A values for HCl concerted elimination reactions.¹⁶

The least squares criterion was applied to determination of the activation energy and pre-exponential factor. A normalizing function

$$F = \sum_N [(\Delta C/C_o)_{\text{exp}} - (\Delta C/C_o)_{\text{calc}}]^2$$

was introduced, as well as its logarithmic analog

$$Fl = \sum_N [\ln(\Delta C/C_o)_{\text{exp}} - \ln(\Delta C/C_o)_{\text{calc}}]^2$$

At that $(\Delta C/C_o)_{\text{calc}} = A * S * \Delta t$, where

$$S = \sum_{t=0}^{t_{\text{max}}} \{ [\sum_{V_i} (\exp(-E_\alpha/RT(V_i)/T(V_i)))] / \sum_{V_i} 1/T(V_i) \} \quad (13)$$

It is known that the least squares criterion is applied to exponential approximation of function F , and also Fl is a function of two variables E_α and A , and its minimum satisfies those values of E_α and A that lead to the best agreement between the N experimental data and calculations. To determine the linear parameter (A) a standard procedure of differentiation by this parameter and finding zero of this derivative is used. Thus, each fixed value of energy has a corresponding unique value of pre-exponent at which the function is minimum:

$$A_{\text{min}}(F) = \sum_N [(\Delta C/C_o)_{\text{exp}} * S / \sum_N S^2 * \Delta t] \quad (14)$$

$$A_{\text{min}}(Fl) = \sqrt[N]{\prod_N [(\Delta C/C_o)_{\text{exp}} / (\Delta t * S)]} \quad (15)$$

The minimal value of F and Fl has a corresponding analogous condition “equal-to-zero-of-derivative” by the nonlinear parameter E_α . It is impossible, however, to determine from this condition this nonlinear parameter in the explicit form. Therefore, the methods of numeric minimization of single-value function (in this case $F[E_\alpha, A_{\text{min}}(F)]$ and $Fl[E_\alpha, A_{\text{min}}(F)]$)¹⁷ were applied to determine the E_α value. Computations of F and Fl were done for E_α in the range of 35 ÷ 70 kcal/mol and A values according to expressions (14) and (15). The minimum for both, F and Fl , for the mixture at $P_{\text{total}} = 4$ Torr was found at $E_\alpha = 53.0$ kcal/mol, $A = 3.4 * 10^{12} \text{ s}^{-1}$; and for the mixture at $P_{\text{total}} = 2$ torr at $E_\alpha = 52.5$ kcal/mol, $A = 2 * 10^{12} \text{ s}^{-1}$.

Computations of $F(E_\alpha, A)$ and $Fl(E_\alpha, A)$ values in the lattice sites with alternating pitch covering the above E_α and A range show that in this region both functions have the only explicit minimum coinciding with the mentioned one. Thus, the present method leads to an unambiguous determination of the activation energy and the pre-exponential factor corresponding to the experimental data and well agreeing with literature data.⁵⁻⁷

Figure 2 shows the calculated values of $\ln(\Delta C/C_o)_{\text{calc}}$ for all experimental values of E_{abs} expressed via T_{VTR} parameter according to expression (11) under initial “mosaic” temperature distribution of the suggested model (solid line), and values of $\ln(\Delta C/C_o)_{\text{clcltd}}$ for the homogeneous heating model (dashed line). Computations were done with the use of the values of Arrhenius parameters E_α and A that we have found. The second model yields the conversion degrees 1 to 1.5 orders of magnitude lower than the first one, and is obviously in disagreement with the experimental results. The carried-out assessment shows that if the absorbed energy (E_{abs}) is distributed inhomogeneously over the cell volume, then there are zones where the temperature of the gas exceeds considerably the T_{VTR} value. It is these regions that

make the decisive contribution to the total destruction degree of difluorochloromethane; this is due to the exponential relation between the rate constant and temperature.

The kinetic model suggested in this paper describes with good approximation the real PHLP process, and enables one to unambiguously determine the Arrhenius parameters of the homogeneous thermal destruction of the reactant. This method is applicable for research into pyrolytic reactions of a wide scope of reactants at higher temperatures.

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