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Gas-Phase Oxidation of Vinyltrifluorosilane with Nitrogen Dioxide under the Action of a Pulse CO_2 Laser

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Abstract—A chemical reaction between $C_2H_3SiF_3$ and NO_2 induced by radiation from a pulse CO_2 laser was studied by mass spectrometry and IR spectroscopy. The composition of gaseous products was determined. A macrokinetic approach was developed to study bimolecular reactions initiated by pulsed IR radiation. The procedure developed allowed us to answer the question of whether the test reaction occurs under conditions when the molecules of only one reactant are vibrationally excited or under conditions of equal vibrational temperatures. The use of this approach to the reaction between $C_2H_3SiF_3$ and NO_2 demonstrated that its acceleration was due to the equilibrium heating of the system.

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INTRODUCTION

The use of high-power IR radiation makes it possible to generate superequilibrium concentrations of vibrationally excited molecules, thereby stimulating the occurrence of chemical reactions [1]. The appearance of new frequency-tuned IR laser radiation sources, such as powerful semiconductor lasers and free electron lasers [2], is causing a rebirth of interest in these studies. The selective stimulation of chemical reactions used for isotope separation or laser purification is the most attractive capability.

There are two essentially different schemes for controlling chemical processes with the use of IR laser radiation. In the first case, laser radiation causes sufficiently strong molecular excitation to result in dissociation [3]. A unimolecular reaction is stimulated in this manner. This suggests the absorption of a large number of laser photons (the phenomenon of multiphoton IR excitation) or the excitation of high vibrational levels upon the absorption of a laser photon (overtone excitation).

The other approach consists in the use of comparatively low molecular excitation, which does not cause dissociation but increases the rate of the subsequent reactions with the participation of the excited molecule. This approach can be referred to as the laser control of bimolecular reactions. The most interesting results in this area were obtained in a study of the interaction of small molecules with atoms and free radicals [4].

The laser acceleration of a bimolecular reaction between stable polyatomic molecules is of the greatest practical importance. Studies in this area have been started a long time ago [5]. At the outset, the question arose as to whether the action of IR laser radiation is thermal or nonthermal, that is, whether it is due to a nonequilibrium concentration of vibrationally excited molecules or equilibrium heating. As of now, it has been found that, with the use of continuous-wave IR lasers, there is a limiting pressure above which radiation can affect the occurrence of gas-phase reactions only because of an increase in the equilibrium temperature. The characteristic value of this limiting pressure varies from several tens to hundreds of Pa [6, 7]. The use of pulse lasers eliminates this restriction and makes it possible to exert a nonthermal effect of laser radiation at higher pressures. However, the problem of a thermal or nonthermal character of the effect of radiation should be individually solved for each particular reaction.

In this work, we propose a procedure for kinetic analysis of a bimolecular reaction initiated by pulse laser radiation. It allowed us to study reactions occurring either under vibrational nonequilibrium conditions or under full equilibrium conditions. This procedure was used to study of a model reaction of vinyltrifluorosilane ($C_2H_3SiF_3$) with nitrogen dioxide (NO_2). As a model, this reaction has a number of advantages. The $C_2H_3SiF_3$ is very efficiently excited by CO_2 laser radiation because of the presence of the SiF_3 group [8]. At the same laser radiation density, $C_2H_3SiF_3$ absorbs more energy than SF_6 by a factor of 3–5 [9]. At the same time, the presence of the unsaturated $–C_2H_3$ fragment in the molecule imparts a certain chemical activity to this molecule. It is believed that $C_2H_3SiF_3$ enters into reactions at the double bond similarly to hydrocarbons from the ethylene series. In particular, vinylfluorosilane can be oxidized by nitrogen dioxide. The presence of an unpaired electron in the NO_2 molecule impart a high reactivity to it [10–13].

It was found experimentally that $C_2H_3SiF_3$ did not react with NO_2 at room temperature and a reactant pressure of ~10^2 Pa. However, the irradiation of a mixture of $C_2H_3SiF_3$ and NO_2 with a pulse CO_2 laser caused irreversible chemical changes. The energy density used in this case was insufficient for the dissociation of vinyltrifluorosilane; this fact suggests a chemical character of its interaction with nitrogen dioxide.

EXPERIMENTAL

The experiments were performed under batch conditions at room temperature; the pressure of gas samples was no higher than 10^3 Pa. A glass vacuum system, which was designed for the synthesis, storage, and puffing of substances, was equipped with a cylindrical Pyrex cell 42 cm in length and 3 cm in diameter with plane-parallel windows of NaCl. The cell was connected to the ion source of an MX 1303 magnetic mass spectrometer through a small-diameter (~20 μm) diaphragm; this allowed us to monitor the composition the sample at any point in time. It was also possible to automatically record the spectra obtained in the course of periodical scanning over a specified range of mass numbers. The pressure in the system was controlled with a Baratron R227A pressure gage, and the temperature was measured with a thermocouple sensor. The synchronized recording of a p–T diagram allowed us to obtain information on the phase component composition of the sample.

The cell was arranged along the optical axis of a pulse CO_2 laser with energy varied to 3 J/pulse [14]. The laser pulse had a shape characteristic of these lasers: the main peak with a duration of 200 ns was accompanied by a tail with a duration of about 800 ns. A central portion was separated from the laser beam using a diaphragm 1 cm in diameter and used for the irradiation of the reaction cell. Laser radiation was not focused. The radiation energy was measured using a power meter and a pyroelectric detector both before and behind the reaction cell.

The preparation of vinyltrifluorosilane was described elsewhere [8]. Nitrogen dioxide used in this study was prepared by the reaction $2NO + O_2 \longrightarrow 2NO_2$ and purified by repeated freeze–thawing fractionation. A mixture of the substances was introduced into the cell and irradiated with a laser. To control the degree of conversion and to determine the composition of products, IR spectroscopic analysis was performed on a Bruker Vector 22 Fourier transform spectrometer with a resolution of 1 cm^{-1}. The substances were analyzed in a cell 18 cm in length and 3 cm in diameter. The IR spectra were measured over a range of 400–4000 cm^{-1} before and after laser irradiation.

Quantum-chemical calculations for the geometry optimization of reactants, products, and intermediate species and a search for the transition state were performed using the Gaussian-98 program package [15] employing the hybrid density functional theory DFT/b3lyp method with the 6-311++ basis set. The parameters of the transition complex were determined using the QST2 procedure.

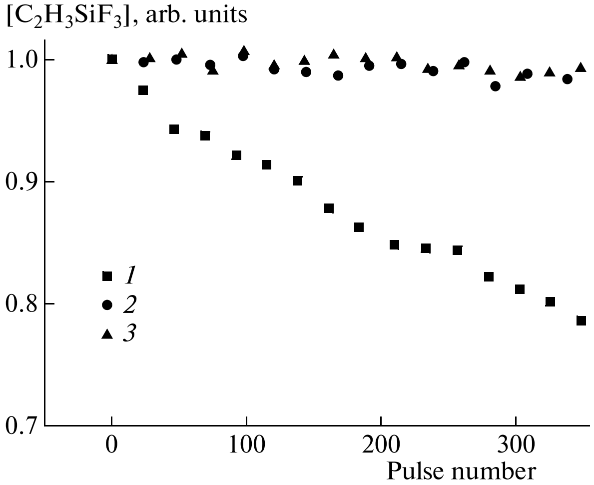


Fig. 1. Consumption of $C_2H_3SiF_3$ upon the irradiation of the reaction cell with a CO_2 laser: (*1*) a mixture of $C_2H_3SiF_3$ (60 Pa) and NO_2 (240 Pa); (*2*) individual $C_2H_3SiF_3$ (60 Pa); (*3*) a mixture of $C_2H_3SiF_3$ (47 Pa) and SO_2 (200 Pa). A laser with a pulse energy density of 0.56 J/cm^2 was tuned to the R12 line (970.5 cm^{-1}); the pulse repetition frequency was 0.5 Hz.

RESULTS

Acceleration of the Reaction of $C_2H_3SiF_3$ with NO_2 under the Action of Laser Radiation

We found that $C_2H_3SiF_3$ and NO_2 do not react with each other at room temperature. For this purpose, we recorded the mass spectrum and p–T diagram of a mixture of $C_2H_3SiF_3$ and NO_2 at partial pressures of 70 Pa and allowed the mixture to stand in the reaction cell for 1 h; then, we performed a repeated analysis, which demonstrated the absence of changes from the system.

The action of CO_2 laser radiation caused a chemical reaction in the $C_2H_3SiF_3$–NO_2 system. Figure 1 shows changes in the concentration of vinyltrifluorosilane upon the irradiation of its mixture with nitrogen dioxide in the absence of multiphoton dissociation. The concentration of vinyltrifluorosilane was determined by mass spectrometry from a signal with m/z = 112 due to the molecular ion $C_2H_3SiF_3^+$. It can be seen that the degradation of $C_2H_3SiF_3$ did not occur at an energy density of 0.56 J/cm^2 in a laser tuned to the R12 line (970.54 cm^{-1}) near a linear absorption maximum of $C_2H_3SiF_3$ (antisymmetric vibration ν_8 (a') and antisymmetric vibration ν_{16} (a'')) [8]. However, in the presence of NO_2, the concentration of $C_2H_3SiF_3$ began to decrease as the laser was turned on.

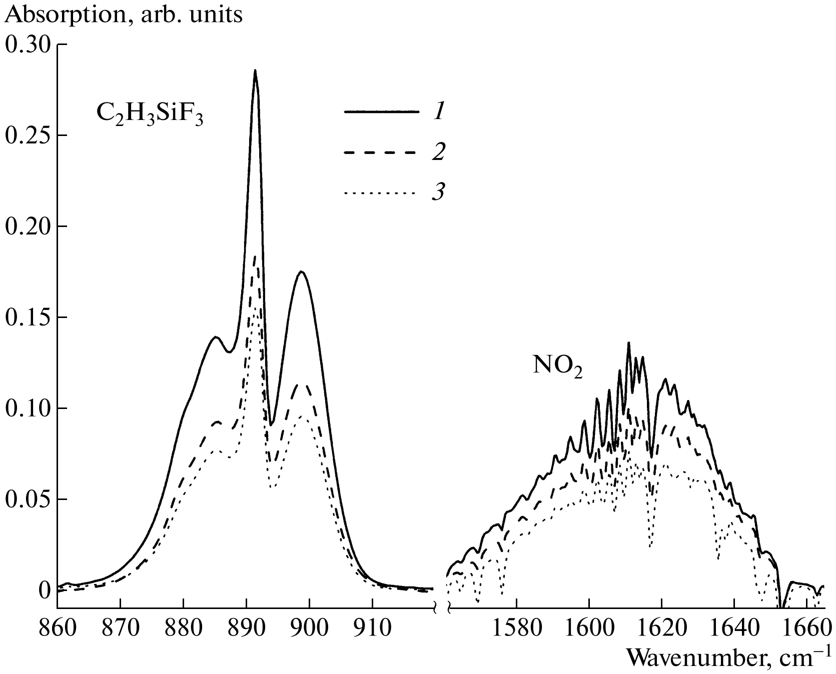


Fig. 2. Fragments of the IR spectrum of a mixture of vinyltrifluorosilane (40 Pa) and nitrogen dioxide (230 Pa): (*1*) before irradiation, (*2*) after irradiation for 20 min, and (*3*) after irradiation for 40 min. A laser with an energy of 0.56 J/cm^2 was tuned to the R12 line; the pulse repetition frequency was 0.5 Hz; the cell length was 18 cm.

At a total pressure of 300 Pa in a mixture, $C_2H_3SiF_3$ molecules undergo several collisions during the time of a laser pulse. To exclude the explanation of the observed results by a decrease in the efficiency of the multiphoton excitation of $C_2H_3SiF_3$, which leads to dissociation, we performed experiments in which a knowingly inert component—sulfur dioxide—was the second component of a mixture. As can be seen in Fig. 1, $C_2H_3SiF_3$ was not consumed upon the addition of sulfur dioxide. The numbers of the degrees of freedom in SO_2 and NO_2 molecules are the same; the vibrational frequencies of these molecules are also comparable. Assuming that collisions with SO_2 and NO_2 molecules equally affect the process of multiphoton excitation, we conclude that the dissociation of $C_2H_3SiF_3$ does not occur both in a mixture and in an individual state.

The occurrence of a chemical reaction was also supported by IR-spectrometric analysis. Figure 2 shows changes in the IR spectrum of a mixture of $C_2H_3SiF_3$ and NO_2 in the course of laser irradiation. A band at 890 cm^{-1} corresponds to symmetrical vibrations in the SiF_3 group of the vinyltrifluorosilane molecule [8], whereas absorption at 1615 cm^{-1} belongs to the antisymmetric stretching vibration of nitrogen dioxide. Upon the laser irradiation of a mixture of $C_2H_3SiF_3$ with NO_2, the concentrations of both of the components decreased.

Product Composition

The mass-spectrometric analysis of a reaction mixture during and after laser irradiation suggests its complex composition. Many new peaks appear in the mass spectrum. Attempts to perform the low-temperature fractionation of a reaction mixture were unsuccessful: after freezing to −196°C and repeated puffing to the cell, new lines disappeared from the mass spectrum of the mixture. It is likely that silicon-containing products form nonvolatile polymers in a condensed phase. The main result of the low-temperature fractionation was the identification of nitrogen monoxide, whose vapor has a sufficiently high volatility at a liquid nitrogen temperature.

The newly formed peaks in the mass spectrum were attributed by comparing with the available mass spectra of substances taking into account the atomic weight composition of the starting mixture (Table 1). Ethinyltrifluorosilane (C_2HSiF_3) and silicon tetrafluoride (SiF_4) belong to the silicon-containing products (their mass spectra are known). Compounds containing the Si–O bond were also detected, namely, trifluorosilanol ($HOSiF_3$) and hexafluorodisiloxane ($O(SiF_3)_2$). In addition, a product formally corresponding to the addition of an oxygen atom to vinyltrifluorosilane was identified; hypothetically, this is vinyl trifluorosilyl ether ($F_3Si–O–CH=CH_2$). Reacted nitrogen dioxide was mainly converted into the monoxide NO.

Table 1. Identification of products of the reaction of CH_3SiF_3 with NO_2 based on the results of mass-spectrometric analysis

Mass number (*m/z*)	Ion	Product
186	$F_3Si–O–SiF_3^+$	Hexafluorodisiloxane ($F_3Si–O–SiF_3$)
167	$F_3Si–O–SiF_2^+$	Hexafluorodisiloxane ($F_3Si–O–SiF_3$)
128	$F_3Si–O–CH=CH_2^+$	Vinyl trifluorosilyl ether
126	$F_3Si–O–C_2H^+$	Vinyl trifluorosilyl ether
110	$F_3Si–C≡CH^+$	Ethyltrifluorosilane ($F_3Si–C≡CH$)
104	SiF_4^+	Silicon tetrafluoride (SiF_4)
102	$F_3Si–OH^+$	Trifluorosilanol ($F_3Si–OH$)
85*	SiF_3^+	–
83	$F_2Si–OH^+$	Trifluorosilanol ($F_3Si–OH$)
44	N_2O^+, CO_2^+	Nitrogen hemioxide or carbon dioxide
43	$C_2H_3O^+$	Vinyl trifluorosilyl ether
30	NO^+	Nitrogen monoxide (NO)
29	HCO^+	Vinyl trifluorosilyl ether
28	CO^+, N_2^+	Nitrogen hemioxide, carbon dioxide, or nitrogen
26	$C_2H_2^+$	Acetylene (C_2H_2)
25	C_2H^+	Acetylene (C_2H_2)
18	H_2O^+	Water (H_2O)

* Uncharacteristic peak, which can be due to various molecules.

The quantitative analysis of a mixture is difficult to perform because of the impossibility of low-temperature separation, the absence of the published mass spectra of individual substances, and the mutual superposition of peaks due to various components. We attempted to perform gas-chromatographic analysis in order to separate and identify the products. However, because of the low concentrations of mixture components after dilution with a carrier gas, we failed to obtain any additional information.

The main silicon-containing products were identified by IR spectroscopy in the region of characteristic absorption due to Si–F vibrations. Figure 3 shows the IR spectra of reaction products obtained by subtracting the spectrum of unreacted $C_2H_3SiF_3$ from the spectra of the reaction mixture before and after irradiation. The individual spectra of ethinyltrifluorosilane (C_2HSiF_3) and silicon tetrafluoride (SiF_4) are also shown. It can be seen that bands at 893.0 and 998.1 cm^{-1} in the spectrum of products belong to ethinyltrifluorosilane, whereas SiF_4 makes the main contribution to absorption at 1029.5 cm^{-1}. The consumption of vinyltrifluorosilane was 34%, which corresponds to a partial pressure of 22 Pa under constant volume conditions. The partial pressures of the resulting ethinyltrifluorosilane and SiF_4 were 2.8 and 11 Pa, respectively.

Reaction Mechanism

The composition and nature of the final products (SiF_4, C_2H_2, and C_2HSiF_3) suggest a complex reaction mechanism. Published data on the formation of dinitro derivatives are available [10]. It is likely that an analogy between vinyltrifluorosilane and unsaturated hydrocarbons is incomplete. The course of the reaction in our experiments is closest to data published by Chao and Jaffe [11], who proposed a reaction scheme for ethylene oxidation with nitrogen dioxide (Scheme 1). At the first step, the electrophilic addition of the NO_2 molecule occurs with double bond opening and the formation of a carboradical. It is believed that, in a gas phase, intermediate **1** had time to rearrange before a collision with the next NO_2 molecule. In this

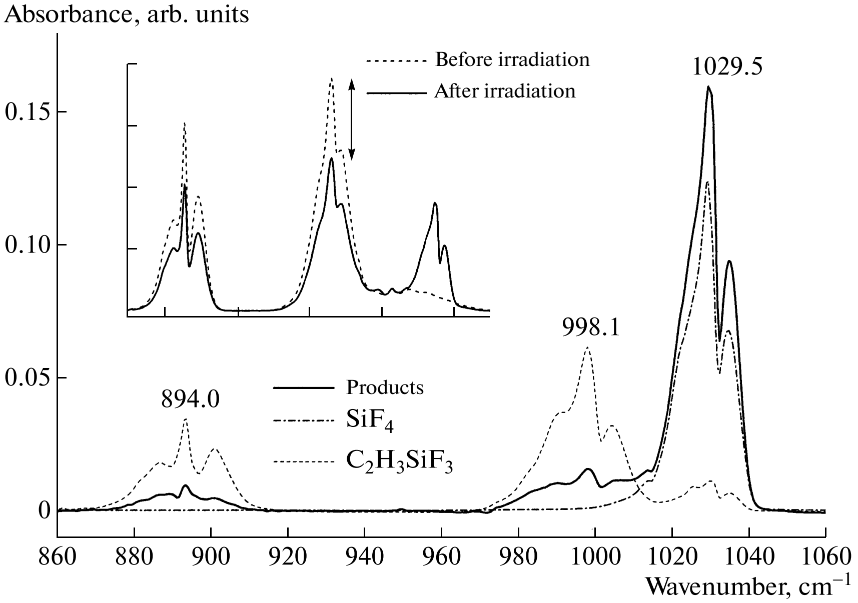
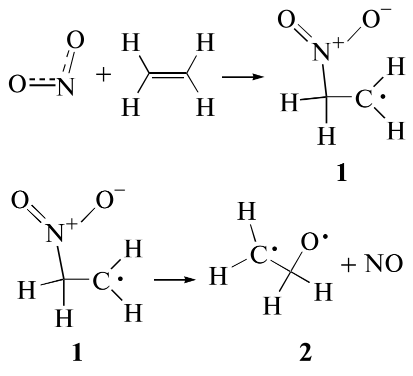


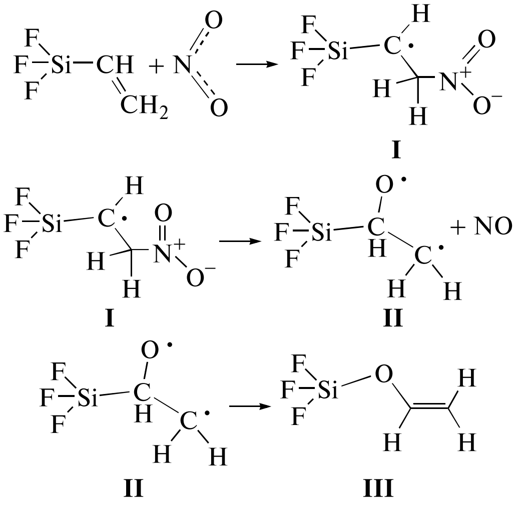
Fig. 3. Identification of reaction products based on IR spectra. Top: the spectra of the reaction mixture of $C_2H_3SiF_3$ (65 Pa) and NO_2 (285 Pa) before and after laser irradiation with an energy density of 0.51 J/cm^2. Bottom: the spectrum of products minus the contribution of unreacted $C_2H_3SiF_3$ and the spectra of C_2HSiF_3 and SiF_4.

case, a nitrogen monoxide molecule is eliminated and biradical **2** is formed. A further rearrangement of **2** can result in the formation of stable products—epoxide and acetaldehyde.

It is likely that the reaction occurs by a similar mechanism in the interaction of $C_2H_3SiF_3$ with NO_2 (Scheme 2). However, in this case, the trifluorosilyl group, which is responsible for the direction of addition, has a considerable effect. The quantum-chemical calculations of the total atomization energy of optimized configurations demonstrated that the formation of α-radical **I** rather than its β isomer is more favorable at the first step of addition. This effect is explained by $(\sigma^*\text{-p})_\pi$ conjugation between the antibonding orbital of the Si–C σ bond and the *p* orbital with an unpaired electron of the α-carbon atom [16]. Rearrangement with the elimination of an NO molecule should be similar to that in the case of ethylene; however, the subsequent rearrangement of biradical **II** occurs under the action of the SiF_3 group. The formation of vinyl trifluorosilyl ether **III** is a thermodynamically favorable direction [17]; the traces of this ether were detected in the mass spectra of reaction products. It is likely that the occurrence of the reaction along this path is hindered by kinetic barriers, and radical reactions developed with the participation of biradical **II** under conditions of an excess of NO_2 lead to the for-



Scheme 1. Mechanism of ethylene oxidation with nitrogen dioxide proposed by Chao and Jaffe [11].



Scheme 2. Mechanism of the reaction of vinyltrifluorosilane with nitrogen dioxide.

mation of final products, as described by Chao and Jaffe [11]. The appearance of ethinyltrifluorosilane can be explained by the elimination of a water molecule from intermediate **II**. The formation of SiF_4 can result from deeper oxidation that leads to trifluorosilyl radicals [11]. The $^{\bullet}SiF_3$ radicals tend to the disproportionation $^{\bullet}SiF_3 + {}^{\bullet}SiF_3 \longrightarrow SiF_4 + SiF_2$. The formation of N_2O, NO, CO_2, and H_2O supports this hypothesis.

The rate-limiting step of the overall process is the addition of NO_2 to the $C_2H_3SiF_3$ molecule to form radical **I** (Scheme 2). Figure 4 shows the calculated energy profile of this step. The reaction rate constant is $k = 3 \times 10^{-14}\exp(-48000/RT)$ cm^3/s, as calculated using the transition state theory.

At room temperature, $k \approx 10^{-22}$ cm^3/s; this corresponds to a characteristic reaction time of about a day under experimental conditions. Evidently, laser excitation considerably increases the rate of reaction. However, several mechanisms of this acceleration can occur.

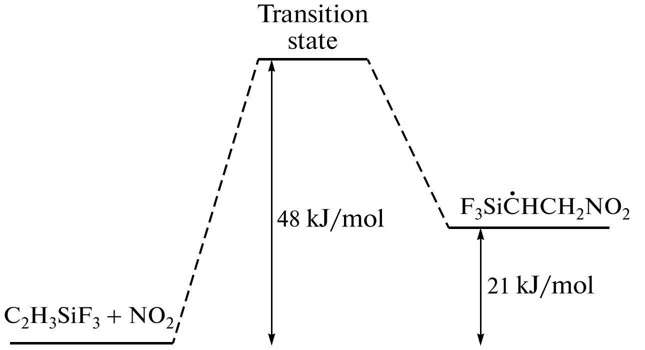


Fig. 4. Energy diagram for NO_2 addition to $C_2H_3SiF_3$.

KINETIC MODEL OF VIBRATIONAL ENERGY CONVERSIONS

Energy exchange processes are an integral part of nonequilibrium reactions. Under conditions of a highly disturbed Maxwell–Boltzmann distribution, a kinetic consideration cannot be performed without introducing relaxation equations [18]. Vibrational energy conversion processes are of the greatest interest. In the case of vibrationally excited polyatomic molecules, there is a velocity distribution of various processes [19]. The VV' exchange is most rapid; the rate of this exchange can be higher by several orders of magnitude than the rate of vibrational–translational VT relaxation (henceforth, we consider an intramolecular equilibration). The difference between the rates of VV' and VT relaxations allowed us to introduce vibrational temperatures, which characterize the energy content of individual sorts of molecules or even individual vibrational modes (if intramolecular relaxation is hindered).

To clarify the role of laser excitation in the acceleration of the test reaction, we used a simplified model of vibrational energy conversion after a laser pulse. The kinetic model does not pretend to quantitatively describe the occurring processes; the aim of the kinetic consideration is to predict the dependence of the rate of reaction on the ratio between reactant concentrations or on the total pressure of the mixture.

For the test two-component system, we introduced equations to describe the energy contents of the vibrational degrees of freedom of $C_2H_3SiF_3$ and NO_2 molecules. Table 2 summarizes the notation used in the model. The translational and rotational degrees of freedom of all molecules are considered as an individual reservoir:

$$\frac{d\varepsilon_A}{dt} = \sigma IA - k_1 B\varepsilon_A + \tilde{k}_1 A\varepsilon_B$$
$$- k_{VT}^{A}(A + B)\varepsilon_A + \tilde{k}_{VT}^{A} A\varepsilon_R - \frac{\varepsilon_A}{\tau};$$

$$\frac{d\varepsilon_B}{dt} = k_1 B\varepsilon_A - \tilde{k} A\varepsilon_B$$
$$- k_{VT}^{B}(A + B)\varepsilon_B + \tilde{k}_{VT}^{B} B\varepsilon_R - \frac{\varepsilon_B}{\tau};$$

$$\frac{d\varepsilon_R}{dt} = k_{VT}^{A}(A + B)\varepsilon_A + k_{VT}^{B}(A + B)\varepsilon_B$$
$$-\left(\tilde{k}_{VT}^{A} A + \tilde{k}_{VT}^{B} B\right)\varepsilon_R - \frac{\varepsilon_R}{\tau}.$$

The term σIA corresponds to the laser pumping of the system, and the last terms of the equations characterize energy dissipation due to heat transfer to reactor walls.

A change to equations for the temperatures T_A, T_B, and T_R considerably simplifies the form of a set of equations. For this purpose, we use the relationships $\varepsilon = c_A A T_A$, $\varepsilon_B = c_B B T_B$, and $\varepsilon_R = c_R(A + B)T_R$. In addition, we introduce the relationships $k_1 c_A = \tilde{k}_1 c_B$, $k_{VT}^{A} c_R = \tilde{k}_{VT}^{A} c_R$, and $k_{VT}^{B} c_A = \tilde{k}_{VT}^{B} c_R$, which follow from the equality of the rates of forward and reverse reactions in an equilibrium. We obtain the following set of equations:

$$\frac{dT_A}{dt} = \frac{\sigma I}{c_A} - k_1 B(T_A - T_B)$$
$$- k_{VT}^{A}(A + B)(T_A - T_R) - \frac{T_A}{\tau};$$

Table 2. Notation used in the kinetic model

ε_{A}	Bulk energy density in the vibrations of $C_2H_3SiF_3$ (the energy is measured in laser radiation photons)
c_{A}	Vibrational heat capacity of $C_2H_3SiF_3$ (measured in laser radiation photons per kelvin)
T_{A}	Vibrational temperature of $C_2H_3SiF_3$
ε_{B}	Bulk energy density in the vibrations of NO_2
c_{B}	Vibrational heat capacity of NO_2
T_{B}	Vibrational temperature of NO_2
ε_{R}	Bulk thermal energy density of translational and rotational motions of $C_2H_3SiF_3$ and NO_2 molecules
A, B	Bulk densities of $C_2H_3SiF_3$ and NO_2 particles, respectively
σ	Laser-radiation absorption cross section
I	Laser-radiation photon flux density
τ	Gas cooling time
k_1, $\tilde{k}_1$	Constants of forward and reverse VV transfer between $C_2H_3SiF_3$ and NO_2, respectively
$k_{\mathrm{VT}}^{\mathrm{A}}$, $\tilde{k}_{\mathrm{VT}}^{\mathrm{A}}$	Forward and reverse VT relaxation constants of $C_2H_3SiF_3$ molecules
$k_{\mathrm{VT}}^{\mathrm{B}}$, $\tilde{k}_{\mathrm{VT}}^{\mathrm{B}}$	Forward and reverse VT relaxation constants of NO_2 molecules

$$\frac{dT_{\mathrm{B}}}{dt} = \frac{c_{\mathrm{A}}}{c_{\mathrm{B}}} k_1 A(T_{\mathrm{A}} - T_{\mathrm{B}}) - k_{\mathrm{VT}}^{\mathrm{B}}(A + B)(T_{\mathrm{B}} - T_{\mathrm{R}}) - \frac{T_{\mathrm{B}}}{\tau};$$

$$\frac{dT_{\mathrm{R}}}{dt} = \frac{c_{\mathrm{A}}}{c_{\mathrm{R}}} k_{\mathrm{VT}}^{\mathrm{A}} A(T_{\mathrm{A}} - T_{\mathrm{R}}) + \frac{c_{\mathrm{B}}}{c_{\mathrm{R}}} k_{\mathrm{VT}}^{\mathrm{B}} B(T_{\mathrm{B}} - T_{\mathrm{R}}) - \frac{T_{\mathrm{R}}}{\tau}.$$

The temperatures T_{A}, T_{B}, and T_{R} are measured with reference to room temperature. We consider a laser pulse to be very short. This results in the starting conditions $T_{\mathrm{A}} = T_{\max} = \frac{E}{c_{\mathrm{A}} A}$ and $T_{\mathrm{B}} = T_{\mathrm{R}} = 0$, where E is the number of laser radiation photons absorbed in a unit volume. The solution can be found analytically taking the VT relaxation constants to be equal: $k_{\mathrm{VT}}^{\mathrm{A}} = k_{\mathrm{VT}}^{\mathrm{B}} = k_{\mathrm{VT}}$.

The solution has the form

$$T_{\mathrm{A}} = T_{\max}\left\{\frac{c_{\mathrm{B}}B}{c_{\mathrm{A}}A + c_{\mathrm{B}}B}\exp\left(\frac{t}{\tau_{\mathrm{VV'}}}\right) + \frac{c_{\mathrm{A}}A}{c_{\mathrm{A}}A + c_{\mathrm{B}}B}\frac{c_{\mathrm{R}}(A + B)}{c_{\mathrm{A}}A + c_{\mathrm{B}}B + c_{\mathrm{R}}(A + B)} \times\exp\left(-\frac{t}{\tau_{\mathrm{VT}}}\right) + \frac{c_{\mathrm{A}}A}{c_{\mathrm{A}}A + c_{\mathrm{B}}B + c_{\mathrm{R}}(A + B)}\right\}\exp\left(-\frac{t}{\tau}\right); \quad (1)$$

$$T_{\mathrm{B}} = T_{\max}\left\{\frac{c_{\mathrm{A}}A}{c_{\mathrm{A}}A + c_{\mathrm{B}}B}\exp\left(\frac{t}{\tau_{\mathrm{VV'}}}\right) + \frac{c_{\mathrm{A}}A}{c_{\mathrm{A}}A + c_{\mathrm{B}}B}\frac{c_{\mathrm{R}}(A + B)}{c_{\mathrm{A}}A + c_{\mathrm{B}}B + c_{\mathrm{R}}(A + B)}\exp\left(-\frac{t}{\tau_{\mathrm{VT}}}\right) + \frac{c_{\mathrm{A}}A}{c_{\mathrm{A}}A + c_{\mathrm{B}}B + c_{\mathrm{R}}(A + B)}\right\}\exp\left(-\frac{t}{\tau}\right); \quad (2)$$

$$T_{\mathrm{R}} = T_{\max}\left\{\frac{c_{\mathrm{A}}A}{c_{\mathrm{A}}A + c_{\mathrm{B}}B + c_{\mathrm{R}}(A + B)} \times\left[1 - \exp\left(-\frac{t}{\tau_{\mathrm{VT}}}\right)\right]\right\}\exp\left(-\frac{t}{\tau}\right). \quad (3)$$

The relaxation times are expressed in the following manner:

$$\frac{1}{\tau_{\mathrm{VV'}}} = k_1 B + k_1\frac{c_{\mathrm{A}}}{c_{\mathrm{B}}}A + k_{\mathrm{VT}}(A + B); \quad (4)$$

$$\frac{1}{\tau_{\mathrm{VT}}} = k_{\mathrm{VT}}\frac{c_{\mathrm{R}}(A + B) + c_{\mathrm{A}}A + c_{\mathrm{B}}B}{c_{\mathrm{R}}}. \quad (5)$$

Deriving the rate equations, we hypothesized that the vibrational heat capacity is constant. Figure 5 shows the dependences of the vibrational energies of $C_2H_3SiF_3$ and NO_2 on vibrational temperature, as calculated in a harmonic approximation. As can be seen, these dependences can be considered approximately linear over a wide range of temperatures. The slope of

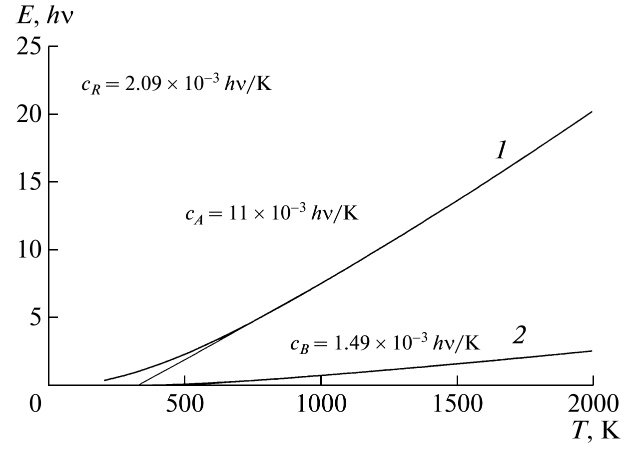


Fig. 5. Temperature dependence of the vibrational energies of (*1*) vinyltrifluorosilane and (*2*) nitrogen dioxide molecules. The numerical values of the heat capacities c_A, c_B, and c_R are specified.

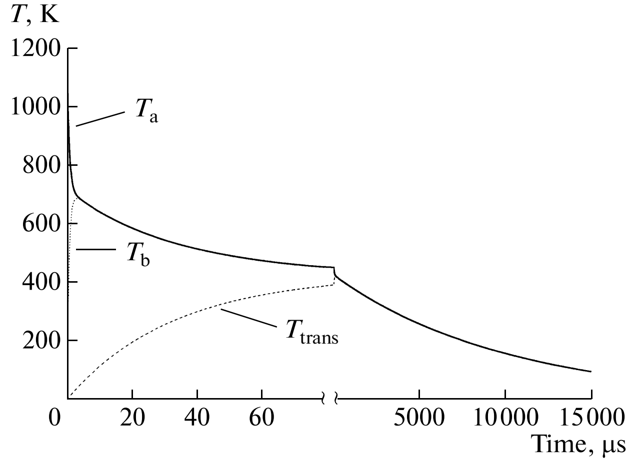


Fig. 6. Solution of the set of equations for vibrational temperatures. The calculated values of the parameters c_A, c_B, and c_R and typical values of the parameters A and B were used. The pressures of $C_2H_3SiF_3$ and NO_2 were 40 and 200 Pa, respectively. The pulse energy corresponds to the absorption of 10 hν per molecule of $C_2H_3SiF_3$.

the corresponding straight lies in Fig. 5 corresponds to the heat capacities c_A and c_B. Figure 5 also specifies the heat capacity c_R, which results with consideration for translational ($3/2k$) and rotational ($3/2k$) degrees of freedom, in the units of hν/K.

To illustrate the general pattern of relaxation processes, Fig. 6 shows the vibrational temperatures T_A and T_B and the translational–rotational reservoir temperature calculated from the above equations as functions of the elapsed time from the start of a laser pulse. Typical concentrations of $C_2H_3SiF_3$ and NO_2 were used. The laser beam energy corresponds to the absorption of ten photons per molecule of $C_2H_3SiF_3$. The rate constants of VV' exchange and VT relaxation were taken to be $k_1 = 1 \times 10^{-11}$ and $k_{VT} = 3 \times 10^{-13}$ cm^3/s, respectively.

Figure 6 clearly shows that there are three steps of vibrational relaxation. The shortest first step characterizes intermolecular VV' transfer, which occurs immediately after the excitation of vinyltrifluorosilane molecules. The VV' exchange comes into play during the action of a laser pulse and lasts for a few microseconds. At the second step, the vibrational temperatures of vinyltrifluorosilane and NO_2 are the same; however, the common vibrational temperature is strongly different from the translational temperature. At this step, slower VT relaxation occurs. The thermal energy of molecular motion increases. At the final step of the process, the system reaches a complete equilibrium and slowly cools to lose energy to the walls of a reaction cell. The characteristic time of cooling was a few milliseconds under conditions of our experiments.

In reactions initiated by laser radiation, it is of considerable importance at which step of vibrational relaxation chemical reaction occurs. The most interesting situation is that the reaction occurs at the first step, which is characterized by different vibrational temperatures of mixture components. In this case, the reaction can be selectively stimulated and vibrationally excited vinyltrifluorosilane molecules interact with cold NO_2 molecules even before the completion of energy transfer processes. If the reaction occurs in the course of the second or third step of relaxation, selective reactions cannot be performed.

Dependence of the Rate of Reaction on the Degree of Dilution

We determined the rate of reaction γ as the relative decrease in the concentration of vinyltrifluorosilane per pulse (Δ*n*):

$$\gamma = \frac{\Delta n}{A} = \int Bk(T_A, T_B)\,dt = \frac{Bk_{\text{eff}}}{f},$$

where $k(T_A, T_B)$ is the rate constant of a bimolecular reaction, which depends on vibrational temperatures; f is the laser pulse repetition frequency; and

$$k_{\text{eff}} = f\int k(T_A, T_B)\,dt. \tag{6}$$

Studying the dependence of the rate of reaction on the degree of dilution of the mixture, we can determine whether the reaction really occurs at the first step, which is characterized by different vibrational temperatures of mixture components. Indeed, for mixtures with an excess of NO_2, from Eqs. (1) and (4), we obtain

$$T_A = T_{\max}\exp\left(-\frac{t}{\tau_{VV'}}\right)\exp\left(-\frac{t}{\tau}\right) \text{ and } \frac{1}{\tau_{VV'}} \approx k_1(A + B).$$

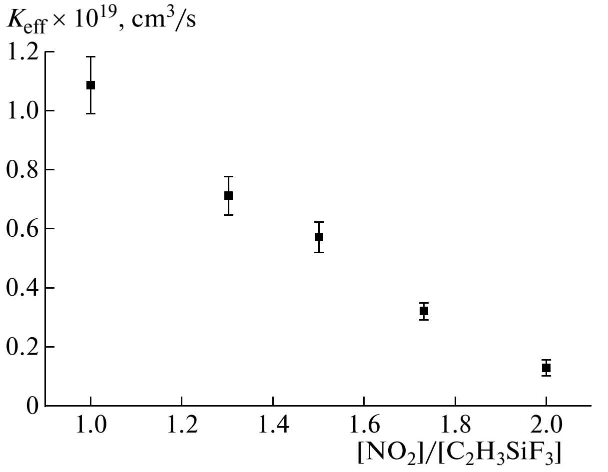


Fig. 7. Dependence of the effective rate constant on the ratio between reactants at a constant total pressure of 200 Pa. A laser with an energy of ~0.6 J/cm^2 was tuned to the R14 line.

The initial vibrational temperature of vinyltrifluorosilane molecules T_{max} depends on the absorption cross-section and energy flux density of laser radiation. The duration of the first step $\tau_{VV'}$ depends on only the constant of VV' transfer and the total concentration of particles in the irradiated volume. Thus, if the laser pulse energy and the total concentration of $C_2H_3SiF_3$ and NO_2 are kept constant, the time dependence of vibrational temperature T_A remains unchanged. Correspondingly, the effective rate constant found from Eq. (6) remains constant.

Dependence of the Rate of Reaction on the Total Pressure

The character of the dependence of the rate of reaction on total pressure will answer the question of whether the reaction occurs under conditions of strongly different vibrational and translational temperatures (second step in Fig. 6) or in full equilibrium (third step in Fig. 6).

If the mixture composition is maintained constant and the total pressure P is increased, the VT relaxation time decreases: $\tau_{VT} \sim 1/P$ (Eq. (5)). The cooling time of a gas mixture also depends on pressure; however, the character of this dependence is essentially different. Thermal relaxation is a diffusion process; therefore, an increase in the pressure results in an increase in τ. The characteristic time of gas cooling in a cylindrical vessel of radius R is described by the equation $\frac{1}{\tau} = \frac{5.78\kappa}{R^2}$, where κ is the thermal diffusivity [20]. At a constant mixture composition, the thermal diffusivity is inversely proportional to pressure; therefore, the cooling time is $\tau \sim P$.

The initial temperature T_{max} of vinyltrifluorosilane depends on the absorption cross-section and energy flux density of laser radiation. Thus, at a constant laser energy and a change in the total pressure of the mixture, the solution of a set of equations for vibrational temperatures (Eqs. (1)–(3); Fig. 6) changes only as a consequence of changes in the duration of individual steps. A decrease in the concentration of vinyltrifluorosilane per pulse depends on total pressure as

$$\Delta n = kAB\tau_{VT} \propto P^2P^{-1} = P,$$

if the reaction occurs under conditions of a strong difference between vibrational and translational temperatures, and

$$\Delta n = kAB\tau_{VT} \propto P^2P^{1} = P^3,$$

if the reaction occurs under conditions of equilibrium heating.

Hence, it follows that a simple criterion allows us to distinguish the roles of these steps in the test reaction: if a chemical transformation occurs under conditions of a strong difference of the vibrational temperature from the translational one, the rate of a bimolecular reaction is a linear function of pressure, $W \sim P$. If the reaction occurs under full equilibrium conditions, the cubic relation is obeyed: $W \sim P^3$.

Note that the criterion proposed for the determination of the roles of various vibrational relaxation steps is based on only the general concepts of relationships between the rates of V–V' and V–T processes, and particular values of vibrational relaxation rates are not used in it.

EXPERIMENTAL DEPENDENCE OF THE RATE OF REACTION ON THE DEGREE OF DILUTION AND TOTAL PRESSURE

The proposed criterion was applied to the test system. The energy density in a pulse and the laser generation frequency were kept constant; the reaction mixtures contained an excess of nitrogen dioxide. To calculate the effective relaxation time, the concentration of vinyltrifluorosilane as a function of the number of pulses was measured by mass spectrometry. The initial portion of kinetic curves was approximated by a first-order equation with respect to $C_2H_3SiF_3$:

$$A(n) = A_0\exp(-\gamma n).$$

The effective rate constant was determined as

$$k_{eff} = \gamma/B.$$

The observed second-order rate constant decreased as the degree of dilution was increased (Fig. 7). Therefore, the reaction occurs under conditions when the vibrational temperatures of both of the components in the system were equalized. Under these conditions, an increase in the degree of dilution caused a decrease in the energy stored in the vibrational reservoir and a decrease in the vibrational temperatures T_A and T_B.

To evaluate the orders of magnitude of T_A, T_B, and T_{trans}, we measured the amount of absorbed energy. Under standard experimental conditions, absorption weakly depended on reactant concentrations, and it was about 20 photons of CO_2 laser radiation per vinyltrifluorosilane molecule at an energy flux density of 0.56 J/cm^2. Thus, the real temperature was somewhat higher than that shown in Fig. 6.

We measured the dependence of the rate of reaction on the total pressure of reactants under conditions of a twofold excess of NO_2. The rate considerably increased as the concentrations of reactants were increased. The found numerical values of pseudo-first-order rate constants allowed us to calculate the absolute initial rate and to determine the overall order of reaction (Fig. 8), which was 2.7. This value is very close to that expected on equilibrium heating.

Thus, the above kinetic analysis suggests that the chemical reaction occurs with the participation of excited molecules of both of the reactants. In this case, the system occurs at the third step of vibrational energy relaxation, that is, under conditions of a full thermal equilibrium. It is likely that the acceleration of reaction was due to the overcoming of an activation barrier and it can be described by an Arrhenius equation.

Thus, in this work, we studied the gas-phase reaction of vinyltrifluorosilane and nitrogen dioxide that occurs under the action of IR laser radiation. We analyzed the reaction products and proposed a mechanism of their formation. It is believed that the addition of an NO_2 molecule at the double bond of vinyltrifluorosilane is a rate-limiting step and laser excitation changes the rate of this process.

We developed a theoretical model for the conversion of vibrational energy in terms of internal temperatures; this model allowed us to relate characteristic relaxation times to the molecular properties of reactants. An analysis of kinetic curves allowed us to reveal three steps of vibrational relaxation: the step of the vibrational excitation of absorbing substance molecules, the step where the vibrational temperature of reactants is strongly different from the translational temperature, and the step of the equilibrium heating of the system. We proposed a kinetic analysis procedure for the detection of a step at which a chemical reaction occurs. We found that, in the test case, the acceleration of reaction was due to the equilibrium heating of the system.

We hope that the developed approach will be helpful in the subsequent studies of laser-stimulated bimolecular reactions. It is very attractive to find and examine a system in which the rate constant specifically depends on vibrational temperature.

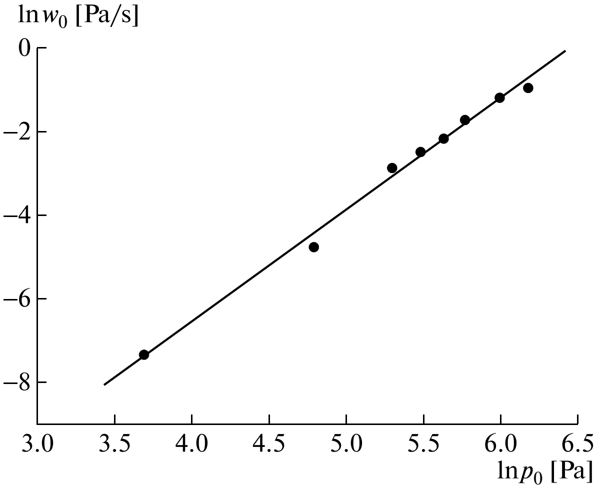


Fig. 8. Determination of the overall order of reaction from the dependence of the logarithm of the initial reaction rate w_0 on the logarithm of the total pressure P_0 of the reaction mixture at the reactant concentration ratio $[NO_2]/[C_2H_3SiF_3] = 2 : 1$.

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