Fast Reactions of Atom Substitution from Polyatomic Molecules and Solid Salts by Thermally Equilibrated Atomic Reactants

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Abstract—A new class of fast thermal gas-phase reactions of the direct substitution of atoms in polyatomic molecules by atomic reactants is discovered. The Arrhenius parameters are determined for the reactions of atomic deuterium with a number of hydrogen-containing compounds, occurring via the direct substitution of hydrogen atoms and via the abstraction of hydrogen atoms. Fast substitution of alkali metal atoms from the crystals of their salts for the reaction chain carriers of hydrogen flames is found. The importance of reactions of these types in chain combustion is demonstrated. The kinetic isotope effects of hydrogen atom abstraction from hydrocarbon molecules by hydrogen and deuterium atoms are studied. A method for the kinetic studies of free atoms and radicals is developed, which takes into account the role of longitudinal diffusion in the jet and does not require the knowledge of the concentrations of atoms and radicals or the rate constants of other reactions.

INTRODUCTION

Any homolytic gas-phase reaction of thermally equilibrated free atoms with valence-saturated molecules were associated until recently with one of the following processes:

(a) The abstraction of an atom from a molecule and its addition to the attacking atom:

$$Y + R_iX = YX + R_i^{\cdot}; \qquad (I)$$
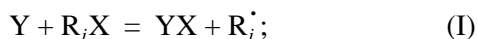
(b) The abstraction of a radical with the formation of another radical and a new molecule:

$$Y + R_1R_2 = R_1Y + R_2^{\cdot}; \qquad (II)$$
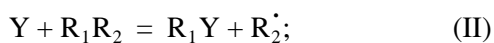
(c) The addition to a multiple bond:

$$Y + R_3X(+M) = R_3XY^{\cdot}(+M). \qquad (III)$$

In these reactions, Y and X are atoms; $R_i^{\cdot}$, $R_2^{\cdot}$, and $R_3XY^{\cdot}$ are polyatomic radicals; R_iX and R_1R_2 are valence-saturated molecules; R_3X is a molecule with a multiple bond (C=C); and M is a third species or a solid surface which accepts excess energy of a molecule formed in reaction (III) (see, for instance, [1–11]).

Only these types of reactions are considered in the studies of elementary reactions and mechanisms of complex processes by the method of isotopes, in the study of kinetic isotope effect, and by other methods [2–11].

This work reports the results of kinetic studies of fast homolytic gas-phase reactions of the direct substi-

tution of atoms in polyatomic molecules, which were discovered by us:

$$Y + RX = RY + X. \qquad (A)$$

The possibility of reactions of this type in atomic–molecular processes was not taken into account earlier because it was generally assumed that these reactions virtually do not occur, unlike liquid-phase nucleophilic substitution reactions. For instance, monographs [1, 2, 5] point out that the activation energies of reactions (A) for hydrocarbons with the participation of hydrogen and deuterium atoms are higher than 145 kJ/mol, which is more than 100 kJ/mol higher than the activation energies of reactions (I) [11]. This high activation energy means that, at temperatures below 700 K, the substitution of an atom in a molecule is more than seven orders of magnitude slower than the reaction of atom abstraction (I) and five to six orders of magnitude slower than reactions (II). Obviously, in this case, reactions (A) cannot occur because initial reactants are consumed by other reactions, including (I) and (II). The value of the activation energy mentioned in [1, 5] was later used by several other authors for interpreting their experimental data (see below).

Obviously, the reactions of direct substitution of atoms considered here differ substantially from stepwise substitution both in the dynamics of an elementary act and in kinetics. Early studies neglected this fact. For instance, Ogg and Polanyi [12] proceeded from the studies of racemization of optically active 2-iodobutane in the gas-phase reaction with atomic iodine and draw the conclusion that the substitution reaction occurs with

the Walden inversion of configuration, that is, in one step:

$$I + d\text{-}sec\text{-}C_4H_9I = l\text{-}sec\text{-}C_4H_9I + I.$$
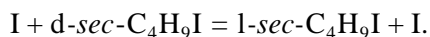
However, the possibility of a stepwise reaction was not excluded; that is, the preliminary abstraction of an iodine atom from the molecule and further reaction of the radical with I_2 or recombination with an iodine atom via the following sequence of reactions:

$$I + d\text{-}sec\text{-}C_4H_9I$$

$$\longrightarrow\ sec\text{-}C_4H_9^{\cdot} + I_2 \longrightarrow I + l\text{-}sec\text{-}C_4H_9I.$$
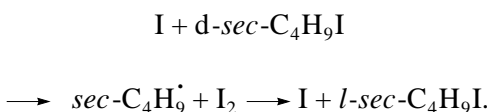
These reactions also lead to racemization. Data on the inhibition of the exchange process by oxygen support the stepwise mechanism [13]. The authors of that work reasonably explain this by the fact that racemization occurs with the participation of butyl radicals, which are consumed in the competing reaction in the presence of oxygen and form butylperoxy radicals.

In monograph [4] devoted to the kinetics of various atomic–molecular reactions, the possibility of reactions (A) is completely ignored. At the same time, the monograph provides an estimate of the activation energy for reactions (II) with the cleavage of the C–C bond (58–60 kJ/mol). The monograph points out that hydrogen atom abstraction from a hydrocarbon molecule is a faster reaction than radical abstraction no matter what the attacking species is, a free atom or a free radical.

The possibility of gas-phase reactions of type (A) was considered in some very early papers on the reactions of deuterium atoms [14–17]. It was pointed out that the amounts of deuterated products formed in these experiments are large. Farkas and Melville [15] studied the formation of molecular products of the reaction between free deuterium atoms, obtained by the dissociation of D_2 photosensitized by mercury, in the mixtures of NH_3, CH_4, and water vapor. The formation of deuterated ammonium and methane observed above a certain temperature was explained by the substitution of hydrogen atoms in the initial molecules. The authors motivated this by the fact that the quantum yield was higher than unity at $T > 500$ K. However, they noted that the quantum yield was only slightly higher than unity, and one cannot be sure that the formation of a deuterated water molecule is due to the direct substitution reaction rather than to the reaction between an excited mercury atom and H_2O and further steps. Steacie [3] pointed to the fact that the values of quantum yields were overestimated in [15] and cannot provide evidence for the substitution reaction. Note also the following circumstances. Indeed, the reaction of hydrogen atom abstraction from a molecule, as well as the recombination of the radical formed with deuterium atoms, cannot themselves lead to quantum yields higher than unity. When

a substitution reaction, e.g.,

$$D + NH_3 = NH_2D + H$$
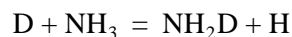
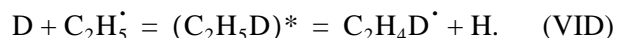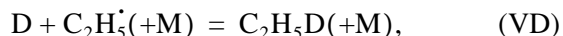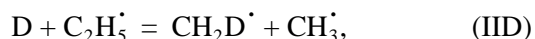and a reaction between H and D_2

$$H + D_2 = HD + D$$
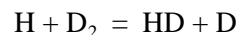
alternate, the number of deuterated ammonium molecules per one absorbed quantum can be higher than unity. However, the fact that the quantum yield is higher than unity does not prove that the substitution reaction occurs. Indeed, in the above reactions, this may also happen when the mechanism does not involve the substitution step at all and when the following reactions alternate:

$$D + NH_3 = DH + NH_2^{\cdot}, \quad NH_2^{\cdot} + D_2 = NH_2D + D.$$
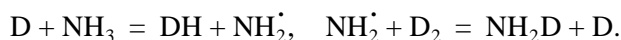
The rate constant of the first reaction here is lower than the rate constant of the reverse reaction [18], and the latter is equal to the rate constant of the second reaction with an error equal to the kinetic isotope effect. Therefore, the $NH_2^{\cdot}$ radicals formed in the first reaction also rapidly react with D_2 and form atomic deuterium. In this chain mechanism, the quantum yield is equal to the chain length and is higher than unity. An analogous mechanism accounts for the data reported in [15] on methane deuteration. Thus, even if the reported quantum yields [15] were higher than unity, they could not prove the substitution reaction.

Reactions (A), including those with water vapors, were initially tolerated in [16, 17]. However, in further papers ([19, 20]) one of the authors (Steacie) interpreted the results without taking into account this reaction, and he asserts in his monograph [3] that the substitution reactions are unreal.
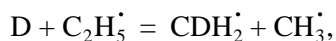
The authors of [14, 19, 20], who studied the reactions of atomic deuterium with alkanes, explained the formation of deuterated hydrocarbons by sole hydrogen abstraction followed by atomic cracking and recombination (the mechanism of stepwise substitution). For instance, the reaction with ethane is described as follows:

$$D + C_2H_6 = DH + C_2H_5^{\cdot}, \qquad \text{(ID)}$$

$$D + C_2H_5^{\cdot} = CH_2D^{\cdot} + CH_3^{\cdot}, \qquad \text{(IID)}$$

$$D + CH_3^{\cdot}(+M) = CH_3D(+M), \qquad \text{(IIID)}$$

$$D + CH_2D^{\cdot}(+M) = CH_2D_2(+M), \qquad \text{(IVD)}$$

$$D + C_2H_5^{\cdot}(+M) = C_2H_5D(+M), \qquad \text{(VD)}$$

$$D + C_2H_5^{\cdot} = (C_2H_5D)^* = C_2H_4D^{\cdot} + H. \quad \text{(VID)}$$

Thus, the formation of a hydrogen atom in the above scheme (reaction (VID)) is only the result of the decomposition of a quasimolecule, which was formed

by the recombination and had no time for stabilization by collision with a third species or a solid surface. Although a partially deuterated ethyl radical and a deuterated product are formed in this reaction scheme along with a hydrogen atom, the substitution reaction is not taken into account.

In connection with the above, note that handbook [21] provides the activation energies and the rate constants that were mistakenly assigned to the hydrogen substitution reactions in hydrocarbon molecules on behalf of the authors of [14, 19, 20, 22], whereas it was noted in the cited papers that these activation energies and the rate constants are calculated from the overall rate of the formation of all deuterated products via all reactions considered there, and reaction (A) was not among them. Accordingly, the authors of the cited papers stressed that they assign these kinetic parameters to the overall process rather than to separate reactions. For instance, the authors of [14, 22] took into account only the following parallel reactions of deuterated ethane formation, which are radical recombination and disproportionation:

$$D + C_2H_5^{\cdot}(+M) \ = \ C_2H_5D(+M),$$

$$D + C_2H_5^{\cdot} \ = \ CDH_2^{\cdot} + CH_3^{\cdot},$$

$$CDH_2^{\cdot} + CH_3^{\cdot} \ = \ C_2H_5D.$$
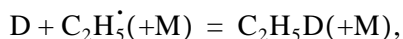
Moreover, the authors of [3, 19, 20] specially noted that reactions of type (A) do not occur.

The possibility of the direct substitution of atoms from organic compounds by thermally equilibrated atomic reagents was negated in [23–25]. These papers were devoted to the studies of reactions of atomic tritium that have an increased kinetic energy (>2.7 eV). To obtain these "hot" atoms, a mixture of TBr, CH_4, and Br_2 was irradiated with UV. The ratio of the rates of hydrogen atom abstraction from the hydrocarbon molecule and the substitution of these atoms was judged from the value of the ratio of concentrations of two final products (HT and CH_3T) determined by chromatography. Based on these data and referring to monographs [1, 3], the authors of [23–25] claimed that the substitution of hydrogen atoms is much slower than their abstraction. The reaction rate constants were not determined. Obviously, the ratio of the rates of substitution and abstraction with the participation of hot atoms does not provide evidence for the value of this ratio in the case of thermally equilibrated atoms. Besides that, the authors of [23–25] overestimated the amount of HT assigned to hydrogen abstraction, because they did not take into account that these molecules are also formed in the reaction between hydrogen atoms substituted from a hydrocarbon molecule and TBr, which is the initial reactant. HT formation by the reaction of H with T_2 following the step

$$T + TBr \ = \ T_2 + Br$$
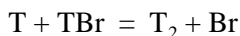
was not taken into account either. Moreover, judging from the text of the cited article, T_2 formation in the above reaction was also neglected. Thus, the overall amount of molecules containing tritium (HT and T_2) was only assigned to HT, and this was an additional factor in overestimating the fraction of the abstraction reaction.

Menzinger and Wolfgang [26] assumed that the substitution of a hydrogen atom in a hydrocarbon molecule is only observed if the energy of atomic tritium obtained by the β-decay of T_2 is higher than 1 eV. However, this conclusion can be a result of the very short residence time of the reaction mixture in the reaction zone. This residence time was not specified and it cannot be estimated from other data reported in [26].

The authors of [27–29] obtained hot deuterium atoms via tritium β-decay and found that the reaction of deuterium and methane forms deuterated hydrocarbons. They explain their finding by the abstraction of a hydrogen atom and further recombination of the methyl radical and atomic deuterium rather than by hydrogen atom substitution. The authors of [27] found in a similar experiment that other deuterated methanes are formed in addition to monodeuterated methane. They suggested that ionizing radiation might lead to the formation of deuterated methanes via the formation of CH_4^+ and CH_5^+. They also assumed that the addition of ammonium removed complexities associated with the ionization under the action of β-rays. Deuterated methanes found in the absence of ionization are explained by the abstraction of a hydrogen atom and further recombination of deuterium atoms and a hydrocarbon radical. The substitution reaction was not considered.

In most studies where tritium was used, the authors paid attention to the fact that data are hard to interpret because of the presence of charged species. Martin and Willard [30] noted that it is almost impossible to distinguish between the substitution and abstraction reactions when hot atoms are used. When authors claim that the substitution of an atom from a molecule is impossible, most of them make references to [1, 3, 5], where the occurrence of reactions (A) with a noticeable rate is negated.

Shatz et al. [31] reported a very high activation energy for reaction (A) when they consider the interaction of atomic deuterium with H_2O molecules in the gas phase and neglect substitution. Ingold and Roberts [32] also assumed that the substitution of a hydrogen atom from CH_4 is very slow and proposed to search for reactions of this type in more exothermic processes than those considered earlier. Monographs devoted to the theory of elementary reactions and chemical kinetics, including those that consider transition state theory [7, 9, 33–35], did not consider the possibility of reactions (A). Only Kondrat'ev and Nikitin [35] provide a reference to [16, 17], although the authors of these

papers started to deny the possibility of reactions (A) soon after these papers had been published.

Thus, all researchers, including those who did not exclude substitution reactions in their early papers, have accepted that reactions (A) are very slow and interpreted their results of studying H, D, and T reactions with polyatomic molecules without taking into account these steps.

Despite current understanding, we directly detected and studied fast thermal reactions (A) of the direct substitution of atoms from polyatomic molecules in their interactions with thermally equilibrated atomic reactants using the ESR method [36–40]. We found that these reactions are even faster than most reactions of atom or radical abstraction from molecules (reactions (I) and (II)). ESR spectroscopy used in these studies enabled the selective registration of free hydrogen and deuterium atoms and the determination of their concentrations.

The data from [36–40] are discussed below together with new results obtained in this study on the homogeneous and heterogeneous reactions of hydrogen and deuterium atoms that are the direct substitution of atoms in a molecule and the substitution of metal atoms from solid salts. The results of the primary kinetic isotope effect in the reactions of abstraction by hydrogen and deuterium atoms from closed-shell molecules are also presented.

THE ROLE OF LONGITUDINAL DIFFUSION IN KINETIC STUDIES OF FREE ATOMS AND RADICALS IN A JET

In addition to elucidating the possibility of the reactions of direct substitution of atoms from polyatomic molecules, the goal of our studies was to determine the kinetic parameters of these processes and compare them with the corresponding parameters of abstraction reactions. Reactions were carried out in jet conditions. Jet methods in kinetic studies offer substantial advantages, but they are associated with complications due to the effect of longitudinal diffusion of reactants on the profiles of their concentrations. This effect is considerable in fast reactions, in which case the concentration gradients along the jet are high. As a result, a change in the concentration of reacting species due to their diffusion becomes comparable with a change due to an intrinsic chemical reaction. When the effect of diffusion on the concentration profile of the reaction system is taken into account correctly using previously known methods, equations for the calculation are very complex and require the knowledge of kinetic and diffusion parameters, while ignoring longitudinal diffusion is correct for limited ranges of low temperatures, low concentrations, and low flow rates. Below, we describe a method, which we have developed, that makes it possible to reduce constraints and complications.

It is known that, in a stationary one-dimensional jet, the concentration of a substance consumed by a first-order reaction is determined by the equation

$$\frac{d}{dx}\left(D\frac{dn}{dx}\right) - v\frac{dn}{dx} - kn = 0, \qquad (1)$$

where x is the coordinate along the jet, D is the diffusion coefficient of a reactant, n is the concentration, k is the reaction rate constant, v is the linear rate of a jet (see, for instance, [41]). If the diffusion coefficient is independent of x (for instance, the mixture composition and the pressure along the jet change insignificantly), then this equation can be described in the following form:

$$D\frac{d^2n}{dx^2} - v\frac{dn}{dx} - kn = 0. \qquad (2)$$

The general solution to this equation is

$$n = C_1\exp(\beta_1 x) + C_2\exp(\beta_2 x), \qquad (3)$$

where β_1 and β_2 are the solutions to the characteristic equation corresponding to differential equation (2); C_1 and C_2 are constants. Taking into account the boundary conditions $n_{t \to \infty} = 0$ and $n_{x = 0} = n_{t = 0}$, where t is time, we obtain

$$n = n_{t = 0}\exp(\beta_1 x). \qquad (4)$$

The value β_1 is determined by the equation

$$\beta_1 = (k/v)(kD/v^2 - 1). \qquad (5)$$

Because $v = x/t$, Eq. (5) can be presented in the following form:

$$\beta_1 x = kt(kD/v^2 - 1). \qquad (6)$$

It can be seen from Eqs. (4) and (6) that $n = n_{t=0}\exp(-kt)$ only if

$$kD/v^2 \ll 1; \qquad (7)$$

that is, the longitudinal diffusion can be neglected when one considers reaction kinetics only if inequality (7) is fulfilled. The higher the rate constant in inequality (7), the higher should be the jet rate to meet this condition. When studying fast reactions, this requirement complicates the experiment and necessitates taking into account the pressure along the flow and rate gradients across the jet.

When the above expressions are used for taking into account longitudinal diffusion by traditional methods, it is necessary to know the diffusion coefficient and the rate constants of reactions that enter the expression for calculation, including Eq. (5). In the quantitative kinetic studies of a reaction, the rate constant is an unknown value. The motivated neglect of longitudinal diffusion in the traditional approach requires checking inequality (7) and, therefore, assumes the knowledge of the rate constant, which is sought, and the value of D. We developed a method of kinetic studies that allows one to take into account longitudinal diffusion over a

wide range of temperatures and concentrations not requiring the knowledge of any rate constants and diffusion coefficients. Along with the determination of rate constants, the method allows the independent determination of the role of longitudinal diffusion and the diffusion coefficients of atoms and radicals. Below, we describe this method together with the procedure of measurements.

EXPERIMENTAL

Experiments were performed in jet vacuum systems combined with EPR-2M or EPR E-104A (Varian) spectrometers (depending on the reaction series). Hydrogen and deuterium atoms were obtained with radio-frequency and microwave discharges (13.6 MHz and 2.4 GHz) in jets H_2 and D_2, respectively, with helium. An atomic reactant, strongly diluted with the inert gas, passed from discharge section *1* of a quartz tube (Fig. 1) through nozzle *2* into a reactor. Side nozzle *2'* was necessary for the admission of a molecular reactant or the inert gas into the reaction zone. After the reaction zone, the mixture passed through a cavity of spectrometer (*5*). An electric furnace with bifilar winding (*3*) provided the uniform distribution of temperature in the reaction zone. The rates of gaseous flows were controlled by valves and measured using flowmeters with an accuracy of ±2%; the jet was laminar. The pressure was measured with the same accuracy at the beginning and at the end of the reaction zone.

The experimental procedure was as follows. A molecular reactant diluted with an inert gas was added in excess over an atomic reactant through a side nozzle to the jet of atomic reactant, which entered from the discharge zone. When the jet left the reaction zone, the relative concentration of atomic component was measured. Then, at the constant parameters of the jet, the molecular reactant was replaced by the same amount of inert gas, and the concentration of atomic reactant was measured again. Because the molecular reactant (hydrocarbon, RH) was taken in excess over the atomic reactant, we were able to take into account only the consumption of atomic reactant. Then, the value of k in Eqs. (1)–(5) is

$$k = k_{het} + bk_{RH}[RH], \qquad (8)$$

where k_{het} and k_{RH} are the rate constants of the heterogeneous decay of atoms and their reaction with the molecular reactant, respectively, and b is the number of atoms consumed by the reaction of one RH molecule (that is, the stoichiometric coefficient). The value of b was determined by mass spectrometric analysis of reaction products. According to Eqs. (4) and (5), a decrease in n in the presence of the molecular reactant corresponds to the equation

$$\ln \frac{n_{t=0}^{RH}}{n^{RH}} = kt \left(1 - \frac{kD^{RH}}{v^2} \right) + B. \qquad (9)$$
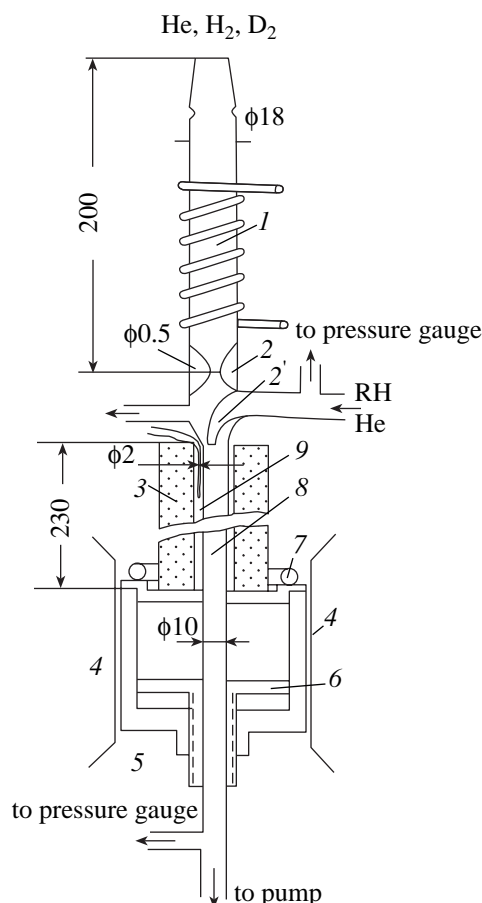
Fig. 1. Reactor with a discharge section: (*1*) discharge section; (*2, 2'*) nozzle; (*3*) electric furnace; (*4*) magnet poles; (*5*) spectrometer cavity; (*6*) mobile bottom cover of a cavity; (*7*) tube for water cooling; (*8*) reactor; and (*9*) thermocouple. Dimensions are given in millimeters.

The value of B takes into account the consumption of atomic reactant after the jet left from the constant-temperature zone and before it reached the registration point (that is, the center of the spectrometer cavity). This area is an order of magnitude shorter than the constant-temperature reaction zone. Moreover, because of a decrease in temperature in this area, the reaction drastically slows down due to a decrease in the rate constant. Therefore, the consumption of atoms after the jet left the constant-temperature zone can be neglected without loss of accuracy; that is, B is much smaller than the first term on the right-hand side of Eq. (9) in agreement with the results of measurements (see below).

When the molecular reactant is replaced by an equal amount of the inert gas, the consumption of the atomic reactant is due to recombination, and a decrease in n is determined by the expression

$$\ln \frac{n_{t=0}^0}{n^0} = k_{het}t \left(1 - \frac{k_{het}D^0}{v^2} \right) + B^0, \qquad (9a)$$

where (similarly to B) B^0 takes into account the consumption of atomic reactant after the jet left from the constant-temperature zone in the absence of the molecular reactant.

The superscripts RH and 0 correspond to the cases when the molecular reactant or the inert gas, respectively, is added to the jet leaving the discharge zone. Since the molecular and atomic reactants are strongly diluted with the same inert gas, the values of D^0 and D^{RH} are very close. Taking into account Eq. (8), the difference of Eqs. (9) and (9a) can be presented in the following form, which is convenient for the processing of experimental data:

$$\frac{1}{[RH]_t} \ln \frac{n^0}{n^{RH}} = bk_{RH} - \frac{D^{RH}}{v^2}$$

$$\times \left(k_{RH}^2 b^2 [RH] + 2k_{RH} bk_{het} - \frac{k_{het}^2}{[RH]} \frac{D^0 - D^{RH}}{D^{RH}} \right). \quad (10)$$

Here, n^0 and n^{RH} are the concentrations of atomic reactant when it leaves the reaction zone in the experiments with the inert gas and molecular reactant, respectively, added through a side nozzle. The left-hand side of this equation contains only measurable values. The rate of the jet is also directly measurable. It is seen from this equation that, when the molecular reactant concentration and the gas pressure are kept constant and the jet rate is varied, one can determine the bk_{RH} value for each chosen temperature. This value is equal to the free term in the linear dependence of the left-hand side on $1/v^2$. Thus, to determine the rate constant of the reaction between atoms and the molecular reactant, there is no need to know any values other than those measured in this experiment. Note also that the atomic reactant concentration enters the calculation formula in the form of the ratio n^0/n^{RH}; that is, the absolute values of concentrations of these active species need not be known.

By treating the reactor surface by, for instance, hydrofluoric acid, conditions can be achieved when the rate of the heterogeneous consumption of the atomic reactant is much lower than the rate of its consumption in the reaction with the molecular reactant. Therefore, Eq. (10) can be simplified as follows:

$$\frac{1}{[RH]_t} \ln \frac{n^0}{n^{RH}} = bk_{RH} - \frac{b^2 k_{RH}^2}{RT} D_0^{RH} 760 \frac{f}{v^2}, \quad (11)$$

where f is the molar fraction of RH molecules, R is the gas constant, T is the temperature, and the subscript at D_0^{RH} indicates that this value refers to $P = 760$ torr [37, 39].

Thus, by carrying out experiments under the conditions when the heterogeneous consumption of atoms is much slower than their homogeneous consumption, one may use the linear dependence of the left-hand side of Eq. (11) on $1/v^2$ to determine a value of bk^{RH} equal

to the free term. In this case, it is not necessary to keep the initial concentrations constant when varying the rate of a flow. The ratio of the slope and the free term can be used to determine the diffusion coefficient. At the same time, the slope of the line in the coordinates of Eq. (11) is an indicator of the role of longitudinal diffusion in changes of the concentrations of atomic reactant in the flow. When the inequality (7) is fulfilled (the role of longitudinal diffusion is insignificant), the straight lines are horizontal. Under these conditions, Eqs. (10) and (11) are simplified and take the following form:

$$\ln \frac{n^0}{n^{RH}} = bk_{RH}[RH]t + B - B^0. \quad (12)$$

Because the above equations for calculation involve the concentrations of the atomic reactant only in the form of a ratio, not only the accuracy of the method is high, but also any method for the registration of an atomic reactant can be used if the sensor signal intensity is proportional to the concentration. Since the primary goal of this study was to check the possibility of the direct substitution of atoms from polyatomic molecules and to determine the parameters of these reactions, we chose the ESR method, which is highly selective to gas-phase paramagnetic species, including hydrogen and deuterium. An important advantage of this method is also that the reaction mixture need not be taken out of the reaction zone to, for instance, an ionization chamber to determine the concentrations of atomic reactants. Neither is it necessary to introduce any accessory or affect the reaction in some other way.

Note that the procedure of alternating the supply of the molecular reactant and an inert gas through the side nozzle was described in [42], where the rate constant of the reaction $O + H_2 = OH^{\bullet} + H$ was determined. The concentration of atomic oxygen was determined in [42] using special reaction of chemical titration by nitrogen oxide, which is accompanied by chemiluminescence. However, Clyne and Trush [42] restricted themselves to using Eq. (12), which does not take into account longitudinal diffusion. Besides that, the reaction time was varied by changing the length of a reaction zone. Because the properties of the reactor surface that determine the efficiency of heterogeneous decay of atoms and radicals depend on the concentration of species in the gas phase (see, for instance, [43–45]), which changes along the jet, variations in the reaction zone length lead to some uncertainties in the results of rate constant determination. The consideration of this fact is very important if the heterogeneous reactions of atoms occur at a high rate. Therefore, we varied the reaction time by changing the rate of a jet at a constant length of the reaction zone. A very slight change of it due to temperature variations from one series of measurements to another was specially taken into account.

The temperature was measured using a chromel–alumel thermocouple placed between the reactor and a

furnace (Fig. 1). Electrolytic hydrogen and deuterium were used. To remove olefin traces in the hydrocarbons, the latter passed through a trap with bromine water. For further purification, gas passed through a trap with a concentrated solution of KOH and condensed in a trap cooled with liquid nitrogen. The middle fraction of the evaporated gas was allowed to pass to the reservoir of the vacuum setup.

Due to the presence of a nozzle between the sections of the reaction and discharge, the gas pressure in the discharge section was about twice as high as the pressure in the reaction zone. Such a pressure difference prevented the gas from passing from the reactor to the discharger and allowed a variation in the reactor pressure without any considerable change in the discharger pressure. In the reaction zone, the concentration of atomic reactants and the mixture pressure were low enough to neglect the homogeneous recombination of atoms with high accuracy. To suppress the recombination of atoms on the reactor walls, the quartz tube in the reaction zone was washed with hydrofluoric acid.

Excited, metastable hydrogen and deuterium atoms in a jet after the discharge zone were absent because, in collisions of these atoms with the species of the gaseous mixtures, they transfer from the metastable $2s$-state to the energetically close $2p$ state, from which they further rapidly transfer to their ground $1s$ state (allowed transition). The transition from the metastable $3s$ state to the ground state occurs in a similar way. This pathway of fast deactivation of metastable atoms in the s states was considered in [46]. After leaving the discharge zone and before mixing with a molecular reactant, hydrogen and deuterium atoms participate in more than 10^5 collisions. This is many thousands times greater than is necessary for the deactivation of metastable states via intermediate p-states according to the above mechanism. An indicator of the absence of excited atoms in the reaction zone is, for instance, the fact that the rate constants of abstraction reactions determined in generating the atomic reactant using a discharge agree well with those determined by radically different methods where no discharge was used and hydrogen atoms were formed in a chemical chain reaction (see below).

Atomic hydrogen was registered using the ESR spectrum ($g = 2.003$) consisting of two identical components at a distance of 509 Oe from each other. Spectrum splitting is due to the hyperfine interaction of electron and proton spins. Atomic deuterium was also registered using the ESR spectrum. As it is known, the latter consists of three identical components stipulated by the hyperfine interaction of the electron and nucleon-deuteron spins. The distance between the components is 83 and 90 Oe from the sides of lower and higher fields, respectively. The strong difference between the ESR spectra of free hydrogen and deuterium atoms enabled easy identification of these species. The sensitivity of spectrometers made it possible to observe changes in their concentrations with high accu-
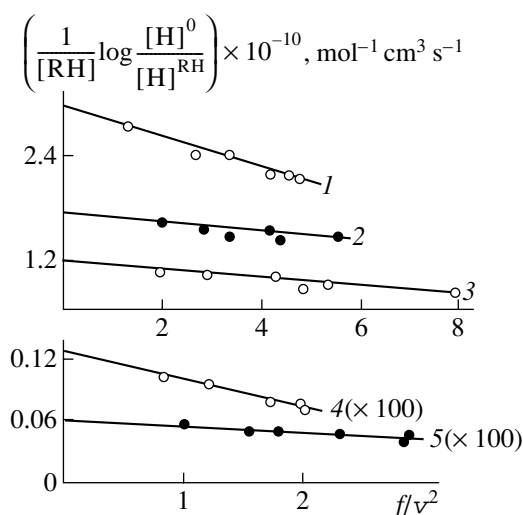
Fig. 2. Dependence of $\dfrac{1}{[RH]}\log\dfrac{[H]^0}{[H]^{RH}}$ on $f/v^2 = \alpha[RH]/Pv^2$ (where RH is C_3H_8) at temperatures, K: (*1*) 368 ($\alpha = 7.46 \times 10^{14}$), (*2*) 345 ($\alpha = 6.32 \times 10^{14}$), (*3*) 321 ($\alpha = 5.06 \times 10^{14}$), (*4*) 443 ($\alpha = 13.06 \times 10^{14}$), and (*5*) 404 ($\alpha = 11.1 \times 10^{14}$). Ordinates of lines *4* and *5* are decreased by a factor of 100.

racy. The ratio of the concentrations of atomic reactants in the computational equations was replaced by the ratio of signal intensities in the spectrum. The reaction time was determined by the consumption of a gaseous mixture taking into account the temperature, the diameter of the reaction tube, and the length of the reaction zone.

RESULTS AND DISCUSSION

The results of studies of reactions of atomic hydrogen and deuterium with ethane and propane are given below. These results are used further to interpret data on the detection and study of homolytic reactions of class (A).

Reactions of Atomic Hydrogen with Hydrogen-Containing Molecules

As Figure 2 shows, in the case of propane, the $(1/[RH])\log\{[H]^0/[H]^{RH}\}$ value linearly depends on $f/v^2 = \alpha[RH]/Pv^2$ with the negative slope in good agreement with Eq. (11). The values of intercepts on the ordinate axis were used to determine the bk values. With a decrease in the temperatures of runs (and with a corresponding decrease in the rate constant), the slopes of the straight lines also decreased, pointing to a weakening of the role of longitudinal diffusion. Below 313 K, the straight lines in the coordinates of Eq. (11) are almost horizontal, showing that the role of diffusion is insignificant. At these temperatures, the experimental
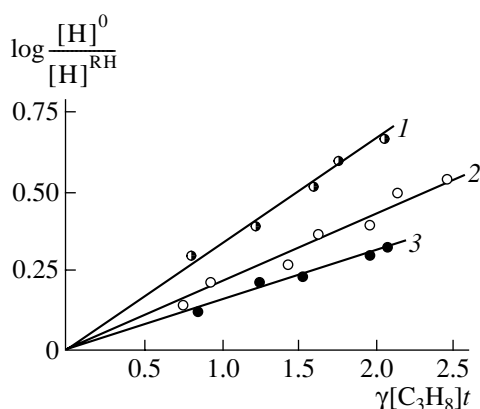
Fig. 3. Dependence of $\log(\,[H]^0/[H]^{RH})$ on $\gamma[C_3H_8]t$ at temperatures, K: (*1*) 313 ($\gamma = 12.82 \times 10^9$), (*2*) 295 ($\gamma = 9.39 \times 10^9$), and (*3*) 284 ($\gamma = 8.97 \times 10^9$); γ is a scaling factor.

Fig. 4. Temperature dependence of the rate constant of hydrogen atom reaction with C_2H_6 (k_{1H}): (*1*) obtained in this work, (*2*) using the method ignition limits [37, 39, 50], and (*3, 4*) obtained in [48, 49].

data are also described well by Eq. (12), which is evident from the proportionality of $\log([H]^0/[H]^{RH})$ to $\gamma[RH]t$ (Fig. 3). At these temperatures, bk was determined both from the intercepts on the ordinate axis in the coordinates of Eq. (11) (Fig. 2) and from the slopes of lines in Fig. 3. The straight lines pass through the origin of coordinates in this figure attesting that the value of $B\text{–}B^0$ is equal to zero. That is, after the jet leaves the constant-temperature zone, the consumption of atomic reactant indeed becomes insignificant. Note that, at $T > 320$ K, Eq. (12), which does not take into account longitudinal diffusion, does not describe the reaction kinetics: the experimental values $\ln([H]^0/[H]^{RH})$ deviate more and more drastically downwards from the linear dependence with an increase in $[RH]t$, whereas Eq. (11) describes well the results of measurements over the whole temperature interval (Fig. 2).

Equations (11) and (12) describe the kinetics of other reactions as well, including the reaction of H with C_2H_6 [37].

The obtained data agree well with [3, 47] and show that, at pressures lower than several hundreds of kilopascals, a reaction such as

$$H + C_2H_6 = H_2 + C_2H_5^{\cdot} \qquad (IH)$$

is rapidly followed by the steps of cracking and recombination

$$H + C_2H_5 = 2CH_3^{\cdot}, \qquad (IIH)$$

$$H + CH_3^{\cdot}(+M) = CH_4(+M), \qquad (IIIH)$$
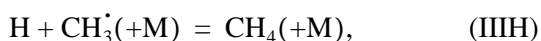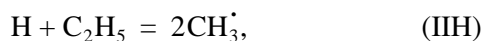
where M is the third species that accepts excess energy.

It follows from this mechanism that, in the reaction of atomic hydrogen with ethane, the stoichiometric coefficient b equals 4. This is evident from the fact that the amount of methane formed is twice as high as the
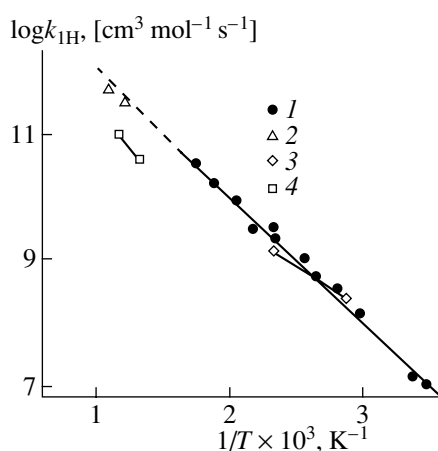
amount of consumed ethane. Owing to the similar set of reactions for the reaction of hydrogen atoms with propane, the coefficient b equals 6.

The results of the determination of the rate constant of reaction (IH) between atomic hydrogen and ethane obtained by the method described above are presented in Fig. 4 in the Arrhenius coordinates. The rate constant thus obtained is $(8.13 \pm 2.1) \times 10^{13}\exp[-(4650 \pm 340)/T]$ cm^3 mol^{-1} s^{-1}. This value agrees well with data obtained in [37, 39, 50] by a variant of the method of ignition limits developed by us earlier, which does not require a knowledge of the rate constants of any other reactions. The above value is also confirmed by the results obtained more recently using radically different methods and coincides with the value recommended in up-to-date reference literature in the interval of temperatures considered here [51, 52]. All these results provide further evidence for the accuracy of the method described above. Specifically, this is evidence for the absence of excited species in the reaction zone. Data reported in [48, 49] and shown in Fig. 4 illustrate the scatter of the rate constant values, which took place before our publications [36, 37, 50].

Thus, the method enables a high-accuracy study of the reaction kinetics and the determination of rate constants. Note that the accuracy of the method also makes it possible to determine a change in the ratio of the rate constants of the reactions of hydrogen atoms in methyl and methylene groups of propane by varying the temperature. This change is due to small variations in the activation energies of hydrogen atoms at the primary and secondary carbon atoms in a hydrocarbon molecule.

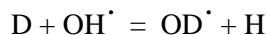*Reactions of Atomic Deuterium with Hydrogen-Containing Molecules*

It was found in the experiment with atomic deuterium that, with the replacement of the inert gas intro-

duced through a side nozzle by the equivalent amount of molecular reactant, the rate of deuterium atom consumption increases to a greater extent than the rate of atomic hydrogen consumption in analogous experiments carried out with atomic hydrogen under the same conditions and with the same molecular reactant. This result itself differs substantially from data reported in [19], where it was claimed that deuterium atoms are consumed more slowly than hydrogen atoms in the reaction with a hydrocarbon. The fast consumption of deuterium atoms in the presence of a hydrocarbon is accompanied by the appearance of atomic hydrogen, which is registered by its ESR spectrum. Free hydrogen atoms are formed only when a hydrogen-containing molecular reactant is added through a side nozzle to the jet containing atomic deuterium. Besides that, when the supply of D_2 to the discharge is discontinued, atomic hydrogen is not observed despite the supply of RH into the reactor through a side nozzle. Thus, the formation of atomic hydrogen is only due to the reaction of atomic deuterium with the molecular reactant. The amount of hydrogen atoms formed in the reaction of deuterium atoms with the molecular reactant reaches several tens of percent of the amount of consumed deuterium.

The appearance of atomic hydrogen in substantial amounts is observed in the reactions of atomic deuterium even with compounds from which hydrogen abstraction is virtually excluded under given conditions. An example is the reaction with water vapor at room temperature. The reaction

$$D + H_2O = HD + OH^{\cdot} \qquad (VIID)$$

is endothermic and the enthalpy increases more than by 56 kJ/mol [18]. The activation energy of the reverse reaction (VIID) is 22 kJ/mol [51] (accurate to the value of the kinetic isotope effect). Therefore, the height of the activation barrier of reaction (VIID) is 78 kJ/mol. This means that, for the time required for the reaction mixture to pass through a reactor at room temperature, the consumption of deuterium atoms by reaction (VIID) is several orders of magnitude lower than the threshold of the registration of a decrease in the concentration of theses atoms. Meanwhile, the experiment shows not only significant consumption of deuterium atoms but the appearance of atomic hydrogen in large amounts as well. Because abstraction reaction (VIID) and the subsequent reaction

$$D + OH^{\cdot} = OD^{\cdot} + H$$

do not occur under these conditions, then the formation of atomic hydrogen results from its substitution from H_2O molecules in their reaction with atomic deuterium.

Obviously, the shorter the time during which the mixture is in the reaction zone and the lower the temperature, the smaller the portion of hydrogen atoms is consumed after their formation. Therefore, with an increase in the flow rates and a decrease in temperature the ratio of the amount of hydrogen atoms to the

amount of deuterium atoms consumed in the reaction with the hydrocarbon (ethane) and alkyl radicals increases; i.e, the ratio $[H]/([D]^0 - [D]^{RH})$ increases. Under certain conditions, this ratio reaches 0.85 (that is, 85% of consumed deuterium is replaced by atomic hydrogen).

The rates of hydrogen atom substitution are much higher than the rates of abstraction reaction (I) from all organic compounds studied by us. This is further evidence for the formation of atomic hydrogen in the reactions with these compounds not via the stepwise mechanism

$$D + CH_3^{\cdot} = (CH_3D)^* = CH_2D^{\cdot} + H, \qquad (VIIID)$$
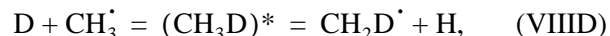
but via direct substitution. Indeed, the rate of consecutive reaction (VIIID) is limited by the rate of $CH_3^{\cdot}$ formation, which is much slower than the apparent reactions of deuterium with the molecular reactant and atomic hydrogen formation.

Thus, our experiment shows that, along with reactions (ID)–(VID), the following fast reaction of hydrogen atom substitution occurs:

$$D + RH = RD + H. \qquad (A_1)$$

In the derivation of the calculation formula for the determination of the rate constants, reaction (A) was taken into account together with reactions (ID)–(IVD). Obviously, by analogy with atomic deuterium, atomic hydrogen can also substitute for a deuterium atom in a polyatomic molecule. However, because in this experiment the initial concentration of atomic deuterium and, consequently, the concentration of deuterated products is much lower than the concentration of C_2H_6, the substitution of deuterium atoms for atomic hydrogen can be neglected with a high degree of accuracy. Taking this into account for the reaction with ethane, we obtain the following expression based on the reaction scheme for deuterium, which is analogous to Eq. (11) under the conditions when the role of longitudinal diffusion is substantial:

$$\frac{1}{[RH]t}\ln\frac{[D]^0}{[D]^{RH}} = 4k_{1D} + k_A \\ - \frac{(4k_{1D} + k_D)^2 760 D_0^{RH}}{RT}\frac{f}{v^2} \qquad (13)$$

and analogous to Eq. (12) under the conditions when the role of this factor is insignificant:

$$\ln\frac{[D]^0}{[D]^{RH}} = (4k_{1D} + k_A)[RH]t. \qquad (14)$$

The proposed method and the results of measurements allow the separate determination of the rate constants of hydrogen substitution and abstraction reactions of the hydrogen-containing molecule with atomic deuterium. Taking into account the amount of substi-
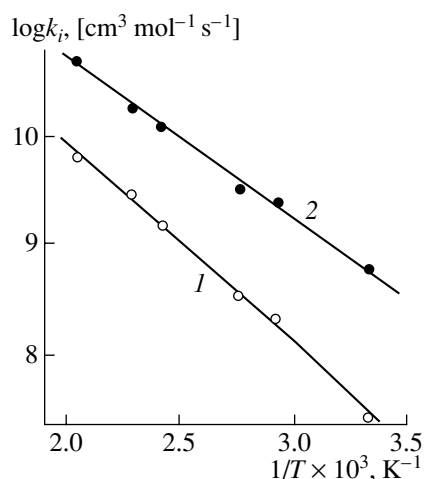
Fig. 5. Temperature dependence of (*1*) k_{1D} and (*2*) k_D for deuterium atoms with ethane.

tuted atomic hydrogen, we obtain the following expression for the reaction of hydrogen atom abstraction from the initial molecule with the formation of HD:

$$\frac{1}{[RH]}\ln\frac{[D]^0}{[D]^{RH}+[H]} = 4k_{1D} - \frac{16k_{1D}^2}{RT}D760\frac{f}{v^2}. \quad (15)$$

Equations (13)–(15) were obtained taking into account that hydrogen atoms substituted in reaction (A) are consumed in reactions (IH)–(IIIH) and in the reactions of heterogeneous recombination. Unlike Eq. (12), formula (15) describes the consumption of atomic deuterium only in abstraction reaction (ID) and subsequent steps (IVD), (VD), and (VID). Therefore, the linear dependence of the left-hand side of Eq. (15) on f/v^2 enables direct determination of the k_{1D} value. Under the conditions when the role of longitudinal diffusion is insignificant (as is evident from the absence of the slopes of the straight lines), this equation takes a simpler form:

$$\ln\frac{[D]^0}{[D]^{RH}+[H]} = 4k_{1D}[RH]t. \quad (16)$$

By subtracting Eq. (16) from Eq. (14), we obtain

$$\ln\left(1 + \frac{[H]^{RH}}{[D]^{RH}}\right) = k_A[RH]t. \quad (17)$$

It is seen from this equation that the value k_A can be determined from the slope of the linear dependence of the left-hand side on $[RH]t$. In the processing of the data, the ratio of the concentrations of atomic hydrogen and deuterium was replaced by the ratio of signal intensities in the spectra taking into account the fact that the signals of atomic deuterium are somewhat broader and that its spectrum contains three components, unlike the spectrum of hydrogen atoms consisting of two components.

In the experiments with atomic deuterium, the temperature was varied from 343 to 489 K and the pressure was varied from 1.3×10^2 to 4×10^2 Pa. Table 1 shows the values of rate constants for reactions (ID) and (A), their ratios, and the overall rate constant at different temperatures obtained using Eqs. (13)–(16).

Figure 5 shows the results in the Arrhenius coordinates. The following temperature dependences were obtained for the rate constants of reactions (ID) and (A) of deuterium atoms with ethane (cm³ mol⁻¹ s⁻¹):

$$k_{1D} = (34.9 \pm 1.2) \times 10^{13}\exp[-(4200 \pm 400)/T],$$

$$k_A = (3.6 \pm 0.4) \times 10^{13}\exp[-(3300 \pm 350)/T].$$

It is seen from the ratio of the overall rate constant $k_D = 4k_{1D} + k_A$ to $4k_{1D}$ that the apparent fast consumption of deuterium atoms cannot be explained by the abstraction reaction and consequent cracking and recombination reactions. Indeed, even if all hydrogen atoms in the ethyl and methyl radicals were exchanged with deuterium in reaction (VIIID), the rate constant of the overall reaction of atomic deuterium (k_D) with ethane and radicals would be only 9/4 times higher than $4k_{1D}$. Meanwhile, as can be seen from the above data, the k_D value is greater than $4k_{1D}$ from 2.6 to 4.6 times (i.e. from 10.4/4 to 18.4/4 times) over the whole temperature interval considered here. The lower the temperature, the greater the difference between these values. Thus, the substitution of a hydrogen atom in the molecular component has the most pronounced contri-

Table 1. Kinetic parameters of deuterium atom reactions with ethane

Parameter	Temperature, K					
	300	343	364	415	439	489
$k_{1D} \times 10^{-8}$, cm³ mol⁻¹ s⁻¹	0.28	2.2	3.6	15.1	29.0	63.2
$k_A \times 10^{-8}$, cm³ mol⁻¹ s⁻¹	6.2	25.1	30.7	118.6	182.0	453.0
k_A/k_{1D}	22.2	11.1	8.5	7.8	6.3	7.2
k_D, cm³ mol⁻¹ s⁻¹	7.2	33.9	45.1	179.0	298.0	705.0
$k_D/4k_{1D}$	4.6	3.8	3.1	2.9	2.6	2.8

bution to the overall consumption of atomic deuterium in the reaction with the molecular component.

Analogous fast substitution of hydrogen atoms was found in the studies of reactions of atomic deuterium with other hydrogen-containing compounds, such as methane, propane, ethanol, acetone, and water vapor. The results of kinetic studies of reactions of hydrogen and deuterium atoms with propane via directions (ID) and (A) are presented in Fig. 6. It can be seen, that the rate of the substitution reaction is much higher than the rate of atom abstraction in this case as well.

When considering various molecular reactants, the k_A/k_{1D} ratio is higher for a reactant from which abstraction of a hydrogen atom is more difficult.

In the experiments with water vapor, helium was bubbled through a saturator filled with distilled water before passing to the side nozzle of the reactor. Saturation was carried out at a temperature, which was higher than the necessary value to achieve the desired concentration of water vapor. Then, a flow of helium and water vapor passed through a trap packed with glass balls at a lower temperature to obtain the desired concentration of water vapor. Other details of the procedure were the same as described above. Thus obtained, the rate constant of the reaction

$$D + H_2O = DOH + H \qquad (IXD)$$
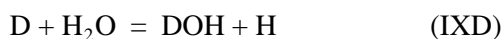
was 5×10^6 cm^3 mol^{-1} s^{-1} at room temperature, which corresponds to an activation energy no higher than 38 kJ/mol at a normal value of the preexponential factor. This is more than 40 kJ/mol lower than the activation energy of hydrogen abstraction. Correspondingly, in the cases considered here, the rate constant of substitution is millions of times higher than the rate constant of the abstraction reaction.

Note that the results of potential energy surface calculations [31] and the activation energy obtained in that work (38.8 kJ/mol) agree well with the experimental value obtained by us earlier for the rate of hydrogen substitution in H_2O. However, the authors of [31] were unfamiliar with our experimental data [39, 53] on the fast substitution of H in H_2O at room temperature and claimed that, contrary to their calculated data, the activation energy of hydrogen atom substitution H should be much higher than their calculated value.

To find out whether heterogeneous factors contribute to the discovered substitution reactions of hydrogen atom in polyatomic molecules, we studied reactions of hydrogen and deuterium atoms with ethane in a special series of experiments using a quartz reactor, whose surface properties were varied by chemical modification. In one series of experiments, the surface was washed with hydrofluoric acid, and in the other series, the surface was covered with sodium tetraborate. Obviously, the surface of sodium tetraborate, an alkali metal salt with a weakly acidic anion, differs substantially from quartz glass treated with hydrofluoric acid in its chemical properties and structure. Measurements at 295 and
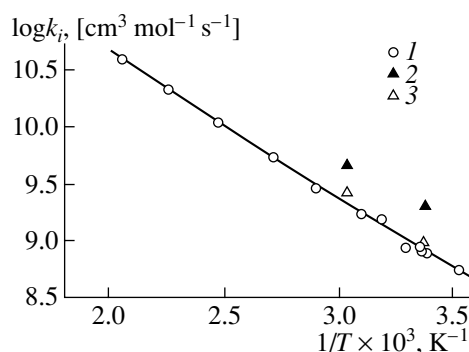

Fig. 6. Dependence of the rate constants for reactions of (*1*) hydrogen and (*2, 3*) deuterium atoms with propane: (*2*) k_A and (*3*) k_{1D}.

393 K showed that the values of the overall rate constant k_D (and, hence, k_A) are independent of the surface material with an error of 10–15%, and the substitution reaction thus occurs in the gas phase.

A great difference in the rates of reactions (A) and (I) and the absence of correlations between the activation energies and enthalpies show that these are different types of reactions with different transition states. Most probably, the spontaneous substitution of a hydrogen atom by deuterium in hydrocarbon molecules occurs as an attack of a deuterium atom on a carbon (rather than hydrogen) atom of a hydrocarbon. Our data show that this attack only results in the C–H bond cleavage rather than C–C bond cleavage, and deuterium substitutes for a hydrogen atom in the initial molecule. Indeed, it can be easily shown that, in the case of C–C bond cleavage in the reaction of a hydrogen atom with ethane, the stoichiometric coefficient would be equal to 2, and it would be equal to 4 in the case of propane. However, it was shown above that the experimental stoichiometric coefficient in the reaction of hydrogen atom with ethane is 4. This indicates that reactions (IH), (IIH), and (IIIH) occur. In the reaction with propane, the stoichiometric coefficient is 6 due to an analogous mechanism, which also involves propyl radicals.

The above experimental data on hydrogen atom abstraction by hydrogen and deuterium from the ethane molecule correspond to the kinetic isotope effect expressed as follows:

$$k_H/k_D = 2.08\exp(-450/T).$$

Consideration of reactions (A) also makes it possible to explain data from [54], where it was found that the products of olefin hydrogenation in the mixture of atomic hydrogen and molecular deuterium are partially deuterated. Some of the product molecules contain more than one deuterium atom. The authors of [54] explained this assuming that the free valence of a carbon atom in the free radical simplifies the exchange of deuterium with hydrogen atoms connected to this carbon atom. This assumption was not supported by

proper arguments and contradicts results obtained in the studies of reactions of molecular deuterium with photochemically generated alkyl radicals [55]. When fast reactions (A) are considered, these data are easier to explain. Indeed, because the activation energy of reaction

$$H + D_2 = HD + D$$
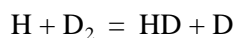
is not high (~30 kJ/mol), the reaction system studied in [54] also contains atomic deuterium, which undergoes the addition to an olefin molecule and enters reaction (A) with the hydrogenation product. The number of deuterium atoms in the deuterated product molecule is determined by the number of times it enters reaction (A).

The discovery of fast gas-phase homolytic substitution reactions of the S_N^2 type (A) suggests reconsidering ideas that negate the occurrence of such reactions. Specifically, the high rate constants of reactions (A) obtained experimentally and the low activation energies show that the calculated values reported in [1, 2, 5] cannot be a reason to deny reactions of this type. The high rates of reactions (A) also point to the necessity of taking them into account when studying the mechanisms of complex chemical processes accompanied by the formation of atoms and radicals, using isotopically labeled molecules, as well in the theory of elementary chemical reactions.

Direct Substitution Reaction in the Process of Carbon Disulfide Combustion

As expected, the direct homolytic substitution of atoms from polyatomic molecules is not restricted to substitution reactions of hydrogen atoms. To explain the specific features of carbon disulfide oxidation, we supplemented the chemical scheme of the process containing the step of active species multiplication [56],

$$S + O_2 = SO + O, \qquad (IV)$$
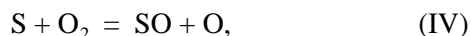
by the thermoneutral reaction of direct substitution of a sulfur atom from the CS_2 molecule:

$$O + CS_2 = COS + S. \qquad (V)$$
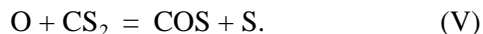
This made it possible to explain the presence of self-ignition limits. Unlike the limit of nonthermal flame propagation, these limits are known to be determined by the competition of the reactions of active intermediate species that follow the first kinetic order with respect to the concentrations of these species. Reaction (V) together with (IV) provides such chain branching. The value of the rate constant of reaction (V), equal to 1.84×10^{11} cm^3 mol^{-1} s^{-1} at 298 K [57], determined later shows that this reaction is so fast that, together with (IV), it can provide a rate of linear chain branching corresponding to the observed values of self-ignition.

Simulations of a set of equations corresponding to the reaction scheme that also takes into account nonlinear chain branching [56] made it possible to describe the limits and the rate of nonthermal flame propagation of CS_2 and O_2.

Note that, in contrast to reaction (VIID) of atomic deuterium with water vapor, which is the only reaction of the observed formation of atomic hydrogen at low temperatures, the formation of atomic sulfur in the reaction mixture $O + CS_2$ does not provide compelling evidence for substitution reaction (V). Indeed, fast reactions

$$O + CS_2 = SO + CS \quad \text{and} \quad O + SO = O_2 + S \quad (VI)$$

occur one after another at high rates in such a mixture and result in the formation of free sulfur atoms [56], while the presence of self-ignition limits of the reaction of CS_2 with O_2 unambiguously points to the fact that, along with chain branching, which has the second overall kinetic order with respect to the concentrations of active intermediate species (with nonlinear branching) and stipulates nonthermal flame propagation, the reaction of linear branching also occurs. It is the substitution reaction (IV), which is characterized by the first order with respect to the active intermediate species (oxygen atom), and provides linear branching together with reaction (V).

Reaction (V) is an example illustrating that fast homolytic reactions of atom substitution from polyatomic molecules may involve atoms other than atomic hydrogen or its isotopes, as well as other molecules. These reactions may play an important role in the process of chain combustion and pyrolysis.

Heterogeneous Reactions of Atomic Substitution in a Chain Process

Atomic substitution is also observed in the reactions of gas-phase atomic reactants with solids. The substitution by atomic hydrogen, formed in a rarefied flame of H_2 with O_2, for sodium and potassium atoms to the gas phase from the respective solid chlorides was found in [58].

A quartz reactor and the registration system are described in Fig. 7. A quartz cylinder was placed into the reactor. The internal surface of the cylinder was covered with a salt to be studied. The reactor design allowed us to vary the position of a cylinder with respect to the gas inlet (positions *A* and *B* in Fig. 7). This was necessary for the determination of the contributions of reactions of the atomic reactant with the solid salt and its vapors. The pressure of the mixture and temperature were varied from 300 to 500 Pa and from 543 to 783 K, respectively. Gas-phase alkali metal atoms were directly registered by the method of emission spectroscopy using an OSA-500 multichannel analyzer of optical spectra (with a resolution of 1.4 Å/channel) equipped with a system for signal accumulation. In special runs where atomic hydrogen was obtained by H_2 dissociation, sodium atoms were registered in the gas phase by the method of resonance fluorescence. Fluo-
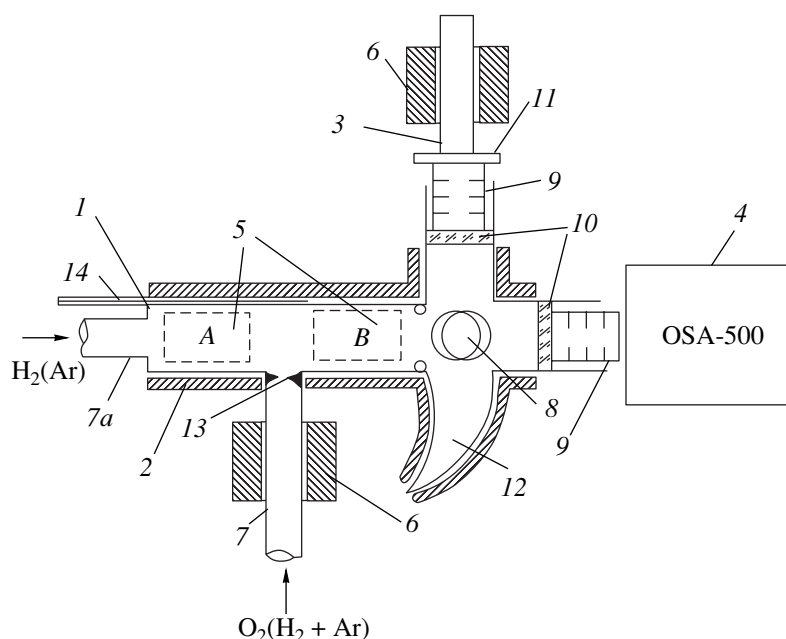
Fig. 7. Reactor for the registration of metal atom substitution from their salts: (*1*) reactor, (*2*) electric furnace, (*3*) resonance lamp, (*4*) spectral analyzer, (*5*) positions of a mobile tube covered with a chloride, (*6*) microwave discharger, (*7*) inert gas charge tube, (*7a*) H$_2$ (and Ar) charge tube, (*8*) communication lines for pumping, (*9*) collimator, (*10*) quartz windows, (*11*) diaphragm, (*12*) light trap, (*13*) nozzle, and (*14*) thermocouple.

rescence of atomic sodium escaped to the gas phase was excited by high-frequency discharge irradiation in a quartz lamp containing NaCl (or metallic sodium in some runs) and filled with a mixture of N$_2$ (0.1 torr) and Ar (2.0 torr). This source provided radiation at a wavelength of 589 nm.

The reaction mixture was supplied from the flame into the reactor through side inlet *7*. It is known that, in the combustion of the stoichiometric or hydrogen-reach mixtures of H$_2$ and O$_2$, hydrogen atoms are almost the only active intermediate species participating in heterogeneous reactions, because their concentration is much higher than the concentration of oxygen atoms and O H$^{\bullet}$ radicals and because they are more mobile. In the runs with a mobile cylinder with NaCl (or KCl) in position *A*, hydrogen atoms only contacted salt vapors carried by a flow of inert gas passing from inlet *7a*, while in the runs with the cylinder in position *B*, hydrogen atoms also contacted the solid salt. Special measurements were performed to ensure the constant flow of salt vapors carried with a jet passing through inlet *7a* along the whole length of the reactor: when the internal cylinder was in position *A*, the value of the resonance fluorescence signal and the intensity of Na atom radiation were independent of the distance between the cylinder and the place where atomic hydrogen was introduced, that is, nozzle *13*. Because the temperature was constant along the reactor axis, a comparison of signal intensities made it possible to determine the contribution of the heterogeneous reaction to the formation of Na and K atoms in the gas phase.

In the runs where atomic hydrogen was obtained with a discharge, the radiation of excited sodium atoms and the signal of resonance fluorescence of these atoms in the ground state were registered. Sodium atoms appear in the gas phase only if atomic hydrogen is available. When the flow of hydrogen atoms through side inlet *7* is discontinued, the signals of sodium and potassium atoms in the ground and excited states disappear.

The pressures of argon supplied through inlet *7a* and a mixture coming from the discharge zone through a side tube *7* were 0.55 and 1.10 torr, respectively, in the first series of experiments and 1.87 and 3.73 torr in the second series. Table 2 shows as an example the results of measurements of radiation intensity (I^*) and the signal of resonance fluorescence (I_{RF}) of atomic sodium at a gas temperature of 718 K in two series of runs, where atomic hydrogen was obtained in a discharge.

These data show that, if hydrogen atoms interact not only with the solid salt but also with NaCl vapors, the concentration of sodium atoms in the ground state registered by the method of resonance fluorescence is 12–13 times higher. In this case, the concentration of excited sodium atoms is also much higher, although deactivation makes this effect smoother.

In the study of NaCl interaction with atomic hydrogen formed in a flame, molecular hydrogen was supplied from the butt-end of the reactor, whereas oxygen was supplied through a side inlet. Ignition and combustion occurred to the right of the nozzle. When the cylinder covered with NaCl was in position *B*, atomic

Table 2. Dependence of radiation and resonance fluorescence intensities for sodium atoms on the cylinder position (*A* and *B* in Fig. 7)

Signal	Intensity, rel. units			
	A	*B*	*A*	*B*
	Series 1		Series 2	
I^*	172	444	27	124
I_{RF}	27	362	10	120

Table 3. Dependence of luminescence intensity (rel. units) for atoms (Na and K) substituted from their solid salts NaCl and KCl on the position of the cylinder under conditions of rarefied flame

Cylinder position	NaCl	KCl	KCl
	Wavelength, nm		
	589	767	770
A	1953	345	273
B	5407	1030	815

sodium was registered both in the gas phase in the excited and ground states. In analogous experiments with KCl, atomic potassium was registered. When the surface contacted the fuel mixture in the absence of flame, metal atoms were not registered in the gas phase. To eliminate the effect of the internal cylinder on the flame geometry, two identical cylinders were put into the reactor in positions *A* and *B* in special runs. The inner surface of one of them was covered with NaCl and that of the other, with KCl. The role of the heterogeneous reaction in the appearance of an alkali metal in the gas phase was judged on the basis of changes in the luminescence signal intensities in positions *A* and *B* when cylinders changed places. The ratio of luminescence signal intensities in positions *A* and *B* correlates with the corresponding ratio of resonance fluorescence intensities. Table 3 exemplifies one experimental series.

It is seen again from these data that, if hydrogen atoms contact the solid salt, the concentrations of both alkali metals are much higher than in the case of interaction with salt vapors only. Thus, the reaction with the solid salt is the main channel for metal to escape into the gas phase. The appearance of yellowish color in the hydrogen flame in glass tubes can be explained by the substitution of sodium atoms from the glass. These atoms radiate the characteristic *d*-line on excitation in a flame. Note that after our work [58], the escape of sodium atoms from solid salts to the gas phase under flame conditions was also observed in [59].

The escape of Na and K atoms during the interactions of their salts with atomic hydrogen obtained in a flame or in a discharge is accompanied by a change in the color of the surface. It became dark purple. Fast substitution of an alkali metal atom from its salt described above is one of the pathways for the chemical modification of the surface in the course of a chain process. Obviously, surface changes under the action of a chain process affect in their turn the characteristics of combustion in general. In the general case, gas-phase reactions of substituted metal atoms should also be taken into account. Considerable changes in the features of hydrogen combustion in oxygen in reactors with surfaces covered with NaCl and KCl [60] is an example of manifestation of modifications in the surface state and its role.

Obviously, the transition of atoms from a solid matrix to the gas phase under the action of an atomic reactant can also take place in other process with the participation of free atoms, including other chain processes.

CONCLUSION

Thus, when atomic reactants react with polyatomic molecules, fast direct substitution reactions occur along with atom abstraction reactions. The elucidation of kinetics and mechanisms of these homolytic reactions, including the configurations of transition states, is one of the topical problems in the theory of elementary reactions. This problem is also of interest for understanding the mechanisms and kinetics of gas-phase processes occurring with the participation of free atoms and radicals, such as pyrolysis and combustion. The reactions of metal atom substitution from their salts by atomic gas-phase reactants are of interest for both topochemistry and gas-phase pyrolysis and combustion processes.

REFERENCES

1. Glasstone, S., Laidler, K.J., and Eyring, H., *The Theory of Rate Processes*, New York: Princeton Univ., 1941.

2. Waters, W., *The Chemistry of Free Radicals*, Oxford, 1946.

3. Steacie, E.W.R., *Atomic and Free Radical Reactions*, New York: Reinhold, 1954, vol. 2.

4. Semenov, N.N., *O nekotorykh problemakh khimicheskoi kinetiki i reaktsionnoi sposobnosti* (On Some Problems of Chemical Kinetics and Reactivity), Moscow: Akad. Nauk SSSR, 1958.

5. Kondrat'ev, V.N., *Kinetika khimicheskikh gazovykh reaktsii* (Kinetics of Chemical Gas-Phase Reactions), Moscow: USSR Academy of Sciences, 1958.

6. Melander, L., *Isotope Effects on Reaction Rates*, New York, 1961.

7. Kondrat'ev, V.N., Nikitin, E.E., Reznikov, A.I., and Umanskii, S.Ya., *Termicheskie bimolekulyarnye reaktsii v gazakh* (Thermal Bimolecular Reactions in Gases), Moscow: Nauka, 1976.

8. Emanuel', N.M. and Knorre, D.G., *Kurs khimicheskoi kinetiki* (Chemical Kinetics), Moscow: Vysshaya Shkola, 1984.

9. Eyring, H., Lin, S.H., and Lin, S.M., *Basic Chemical Kinetics*, New York: Wiley, 1980.

10. Fujisaki, N., Gaumann, T., and Ruf, A., *Ber. Bunsen-Ges. Phys. Chem.*, 1986, vol. 90, no. 2, p. 375.

11. Baulch, D.L., Cobos, C.J., Cox, R.A., *et al.*, *Combast. Flame*, 1994, vol. 98, no. 11, p. 59.

12. Ogg, R.A. and Polanyi, M., *Trans. Faraday Soc.*, 1935, vol. 31, no. 2, p. 482.

13. Bujuke, J.E., Pratt, M.W.T., and Noyes, R.M., *J. Am. Chem. Soc.*, 1961, vol. 83, no. 7, p. 1547.

14. Morikawa, K., Benedict, W.S., and Taylor, N.S., *J. Chem. Phys.*, 1937, vol. 5, no. 1, p. 212.

15. Farkas, A. and Melville, H.W., *Proc. R. Soc.*, 1936, vol. 157, no. 3, p. 625.

16. Geib, K.H. and Steacie, E.W.R., *Trans. Roy. Soc. Can.*, 1935, vol. 3, no. 1, p. 91.

17. Geib, K.H. and Steacie, E.W.R., *Z. Phys. Chem.*, 1935, vol. 29, no. 1, p. 215.

18. Corchado, J.C. and Garscia, J.E., *J. Chem. Phys.*, 1997, vol. 106, no. 10, p. 4013.

19. Shiff, H.J. and Steacie, E.W.R., *Can. J. Chem.*, 1951, vol. 29, no. 1, p. 1.

20. Steacie, E.W.R. and Phillips, N.W.F., *J. Chem. Phys.*, 1936, vol. 4, no. 8, p. 461.

21. Kondrat'ev, V.N., *Konstanty skorosti gazofaznykh reaktsii* (Rate Constants of Gas-Phase Reactions), Moscow: Nauka, 1970.

22. Trenner, N.R., Morikawa, K., and Taylor, H.S., *Z. Chem. Phys.*, 1937, vol. 5, no. 1, p. 203.

23. Chon, C.C. and Rowland, F.S., *J. Am. Chem. Soc.*, 1966, vol. 88, no. 11, p. 2612.

24. Roor, J.W. and Rowland, F.S., *J. Chem. Phys.*, 1967, vol. 46, no. 11, p. 4299.

25. Chon, C.C. and Rowland, F.S., *J. Chem. Phys.*, 1969, vol. 50, no. 6, p. 2763.

26. Menzinger, M. and Wolfgang, R., *J. Am. Chem. Soc.*, 1967, vol. 89, no. 24, p. 5992.

27. Estrup, P.J. and Wolfgang, R., *J. Am. Chem. Soc.*, 1960, vol. 82, no. 11, p. 2661.

28. Firestone, R.F., Lemr, C.F., and Trudel, C.F., *J. Am. Chem. Soc.*, 1962, vol. 84, no. 12, p. 2279.

29. Lawrence, R.H. and Firestone, R.F., *J. Am. Chem. Soc.*, 1966, vol. 88, no. 19, p. 4564.

30. Martin, R.M. and Willard, J.N., *J. Chem. Phys.*, 1969, vol. 40, no. 7, p. 3007.

31. Shatz, G.C., Colten, M.C., and Grant, J.L., *J. Phys. Chem.*, 1984, vol. 88, no. 14, p. 2971.

32. Ingold, K.U. and Roberts, B.P., *Free-Radical Substitution Reactions*, New York: Wiley, 1971.

33. Nikitin, E.E., *Teoriya elementarnykh atomno-molekulyarnykh protsessov v gazakh* (The Theory of Elementary Atomic-Molecular Processes in Gases), Moscow: Khimiya, 1970.

34. Semiokhin, I.A., Strakhov, B.V., and Osipov, A.I., *Kurs khimicheskoi kinetiki* (Chemical Kinetics), Moscow: Mosk. Gos. Univ., 1995.

35. Kondrat'ev, V.N. and Nikitin, E.E., *Khimicheskie protsessy v gazakh* (Chemical Processes in Gases), Moscow: Nauka, 1981.

36. Azatyan, V.V. and Filippov, S.B., *Dokl. Akad. Nauk SSSR*, 1969, vol. 184, p. 625; *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, no. 5, p. 1186.

37. Azatyan, V.V., *Dokl. Akad. Nauk SSSR*, 1972, vol. 203, p. 137.

38. Azatyan, V.V., Filippov, S.B., and Khachatryan, M.S., *Kinet. Katal.*, 1971, vol. 12, no. 1, p. 17.

39. Azatyan, V.V., *Doctoral (Chem.) Dissertation*, Moscow: Inst. of Chem. Phys., 1978.

40. Azatyan, V.V., Gazaryan, K.G., and Garibyan, T.A., *Kinet. Katal.*, 1987, vol. 29, no. 1, p. 38.

41. Frank-Kamenetskii, D.A., *Diffuziya i teploperedacha v khimicheskoi kinetike* (Diffusion and Heat Transfer in Chemical Kinetics), Moscow: Nauka, 1987.

42. Clyne, M.A.A. and Thrush, B.A., *Proc. R. Soc.*, 1963, vol. 275A, p. 599.

43. Azatyan, V.V., *Usp. Khim.*, 1985, vol. 54, no. 1, p. 33.

44. Azatyan, V.V., *Zh. Fiz. Khim.*, 1998, vol. 72, no. 3, p. 391.

45. Azatyan, V.V., *Kinet. Katal.*, 1999, vol. 40, no. 2, p. 180.

46. Kampaneets, A.S., *Teor. Eksp. Khim.*, 1972, vol. 8, no. 1, p. 147.

47. Kazmi, H.A. and Le Roy, D.J., *Can. J. Chem.*, 1964, vol. 42, no. 5, p. 1145.

48. Berlie, M.K. and Le Roy, D.J., *Disc. Faraday Soc.*, 1953, vol. 14, no. 1, p. 50.

49. Panfilov, V.N. and Voevodskii, V.V., *Kinet. Katal.*, 1965, vol. 6, no. 4, p. 577.

50. Azatyan, V.V., *Dokl. Akad. Nauk SSSR*, 1971, vol. 196, no. 3, p. 617.

51. Tsang, W. and Hapson, R.F., *J. Phys. Chem. Ref. Data*, 1986, vol. 15, no. 3, p. 1087.

52. Baulch, D.L., Cobos, C.J., Cox, R.A., *et al.*, *Combust. Flame*, 1994, vol. 98, no. 1, p. 59.

53. Azatyan, V.V., Grigoryan, F.A., and Filippov, S.B., *Kinet. Katal.*, 1972, vol. 13, no. 6, p. 1389.

54. Voevodskii, V.V., Lavrovskaya, G.K., and Mardaleishvili, R.E., in *Voprosy khimicheskoi kinetiki, kataliza i reaktsionnoi sposobnosti* (Problems of Chemical Kinetics, Catalysis, and Reactivity), Moscow: USSR Academy of Sciences, 1955, p. 40.

55. White, E. and Steacie, *J. Chem. Phys.*, 1953, vol. 21, p. 933.

56. Azatyan, V.V., Novozhilov, B.V., Posvyanskii, V.S., and Semenov, N.N., *Kinet. Katal.*, 1976, vol. 17, no. 6, p. 1386.

57. Atkinson, R., Baulch, D.L., Cox, R.A., *et al.*, *J. Phys. Chem. Ref. Data*, 1997, vol. 26, no. 6, p. 1329.

58. Rubtsov, N.M., Azatyan, V.V., Borodulin, R.R., *et al.*, *Khim. Fiz.*, 1984, vol. 3, p. 1789.

59. Baulch, D.L., Griffiths, J.F., and Richer, R., *Combust. Flame*, 1991, vol. 85, nos. 1–2, p. 271.

60. Azatyan, V.V., Sklyarenko, V.I., and Shavard, A.A., *Khim. Fiz.*, 1982, vol. 1, no. 12, p. 1704.