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The Reactivity of Hydrogen Atoms

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Theoretical ideas about the reactions of thermal and "hot" hydrogen atoms are examined and experimental data, characterising the mode of reactions involving hydrogen atoms with different energies, are presented.
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I. INTRODUCTION

The hydrogen atom is the simplest chemical species and has for a long time attracted the attention of investigators endeavouring to understand elementary chemical processes. On the other hand, the role of hydrogen atoms in many processes occurring naturally or induced artificially is generally known: in space and in the upper layers of the atmosphere, in radiation chemistry and photochemistry, in the pyrolysis of substances, in hydrogenation reactions, in plasmas, and in thermonuclear processes. There is reason to believe that organic substances are formed on the planets of the solar system as a result of reactions of hydrogen atoms[1].

There are several ways of obtaining hydrogen atoms (and the atoms of hydrogen isotopes—deuterium and tritium): thermal dissociation, electric discharge, photolysis, radiolysis, nuclear reactions, and an acceleration technique. In the thermal dissociation of molecular hydrogen, one obtains thermal atoms and, since the source region is at a high temperature, approximtely 10% of the atoms are obtained with an energy of approximately 0.3-0.5 eV.[2] In the remaining instances, hydrogen atoms have a non-equilibrium distribution. In an electric discharge there is a possibility of the formation of excited atoms[3]. Hydrogen atoms in certain quantum states are obtained by the electron impact method[4] or in a proton transfer reaction[5]. Hydrogen atoms appear when gas flows from an ultrasonic nozzle[6]. Owing to the dissociation of C—H bonds, the radiolysis of hydrogen-containing organic compounds results in the appearance of hydrogen atoms with an energy of 1—3 eV.[7] In photolytic experiments the energy of hydrogen atoms varies from 0.1 to 6 eV.[8] Recoil tritium atoms with energies of 0.19 and 2.7 MeV can be obtained by the nuclear reactions $^3He(n,p)^3H$ and $^6Li(n,\alpha)^3H$.[9] The technique of "chemical" accelerators makes it possible to obtain hydrogen atoms with energies in the range from approximately 1 to 200 eV[10] and to investigate the angular distribution of the reaction products[11]. Thus present day investigators are able to obtain hydrogen atoms with energies ranging from approximately 0 to 2.7 MeV. There is a prospect of investigating reactions with reactants having different energies and known quantum states.

According to the classical Arrhenius equation, with increase of temperature (collision energy) the probability of the reaction should tend to a value equal to the steric factor. However, if high-energy atoms are generated in the system, the reactions do not obey the Arrhenius kinetics; the steric factor increases[12] when the probability of the reaction depends in a complex manner on the collision energy[12,13]. Thus the reactions occurring at different relative collision energies cannot be described in terms of a single mechanism.

Ideas borrowed from collison physics and nuclear physics throw a significant light on the nature of chemical reactions. This concerns concepts such as the reaction cross-section and the excitation function. The cross-section of a chemical reaction reflects its probability for a specific quantum state of the initial reactants and final products, while the excitation function describes the dependence of the cross-section on the collision energy. By integrating over all possible states, one obtains the overall reaction cross-section and, on multiplying by the relative velocity of the reacting species, one finds the rate coefficient—a quantity analogous to the rate constant for a chemical reaction. For the equilibrium distribution of the reacting species with respect to energies, the rate coefficient is the rate constant for the chemical reaction.

Appreciable advances have been made in recent years in the study of the excitation functions $\sigma(E)$ of chemical reactions in general and of the reactions of hydrogen atoms in particular. The chemical reaction thresholds have been determined; it has been shown that $\sigma(E)$ corresponding to a specific energy has a maximum, beyond which it decreases to $\sigma(E) \cong 0$. Taking this into account, it is possible to classify the interactions of hydrogen atoms which are generated in some way in the medium in terms of their energies and the nature of their energy spectrum. If the spectrum is of the Boltzmann type, then usually only a small proportion of the atoms enter the region $E_1 \leq E \leq E_2$, where the function $\sigma(E)$ is determined. In this case the classical description based on the Arrhenius equation is entirely applicable in the region of "moderate" temperatures (200—500 K). At low temperatures quantum corrections for the wave properties exhibited by the hydrogen atoms are necessary, while at high temperatures account must be taken of the breakdown of the Boltzmann distribution as a consequence of the "burning away" of the active species.

If atoms with an energy in the region $E_1 \leq E \leq E_2$ are generated in the system where the function $\sigma(E)$ is determined (this is usually 0.1—10 eV) and if there is no equilibrium in the energy distribution of the atoms, then the Arrhenius equation is inapplicable to the description of the kinetics of the reactions of such species, which are referred to as "hot". The reaction can occur in the first collision and also subsequently when the atom has lost part of its energy, but subject to the condition that the residual energy of the atom lies within the limits of the region $E_1 \leq E \leq E_2$. If atoms with $E > E_2$ act on a given substance, then in the first collision the reaction is impossible and the atoms must be retarded until the energy is $\leq E_2$. Subsequently the reaction proceeds

in the same way as that with atoms generated in the range of energies $E_1 < E \leq E_2$.

The rate of a reaction involving species with an energy can be expressed by the general equation

$$w = \int_{E_1}^{E_2} p(E')\, n(E, E')\, \mathrm{d}E' \,, \qquad (1)$$

where $p(E')$ is the probability of the reaction for a collision energy $E = E'$ and $n(E,e')$ is the collision density (the number of collisions per unit time per unit volume). The collision density in the range of energies dE' near E' in general depends on the energy of the species E, falling within this range on retardation.

If $E > E_1$, the probability of the reaction of thermal atoms is assumed to be independent of the collision energy; the collision density is calculated from the Boltzmann distribution of the species with respect to energies. Hence it is possible to derive the Arrhenius law from Eqn.(1). For "hot" species, the assumption that the reaction probability is independent of the energy is invalid, because a considerable proportion of the species (if not all) have an energy $E \gg E_1$. However, in an analytical form, the $p(E)$ relation is as a rule unknown, so that the concept of integral probability is used in the solution of Eqn.(1) and the function $n(E,E')$ is found by solving the transport equation for the species with certain assumptions about the nature of the retardation process.

The advances in the chemistry of thermal hydrogen atoms described in Dubinskaya's[14] and Thrush's[15] reviews and the reactions of "hot" atoms considered in a number of other reviews[16–20] will be touched on in the present survey only where necessary. Attention is concentrated on new investigations and also on studies which had not been considered before.

II. REACTIONS OF THERMAL HYDROGEN ATOMS

1. Modern Ideas about the Reactivity of Thermal Hydrogen Atoms

The reactivity of hydrogen atoms has always been and still is the subject of extensive investigations. In view of its characteristic features—a light nucleus with a single electron—the hydrogen atom constitutes a system suitable for testing the validity of any physicochemical theory of reactivity and the existence of hydrogen isotopes permits the study of quantum and isotope effects in the kinetics of chemical reactions[21]. The commonest reaction of hydrogen atoms is of the type $A + BC \rightarrow AB + C$, i.e. a bimolecular substitution reaction (when C contains more than one atom, this is referred to as the abstraction reaction). The transition state (TS) theory has found the most extensive applications in the description of bimolecular reactions. A deficiency of this theory for atom–molecule reactions consists in the neglect of the tunnelling effect, which leads to unduly low calculated reaction rate constants at low temperatures. The "quantum-mechanical" rate constant is as a rule 1–2 orders of magnitude greater than the constant calculated on the basis of the TS theory[22].

The introduction of various corrections, as well as calculations by the method of trajectories, significantly improve the agreement between the classical and quantum-chemical calculations. A version based on a simple physical modification of the usual tunnel corrections is used, which consists in the fact that, instead of the movement of the representative point in the saddle area of the potential surface, one calculates its path along the curve connecting the classical turning points[23]. This leads to the narrowing of the calculated barrier to reaction compared with that obtained on moving along the potential energy maximum. This reaction pathway is shorter, which improves the agreement with quantum-mechanical calculations, for example, for reactions of the type

$$H + H_2 \rightarrow H_2 + H \,. \qquad (2)$$

However, in the study of the role of various corrections in the TS theory it has been shown that, although the Wigner relation usually employed has no rigorous theoretical proof, it is more consistent than any other for a wide set of reactions[23]. An attempt has been made[24] to take into account the vibrational non-adiabatic conditions in the abstraction reaction and the possibility of tunnelling within the framework of the TS quantum theory. It has been suggested that the "best" tunnelling path, common to all reactions, does not exist.

Tunnelling corrections are introduced as a rule within the framework of the "direct" mechanism of the TS theory: one considers the surface dividing the space of the reactant products in which there is a single trajectory of the movement of the representative point. This model is valid for energies which do not greatly exceed the threshold energy E_1. On the other hand, the majority of reactions proceed via the formation of a long-lived complex[25]. In the theory combining both concepts of bimolecular reactions (the "direct mechanism" and the "long-lived complex") expressions have been derived for the probability of reaction and it has been shown that they can be deduced from a general model[26]. The application of this model to the reaction between H and H_2 has been considered[27].

Starting from the 1950's the molecular orbital (MO) method began to be incorporated in chemical kinetics. A general approach based on the MO method to the abstraction reactions has been developed[28,29]. Here one uses concepts such as the stabilisation energy of the radical ΔE, the delocalisability D_r, and also the concept of the linear relation between E_a and ΔE:

$$E_a = A - B \cdot \Delta E; \; D_r = \sum_j (C_r^j)^2; \; \Delta E = C \cdot D_r$$

where C_r^j is the coefficient of the atomic orbital (AO) in the jth molecular orbital; the summation is carried out over all occupied and unoccupied MO: A, B, and C are constants.

If one considers a series of substances, for example, hydrocarbons, then the product of the abstraction reaction is H_2 and E_a should depend solely on the stabilisation energy of the radicals ΔE. The higher the stability of the radical obtained, the lower the activation energy for the reaction—a fact which has long been known in chemical kinetics[30]. However, it was not until the 1960's that it was possible to characterise the stability of chemicals quantitatively by introducing the concept of delocalisability[31], which was calculated by the MO method[31,32]. The value of the calculations lies in the accuracy and reliability of the evaluation of the coefficients of the AO. Approximate quantum-chemical methods are usually employed and only a qualitative correlation between E_a and $\Delta E(D_r)$ is obtained[31–33].

In general the MO method usually provides a description of the reactions at an adequately high qualitative level. Satisfactory results have been obtained by combining the MO method with the technique of correlation diagrams, whose construction is based on the principle of the conservation of orbital symmetry in the reaction[34]. The hydrogen abstraction reactions are symmetry-allowed and the reactivity of the C–H bond in various compounds with respect to the given reaction is determined by the electron density in the occupied and unoccupied MO of the initial molecules and by the delocalisation energy of the unpaired electron in the radical formed.

Correlation diagrams assist in understanding the course of the reaction. The abstraction reaction takes place in three stages[35]: in the first stage an electron is transferred from the RH molecule to a partially occupied orbital of the H atom and in the second stage an electron is transferred from the H atom to the lowest vacant orbital of the molecule (the spin-delocalisation stage). A charge is then accumulated in the region between the hydrogen atoms and the C–H bond is formed by the "local triplet" of two electrons, which is responsible for the dissociation of the C–H bond in the concluding, third reaction stage. The process described proceeds most readily under the conditions of an axial attack.

The application of the principle of conservation of orbital symmetry to the abstraction reaction does not account for the origin of the activation energy but makes it possible to understand certain details of the formation and dissociation of the bonds. A more general principle of the description of chemical reactions, consisting in the fact that the reaction is regarded as allowed if the distortions occurring on a given pathway do not give rise to new nodal planes in the wave functions, has now been proposed. The principle of the conservation of orbital symmetry is a special case of a more general principle[36]. The fundamental feature of the proposed analysis of the reactions is the introduction of an operator which satisfies the requirements of the prohibition of a change in nodal structure (mapping operator). The reaction is allowed if the mapping function and the wave function of the putative product overlap.

Some investigators have developed an even more general approach to the study of the kinetics of chemical reactions[37–39]. On the basis of the general principles of wave mechanics, they assume that the probability of the reaction is proportional to the overlap integral of the wave functions of the initial and final states of the species. There is then no need to consider the usual reaction path as the movement of a point on the potential energy surface, to construct correlation diagrams, and to introduce corrections for reactions via other mechanisms, for example the tunnelling mechanism: within the framework of the proposed theory, the tunnelling process is inherently included. The conclusion that heat is evolved in an exothermic reaction mainly in the form of the internal energy of molecules is one of the consequences of the wave theory of chemical reactions, which has been confirmed experimentally.

2. The Reactions of Hydrogen Atoms with Inorganic Substances

An enormous number of studies have been made on reaction (2) and its isotopic variants. One of the latest reviews[21] considers the application of the collision theory to the activated complex theory taking into account the quantum and isotope effects. The reaction dynamics have been considered in a review[40] as a consequence of trajectory calculations. Quantum-mechanical calculations have been made on the cross-sections of reaction collisions and the differential cross-sections. the reaction threshold. and the quantum state of the products have been evaluated. Theoretical studies are usually preformed on the basis of a variant of the TS theory taking into account tunnelling effects at temperatures $T < 450$ K. A satisfactory agreement with experiment is then achieved[41]. Thus the isotope effects of the reactions between D and H_2 and between H and D_2 have been calculated[42] for the range 200–4000 K. An analogous study has been made for the reactions between H and H_2 and between D and D_2.[43]

Quantum-chemical calculations make it possible to calculate the reaction thresholds and to consider the reaction dynamics and the population of the states of the products. A three-dimensional quantum-chemical study has been made[44] of the reaction $D + H_2 \rightarrow HD + H$; the reaction threshold was estimated as 0.27 ev (which virtually agrees with experiment) and intense back-scattering (ricochet) and population of the lowest levels of the HD molecule were predicted.

Reactions of the type $X + H_2 \rightarrow$ and $H + X_2 \rightarrow$, where X = H, D, or ^3H, have been investigated by the method of classical trajectories for collinear collisions and for the three-dimensional case[45]. In the first case the reaction thresholds for different isotopes differ little (0.27–0.28 eV), but in the second case the differences are significant (for the reactions of H atoms with H_2, D_2, and $^3H_2$, the thresholds are 0.271, 0.192, and 0.157 eV respectively). The calculations showed that between 0.3 and 0.45 of the collision energy is converted into the internal energy of the product. It is of interest to note that the differences in the reactivity, which are usually attributed to thermal effects, are accounted for in this instance by simple dynamic effects on collision between the species.

A detailed experimental study of the reactions of hydrogen atoms with hydrogen molecules (and the molecules of its isotopes) has been made by the usual thermal techniques. However, only studies in beams make it possible to obtain information about the fine details of the reaction mechanisms and to answer the questions which modern theories of reactivity cannot answer. In connection with apparatus difficulties, only as late as 1970 was it shown that HD, the product of the reaction between D and H_2, is scatterd "backwards" in the centre of mass system and that the internal excitation of molecules is low[46]. Since hitherto it has not been possible to overcome the difficulties associated with the experiments in beams, particularly in the detection of products, it has been suggested that the reactions of hydrogen atoms with tritium molecules, i.e. $X + {}^3H_2 \rightarrow$ (X = H or D), be investigated with detection of the products on the basis of their radioactivity[47]. The forward scattering of tritium atoms in the reaction

$$H + {}^3H_2 \rightarrow H^3H + {}^3H$$

and the back-scattering of H^3H molecules were observed, i.e. the direct abstraction reaction was noted. The above report[47] contains valuable information about the angular distribution of products, but there are no data on the distribution with respect to velocities, which precludes any conclusions concerning the form of the potential energy surface.

At ultralow temperatures the hydrogen atoms in the molecular hydrogen matrix are stabilised[48] and at $T < 1$K an average concentration of hydrogen atoms of 0.01% was attained. Since the radicals were obtained in solid H_2 with the aid of the β-decomposition of ^3H, the local concentration [H] was much higher. The temperature T_R at which the H_2 specimen containing H atoms becomes unstable and spontaneous (or stimulated) evolution of energy takes place has been found. It has been noted that T_R decreases with increasing storage time of the specimens. The authors[48] concluded that the regions of a high concentration of H atoms behave similarly to ferromagnetic domains. Subsequently a study was made of the kinetics of the accumulation of hydrogen atoms in solid H_2 containing 2% $^3H_2$ at $T < 1$ K.[49] Hydrogen atoms are stabilised by the reactions

$$H + {}^3H_2 \rightarrow H^3 \cdot H_2 \quad \text{and} \quad H + H^3H \rightarrow H_2 \cdot {}^3H.$$

It was found that at $T \cong 0.17$ K the limiting concentration is $[H] \cong 5 \times 10^{19}$ atoms cm^{-3} or 2×10^{-3}M, i.e. a high concentration of hydrogen atoms is not reached.

A study of reactions of the type $H + X_2 \rightarrow$ (X = halogen) by methods of classical and quantum mechanics showed that the main discrepancy between their results occurs near the threshold owing to the neglect of the contribution of complex trajectories in the classical treatment of the reaction pathway[50,51]. The classical description with a more "accurate" treatment of the region of the threshold (for example with optimisation of the transition state) gives rise to a good agreement of the rate constants with experimental values for the reactions of hydrogen atoms with HBr, ^{3}HBr, F_2, and Cl_2.[52] The "accurate" treatment consisted in employing in the calculations two dividing surfaces: one for energies less than the energy at the saddle point and the other for higher energies.

Modern experimental data (vibrational excitation of products, rate constants, rate constant ratios, angular distribution) permit the calculation of parameters characterising the potential energy surface, for example, for the reaction between D(H) and X_2, where X = Cl or muonium[53]. In certain cases the same reaction products can be obtained via different channels, for example:

$$H + XY \begin{cases} \rightarrow H\cdots XY \rightarrow HX + Y & (3) \\ \rightarrow X{-}Y \rightarrow HX + Y \\ \quad \vdots \\ \quad H & (4) \end{cases}$$

Reaction (3) proceeds via the "direct" mechanism and reaction (4) involves the insertion mechanism. Theoretical study showed that the probability of reaction (3) increases and that of reaction (4) falls with increasing translational energy of the hydrogen atom[54].

A few studies of the interaction of hydrogen atoms with inorganic compounds have been described in the literature. Langmuir was the first to show[55] that atomic hydrogen reacts with phosphorus and reaction parameters have been given in a review[56] †:

$$H + NO_2 \xrightarrow{k} OH + NO, \quad \Delta H^0_{298} = 122 \text{ kJ mol}^{-1}, \quad k_{300} = 2\cdot 10^{13} \text{ cm}^3 \text{ s}^{-1} \text{ mol}^{-1};$$

$$H + ClNO \xrightarrow{k'} HCl + NO, \quad \Delta H^0_{298} = -273 \text{ kJ mol}^{-1}, \quad k' \simeq k.$$

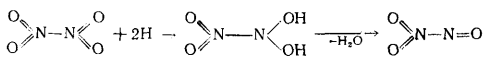
The addtion of H atoms to O_2 and NO_2 has been considered[57] and the rate constants for the reactions of H and D atoms with NO_2, N_2H_4, Cl_2, NOCl, HBr, and DBr in the range 200–700 K have been published[58–62].

In the reaction of hydrogen atoms with carbon[63] in the range 300–1220 K the formation of CH_4 (91%), C_2H_6 (8.4%), C_3H_8 (0.6%), and secondary products (C_2H_4, C_3H_6, and C_4 hydrocarbons) has been observed[63]. With increase of temperature, the yield of hydrocarbons rose and the temperature dependence of the yield of CH_4 revealed three stages of the reaction, for which the activation energies were found: 4.5 ± 1.2, 0.15 ± 0.05 and 0.94 ± 0.20 kcal mol^{-1} for the temperature ranges 1000–1200, 500–1000, and 300–500 K respectively. At 300 K approximately 1% of hydrogen atoms interact with carbon, being converted into hydrocarbons; at 1220 K this fraction reaches 4%. Methane, being the primary reaction product, can probably react further with atomic hydrogen to form other hydrocarbons[54].

On interaction of hydrogen (and deuterium) atoms with solid N_2O_4 at 77–100 K, the following reaction was observed[65]:

$$N_2O_4 + 2H \rightarrow N_2O_3 + H_2O .$$

The authors[65] believed that the preferred mechanism of the reaction involves the reduction of nitrogen:



† Here and henceforth the units of energy are given in the same way as in the original communications.

Interesting studies have been made on the interaction of hydrogen atoms with cobalt(III) and copper(II) complexes[66]. It has been shown that for cobalt compounds the reduction of the complex-forming agent is preceded by a stage involving the dehydrogenation of the coordinated ligand. The reaction results in the formation of molecular hydrogen and a coordinated radical, which reduces cobalt(III) to cobalt(II) at the instant of its formation. The reduction of copper(II) in its complexes with aminoacids, which may be regarded as square-planar compounds, proceeds via an intermediate stage in which a hydride complex is formed, omitting the dehydrogenation of the coordinated ligand:

where R is the aminoacid residue. As was to be expected, the rate constant for this reaction is independent of the chemical nature of the coordinated residues (glycine, alanine, and valine).

Since targets made up of substances subjected to the action of atomic hydrogen are as a rule deposited on glass, the interaction of glass with hydrogen atoms is of particular interest. Langmuir showed[55] that the rate of absorption of hydrogen by glass depends on the temperature of the source of atoms—a heated tungsten spiral, on the purity of the surface of the glass, and on its temperature. Later it was demonstrated[67] that only atomic hydrogen is absorbed; the absorption takes place at a temperature of the source of atoms ≥1300 K and only when the glass is cooled to 80 K. After heating the glass, the atoms recombine and the hydrogen is partly removed from its surface. Since repeated cooling of the glass (without atomisation) does not alter the hydrogen pressure, it follows that molecular hydrogen is desorbed. The H_2O, CO_2, and O_2 impurities are always present on the surface of the glass and prevent the adsorption of atomic hydrogen, being fully removed only after prolonged heating at approximately 600 K. The maximum number of atoms is approximately 1.5×10^{15} atoms cm^{-2},[55] while the number of tritium atoms on molybdenum glass is approximately 1×10^{16} atoms cm^{-2}, the sorption on glass being accompanied by the exchange of tritium for protium[68].

It has been found[69] that hydrogen atoms populate two states. The first state ($E_a = 25$ kcal mol^{-1}) is characterised by the formation of chemical bonds on the surface of the glass. The second rate ($E_a = 6.6$ kcal mol^{-1}) is determined by the van der Waals forces retaining the hydrogen atoms near the chemisorbed atoms. The populations of the two states are approximately the same. The rate of capture of thermal hydrogen atoms by Pyrex glass at 77 K and an initial hydrogen pressure of 5×10^{-2} mmHg is 2.8×10^{15} atoms cm^{-2} s^{-1}.[69] The adsorption of hydrogen atoms on zeolites depends greatly on the amount of water adsorbed on the surface[70], which can apparently be accounted for by the stabilisation of atoms on the acid surface centres. It may be that an analogous process also occurs on glass. Indeed the rate of capture of hydrogen atoms by glass differs by a factor of four for dry and wet surfaces[68].

In general the method of preliminary treatment of the surface has a major influence on the adsorption properties of the glass. The process is characterised in terms of the concept of the "recombination coefficient" γ, which is equal to the ratio of the number of atoms recombining on the surface to the total number of atoms impinging against the surface during the same period[71]. With increase of the temperature, we have $\gamma \rightarrow 1$.[15] Treatment of the glass with hydrofluoric or phosphoric acid reduces the value of γ.[72,73].

Treatment with acid apparently leads to an increase in the concentration of adsorbed atoms existing in a chemical state such that the atoms are incapable of impact recombination[68]. These conclusions have been confirmed by EPR data for the chemical state of sorbed hydrogen atoms. It has been found[72] that, as a result of sorption, the electron of the hydrogen atom is partly transferred to the *p* orbital, i.e. the properties of the sorbed species are altered (for example, the electrical properties of the solid phase, as a consequence of electron transfer to the valence band[74]). When tritium is used, this can be manifested by isotope exchange between ^3H and the molecules of substances containing "labile" hydrogen atoms[68,75].

Among reactions of hydrogen atoms with metals, the most detailed studies have been made of those with silver films on glass[76], the adsorption of hydrogen atoms on silver proceeding without an activation energy, and with sodium films at 78–178 K,[77] where low activation energies were observed. The efficiencies of the adsorption on palladium[78] of hydrogen atoms obtained in an electric discharge and by thermal dissociation have been compared. In the latter case a high efficiency was achieved and the ratio H/Pd was approximately 0.9, while the activation energy for the sorption of hydrogen by palladium proved to be 26.8 kcal mol^{-1}.

Qualitative conclusions have also been reached concerning the rates of reaction of hydrogen with COS, HN_3, and with a whole series of metals (Li, Na, Hg, Gd, Ga, Ca, Ba, Bi, Zn, Cu, and Mg) on the basis of observations of the changes in the hydrogen pressure in the system[79], but little information can be derived from these data.

It is of interest to use hydrogen atoms to investigate the surfaces of crystals[80]. The scattering from LiF crystals has been studied with the aid of monochromatic atoms. The Debye–Waller factor and the force parameter of the Morse function have been calculated from experimental data.

3. Reactions of Hydrogen Atoms with Organic Substances

(*a*) *Saturated aliphatic and cyclic hydrocarbons.* Theoretical studies on the reactions of hydrogen atoms have usually been made for the simplest hydrocarbon (methane) and in quantum-chemical calculations account has been taken of the polarisation of wave functions[81], which leads to a better agreement with experiment than the use of the London–Eyring–Polanyi–Sato (LEPS) potential[82]. The hydrogen abstraction reaction is believed to occur in a collinear collision and the exchange (substitution) is thought to proceed via a "trigonal bipyramidal" complex[81]. Since the latter process has $E_{thresh} \cong 35$ kcal mol^{-1}, it can only be induced by "hot" atoms. Theoretical studies on reactions with other hydrocarbons are limited by the possibilities of modern methods: in essence there have only been calculations by the MO method using the relation between the activation energy and certain reactivity indices, for example delocalisability[31–33].

The reactions of thermal hydrogen atoms with hydrocarbons may involve a process leading to the exchange of atoms but not via a single-stage substitution mechanism, involving instead consecutive abstraction and recombination reactions. Such reactions can be followed with the aid of an isotope technique. Apparently Shores and Moser[83] were the first to show that thermal tritium atoms can interact with saturated compounds such as n-hexane and cyclohexane. The kinetics of these reactions have not been studied and the reaction products have not been identified. The abstraction of a hydrogen atom from isobutane has been demonstrated[84].

The effect of thermal tritium atoms on propane has been studied in greater detail[85]. The activation energy for the reaction

$$H + C_3H_8 \rightarrow H_2 + C_3H_7^{\cdot}$$

is 7.1 kcal mol^{-1} at 480 K [86] and diminishes somewhat with decrease of temperature as a consequence of the different temperature dependences of the rates of reaction of hydrogen atoms with the CH_3 and CH_2 groups of propane. [^3H] propane can be formed as a result of a two-stage process—the formation of the propyl radical and its subsequent recombination, for which less energetic atoms are responsible, and also as a result of the direct substitution of hydrogen by tritium. The mechanism of the formation of side products, among which methane, ethane, ethylene, and propene have been found, can be represented schematically as follows:

$$H + C_3H_7^{\cdot} \rightarrow CH_3^{\cdot} + C_2H_5^{\cdot},$$
$$H + C_2H_5^{\cdot} \rightarrow 2CH_3^{\cdot},$$
$$H + CH_3^{\cdot} + A \rightarrow CH_4 + A \text{ etc.},$$

i.e. the rupture of C–C bonds in the radicals on collision of the latter with thermal hydrogen atoms is apparently possible. In addition one must take into account the occurrence of rapid substitution (exchange) reactions leading to the preferential rupture of secondary C–^3H bonds in alkanes[87].

The primary reaction of hydrogen atoms with cyclopropane[88] is the abstraction of hydrogen with formation of the cyclopropyl radical, the subsequent addition of hydrogen to which results in the formation of excited cyclopropane molecules. The excited molecules isomerise with formation of propene. Since the excitation energy after the addition of a hydrogen atom to the cyclopropyl radical is greater by approximately 35 kcal than the activation energy for the isomerisation of cyclopropane to propene, the probability of this process is fairly high.

The abstraction reaction has also been observed in the interaction of a stream of hydrogen atoms at a temperature of 2000 K with a cyclohexane target at 77 K; the activation energy for the abstraction of hydrogen was 6–8 kcal mol^{-1}.[89] This is the primary reaction and is followed by a disproportionation reaction (between a tritium atom and a cyclohexyl radical) with formation of cyclohexane, the addition of a tritium atom to which accounts for the appearance of labelled cyclohexyl radicals in subsequent processes. When the target is heated, the reactions of cyclohexyl radicals—disproportionation, recombination, and addition to a double bond—occur near the polymorphic transition temperature (160–190 K), which can be explained by the self-diffusion occurring near the phase transition temperatures[90]. The ratio of the disproportionation and recombination rate constants (k_{dispr} and k_{rec} respectively) for the cyclohexyl radicals at 77 K is approximately 5 ± 1, while E_a(rec.)–E_a(dispr.) $\cong$ 300–400 cal mol^{-1}. In a study of the temperature dependence of the destruction of cyclohexyl radicals in the range 70–145 K, it was found[91] that the yield of bicyclohexyl increases with increase of temperature, the increase being sharp as the phase transition temperature of cyclohexene is traversed and $k_{dispr}/k_{rec} \propto T^{-5.1}$. It has been suggested[91] that the "heating" of the molecular movement in the phase transition is manifested most effectively in the radical recombination reaction.

It is of interest that a high reactivity in the hydrogen abstraction reactions has been observed for a series of silanes [SiH_4, Si_2H_6, CH_3SiH_3, $(CH_3)_2SiH_2$] compared with the hydrogen analogoues[92,93]. Apparently the difference can be accounted for by the difference between the activation energies, since the pre-exponential factors are similar in the two cases and the decrease of the activation energy corresponds to the decrease of the Si–H bond energy.

(*b*) *Unsaturated hydrocarbons.* There have been few theoretical studies on the reactions of hydrogen atoms with unsaturated compounds. As a rule, they are confined to an examination of correlations between the rate constants and reactivity indices, for example, the localisation energy, calculated by simple MO methods. The height of the barrier to the reaction involving the addition of a hydrogen atom to ethylene has been calculated only recently by the Hartree–Fock method with optimisation of the geometry. The calculated barrier (5.1 kcal mol^{-1}) is close to the experimental value[94].

A number of investigators have proposed mechanisms of the possible reactions, devised by analysing the products of the reactions of hydrogen atoms with hydrocarbons, and also reaction parameters and EPR data[95–105]. These mechanisms have many features in common: in the first stage the hydrogen atom addition process results in the formation of radicals[96,104], which is followed by rapid secondary reactions—the disproportionation and recombination of the radicals with one another or with hydrogen atoms and, in the case of deuterium and tritium atoms, disproportionation and recombination of mixed radical species take place. Furthermore, in virtually all cases dimerisation reactions are observed, but the relative rate of the latter is low. For example, the ratio of the amount of propane obtained in the reaction of hydrogen atoms with propene to the amount of the dimerisation product (2,3-dimethylbutane) is approximately 9,[105] while the ratio to the total amount of all the hexane isomers obtained is approximately 11.[103]

For hydrocarbons with a carbon chain longer than that of propene, account must be taken of specific reactions associated with the position of the double bond. For example, a shift of the double bond with formation of *trans*-but-2-ene is characteristic of the reactions of hydrogen atoms with but-1-ene. The reactions of hydrogen atoms with buta-1,2-diene and buta-1,3-diene lead to different final products, since the addition of hydrogen to buta-1,3-diene can involve either double bond, while the "non-terminal" addition to buta-1,2-diene is energetically unfavourable, which leads to the formation of but-2-ene as the main product.

In the deuteration of a solid olefin there is a possibility of H–D exchange between the hydrogen atoms and the free alkyl radicals[106,107]:

$$\dot{R}_H + D \rightarrow \dot{R}_{(D)} + H \ .$$

On passing to unsaturated cyclic compounds, the same features are observed as for olefins. Thus, when tritium atoms reacted with cyclohexene[108], an addition reaction was observed and cyclohexane, cyclohexene, and bicyclohexyl, obtained as a result of consecutive recombination–disproportionation reactions, were found among the labelled reaction products. At low temperatures the rate constant for the recombination reaction is lower than that for the disproportionation reaction, but k_{rec} increases faster than k_{dispr} with increase of temperature. The activation energy for the addition of hydrogen atoms to cyclohexene is approximately 1.5–3.5 kcal mol^{-1},[108] which is consistent with the calculation based on the Semenov–Polanyi rule.

When tritium atoms were allowed to react with cyclohexylcyclohexene isomers, the formation of isomeric compounds together with hydrogenation products was observed. Furthermore, the proportions of the products and the ratios k_{dispr}/k_{rec} depend on the nature of the solvent, i.e. are related to the different rigidities of the maxtrix[109].

(*c*) *Compounds containing functional groups.* In the reactions of hydrogen atoms with alcohols the main process is the abstraction of hydrogen from the carbon atom in the α-position relative to the OH group and the subsequent formation of alkanes and aldehydes[110–112]:

$$H + CH_3OH \rightarrow H_2 + \dot{C}H_2OH \xrightarrow{H} \dot{C}H_3 + OH \ ;$$

$$H + CH_3CH_2OH \begin{cases} \rightarrow H_2O + C_2H_5 \xrightarrow{H} C_2H_6^* \rightarrow 2CH_3 \begin{cases} \rightarrow C_2H_6 \\ \xrightarrow{H} CH_4 \end{cases} ; \\ \rightarrow CH_3\dot{C}HOH + H_2 \begin{cases} \xrightarrow{H} CH_3CHO \\ \xrightarrow{H} CH_3\dot{C}H \rightarrow C_2H_4 \end{cases} ; \end{cases}$$

$$H\,(D) + CH_2{=}CHCH_2OH \rightarrow CH_2{=}C\dot{H}CHOH + H_2\,(HD) \ .$$

t-Butyl alcohol, where the abstraction of the OH group is the dominant process, constitutes an exception. The rate constants for the primary reactions are presented in Table 1. The secondary reactions are determined by the nature of the radical obtained. Thus the addition reaction with formation of propanol and propionaldehyde predominates for allyl alcohol.

Table 1. The rate constants for the reactions of hydrogen atoms with aliphatic alcohols [$k = A \exp(E/RT)$].

Alcohol	A, cm^3 s^{-1} mol^{-1}	E, cal mol^{-1}	References
CH_3OH	$6.5 \cdot 10^{12}$	5440±150	[110]
	$1.3 \cdot 10^{13}$	5260	[212]
C_2H_5OH	$(4.2 \pm 0.4) \cdot 10^{19}$	4200±300	[112]
$(CH_3)_3COH$	$(4.0 \pm 0.4) \cdot 10^{13}$	8200±650	[112]

The mechanism of the reaction of hydrogen atoms with dimethyl ether has been published[110]:

$$H + CH_3OCH_3 \rightarrow \dot{C}H_2OCH_3 + H_2$$

$$CH_3OCH_3^* \rightarrow \dot{C}H_3 + \dot{O}CH_3 \begin{cases} \rightarrow CH_2O + H_2 \\ \rightarrow \dot{C}H_3 + OH \end{cases} .$$

According to the authors, the identity of the activation energies for this reaction and the reaction of atomic hydrogen with CH_3OH indicates the similarity of the mechanisms of these processes.

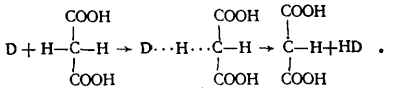
A characteristic reaction of hydrogen atoms with nitrocompounds (nitromethane, nitrobenzene, nitroethylene, and nitroisopropene) is the addition of a hydrogen atom to the nitro-group.

$$H + R{-}N\!\!<\!\!\begin{matrix}O\\O\end{matrix} \rightarrow R{-}\dot{N}\!\!<\!\!\begin{matrix}O\\OH\end{matrix} \ ,$$

which is a more effective hydrogen atom acceptor than the benzene ring and the C = C bond[113]. The NCO and NCS groups also effectively capture hydrogen atoms and the mode of reaction in this instance depends significantly on the nature and position of the subsequent substituent (if such exists) relative to the NCO (NCS) group. Thus a hydrogen atom adds to the benzene ring of phenyl isocyanate, but, after the introduction of a second functional group into the latter (CH_3, NO_2, $OCNC_6H_4CH_2$), the double bond of the NCO or NO_2 groups is attacked[113], since the second substituent alters significantly the distribution of electron density in the molecule.

When malonic and methylmalonic acids react with thermal hydrogen atoms, the C–H bond is ruptured, the dissociation of a carbon–carbon bond is not observed[114,115], and the

hydrogen atom of the methylene group is abstracted:



A similar reaction is characteristic also of malonamides.

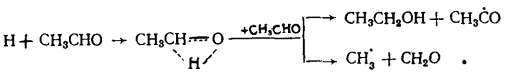
If the initial acid contains double bonds, the latter are hydrogenated. For example, it has been observed that the main process in the reaction involving oleic acid[116] is the formation of stearic acid and the ratio of the contributions of the addition and substitution reactions was approximately 2.6.

The reaction of atomic hydrogen with aldehydes proceeds in the same way as for carboxylic acids, i.e. involves the abstraction of a methylene hydrogen atom, which leads to the formation of keten, methane, ethane, and carbon monoxide[117]:

$$\begin{aligned}
&H + CH_3CHO \xrightarrow{k_1} CH_3\dot{C}O + H_2 ,\\
&CH_3\dot{C}O + H - \begin{cases} \xrightarrow{k_2} CH_3 + CHO \\ \xrightarrow{k_3} CH_2CO + H_2 \end{cases},\\
&CHO + H \rightarrow CO + H_2 ,\\
&H + CH_3 + A \rightarrow CH_4 + A ,\\
&2CH_3 \rightarrow C_2H_6 ,\\
&H + CH_2CO \rightarrow CH_3 + CO ,
\end{aligned}$$

where $k_2/k_3 \cong 4.7$ and $k_1 = (2.6 \pm 0.2) \times 10^{12} \exp(-2600/RT)$ is close to the corresponding rate constant for the reaction of atomic hydrogen with methanol.

Virtually none of the communications concerning the action of atomic hydrogen on compounds containing the carbonyl group provides information about the addition of hydrogen atoms to the C=O bond. An impression has been created that the C=O bond differs so much from the C=C bond that the addition reaction is impossible. Only recently[118], in a study of the reactions between atomic hydrogen and acetaldehyde, was ethanol detected as the reduction product. To account for its formation, the authors[118] proposed the following mechanism:



The excess energy evolved in the addition of hydrogen (21 kcal mol^{-1}) is sufficient for the occurrence of the above reactions.

When tritium atoms act on $C_5H_{11}X$ (X = SH, NH_2, OH, or COOH) at 77 K, pentane is formed, whose tritium content is correlated with the bond energies of the substituents[119].

(*d*) *Aromatic and Heterocyclic compounds.* When thermal hydrogen atoms react with aromatic compounds, the main reaction is the addition of a hydrogen atom to the benzene ring with formation of radicals of the cyclohexadienyl type[120]. Such reactions have been observed for a large number of substances[121-127], but in many instances the competitive abstraction of a hydrogen atom from the substituent or its addition to the C=C bond of the side chain takes place. For halogenotoluenes, the rate constant for the abstraction of a benzyl hydrogen atom is close to the value determined by diffusion[128].

The rates of abstraction reactions involving mesitylene, tetralin, phenylcyclohexane, and thiophenol are comparable to the rate of addition to the benzene ring and, in the case of phenol and benzyl alcohol, the abstraction of the OH group takes place together with addition to the benzene ring:

$$R{-}OH + H \rightarrow R^{\cdot} + H_2O .$$

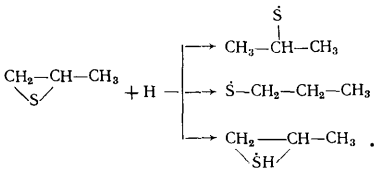
The difference between the activation energies for the abstraction and addition reactions is 0.5 kcal mol^{-1}.[129] For aniline and benzyl chloride, the abstraction reactions are the main processes, while in the case of nitrobenzene and nitrosobenzene the reactions involving addition to the ring are not observed at all. Hydrogen atoms add almost completely to the N=O bond.[123]

When hydrogen atoms attack the side group, π-electron radicals are formed in which there is resonance interaction, according to EPR data, of the unshared electron with the π-electron system of the ring (phenol, which gives rise to σ-radicals, is an exception).

The kinetics of the accumulation of radicals are described satisfactorily in this case by a model taking into account the diffusion of hydrogen atoms from the gas phase to the solid phase and the occurrence of a first-order chemical reaction[97]. The low rate of accumulation of radicals observed for a series of substituted benzenes (amines and alcohols) compared with benzene is apparently associated with the fact that in these substances the diffusion coefficient of hydrogen atoms is low owing to the presence of hydrogen bonds[130].

When tritium atoms react with benzene at 77 K, ≤5% of the labelled parent compound is formed, while the remaining products are hydrogenation products, mainly [^{3}H] cyclohexene, which indicates a low rate of the disproportionation reaction[131]. Under the same conditions, considerable amounts of [^{3}H] toluene are formed from toluene[132]. In the reactions with benzene derivatives there is a possibility of the substitution of functional groups[133].

For heteroaromatic compounds, the same processes have been observed as for aromatic systems, i.e. the addition of a hydrogen atom to the unsaturated bonds in the ring[134]. For certain sulphur compounds, for example, methylthiiran, the addition of a hydrogen atom to the sulphur heteroatom has been observed[135]:



In the general case the dissociation of the C–H bond in the α-position relative to the heteroatom is characteristic of saturated heterocyclic compounds[126,135].

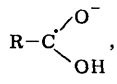
(*e*) *Polymers.* Substances of this class react with hydrogen atoms either with abstraction of hydrogen from the saturated molecules or via addition to the benzene ring, for example, in polystyrene[136], polymethylstyrene, and poly(ethylene terephthalate)[137,138]. Data for radicals detected by EPR in high-molecular-weight compounds have been examined in detail in two studies[139,140].

The activation energies for the abstraction of a hydrogen atom from the main polymer chain are, for example 2 and 1.2 kcal mol^{-1} for the reactions involving polyisobutylene and poly(ethylene oxide) respectively at 100–150 K and the temperature dependence of the rate constants does not obey the Arrhenius law[134]. These facts were explained by the considerable contribution of the tunnel transfer of hydrogen atoms to the rate of the process[141].

(f) Biologically active substances. The interaction of hydrogen atoms with biologically active compounds has been little studied. Moser and coworkers[75] were the first to obtain labelled sucrose, glucose, and starch by acting on frozen targets with "heated" tritium atoms. The reaction is believed to proceed in two stages: with abstraction of a hydrogen atom and subsequent recombination with a tritium atom. The same method has been used to obtain [^{3}H] alanine[142] and [^{3}H] ribonuclease[143] with a fairly high specific activity. Tritium-labelled adrenocorticotropin[144], morphine[145], and valine[116] with specific activities of 15, 2.7, and 3 mc mmol^{-1} respectively and certain peptides[146] have been obtained under the conditions of a microwave discharge. [^{3}H] ribonuclease with a specific activity of 1.5–3.5 mc mmol^{-1} has been obtained under conditions where tritium atoms were generated in a silent electric discharge[147]. A high specific activity of biologically active compounds can be achieved using an arc discharge[148].

The complexity of the study of the mechanism of the interaction of hydrogen atoms with biological objects consists primarily in the presence in the latter of numerous functional groups and also of secondary and tertiary structures in proteins. The steric factor plays here a significant role and the conclusion that such reactions occur on the surfaces of large molecules is particularly important in this connection[75, 115].

The formation of radicals from aminoacids (Table 2) is associated, as usual, with abstraction of hydrogen atoms from saturated molecules and their addition to unsaturated and aromatic molecules. However, the hydrogenation of aromatic bonds in the ring is negligible for phenylalanine[116], although radicals of the cyclohexadienyl type have been detected in reactions of atomic hydrogen with aromatic aminoacids (phenylalanine, tyrosine, and tryptophan)[149]. For proline, ring opening has been noted[150]. Furthermore, there is a possibility of deamination (and decarboxylation) processes associated with the addition of hydrogen atoms to the amino-group[142] (or with formation of radicals of the type



, which can be stabilised by protonation[151]).

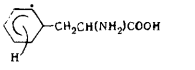
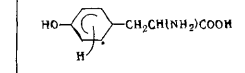
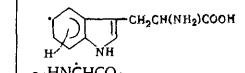
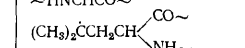
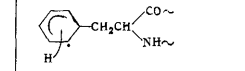
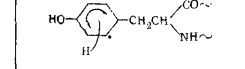
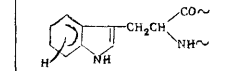
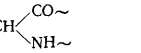
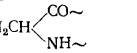
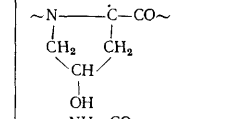
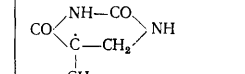
The action of hydrogen atoms on the peptide bond, leading to the formation of molecular fragments with a lower molecular weight, is important for polyaminoacids. The presence of aromatic aminoacid molecules in the chain leads to a greater stability of the polypeptide[152].

An important but little investigated process is the intramolecular distribution of tritium in labelled molecules obtained on treatment with tritium atoms. The α-, β-, and γ-positions in [^{3}H] valine contain 7.1, 32.7, and 60.2% of tritium respectively[116]. The predominant concentration of tritium in the β-position has also been observed in labelled L-isoleucine and L-alloleucine[152], which is due to differences between the bond energies and the activation energies for the abstraction of hydrogen from different positions in the molecule. In the cleavage of [^{3}H] ribonuclease[147] into individual aminoacids, the greatest proportion of tritium was found in methionine, glycine, and histidine, while the tritium content in threonine, serine, and arginine proved to be insignificant.

Apart from labelled parent compounds, products resulting from deamination, carboxylation, and the abstraction of the OH group, with a high specific activity, have been detected in the interaction of tritium atoms (0–0.2 eV), obtained by the thermal dissociation method, with aromatic aminoacids (tyrosine and phenylalanine)[154].

Tritium atoms with an average energy of approximately 0.02 eV mainly abstract hydrogen atoms from the β-position in the side chains of phenylalanine and tyrosine[155,156] which agrees qualitatively with calculations by the MO method[157,158].

Table 2. The radicals formed in the interaction of hydrogen atoms with certain biologically active compounds.

Compound	T, K	Radical	References
Glycine	298	$^+H_3NĊHCOOH$	[152]
Alanine	298	$CH_3ĊHCOOH$	[152]
Leucine	298	$(CH_3)_2ĊCH_2CH(NH_2)COOH$	[152]
Phenylalanine	77–300		[149]
Tyrosine	77–300		[149]
Tryptophan	77–300		[149]
Polyglycine	77–300	~$HNĊHCO$~	[150]
Polyalanine	77	$CH_3ĊHCO$~	[150]
Poly-DL-alanine	77	~$HNĊ(CH_3)CO$~	[150]
Poly-L-serine	77	~$HNĊHCO$~	[150]
Poly-DL-leucine	77–300		[150]
Poly-L-phenylalanine	77–300		[149]
Poly-L-tyrosine	77–300		[149]
Poly-DL-tryptophan	77–300		[149]
Poly-L-methionine	77	$ṠCH_2CH_2CH$	[150]
Poly-L-lysine	77	~$HNĊHCO$~	[150]
Poly-L-proline	77–300	$ĊH_2CH_2CH_2CH$	[150]
Poly-L-hydroxyproline	77–300		[150]
Thymine, dihydrothymine	160–300		[153]
Penicillamine	160–300	$HOCOCH(NH_2)C(CH_3)_2Ṡ$	[115]

In the temperature range 30–200 K tritium atoms also react with aminoacids and the experimental activation energies for these reactions are close to zero and below 60 K the limit of the chemical reaction rate is reached[156,159]. This makes it possible to suggest the occurrence of tunnel reactions and to estimate the parameters of the barrier. The probabilities of reactions involving the abstraction of hydrogen from different aminoacids by tritium atoms at 300 K have been compared[160] with the reactivity indices—the boundary electron density and delocalisability, a satisfactory qualitative agreement being found.

III. REACTIONS OF "HOT" HYDROGEN ATOMS

1. Models of Chemical Reactions Involving "Hot" Hydrogen Atoms

Theoretical studies of the reactions of atoms having an excess of kinetic energy have developed in two directions. On the one hand, attempts have been made to relate the yields of reactions to the characteristics of the moderation process and on the other it was endeavoured to understand the details of the mechanism of the elementary chemical reaction under the conditions of high energy.

In Eqn.(1) the probability of the reaction $p(E)$ can be represented by the relation

$$p(E)=\sigma_r(E)/[\sigma_r(E)+\sigma_n(E)],$$

where $\sigma_r(E)$ is the "reaction" collision cross-section, i.e. the cross-section of the collision leading to reaction, and $\sigma_n(E)$ is the cross-section of the "non-reaction" collision in which the "hot" atom loses energy without entering into a reaction with formation of a stable product. The main efforts were concentrated on the search for an analytical expression for $n(E,E')$. Thus Estrup and Wolfgang[161] used the ideas of the physics of the moderation of neutrons, from which it followed that, for neutral species generated with $E \gg E_2$ (E_2 is the "upper limit" to the occurrence of chemical reactions), the energy spectrum of the species can be described by the Fermi function

$$n(E, E')\,dE'=n(E')\,dE'=dE'/\alpha E',$$

where α is the average loss of energy determined as the retardation coefficient for two consecutive collisions: $E_{i+1}=E_iE^{-\alpha}$. An expression for α can be obtained by specifying the moderation mechanism. Since the form of the function $p(E)$ is not clear, the parameter

$$I=\int_0^\infty p(E)\,dE,$$

called the integral reaction probability, was introduced[162].

Using the concepts enumerated above, an expression was obtained for the yield of the reaction:

$$R=1-\exp\left(-\frac{f}{\alpha}I\right),$$

which is at present widely used in the chemistry of "hot" atoms (f is the geometrical probability of the collision calculated from the mole fractions of the substances and the covalent atomic radii). Subsequently the equation was supplemented by corrections for the influence of added substances and for the phenomenon of the "combustion" of the species in the course of the reaction[163]. The Wolfgang equation agrees satisfactorily with experiment, i.e. a relation of the type

$$-\ln(1-R)=\frac{f}{\alpha}I$$

persists when the ratio f/α is varied within wide limits.

The ratio f/α has been calculated from the experimental conditions and the efficiency of moderation. The quantity I has been determined graphically. The integral probabilities of many reactions of "hot" ^3H atoms have been found in this way. Thus $I=0.1$ for the reaction $^3H+CH_4 \rightarrow CH_3^3H+H$, i.e. approximately one of ten collisions leads to reaction[161]. The possibility of using the ideas of the physics of the moderation and reactions of neutrons for chemical reactions proved to be fruitful, because it was possible to replace the reaction cross-section by the integral probability and the moderation process by a simple collision model.

The Wolfgang equation holds better the higher the initial energy of the atoms and the smaller the influence of non-elastic collisions. In studies since 1969 α has been calculated on the basis of a retardation scheme for rigid spheres. Subsequently account was taken in the moderation model of the possibility of "soft" collisions and it was found that the reaction yield should increase for a "softer" potential[164]. After taking into account the scattering anisotropy, it was shown that α decreases under these conditions, but the form of the collision density function remains unaltered[165].

The models examined are valid for energy ranges remote from the energy of the source of "hot" atoms, i.e. $E \ll E_0$ (but $E_0 \gg E_2$)[166]. In the theory developed by Porter[167-169] these limitations were removed by solving the equation for the reaction probability as a function of energy; account was also taken of the thermal movement of the target species. Porter's equation for the yield of the reaction with formation of the ith product is

$$R_i(E)=p_i(E)+\left[1-\sum_j p_j(E)\right]\int_0^\infty R_i(E')\,W(E, E')\,dE', \qquad (5)$$

where $p_i(E)$ is the probability of the formation of the product in the first collision, $[1-\sum_j p_j(E)]$ the probability of avoiding reactions with formation of all the products, $W(E,E')$ the probability of a change in the energy of the atom ($E \rightarrow E'$) in a non-reactive collision, and $p_i(E')$ the probability of the reaction in the collision of reactants with $E=E'$. Porter derived Eqn.(5) by a rigorous mathematical procedure, although it can be formulated on the basis of the most general intuitive considerations. An analytical solution of this equation is possible on the assumption of a simple moderation model, namely collisions of the bard sphere type[170].

Thomsen[171] treated the reactions differently. His formulation of the problem differs by the fact that, instead of seeking a solution for the stationary distribution of "hot" atoms, he suggested that one determine the probability of the reaction for an individual atom in the course of its moderation. The moderation process was then modelled as a continuous process.

Theoretical studies have shown that the atomic spectrum depends greatly on the properties of the medium. It was concluded that the probabilities of the reactions of "hot" atoms with different substances should be compared by studying experimentally the yields of reactions in the presence of a moderating substance. Naturally the inert gases were chosen for this purpose. Different variants of stochastic methods began to be used for quantitative estimates. In particular, the collision densities at different temperatures of the gas medium have been calculated for ^3H atoms with "intermediate" energies (0.5–2 eV) and for three potentials (the solid sphere, Lennard–Jones, and $1/r^6$ potentials). It was shown that, for an energy of the source of 0.5 eV, oscillations in collision density are observed, which had been predicted theoretically for the moderation of neutrons[172], and for $E < 0.5$ eV a rapid approach to the collision density corresponding to the $1/E$ spectrum is observed. The influence of temperature is manifested by the fact that, in the energy distribution spectrum of the species, a "tail" appears in the high-energy region for $E > 0.5$ eV.[173]

Subsequently a stationary model of the moderation of "hot" species was proposed in which a Maxwell distribution of "hot" atoms with an average temperature $T_R(t)$, depending on the time elapsed from the instant of generation of the atoms, was assumed[174]. A stationary state obtains when $dT_R(t)/dt=0$. An analytical solution of the Boltzmann equation for the transport of the species is then possible, and the final expression is similar to the Arrhenius equation.

The condition for the attainment of a stationary state up to the instant when chemical reactions begin to occur to an appreciable extent is very important for the application of this model. However, it has been established by the Monte Carlo method that the stationary states do not obtain a retardation[175,176]. A study was therefore undertaken with the aim of a more accurate solution of the Boltzmann equation and a clear-cut framework has been found for the application of the proposed theory: the time scales in the description of the moderation processes and the reactions must be separated[177]. Conditions have been established under which the solution of the Boltzmann equation satisfies the calculations by the Monte Carlo method or agrees with the distribution of the species with respect to velocities corresponding to a Maxwell distribution at an effective temperature[178].

The transfer of the ideas of nuclear physics to moderation and the reactions of chemical species proved so productive that investigators were inspired to consider more far-reaching analogies between chemical and nuclear reactions. The description of resonance reactions involving neutrons is widely used in nuclear physics. The Breit–Wigner formula relates the reaction cross-section to the resonance parameters. It has been suggested that resonance scattering cross-sections and reactions involving a polyatomic molecule correspond to the resonance cross-section for the scattering of the "hot" atom by the attacked atom in the molecule and the case where the cross-sections for the reactive and non-reactive collisions of the "hot" atom with a molecule involve only one Breit–Wigner resonance was examined[37].

These qualitative ideas required a rigorous mathematical justification, which was subsequently provided[38]. The following expression has been obtained for the yield of the "hot" reaction:

$$R \propto \Gamma/\beta ,$$

where Γ is the width of the resonance, $\beta = \mu'/(\mu' + m)$ the "isotope" factor associated with the masses of the interacting atoms and characterising the degree of localisation of the "hot" reaction, μ' the mass of the part of the molecule involved in the formation of the resonance state, and m the mass of the "hot" atom. The authors[38] believe that the similarity of the mass μ' to the mass of the attacked atom (μ' was calculated from the isotope effect in the reactions involving the abstraction of hydrogen by "hot" tritium atoms) constitutes significant evidence for the occurrence of resonance in the reaction. The value of the proposed interpretation of the mechanism of "hot" reactions consists in the fact that, within the framework of the theory, one can find an explanation of the marked influence of the electronic structure of the molecules and of the difference between the bond energies on the yield of the reaction—a fact which is well known in the chemistry of "hot" species[179–181].

We shall consider the achievements of the theoretical studies in the chemistry of "hot" atoms in relation to two reactions, namely $H + H_2 \rightarrow H_2 + H$ and $H + CH_4 \rightarrow CH_3 + H_2$, and also substitution reactions of the type $^3H + CH_4 \rightarrow CH_3{}^3H + H$.

2. The $H + H_2 \rightarrow H_2 + H$ Reaction and Its Isotopic Variants

The ratio of the integral probabilities of the reactions of "hot" recoil atoms, i.e.

$$^3H + HD \left\langle \begin{array}{l} \rightarrow H^3H + D \\ \rightarrow D^3H + H \end{array} \right. ,$$

has been calculated[170] as $I_{H^3H}/I_{D^3H} = 0.62 \pm 0.06$; the corresponding value, calculated in another study[182] from the results of trajectory calculations, proved to be 0.7 ± 0.1.

For the reactions $^3H + H_2 \rightarrow H^3H + H$ and $^3H + D_2 \rightarrow D^3H + D$, experiment yielded $I_{H^3H}/I_{D^3H} = 1.14 \pm 0.06$, while the calculated value is 1.18 ± 0.05. Since a satisfactory agreement has been observed between the calculated and experimental data, it is reasonable to consider in greater detail the essential features of the calculations yielding valuable information about the details of the reaction mechanisms.

The potential surface for a reaction of the type $A + BC \rightarrow$ was constructed[182] on the basis of the Morse function taking into account the energy levels obtained in the solution of the secular equation and neglecting overlap (the Hückel method)[182]:

$$U = E_1 + E_2 + \sum_{ij} H_{ij};\ H_{ij} = -D_{ij} \exp\left[-\beta_{ij}(r_{ij} - r_{0ij})\right] ,$$

where D_{ij} is the dissociation energy, β_{ij} the Morse constant, and r_{0ij} the equilibrium distance. The usual procedure was used in the subsequent calculations. It was found that, for low energies of the ^3H atoms (approximately 10 eV), the reaction cross-sections are a maximum for attack along the H–H (H–D, D–D) bond. For energies of approximately 35 eV, the cross-section is a maximum when attack takes place at right-angles to the H–H bond. This collision, leading to the abstraction of an atom (the "stripping" mechanism), is related to the "spectator" model: the process takes place in such a way that one atom is assumed to be abstracted, while another behaves as a passive witness of the event. On further increase of E to approximately 100 eV, the cross-section shifts towards collision angles $>\pi/2$, which indicates back-scattering of the reaction product ("rebound stripping"). In this process the third atom is a partner in the removal of the excess energy transferred by the "hot" atom on collision. The product molecule, formed as a result of this process, has a lower energy than the molecule obtained via the "spectator" mechanism (for the same collision energy).

Detailed calculations for reactions of the type

$$^3H + HD \left\langle \begin{array}{l} \rightarrow H^3H + D \\ \rightarrow D^3H + H \\ \rightarrow {}^3H + D + H \end{array} \right. \qquad (6)$$

have been made recently[170] by the trajectory method up to $E_H = 60$ eV and cross-sections [including the cross-section of reactions (6)] and the integral probabilities of reactions have been obtained taking into account the contribution of non-elastic collisions to the atom moderation spectrum. It was found that the calculated ratio $I_{H^3H}/I_{D^3H} = 0.7$ agrees fairly well with the results of calculations based on simpler mechanisms (collision of the solid sphere type) and with experiment only in the region of low energies (of the order of several eV). For ^3H atoms with $E = 60$ eV, the calculated ratio $I_{H^3H}/I_{D^3H} = 1.8$, which is greater than the experimental value (for "hot" recoil atoms) and the value calculated on the basis of a simpler model (0.8). According to the authors[170], the reason for this discrepancy consists in the fact that their model is based on the assumption of a small role of secondary dissociation reactions of the H^3H and ^3HD molecules. The agreement between the calculations based on the simple model and experiment is apparently attained as a result of the superposition of two errors—associated with the use of an incorrect function for the energy distribution of atoms (its calculation was based on the assumption of a moderation mechanism in accordance with the law governing hard sphere collisions) and the neglect of secondary dissociation.

Thus an exact description of the mechanism of even the simplest reactions is still not available, although there is no doubt that computational methods involving computers have thrown much light on it.

3. The Reaction $H + CH_4 \rightarrow H_2 + CH_3$ and Its Isotopic Variants

The abstraction reaction involving thermal hydrogen atoms is well known. For "hot" H*, D*, and ^3H* atoms, obtained by photolysis or via a nuclear reaction, channels other than the abstraction reaction

$$^3H + CH_4 \rightarrow CH_3 + H^3H, \quad (7)$$

have been discovered, namely

$$^3H + CH_4 \rightarrow CH_3{}^3H + H, \quad (8)$$

$$^3H + CH_4 \rightarrow CH_3 + H + {}^3H, \quad (9)$$
$$^3H + CH_4 \rightarrow CH_2{}^3H + 2H.$$

The calculation thresholds for the abstraction and substitution reactions, equal to 0.66 and 1.54 eV,[183] agree with experimental values of 0.3 and 1.5 eV.[6,184,185]. Experiments with $CH_4 + CD_4$ mixtures showed that $(H^3H/CH_4) : (H^3H/CD_4) = 1.4$, i.e. that CD_4 is somewhat less reactive in the abstraction reaction than CH_4. The ratio $(CH_3{}^3H/CH_4) : (CD_3{}^3H/CD_4) = 6.9$ shows that CD_4 is significantly less reactive in the substitution reaction than CH_4.[186]

In the first trajectory studies the CH_3 group was approximated by a structureless unit with a mass of 15 and the LEPS potential was adopted as the potential energy surface[187]. It was found that the abstraction and substitution reactions are of the "direct" and "concerted" type, i.e. they proceed without the formation of a long-lived complex: the length of the bond dissociated increases monotonically with the simultaneous formation of a new bond. This process is apparently valid for $E \cong 1.5$–2 eV. For a higher energy (~10–15 eV), abstraction again predominates, but the mechanism is in this instance different—this is a "stripping" reaction. Since the CH_3 group has been represented by a single species, the problem of the details of the mechanism (whether or not the Walden inversion occurs) was not discussed in the above investigation[187].

Certain theoretical evidence for the mechanism of the Walden inversion has been obtained by considering the movements of all the atoms in the reaction between H and CH_4 along an empirical potential surface (no account was then taken of the interaction between the displaced H atom and the other three hydrogen atoms)[188,189]. The threshold of the abstraction reaction has been estimated as 0.4 eV and the cross-section is a maximum ($3.5\ Å^2$) for 2.7 eV. The authors showed that the calculated ratio of the probabilities of reactions (8) and (7) is not 0.25, as was observed in the experiments. Since it was assumed in the calculations that there is no Walden inversion, the above discrepancy throws doubt on the validity of this assumption.

In subsequent studies this limitation in the interaction between atoms was abandoned and all the hydrogen atoms began to be regarded as equivalent. It was shown[190] that the substitution of hydrogen and deuterium in the reaction between ^3H and CH_2D_2 involving the Walden inversion must be equally probable, which agrees with experimental results[9,186]. However, the calculations were performed using data for the reactions of tritium atoms with CH_4 and CD_4, i.e. semiempirically. These studies were followed by a series of investigations by MO methods in terms of various approximations, which yielded contradictory information about the role of the Walden inversion in the reaction mechanism[191,192].

The most detailed study has been made by Raff[82], who calculated the minimum on the CH_5 potential energy surface and calculated the cross-sections by the method of trajectories. It was found that the threshold of the abstraction reaction corresponds to 0.25 eV, while that of the substitution reaction corresponds to 1.5–1.6 eV. The cross-section of the abstraction reaction is a maximum at 1.5 eV and that of the substitution reaction is a maximum at 6 eV. The fragmentation process (9) begins according to these calculations at $E \cong 5$ eV and reaches a maximum at 10 eV, its probability decreasing slowly up to 40 eV. In the substitution reactions there is not more than 50% inversion, i.e. the Walden inversion does not constitute the only reaction mechanism. This conclusion was reached after considering the ^3H–C–H angles in trajectory studies of substitution reactions. In order to compare the results of the calculations with the results of experiments carried out previously for recoil atoms, Raff used Porter's equation for a stationary target[167] in conjunction with his own data obtained from trajectory studies. The limit of the ratio $H^3H/CH_3{}^3H$ (for high values of E), equal to 0.79, proved to be in excellent agreement with Wolfgang's experimental data for recoil atoms[18]. The ratio $CD_3{}^3H/D^3H$ proved to be somewhat smaller than the experimental value. Agreement with experimental data has not been achieved for photolytic atoms ($E \cong 2.8$ eV): calculation yielded $H^3H/CH_3{}^3H = 8.7$, while the experimental value is ~4. This may be because the Walden inversion mechanism plays a major role for a low energy.

4. Abstraction Reactions and the Influence of the Bond Energy on Their Yield

In the chemistry of "hot" tritium atoms the influence on the abstraction reaction of a small change in the bond energy E_b of the abstracted atom is well known[9,180] and the cause of this phenomenon has been the subject of discussions[17,162,179–181,193]. According to one concept, the influence of the bond energy is seen when an intermediate collision complex is formed, while according to another this happens when the abstraction reaction proceeds via a "stripping" mechanism analogous to the familiar mechanism of nuclear reactions. The fact that the bond energy must influence the probability of the abstraction reaction when a collision complex is formed is so evident that it does not require elucidation. However, numerous data have shown that the reactions of "hot" atoms proceed via a "direct" mechanism. Therefore this explanation is not satisfactory.

The "stripping" mechanism explains the dependence of the abstraction cross-sections on the bond energy by the fact that the lower the value of E_b the greater the target distance over which an atom can be "stripped off", i.e. for the same reaction time the process can occur with a higher energy of the "hot" atom. Hence one may conclude that the excitation function for a chemical abstraction reaction $\sigma_{abs}(E)$ is determined over a wider energy range than the function for the substitution reaction $\sigma_{subs}(E)$, where the role of the bond energy is manifested to a much smaller extent. There is little information in the literature about the experimental measurement of the $\sigma_{abs}(E)$ and $\sigma_{subs}(E)$ relations over a wide energy range. Calculations by the method of trajectories using semiempirical potential energy surfaces have shown that the bond energy influences the cross-section for the abstraction reaction by altering the height of the barrier (confirmation of the Semenov–Polanyi rule). We may note yet another important factor, which follows from these calculations: for a lower barrier, the reaction takes place over longer target distances; for a high barrier (approximately

0.5 eV), the probability of the reaction diminishes with increase of the impact parameter and for a low barrier (approximately 0.2 eV) there is a probability maximum. Hence it follows that the conclusion concerning the dynamics of the abstraction reaction treated as a "stripping" process has been confirmed by trajectory calculations[179]

5. Substitution Reactions

Substitution reactions of the type $RX + H^* \rightarrow RH + X$ (X = H, etc), which are not observed in thermal chemistry, have aroused the greatest interest. It has been established that such a reaction results in the formation of vibrationally excited molecules, which decompose at low pressures. In the theoretical calculations of the yield of substitution reactions corrections are introduced for decomposition based on the ratio of the energy converted on collision into the internal energy of the molecules and the dissociation energy. The dependence on pressure and the concentration of other species is obtained experimentally and the contribution of the decomposition process is estimated. For the reactions of recoil tritium atoms with CH_3X (X = F, Cl, Br, or H), the observed yields of the product $CH_2{}^3HX$ were 58 ± 2, 40 ± 2, 33 ± 3, and 83 ± 3% respectively and the values corrected for decomposition (primary yields) were 64 ± 3, 75 ± 3, 78 ± 5, and 100 ± 5% relative to the yield of cyclo-$C_4H_9{}^3H$ formed from cyclo-C_4H_{10} used as a standard.

The results agree with the "impact" model[194]: the greater the radius of the shielding atom, the lower the yield of the hydrogen substitution reaction. However, conclusions corrected for decomposition indicate the opposite relation. Apparently the description of the substitution process adopted previously, in which account was taken only of the physical characteristics of the system—the masses of the atoms, their dimensions, the bond angles, and the angles of attack—is inadequate. More far-reaching driving forces were manifested in the substitution reaction, for example, the mutual influence of the atoms in the molecule on the reactivity of the "hot" atoms. The concept of the decisive influence of the electronegativity of the substituents on the hydrogen substitution process has been put forward[193]. The probability of the substitution of hydrogen depends on the electron density in the C–H bond: in CH_3F it is a minimum, which leads to the lowest yield of the substitution reaction. The yields of substitution reactions of the atoms X are 4.4, 7.1, 12.0. and 7.7%, which agrees with the changes in the C–X bond energy and not in the collision diameters, as was assumed previously on the basis of the collision model.

Certain details of the substitution processes become more understandable when isotope effects are investigated[9,186,190,193,195]. It has been found that the isotope effect in the substitution of H and D by ^3H is 1.30 ± 0.03 for different compounds. Initially this was attributed to differences between the retarding capacities of substances, which induce changes in the frequency of the collisions of "hot" atoms with molecules. However, for substances such as $(CH_3)_3CH$ and $(CH_3)_3CD$, $(CD_3)_3CH$, and $(CD_3)_3CD$, the isotope effects proved to be identical. Furthermore, the isotope effect in the substitution of fluorine in CH_3F and CD_3F is 1.4 ± 0.05.[196] Thus the isotope effect is manifested not only in the first stage of the process (the dislodgement of an atom), but also in the second stage involving the formation of a bond with the molecular residue. The formation of a bond in the substitution reaction obeys the "inertial" mechanism: the lighter the residue, the higher the rate of formation of a bond[194].

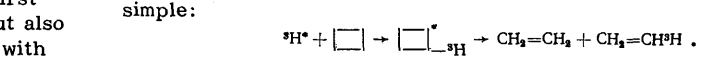
It would be very interesting to investigate the isotope effects in CH_2D_2: if the direct substitution process, i.e. the dislodgement of an atom, plays the main role, the isotope effect should be approximately 1.3, while in the case where the second stage (bond formation) is important, the yield of the substitution of deuterium should be approximately 10% higher by virtue of the "inertial" mechanism[17]. The technical difficulties in the separation of CH_2D^3H and CH^3HD_2 have now been overcome and it has been shown that their yields are identical, which demonstrates that both mechanisms operate, acting in opposite directions. The isotope effect for atoms with a lower energy is much greater: thus the ratio $(CH_3{}^3H/CH_4) : (CD_3{}^3H/CD_4)$ proved to be approximately 7 for ^3H atoms with $E = 2.8$ eV in the $CH_4 + CD_4$ mixture, the values for CH_3D and CH_2D_2 being 2.4 and 1.0. The overall yield of the substitution reaction falls with increase of the number of deuterium atoms in the molecule. The probability of the substitution reaction for an H atom is 1.6 ± 0.2 times greater than for a D atom regardless of whether the atom is substituted or remains in the residual radical, i.e. the two-stage mechanism of the substitution process has been confirmed[9].

The experimental threshold energy of the substitution of hydrogen in hydrocarbons by its isotopes is 1.5 eV.[184,186] For the substitution of hydrogen in 1-chlorobutane by ^3H atoms accelerated in a "chemical" accelerator, $E_{thresh} = 1.2$ eV has been obtained with a maximum reaction cross-section at 8 eV.[196] The threshold energy of the substitution of H by ^3H agrees with Eyring's theoretical estimate[197] for the substitution of H by D in CH_4, based on the assumption of an inversion mechanism. This was confirmed by certain subsequent investigations[190–191], but in others it was pointed out that a threshold energy of the substitution process of approximately 1.6 eV is obtained if the extent of inversion is not greater than 50%.[82] For bulky substituents in methane, the conservation of the initial configuration in substitution reactions has been demonstrated for a fairly large number of examples. This provided Wolfgang with justification to formulate, by analogy with the familiar Franck–Condon principle, the "golden rule of hot chemistry": "If the time required for the migration of atoms (with formation of a given reaction product) is greater than the collision time, the reaction is forbidden".[194]

One of the interesting features of the substitution reaction is the formation of excited molecules. The problem arises whether the energy is distributed among the degrees of freedom in such molecules before decomposition or before deactivation. Studies have shown that, as a result of the substitution of an H atom by a recoil ^3H atom, the molecules are vibrationally excited up to an energy of 5 eV, [16] and the hypothesis of a statistical distribution of energy proves to be valid. Indeed, according to the unimolecular decomposition theory[198], the probability of the decomposition is proportional to the energy excess over E_a:

$$k \simeq A[(E - E_a)/E]^{s-1},$$

where $s = \frac{1}{2}(3N-6)$ and N is the number of atoms in the molecule involved in the process. The probability of decomposition can be estimated from the yields of products and E_a is known from the "usual" chemistry. $E \cong 5$ eV have been calculated for the reactions of ^3H with cyclobutane[199] and methylcyclohexene[198]. In this case, the reaction mechanism is simple:



In a later study it was established that the reaction products can be obtained not only via unimolecular decomposition but also via a direct substitution reaction[200], i.e. after the substitution of H by ^3H the molecule can decompose until the

collision energy is uniformly distributed among all the vibrational degrees of freedom. This process can be described as a reaction involving the direct substitution of a group of atoms.

6. Addition Reactions

The reactions involving the addition of thermal hydrogen atoms to double bonds are accompanied by the liberation of a vibrational energy of approximately 30 kcal mol^{-1}. Some investigators have been interested in the possibility of obtaining superexcited radicals by the addition of "hot" atoms. In a series of studies[12,201], performed using photochemical atoms with $E = 1.8$ eV, the formation of such radicals was demonstrated by comparing the rate coefficients for the characteristic reactions of the radicals—the abstraction of hydrogen and recombination.

According to the Arrhenius equation, the probability of the reaction should approach the value of the steric factor as the interaction energy of the species increases. However, it has been shown in a number of investigations that the steric factors for the addition of hydrogen to ethylene increase by three orders of magnitude on passing from the thermal energy of hydrogen atoms, corresponding to room temperature, to 6 eV.[12] An analogous behaviour has been observed for the recoil tritium atoms in a cyclohexane-cyclohexene mixture[202]: the ratio of the rate coefficients for the abstraction and addition reactions was 0.34 ± 0.01, which exceeds by a factor of 100 the corresponding ratio for thermal atoms and by a factor of 5–20 the ratio of hydrogen atoms obtained in radiolysis under the influence of radiations of different types. The fraction of "hot" hydrogen atoms in the overall yield of hydrogen atoms in radiolysis (<15%) has been estimated from the data of Kukin and Filatov[202]. An analogous result had been obtained earlier for the CH_3OH–C_6H_6 mixture, where the corresponding ratio of the abstraction and addition rate constants was close to unity, while in radiolysis it was approximately 10^{-2}.[203] This agrees with quantitative estimates of the contribution of the reactions of "hot" atoms obtained in radiolysis to the yield of H_2.

Since the steric factor for an abstraction reaction involving thermal hydrogen atoms is 0.1–1 and that for an addition reaction is 10^{-3}–10^{-4}, it follows that k_{abs}/k_{add} should be 10^{-2}–10^{-4} for $E \gg E_a$. Since the experimental ratios of the rate coefficients for "hot" atoms are close to unity, the steric factors for the reactions apparently also depend on the energy.

7. Other Reactions of "Hot" Hydrogen Atoms

The reactions of "hot" hydrogen atoms not observed in the "usual" thermal chemistry have been noted in a number of studies: reactions involving the substitution of groups of atoms[9,17,162,204] and the dissociation of C–C bonds[205–207]. Certain polymerisation reactions with participation of "hot" tritium atoms have been studied[208,209]. These reactions, first noted for recoil tritium atoms, were subsequently investigated with the aid of the acceleration technique[10,210]. The energy thresholds of certain reactions, for example, the cyclohexane ring opening reaction (approximately 4.5 eV), have been found[210]. There are at present no clear ideas in the literature concerning the mechanisms of the above processes.

In the study of chemical processes from the standpoint of elementary reaction collision steps, the knowledge of the reaction cross-section is the most valuable. Classical experimental chemistry operates with the concept of the rate constant which is identical with the rate coefficient for the Maxwell–Boltzmann distribution of species. Information about the cross-section cannot be obtained from numerical rate constants, since the cross-section is a characteristic of the reaction for specific quantum states of the reactants and products.

The possibility of the calculation of the cross-sections and of estimating other reaction characteristics has been considered in detail in a review[211], where a table of the rate coefficients, the integral probabilities, and the cross-sections of the reactions of hydrogen atoms obtained by various procedures is compiled.

IV. CONCLUSIONS

Thermal hydrogen atoms exhibit a high reactivity up to approximately 30 K in relation to compounds of virtually all classes. The view that the reactions at low temperatures proceed via a tunnel mechanism is generally accepted, although it has been suggested that the deviation from the Arrhenius relation at low temperatures can be caused by a change in the activation energy in the solid state.

Significant advances in the understanding of the mechanisms of reactions involving hydrogen atoms have been made by virtue of the development of physical ideas about the reaction dynamics. The MO methods in combination with computer calculations are widely used. Calculations of the potential energy of the interaction of six bodies have now become possible, which greatly extends the applied scope of the calculations.

Apart from the familiar reaction channels, the following new channels have been established for "hot" hydrogen atoms: the substitution of atoms and groups of atoms. Since the products of the unimolecular decomposition of the initial molecules are present in the reactions of "hot" atoms, it is believed that substitution results in the formation of vibrationally excited molecules, the probability of the decomposition of which can be calculated. "Hot" atoms can add to the double bond with formation of vibrationally "superexcited" radicals. Concepts such as the reaction rate coefficient (and not the rate constant, since there is no Boltzmann distribution with respect to the energies), the reaction probability, and the reaction cross-section serve as quantitative characteristics of "hot" reactions. Their dependence on the collision energy is significant.

Studies with "hot" atoms stimulated the investigation of the dependence of reaction probability on the energy of the colliding species. A successful development of the relevant studies requires the theoretical knowledge of the form of the potential surfaces for the reactions. The dependence of the reaction cross-sections on the energy can be obtained by the method of trajectories. The conversion of the cross-sections into reaction probabilities and yields presents no difficulties. On the other hand, if account is taken of the orientation of the molecule relative to the velocity vector of the attacking species, it is possible to obtain the dependence of the differential reaction cross-section on the angle of attack. However, this is applicable only to a quantitative description of simple reactions. For more complex processes, there is a possibility of only a qualitative comparison with experiment. Nevertheless, computational methods have contributed much to the understanding of the dynamics of chemical reactions. Apparently Mulliken was right in predicting the onset of the era of "computing"chemists who will resort to computers in their hundreds and will achieve thereby a significant understanding of the reaction mechanisms.

Experimental studies with "hot" species require the construction of complex accelerators, because the traditional methods for the generation of species (photolysis, radiolysis, and nuclear reactions) cannot yield a stream of monochromatic atoms with a specified energy and the value of such experiments is therefore theoretically low. Information about the quantum states of the reactants and products is essential for a comparison of experimental data with theoretical calculations. This also requires a quantitatively new development of experimental techniques.

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