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The Interaction of Hydrogen Atoms with Solid Organic Substances

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The mechanisms and kinetics of reactions occurring when solid organic compounds of different structures (low-molecular- and high-molecular-weight substances) are acted upon by "thermal" hydrogen atoms are examined. Models and kinetic schemes proposed for the description of the interaction of solid organic substances with gaseous atomic hydrogen are analysed. The majority of the results summarised in the review refer to the path and rate of the primary chemical step in the interaction. Particular attention has been devoted to reactions of the type $H + RH \rightarrow H_2 + R$, the kinetic constants of which have been measured only in recent years. These data are treated on the basis of the hypothesis of a tunnel mechanism for the transfer of a hydrogen atom at a low temperature. The review also deals with the results of studies of the low-temperature reactions of free radicals with hydrogen atoms and with one another.
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I. INTRODUCTION

The study of the interaction of atomic hydrogen with solid organic substances was initiated in 1958 by Klein and Scheer[1,2], who established that hydrogen atoms add to frozen olefins at a high rate at 77 K. More than 100 studies devoted to the paths and rates of the reactions of atomic hydrogen with solid organic substances have already been published. They are important for the determination of the nature of the elementary steps in the free-radical processes and for the elucidation of the rules relating the structures of the reactants to their reactivities. Furthermore, the study of the reaction of hydrogen atoms with solid organic substances is essential for the understanding of the kinetics and mechanisms of low-temperature chemical reactions as well as heterogeneous processes in systems, frequently encountered in practice, which comprise atomic species in the gas phase and a solid substance.

The knowledge of detailed mechanisms and characteristics of the elementary reactions between the atomic hydrogen and solid organic substances plays a particularly important role in the solution of problems arising in the study of the action of high-energy radiation on such substances. Under the influence of ionising radiation, C–H bonds are ruptured in organic compounds and the reactions of the resulting hydrogen atoms influence the yields of radiolysis products and the radiation stability of the substances.

The reactions of atomic hydrogen with solid organic substances are studied by a wide variety of methods: monitoring of the changes in the pressure of molecular hydrogen, chromatographic or mass-spectrometric analysis of reaction products, and study of the exchange between the gas and solid phases during the interaction of hydrogen isotopes (deuterium and tritium) with frozen hydrocarbons. Lomanov et al.[3] developed the method of kinetic calorimetry for the simultaneous measurement of the heat evolved in the reaction layer and of the amount of hydrogen absorbed. EPR spectroscopy is widely used in the study of reactions of atomic hydrogen with solid organic substances. The free-radical reaction products are identified and their concentration and the concentration of hydrogen atoms are determined by EPR.

Another microwave spectroscopic method is based on the use of a hydrogen maser, the sensitivity of which is higher by approximately 4 orders of magnitude than that of an EPR spectrometer. This makes it possible to investigate reactions in the presence of a very low concentration of atomic hydrogen. It has been suggested[4] that the hydrogen maser be used under pulsed conditions to investigate not only chemical reactions but also the steps preceding them, namely the physical and chemical adsorption of atomic hydrogen on the surface of a solid (from the change in the hyperfine state of the hydrogen atom).

Atomic hydrogen is usually obtained either in the gas phase or is generated directly in the solid substance. The most suitable methods for the generation of atomic hydrogen in the gas phase are thermal decomposition and the dissociation of molecular hydrogen in the gas discharge. The latter procedure is more convenient and effective. The generation of hydrogen atoms in an electrodeless high-frequency or ultrahigh frequency discharge is particularly common. The methods for the generation of hydrogen in the gas phase and the procedures for the measurement of their concentration have been examined in a review[5].

Radiation and photochemical methods are used to generate hydrogen atoms directly in the solid. Among the latter procedures, the method involving the ultraviolet irradiation of frozen aqueous solutions of acids (H_2SO_4 and H_3PO_4) containing small amounts of $FeSO_4$ has come to be most widely used[6,7]. Ultraviolet irradiation of such systems leads to the oxidation-reduction reaction

$$Fe^{2+} + H_2O + h\nu \rightarrow Fe^{3+} + OH^- + H^{\cdot} \quad .$$

The hydrogen atoms produced are stabilised at 77 K, but, on raising the solution temperature to 90–120 K, they become mobile and can react with the solute.

The methods available for the investigation of the interaction of atomic hydrogen with solid organic substances have made it possible to establish fairly reliably the paths of the reactions and in certain cases also to measure their rates. The review presents results referring solely to thermalised hydrogen atoms. The extensive literature on the radiolysis of solid organic substances, from which data for the reactions of atomic hydrogen may be obtained, is not dealt with because radiolysis may entail the formation of "hot" hydrogen atoms.

II. PROCESSES IN SYSTEMS H(GAS) + SOLID ORGANIC SUBSTANCE

1. Models for the Description of Processes

The chemical interaction of hydrogen atoms with organic compounds can be described by the following fundamental equations:

$$M + H \xrightarrow{k_1} R, \quad (1)$$

$$RX + H \xrightarrow{k_2} R + HX, \quad (2)$$

$$R + H \xrightarrow{k_3} RH, \quad (3)$$

$$R + H \xrightarrow{k_4} \rangle C{=}C \langle + H_2, \quad (4)$$

$$R + R \xrightarrow{k_5} R{-}R, \quad (5)$$

$$R + R \xrightarrow{k_6} \rangle C{=}C \langle + RH, \quad (6)$$

$$H + H \xrightarrow{k_7} H_2, \quad (7)$$

where **M** and **RX** are molecules of unsaturated and saturated compounds respectively. Depending on the structure of the initial molecules, the primary step in the interaction is either the addition reaction (1) or reaction (2) involving the abstraction of an atom or groups of atoms. The transfer of a hydrogen atom (**X** = H) constitutes a special case of reactions of the second type. For certain compounds with complex structures, there is a possibility of the simultaneous occurrence of reactions (1) and (2) (see Section III). The free radicals generated in the primary step react further with hydrogen atoms [reactions (3) and (4)] and with one another [reactions (5) and (6)]; these secondary reactions of free radicals proceed via recombination [reactions (3) and (5)] or disproportionation [reactions (4) and (6)] mechanisms. Reactions (4) and (6) lead to the formation of molecules with double bonds.

Since the reactant is in the solid phase, physical processes such as diffusion, dissolution or adsorption of hydrogen atoms, and elementary steps involving the migration of the reacting solid-phase species (molecules and free radicals), in the first place their translational diffusion, play an important role in the kinetics. One should also bear in mind that many parameters, for example, diffusion coefficients, may vary as the reaction proceeds, owing to the change in the structure of the initial substance. The fundamental differential equations describing the interaction of hydrogen atoms with an unsaturated compound are presented below [a one-dimensional model is considered; it is assumed that reactions (4) and (6) result in the formation of unsaturated compounds having the same structure as the initial substance]:

$$\frac{\partial [H]}{\partial \tau} = D_H \frac{\partial^2 [H]}{\partial x^2} - k_1 [M][H] - (k_3 + k_4)[R][H] - k_7 [H]^2, \quad (8)$$

$$\frac{\partial [M]}{\partial \tau} = D_M \frac{\partial^2 [M]}{\partial x^2} - k_1 [M][H] + k_4 [R][H] + k_6 [R]^2, \quad (9)$$

$$\frac{\partial [R]}{\partial \tau} = D_R \frac{\partial^2 [R]}{\partial x^2} + k_1 [M][H] - (k_3 + k_4)[R][H] - (k_5 + k_6)[R]^2, \quad (10)$$

where k_1, k_2, k_3, etc. are the rate constants for the above reactions, [H], [M], and [R] are respectively the concentrations of hydrogen atoms, reacting molecules, and free radicals, and D_H, D_M, and D_R are the diffusion coefficients of these species. In the general case the concentrations and diffusion coefficients are functions of the distance x from the surface of the specimen (Fig. 1) and the time τ.

The above equations must be supplemented by the analogous material balance equations for the molecular hydrogenation products (**RH** and **R–R**). The solution of the complete system of equations is difficult, but it is quite feasible with the aid of a computer. Thus Rappe et al.[8] calculated on a computer the time variation of the quantity $\partial[H]/\partial\tau$ for frozen (77 K) isobutene, taking into account reactions (1), (3), (4), (6) and (7), which occur in this system, and the diffusion of all the reacting species (hydrogen atoms, isobutene molecules, isobutyl radicals, isobutane molecules), and in the first version of the calculation it was assumed that the diffusion coefficients are constant throughout the hydrogenation process. The calculated variation of $\partial[H]/\partial\tau$ with τ agrees with the experimental variation along the initial section; at more advanced stages of the reaction the measured rate decreases faster than would follow from the results of the calculation. In order to account for the discrepancy, the authors suggested that the presence of isobutane leads to a decrease of either (1) the rate of diffusion of hydrogen atoms and of all the solid-phase reacting species or (2) the solubility of hydrogen atoms. When either of these possibilities was taken into account, satisfactory agreement between the experimental and calculated data was achieved. However, one should note that the reaction rate constants and diffusion coefficients used in the calculation have not been measured experimentally in most cases and are not always reliable. For this reason, the results must be treated with a certain amount of caution.

It is seen from the above example that the correct description of the interaction of hydrogen atoms with solid organic substances requires the knowledge of many constants for chemical and physical processes. In practice, in order to simplify the problem, use is made of approximate models. Among all the transport phenomena, commonly only the diffusion of atomic hydrogen is taken into account, while the diffusion of molecules and free radicals is neglected (the H-diffusion model[8–10]).

It is usually assumed that $\partial[H]/\partial\tau = 0$. Then

$$D_H \frac{\partial^2 [H]}{\partial x^2} = k_1 [M][H] + k_3 [R][H] + k_4 [R][H] + k_7 [H]^2. \quad (11)$$

The distribution of the concentration of atomic hydrogen in the layer of the given substance, where a whole series of reactions take place simultaneously, is complex. We shall confine ourselves to an examination of two special cases which are encountered in practice.

(a) The distribution of the concentration of atomic hydrogen determined by the rate of recombination of hydrogen atoms [reaction (7)]. One can state *a priori* that this mechanism should obtain for saturated compounds (such as alkanes) at very low temperatures (< 80 K):

$$D_H \partial^2 [H]/\partial x^2 = k_7 [H]^2, \quad (12)$$

$$[H] = \{[H]_0^{-1/2} + (k_7/6D_H)^{1/2} x\}^{-2}, \quad (13)$$

where $[H]_0$ is the concentration of atomic hydrogen on the surface of the specimen for $x = 0$.

(b) The consumption of atomic hydrogen is determined by reaction (1) or (2) (depending on the structure of the initial substance). This special case corresponds to compounds reacting with atomic hydrogen at a high rate. These include in the first place unsaturated and many saturated compounds at temperatures $\geqslant 100$ K (see Section VI). Eqn. (11) transforms into

$$D_H \partial^2 [H]/\partial x^2 = k_1 [M] [H], \quad (14)$$

$$[H] = [H]_0 \{\mathrm{ch}\,(k_1 [M]/D_H)^{1/2} x - \mathrm{th}\,(k_1 [M]/D_H)^{1/2} l \cdot \mathrm{sh}\,(k_1 [M]/D_H)^{1/2} x\}. \quad (15)$$

The measured parameters are usually the rate of change of the pressure of molecular hydrogen (when the reactions proceed in a closed system) and the rate of formation of free radicals. The corresponding equations for the rate of addition are

$$-2\frac{dH_2}{d\tau} = \int_0^l \{k_1 [M] [H] + (k_3 - k_4) [R] [H]\} s\, dx, \quad (16)$$

$$\frac{dN}{d\tau} = \int_0^l \{k_1 [M] [H] - (k_3 + k_4) [R] [H] - (k_5 + k_6) [R]^2\} s\, dx, \quad (17)$$

where H_2 is the total number of hydrogen molecules in the system, N the number of free radicals in the specimen, s the surface area of the specimen, and l its thickness. On substituting the expressions for [H] [Eqns. (13) and (15)] in these equations, it is possible to obtain the dependence of the rates of the processes on $[H]_0$ and D_H for the two cases considered.

We shall deal with the more interesting case (b). The initial rate of consumption of molecular hydrogen is

$$2\left(\frac{dH_2}{d\tau}\right)_0 = \int_0^l k_1 [M] [H] s\, dx = (D_H k_1 [M])^{1/2} [H]_0 s\, \mathrm{th}\,(k_1 [M]/D_H)^{1/2} l. \quad (18)$$

It is assumed that $[H]|_{x=0} = [H]_0$ and $\partial[H]/\partial x|_{x=l} = 0$. For a very thin layer, we have

$$-2\left(\frac{dH_2}{d\tau}\right)_0 = k_1 [H]_0 [M] sl. \quad (19)$$

An analogous expression is obtained for the initial rate of accumulation of free radicals:

$$(dN/d\tau)_0 = k_1 [H]_0 [M] sl. \quad (20)$$

Thus the initial rate of reaction for thin-layer specimens is proportional to their thickness, the concentration of hydrogen atoms, and the concentration of the reactant. For a thick-layer specimen, Eqn. (18) becomes

$$-2\left(\frac{dH_2}{d\tau}\right)_0 = [H]_0 s (D_H k_1 [M])^{1/2}, \quad (21)$$

i.e. the initial rate of change of the pressure of molecular hydrogen is independent of the thickness of the specimen and is proportional to the concentration of atomic hydrogen and the square root of the concentration of the reactant.

The model involving the diffusion of hydrogen atoms is suitable for the description of the interaction with solid organic compounds, whose molecules have no mobility or their mobility is restricted. For low-molecular-weight compounds, the temperature range in which it is possible to employ the H-diffusion model depends on the melting point (T_m) and usually includes temperatures $T \leqslant T_m/2$. For high-molecular-weight compounds, the upper limit of this temperature range is approximately $T_g - 20°$, where T_g is the glass point of the amorphous polymer, or is close to the melting point of the crystalline polymer.

The given model is sometimes applicable also to hydrocarbons with a low melting point, such as, for example, propene and isobutene. The foregoing refers to thin films of olefins. Thus it has been found that[8] the initial rate of absorption of molecular hydrogen by isobutene ($l \leqslant 0.5$ m) at 77 K varies linearly with the concentration of atomic hydrogen in the gas phase and with film thickness. The linear dependence of $dH_2/d\tau$ on l has also been observed for propene[9]. For thick films of olefins (~ 1 μm), the rate ceases to depend on film thickness, approaching a constant value[9].

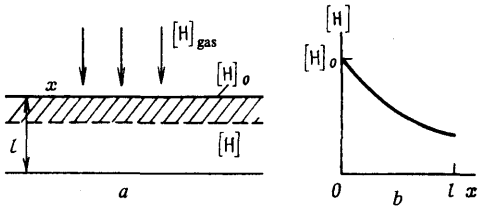


Figure 1. Schematic representation of the interaction of hydrogen atoms (gas) with a solid (*a*) and variation of the concentration of hydrogen atoms in a layer with a thickness l (*b*).

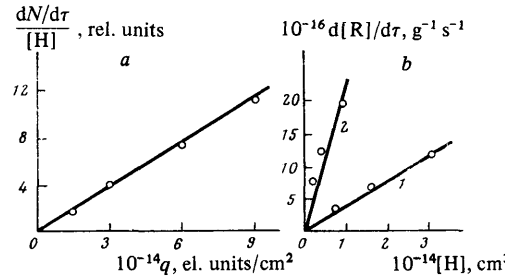


Figure 2. Dependence of the initial rate of formation of free radicals in polyisobutylene adsorbed on aerosil (s_{sp} = 200 $m^2\ g^{-1}$) on the number of elementary units (q) of the polymer (*a*) and the concentration of atomic hydrogen in the gas phase (*b*): *a*) $T = 100$ K, the number of radicals and the number of elementary units are referred to unit surface of aerosil; *b*) $q = 6 \times 10^{14}$ elementary units per cm^2, $T = 115$ K (line *1*) and 163 K (line *2*).

However, studies of the interaction of atomic hydrogen with thick propene films established a whole series of facts, which could not be explained within the framework of the H-diffusion model and indicated a high diffusion coefficient of the olefin. It was found that (1) the initial rate of reaction is proportional to [M] and not $[M]^{1/2}$, as would follow from Eqn. (21),[1] (2) the rate depends on the type of matrix in which the olefin is located[11], the consumption of molecules in rigid matrices being proportional to $\tau^{1/2}$ and not τ, and (3) when the hydrogenation is interrupted and the supply of atomic hydrogen is then resumed, the rate of reaction increases significantly[12]. The low

concentration of free-radical products of propene and isobutene hydrogenation, which cannot be measured by EPR ($\leqslant 6 \times 10^{17}$ g^{-1}) also constitutes indirect indication of the mobility of olefins. The surface reaction model has been put forward to account for the observed phenomena[8,11]. It is suggested that the reaction proceeds on the surface where the concentration of hydrogen atoms is $[H]_0$, while the concentration within the layer is zero. The model takes into account the diffusion of the reacting substance from the bulk of the layer onto the surface, and it is assumed that the diffusion coefficient is independent of the composition of the layer and the duration of the process. According to the model, the initial rate of absorption of hydrogen is independent of the thickness of the layer and is proportional to the concentration of the reactant and hydrogen atoms:

$$-2\left(\frac{dH_2}{d\tau}\right)_0 = k_1 [H]_0 [M]s \quad . \tag{22}$$

At more advanced stages of the process there is a possibility of two limiting cases where the rate is determined by (a) the chemical reaction [(1) or (2)] on the surface and (b) the diffusion of the reactant. If the rate of the process is limited by that of the reaction, Eqn. (22) is applicable, and, when it is limited by the rate of diffusion, we have

$$\Delta H_2 \simeq (D_M \tau/\pi)^{1/4}. \tag{23}$$

The model agrees satisfactorily with experimental data for thick films at advanced stages in the hydrogenation of propene in different matrices[11].

Systems where the reacting molecules are adsorbed on the surface of an inert carrier constitute the simplest case[13-15]. When such specimens are used, all the reactions take place on the surface and one may disregard the diffusion of hydrogen atoms and the reacting species.

The adsorbent is usually aerosil (SiO_2) with a high specific surface ($\geqslant 200$ m^2 g^{-1}); it is a non-porous fine-grained powder (particle size between 4 and 40 nm), which readily adsorbs organic substances. The specific surfaces of the specimens are the same as the specific surface of the initial aerosil when the adsorbed amounts correspond to approximately 1–2 molecular layers (5–10 μmole m^{-2}). The reaction kinetics may be described by Eqns.(19) and (20), which are valid for a very thin layer of reactant (in this case the average thickness of the layer l corresponds to only 1–2 molecular diameters).

For low surface coverages of aerosil, the amount of free radicals formed varies linearly with the amount of adsorbed polymer (Fig. 2*a*). For high coverages, the linearity breaks down. Fig. 2*b* shows that the initial rate of accumulation of radicals for the polymer adsorbed on a thin layer of aerosil, as well as for olefin films, is proportional to the concentration of hydrogen atoms in the gas phase.

2. The Mechanisms of Elementary Chemical Reactions for Certain Compounds

The compositions of the molecular hydrogenation products have been analysed for the simplest olefins and the mechanisms of chemical reactions leading to hydrogenation have been fairly reliably established[8,9,11,12,16-22]. When propene is acted upon by atomic hydrogen, mainly propane and dimethylbutane are formed. In soft matrices (propene, propene + propane, propene + n-butane), reactions (1), (5), and (6) take place and of the two reactions of isopropyl radicals with each other disproportionation is the dominant process[9,11,20-23]. The rates of reactions (3) and (4) are insignificant, but their role increases in rigid matrices, where the probability of the interaction of free radicals with one another is reduced. Thus in solid mixtures of propene with isopentane[24] and *cis*-butene[11] and in propene adsorbed on quartz[18] isopropyl free radicals are destroyed mainly via reactions (3) and (4).

In order to determine the sequence of the elementary processes occurring in the hydrogenation of olefins, some investigators[21,24-26] studied the deuterium–hydrogen exchange between the gas and solid phases. It was found that, when propene is acted upon (at 77 K) by deuterium atoms, hardly any HD is formed[25]. On the other hand, when butene, isobutene, 2-methylbut-1-ene, and 3-methylbut-1-ene are bombarded by atomic deuterium, H–D exchange takes place at a high rate[25,27]. Its rate for isobutene is close to the rate of absorption of deuterium. The isotope exchange may be caused by the two reactions:

$$R + D \rightarrow \text{olefin} + HD + 60 \text{ kcal mole}^{-1}, \tag{24}$$

$$R + D \rightarrow R_D + H + 0 \text{ kcal mole}^{-1}. \tag{25}$$

Here R_D is a free radical containing a D atom.

The simultaneous study of heat evolution and the amount of absorbed deuterium in the case of isobutene showed[25] that the H–D exchange must be due to a thermally neutral process, i.e. reaction (25). The authors therefore believe[25,27] that the mechanism involving reactions (1)–(7), occurring when solid olefins are acted upon by atomic hydrogen, should be supplemented by the exchange between free radicals and hydrogen atoms. However, the possibility of such an energetically unfavourable process requires further experimental confirmation.

The interaction of atomic hydrogen with many high-molecular-weight [polyisobutylene, polypropylene, poly(methyl acrylate), etc.] and low-molecular weight (n-hexadecane, malonic acid) compounds at a fairly low temperature may be described by reactions (2)–(4). This conclusion is based on the results of kinetic studies by EPR[14,15,28]. The curves representing the variation of the concentration of free radicals in the substances enumerated above are described by the equation

$$\frac{d[R]}{d\tau} = k_2 [H][RH] - (k_3 + k_4)[H][R]. \tag{26}$$

Similarly the rate of formation of free radicals in unsaturated compounds may be represented by the expression

$$\frac{d[R]}{d\tau} = k_1 [H][M] - (k_3 + k_4)[H][R]. \tag{27}$$

A simultaneous study of the rate of accumulation of free radicals and of the rate of change of pressure in the system makes it possible to determine which of the two reactions [(3) or (4)] predominates. For unsaturated compounds, the rate of absorption of hydrogen is

$$-2\frac{dH_2}{d\tau} = k_1 [H][M] + (k_3 - k_4)[H][R]. \tag{28}$$

Under the conditions of a steady-state concentration of free radicals, we have

$$-\frac{dH_2}{d\tau} = \frac{k_1 k_3}{k_3 + k_4}[H][M]. \tag{29}$$

Two extreme cases are possible:

when $k_3 \gg k_4$ $\quad -dH_2/d\tau = k_1 [H][M]$,
when $k_3 \ll k_4$ $\quad -dH_2/d\tau \approx 0$.

The nature of the kinetic curves for polystyrene[29] (Fig. 3) shows that in this instance $k_3 \gg k_4$, i.e. the interaction of atomic hydrogen with polystyrene includes only two chemical reactions [(1) and (3)].

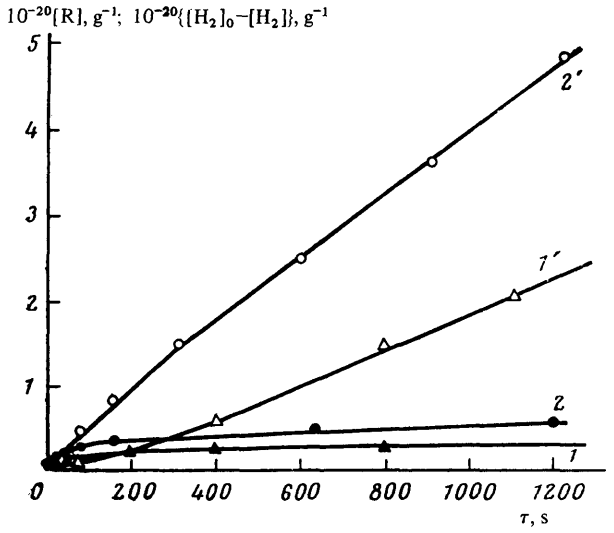


Figure 3. Kinetic curves for the variation of the concentration of free radicals (lines *1* and *2*) and the absorption of molecular hydrogen (lines *1′* and *2′*) in the interaction of atomic hydrogen with polystyrene at 123 K (lines *1* and *1′*) and 163 K (lines *2* and *2′*).[29] The amounts of free radicals and H_2 molecules are referred to unit mass of the polymer.

3. The Depth of Penetration of Hydrogen Atoms into a Layer of a Solid Organic Substance

The relation between the rates of diffusion and chemical reactions in the layer of reactant determines the depth of penetration of atomic hydrogen δ into this substance. Thus δ depends on the chemical structure of the reactants, their physical properties, and, finally, temperature. It can be measured by various experimental methods, including EPR. Since in thick layers hydrogen atoms penetrate only into a layer with a thickness δ, free radicals are likewise formed only in this layer. The average concentration of radicals in such specimens therefore differs from the local concentration in the δ layer: $[R]_{av} = [R]_{loc} s\rho\delta$ (here s is the specific surface of the specimen and ρ its density). Knowing the average and local concentrations of free radicals, it is possible to determine δ. $[R]_{av}$ is measured directly by EPR, while $[R]_{loc}$ is found by studying the broadening of EPR spectra with increasing amount of free radicals, which is due to the dipole–dipole spin interaction. The width of an individual line in the EPR spectrum usually varies linearly with the concentration of radicals (Fig. 4) and $[R]_{loc}$ can be calculated from the equation[30]

$$\Delta H = \Delta H_0 + 5 \cdot 10^{-20} [R]_{loc}, \qquad (30)$$

where ΔH_0 is the intrinsic width of the individual spectral line and ΔH the width of the same line increased owing to the dipole–dipole interaction.

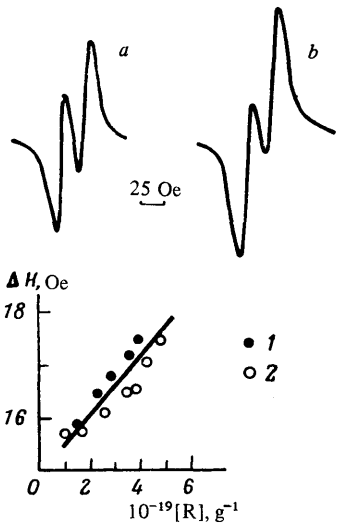


Figure 4. Dependence of the width of an individual line in the EPR spectrum of polyisobutylene radicals on the concentration of the latter[33]. Reaction temperature 145 K (*1*) and 123 K (*2*). The upper part of the figure represents the EPR spectra of free radicals at 145 K. Duration of exposure to the action of hydrogen atoms: *a*) 40 s; *b*) 400 s.

Table 1. The depth of penetration by hydrogen atoms into certain solid organic substances.

Substance	*T*, K	$10^5\delta$, cm	References
Propane	77	10	1
Propene	77	1—10	1
Propene	77	0.2	27
Polystyrene	295	1	31
Thymine	295	2—3	32
Poly(methyl methacrylate)	100	0.2	33
Poly(vinyl acetate)	120	0.1—0.2	33

Table 1 presents the values of δ for certain organic substances. Those for thymine and poly(methyl methacrylate) were determined by the method described above.

The depth of penetration by atomic hydrogen in solid organic substances of different chemical structures in the temperature range 77–300 K is 10^{-6}–10^{-5} cm (Table 1). Only for propane is δ greater (10^{-4} cm), which can be accounted for by the high rate of diffusion of atomic hydrogen in this substance compared with the rate of destruction of hydrogen atoms on recombination and chemical interaction with propane.

In estimating the values of δ for propene at 77 K the authors of the first investigations[1] did not take into account the possibility of the diffusion of the olefin to the surface of the film, which led to unduly high values of δ. In a

later study[11], where an olefin-diffusion model was considered, the estimated δ amounted to only a few molecular diameters.

III. THE PRIMARY CHEMICAL STEP IN THE INTERACTION OF ATOMIC HYDROGEN WITH ORGANIC COMPOUNDS OF DIFFERENT CLASSES

1. The Paths of Reactions (1) and (2)

The path of the chemical reaction can be determined from the EPR spectra of free radicals (Fig. 5) and by analysing molecular products. In most cases the hyperfine structure of EPR spectra is susceptible to elucidation and the directions of reactions (1) and (2) have been established reliably. Since this information is given in a monograph[34] and it is only briefly discussed in the present review, emphasis is laid on the results obtained after the publication of the book by Pshezhetskii et al.[34]

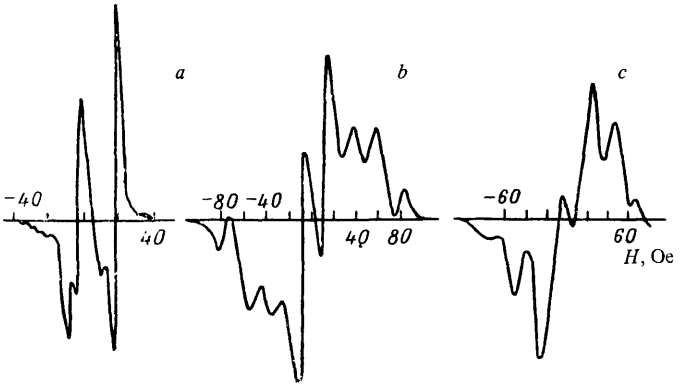


Figure 5. EPR spectra of the free radicals arising as a result of the reaction H + RH → H_2 + R at 110–115 K: *a*) malonic acid; *b*) n-hexadecane; *c*) polypropylene.

The principal data for addition reactions (1) are summarised in Tables 2–4. Hydrogen atoms add at 80–140 K to multiple bonds of different types: C=C, C≡C, C=O, C≡N, N=O, $N\begin{matrix}O\\O\end{matrix}$, N=C=O (Table 2). For olefins and monomers of the vinyl type (methyl methacrylate, vinyl acetate, etc.), the energy of a C–H bond involving a primary carbon atom is greater by several kilocalories than for a bond involving a secondary carbon atom, and hydrogen atoms add mainly to a terminal carbon atom (in conformity with the empirical Markovnikov rule).

Analysis of the molecular olefin hydrogenation products made it possible to determine the relative reactivities of two carbon atoms linked by a double bond. Table 3, which presents data for certain olefins at 90 K, shows that the rate of addition of a hydrogen atom to a primary carbon atom (propene) exceeds by a factor of approximately 100 the rate of addition to a secondary carbon atom. The difference between the rates of addition to primary and tertiary carbon atoms is greater still—it is illustrated by the example of isobutene. Data for the relative reactivities at other temperatures can be found below in Table 8, which also presents values obtained in the study of the effect of atomic deuterium on olefins.

Table 2. The free-radical products of the interaction of atomic hydrogen with unsaturated solid organic compounds [reaction (1)].

Compound	T, K	R	References
	>C=C<		
CH_2=CH_2	77–90	$CH_2\dot{C}H_2$	7, 26, 35, 36
CH_2=CH–CH_3	77	$CH_2\dot{C}HCH_3$	9, 20, 35
CH_2=C$(CH_3)_2$	77–90	$CH_2\dot{C}(CH_3)_2$	8, 35, 37
CH_2=CHX	77	$CH_2\dot{C}HX$	38, 39
(X=OCOCH$_3$, –C≡N C_6H_5, COOH, $CONH_2$)			
CH_2=C(CH_3)X (X=COOCH$_3$, C≡N COOH, $CONH_2$)	77	$CH_2\dot{C}(CH_3)X$	38, 39
CH(CH_3)=CH(COOH)	77	$CH_3CH\dot{C}H(COOH)$	39
C(CH_3)(COOH)=CH(COOH)	77–300	$\dot{C}(CH_3)(COOH)CH_2(COOH)$	40
CH_2=CH–CH=CH_2	77	CH_2=CH–$\dot{C}H(CH_2)$⇄ ⇄$\dot{C}H_2$CH=CH(CH_3)	36
	–C≡C–		
CH≡CH	90	CH_2=$\dot{C}H$	7
CH≡C(COOH)	77	CH_2=$\dot{C}$(COOH)	41
C(COOX)≡C(COOX) (X=H, CH_3)	77	CH(COOX)=$\dot{C}$(COOX)	41
CH≡CCH_2X(X=Cl, Br)	77	$\dot{C}H$=$CHCH_2$X	41
	>C=O		
H_2C = O	90–120	$H\dot{C}$=O	7
$CH_3C(=O)H$	77	$CH_3\dot{C}H(OH)$	38
		$CH_3CH_2O\cdot$	
$CH_3C(=O)CH_3$	77	$CH_3\dot{C}(OH)CH_3$	38
		$CH_3CH\dot{C}H_3$ (O·)	38
	–C≡N		
$[-CH_2-CH(C{\equiv}N)-]_n$	140	$[-CH_2-\dot{C}(C{\equiv}NH)-]_n$	42
	–N=O		
C_6H_5NO	113	$C_6H_4\dot{N}$–OH	43
	$-N\begin{matrix}O\\O\end{matrix}$		
$C_6H_6NO_2$	140	$C_6H_5\dot{N}O$(OH)	44
CH_3NO_2	140	$CH_3\dot{N}O$(OH)	44
CH_2=$CHNO_2$	140	CH_2=CH–$\dot{N}$=O(OH)	44
CH_2=$C(CH_3)NO_2$	140	CH_2=$C(CH_3)$–$\dot{N}$=O(OH)	44
	–N=C=O		
CH_3N=C=O	113	CH_3NH–$\dot{C}$=O	45
O=C=N–$(CH_2)_6$–N=C=O	123	O=C=N–$(CH_2)_4$–$\dot{N}$–CH=O	45
(O=C=N–$C_6H_4)_2CH_2$	113	R–$\dot{N}$–CH=O	45

Nitro- and nitroso-groups behave as active acceptors of hydrogen atoms. The addition to a nitro-olefin (nitroethylene, isonitropropene) is selective: virtually only the N=O bonds react. The interaction of the N=C=O and N=C=S groups with hydrogen atoms entails the rupture of the N=C bond and the site of addition (the nitrogen or carbon atom) depends on the nature of the substituent at these bonds[45].

Hydrogen atoms react very readily with benzene and its derivatives: toluene, biphenyl, phenol, hydroquinone, anisole, etc., with formation of radicals of the cyclohexadienyl type[36,38,46–54]. The EPR spectra of the free radicals arising in these substances are usually poorly

resolved and it is not always possible to determine their structure. However, the available data nevertheless permit the conclusion that hydrogen atoms add to the majority of benzene derivatives in the *ortho*- and *para*-positions relative to the substituent (Table 4). 1,3-Disubstituted benzenes react with hydrogen atoms more readily than the 1,2- or 1,4-substituted derivatives[50]. Heterocyclic compounds with aromatic properties, such as furan, thiophen, and their derivatives (Table 4), combine with hydrogen atoms in the 2-position.

Table 3. The relative reactivities of carbon atoms in olefins at 90 K (k_1 and k_1' are the rate constants for the addition of a hydrogen atom to carbon atoms shown to the left and to the right of the double bond respectively)[37].

Olefin	k_1/k_1'
$CH_2=CH-CH_3$	126
$CH_2=C(CH_3)_2$	1000
$CH_3-CH=C(CH_3)_2$	115

Many compounds are involved in hydrogen atom transfer reactions when they interact with atomic hydrogen (Table 5). The free radicals arising in aniline[47], thiophenol[47], allyl alcohol[38], and other compounds as a result of the dissociation of the N–H, S–H, and C–H bonds are to a large extent stabilised owing to conjugation and the reactions therefore proceed at a high rate even at low temperatures. The C–H bonds in other compounds, particularly paraffins, are comparatively strong and the activation energy for a reaction of the type $H + RH \rightarrow H_2 + R$ is 6–9 kcal mole^{-1}.[60] For this reason, it is frequently claimed (see, for example, Refs. 34 and 61) that such reactions cannot be detected at low temperatures (near the boiling point of nitrogen).

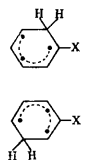
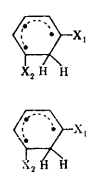
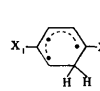
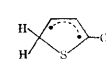
However, studies carried out by the EPR method in recent years revealed the abstraction of hydrogen atoms at a low temperature (in many instances down to 77 K) from a wide variety of compounds, such as cyclohexane, malonic acid, glucose, mannose, and other monosaccharides, tetrahydrofuran, etc. (Table 5). This reaction was observed when many polymers, for example, polyethylene, polypropylene, polyisobutylene, etc. were acted upon by atomic hydrogen[42]. As was to be expected, the site of attack is determined by the weakest C–H bond.

For certain compounds with a complex structure, containing several functional groups, there is a possibility of competition between different modes of reaction. For example, the addition of atomic hydrogen to the aromatic ring and the abstraction of a hydrogen atom from the substituent take place simultaneously in thiophenol, mesitylene, benzyl alcohol, etc.[47,49] When but-2-ene is acted upon by atomic hydrogen, secondary butyl (addition to the double bond) and methylallyl (abstraction of a hydrogen atom from the terminal methyl group) radicals are formed in proportions of 40 : 60.[62] Very many similar examples may be quoted.

Numerous studies have been devoted to the interaction of atomic hydrogen with compounds of biological interest: amino-acids and purine and pyrimidine bases (see the monograph of Pshezhetskii et al.[34] and other reports[32,57,63–73]).

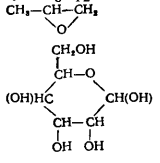
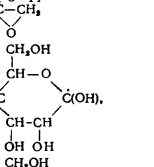
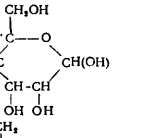
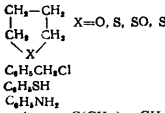
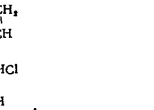
There are numerous data on the modes of reaction of atomic hydrogen with macromolecules. Atomic hydrogen adds to the benzene rings of polymers such as polystyrene, polymethylstyrene, poly(ethylene terephthalate), polyphenylalanine, etc.,[29,31,42,53,54,68] and to the nitrile group of polyacrylonitrile[42]. As already mentioned, atomic hydrogen is abstracted from the main polymer chain in polyethylene, polypropylene, poly(methyl acrylate), poly(methyl methacrylate), polyisobutylene, and certain other polymers[42]. Bombardment of the polymers with hydrogen atoms sometimes leads to the dissociation of C–C bonds with elimination of the side group (poly-L-lysine, poly-L-serine), C–N bonds (poly-L-alanine, poly-L-proline), and C–S bonds (poly-L-methionine)[68,69].

Table 4. The interaction of atomic hydrogen with aromatic compounds [reaction (1)].

	Compound	T, K	R	Refs.
		77—130		36, 38, 46—48
	X=OH, OCH_3, SO_3H X=CH_3 X=CH_2OH, NH_3^+ X=Cl	90 113 90 130		48 49 48 47
	X_1=OH, X_2=OH X_1=OH, X_2=OCH_3	90 90		48
	X_1=X_2=OH X_1=OH, X_2=COOH X_1=COOH, X_2=$C(CH_3)_2$	90 298 298		48 48 50
	X_1=X_2=OH, OCH_3 X_1=COOH; X_2=$C(CH_3)_2$ X_1=COOH, X_2=Cl X_1=COOH, X_2=Cl X_1=X_2=COOH	90 298 187 298 298		48 50 51 50 50
		90		48
		130		47
		130		47
		143		52

Thus at a low temperature atomic hydrogen enters into a wide variety of reactions with the molecules of solid organic substances. It has been established for many compounds that the structures of the free radicals obtained on bombardment with hydrogen atoms and under the influence of high-energy radiation are the same[34,39,41,50,57]. One must therefore suppose that many free radicals, arising in the radiolysis of solid organic substances and responsible for the alteration of their properties, are formed via reactions involving atomic hydrogen.

Table 5. The free-radical products of the interaction of atomic hydrogen with saturated solid organic compounds [the reaction H + RH → H_2 + R].

Compound	T, K	R	Refs
CH_3OH	90	$\dot{C}H_2OH$	55
CH_3CH_2OH	77—90	$CH_3\dot{C}HOH$	38, 55
$(CH_3)_2CHOH$	77—90	$(CH_3)_2\dot{C}OH$	38, 55
$(CH_3)_2CH(COOH)$	99	$(CH_3)_2\dot{C}(COOH)$	55
$CH_2(COOH)_2$	90—298	$\dot{C}H(COOH)_2$	15, 55, 56
$CH_2(CONH_2)_2$	298	$\dot{C}H(CONH_2)_2$	56
$CH(CH_3)(COX)_2$, X=OH, NH_2	298	$CH_3\dot{C}(COX)_2$	56
$(COOH)CH_2C(CH_3)_2(COOH)$	298	$(COOH)\dot{C}HC(CH_3)_2(COOH)$	40
$(COOH)CH(CH_3)CH(CH_3)(COOH)$	298	$(COOH)\dot{C}(CH_3)CH(CH_3)(COOH)$	40
$n\text{-}C_{16}H_{34}$	77—173	$n\text{-}C_{16}H_{33}$	15
$NH_3^+CH_2(COOH)$	298	$NH_3^+\dot{C}H(COOH)$	57
$(CH_3)_2CHCH_2CH(NH_2)(COOH)$	298	$(CH_3)_2\dot{C}CH_2CH(NH_2)(COOH)$	57
$(COOH)C_6H_4CH(CH_3)_2$	298	$(COOH)C_6H_4\dot{C}(CH_3)_2$	50
cyclo-C_6H_{12}	133	cyclo-C_6H_{11}	58
$CH_3—CH(O)—CH_2$	113	$CH_3—\dot{C}(O)—CH_2$	58
	110—120		59
			
 X=O, S, SO, SO_2	113—133		58
$C_6H_5CH_2Cl$	130	$C_6H_5\dot{C}HCl$	47
C_6H_5SH	130	$C_6H_5\dot{S}$	47
$C_6H_5NH_2$	130	$C_6H_5\dot{N}H$	47
polymers-$C(CH_3)_2$-CH_2–	77—233	$—C(CH_3)_2—\dot{C}H—$	42, 13, 14
$—CH_2CH_2O—$	99—145	$—CH_2\dot{C}HO—$	42, 13
$—CH_2CH(CH_3)—$	96—173	$—CH_2\dot{C}(CH_3)—$	42, 28
$—CH_2CH(COOCH_3)—$	77—223	$—CH_2\dot{C}(COOCH_3)—$	42, 28
$—C(CH_3)(COOCH_3)CH_2—$	96—203	$—C(CH_3)(COOCH_3)\dot{C}H—$	42, 28

radicals, alteration of the concentration of the initial compound. In all cases it is assumed that $[H]_0 = [H]_{gas}$, i.e. that the concentration of atomic hydrogen in the surface layer of the substance is equal to its concentration in the gas phase—$[H]_{gas}$ is usually determined by EPR.

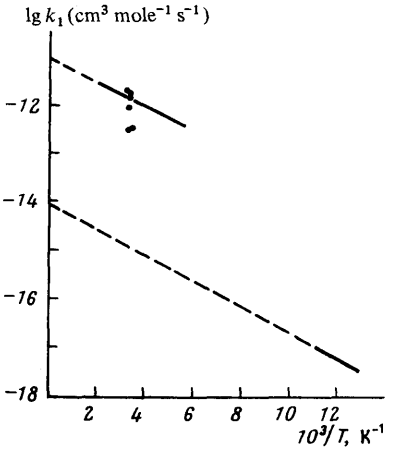


Figure 6. Temperature dependence of the rate constant k_1 for the reaction H + C_3H_6 → C_3H_7 (for explanation, see text).

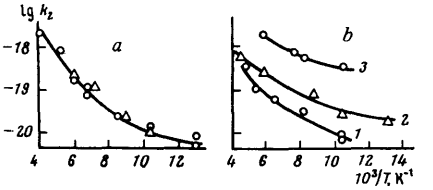


Figure 7. Temperature dependence of the rate constant k_2 for the reaction H + RH → H_2 + R[14,28]: *a*) polyisobutylene, the triangles denote the values of k_2 for the reaction D + RH → HD + R; *b*) [1) poly(methyl methacrylate); 2) poly(methyl acrylate); 3) polypropylene]. The constants are referred to a single reacting C-H bond.

2. Kinetic Constants for Reactions (1) and (2)

The rate constants for all the elementary reactions (1)–(7) have not as yet been determined. The majority of the available kinetic data refer to reactions (1) and (2); the most reliable results have been obtained in studies of the interaction of hydrogen atoms with thin films of olefins[8,9] and with substances adsorbed on the surface of aerosil[13-15,28,29]. The latter method is particularly promising, because it makes it possible to eliminate completely all kinds of diffusion-dependent complications and to measure directly the rate of reaction (1) or (2).

The rate constants for reactions (1) and (2) are calculated from the initial rate of any one of the following processes: absorption of hydrogen, accumulation of free

Kinetic data for reaction (1) are presented in Table 6 and in Fig. 6 and those for reaction (2) are in Table 7 and in Figs. 7 and 8. For thin films and substances adsorbed in an approximately monomolecular layer on aerosil, the effective activation energy represents the difference between the activation energy for the reaction and the heat of adsorption of atomic hydrogen:

$$E_{eff} = E - Q_{ads}. \qquad (31)$$

It has not so far been possible to measure Q_{ads}, but one may suppose that it is small for solid organic substances and that the reactions on the surface proceed with participation of hydrogen atoms arriving directly from the gas phase. In this case $E_{eff} \simeq E$.

For thick films (acetylene, methylbutene, etc.) and for powders with a small specific surface (thymine, dihydrothymine, etc.), the energy E_{eff} characterises a fairly complex process, including diffusion and dissolution of atomic hydrogen in the given substance. According to the model described by Eqn. (21),

$$E_{eff} = [(E + E_{dif})/2] - Q_{ads}. \qquad (31')$$

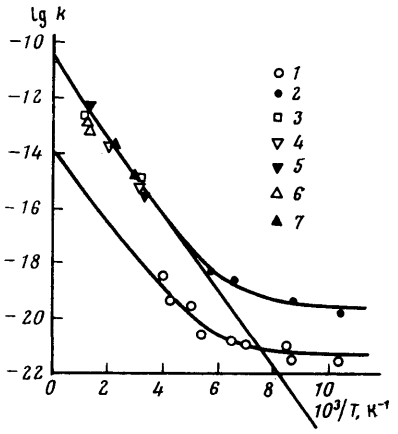


Figure 8. Temperature dependence of the rate constants for different reactions: 1) H + $CH_2(COOH)_2 \rightarrow H_2 +$ $\dot{C}H(COOH)_2$; 2) H + n-$C_{16}H_{34} \rightarrow H_2$ + n-$C_{16}H_{33}$ (Dubinskaya and Yusubov[15]); 3)–7) H + n-$C_4H_{10} \rightarrow H_2$ + n-C_4H_9 (Kondrat'ev[60]). The constants refer to a single methylene group.

Table 6 shows that the values of k_1 calculated for propene at 77 K from the rate of change of its concentration agree with one another, but differ from the values determined by another method—from the decrease in the H_2 pressure.

It is noteworthy that in the determination of k_1 from the change in the initial concentration of the reactant, the relative rates of the subsequent reactions (3)–(6) are used. However, analysis has shown that a change by a large factor in the ratio of the rate constants for these reactions has little effect on the calculated k_1. For this reason, the possible inaccuracies in the determination of the role of secondary free-radical reactions can be the cause of the differences between the values of k_1 found by these two methods.

The rate constants for the reaction of atomic hydrogen with solid propene at low temperatures are compared in Fig. 6 with the values measured in the gas phase at elevated temperatures. The upper continuous straight line (177–434 K) was plotted using the results of Kurylo and Preston[75]. The constants at 177–300 K are trustworthy, because they were measured under conditions excluding possible errors associated with side reactions (the abstraction of hydrogen atoms from propene, the decomposition of excited propyl radicals, etc.). The data of other workers at room temperature (circles), summarised by Jones et al.[5] and Kondrat'ev[60], are also presented. The lower straight line refers to the reaction of atomic hydrogen with solid propene and was plotted using the following values: $E_1 = 1.5$ kcal mole^{-1} and $k_1(77\ K) = 3 \times 10^{-18}$ cm^3 s^{-1}, which we believe to be the most trustworthy. Fig. 6 shows that the activation energies in the gas and solid phases are similar, but the pre-exponential factor in the Arrhenius equation for the reaction with solid propene is appreciably lower (by three orders of magnitude).

The values of k_1 for polystyrene at a low temperature, determined by two different methods (from the initial rate of formation of free radicals and from the decrease of the

Table 6. Critical constants for the addition of atomic hydrogen to certain unsaturated compounds.

Compound	Characteristics of specimen	Measured parameter	T, K	k_1, cm^3 s^{-1}	Temp. range**	E_{eff}, kcal mole^{-1}	Refs.
Propene	film, $l = 10^{-5}$ cm	$-dH_2/d\tau$	77	$\sim 8 \cdot 10^{-17}$*	—	—	9
	film, $l = 10^{-4}$ cm	$-d[M]/d\tau$	77	$\sim 4 \cdot 10^{-18}$*	77—100	1.5	20
	film, $l = 6 \times 10^{-4}$ cm	$-d[M]/d\tau$	77	$3 \cdot 10^{-18}$	—	—	17
	film, $l = 10^{-4}$-10^{-3} cm	$-dH_2/d\tau$	—	—	63—78	<0.5	74
Isobutene	film, $l = 10^{-4}$-10^{-3} cm	$-dH_2/d\tau$	77		63—78	<0.7	74
	film, $l \approx 10^{-5}$ cm	$-dH_2/d\tau$	77	$5 \cdot 10^{-18}$	—	—	8
3-Methylbut-1-ene	film, $l = 10^{-4}$-10^{-3} cm	$-dH_2/d\tau$	—	—	63—78	3.0	74
2-Methylbut-1-ene	film, $l = 10^{-4}$-10^{-3} cm	$-dH_2/d\tau$	—	—	63—78	2.8	74
Acetylene	film, $l = 10^{-4}$-10^{-3} cm	$-dH_2/d\tau$	—	—	63—78	1.0	74
Toluene	film, $l = 10^{-4}$-10^{-3} cm	$-dH_2/d\tau$	—	—	78—160	0.7	74
Phenylacetylene	film, $l = 10^{-4}$-10^{-3} cm	$-dH_2/d\tau$	—	—	78—150	0.5	74
Thymine	powder, particle size 60–100 μm	$d[R]/d\tau$	—	—	120—330	1.2	72
Uracil	aerogel ("fluff")	$d[R]/d\tau$	—	—	190—300	2	73
	powder, particle size 60–100 μm	$d[R]/d\tau$	—	—	190—300	1.5	73
Polystyrene	aerogel, $s_{sp} = 20$ m^2 g^{-1}	$d[R]/d\tau$	295	$7 \cdot 10^{-18}$	—	—	53
	polymer adsorbed on aerosil in a monomolecular layer, $s_{sp} = 200$ m^2 g^{-1}	$d[R]/d\tau$	77	$5 \cdot 10^{-20}$			
		$d[R]/d\tau$	123	$11.5 \cdot 10^{-19}$	77—163	1.3	29
		$-dH_2/d\tau$	123	$9.8 \cdot 10^{-19}$			

*The concentration of hydrogen atoms was calculated and not measured (see text).
**Temperature range in which the activation energy E_{eff} was measured.

pressure of molecular hydrogen) agree satisfactorily (Table 6). The dependence of the rate constant for the addition of atomic hydrogen to polystyrene on temperature in the range 77–163 K may be represented by the expressions $k_1 = 10^{-15.8\pm0.4} \exp[(-1300 \pm 200)/RT]$ cm^3 s^{-1}.[29] These data refer to polystyrene adsorbed in an approximately monomolecular layer on the surface of aerosil ($s_{sp} \simeq 200$ m^2 g^{-1}) and the measured kinetic constants presumably characterise the rate of the chemical reaction itself.

Table 7. Kinetic constants for the reaction H + RH → H_2 + R (the constants k_2 were determined throughout for one reacting C–H bond).

Reacting compound	T, K	E_{eff}, kcal mole^{-1}	k_2, cm^3 s^{-1}	Refs.
Deuteropolyethylene*	170—430	2—3	—	76
Dihydrothymine**	140—330	2.5	—	72
Dihydrouracil***	190—300	2	—	73
Malonic acid	96	0.6	$1.8\cdot10^{-22}$	15
	253	6.0	$1.3\cdot10^{-19}$	
n-Hexadecane	77	0.4	$1.5\cdot10^{-21}$	15
	173	3.2	$2.2\cdot10^{-19}$	
Poly(methyl acrylate)	77	0.3	$1.8\cdot10^{-20}$	28
	223	2.0	$5.2\cdot10^{-19}$	
Poly(ethylene oxide)	99		$1.6\cdot10^{-21}$	13
Poly(methyl methacrylate)	96	0.4	$7.5\cdot10^{-21}$	28
	203	2.2	$3.2\cdot10^{-19}$	
Polypropylene	96	0.3	$3.2\cdot10^{-19}$	28
	173	1.3	$1.6\cdot10^{-18}$	
Polyisobutylene	77	0.4	$5.5\cdot10^{-21}$	14
	233	4.0	$2\cdot10^{-18}$	

*Specimen in the form of a powder.
**Powder with a particle size of 60–100 μm.
***Aerogels; in the remaining cases the substance was adsorbed on aerosil.

It is of interest to compare the constants k_1 for different compounds at a single temperature; unfortunately only a limited number of such data are available. Table 6 shows that the rate constants for the addition of atomic hydrogen to propene and isobutene (77 K) are approximately the same and exceed the corresponding constant for the addition to the benzene rings of polystyrene by two orders of magnitude. The ratio of the rates of addition of atomic hydrogen at 90 K to the CH_2 = CH– (propene and but-1-ene) and –CH=CH–(*trans*-but-2-ene) bonds is ten[37]. An approximately the same ratio of the rates is observed for the addition of atomic hydrogen to the terminal and inner double bonds in hexa-1,4-diene[37].

Interesting results were obtained in a kinetic study of reaction (2): H + RH → H_2 + R (Table 7 and Figs. 7 and 8). The rate of reaction and the concentration of hydrogen atoms (in the gas phase) were in all cases measured by EPR. The majority of kinetic data refer to substances adsorbed in a thin layer (not more than 5–10 μmole m^{-2}) on aerosil with a specific surface of 200 m^2 g^{-1}.

The principal characteristic feature of the low-temperature reaction H + RH → H_2 + R is the absence of a linear dependence of $\lg k_2$ on $1/T$. The plot of $\lg k_2$ against $1/T$ is a concave curve[14,15,28], i.e. the rate constant diminishes much more slowly than would follow from the Arrhenius law as the temperature is reduced. The concave shape of the curves is pronounced in those cases where it was possible to investigate the reaction over a comparatively wide range of temperatures, for example, for polyisobutylene (Fig. 7*a*) and malonic acid (Fig. 8, curve *1*).

The rate constants for reactions at a low temperature are high [thus the values of k_2 at 77 K for n-hexadecane, poly(methyl methacrylate) and polyisobutylene are in the range 10^{-21}–10^{-20} cm^3 s^{-1}] and exceed by many orders of magnitude the values which would be expected if the Arrhenius law held. Fig. 8 compares the rate constants for the reactions of atomic hydrogen with the methylene groups of n-hexadecane (solid phase, 77–188 K) and n-butane (gas phase, 300–500 K).

The plot shows that the rate constant for the reaction at 77 K exceeds the extrapolated value by ten orders of magnitude. At 77–120 K the reaction rate is almost independent of temperature. The effective activation energy in this temperature range is < 1 kcal mole^{-1}.

3. Isotope Effects in Reactions (1) and (2)

As mentioned at the beginning of Section III, the ratio of the rate constants for the addition of atomic hydrogen in the two possible positions relative to the $\rangle C{=}C \langle$ double bond [reactions (1) and (1′)] depends on the nature of the substituents at the carbon atoms (Table 3). The ratio increases when the olefin is acted upon by atomic deuterium; under these conditions, the greater the ratio k_1/k_1', the greater the isotope effect (Table 8)[37]. It has been established[37] that, when atomic hydrogen reacts with propene and deuteropropene, the relative rates of reactions (1) and (1′) are the same, i.e. there is no isotope effect.

Table 8. The isotope effects in reactions involving the addition of hydrogen and deuterium atoms to olefins[37] (k_1 and k_1' are the rate constants for the addition of hydrogen or deuterium atoms to carbon atoms shown to the left and to the right of the double bond respectively).

Olefin	T, K	$(k_1/k_1')_H$	$(k_1/k_1')_D$	$\frac{(k_1/k_1')_D}{(k_1/k_1')_H}$
CH_2=CH–CH_3 or CD_2=CD–CD_3	90	126	398	3.1
	77	167	575	3.4
CH_3–CH=CH–CH_2–CH_3 (cis)	90	1.48	1.46	1.0
CH_3–CH=C$(CH_3)_2$	77	115	234	2.0
	90	115	233	2.0
	113	102	155	1.5
	143	53	75	1.4

The rate of the reaction H + RH → H_2 + R hardly changes when hydrogen atoms are replaced by deuterium[77]. The rate constants for the reactions in these two instances are plotted in Fig. 7*a*. Evidently all the points lie on a single curve. On the other hand, the rate of the hydrogen atom transfer reaction is very sensitive to isotope substitution in the structure of the reacting molecule[28,77]. Fig. 9 presents data for the kinetic isotope effects in the reactions of atomic hydrogen with poly(methyl methacrylate) and deuteropoly(methyl methacrylate) (all the hydrogen atoms

have been replaced by deuterium atoms and the deuterium content in the isotope-substituted position is 98.9%). The measured isotope effects (curve *1*) are compared with the values calculated from the equation $k_H/k_D \simeq \exp(0.15\, h\nu_{C\text{-}H}/kT)$ (Here $\nu_{C\text{-}H} = 9 \times 10^{13}$ s^{-1} is the stretching vibration frequency of the C–H bonds, h the Planck constant, and k the Boltzmann constant)[78]. Fig. 9 shows that the experimental values exceed the calculated data over the entire temperature range (165–300 K), the discrepancy increasing at low temperatures. The calculated isotope effect at 165 K is 45, while the experimental value is $\geqslant 260$.

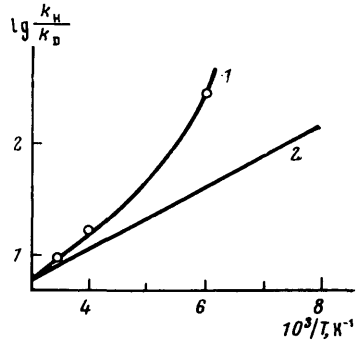


Figure 9. Temperature dependence of the isotope effect k_H/k_D for the reactions of hydrogen atoms with poly(methyl methacrylate) and deuteropoly(methyl methacrylate)[28]: 1) experimental values; 2) linear plot based on calculated values (see text).

Thus kinetic isotope effects of two types were observed—those associated with the replacement of (1) atomic hydrogen by atomic deuterium and (2) of H atoms by D atoms in the structure of the reacting molecule. Isotope effects of the first type are characteristic of addition reactions where the second effect is absent, while the situation is reversed in hydrogen atom transfer reactions.

IV. QUANTUM-MECHANICAL EFFECTS IN LOW-TEMPERATURE REACTIONS

The possible role of the tunnel effect in chemical kinetics has been frequently discussed theoretically[79–82]. It has been shown experimentally that tunnelling must be taken into account in a whole series of reactions involving electron transfer (oxidation-reduction reactions and radiation-chemical and photochemical processes). The mass of the hydrogen atom exceeds that of the electron by a factor of 1841, which reduces sharply the probability of the passage of H through the barrier. For this reason, the tunnel effect in reactions involving the transfer of a proton or a hydrogen atom can be manifested distinctly only at low temperatures. A number of kinetic consequences arise from the possible tunnel migration of a hydrogen atom through the barrier: deviations from the Arrhenius law, extremely large isotope effects when the H atom in the structure of the reacting molecule is replaced by a D or T atom (k_H/k_D or k_H/k_T), a nonlinear relation between $\lg(k_H/k_D)$ and $1/T$, etc. These facts were established in a study of the interaction of hydrogen atoms with solid organic substances at low temperatures, namely H + RH → H_2 + R. The tunnel mechanism of this reaction is confirmed by calculations of the dependence of the reaction rate constant on temperature, taking into account the passage through the barrier.

The reaction rate constant can be represented in the usual Arrhenius form:

$$k = A\gamma \exp(-V/RT), \tag{32}$$

where V is the height of the potential barrier in the reaction, A the pre-exponential factor, and $\gamma = w_{qu}/w_{cl}$ the correction for tunnelling or the "tunnel" correction (w_{qu} and w_{cl} are the "quantum" and "classical" reaction rates).

An exact calculation of the "tunnel" correction is impossible without knowing the potential surface for the reaction. Simplified models are used in approximate calculations. It is assumed to a rough approximation[79,82] that the activation barrier is one-dimensional and that the system is in thermal equilibrium. For such a system, we have:

$$\gamma = \exp\frac{V}{kT}\int_0^\infty \frac{1}{kT} G(W) \exp\left(-\frac{W}{kT}\right) dW, \tag{33}$$

where W is the energy of the reacting species, $G(W)$ the probability of the tunnel reaction or the permeability of the barrier, which depends only on its width and height when its shape is specified, and k is the Boltzmann constant.

The experimental data for the reaction H + RH → H_2 + R at low temperatures agree satisfactorily with the results of the calculation carried out in accordance with this model[13,15,83]. In the calculations the barrier was assumed to have the parabolic shape; Bell[80] obtained an exact solution of the integral Eqn. (33) for such a barrier:

$$\gamma = \frac{e^\alpha}{\beta - \alpha}(\beta e^{-\alpha} - \alpha e^{-\beta}). \tag{34}$$

Here

$$\alpha = V/kT,\ \beta = \frac{2\pi^2}{h} d \cdot (2mV)^{1/2},$$

where d is the effective half-width of the barrier, m the reduced mass of the tunnelling species, and h the Planck constant.

The rate constants calculated for the reactions involving malonic acid and n-hexadecane (continuous curves) are compared in Fig. 8 with the measured values (designated by circles). The parameters of the barrier and the pre-exponential factors used in the calculation are listed in Table 9. It is striking that the rate constants for the reactions involving n-butane and n-hexadecane (per methylene group) fit on a single smooth $\lg k - 1/T$ curve, which satisfies the parameters listed in Table 9 for the reaction

$$H + C_nH_{2n+2} \rightarrow H_2 + C_nH_{2n+1}.$$

Thus the temperature dependence of the rate of this reaction may be accounted for over a very wide range (100–1000 K) on the assumption that the potential surface for the reaction remains unchanged on passing from the gas phase (330–1000 K) to the solid phase (100–173 K) and that the deviation from the Arrhenius law is due to the tunnel mechanism of the reaction at a low temperature.

Table 9 also presents the parameters of the activation barrier for a number of other reactions for which the appropriate calculations have been made[83]. In all cases the calculated and experimental results agreed satisfactorily. The effective half-widths of the barriers in these

reactions are in the range 0.5–0.65 Å (Table 9) and are comparable with the values calculated by Caldin[82] for proton transfer in the liquid phase.

Table 9. Certain parameters adopted in the calculation of the "tunnel" correction (parabolic barrier)[83].

Reaction	T, K	V, kcal mole^{-1}	d, Å	A, cm^3 s^{-1}
$\dot{H}+-(CH_3)_2C-CH_2-C(CH_3)_2- \rightarrow$ $\rightarrow H_2+-(CH_3)_2C-\dot{C}H-C(CH_3)_2-$	100—180	6.0	0.65	$5\cdot10^{-11}$
$\dot{H}+-CH_2CH_2O- \rightarrow H_2+-CH_2\dot{C}HO-$	100—150	6.7	0.57	$5\cdot10^{-11}$
$\dot{H}+C_nH_{2n+2} \rightarrow H_2+C_nH_{2n+1}$	100—1000	7.0	0.58	$3\cdot10^{-11}$
$\dot{H}+CH_2(COOH)_2 \rightarrow H_2+\dot{C}H(COOH)_2$	100—250	6.1	0.51	10^{-14}

Thus calculations carried out in terms of a rough approximation showed that the rate constants for the reaction H + RH → H_2 + R and the form of the temperature dependence of lg k_2 can be satisfactorily explained on the assumption of tunnelling.

Calculations of the ratios k_1/k_1' for the addition of atomic hydrogen to olefins have been carried out taking into account tunnelling (Table 8).[37] It was assumed in these calculations that the addition to two carbon atoms can be described by two one-dimensional barriers, taking into account the asymmetry of the barriers. The parameters of each barrier were varied as follows: the height from 1.2 to 4.5 kcal mole^{-1} and the effective half-width from 0.25 to 0.75 Å. The authors[37] were unable to achieve the agreement of all the experimental k_1/k_1' ratios at different temperatures with the calculated values whatever the combination of the quantities characterising the height and width of the barrier (the calculations were performed for rectangular and Eckart forms of the barrier). Nevertheless one may agree with the authors' conclusions that tunnelling is the only mechanism which permits an explanation of the isotope effects observed in the addition reaction. The discrepancies between the experimental and calculated values are probably associated with the fact that the one-dimensional barrier model is relatively unsuitable for the description of the reaction in the present instance.

V. REACTIONS OF FREE RADICALS WITH HYDROGEN ATOMS AND WITH ONE ANOTHER AT A LOW TEMPERATURE

Hydrogen atoms react with free radicals at a low temperature via recombination [reaction (3)] and disproportionation [reaction (4)] mechanisms. The elementary constants k_3 and k_4 for low-molecular-weight free radicals have not been measured, but attempts have been made[22,24] to estimate the ratios of these constants for certain systems. The few available data for reactions of the type R + H are summarised in Table 10, which shows that the disproportionation reaction predominates for alkyl radicals at a low temperature. This conclusion applies also to isotope-substituted radicals, without hydrogen atoms, such as C_3D_6T.

The overall rate constants for the reaction with atomic hydrogen ($k_3 + k_4$) were measured in the range 77–220 K for polymeric free radicals of different structures[28]. To a first approximation, the temperature dependence of $k_3 + k_4$ obeys the Arrhenius law. The activation energies for the reactions are in the range 0.4–0.9 kcal mole^{-1} and the pre-exponential factors are in the range $10^{-14.3}$–$10^{-15.6}$ cm^3 s^{-1} (Table 11), i.e. are smaller by 2–4 orders of magnitude than the collision numbers Z for the systems investigated ($Z \simeq 10^{-11}$ cm^3 s^{-1}).

Table 10. The ratios of the rate constants for the disproportionation and recombination reactions.

Reactions	T, K	k_4/k_3	References
H + s-C_4H_9	90	1.9	22
T + iso-C_3H_6T	63	3.55	24
T+C_3D_6T	63	3.05	24

Table 11. Parameters of the Arrhenius equation for the reaction between R(ROO) and atomic hydrogen[28,29].

Polymeric free radicals	Temp. range, K	E, kcal mole^{-1}	$-\lg A$ (cm^3 s^{-1})
$-C(CH_3)_2-\dot{C}H-C(CH_3)_2-$	77—163	0.4	~15.6
$-C(CH_3)(COOCH_3)-\dot{C}H-C(CH_3)(COOCH_3)-$	96—203	0.9±0.3	14.7±0.3
$-CH_2-\dot{C}(COOH)_2-CH_2-$	77—223	0.5±0.2	15.5±0.3
$-CH_2-\dot{C}(CH_3)-CH_2-$	96—173	0.5±0.3	14.4±0.5
$-CH_2-C(C_6H_5)-CH_2-$	77—163	0.8±0.1	14.3±0.3
ROO· poly(vinyl acetate)	113—173	1.2±0.1	14.8±0.1

These values were obtained from the analysis of kinetic curves for the accumulation of free radicals, which does not allow the separate determination of k_3 and k_4. In order to discover which reaction predominates—recombination or disproportionation—additional measurements are necessary using other methods (analysis of molecular products, the study of the deuterium–hydrogen exchange, monitoring of the pressure variation, etc.). It has been possible to establish for polystyrene[29] that free radicals (of the cyclohexadienyl type) interact with hydrogen atoms (at 123–163 K) via a recombination mechanism, which leads to partial hydrogenation of the aromatic rings. Presumably this reaction is the cause of the appearance of cyclohexadiene rings, which were detected by infrared spectroscopy in polystyrene irradiated by fast electrons[84].

The free radicals arising as a result of reactions (1) and (2) can react not only with hydrogen atoms but also with one another. The rate of reaction of the radicals in the solid phase is usually limited by their mobility. The kinetics and mechanism of the destruction of free radicals in the solid phase constitute an independent problem and numerous studies have been devoted to it. We shall consider only the question of the relative rates of the reactions leading to the destruction of free radicals when they interact with one another: the recombination [reaction (5)] and disproportionation [reaction (6)] reactions. The ratios k_{disp}/k_{rec} (k_6/k_5) for the free radicals formed when solid organic compounds are acted upon by hydrogen or tritium atoms are listed in Table 12, which also includes the

values for the free radicals obtained by other methods. Analysis of these data reveals the following fundamental features.

(1) The ratio k_{disp}/k_{rec} depends on the structure of the radicals. For primary alkyl radicals (methyl–ethyl, ethyl–ethyl), the ratio is small and amounts to 0.2–0.3 at 80–90 K, i.e. the recombination reaction predominates. For secondary radicals (isopropyl, s-butyl, s-pentyl, cyclohexyl), the ratio k_{disp}/k_{rec} increases and is in the range 2–11 according to different data. The difference between the relative rates of disproportionation and recombination is even greater for tertiary butyl and pentyl radicals. The disproportionation reaction is virtually the only pathway to the destruction of these radicals at a low temperature.

Table 12. The ratios of the rate constants for the disproportionation and recombination reactions in the solid-phase interaction of certain free radicals with one another.

Free radicals[a]	T, K	k_{disp}/k_{rec}	Matrix	References
$\dot{C}H_3+\dot{C}_2H_5^*$	82	0.174	$CH_3N_2C_2H_5$	
	82	0.183	iso-octane	85
	82	0.196	glycol	
$2\dot{C}_2H_5^*$	89	0.198	azoethane	
	89	0.309	toluene	
	89	0.325	propanol	
	79	0.304	toluene	86, 87
	78	0.187	azoethane	
	78	0.327	glycol	
$\dot{C}_2H_5+\dot{C}_2H_4T$	63	0.83	ethylene	
$2\dot{C}_2H_4T$	63	0.77	ethylene	26
$2\dot{C}_2D_4T$	63	0.75	ethylene	
2iso-$\dot{C}_3H_7$	90	6	propane	37
	77	8—10	propane, butane	9, 20, 21, 37
	77	3	propene	17
	77	2*	azoisopropane	22
	63	22	propane	37
2iso-$\dot{C}_3H_6T$	77	5.5	propene	23
	63	5.9	propene	
2s-$\dot{C}_4H_9$	90	11	propane	22
2t-$\dot{C}_4H_9$	90	500	propane	37
2s-$\dot{C}_5H_{11}$	90	6,4	propane	88
$2CH_3\dot{C}HCH_2CH{=}CH_2$	90	7.6	propane	88
2t-$\dot{C}_5H_{11}$	90	1566	propane	89
t-$\dot{C}_5H_{11}$ + s-$\dot{C}_4H_9$	90	35	propane	89
2cyclo-$\dot{C}_6H_{11}$	160—190	5	cyclohexane	90
	112	2.7	cyclohexene	91
	77	49	cyclohexene	91
	77	1	cyclohexane	35
$2CH_3-\dot{C}H-CH{=}CH_2$	90	<0.01	propane	88
$2CH_3-\dot{C}H-CH{=}CH(CH_3)$	90	<0.01	propane	88
$2CH_3-\dot{C}(CH_3)-CH{=}C(CH_3)_2$	90	<0.01	propane	88

[a]The free radicals were generated by exposing the corresponding olefin or diene to hydrogen or tritium atoms; in the instances denoted by asterisks the free radicals were obtained by the photodecomposition of azo-compounds.

In contrast to alkyl radicals, allyl radicals are destroyed exclusively via a recombination mechanism (Table 12).

(2) The ratio k_{disp}/k_{rec} is sensitive to the nature of the matrix in which the free radicals are present. The physical state of the substance in which the radicals are distributed plays an important role under these conditions. Thus the ratios and the rates of recombination and disproportionation are different in vitreous and crystalline matrices[92].

(3) The ratio k_{disp}/k_{rec} increases as the temperature is reduced, which indicates a higher activation energy for the recombination reaction than for the disproportionation reaction. It follows from the data in Table 12 that the difference $E_{rec} - E_{disp}$ usually amounts to several hundreds of cal mole^{-1}.

Similar features, albeit not quite so pronounced, are also observed for the reactions of free radicals with one another in the liquid phase[93,94]. The ratio k_{disp}/k_{rec} also depends in this case on the structure of the reacting radicals and on the type of solvent, increasing as the temperature is reduced.

Thus fairly extensive experimental data concerning the nature of the interaction of free radicals with one another in the solid phase, analysis of which is useful in the study of the mechanisms of solid-phase reactions and for the elucidation of the structure of the transition complex in recombination and disproportionation reactions, have now accumulated. It has been suggested at one time that these two reactions have a common transition complex, which aroused controversy and stimulated a number of investigations[94]. The dependence of k_{disp}/k_{rec} on the nature of the matrix and temperature (Table 12) shows that the hypothesis of two types of transition complex is more correct. This problem is discussed in greater detail in a special review[94].

VI. DIFFUSION AND RECOMBINATION OF HYDROGEN ATOMS IN SURFACE LAYERS

Data on the diffusion, solubility, adsorption, and recombination of hydrogen atoms in solid organic substances are important for understanding the mechanism of the interaction of gaseous atomic hydrogen with such substances. Unfortunately there is almost no information of this kind, mainly owing to the lack of direct methods of measurement. For this reason, this last section represents merely an attempt at a compilation in one place of the scattered values which are sometimes rough estimates based on indirect data.

Table 13. The diffusion coefficients D and rate constants for the recombination of hydrogen atoms (k_7) in frozen hydrocarbons at 77 K.

Hydrocarbon	D, cm^2 s^{-1}	k_7, cm^3 s^{-1}
Propene	$3\cdot10^{-7}$ (27)	$2\cdot10^{-14}$
Propane	$2\cdot10^{-4}$	$\sim10^{-11}$
n-Butane	$5\cdot10^{-4}$ (9)	$3\cdot10^{-11}$
Isobutene	$2\cdot10^{-3}$ (8)	$1\cdot10^{-10}$ ($2\cdot10^{-12}$ (8))

Note. Figures in round brackets denote references (Ed. of translation).

The diffusion coefficients of hydrogen atoms in certain frozen hydrocarbons are listed in Table 13. The estimates of D are based on the H-diffusion model where no account was taken of the mobilities of other reacting species (see Section II), so that the tabulated values do not correspond entirely to real systems.

The recombination rate constants k_7 for hydrogen atoms in a layer of frozen hydrocarbon (Table 13) were calculated on the hypothesis that each collision leads to interaction and that the rate of reaction (7) is limited by the

diffusion of hydrogen atoms. Then

$$k_7(\text{cm}^3\,\text{s}^{-1}) = 4\pi\rho D\,, \qquad (35)$$

where ρ is the collision radius of the hydrogen atom, assumed to be 0.5 Å in the calculations.

Table 13 also lists the value $k_7 = 2 \times 10^{-12}$ proposed for isobutene[8].

The values of D and k_7 for propane were estimated from calorimetric measurements[3,27]. The heat evolved in a layer of propane amounts to 6% of that evolved in a layer of propene with the same thickness. Assuming that the evolution of heat is caused in the first case by hydrogenation and in the second by reaction (7) (as will be shown below, this is apparently true), one can write

$$w_7/w_{\text{hydr}} = 0.06\ Q_{\text{hydr}}/Q_7 = 0.08$$

where w_7 and Q_7 are the rate and heat of recombination of hydrogen atoms in propane and w_{hydr} and Q_{hydr} are the rate and heat of hydrogenation of propene. Under the experimental conditions, we have

$$w_{\text{hydr}} \simeq 2k_1[\text{H}][\text{C}_3\text{H}_8],\ w_7 = k_7[\text{H}]^2.$$

Hence

$$k_7 \sim \frac{2k_1[\text{C}_3\text{H}_8]}{[\text{H}]} \cdot \frac{w_7}{w_{\text{hydr}}} \simeq \frac{2k_1[\text{C}_3\text{H}_8]}{[\text{H}]} \cdot 0.08 \simeq \frac{0.16k_1[\text{C}_3\text{H}_8]}{[\text{H}]}\,.$$

When $[\text{H}] = 10^{14}$ cm^{-3}, we have $k_7 \simeq 10^{-11}$ cm^3 s^{-1}.

D for propane, calculated by Eqn. (35), is 2×10^{-4} cm^2 s^{-1} and is close to the diffusion coefficient in n-butane.

We shall now trace the fate of hydrogen atoms in a solid reacting substance. The destruction of hydrogen atoms is possible in the course of reactions (1)–(4) and (7). We shall denote by w_{add} the rate of destruction of hydrogen atoms as a result of the chemical reaction with an unsaturated compound M and by w_{abs} the rate of destruction due to the reaction with a saturated compound RH. At a steady-state concentration of free radicals, we have

$$w_{\text{add}} \simeq 2k_1[\text{H}][\text{M}],\ w_{\text{abs}} \simeq 2k_2[\text{H}][\text{RH}].$$

Then

$$w_7/w_{\text{add}} = \frac{k_7[\text{H}]}{2k_1[\text{M}]} \text{ and } w_7/w_{\text{abs}} = \frac{k_7[\text{H}]}{2k_2[\text{RH}]}\,.$$

Thus the ratio of the rates of the corresponding processes is determined by the constants k_7 and k_1 (k_2) and the concentration of atomic hydrogen in the layer of the reacting substance. For frozen olefins (propene, isobutene), $k_7(77\text{ K}) = 10^{-12}$ cm^3 s^{-1}, which is probably close to the real value. The constant $k_1 \simeq 10^{-18}$ cm^3 s^{-1} (Table 6). Hence $w_7/w_{\text{add}} \simeq 10^{-16}[\text{H}]$. Since $[\text{H}] \leq 10^{14}$ cm^{-3} under the experimental conditions, it follows that $w_7 \simeq 10^{-2}w_{\text{add}}$, i.e. hydrogen atoms are destroyed preferentially as a result of the hydrogenation of the olefin.

For the hydrogen atom transfer reaction H + RH → H$_2$ + R (polyisobutylene), $k_2(77\text{ K}) = 5 \times 10^{-21}$ cm^3 s^{-1}. If the value of k_7 is the same as in the previous example, then $w_7/w_{\text{abs}} = 10^{-14}[\text{H}]$. Hence we obtain $w_7 \simeq w_{\text{abs}}$ for $[\text{H}] = 10^{14}$ cm^{-3} and $w_7 < w_{\text{abs}}$ for $[\text{H}] < 10^{14}$ cm^{-3}. Thus under the real experimental conditions the rate of recombination of hydrogen atoms in polyisobutylene at 77 K is comparable to the rate of their destruction via chemical interaction with the polymer. At low concentrations of atomic hydrogen, the destruction of radical species in reactions (2)–(4) predominates.

The heterogeneous recombination of hydrogen atoms on the surfaces of certain organoelemental polymers has been studied in a number of investigations[5,95,101,102]. The rate of destruction of atoms on any surface is characterised by the probability of recombination ϵ, which is defined as the ratio of the rate of heterogeneous recombination to the frequency of the impacts by atoms on the surface. It is usually believed[5] that the rate of recombination of hydrogen atoms on the surfaces of polymeric films obeys (as for Pyrex) first-order kinetics, but this conclusion requires further confirmation and ϵ may depend on the concentration of atomic hydrogen in the gas phase. The probabilities of the recombination of atomic hydrogen on the surfaces of certain polymers at room temperature are listed below:

Polymer	ϵ	Literature
Polytetrafluoroethylene	10^{-4}	95
	$\sim 10^{-6}$	101
Polychlorotrifluoroethylene	$4 \cdot 10^{-4}$	95
Chloromethylsilane polycondensation products (Drifilm)	$4 \cdot 10^{-4}$	95
	$2 \cdot 10^{-5}$	102

The rate of hydrogenation of propene hardly changes when it is coated by a thin film of propane[1,3,27], which indicates a low rate of recombination of hydrogen atoms in the propane layer. According to Ponomarev's estimate[27], the probability of the recombination of atomic hydrogen on the surface of propane (at 77 K) is 6×10^{-5}.

There are no other more detailed literature data for the rates and mechanisms of the recombination of hydrogen atoms on the surfaces of solid organic substances. We believe that research on the heterogeneous recombination of atomic hydrogen at low temperatures, where its rate still depends on the heat of the physical adsorption of hydrogen atoms on the surface of the substance, is urgently required. One may hope that such research will make it possible to estimate the heats of adsorption of various compounds and to approach more closely the mechanisms of the chemical reactions of atomic hydrogen with solid organic substances.

VII. CONCLUSION

The interaction of thermal hydrogen atoms with a wide range of solid organic substances has been investigated. The mechanisms of the reactions leading to the formation of free radicals have been unambiguously established for the vast majority of the compounds. The mode of these reactions is determined by the chemical structure of the reactant and is as a rule the same in the gas and liquid phases. However, in those cases where there is a possibility of two or more reaction pathways, the low-temperature reaction in the solid phase proceeds via the pathway which requires the lowest activation energy. For example, the main pathway in the reaction of atomic hydrogen with toluene at 113 K involves addition to the aromatic ring[49]: H + $C_6H_5CH_3$ → $C_6H_6CH_3$, whereas in the gas phase at high temperatures hydrogen atoms are abstracted from the methyl group[96] and the reaction H + $C_6H_5CH_3$ → C_6H_6 + CH_3 takes place[97].

The ratio of the rate constants for the addition of hydrogen atoms in two different positions relative to the double bond of the olefin increases as the temperature is reduced. Thus the ratio for propene increases from 21 (300 K, gas phase) to 189 (63 K, solid phase)[37]. These two examples therefore show that the reactions are more selective at a low temperature.

The specific features of the solid phase and low temperatures affect the kinetics of the individual stages of the interaction of atomic hydrogen with solids; they are manifested in two ways. On the one hand, the mechanism of the chemical reactions is simplified, since many secondary free-radical processes occurring in the gas phase do not take place in the solid phase at fairly low temperatures

owing to the limited mobility of the molecules and free radicals. Furthermore, vibrationally excited species are formed in the gas phase, while the solid phase promotes their effective deactivation. For this reason, reactions involving the decomposition of excited species as well as possible reactions of hot radicals[5,61,98,99] are ruled out when the kinetics of solid-phase processes are considered.

On the other hand, the occurrence of the reactions in the solid phase and at low temperatures complicates the determination of their elementary rate constants. Under these conditions, the process kinetics depend on the rates of a number of physical stages, primarily diffusion, adsorption, and the dissolution of hydrogen atoms in the solid substance. In a more detailed approach one must take into account also the molecular motions in the solid phase; translation, rotations, etc.

The kinetic data obtained hitherto make it possible to infer the rate of interaction of hydrogen atoms with solid organic compounds as a whole and the rates of its individual stages. The kinetics of the reactions of atomic hydrogen at a low temperature are characterised by specific features associated with the manifestation of quantum effects. At low temperatures below a critical value T_{cr}, the rate of the reactions via the tunnel mechanism exceeds by a large factor the rate of the classical Arrhenius reaction. T_{cr} is proportional to the square root of the height of the potential barrier[79], so that at $T > 77$ K the tunnel effect is manifested most distinctly by reactions with large activation energies—the hydrogen atom transfer reactions. The following characteristics, which are the kinetic consequences of the transfer of a hydrogen atom via the tunnel mechanism, have been established for the $H + HR \rightarrow H_2 + R$ reaction at 77–220 K: high rate constants at 80–100 K (10^{-19}–10^{-22} cm^3 s^{-1}), low effective activation energies at these temperatures (< 1 kcal $mole^{-1}$), failure to obey the Arrhenius law, extremely large kinetic isotope effect when RH is replaced by RD, and a non-linear dependence of $\lg(k_H/k_D)$ on $1/T$. One should note that the deviation from the Arrhenius law, due to the effect of the tunnel transfer of a hydrogen atom on the rate of the given reaction, is observed also at higher temperatures in the gas phase. However, the deviation at high temperatures is insignificant and can be observed only when kinetic data are analysed over an extended temperature range (300–1800 K)[100]. At a low temperature, the $\lg k - 1/T$ curves are distinctly concave (Figs. 7 and 8).

For reactions of atomic hydrogen with unsaturated compounds, the ratio of the rate constants for addition in two possible positions relative to the double bond of the olefin increases when hydrogen atoms are replaced by deuterium atoms. This isotope effect also indicates a tunnel mechanism of the addition reaction at a low temperature. Other kinetic manifestations of tunnelling, analogous to those described above, for hydrogen atom transfer reactions are to be expected at temperatures below 77 K, because the activation energy and hence also T_{cr} are lower for the addition reactions.

The studies of the kinetics of the interaction of atomic hydrogen with solid organic substances have established certain facts, which indicate a specific character of the chemical process in the solid phase. Thus the pre-exponential factor in the Arrhenius equation for reactions involving the addition of hydrogen atoms to unsaturated compounds (propene, polystyrene) and H + R reactions are smaller by 3 – 4 orders of magnitude than the collision number. Interesting data have been obtained concerning the pathways in the reactions of alkyl radicals with one another. Although recombination is energetically more favourable than disproportionation, alkyl radicals are destroyed in the solid phase mainly via a disproportionation mechanism and the ratio k_{disp}/k_{rec} depends very markedly on the structure of the matrix.

After the manuscript had been sent to the printers, Ovchinnikova[103] published a study, in which the probabilities of tunnelling in the reaction $H + H - \overset{|}{\underset{|}{C}} - \rightarrow H_2 + \overset{|}{\underset{|}{\dot{C}}}-$ were calculated for a three-dimensional barrier. The exact quantum-mechanical solution of the problem was replaced by approximate calculations based on the classical S-matrix method. Comparison of the tunnelling probabilities for vibrational-adiabatic one-dimensional and three-dimensional barriers established that non-adiabatic effects significantly increase the probability of the tunnel reaction. Parameters of the model were selected for which the experimental data[28] (the dependence of the rate constant for the hydrogen transfer reaction on temperature and the isotope effects) agree with the results of the calculation.

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