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THE MECHANISM OF THE ELEMENTARY ACT OF HOT REACTIONS

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I. INTRODUCTION

Hot atom chemistry dates from the discovery, made by Szilard and Chalmers in the nineteen-thirties, that as a result of a nuclear reaction, radioactive atoms leave the original molecule and are found partly in a chemical form which can be separated from the initial form. Fermi showed that the reactivity of these atoms is associated with the considerable recoil impulse produced when the second particle is ejected in the nuclear process. Although the first work in the field of the chemistry of hot atoms (as atoms exhibiting appreciable kinetic energy came to be called) was devoted chiefly to the practical utilisation of the Szilard–Chalmers method for the preparation of enriched specimens of radioelements, the main attention was subsequently directed to the secondary effects associated with the chemical action of hot atoms. Here two directions have been distinguished.

Part of the work is carried out with the aim of finding an effective method for preparing labelled compounds, particularly those which are difficult to obtain by ordinary chemical synthesis or by isotopic exchange. The possibilities of the hot synthesis of organic compounds labelled with tritium and carbon have been discussed in reviews by Nesmeyanov and coworkers[1–3].

Another direction in hot atom chemistry involves the investigation of the mechanism of the elementary act of the atom–molecule collision and the subsequent reactions brought about by the transfer of the excess of energy from the atom to the molecule. Since the publication of reviews by Nesmeyanov and Borisov[4,5] in 1957 and earlier, no attempt has been made in the Soviet literature to examine the achievements made in this direction. The present paper examines the results obtained in recently published work. Particular attention is paid to the theoretical interpretation of the results. The review does not reflect completely all directions of study in hot atom chemistry: the main attention is paid to work whose results lead to definite conclusions regarding the mechanism of hot reactions.

At the present time, hot atom chemistry is attracting increasing attention as a branch of high-energy chemical kinetics. This is indicated by the two international conferences held in Prague in 1960 and in Vienna in 1964.

II. SOME PHYSICOCHEMICAL PRINCIPLES OF HOT ATOM CHEMISTRY

1. The Possibility of Applying the Theory of Absolute Reaction Rates to High-Energy Chemical Processes

The first problem arising in the theoretical interpretation of the results of experiments in hot atom chemistry is the extent to which the ideas of an intermediate complex as the transition state of the reacting atom–molecule system are applicable to the reactions of high-energy atoms. The Arrhenius–Eyring equation is:

$$k \simeq z \exp[-E/RT] \simeq pz \exp[-E/RT] \simeq \chi pz \exp[-E/RT], \quad (1)$$

where z is the number of active collisions, p a steric factor, and χ the transmission coefficient, with $\chi = \rho\sigma$, where ρ is the probability of transition between potential surfaces, and σ the reflection coefficient (the reflection coefficient is related to the rate of deactivation in the transition state). This equation can be used to calculate reaction rate constants if the following conditions are satisfied: (1) the reaction A + BM → [AB]M → AB + M is adiabatic, that is, takes place on one potential surface; (2) the potential energy surface has a range corresponding to the existence of the activated complex; (3) equilibrium is established between the reacting substances and the complexes; and (4) the transmission coefficient is constant and close to 1.

Lack of agreement between experimental data and theoretically calculated values for the rates of chemical reactions is attributed to the fact that the intermediate and final products are formed initially with an irregular distribution of energy in the vibrational degrees of freedom. Vibrational--rotational non-equilibrium distributions may also arise as a result of inelastic collisions of the second type (extinction of electronic-excited states on collision). Deviations from "ordinary" kinetics are observed in processes accompanying the combustion of reactive fuels, rapid explosion reactions, etc.[6]

The pictorial model representation of a chemical reaction as the movement of a configurational point over a potential energy surface[7,8] is untenable in the study of reactions initiated by the collisions of fast atoms, in which the duration of the interaction is much less than the rate of energy transfer from the local point of collision to the molecule as a whole. From this it follows that conditions 1–4 can hardly be applicable to reactions initiated by the collisions of hot atoms, in view of the marked non-equilibrium character of the process of energy transfer on collision. Theoretical studies of non-equilibrium processes are at present in the development stage[9,10].

A specific feature of hot atoms is that they approach the range of the energy of chemical interaction "from above", from the direction of higher energies. On retardation, the hot atom passes successively through energy levels until it falls into an energy range below the activation energy for the reaction. In ordinary kinetics, the atoms which reach $E = E_{act}$ "from below" (that is, the active atoms) are able to take part in a chemical interaction which proceeds on a definite surface corresponding to $E = E_{act}$. The hot atom has at its disposal a set of potential surfaces (possibly with facilitated transition between them) and this makes it very difficult to calculate the probability of chemical interaction by means of a model which represents the

course of the reaction in the form of the movement of a configurational point.

Since the reaction of hot atoms with molecules leads to their stabilisation in definite chemical forms, some hot atom–molecule transition state must exist.

The aim of hot atom chemistry is to determine the nature of this transition state and the energy at which bond formation between the hot atom and the molecule takes place, and to investigate the influence of various factors on the course of hot reactions.

2. Reactions of Excited Molecules and Processes of Excitation Energy Transfer

As shown in Section I.1, the ideas of "ordinary" kinetics provide little basis for understanding the high reactivity of hot atoms. Irrespective of the way in which a chemical bond is formed by a hot atom on collision with a molecule, however, it is undoubtedly the case that the primary "labelled" molecule is excited. Stabilisation of this molecule can take place only with dissipation of the excitation energy. Most information on this question, particularly in recent years, has been given by radiation chemistry. The deviations, observed in a number of studies, from the law of radiation-chemical additivity in the radiolysis of binary systems can be attributed to a process involving the transfer of the excess of energy from the initially excited molecule fragments[11–15]. Analysis of experimental data on "large" and "small" deviations from additivity showed that in the first case the rate of transfer of energy is greater than the number of collisions with inhibitor by a factor of at least 10 (inhibitor concentration < 0.01 M). It is evident that the excitation energy is "thrown" 50–70 Å during the lifetime of the excited molecule. These processes can take place only under conditions where the excitation spectra of two components of the mixture overlap. This condition can be realised in practice by selecting substances with similar chemical structures.

If the action of radiation on a substance leads to the formation of molecular ions, the solution of the problem of energy transfer becomes possible if the following conditions are satisfied: (1) the inhibitor has a complex system of levels (an almost continuous spectrum) in the region of the excitation energy of the main component; (2) the medium is transparent, that is, the excitation levels of the molecular fragments (in particular, ions) formed during radiolysis lie below the first excitation electronic level of the main molecule. Brodskii[13] showed that the probability of inhibition is determined by the equation

$$W = kN^{2/3}\left(1 + \frac{N^{2/3}}{\omega^2} + \frac{N^{4/3}}{\omega^4}\right), \qquad (2)$$

where N is the concentration of inhibitor, and ω the excitation energy. The available experimental data show good agreement with Eqn. (2) over a wide range of concentrations. Since the excitation energy cannot always be determined accurately, use is made of another equation, previously established experimentally:

$$G = kr^3 = k\left(\frac{1}{\sqrt[3]{N}}\right)^3, \qquad (3)$$

where G is the radiation yield, and r the mean distance between the inhibitor molecules, expressed in the number of molecules of the main substance. Eqn. (3) is a first approximation of the more general equation (2). The physical nature of the phenomenon described by Eqn. (2) is the existence of a mechanism of energy transfer analogous to sensitised fluorescence–non-radiative electromagnetic transition[15].

"Small" deviations from additivity are attributed to the direct transfer of energy through the formation of a donor–acceptor complex according to the scheme: $A^* + B \rightarrow \rightarrow [AB]^* \rightarrow A + B$, where the complex breaks down to non-excited particles.

Simple energy transfer on collision $A^* + B \rightarrow A + B^*$ either is very difficult or does not take place at all. This important experimental fact was established in an analysis of the radiation-chemical yields in the cyclohexane–benzene system and in the study of the intensity of fluorescence in the cyclohexane–terphenyl, benzene–terphenyl, and cyclohexane–benzene–terphenyl systems[11]. Since the chief primary particles in radiolysis are excited and ionised molecules, the part played by benzene in the complex $[AB]^*$ is assumed to involve the following processes: (1) the benzene brings about the conversion of the electronic excitation of the cyclohexane molecules; and (2) the benzene removes the charge from the cyclohexane molecule, since the ionisation potential of benzene is lower by 1.8 eV.

From the viewpoint of the formation of donor–acceptor complexes, it is also possible to explain the "large" deviations from additivity, observed at low concentrations of added acceptor, if we assume the existence of associates consisting of molecules of the main substance; in this case the collision of an inhibitor molecule with an associate is equivalent to a collision with an initially excited molecule.

The explanation of the results of radiolysis, however, even for a well-studied system such as the cyclohexane–benzene system, is ambiguous, since the benzene may react with thermal hydrogen atoms:

$$C_6H_6 + H^{\cdot} \rightarrow C_6H_7^{\cdot} \rightarrow \text{polymer}$$

(pyridine shows analogous behaviour in mixtures with benzene[16]).

Moreover, according to Swallow's hypothesis[17] (based on the data of Inokuti on cross-sections for the interaction of electrons with benzene molecules), radiation may be selectively absorbed in a mixture of two components, so that the concentration dependence of the yields of radiolysis products shows marked departure from linearity. Thus departure from additivity in the radiolysis of binary systems does not provide sufficient basis for concluding that energy transfer from the initially excited molecules occurs and influences the yield of radiolysis products.

If Swallow's model were applicable, the radiolysis of a cyclohexane–benzene binary mixture in the gaseous phase at low pressures should give the same effect as that given in the liquid phase. Since the gas-phase radiolysis showed differences from the regular features observed for condensed systems[18], doubt was cast on the applicability of Swallow's hypothesis.

Since the transfer of excitation energy assumes the existence of long-lived states — and this has not been proved spectroscopically — some authors suggest that the deviation from the law of radiation-chemical additivity is due to the formation of hot hydrogen atoms during radiolysis. The energy of the hydrogen atoms formed during radiolysis varies from fractions of 1 eV to 1–3 eV. These atoms are capable of detaching hydrogen from organic compounds with consequent breakdown of the primary distribution of radiolysis products[19,20].

The most appropriate viewpoint is that which allows for the principal effects observed: one of the observed (or assumed) effects may play a major part, depending on the nature of the compounds and the relative concentration of the components[21].

The processes of excited molecule stabilisation are apparently accompanied by intramolecular energy transfer. This was proved by experiments on the radiolysis of alkylbenzenes. The yield of radicals from the compounds C_6H_5R (where R= alkyl) is less than that from the mixture C_6H_6 + RH. This indicates a process of effective energy transfer from the side chain into the phenyl ring. At the same time, analysis of the radiolysis products of alkylbenzenes indicated that the greatest tendency to undergo rupture is shown by the bond formed by the second carbon atom in the side chain, that is, the $C_6H_5CH_2^{\cdot}$ radical is formed in highest yield, irrespective of the length of the chain. This can be attributed to transfer of excitation energy from the benzene ring into the side chain, or simply to the high "vulnerability" of the α position in intramolecular energy migration.

The yields of the products of hot reactions also show deviation from the additivity law, suggesting that the process of energy transfer from the excited labelled products takes place.

3. The Retardation of Hot Atoms (Physical Interpretation)

It has recently been assumed that the retardation of hot atoms in the range of energies in which the reactions of hot atoms do not take place obeys the laws derived from the assumption of elastic particle collisions. In this case the retardation spectrum can be calculated using the equations describing the process of neutron thermalisation[22,23].

The fraction of the energy remaining on a recoil atom (m) after collision with another atom (M) is

$$E'/E = \frac{m^2 + M^2 + 2mM\cos\theta}{(m+M)^2}. \quad (4)$$

The minimum fraction is

$$\alpha = \left(\frac{m-M}{m+M}\right)^2. \quad (5)$$

The loss of energy or the fraction of the energy transferred to an atom of the medium is equal to

$$E''/E = \frac{2mM}{(m+M)^2}(1-\cos\theta). \quad (6)$$

The maximum loss is

$$\beta = \frac{4mM}{(m+M)^2}, \quad (7)$$

where θ is the scattering angle of the centre of mass in the system. The extent of the deviation from spherical scattering can be estimated from the mean value of the cosine of the angle of scattering in a laboratory system of coordinates ($\overline{\cos\varphi}$):

$$\overline{\cos\varphi} = \int_0^{\pi} \cos\varphi\,\lambda(\theta)\,d\theta = \int_0^{\pi} \frac{(M\cos\theta + m)}{\sqrt{m^2 + M^2 + 2mM\cos\theta}} \frac{1}{2}\sin\theta\,d\theta, \quad (8)$$

where $\lambda(\theta)d\theta$ is the probability of scattering.

For the case of the retardation of tritium recoil atoms in a hydrogen-containing medium, expression (8) becomes

$$\overline{\cos\varphi} = \frac{1}{2}\int_{-1}^{+1} \frac{y+3}{\sqrt{1+6y+9}}\,dy, \quad (9)$$

where $y = \cos\theta$, and $dy = -\sin\theta d\theta$.

Solution of integral (9) gives $\overline{\cos\varphi} = 0.9$, that is, the scattering of tritium recoil atoms in hydrogen-containing media is markedly anisotropic.

The number of collisions necessary for retardation of a given energy E from an initial energy E_0 is

$$k = \frac{\ln\frac{E_0}{E}}{\xi}, \quad (10)$$

where ξ is the logarithmic energy decrement

$$\xi = \overline{\ln\frac{E}{E'}} = 1 + \frac{\alpha}{1-\alpha}\ln\alpha. \quad (11)$$

For a chemical two-component compound or binary mixture of substances, the logarithmic decrement is

$$\xi = f_1\xi_1 + f_2\xi_2 = \frac{N_1\sigma_1\xi_1 + N_2\sigma_2\xi_2}{N_1\sigma_1 + N_2\sigma_2}, \quad (12)$$

where $N_1\sigma_1$ and $N_2\sigma_2$ are the macroscopic scattering cross-sections ($N\sigma = \Sigma_s$), N_1 and N_2 the mole fractions, σ the microscopic scattering cross-section, and f_1 and f_2 the geometric probabilities of collision with the first and second components of the mixture.

The beam of hot atoms which have reached the energy level E is defined by the expression

$$n(E) = \frac{q}{\xi E\Sigma_s}, \quad (13)$$

where q is the number of recoil atoms generated, in $cm^3 \times s^{-1}$. Expression (13) is applicable if $E \ll E_0$, that is, if the recoil atom has undergone at least several collisions with other atoms. A more precise criterion for the applicability of Eqn. (13) is that $E < \xi^3 E_0$. If this is not so, it is necessary to make allowance for the fact that the function $n(E)$ shows discontinuities at $E = \xi^n E_0$, where $n = 1, 2, 3\ldots$ (collision density oscillations).

A more accurate hot atom distribution than that given by formula (13) can be found by the two-group approximation method (Placzek[22] and Temkin[13]). The equations obtained are extremely cumbersome, and simple expressions can be obtained only when the tracks of the hot atoms overlap. This last condition is not satisfied, however, for hot atoms obtained by nuclear reactions.

Eqn. (13) is applicable to the retardation of recoil atoms on atoms with similar masses, and also when it is desired to find the value of $n(E)$ at a distance from the initial recoil energy. These conditions are generally realised in the study of reactions brought about by hot atoms.

If the hot atoms undergo chemical reactions in the energy range from E_2 to E_1, the retarded atom spectrum loses a fraction of recoil atoms equal to

$$1 - \exp\left[-\int_{E_1}^{E_2} \frac{p(E)}{\xi}\frac{dE}{E}\right], \quad (14)$$

where the exponent expresses the probability of avoiding hot reactions in the range E_2–E_1, and $p(E)$ is the chemical reaction excitation function. The latter is dependent on

energy and apparently has resonance character. This makes it possible to apply the basic formulae from the theory of neutron retardation (4)–(14) not only to the case of retardation through collision, but also to the derivation of equations for the yields in chemical reactions of hot atoms.

The theory of neutron retardation as applied to the collisions of hot atoms was recently developed by Hsiung and Gordus[24] for isotropic and anisotropic scattering with selection of two interaction potentials (rigid-sphere collisions and Lennard-Jones potential). It was shown that isotropic scattering with respect to the centre of mass with selection of the Lennard-Jones interaction potentials is achieved only for simple atomic systems (H + H_2, H + He) and then naturally coincides with the isotropic scattering for the elastic scattering of particles. For more complex systems, for example, the collision H + CH_4, the deviation from isotropy is significant. Thus in real systems where retardation of hot atoms takes place, the loss of energy will be dependent on the energy.

If by definition $\xi = \overline{\ln \frac{E}{E'}}$, Eqn. (11), we have

$$\xi = \int_{\alpha E}^{E} \ln \frac{E}{E'} \lambda(E, E')\, dE,$$

where $\lambda(E, E')$ is the scattering function[24]. Eqn. (11) was obtained for isotropic scattering with respect to the centre of mass, when the probability of scattering is

$$\lambda(E, E') = \frac{1}{2} \sin\theta d\theta.$$

III. CHEMICAL REACTIONS OF HOT ATOMS

The general considerations discussed in Section II naturally do not resolve the problems facing hot atom chemistry. The theory of the kinetics of the reactions of hot atoms includes many problems, each of which is still far from being solved (non-equilibrium processes of energy transfer in hot-atom collisions, the dissociation of molecules, reaction excitation function, etc.). This explains the difficulty and ambiguity of the interpretation of results in hot atom chemistry. In recent years some progress has been made in this direction. Special experiments aimed at investigating the part played by individual factors influencing the yield of hot reactions have eliminated to a considerable extent the ambiguity and indefinite nature of the results.

The greatest number of papers has been published on the chemistry of hot atoms of tritium, the halogens, and carbon in organic systems, by Rowland and coworkers[25], Wolfgang and coworkers[26], Willard and coworkers[27], Nesmeyanov and coworkers[3,28–30], and Wolf and coworkers[31].

1. Mechanism of the Reactions of Hot Tritium Atoms

It is now regarded as firmly established that in reactions of hot atoms no transition complex with regular energy distribution exists; this also follows from the theory of the non-equilibrium processes of kinetic energy transfer on collision between a hot atom and a molecule. An exception is those systems in which, after the primary act of collision and transfer of energy, states with lives long enough (10^{-7}–10^{-8} s) for the even distribution of energy throughout the degrees of freedom are produced†. The substances which have been studied in this connection include cyclopropane[32], cyclobutane[33], and unsaturated compounds[34–36].

The reactions of tritium recoil atoms with molecules containing saturated carbon–carbon bonds generally take place by direct single-stage interaction between the recoil atom and individual atoms (more accurately, chemical bonds‡); this primary process does not involve other atoms. The latter merely provide the spatial limitation in the attack by the hot atom.

With this approach to the mechanism of the reactions of hot atoms, it becomes possible to compare the results of experiments with calculation. The main assumptions of the theory[37] are as follows. Of the total number of hot atoms (N_s) only part (N_h) react in the energy range E_2–E_1, in which the probability of chemical reaction on collision $p_i(E)$ differs from zero:

$$R_{ij} = N_h / N_s = \int_{E_1}^{E_2} f_j p_i(E)\, n(E)\, dE, \qquad (15)$$

where R_{ij} is the yield of the i-product of the hot reaction from the j-component, f_j the probability of collision with the given component, $f_j = N_j \sigma_j / \Sigma N\sigma$ (N_j is the mole fraction of the j-component, and σ_j the collision micro-cross-section), $n(E)dE$ the hot atom spectrum (the number of collisions between E and $E + dE$), and $p_i(E)$ the probability of reaction on one collision with a molecule of the j-component with the formation of the i-labelled product. It is evident that in the range $E > E_2$, $n(E)$ is equal to the flow of hot atoms in the absence of absorption, that is, it can be calculated from formula (13): $1/\xi E$ (Σ_S is assumed to be constant). When chemical reactions take place, the atoms taking part in the chemical reactions are "eaten out" of the spectrum in the range E_2–E_1. It is assumed that the fraction of atoms not taking part in the reaction is proportional to

$$\exp\left[-\int_{E}^{E_2} f\, p(E)\, n(E)\, dE\right] \qquad (16)$$

[see Eqn. (14)]. The flow of hot atoms when chemical reactions take place is then equal to

$$n(E) = \frac{1}{\xi E}\left\{\exp\left[-\Sigma \int_{E}^{E_2} f p(E)\, n(E)\, dE\right]\right\} \qquad (17)\S$$

(the sum with respect to all components of the mixture).

Substitution of Eqn. (17) into (15) and expansion of integral $\int_{E_1}^{E_2} \frac{p(E)}{E} dE$ into a series leads to an expression of the form

$$R = 1 - \exp\left[-\frac{f}{\xi} I\right], \qquad (18)$$

† In this case also, however, the primary act does not involve the formation of an intermediate complex. Here a "pseudo-complex" is formed, since the course of the reaction is determined by the second, slow stage of energy redistribution.

‡ See p. 685 for more details.

§ The integral in expression (17) is the resonance integral in the theory of neutron retardation[22,23]; see elsewhere[28,38] for more details.

where

$$I = \int_{E_1}^{E_2} \frac{p(E)}{E} dE. \qquad (19)$$

The quantity R signifies the yield of all products containing recoil atoms and formed by hot reactions. For the yield of an individual labelled compound from a two-component system (the second component being an inert moderator), we obtain the expression

$$R_{1i} = \frac{f_1}{\xi} I - \frac{f_1^2}{\xi^2} K, \qquad (20)$$

where

$$I = \int_{E_1}^{E_2} \frac{p_i(E)}{E} dE, \qquad (21)$$

and

$$K = \int_{E_1}^{E_2} \frac{p_i(E)}{E} \left[\int_{E}^{E_2} \frac{p(E)}{E} dE \right] dE. \qquad (22)$$

Here $p_i(E)$ is the probability of a hot reaction on one collision between a hot atom and a molecule with the formation of an i-labelled product, and $p(E)$ the probability of formation on collision of all labelled products. If the second component is not inert, we have

$$K = \int_{E_1}^{E_2} \frac{p_i(E)}{E} \left[\int_{E}^{E_1} \frac{f_1 p_1(E) + f_2 p_2(E)}{E} dE \right] dE,$$

where $p_2(E)$ is the probability of chemical reaction with the formation of all labelled products on collision with a molecule of the second component.

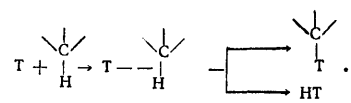
It follows from (20) that the dependence of $(\xi/f)R_{1i}$ on f/ξ should be given by a straight line. The intercept on the axis of ordinates gives the value of the integral (21), that is, the probability of chemical reaction with the formation of a definite labelled product, and the slope gives the value of integral (22) as the probability that the hot atom enters any chemical compound in general.

This model was verified for the case of hot tritium atoms in the methane–inert gas system. The mean value of the probabilities of the hot chemical reaction of tritium atoms with methane with the formation of CH_3T:

$$\overline{p(E)} = I/\ln \frac{E_2}{E_1}, \qquad (23)$$

was found to be 0.12. The quantities f and ξ were calculated from the masses and dimensions of the atoms and molecules in the approximation corresponding to elastic transfer of energy.

It was shown that the mechanism of elastic collisions is not applicable to the reactions of hot tritium atoms[39]. An important problem in this connection is the following: how does the transfer of energy from the hot atom to the molecule, leading to chemical reaction, take place? The agreement between the experimental data and calculation according to formula (20) for the yield of the product of hydrogen replacement is best[40] if it is assumed that the tritium atom collides with a mass which is smaller than the mass of the methane molecule but greater than the mass of the hydrogen atoms. If the role of this "effective mass" is assigned to the chemical bond between the atoms in organic compounds, the process of formation of compounds labelled with tritium can be represented schematically as follows.



This conclusion follows from the following experimental facts: (1) the yield of product formed by the rupture of any bond is proportional to the total number of bonds of this type; the ratio of the yields HT/CH_3T in the reactions of hot tritium atoms with carboxylic acids[41] and alcohols[42] is directly proportional to the ratio: (number of C–H bonds) ÷ ÷ (number of $C-CH_3$ bonds); (2) the reactions of tritium recoil atoms are not accompanied by Walden inversion[43] and the isomeric configuration is also preserved[32,33,44]; (3) 90% of the activity of the tritium is distributed between the labelled mother compound RT and active hydrogen HT. The ratio of the yields HT/RT (hydrogen abstraction/hydrogen replacement) in the reactions of hot tritium atoms with hydrocarbons agrees with the expression

$$\frac{HT}{RT} = \frac{n}{n_1(1-\Omega) + n_2(1-\Omega)^2 + n_3(1-\Omega)^3}, \qquad (24)$$

where n is the total number of hydrogen atoms in the molecule, Ω the steric hindrance in the reaction of hydrogen replacement, and n_1, n_2, and n_3 the numbers of primary, secondary, and tertiary hydrogen atoms.

The experimental data are compared with the results calculated from formula (24) in Table 1.[26]

These facts give grounds for concluding that hot tritium atoms react with the bonds between the C and H atoms and that attack along the C–H bond (more accurately, at small angles to this bond; in this case there is no steric hindrance so that the yield of HT is proportional to the total number of hydrogen atoms) leads to the abstraction of

TABLE 1. The part played by steric factors in the abstraction and replacement of hydrogen by hot tritium atoms.

Substance (hydrocarbon)	Abstraction / replacement: calculated ratio	observed experimentally
CH_4	1	1
C_2H_6	$\frac{1}{1-\Omega} = 1.82$	1.82
	$\frac{1}{1-\Omega} = 1.82$	1.40
	$\frac{10}{9(1-\Omega)+(1-\Omega)^3} = 1.95$	1.95
	$\frac{4}{3(1-\Omega)+(1-\Omega)^3} = 2.05$	2.0
	$\frac{10}{6(1-\Omega)+4(1-\Omega)^2} = 2.2$	2.0
	$\frac{14}{6(1-\Omega)+8(1-\Omega)^2} = 2.4$	3.3
	$\frac{12}{9(1-\Omega)+2(1-\Omega)^2+(1-\Omega)^3} = 2.1$	2.0

Ω is the steric parameter in replacement reactions: $\Omega = 0.45$ is the choice made to give agreement between calculation and experiment for the case of ethane.

hydrogen in the form HT, whereas attack in a perpendicular direction (more accurately, at high angles to the bond; the steric hindrance increases with increase in the angle of attack and amounts to $\Omega = 0.45$ for primary hydrogen) leads to the replacement of hydrogen.

The theory whose main conclusions have been examined above has been called the "collision model" [37]. For the gaseous phase, this model was confirmed for the case of recoil halogen atoms [45-47].

It follows from the collision model that the decisive factors for reactions of hot atoms in the gaseous phase are: the steric hindrance to approach to the bond, the form of the function $p(E)$, and the hot atom spectrum in the range $E_2 - E_1$, where $p(E) > 0$. The value of the bond energy is unimportant from the viewpoint of the "collision model".

The collision model was developed by Wolfgang for multicomponent systems [48] and may now form a basis for the development of a theory of the kinetics of high-energy reactions. The case of the gas-phase reactions of tritium recoil atoms, $^3He(n,p)T$ with ethane, butane, neopentane, and hydrocarbon mixtures with the addition of a moderator has shown [49] the applicability of the Wolfgang equation — a combination of formulae (12) and (18): [48]

$$-1/\ln(1-R) = \xi_p/I + \xi_M/I\,\frac{1-f_p}{f_p}, \qquad (25)$$

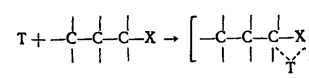
where ξ_p is the mean loss of energy for the collision of tritium with a molecule of the main component, and ξ_M is the same for the collision with a molecule of the inert moderator, for example, helium.

These results [49] show that the ratio of the molar activity of ethane to the molar activity of neopentane for the neutron irradiation of a $^3He + C_2H_6 +$ neo-C_5H_{12} mixture *increases* with *decrease* in the ethane concentration, that is, the reactivity of the ethane molecules in the replacement of H by T increases (or that of neopentane decreases) with decrease in its concentration. The same effect of increase in the relative activity of tritium-substituted ethane is achieved by adding the moderator helium to the mixture being studied (at the same molar ratios). It was concluded that hot reactions are extremely sensitive to change in the spectrum of the retarding atoms, the mean energy losses for retardation in identical substances differing considerably. Data on the magnitude of the energy losses on collision of tritium with molecules of ethane, butane, and neopentane, and also the integral probabilities of chemical reaction with the formation of labelled ethane, butane, and neopentane in the reactions of hot tritium atoms, are given in Table 2 (the data were calculated relative to the value of ξ He — the mean loss of energy by tritium on collision with helium, for example, ξ ethane = $= 3.64\xi$ He).

TABLE 2. Mean energy loss for the collision of hot tritium atoms with ethane, n-butane, and neopentane. Integral probabilities of replacement and abstraction of hydrogen by hot tritium atoms. (Conditions [49]: 1 cm ^3He, 2–4 cm O_2, 1 atm of substances, integral neutron beam 10^{15}).

Hydrocarbon	ξ	I_{RT}	I_{HT}
Ethane	3.64	2.1	0.55
n-Butane	5.05	2.78	0.79
Neopentane	5.8	2.93	0.59

The collision model does not reveal the nature of the phenomenon of energy transfer on collision and formation of a chemical bond, that is, a transition state leading to the hot reaction is excluded. At the same time the concept which considers the process of establishment of chemical bonds through a transition complex is more familiar to the chemist [25]. Since there is no significant difference in the yields of compounds labelled with tritium relative to change in the phase state and pressure in the gaseous phase (that is, deactivating collisions after the "marking" process do not influence the distribution of the activity), this complex should exist for a period of not more than 10^{-13}–10^{-14} s ("collision complex"), that is, for the duration of one or two vibrations of the bond:



The breakdown of the "collision complex" may be determined by the C–X bond energy, but the bond energy is apparently not so important. The reaction of hot atoms takes place in the range 15 eV–E_{act}, and the recoil atoms approach "from above" the energy values where the probability of reaction has maximum values. A change in the magnitude of the bond energy by several tenths of an electron volt cannot greatly influence the yield of labelled compound, since the greater part of the reactions are assumed to take place in the range 3–8 eV. Since the abstraction (of hydrogen) takes place at lower energies than substitution, as observed in experiments to find models for the collisions of atoms and molecules in the tritium + hydrocarbon system (tritium gas at $t = 1200$–$1800°$), [50] change in the C–X bond energy should be revealed as a change in the yield of the abstraction (in the form XT).

In fact, Rowland, the author of the latest theory, was able to show that the proportion of the activity of the tritium in the form HT is consistent with the energy of the C–H bond [51]; a paradoxical feature is that neopentane was not "fitted" into the relationship found for other hydrocarbons until new data were published on the energy of the C–H bond in neopentane.

It follows from the experiments of Rowland and coworkers [51] that the chemistry of hot tritium atoms gives an accuracy in the determination of the energy of the chemical bond which is no less than that given by the ordinary methods of "ordinary" chemistry.

In this connection, some doubt may be cast on the aspect of the collision theory dealing with the competing reactions of hydrogen abstraction and replacement, particularly for systems in which the hot atom spectrum contains an appreciable proportion of epithermal and "slightly hot" atoms. Such atoms in the range 0.5–3 eV have a greater tendency to take part in hydrogen abstraction, and in this range the C–H bond energy influences the yield of HT.

There are apparently no fundamental contradictions between the "collision model" [26,37] and the "collision complexes" [25]; at any rate, the experimental data can be explained equally successfully from both viewpoints. Let us take an example. Isotopic effects have been observed [39,53-58] in the reactions of tritium recoil atoms with simple dueterated compounds (Tables 3 and 4): the processes of replacement and abstraction of hydrogen by tritium ions

TABLE 3. Isotopic effect in reactions of hot tritium atoms with simple and deuterated compounds[58].

a. Abstraction of HT or DT

Ratio of yields	Substance			
	CH_2D_2	CH_3CD_3	CH_4+CD_4 mixture	CH_3F+CD_3F*
HT/DT	1.32±0.01	1.34±0.01	1.28±0.02	1.26±0.05

b. Replacement of H and D by T

CH_3T/CD_3T	CH_2TF/CD_2TF*	C_4H_9T/C_4D_9T**
1.31±0.05	1.33±0.04	1.21±0.05

* Derived from experiments with mixtures of CH_3F (or CD_3F) and cyclobutane.

** Derived from experiments with mixtures of n-C_4H_{10} (or n-C_4D_{10}) and CH_4.

TABLE 4. Isotopic effect in reactions of tritium recoil atoms with simple and deuterated methyl fluoride[40].

Replacement	Yield of products from		H-system / D-system
	CH_3F	CD_3F	
H (D)	12.4	10.1	1.23±0.02
F	4.2	3.2	1.30±0.02
H (D), F	2.9	2.1	1.4 ±0.06
2 H (2 D)	1.3	0.9	1.4 ±0.09

(Yield given for the total absolute activity of tritium.)

For the abstraction of hydrogen (or deuterium) the isotopic effect = = 1.17 ± 0.03.

take place preferentially by 30% compared with the same processes for deuterium.

Since the loss of energy on retardation is not the same even for a homologous series of substances[49], the magnitude of the isotopic effect is investigated by carrying out experiments on the action of hot tritium atoms simultaneously in a mixture of two substances such that the spectra of the retarded atoms are the same[58]. For example, determination of the yield of CH_2TF from CH_3F and of CD_2TF from CD_3F and calculation of the ratio CH_2TF/CD_2. .TF (Table 3a) were carried out in a study of mixtures of CH_3F and CD_3F with a large quantity of cyclobutane. The yield of CH_3T and CD_3T from CH_4 + cyclobutane and CD_4 + + cyclobutane mixtures was determined in analogous fashion. The ratio CH_3T/CD_3T was found[58] to be equal to 1.31 ± 0.05, which agrees with the ratio $\frac{CH_3T/CD_3T}{CH_4/CD_4}$ obtained from direct experiments with a CH_4 + CD_4 mixture[56].

From the viewpoint of the collision model, the isotopic effect observed in reactions of tritium recoil atoms with methane and deuteromethane can be attributed to a difference in the retarding power of the simple and deuterated compounds[40].

We are however, faced with the question of how the isotopic effect arises in the reaction of hot tritium atoms with CH_2D_2 $\left(\frac{HT}{DT}=1.32\right)$, with CH_3CD_3 $\left(\frac{HT}{DT}=1.34\right)$, and in a CH_4 + CD_4 mixture (CH_3T/CD_3T = 1.26), where the recoil atom spectra are the same for the replacement and abstraction of H and D.

Some part is possibly played by a slight difference in the values of the C–H and C–D bond energies, but it is then difficult to explain the existence of the isotopic effect for the replacement of fluorine by tritium atoms in CH_3F and CD_3F (CH_3T/CD_3T = 1.3 [40]), where the C–F bond energy is the same in both compounds.

Recent work by Rowland and coworkers[57] has shown that in the CH_4 + D_2 system the ratio of the specific activities $DT/D_2/CH_3T/CH_4$ remains unchanged with change in the ratio of the gas pressures by a factor of 15. This indicates, firstly, that the hot tritium atoms not only react with CH_4 in the high-energy range to give CH_3T, but also are effectively retarded, on collision with methane, to low energies, which are, however, higher than the activation energy for exchange with deuterium (0.5 eV); and secondly, that the $p(E)$ curve for the replacement of hydrogen in methane by hot tritium atoms lies in a higher energy range and does not overlap the range for the reaction T + + D_2 = TD + D. This makes possible the appearance of an "integral" isotopic effect associated with the difference in the energy dependence of the probabilities of the chemical reactions, which, like the change in the retardation parameter ξ, explains so successfully the difference in the yields of the products of the replacement (or abstraction) of H and D.

A pictorial representation of the dynamics of the collision of hot tritium atoms with methane molecules may be provided by the collision of "a sphere against a cushion" [57], in which an appreciable proportion of the kinetic energy of the hot atom is lost.

It has now been established that the magnitude of the mean energy loss on collision changes sharply in the range of chemical interaction[49,57]. The corresponding theoretical approach to this problem has already been mentioned (see Section II. 3).

The importance of the study of isotope effects in the reactions of hot tritium atoms is related to the fact that this may reveal the mechanism of bond formation in the reactions of highly energetic atoms with molecules. It is of interest to determine the decisive factor in the production of isotopic differences in the replacement of hydrogen and deuterium by tritium: the process of replacement on collision or the secondary process of bond formation after the ejection of hydrogen and deuterium, that is, whether the important reaction is

(1) $$T+CH_4 \rightarrow CH_3T+H,$$

or the recombination of radicals in direct proximity

(2) $$T+CH_4 \rightarrow CH_3 \,\vdots\, T+H.$$

It is suggested that the answer may be obtained by studying the yields of H and D replacement by tritium in CH_2D_2:

(3) $$T+CH_2D_2 \rightarrow CHTD_2+H,$$

(4) $$T+CH_2D_2 \rightarrow CH_2DT+D.$$

If the chief part is played by direct replacement, the yield of reaction (3) should be 30% greater than the yield

of reaction (4) (since the replacement of hydrogen is preferred to the replacement of deuterium to the extent of 30%). If the main part is played by the secondary isotopic effect (recombination in direct proximity), reaction (4) should be preferred to reaction (3) to the extent of 10%, since on the recombination of radicals in direct proximity to one another, an important part is played by the "inertial mechanism" of replacement, namely: the rate of recombination is greater, the smaller the mass of the fragment (see Section IV. 7). At present, however, the technical difficulties of separating the products of reactions (3) and (4) have not been overcome.

In concluding this section we may note the following feature. The magnitude of the isotopic effect, obtained in the reactions of tritium recoil atoms with simple and deuterated compounds, amounts on the average to 1.3–1.4 (H-system/D-system) and is extremely close to the ratio of the fundamental vibration frequencies of the C–H and C–D bonds (with the assumption that the force constants are equal)

$$\nu_{C-H}/\nu_{C-D} = \sqrt{\frac{f}{m_H}}\Big/\sqrt{\frac{f}{m_D}} = \sqrt{2} \simeq 1.4.$$

This ratio of the rate constants for the chemical reactions of hydrogen and deuterium replacement is obtained if in the transition complex the dimensions of the bond remain unchanged on replacement[59]. For a completely broken bond in the transition complex the kinetic isotopic effect acquires a maximum value of 18. In ordinary chemical reactions, the replacement of hydrogen by deuterium leads to a decrease in the rate of reaction by a factor of 3–8, indicating appreciable deformation of the bond during the reaction[59]. From the above comparison it may be concluded that the "transition state" in a hot reaction has the character of a local collision at the C–H bond in a period of $\sim 10^{-14}$ s, in which the lengths of the C–H and C–D bonds cannot change. Thus the kinetics of hot reactions represent an extreme case of the kinetics of ordinary chemical reactions.

Valuable information on the mechanism of the reactions of hot atoms may be given by experiments to find models for atom–molecule collisions. The first experiments in this direction with tritium atoms heated to 1800° and used to bombard a cyclopropane target[50] showed that the processes of hydrogen replacement take place in a higher energy range than the abstraction processes. This may change our ideas regarding the kinetics of hot atom reactions, particularly the conclusions regarding the mechanism of production of the isotopic effect. An increase in the retarding power of the medium should lead to an increase in the fraction of hydrogen abstraction reactions (the kinetic isotopic effect should increase).

2. Reactions of Hot Halogen Atoms

The energy of halogen recoil atoms obtained by an (n,γ) reaction varies from several dozen to several hundred eV. Some of the atoms can apparently undergo chemical reaction with the medium on the first collisions. In this connection, the chemical state of the recoil atoms which have undergone the nuclear reaction is of considerable importance. The collection of recoil atoms in the gaseous phase[60] has shown that after an (n,γ) reaction the atoms may remain in a metastable state, which leads to charged atoms after an internal conversion process. The process of charge increase takes place after the atom has left the parent molecule. The process is described in more detail as follows. The greater part of the excitation energy of the nucleus after the nuclear reaction is lost by the emission of γ-quanta (several γ-quanta with ~ 1–3 MeV)¶. The remaining fraction is lost by low-energy transitions accompanied by internal conversion. The lifetime of a level with $E > 1$ MeV is 10^{-14} s; the lifetime of transitions with low energies lies in the range 10^{-12}–10^{-5} s. After the ejection of the γ-quantum, for example, with $E \sim 1$ MeV, the atom leaves the molecule, and after 10^{-13} s it is stopped, after having moved a distance of several molecular diameters. Thus hot reactions initiated by part of the excitation energy of the nucleus after neutron capture take place before the start of the process of avalanche charge increase, as a result of the conversion of soft γ-quanta. These conclusions are confirmed by many experimental facts, in particular by data on the proportions of charged atoms (indium and manganese) after an (n,γ) reaction. These proportions are independent of the original form irradiated by the neutrons and amount to 40–60%. This means that the accumulation of positive charge on the atom takes place in a time interval which is longer than that required for rupture of the bond and several first collisions. Wexler and Davies[62,63] found the proportions of charged atoms after an (n,γ) reaction: 25% for ^{82}Br, 12% for ^{80}Br, 21% for ^{38}Cl, and 50% for ^{128}I. The mean charge of the recoil ions was found to be +10 (for ^{80}Br). Intensive supercharging of positive ^{80}Br recoil ions was also observed, the current strength of the resulting negative ions increasing with increase in the density of the medium.

The determination of the fraction of positively charged atoms after radiative neutron capture by the collection of recoil atoms is very imperfect. The probability of energy loss by conversion increases as z^3, whereas experiments with different recoil atoms give approximately the same fraction of charged atoms[60].

It follows from the foregoing that the "hot chemistry" of heavy recoil atoms should make allowance for the possibility of twofold introduction of radioactive atoms into the compounds: firstly as a result of recoil from hard capture γ-quanta, and secondly as a result of the conversion of soft capture γ-rays and the subsequent processes of charge formation on the atom: intramolecular charge transfer — formation of molecular ion — dissociation of molecular ion — formation of recoil ion — chemical reaction of recoil ion.

Suess[64] and later Libby[65] showed that the rupture of the chemical bond in a diatomic molecule uses up a fraction of the recoil energy which depends on the ratio of the masses of the recoil atom and the second atom. The excitation energy used up in the dissociation is found from the difference between the kinetic energy of the recoil atom and the kinetic energy of movement of the centre of gravity of the molecule:

$$E_{\text{excitation}} = E_m - E_M = p^2/2m - p^2/2(m+x) = E_m \frac{x}{M}, \qquad (26)$$

where x is the mass of the second atom, M the mass of the molecule, $M = m + x$, m the mass of the recoil atom, and p

¶ Groshev[61] showed that the proportion of the excitation energy of the nucleus de-excited by photons with $E > 0.5$ times the binding energy of a neutron (α) is close to 80–100% only for atoms with magic numbers of neutrons and protons. As a rule, α = 20–30% for heavy atoms, 30% for chlorine, 70% for sulphur, and 60% for phosphorus.

the impulse of the recoil atom. The condition for bond rupture as a result of the recoil effect has the form

$$E_{\text{recoil}}\frac{x}{M} > \nu, \qquad (27)$$

where ν is the energy of the chemical bond.

Gordus[66] obtained formulae for calculating the condition for ejection of recoil atoms from molecules in terms of the masses of the atoms, the interatomic distances, and the angles between the bonds in polyatomic molecules. In order to obtain approximate data for the case of polyatomic molecules, however, it is possible to use Eqn.(26) and the inequality (27), assuming that x is equal to the mass of the molecular residue. The error amounts to 15–20%. Careful experiments to find the fractions of unbroken bonds in an (n,γ) reaction showed that they amount to approximately 0.3–1% and show good agreement with theoretical estimates. It may therefore be assumed that after an (n,γ) reaction the chemical bond is broken in almost all cases. Sometimes, however, marked deviations from this relationship are observed. For the rupture of the bond in the HBr molecule, according to Eqn. (27), the recoil bromine atom should have a kinetic energy of not less than 312 eV. From approximate calculation of the spectrum of bromine recoil atoms[67] it follows that 85% of all the bromine atoms have a recoil energy less than the dissociation energy. Suess's first experiments[64,68], however, and later careful experiments carried out in the gaseous phase by other workers[69] showed that only ~10% of the activity of the ^{80}Br after an (n,γ) reaction in the HBr + C_2H_2 mixture (with low HBr partial pressure) remains in the form of $H^{80}Br$, whereas we should expect a retention of $H^{80}Br$ of the order of 85%. This indicates the high degree of conversion of γ-rays after the (n,γ) reaction, one result of which is the formation of recoil ions which leave the original molecules as a result of coulombic repulsion. The discovery of the existence of recoil ions played an important part in the postulation of ion–molecular hot reactions, thanks to which it has been possible to explain certain facts, in particular the existence of isotopic effects in (n,γ) reactions[80]. The formation of positively charged recoil ions does not always explain the experimental data, however. Thus in the isomeric transition, $^{80m}Br \rightarrow {}^{80}Br$, the internal conversion coefficient is equal to 90–100%, that is, at least 90% of the ^{80}Br atoms should leave the $H^{80m}Br$ molecule as a result of isomeric transition. Experiments[70] showed that the yield of $H^{80}Br$ from $H^{80m}Br$ amounts to 25%. If in the (n,γ) reaction the kinetic energy is insufficient for rupture of the bond in the HBr molecules, and the ejection of bromine atoms can be attributed to the formation of recoil ions as a result of conversion of the capture γ-rays, how are we to explain the fact that in the case of the isomeric transition in $H^{80m}Br$, where the γ-rays undergo conversion to the extent of 100%, the proportion of unbroken bonds is greater by a factor of 2.5? One possible explanation may be based on the difference in the magnitude of the charge on the ions after the (n,γ) reaction and the isomeric transition (i.t.). In fact, the mean charge of the recoil ions of bromine-80 after the (n,γ) reaction was found to be +10, whereas after i.t., according to Cooper's calculations[71], it amounts to +4.7. Calculations carried out by Magee[72] showed that the HBr^{z+} molecules are stable up to z = +4, and this may explain the fact that an appreciable proportion of the activity of ^{80}Br after i.t. is found in the form of hydrogen bromide.

The mass-spectrometric data confirm the formation of rapidly-moving ions produced by the dissociation of highly charged molecular ions. The kinetic energy of the fragments can be estimated approximately from the difference between the ionisation potentials of the ionised molecule and the fragment ions. Cooper[71] showed that the time taken for the transfer of charge from the K-shell to the valency shell is 10^{-12} s. In this period, an atom in the molecule undergoes 10–100 vibrations, that is, there is a considerable probability of internal charge transfer with the formation of molecular ions. The relative kinetic energy of $^{80}Br^+$ ions from the compound $CH_3{}^{80m}Br$ is 10 times greater than that from $H^{80m}Br$ (on the basis of an equal distribution of charge throughout the molecule). This may explain the fact that the fraction of unbroken bonds in $CH_3{}^{80m}Br$ after i.t. is much smaller than that in $H^{80m}Br$ (3–7%).[70]

It may be assumed that the kinetic energy of recoil ions after i.t., and also as a result of the conversion of soft capture γ-rays, depends on the energy and degree of conversion of the γ-rays, the ratio of the masses of the recoil atom and the remainder of the molecule, and the values of the ionisation potentials of the molecular ions and fragment ions. In the gaseous phase the fraction of unbroken bonds amounts to several percent but in the liquid phase this fraction reaches about 15% (for example, the yield of $CHBr_2{}^{80}Br$ from $CHBr_2{}^{80m}Br$ amounted to 13% in the liquid phase in the presence of appreciable quantities of elemental bromine[73]). This can be related to the "cage" effect, which retains the recoil ion in direct proximity to the molecular residue, or to the process of intermolecular charge removal from the molecular ions, facilitating "survival" of the molecule.

Bromine and iodine recoil atoms initiated by different nuclear processes give the same distributions of activity in the products. However, the initial distributions of the atoms, after, for example, an (n,γ) reaction and isomeric transition, are different: the (n,γ) reaction gives the atom kinetic energy but isomeric transition gives the atom a charge. In the light of the foregoing, it may be assumed that the fact that the atoms show identical behaviour after an (n,γ) reaction and i.t. is due to the same factors. One of these is that the conversion of γ-rays after the (n,γ) reaction produces charged recoil atoms whose behaviour will consequently be the same as that of atoms produced in i.t., for which the coefficient of internal conversion is high. Another reason for the identical behaviour of atoms obtained by different nuclear reactions is based on the opposite assumption that the charged atoms are neutralised, as a result of which the recoil atom spectra may be the same in the range of chemical interaction. The first viewpoint leads to the postulate that an important part is played by ion–molecule reactions (see Ref. 80 for more details), whereas the second leads to the hypothesis which gives preference to the part played by kinetic energy in the hot reaction[28,74,75].

There is a third point of view regarding the source of the high activity of hot atoms. It is suggested that, irrespective of the primary processes, the atoms are obtained with an appreciable electronic excitation energy. It is then necessary to speak of the chemistry of "hot orbital electrons"[76].

Finally, a still valid viewpoint is that which concentrates attention on the radical reactions of recoil atoms with fragments formed on the path of movement and as a result of radiative breakdown produced by the Auger electrons after the conversion process[27,77]. A fundamentally new approach to the explanation of results obtained in hot atom

chemistry in organic media was put forward by Shaw[78] whose calculations showed the influence of local pressure, produced by the hot atom in the retardation zone, on the yield of labelled products. Let us examine briefly the experimental data supporting the different views on the mechanism of hot reactions.

(a) Ion-molecular mechanism. It has been established[45-47] that in the reactions of ^{80}Br and ^{128}I recoil atoms with methane in the gaseous phase in the presence of added inert gases, the yield of labelled products shows good agreement with the equations of Wolfgang's kinetic collision theory (see Section III. 1), confirming the suggestion regarding the reactions of neutral non-excited hot atoms with an excess of kinetic energy. Significant deviation from the equations of the kinetic theory were found in the study of the action of neutrons on an $I_2 + CH_4 +$ + Xe mixture and this was attributed to the transfer of charge from ^{128}I atoms (50% of which are obtained in the charged state after an (n,γ) reaction) in the $^1D_2$ state to xenon, which thus exhibits a quenching action†.

The reaction of excited iodine recoil ions with xenon may compete to an appreciable extent with the ion-molecular reaction involving the introduction of iodine into methane. From this it was found that the fraction of ^{128}I recoil ions after the (n,γ) reaction is 23 ± 3%. The fraction corresponding to true hot reactions (suppressed only by the moderators — inert diluents — He, Ne, and Ar) amounts to 18 ± 2%. The remaining 11% of all the reactions of iodine atoms involve interaction between methane and charged ^{128}I ions in p-states with excitation energy $E < 1.7$ eV, and these are not influenced by the addition of xenon. Study of the hot reactions of ^{80}Br recoil atoms in methane under the same conditions showed that only the kinetic energy influences the yield of products, despite the fact that some of the ^{80}Br atoms are obtained in the charged state after the (n,γ) reaction. In isomeric transition in the ^{80m}BrBr + CH_4 system, the yield of $CH_3{}^{80}$Br is less than that in the (n,γ) reaction (6.8 ± 0.8% and 12.0 ± 1% respectively)[79]. This result was attributed to the high kinetic energy after the (n,γ) reaction. There is another possible explanation, however: if the ^{80}Br recoil atoms are formed in a metastable state with sufficiently long lifetime (greater than the lifetime between collisions in the gaseous phase), only some of these atoms, after their first introduction into the methane molecule, will leave the resulting molecule due to the conversion of γ-rays. These atoms apparently have the same probability of reaction with methane as ^{80}Br atoms from Br^{80m}Br. We should thus expect that the yield of $CH_3{}^{80}$Br after the (n,γ) reaction should be slightly greater than that for the i.t. process. An analogous process should take place with recoil atoms of the ^{82}Br isotope, for which a 6.2-minute isomer has been found‡[77]. This does not solve the problem of the source of the high reactivity of bromine and iodine after a nuclear (n,γ) reaction. It is possible that the kinetic energy plays the most important role: on the production of a charge of +5 on the iodine atom in the CH_3I molecule, its kinetic energy after rupture of the C–I bond is ~9 eV,[77] which is, of course, quite sufficient for the replacement of hydrogen in methane. According to calculations, however, after the replacement of hydrogen in methane by the ^{128}I atom, the $CH_3{}^{128}$I molecule will have too much energy to be stabilised (see Filatov[80] for more details). Thus the ion-molecular mechanism of formation of $CH_3{}^{128}$I in the reactions of ^{128}I recoil atoms with methane is to be preferred.

This was confirmed in subsequent studies of the (n,γ) reaction in the $I_2 + CH_4$ system containing added alkyl iodides, nitric oxide, and benzene[47]. The yield of $CH_3{}^{128}$I on irradiation of the gas-phase systems with neutrons decreased rapidly when alkyl iodides were added; this can be attributed to the transfer of charge to RI, which has a lower ionisation potential than iodine, or to the thermal ion-molecular reaction $I^+ + RI \rightarrow I_2^+ + R$, which was also observed in mass-spectrometric studies. Since iodine atoms do not react with nitrogen monoxide, the inhibition of the formation of $CH_3{}^{128}$I by the addition of NO is due to the transfer of charge to the nitric oxide. The ion-molecular model for the reactions of hot atoms provides an explanation for the low yield (2–4%) of alkyl iodides labelled with ^{128}I in the neutron irradiation of the gaseous mixtures $I_2 + C_2H_6$, $I_2 + C_3H_8$, etc. Alkanes, apart from CH_4, can remove charge from iodine ions in the $^1D_2$, $^2P_1$, and $^3P_0$ states. In actual fact, the addition of ethane to an $I_2 + CH_4$ mixture inhibits the formation of $CH_3{}^{128}$I.[47]

The hypothesis of ion-molecular reactions of hot atoms has proved useful in the explanation of the results of a study of the chemical consequences of β-decay in the liquid-phase systems: $^{132}TeCl_4(^{132}Te \xrightarrow{\beta} {}^{132}I) + C_3H_7X + C_6H_6$ and $TeCl_4 + C_3H_7I + C_6H_5I$ (X = I, Br, or Cl). The recoil energy of the iodine atoms obtained by the β-decay of tellurium is low (0.5 eV) and cannot bring about chemical reactions. Halpern and Sokolovska[81] detected an increase in the specific activity of $C_3H_7{}^{132}$I in the presence of benzene, which they attributed to the transfer of energy from propyl iodides to the benzene molecules. The formation of propyl iodides, however, was regarded as the reaction of $^{132}I^+$ ions with dipolar C_3H_7X molecules, the yield of the product of replacement of X by ^{132}I, as a first approximation, being proportional to the dipole moment of C_3H_7X. The fact that the spectra of the charged fragments formed in isomeric transition and in irradiation by X-rays with E = 40 keV are similar[82] suggests that not only in the chemistry of atoms obtained by i.t., but also in radiation chemistry, we are dealing with hot ions formed by the "coulombic explosion" of highly charged molecular ions.

(b) Kinetic theory of hot reactions of halogen recoil atoms. Some experimental data confirm the idea that before recoil atoms take part in chemical reactions they are neutralised and deactivated. It may thus be suggested that recoil atoms are obtained in the ground state. If we assume that the reactivity of these atoms is determined entirely by their kinetic energy, we can derive equations which permit experimental verification. Examples of such equations for reactions in the gaseous phase are those of Wolfgang, for example, Eqn. (20). Milman[74,75] and Nesmeyanov and coworkers[28] applied these equations to a condensed system. If it is assumed that for condensed systems a good approximation is provided by the elastic-collision model (since the "cage effect" facilitates rapid recombination reactions by radicals in direct proximity to one another), Eqn. (20) becomes

$$R \simeq \frac{\varepsilon}{\nu\xi} \ln \frac{E_0}{\nu} f, \qquad (28)$$

† In the normal state the process of charge transfer is impossible: the ionisation potential of iodine (10.4) is less than that of xenon (12.1). The excitation energy of the $^1D_2$ level (in the ion) is 1.7 eV. The transfer of charge takes place from this level.

‡ Formed in 90% of cases of neutron capture. E(i.t.) = keV. Almost all γ-quanta are converted[27,77].

where ϵ is the energy of removal from the cell, E_0 the initial recoil energy, $\nu = \nu' M/(M-m)$, ν' is the energy of the C–Br chemical bond, M the mass of the molecule, m the mass of the bromine atom, and f, as before, the geometric probability of collision. Eqn. (28) can also be obtained by simple solution of the resonance integral from the theory of neutron retardation, assuming the mechanism of elastic transfer of energy on collision[28].

For a mixture of substances

$$R \simeq f \frac{\varepsilon}{\nu\xi} \ln \frac{E_0}{\nu} = \frac{N\sigma}{\Sigma N\sigma} \frac{\varepsilon}{\nu\xi} \ln \frac{E_0}{\nu}, \qquad (29)$$

where N is the mole fraction of the original compound in the mixture with the second component. It follows from Eqn. (29) that the yield of labelled compound formed by elastic collision is linearly dependent on the mole fraction multiplied by the factor $1/\xi$. In fact, on dilution of C_2H_5Br with chloromethanes, the observed values for the yield of $C_2H_5{}^{82}Br$ on irradiation of the mixtures with neutrons showed good agreement with the results obtained by calculation using formula (29):

$$R = \frac{\varepsilon}{\nu} \ln \frac{E_0}{\nu} \frac{1}{\xi} f = \text{const} \frac{4r_{Br}^2 N}{4r_{Br}^2 N + (1-N)(r_{Br}+r_{Cl})^2 n\xi_{Cl}},$$

where σ is the collision cross-section, ξ_{Cl} the logarithmic decrement for the bromine–chlorine collision, r_{Br} and r_{Cl} are the covalent radii of bromine and chlorine, and n is the number of chlorine atoms in the chloromethane molecule. The dependence of R on f/ξ was found to be linear, in complete agreement with the mechanism of elastic transfer of energy[28]. Shaw and coworkers[83] showed that the results of the chemical reactions of hot bromine atoms in the liquid phase in the $RBr + Br_2$ system can be interpreted in terms of a model which assumes that the reactions involve elastic collisions.

To describe the replacement of hydrogen atoms by the hot atoms of heavy elements, it is possible to use an inelastic-collision model which assumes that the yield depends on the fraction of the energy transferred on inelastic collision through the molecule as a whole, $M/(M+m)$.[28] The threshold minimum value of the kinetic energy of the bromine recoil atom, at which replacement of hydrogen is still possible, is estimated at 6 eV. Difficulties are encountered in the estimation of the upper energy limit of the recoil atom for the replacement of a hydrogen atom in molecules. It may be estimated only approximately at ~10 eV. The minimum kinetic energy necessary to bring about reactions of elastic collision is equal to 12 eV for C_2H_5Br. On the basis of these considerations, it is possible to construct an approximate curve for the cross-sections of elastic and inelastic collisions leading to hot and epithermal replacement of atoms by hot ^{82}Br atoms (Fig. 1). Experiments on the study of the reactions of halogen recoil atoms are now being carried out with allowance for the secondary ionisation of the labelled compound formed in the first stage of the hot reaction. ^{18}F atoms obtained by the photonuclear (γ,n) reaction have excitation levels of 1.13 MeV and 0.94 MeV, with lifetimes $\sim 10^{-10}$ s.[84] Since change in pressure in the CF_4–inert gas system did not lead to a different distribution of ^{18}F activity, the ^{18}F atoms are formed after the (γ,n) reaction in the ground state.

Since the energy of recoil ^{18}F atoms after the (γ,n) reaction amounts to $\sim 10^5$ eV, they may be ionised in the retardation process and thus still enter the range of chemical interaction in the charged state. A special study has been made of this question[84]. From the values of the energy

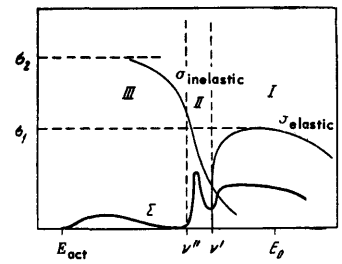


Fig. 1. Probability of chemical reactions of bromine recoil atoms with alkyl bromide molecules. $\sigma_{elastic}$ is the cross-section for elastic collision, $\sigma_{inelastic}$ the cross-section for inelastic collision, $p(E)$ the probability of reactions on one collision, and Σ the cross-section for the hot reaction, equal to

$$p_{elastic}\sigma_{elastic} + p_{inelastic}\sigma_{inelastic},$$

($p_{elastic} = \epsilon/\nu$). In range I the reaction due to elastic transfer of energy takes place:

$$Br^* + C_2H_5Br \rightarrow [C_2H_5 + Br + Br^*]_{cell} \rightarrow C_2H_5Br^*.$$

In range II inelastic collision with the molecule as a whole leads to replacement of hydrogen:

$$Br^* + C_2H_5Br \rightarrow \left[C_2H_5\begin{matrix}Br\\Br^*\end{matrix}\right]_{"complex"} \rightarrow C_2H_4BrBr^*.$$

In range III the reaction of "ordinary" chemistry takes place:

$$Br^* + C_2H_5Br \rightarrow C_2H_4Br + HBr^*.$$

It is possible that the paths of the cross-sections overlap in ranges II and III, and that the reactions of abstraction and replacement of hydrogen are competing reactions, differing only in the values of the probabilities

$$Br^* + C_2H_5Br \rightarrow \left[C_2H_5\begin{matrix}Br\\Br\end{matrix}\right] \begin{matrix}\nearrow C_2H_4Br + HBr^*\\ \searrow C_2H_5Br^* + H\end{matrix}.$$

of the fluorine atoms at which the ionisation processes take place to the maximum extent, calculated from the formula

$$E = {}^1/_2 m \left(\frac{\Delta E\, a}{h}\right)^2 = 2700\,(\Delta E)^2 \text{ eV}\,\S,$$

it follows that the ionisation processes reach a maximum at energies greater than the neutralisation energies, and that at $E < 10^2$ all the atoms are neutral. The results of the chemical action of hot fluorine atoms in the CF_4–inert gases–radical acceptors system, treated from the viewpoint of Wolfgang's kinetic theory, showed[84] that the loss of energy for the collision of fluorine with atoms and molecules is greater than the loss calculated assuming elastic transfer of energy. The fraction of the kinetic energy lost when fluorine collides with argon should be 0.7. Experiment gives 0.94. Comparison of experiment with calculation for collision with a CF_4 molecule gives an even greater discrepancy: calculation gives the value $\xi = 0.36$, whereas experiment gives 1.47 ± 0.28 (relative to the loss of energy on collisions between fluorine and helium). The probability of chemical interaction between fluorine and CF_4 is small: the integral probability of formation of $CF_3{}^{18}F$

§ ΔE is the ionisation potential, a the dimensions of the atom, 7×10^{-8} cm, and m the mass of the fluorine atom.

is smaller by a factor of 16 than the mean loss of energy on collision with CF_4 without the formation of a chemical bond. The probability of replacement of two fluorine atoms with the formation of the radical $CF_2{}^{18}F$ is the same as the probability of the replacement of one atom with the formation of $CF_3{}^{18}F$, and this cannot be explained from the energetic viewpoint, since the replacement of two atoms requires the expenditure of a further 4 eV of energy.

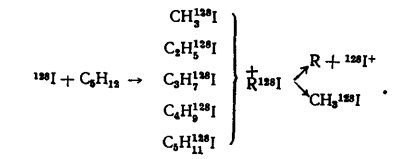
A considerable proportion of the studies which have now been carried out show that the equations of Wolfgang's kinetic theory assist in understanding the processes of energy loss during the retardation of hot atoms and give numerical values for the proportion of the energy lost on collisions with molecules. The retarding powers of different molecules can be compared and are found to be different even for a homologous series of substances. The equations of the kinetic theory can be used to calculate the integral probabilities of the chemical reactions of hot atoms and these are found to be greater by several orders of magnitude than those for ordinary thermal reactions. The next step in the development of reaction mechanism theory may be the determination of the analytical form of the function $p(E)$ — the probability of chemical reaction on one collision — and comparison of calculations with experiment. It is possible that valuable information on the "chemical reaction excitation function" will be provided by studies of the interaction of atoms with molecules in intersecting molecular beams.

(c) Radiative mechanism. The broad spectrum of products formed in the reactions of halogen recoil atoms enabled Willard and coworkers[85,86] to postulate that "nesters of radicals" are formed in the hot atom retardation of radicals" are formed in the hot atom retardation leads to the formation of labelled products. This approach, however, cannot explain a number of facts, including the appreciable yield of labelled products when the experiments are carried out in the gaseous phase. Thus iodine recoil atoms in methane give a 50% yield of $CH_3{}^{128}I$, bromine recoil atoms give ~14% $CH_3{}^{80}Br$, chlorine gives 27%, and tritium gives ~30% CH_3T. At the same time there are certain data which can be explained only from the radiative viewpoint of "random fragmentation" of molecules to form radicals. For example, it was found that the yield of $C_2H_5{}^{128}I$ after an (n,γ) reaction in a 1.4% solution of C_2H_5I in pentane amounts to 41%,[27] whereas neutron irradiation of a mixture of I_2 (0.25 M) with pentane gives a $C_2H_5{}^{128}I$ yield of only 18%. These data can be explained using an "autoradiative model": the distance between the C_2H_5I molecules in the solution is less than the zone corresponding to breakdown brought about by the conversion electrons of soft neutron-capture γ-rays.

The energies of the electrons emitted by ^{128}I are different. A conversion K-electron apparently has an energy of several dozen keV, some of the electrons have an energy equal to the $K-L$ transition without the binding energy of the L-electron, that is, approximately 20 keV, and some of the electrons are emitted with an energy of several keV. The electrons bring about radiative breakdown (ionisation and excitation) among the molecules lying close to the ^{128}I recoil atom which has undergone retardation. The linear transfer of energy by electrons with energies (keV) of 0.1, 1, 10, and 20 is equal to (eV per Å) 3.3, 1.2, 0.23, and 0.13.[27]

Thus the ^{128}I recoil atom which has left the mother molecule after the emission of capture γ-quanta is found, after retardation, in the centre of the zone of breakdown produced by the conversion electrons and characteristic X-rays. The repeatedly drawn-out iodine atoms are rapidly neutralised and subsequently recombine with the surrounding radicals (including radicals of the mother compound) formed as a result of the action of Auger electrons.

The process of ^{128}I marking is possibly more complex than is generally assumed. Allowance must be made for the twofold introduction of iodine atoms into the organic compounds: the iodine recoil atoms first replace hydrogen atoms and groups of atoms in pentane, after which conversion takes place with the formation of iodine recoil ions, which again take part in reaction. A scheme for reaction (5) in accordance with this suggestion is given below:



The ^{128}I ions may again take part in the ion–molecular reaction $^{128}I^+ + C_5H_{12} \rightarrow R^{128}I^+$, whose activation energy is 10–20 kcal lower than that of the corresponding reaction with neutral atoms.

It is at present impossible to analyse the processes of charge transfer in a condensed system. Theoretical calculation of the rate of dissociation of the linear chain of H_2^+ molecules, assuming the existence of intermolecular interaction, showed[87] that dissociation into atoms does not take place if the intermolecular bond is sufficiently strong. From this it follows that the intermediate molecular ions $R^{128}I^+$ may determine the direction of the subsequent reactions of ^{128}I atoms.

(d) Thermodynamic conception of hot reactions in condensed systems. A new approach to the study of the mechanism of hot reactions was developed by Shaw[78]. The equation for the yield of a hot reaction (28) contains the quantity ϵ — the energy of removal from the reaction cell (the energy of formation of a "hole" in the liquid, which a diffusing atom may enter). The magnitude of ϵ can be estimated from photochemical data (0.05 eV). The ratio ϵ/ν amounts to ~0.01. If the absolute calculated yield of a hot reaction is to agree with experiment, it is necessary to assume a considerable number of collisions in the range of chemical interaction (~100) but this cannot be justified. It is suggested[78] that $\epsilon = \Delta E + p\Delta v$, where ΔE is the heat of volatilisation (formation of a "hole"), and $p\Delta v$ the work done against hydrostatic pressure in the formation of a "hole" with volume Δv. For most liquids, for example, C_2H_5Br, $p\Delta v = 8 \times \times 10^{-5}$ eV (p = 1 atm, Δv = 125 Å^3). If an atom with appreciable energy moves in the liquid, the result may be the formation of a zone with increased temperature. If the rate of formation of the zone is high, no significant change in the volume of the zone takes place during the retardation of the hot atom, so that we can examine a thermodynamic parameter $(\partial p/\partial T)v$, which, according to direct experiments[88], is found to be equal to 11.5 atm deg^{-1} for ethyl bromide under normal conditions[78]. The loss of energy by hot bromine atoms was calculated by Shaw on the basis of the model of Capron and Oshima (the method

of Capron and Oshima was described by Nesmeyanov and Borisov[4]). It is suggested that the liberated energy is used up in the formation of a bubble of gas in the liquid and that this rapidly brings about retardation of the hot atom. Calculations show that after a period of $\sim 10^{-12}$ s the pressure in the bubble reaches several thousand kg cm^{-2}, and this alters appreciably the stability of the cell ϵ. At the same time, substitution of the ratio ϵ/ν in formula (28) gives a result which agrees with experiment. Change in temperature during the hot reaction in ethyl bromide is reflected in the magnitude of the pressure: the latter increases with decrease in temperature. An analysis carried out by Shaw shows that the magnitude of the pressure depends to a marked extent on the volume of the hot zone: the pressure increases with decrease in the volume. It may thus be assumed that the introduction of chemically inert retarding agents should increase the yield of mother compound, since in this case the kinetic energy of the hot atom decreases so that the volume of the breakdown zone also decreases.

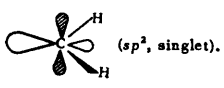
Milman[89] recently observed a relationship between the change in the yield of labelled dibromoethane after an (n,γ) reaction with the points of phase transformation and the change in specific heat and dielectric constant with change in temperature. This indicates a close relationship between the chemical effects of nuclear changes and the physicochemical structure of solids and certain of their properties to which attention has not been paid up to the present.

Thus several approaches have been made to the study of the mechanism of the hot reactions of atoms initiated by nuclear changes. Each approach explains only some of the experimental data, indicating that the mechanism of hot processes is complex and that it is possible to construct a theory showing satisfactory agreement with experiment only by making certain simplications and assumptions which are justified in individual specific cases.

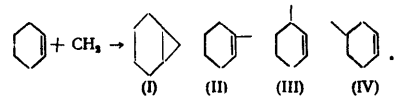
3. Reactions of Hot Carbon Atoms

Unlike halogen and tritium recoil atoms, which react with molecules in the ground states, the determination of the state of carbon (including its chemical form) is more complex. The ground state of the carbon atom is a triplet state (^3P): $|1s^2 2s^2 2p^2|$ ↑↓ ↑↓ ↑ ↑. Conversion into other states involves a considerable expenditure of energy, thus sp^3 hybridisation requires 80–100 kcal. This expenditure is compensated by the energy liberated when carbon forms bonds in the sp^3 state. When hot carbon atoms are formed by the reactions $^{14}N(n,p)^{14}C$, $^{12}C(p,pn)^{11}C$, or $^{12}C(n,2n)^{11}C$, however, the state transition $^3P \rightarrow sp^3$ is brought about by the high kinetic energy accompanying the nuclear reaction.

Some information on the reactivity of a hot carbon atom can be obtained from photochemistry. Experiments on the photolysis of diazomethane have shown the existence of a hot CH_2 fragment in a ground singlet state with one free orbital and one hybridised orbital[90]:

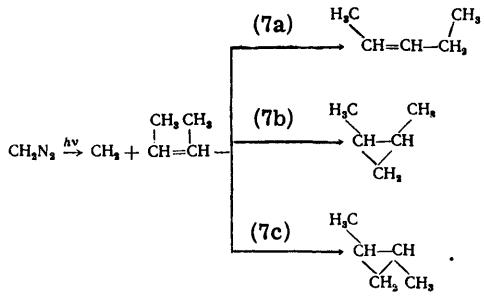

(sp^2, singlet).

On collision with the atoms of the medium, this hot fragment undergoes a singlet–triplet transition[91,92]. The following products are obtained by the photolysis of diazomethane in cyclohexene solution:

(6) 
(I) (II) (III) (IV)

The yields of the products (II), (III), and (IV) are in the ratio 2 : 4 : 4, in complete agreement with the statistical introduction of CH_2 at the C–H bond. The yield of norcarane (I) is much greater than that of the others[92]. The addition of CH_2 across a double bond can take place only if the CH_2 is in the triplet state, since the first excited state of the double bond — the biradical — is a triplet[93]. The formation of norcarane can be explained if we assume a change in multiplicity on the retardation of hot CH_2.

The reactions of hot CH_2 in the gaseous phase confirm the singlet–triplet transition. The photolysis of diazomethane in a medium of *cis*-but-2-ene gives the following products:

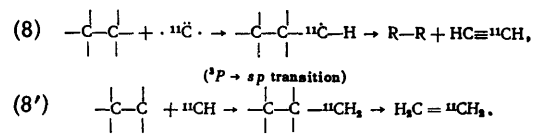


The addition of argon leads to a decrease in the yield of *cis*-pent-2-ene, formed by "insertion" at the C–H bond. The yield of reaction (7b) decreases and that of reaction (7c) increases but the sum of the yields of *cis*- and *trans*-dimethylcyclopropane remains unchanged. Collision with argon is accompanied by the singlet–triplet transition, which then brings about addition at the double bond. The isomerisation in the reactions of hot CH_2 with *cis*-but-2-ene is due to the fact that the products of reactions (7b) and (7c) are formed in the triplet state, for which transition to the ground singlet state is forbidden. There is a definite probability of rotation about the bond within the time corresponding to the transition, equal to 10^{-8}–10^{-7} s. The triplet state of the hot CH_2 obtained after several collisions is confirmed by experiments with the addition of oxygen. The ground state of oxygen is a triplet state and when added in small quantities it reacts effectively with the triplet CH_2 and the products of the addition of CH_2 across the double bond.

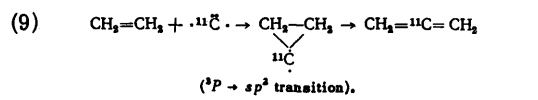
The reactions of hot carbon atoms are now being studied using the isotope ^{11}C obtained from carbon by $(n,2n)$, (p,pn), and (γ,n) reactions, from nitrogen by a (p,α) reaction, from oxygen by a $(p,pn\alpha)$ reaction, and by the reaction of neutron removal when thin targets are bombarded with $^{12}C^+$ ions.

^{11}C recoil atoms, in reactions with saturated and unsaturated hydrocarbons, cyclopropane, or ethylene oxide, give labelled acetylene as chief product (~30% yield)[31,94,95]. In the reactions of ^{11}C recoil atoms with pentane, the chief products are acetylene (22%), ethylene (11%), butane (7%), and n-hexane (26%). If the "insertion" mechanism is

correct, the following reactions should take place in this case:



In the case of unsaturated compounds, considerable yields are obtained of alkenes containing one more carbon atom, for example, the yield of allene from ethylene amounts to 18%:

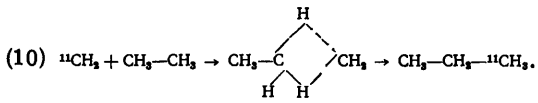


The intramolecular distribution of ^{11}C in allene is now being studied in order to prove the mechanism of addition across the double bond[95].

The addition of retarding agents (nitrogen) did not lead to a decrease in the yield of products. This means that the reactivity of the hot carbon atoms is not due to their kinetic energy. The yield of mother compound in the reactions of hot carbon atoms is extremely low (1.5–2%) and this is not surprising, since elastic collision reactions can hardly compete with the insertion processes. The formation of ethylene from saturated compounds apparently takes place by the insertion of a CH fragment at the C–H bond with subsequent rupture of the C–C bond (reaction 8′).

The low yield of cyclic hydrocarbons in the reactions of carbon atoms with unsaturated compounds (3%)[94,95] is due to the insertion of hot CH_2 at the double bond in the same way as in the reaction initiated by light. In this case, oxygen also inhibits the yield of cyclic products[31].

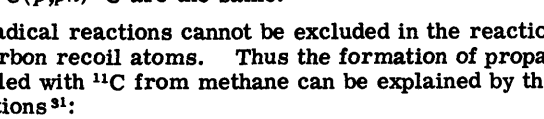
Hot CH_2 are formed by the retardation of carbon recoil atoms in hydrogen-containing media. The increase in chain length is due to insertion at the C–H bond:



The formation of n-hexane from pentane takes place in the same way.

Change in phase state did not lead to any significant redistribution of the activity of ^{11}C in the products[96]. It was found that the primary products formed by insertion at C–H and C–C bonds are excited[96]. The excitation energy is apparently high, since in the condensed phase the yield of the products of the decomposition of the primary excited labelled molecules does not decrease to zero. The yields of the reactions initiated by the nuclear changes $^{12}C(n,2n)^{11}C$ and $^{12}C(p,pn)^{11}C$ are the same.

Radical reactions cannot be excluded in the reactions of carbon recoil atoms. Thus the formation of propane labelled with ^{11}C from methane can be explained by the reactions[31]:



The yield of propane increases with increase in the radiation dose, confirming the radical mechanism, but the yield of ethane does not increase with increase in the dose, contradicting this suggestion.

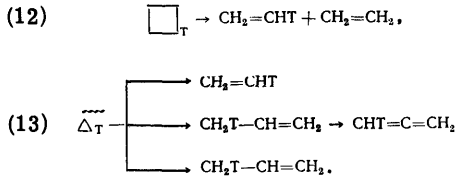
Studies which have been carried out have shown that carbon recoil atoms take part in chemical reactions with molecules in the states C (^3P), CH (sp), and CH_2 (sp^2).

The formation of CH_2 does not depend on the nature of the compound; the reactions of hot carbon atoms always lead to the formation of the same proportion of $^{11}CH_2$ fragments, which undergo insertion reactions in accordance with simple statistics. Kinetic energy plays no significant part in the reactions of hot carbon atoms. The reactions of hot carbon atoms can be represented schematically as follows. Insertion reactions take place irrespective of the nature of the fragment: the insertion of a carbon atom at the C–H bond gives decomposition products, chiefly acetylene; the introduction of the CH methine group at the C–H bond leads to decomposition to ethylene or the formation of an alkene with one carbon atom more than the original molecule; the insertion of CH_2 at C–H and C=C bonds gives hydrocarbons with one atom more than the original molecule. The excitation energy after the insertion process is high, leading to rupture of the nearest C–C bonds. The CH_3 radical is apparently not formed in the retardation of a hot carbon atom. This is confirmed by the fact that no labelled methane molecules were found in the products of the stabilisation of hot ^{14}C atoms[97]. It is true that study of the process $^{14}N(n,p)^{14}C$ is not a sufficiently reliable method for studying the mechanism of the reactions of hot carbon atoms: the appreciable irradiation times required to obtain sufficiently high activities (200–400 h) lead to appreciable radiative decomposition not only of the original products, but also of the products of the hot reactions. Irradiation for short periods in the $NH_3 + CH_4$ system gives acetylene and ethylene, whose yields decrease with increase in the duration of irradiation[98], confirming the above model for the hot reactions of carbon atoms.

IV. EXCITATION ENERGY TRANSFER IN REACTIONS OF HOT ATOMS AND PARAMETERS DETERMINING THE COURSE OF HOT REACTIONS

1. Energy Transfer on Simple Collision

In hot atom chemistry it is an experimentally established fact that the primary labelled products are in an excited state. Thus in the reactions of tritium recoil atoms with cyclopropane and cyclobutane, decomposition of the primary labelled compound is possible[32,33]:



Since change in pressure in the range 0.1–1 atm leads to an increase in the yield of labelled mother molecules, the lifetime of the excited states is estimated at $\geq 10^{-9}$ s. On going to the condensed phase, where the frequency of collision is greater by a factor of 10^3, there is a considerable phase effect for these reactions (Table 5).

TABLE 5. Yield of tritium-labelled products obtained by reaction in cyclobutane in the gaseous $^3He(n, p)T$ and liquid $^6Li(n, \alpha)T$ phases (yield of $\square_T$ + + C_2H_3T taken as 100%).

Conditions	Products					
	$\square_T$	C_2H_3T	HT	$n\text{-}C_4H_9T$	CH_3T	C_3H_6T
9.4 cm□ 2.3 cm O_2 1.4 cm ^3He	50	50	151	3	0.6	0.2
LiF + □ (liquid)	82	19	211	10	5	9.7

Analysis of the data given in Table 5 indicates that in the reactions of tritium recoil atoms with cyclobutane, intermediate molecules in two different states are formed: with a lifetime $>10^{-9}$ s (the yield of the reaction depends on the pressure) and with a lifetime $<5\times10^{-12}$ s (since the change to the liquid phase did not block completely the decomposition of the cyclobutane molecule). The first type of state is a triplet state and the second is a singlet state. The fact that the triplet–singlet transition is forbidden is responsible for the long lifetime of the excited states, and increase in pressure decreases the probability of breakdown of the labelled excited molecules. Since the change to the liquid phase does not reduce the decomposition to zero, however, it must be assumed that there exist highly excited molecules with a short lifetime ($<5\times10^{-12}$ s, singlet), shorter than the time interval between two collisions in the liquid phase.

The removal of the excitation energy apparently takes place from the vibrational levels after the intramolecular conversion of the electronic excitation.

2. Parameters Determining the Course of a Hot Reaction. The Question of the Existence of a Mechanism for the Specific Transfer of Excitation Energy

Nesmeyanov and coworkers[28-30,52,99,100] suggested the existence of an excitation energy transfer depending not so much on the number of collisions as on the nature of the colliding molecules (specific transfer of energy). The deviation from additivity shown by the tritium-labelled products in the binary mixtures: benzene–cyclohexane[100], benzene–pyridine, and pyridine–cyclohexane[30], or by bromine-labelled products in the ethyl bromide–benzene[28] and methylene bromide–benzene[52] systems and by compounds labelled with ^{14}C in the aniline–indole system[29], can be attributed to the transfer of energy from the excited labelled molecules to molecules of an energy "acceptor", analogous to that assumed in radiation chemistry. The analogous relationship for the yields of labelled products observed for the aniline–ethanol (acetone) and acetone–water systems[101] has been examined from other angles, namely from the viewpoint that the yields of the reactions are dependent on the probability of primary interaction and the change in the spectrum of retarded atoms. This viewpoint is also similar to the concept developed in radiation chemistry. Typical curves for the yields of labelled products in binary mixtures of substances are given in Fig. 2.

The yield of labelled product when hot reactions are carried out in a mixture consisting of two components can

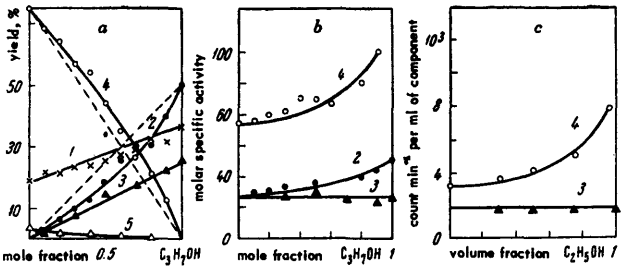


Fig. 2. Radiochemical yields and specific activities of tritium-labelled substances in the C_6H_6–C_3H_7OH binary system: *a*) radiochemical yields: HT (1), $C_3H_7OH(T)$ (2), C_3H_6TOH (3), C_6H_5T (4), and cyclohexene(T) (5) for irradiation of the system: 20 mg Li_2CO_3 + 0.02 ml of C_3H_7OH + C_6H_6 mixtures by a 10^{11} n × × cm^{-2} s^{-1} neutron beam for 6 h at 40°. The total activity recorded was independent of composition[42]; *b*) molar specific activity of components[42] in the C_6H_6–C_3H_7OH binary system; *c*) absolute specific activities of the components of a binary mixture of aniline (4) and ethanol (3). The irradiation was carried out in monitored neutron beams[101].

be found by the Wolfgang–Estrup method[37] (see III. 1) or by solving the resonance integral of the theory of neutron retardation in an absorbing medium[28,38].

If we take

$$\int_{E_1}^{E_2}\frac{p_i(E)}{E}\,dE=\overline{p_i(E)}\ln\frac{E_2}{E_1}$$

[see Eqns. (20) and (22)], we have, with an accuracy up to the constant factors

$$R_{1i}\simeq\left\{\frac{f_1}{\xi}\overline{p_i(E)}-\frac{f_1}{\xi^2}-\overline{p_i(E)}\,[\overline{f_1p_1(E)+f_2p_2(E)}]\right\}\text{const}, \qquad (30)$$

where $R_{1i}=I_{1i}/\Sigma I$, I_{1i} is the activity of the i-labelled product from the first component of the mixture, ΣI the activity of all the labelled products in the system, f_1 the geometric probability of collision with the first component of the mixture, $\overline{p_i(E)}$ the mean probability of chemical reaction on collision with the formation of the i-labelled product from the first component, $\overline{p_1(E)}$ the mean probability of reaction on collision with the formation of all labelled products from the first component, and $\overline{p_2(E)}$ the corresponding probability for the second component. The geometric probability of collision is determined from the relationship

$$f_1=N_1\sigma_1n_1\gamma_1/(N_1\sigma_1n_1\gamma_1+N_2\sigma_2n_2\gamma_2)\quad\begin{matrix}z_1=\sigma_1n_1\gamma_1\\ z_2=\sigma_2n_2\gamma_2\end{matrix}, \qquad (31)$$

where N_1 and N_2 are the mole fractions of the first and second components of the binary mixture, σ_1 and σ_2 the collision micro-cross-sections, n_1 and n_2 the number of reactive points in the molecule at which chemical reactions are possible on collision, and γ_1 and γ_2 the steric-hindrance coefficients for attack. The logarithmic decrement for a mixture of substances can be calculated from formula (12).

Eqn. (30) was obtained[28,38,102] on the basis of the regular features observed in a study of the thermalisation of neutrons when capture processes are taking place, and is applicable if the following conditions are satisfied: (1) the

hot atoms are retarded on atoms of similar mass, or else $E < \xi\, {}^3E_0$, where E_0 is the initial recoil energy; (2) the function for excitation of chemical reactions, $p(E)$, has resonance character; (3) collision between an atom and a molecule is accompanied either by chemical reaction or by scattering with the loss of energy; (4) a hot atom spectrum corresponding to asymptotic collision density $1/\xi E$ can be established; (5) the mean proportion of the energy loss is independent of the energy; and (6) the collision micro-cross-section and steric-hindrance coefficient are independent of the energy. The first four conditions are evidently satisfied in the reactions of hot atoms, and the fifth and sixth conditions can be taken as extremely rough approximations necessary for the analysis of Eqn. (30).

Moreover, we assume that the mean loss of energy is independent of composition (this may be satisfied in particular cases). This facilitates the analysis of Eqn. (30).

Analysis of Eqn. (30) leads to the following conclusions[102]: (1) if $\overline{p_1(E)} > \overline{p_2(E)}$ and $z_1 > z_2$, we find that $d^2R_{1i}/dN_1^2 < 0$ and that the dependence of R_{1i} on N_1 deviates from linearity in a positive direction; (2) if $\overline{p_1(E)} < \overline{p_2(E)}$ and $z_1 < z_2$, we find that $d^2R/dN^2 > 0$, and the dependence of R_1 on N_1 shows a deviation downwards towards the N_1 axis.

The derivative d^2R_1/dN_1^2 does not change sign throughout the whole range of concentrations N_1 from 0 to 1, that is, the dependence of R_1 on N_1 deviates from linearity either upwards or downwards, if $\overline{p_1(E)} > \overline{p_2(E)}$ and $z_1 > z_2$, or $\overline{p_1(E)} < \overline{p_2(E)}$ and $z_1 < z_2$¶. From this analysis it follows that the yields of the labelled products of hot reactions in a binary mixture of substances is non-linearly dependent on concentration and that the dependence may become linear only when $\overline{p_1(E)} = \overline{p_2(E)}$ and $z_1 = z_2$. From this it follows that the explanation of the deviations from additivity shown by the yields of labelled products from the viewpoint of the influence of intermolecular transfer of energy is not unambiguous, since even if the loss of energy does not change with change in concentration, the yield of a hot reaction may be non-linearly dependent on concentration because of differences in the probabilities of chemical interaction. If the retarding power of the medium also changes with change in composition, this will introduce an additional change in the yield of the reactions. The rates of change in R/N at small and large values of N differ by a factor of $(z_1/z_2)^2$. This means that in addition to the ratio between the probabilities of the hot reactions, the yields of labelled products are influenced to a significant extent by such parameters as the collision micro-cross-sections, the number of reactive points in the molecules, and the steric-hindrance coefficients for attack.

Solution of Eqn. (30) for small values of N leads to formulae of the following type[102]:

$$\frac{R_{1i}^1}{R_{1i}^0}\frac{R_{2i}^1}{R_{2i}^0} N_1 N_2 \simeq 1, \qquad (32)$$

$$\frac{R_{1i}^1}{R_{1i}^0} N_1 = \frac{\xi_2}{\xi_1}\frac{z_2}{z_1}, \qquad (33)$$

where R_{1i}^1 and R_{2i}^1 are the yields of the labelled first and second components with the condition that their concentrations are equal to 1 (that is, the yields of labelled components from the pure substances), and R_{1i}^0 and R_{2i}^0 the yields of the first and second labelled components when their concentrations are low (that is R_{1i} when $N_1 \simeq 0.1$, and R_{2i} when $N_2 \simeq 0.1$). Eqn. (32) is confirmed by the experimental data for seven binary systems studied. Significant deviation was found only for the C_6H_{12}–C_6H_6 and C_6H_6–C_5H_5N systems, possibly due to the high probability of the reactions of thermal tritium atoms with benzene and pyridine, one result of which is the formation of a polymer whose activity was not recorded in the experiments[103] (see Section II. 2).

In fact, Rowland and coworkers[104] found that the yield of polymer labelled with tritium in the benzene + + cyclohexane system amounted to 30–40%, depending on the duration of irradiation. It is assumed that the labelled polymer is formed through cyclohexadienyl radicals, whose production was noted earlier[99].

Eqn. (33) can be used to find the ratios $z_1\xi_1/z_2\xi_2$. This ratio is equal to 0.7 for the alcohol–benzene system and 0.5 for the alcohol–cyclohexane system. Thus the analogous ratio for the cyclohexane–benzene system can be found by calculation: 0.7/0.5 = 1.4, which agrees exactly with the value found directly from experimental data on the yields of labelled compounds from a cyclohexane–benzene mixture. This indicates the possibility of using this method to treat the experimental results of studies of the yields of hot reactions in binary mixtures in the condensed phase.

Recently Rowland and coworkers[105] calculated the dependence of R_1 on N_1 by a Monte Carlo method for a number of binary mixtures in the gaseous phase. It was found that the dependence of R_1 on N_1 is determined by $p_1(E)$ and the ratios between σ_1 and σ_2, and ξ_1 and ξ_2, that is, the kinetics of hot reactions are determined by factors such as the probability of reaction, the retardation parameter, and the collision micro-cross-section.

This has a clear physical significance. Let us examine in turn the influence of the parameters determining the formation of the products in hot reactions.

3. The Influence of the Probability of Chemical Reaction on the Yield of the Products of Hot Reactions in a Binary Mixture of Substances

In the range $E \ll E_0$ (more accurately, $E < \xi\, {}^3E_0$) the hot atom spectrum is determined by the expression $1/\xi E$ (Fig. 3). If it is assumed that the probabilities of chemical reaction with the first and second components in the binary mixture of substances are determined in the range E_2–E_1 and depend in resonance fashion on energy (Fig. 3), the spectrum of hot atoms entering the range corresponding to determination of the function $p_{1i}(E)$ "loses" a fraction proportional to $\overline{f_1p_1(E)} + \overline{f_2p_2(E)} - \overline{p(E)}$ is subsequently denoted p. The fraction of hot atoms which can react with the first component with the formation of an i-labelled product (with probability p_{1i}) is equal to $1 - (f_1p_1 + f_2p_2)$. Since the probability of formation of an i-labelled product in the absence of competing processes is proportional to f_1p_{1i}, the yield $R_{1i} \simeq f_1p_{1i} \times (1 - f_1p_1 - f_2p_2)$. From this it follows that with increase in the concentration of the second component in the binary mixture of substances, the hot atom spectrum will show ever-increasing quantities of relatively low-energy atoms at the expense of "removal" of the high-energy fraction of the spectrum in the range E_2–E_1'. The effect of "selective" action of the hot atoms leads to a non-linear concentration dependence for the yields of the labelled products of the hot reactions.

¶ See Nesmeyanov and Filatov[102] for the detailed analysis.

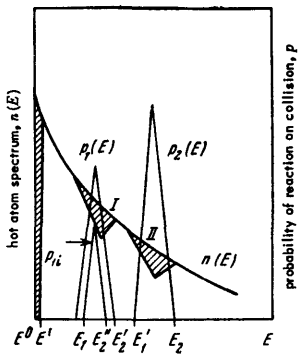


Fig. 3. Dependence of the hot atom spectrum on the probability of chemical reactions in binary mixtures of substances. $p_{1i}(E)$ is the probability of chemical reaction with the first component with the formation of the i-labelled product, $p_1(E)$ the same for the formation of all labelled products, and $p_2(E)$ the probability of reaction with the second component with the formation of all labelled products. The hatched regions (I and II) are the parts of the hot atom spectrum leaving the "game" as a result of chemical reactions. The fraction of hot atoms (II) is proportional to $f_2\overline{p_2(E)}$ and the fraction (I) is proportional to $f_1\overline{p_1(E)}$. The fraction of atoms $1/\xi E\{1 - [f_1p_1 + f_2p_2]\}$ (without allowance for the change in the density of collisions with change in concentration) falls in the energy range $(E_2''-E_1)$ of the function $p_{1i}(E)$. In the range of the spectrum $(E'-E^0)$ the atoms are captured by acceptors of radicals and thermal atoms $E_2 \simeq 10$ eV, $E_1 \simeq 1$ eV, $E^0 \simeq 0.03$ eV.

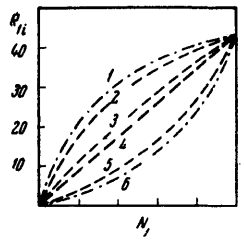


Fig. 4. Yield of labelled first component, formed by hot reactions in a binary mixture of substances, according to the kinetic equation (30), with the conditions that:

1) $p_1 > p_2$, $z_1 > z_2$; 2) $p_1 = p_2$, $z_1 > z_2$;
3) $p_1 > p_2$, $z_1 = z_2$; 4) $p_1 = p_2$, $z_1 = z_2$;
5) $p_1 > p_2$, $z_1 < z_2$; 6) $p_1 = p_2$, $z_1 < z_2$,

where p_1 is the probability of reaction of the hot atom on collision with the first component of the binary mixture; p_2 the same for the second component; z_1 and z_2 the steric parameters; $z_1 = n_1\sigma_1\gamma_1$ for the first component and $z_2 = n_2\sigma_2\gamma_2$ for the second component. R_{1i} is the yield of labelled first component, and N_1 the mole fraction. The following values were selected for the calculation (1, 3, and 5): $p_1 = 0.3$, $p_2 = 0.2$, $z_1 = 0.3$, $z_2 = 0.1$, $p_{1i} = 0.1$, $\xi = 0.6$, and const = 5. For 2, 4, and 6: $p_1 = p_2 = 0.3$. In 3 and 4, $z_1 = z_2 = 0.3$. For $z_1 < z_2$ we took $z_1 = 0.1$ and $z_2 = 0.3$. The choice of the values of p, z, and ξ is not critical. The shape of the dependence of R_1 on N_1 does not depend on the values of p_1, z_1, and p_2, z_2, but only on the relationships between p_{1i}, p_1, z_1 and p_2, z_2.

It is suggested[28,38,101,102] that the existence of this effect, which has been called the "integral effect", explains the *increase in specific activity of any component of the mixture with decrease in its concentration* and also the appearance of an isotopic effect in the reactions of hot tritium atoms in substances such as CH_2D_2, where the mean loss of energy has no influence on the result (see Section III. 1). On the other hand, since $f_1 = N_1\sigma_1n_1\gamma_1/\Sigma N\sigma n\gamma$ [see formula (31)], the rate of change in R_{1i} with change in N_1 (and the rate of change in specific activity with change in composition) is determined by the parameters σ, n, and γ (see Fig. 4).

4. The Influence of the Retarding Power of the Medium on the Yield of the Products of Hot Reactions

According to the kinetic equation (30), for smaller losses of energy, the hot atoms have a higher possibility of taking part in reactions, since there is an increase in the number of collisions in the energy range where $p_{1i} > 0$. On the other hand, if the probabilities of the reactions with the components are different (see Fig. 3), for low fractions of the kinetic energy lost the preferred product will be that for which the probability of formation is displaced towards higher energies (products with p_2). If appreciable proportions of the energy are lost on collision, the hot atom falls into the low energy range in the first collisions and then the $1i$-product will be formed with high probability. This "retardation effect" may lead to an increase in the specific activity of the component on dilution with a second substance[48]. This also follows from the relationship obtained by substituting, in place of f/ξ in Eqn. (3C), the following expression:

$$f/\xi = N_1z_1/[N_1(z_1\xi_1 - z_2\xi_2) + z_2\xi_2] \qquad (34)$$

(ξ_1 and ξ_2 are the mean logarithmic losses of energy on collision with the first and second components respectively)

$$R_{1i} = \frac{N_1z_1}{(N_1z_1\xi_1 + N_2z_2\xi_2)}\overline{p_{1i}(E)} - \frac{N_1z_1}{(N_1z_1\xi_1 + N_2z_2\xi_2)^2}\overline{p_{1i}(E)}\,[N_2z_1\overline{p_1(E)} + N_2z_2\overline{p_2(E)}]. \qquad (35)$$

The dependence of R_{1i} on N_1 is non-linear.

The arguments given in Sections IV. 3 and IV. 4 are valid with the assumption that z and ξ are independent of E. If this is not the case, the analysis of the kinetic equation is more difficult.

5. The Loss of Energy by Hot Atoms in the Range of Chemical Interaction

As noted above, the loss of energy by a hot tritium atom on collision with a methane molecule is greater than that for collision with deuterium, despite the more favourable ratios of the masses of the tritium and deuterium for the transfer of kinetic energy. Chemical interaction apparently takes place on collision between the hot atom and a molecule even if it does not lead to stabilisation of the atom in

any chemical form, that is, "non-reactive" collisions take place with a high cross-section. This process may be called the "chemical scattering" of energy (inelastic collisions). Thus ξ cannot be calculated rigorously from the ratio of the masses and dimensions of the atoms alone. The mean loss of energy on collision should be related to the collision cross-section in the range of chemical interaction energies and should depend on the energy.

According to the theory of neutron retardation, the number of collisions for retardation from E_2 and E_1 is determined by expressions (13). The loss of energy along an infinitely small section of the retardation path can be expressed by the general equation:

$$-dE/dx = LEn\sigma_p, \tag{36}$$

where L is the number of molecules in unit volume, n the number of scattering centres, and σ_p the micro-cross-section of "chemical scattering". From this,

$$x = \ln\left(\frac{E_2}{E_1}\right)\Big/Ln\sigma_p. \tag{37}$$

Dividing (37) by the diameter of the molecule ρ, we obtain the number of collisions with molecul s in the retardation path from E_2 to E_1 (range in fractions of the molecular diameters):

$$k = \frac{\ln(E_2/E_1)}{Ln\sigma_p}\,\frac{1}{\rho}. \tag{38}$$

Equating (38) and (13), we obtain for ξ the expression

$$\xi = Ln\sigma_p\rho. \tag{39}$$

The quantity ξ should be dimensionless, as can be readily verified from (39). In the case of a binary mixture of substances we must substitute in formula (39) the "mean dimensions of the molecules" $\overline{\rho} = N_1\rho_1 + N_2\rho_2$, and the product $Ln\sigma_p$ should be replaced by the sum for both components

$$\xi = (L_1n_1\sigma_{1p} + L_2n_2\sigma_{2p})\,(N_1\rho_1 + N_2\rho_2). \tag{40}$$

Expression (40) gives the relationship between ξ and σ_p.

This analysis shows the complexity of the processes accompanying the retardation and chemical interaction of hot atoms.

Under real conditions, some part is apparently played by several factors: the change in ξ with change in composition produces a change in the density of collisions in the energy range where the probability of reaction is not equal to zero; a difference in the reaction probabilities and the steric parameters of the components of the binary mixtures leads to a change in the spectral distribution of the hot atoms with respect to energies. This change is greater, the greater the difference in the values of the probabilities and the factors $z = n\sigma\gamma$.

The fraction of the energy lost on collisions by the hot atoms ξ is determined by the scattering micro-cross-sections. Since the micro-cross-section increases in the range of chemical interaction energies, the fraction of energy lost also increases.

Thus the independent quantities in formula (30) are $p(E)$, $\sigma(E)$, and, in implicit form, $\sigma_p(E)$. The functions $p(E)$, $\sigma(E)$, and $\sigma_p(E)$ alter the spectrum and density of collisions of the hot atoms, leading to a change in the yields of the hot reactions which is not proportional to the concentration of the original substances. The analytical expression for these functions, which for a given substance depend only on E, is unknown. At present, therefore, we cannot calculate the absolute yield of a hot reaction.

The foregoing does not exclude the possibility that transfer of excitation energy from labelled "newly-formed" molecules influences the yield of the products of hot reactions. Qualitative hypothetical conclusions regarding the existence of this mechanism[30,100] have obtained more rigorous proof. It has been shown[102] that the dependence of the change in the yield of labelled first component (ΔR_1) on the addition of a second component — a hypothetical excitation energy acceptor — is linearly determined by the parameter N_2^3. Since $N_2^3 = 1/r_2$, where r_2 is the distance between the molecules of the excitation energy acceptor, the observed relationship $\Delta R_1 = \text{const} \times N_2^3$ indicates the existence of linear energy transfer throughout the molecules of the acceptor. The part of excitation energy acceptor is played by alcohol molecules in the $C_6H_6 + C_3H_7OH$ and $C_6H_{12} + C_3H_7OH$ systems and by benzene molecules in the $C_6H_{12} + C_6H_6$ system.

The experimental data show that the relationship $\Delta R_1 = CN_2^3$ applies satisfactorily for $N_2 > 0.6$ M. This indicates that the excited molecule of the first component should be surrounded by not less than six molecules of the excitation energy acceptor if the "protection" mechanism is to be effective. It is suggested[102] that at high concentrations of the energy acceptor the chief part is played by energy transfer influencing the rate of deactivation of the excited freshly-formed molecule, whereas at low concentrations the mechanism of "selective" action of the hot atoms predominates.

It may thus be assumed that at present the following parameters and processes determining the kinetics of hot reactions are known: the probability of reaction on collision, the micro-cross-sections of collision and scattering, and, possibly, the transfer of energy from "freshly-formed" labelled molecules.

6. The Possibility of Transfer of Hot Atoms in High-Excitation Reactions

The phenomenon of hydrogen atom transfer was observed in the nineteen-thirties[7] for exchange reactions of the type:

(14) $$H + CH_4 \rightarrow CH_3{-}H{-}H,$$

(15) $$CH_3{-}H{-}H + D \rightarrow HD + CH_4.$$

The methane molecules are hydrogen atom carriers which "catalyse" the process of deuterohydrogen formation. The activation energy of reaction (14) amounts to 10 kcal and the dissociation energy of the "fifth" hydrogen atom is ~17 kcal, that is, the compound $CH_4{-}H$ is fairly stable.

In view of the existence of the processes of charge and excitation energy transfer, and also the above process, it may be assumed that there is a possibility of hot atom transfer from some molecules to others, for example, in the cyclohexane–benzene system after collision between tritium and a benzene molecule — the "catalytic" marking of cyclohexane: $C_6H_5{-}T + C_6H_{12} \rightarrow C_6H_{11}T + C_6H_7$ (compare Section II. 2).

In the RH + ROH system, the alcohol molecules apparently act as tritium atom carriers.

From this viewpoint it is possible to explain the change in the specific activity of certain substances in a mixture

with additives capable of transferring hot atoms. At present, however, we have no proof that such "catalytic" processes take place in hot atom chemistry.

7. The Stereochemistry of Hot Reactions and the Elementary Act of the Establishment of a Bond

It follows from formula (24) that the three-dimensional structure of molecules should influence primarily the replacement of atoms, since this takes place with attack by the hot atom at large angles to the direction of the bond formed by the atom being replaced. In fact, the agreement between the experimental results and calculated data assuming that the steric hindrance for attack $\Omega = 0.45$ in the replacement of a primary atom shows that steric factors play a decisive part in the competing reactions of abstraction and replacement. In attack at large angles to the bond direction, the rotational levels of the molecule are apparently excited. In this connection the mass of the molecule should apparently influence the establishment of a chemical bond following the transfer of energy. This can be readily followed by analysing the yields of the products formed by rupture of the C–C bond in different hydrocarbons. It is found that the tritium recoil atom reacts with the lighter residue of the molecule. Thus in the reaction

$$(16)\qquad T + CH_3{-}CF_3 \rightarrow \begin{cases} CH_3T \\ CF_3T \end{cases},$$

the ratio of the yields CH_3T/CF_3T amounted to 15, whereas in the reaction

$$(17)\quad T + CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_3 \rightarrow \begin{cases} CH_3T + R \\ CH_3{-}CH_2{-}CH_2{-}CH_2T + CH_3^{\cdot} \end{cases},$$

the ratio $CH_3T/CH_3CH_2CH_2CH_2T$ was found to be 2.8 (Table 6). For chlorinated, brominated, and fluorinated methanes, it was also found that the effect of replacement of an atom was preferred to a greater extent, the smaller the mass of the fragment with which the hot atom reacts ("the inertial effect")[106,107].

The period of rotation through an angle θ is related to the moment of inertia (I) by the relationship

$$\tau \simeq 2\theta\sqrt{I/2E}. \qquad (41)$$

Calculation[106] shows that the time required for the rotation of CH_2F through an angle of 1 radian amounts to $\sim 5 \times \times 10^{-14}$ s if the recoil atom communicated several electron volts of kinetic energy to the CH_2F_2 molecule on collision at the C–F bond. This time interval is greater than the duration of the interaction between the hot atom and the C–F bond (10^{-14} s). In fact, the yield of the products obtained by the replacement of fluorine by tritium atoms in CH_2F_2 amounted to fractions of 1%, whereas as a result of the ease of rotation of the methyl group about the centre of inertia in CH_3F the yield of CH_3T amounted to 4.4%.

TABLE 6. Inertial effect in the reactions of hot tritium atoms[106].

Substance	Ratio of yield of CH_3T to the yield of $R_{n-1}H_{2n-1}T$ per C–CH_3 bond
C_3H_8	2.7*
$n\text{-}C_4H_{10}$	1.8
$n\text{-}C_5H_{12}$	2.8
$iso\text{-}C_5H_{10}$	4.7
$neo\text{-}C_5H_{12}$	8.7
$n\text{-}C_6H_{14}$	2.2
For $CH_3{-}CF_3$	Ratio $\frac{CH_3T}{CF_3T} \simeq 15$

* For example, for C_3H_8: $CH_3T/C_2H_5T = \frac{11.0}{4.0} = 2.7$.

In the calculation it is also necessary to allow for the values of the collision cross-sections, the energy of the bonds, and the possibility of removal of the excitation energy. In the series CH_3F, CH_3Cl, and CH_3Br, the yield of CH_3T increases systematically (4.4%, 7.1%, and 12.0%) in accordance with the increasing cross-sections of collision for tritium with the atoms on going from fluorine (0.88×10^{-16} cm²) to chlorine (1.6×10^{-16} cm²) and bromine (1.96×10^{-16} cm²)† – the energy of the C–X bond (X = halogen) also decreases in the above series of compounds, so that the conclusion regarding the influence of collision cross-section is ambiguous; the results show better agreement with experiment, however, for the former model. In the liquid phase the freedom of rotation of the molecules is limited. From the viewpoint of the "inertial effect", the yield of replacement products should decrease, but this is not observed (Table 7): the yield of the chlorine-replacement product increases for both CH_3Cl and CH_2Cl_2. In the liquid phase there is apparently a sharp increase in the survival of labelled molecules as a result of the transfer of energy on collision.

The transfer of energy (non-specific) here is facilitated by the fact that the rotational energy, which is essentially kinetic, is readily converted into energy of translational movement. The rate of removal of the excitation energy is equal to the number of collisions between the atoms and molecules:

$$z = 2/\sqrt{\pi}\,\sigma\, v N_1 N_2 q, \qquad (42)$$

where σ is the collision cross-section for the excited molecule, v the velocity of the particles, N_1 and N_2 are their concentrations, and q is the probability of the process,

TABLE 7. Relative yields of tritium-labelled molecules as a result of the reactions of hot tritium atoms with chloromethanes*.[108]

A

Substance	Yield of products		
	CH_3T	CH_2TCl	CH_2TI
CH_3Cl 9.1 cm, gas	27.8	30.4	40.9
Liquid	45	65	—

B

Substance	Yield of products			
	CH_2TCl	$CHTCl_2$	CH_2TI	$CHTCII$
CH_2Cl_2 8.1 cm, gas	6.9	13.9	15.3	6.4
Liquid	37	44	—	—

* Yield of HT taken as 100%; ^{3}He pressure 1.5 cm; on irradiation in the gaseous phase the ampoules contained I_2.

† The covalent radii were used for the calculation[108].

equal to unity for the conversion of energy of rotation into translational energy and equal to $\sim 10^{-4}$ for the conversion of vibrational energy into translational energy.

Thus for attack at large angles to the bond direction, the rotational levels are excited. The removal of excitation energy takes place effectively on each collision with another molecule, so that increase in pressure leads to an increase in the yield of replacement product. In the case of attack along the bond, the vibrational levels of the molecule are excited. The probability of conversion of vibrational energy into translational energy is smaller by a factor of 10^4 than that for the conversion of rotational energy into translational energy. Thus the yield of abstraction products formed as a result of this attack depends little on pressure, as confirmed by experiment[33].

It is undoubtedly true that in the establishment of a chemical bond the electronic levels of the molecule are also excited. The lifetime of excited electronic states amounts to 10^{-12}–10^{-13} s. This increases to 10^{-9}–10^{-7} s if a change in multiplicity takes place. In a period of $\sim 10^{-8}$ s the molecule is able to undergo approximately 10^5 vibrations and approximately 10^3 rotations. If the internal conversion of electronic excitation takes place readily, there is a definite probability of energy transfer on collision with surrounding molecules (non-specific transfer of energy). Certain substances, for example, benzene, are able to remove excitation energy directly from electronic levels (specific transfer of energy).

In the gaseous phase the time interval between two collisions is inversely proportional to pressure and is equal to $\sim 10^{-7}\ p^{-1}$ s, where p is the pressure in mmHg. At a pressure of 100 mmHg the lifetime of an excited molecule should be greater than 10^{-8} s if deactivation is to take place on collision. In a liquid, the number of collisions per second amounts to $\sim 5 \times 10^{12}$, so that transfer of energy on collision is possible even if short-lived states are excited. The question of the specific transfer of excitation energy in reactions of hot atoms remains open. At present the main task is to establish precise experimental facts indicating that such processes take place.

The next step in the further development of the theory of the elementary acts of chemical reactions at high energies is possibly a quantum-mechanical approach, which here is facilitated by the fact that the reactions of hot atoms take place on local collision in a limited part of the molecule, so that the remaining part of the molecule can be regarded as not taking part in the primary act of establishment of the chemical bond. The first steps in this direction have already been taken[109].

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THE USE OF ELECTRON PARAMAGNETIC RESONANCE FOR THE STUDY OF CATALYSTS

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