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Kinetics of Gas-phase Ion-Molecule Exchange Reactions

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The kinetics of ion-molecule exchange reactions (IMR), which are important in high-energy and analytical chemistry, are discussed, and their special features and the factors influencing the reaction rate are analysed. Special attention is paid to slow IMR with rate constants substantially smaller than the gas-kinetic ion-molecule collision rate.
141 references

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I. INTRODUCTION

The foundations of the kinetics of gas-phase ion-molecule reactions (IMR), a new branch of chemical kinetics, were laid by Tal'roze[1,2]. Since then, interest in IMR has grown very considerably as a result of new developments in radiation chemistry, the physics and chemistry of plasmas and of gas discharges, the chemistry of planetary ionospheres and of interstellar clouds, and other systems in which the molecular composition of an ionised medium is determined mainly by IMR[3-6].

Ion–molecule reactions play an important role in analytical techniques, especially in mass spectroscopy, because they yield simple line spectra which facilitate the analysis of complex organic compounds and their mixtures and from which information on the structure and the energy state of the ions can be obtained[7-10].

Methods based on the study of IMR offer important information on the acid-base properties of molecules in the gas phase: their proton and electron affinity[11,12], the mechanism by which the ions become solvated in a liquid, and the mechanism of the gas-liquid phase transition.

Ion-molecule reactions are a convenient way of experimentally identifying and studying the special features of the elementary chemical acts, and the fundamental nature of the reactivity of the system.

The reacting ions can be obtained relatively simply with different energy distributions (controlled by varying the energy of the ionising radiation) in IMR. An electric field can be used to vary the kinetic energy of the reacting ions and to analyse the resulting ions in terms of their energy. Both the reacting and the resulting ions can be separated and monitored very effectively by mass-spectrometric methods. IMR can be studied without difficulty at flow rates of the order of one ion per second by existing experimental techniques. The sensitivity and selectivity of the method are sufficient to justify detailed studies of IMR under non-equilibrium conditions (which are far less easily undertaken in the case of neutral reacting species). These features of the method explain the important contribution of IMR data to recent developments in the theory of elementary processes.

Experimental methods used in quantitative studies of IMR are fully reviewed in a recent monograph[17], and we shall only discuss a few special aspects of the technique in this review. In the internal ionisation methods[20] both the primary ion and the secondary (product) ion are obtained within the ionisation chamber of the ion source of a mass spectrometer. The most detailed information on the initial vibrational energy distribution of the primary ions is obtained by using photon impact ionisation[21-25]. The pulse method[26], in conjunction with ion trapping[27-30] and ion cyclotron resonance (ICR)[31-34] techniques, allows the reactions of thermal ions to be studied at low pressures. At relatively high pressures other methods are used (plasma decomposition in a flow[35] and ion drift in an electric field[37]).

In the external ionisation methods the primary ions are introduced into the ionisation chamber from outside[20,38-40], thus allowing the kinetic energy of the ion to be determined. These methods include the crossed beam method[41-44], which is particularly convenient for measurements of the angular distribution of the products. Information on the internal energy and structure of the primary ions is obtained by analysing the radiation[45,46], by impact spectroscopy methods[47,48], and by analysing the radiolysis products of gases and of condensed phases.

Several monographs dealing specifically with various aspects of IMR have appeared in recent years[13-19]: the aim of the present review is to examine some of the factors affecting the rate of bimolecular IMR and the kinetics of the elementary processes in these reactions.

II. METHODS OF CALCULATING THE KINETIC PARAMETERS

Mutual polarisation plays an important role in the collision between an ion and a molecule. The Langevin formula can be used to allow for this effect in the expressions for the rate constant and the cross section of ion-molecule collisions[50]:

$$k = 2\pi e(\alpha/\mu)^{1/2} \quad (1)$$

$$\sigma = \pi e(2\alpha/E)^{1/2} \quad (2)$$

where α is the polarisability of the molecule, e is the charge on the electron, μ is the reduced mass, and E is the kinetic energy of the relative motion of the ion and the molecule. When an ion interacts with a molecule which has a constant dipole moment an upper limit for the collision rate can be obtained by the formula[51,52]

$$k = 2\pi e\mu^{-1/2}[\alpha^{1/2} + \mu_D(2/\pi k_B T)^{1/2}] \quad (3)$$

where μ_D is the dipole moment, k_B is Boltzmann's constant,

and T is the absolute temperature. Methods of calculating the rate constants of collisions between ions and atoms (or molecules) with allowance for electronic polarisation, dipole orientation, ion–quadrupole forces, and interactions between induced dipoles are reviewed in a recent monograph[51]. It is often found that the rates of exothermic or thermoneutral exchange IMR are close to the corresponding ion–molecule collision rates[53].

The efficiency of the exchange reaction depends on the shape of the multidimensional potential energy surfaces for the system of colliding particles and on the probability of transitions between these surfaces. Exact calculations of the potential surfaces and of the cross-sections of IMR have been attempted only for very simple systems[54,55].

We shall confine our discussion to the factors directly related to the parameters of the reactants and able to influence the effectiveness of the reactions. The first calculation of the rate constant of an IMR was reported by Eyring and coworkers[56], who applied to the reaction

$$H_2^+ + H_2 = H_3^+ + H \qquad (4)$$

a variant of the transition state method in which only long-range attractive forces are considered, and the effective activation energy is assumed to be determined by the competing effects of the centrifugal force and the attractive force between reactants due to the polarisation of the neutral species. In this model of the interaction, the distance between the reacting species in the activated complex is large, and the rotation of the two reacting particles can be treated as the rotation of uncoupled partners. The vibrational degrees of freedom are assumed to be the same as for the isolated reactants (the molecule and the ion). Therefore the vibrational and the rotational partition functions of the reactants and of the activated complex are simplified in the expression for the rate constant of the reaction, and the rate constant of an exothermic reaction is defined by Eqn.(1) and is equal to the rate constant of the ion–molecule collision process.

We should stress that the first strict calculation[57] of the rate constants of IMR with zero activation energy by the transition state theory appeared in 1978, i.e. many years after Eyring's original paper[56].

Most of the specific calculations of cross sections and rate constants for IMR have relied on the statistical theory, which is particularly convenient for non-activated reactions. This theory assumes strong interactions between all the degrees of freedom in the intermediate complex, making the decomposition of the intermediate complex in any direction allowed by the conservation laws equally probable. The first step in the reaction is the formation of the intermediate complex, within which the energy and momentum of the reactants become statistically distributed over all degrees of freedom up to the instant of decomposition; the second step consists in the decomposition, which depends only on the total energy and momentum, and is independent of the other initial conditions under which the complex was formed.

The statistical theory was first applied to IMR by Tal'roze and Firsov[58,59] in a simplified form which did not allow for conservation of the total momentum, but it was subsequently further developed and expanded[60,61]. In all the calculations the exothermic and thermoneutral IMR were assumed to have zero activation energy, and the rate constant for the formation of the intermediate complex was identified with the rate of ion-molecule collisions. A valuable feature of this variant of the statistical theory is the small number of parameters (relating only to the reactants and products, and not to the collision complex) needed to calculate the full set of characteristics of the elementary act of the IMR.

The statistical theory has been used to calculate the dependence of the rate constants and cross-sections of IMR on the translational and internal energy of the reactants[62,63] and the energy distribution of the products of the IMR.[63,64]

The application of the statistical theory to IMR has been discussed by several reviewers[63,65,66], and the agreement between calculation and experiment has been shown to be good. For example, the steeper fall in the cross-section of exothermic IMR with increase in the kinetic energy of the ions [as compared with the effect predicted by formula(2)] can be explained in terms of the statistical theory by the competing effect of the backward decomposition of the intermediate complex into the initial reactants[58]. The reaction cross-section falls more steeply when the secondary ion can dissociate[67]. The subsequent decomposition reactions can also be described by the statistical theory.

In some systems serious discrepancies are observed between experiment and calculations by the statistical theory. For example, collisions of the type of

$$CH_3CDO^+ + CD_3CDO \rightarrow H_3C{-}C\begin{matrix}O\cdots D\\ +\\ D\cdots O\end{matrix}C{-}CD_3$$

produce a symmetrical complex which should (according to the statistical theory) yield CD_3CDOD^+ and CH_3CDOD^+ as products with equal probabilities. Experimentally[68] we find that CD_3CDOD^+ is formed preferentially, suggesting that the charge in the complex has not been fully delocalised.

Reported differences between calculation and experiment may be due to the following factors:

1) the probability of formation of the intermediate ion–molecule complex is not unity (as is assumed in the theory),

2) the exchange of energy between the different degrees of freedom in the complex is hindered,

3) the potential surface of the IMR includes an energy barrier.

To allow for these factors we need to formulate the theory of IMR in greater detail, and to introduce additional parameters. For exothermic IMR taking place without activation through a "soft" polarisation complex the statistical theory and the activated complex theory give identical results.

In the case of endothermic IMR the statistical theory is applicable only when the collision complex has a stable configuration. For example, the reaction

$$C^+ + H_2 \rightarrow CH_2^+ \rightarrow CH^+ + H \qquad (5)$$

can form the strongly bound complex CH_2^+, whereas the H_4O^+ complex formed in

$$H_2O^+ + H_2 \rightarrow H_3^+ + OH \qquad (6)$$

is unstable. The statistical theory satisfactorily describes the dependence of the cross-section on the kinetic energy near the threshold for reaction (5), but for reaction (6) the same calculation gives unacceptable results[69,70].

Reaction (6) can be described by the activated complex theory on the assumption that the energy threshold is shifted towards the reactants[70]. In general, the activated complex theory is most successfully applied to reactions with a threshold energy when these are "direct" processes, i.e. reactions in which the interaction time of the reactants is small compared to the characteristic time of the redistribution of energy over the degrees of freedom of the system.

The validity of the activated complex theory or of the statistical theory when applied to a specific reaction is determined by the ratio of the height of the energy barrier corresponding to the transition state to the depth of the potential well corresponding to the intermediate complex. A recently developed unified statistical model yields a generalised expression for the rate constant of the reaction which can be

used for direct reactions as well as for reactions taking place through a long-lived complex[71]. This model has not yet been used in the calculations for IMR.

III. STERIC FACTORS AND TEMPERATURE EFFECTS

The low rate constants of some exothermic IMR (as compared to the values predicted by the statistical theory) have been ascribed[72] to the need for a particular mutual orientation of the colliding particles to allow chemical rearrangement in the ion–molecule complex. The following expression is obtained for the differential collision cross-section of the ion and the molecule with an orbital quantum number L:

$$\sigma(L, E) = (2L+1)\pi\hbar^2/2\mu E \ .$$

Noting that only one of the $(2L+1)$ possible projections of the vector for the momentum of the relative motion of the reactants leads to reaction, and that the maximum value L^* is determined by the Langevin capture cross-section according to the formula

$$L^*(L^*+1) = 8\mu^2\alpha e^2 E)^{1/2}\hbar^2$$

for the full cross-section of the reaction produced by the collision of the reactants, we arrive at

$$\sigma(E) = \pi\hbar(\alpha e^2/2\mu^2 E^3)^{1/4} \qquad (7)$$

so that the rate constant is

$$k(E) = \pi\hbar(2\alpha e^2/E)^{1/2}\mu \ . \qquad (8)$$

In the case of a Maxwellian distribution of the velocities of the reacting particles at temperature T the expression for the rate constant becomes

$$k(T) = 3.2(2\alpha e^2/k_B T)^{1/2} \ . \qquad (9)$$

In the case of IMR involving symmetrical reactants the right-hand sides of Eqns.(7)–(9) should be multiplied by the degeneracy factor g, Thus, for the reaction

$$CF^+ + C_3F_8 = CF_2 + C_3F_7^+ . \qquad (10)$$

we have $g = 8$, since any one of the eight fluorine atoms in the C_3F_8 molecule can act as a reaction centre. The calculated[72] rate constant of reaction (10) is 5.2×10^{-11} cm^3 s^{-1}, and the Langevin collision rate constant of the reactants is 1.08×10^{-9} cm^3 s^{-1}. The experimental value[73] of the rate constant for this reaction is 3.7×10^{-11} cm^3 s^{-1}, in good agreement with the calculated value[72]. In IMR in binary mixtures of ethylene and fluorinated ethylenes the rate of the condensation reactions giving $C_3(H,F)_5^+$ and $C(H,F)_3^+$ as products has been shown[74] to be very sensitive to the replacement of H atoms by F atoms. In the $C_2H_4^+ + C_2H_4$ system every collision leads to interaction, whereas in the $CF_2CH_2^+ + CF_2CH_2$ system the rate constant of the corresponding reaction is less than 10^{-12} cm^3 s^{-1}. The presence of the fluorine atoms does not make the reaction thermodynamically forbidden, but it increases the height of the barriers opposing the migration of atoms (H, or F) in the intermediate complex. The high rate constants of reactions similar to (10) but involving hydrocarbons have been explained[72] in terms of the relatively high mobility of H, H^+, and H^- in the intermediate complex (as compared to the mobility of the fluorine atom).

Fast IMR involving the transfer of a fluorine atom have been recently discovered experimentally[75]:

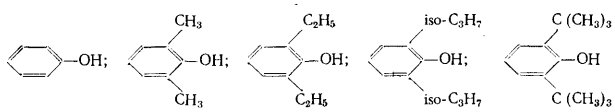
$$CH_3^+ + CH_2F_2 \rightarrow CH_3F^+ + CH_3F$$
$$CH_3^+ + CHF_3 \rightarrow CH_3F + CHF_2^+$$
$$CH_3^+ + CF_4 \rightarrow CF_3^+ + CH_3F \ .$$

The rate constants of these reactions calculated by formula (8) are much lower than the experimental values. Evidently, the validity of formulae (7)–(9) in calculations of the kinetic parameters of IMR must be limited by a number of factors (not merely the mass of the migrating atom). Thus in the collision between an ion and a molecule some of the energy of the relative motion may be converted into vibrational or rotational energy of the reactants, giving a complex in which the reactants can experience many intramolecular collisions. For example, according to the activated complex theory[57] the ion-atomic and a diatomic particle at 300 K and with a potential well of 2 eV gives a complex with a life time equivalent to 100 vibrations (vibration period 3×10^{-13} s). The complex formed by two diatomic species for the same parameters is even longer-lived (3×10^3 vibrations), thus increasing the probability of acheiving a mutual orientation of the reactants favourable to the reaction. However, we should stress that the number of intra-complex conditions is greater in the $CH_3^+...CH_2F_2$ than in the $CF^+...C_3F_8$ system. At present formulae (7)–(9) have been shown to be consistent with experiment only for IMR between neutral and charged unsubstituted fluorocarbons.

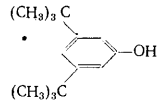
Orientation effects are even more important when the collision has to be followed by the transfer of a large group of atoms (as opposed to the transfer of a single atom). An example is the transfer of the acetyl ion[76], in which the reacting ion is formed by the reaction

$$CH_3COCOCH_3^+ + CH_3COCOCH_3 \rightarrow (CH_3CO)_3^+ + CH_3CO \ .$$

Bursey and coworkers have shown[76] that in the phenol series



the acetylation reaction takes place only with the first three members: the last two compounds do not react because the approach of the $C_6H_9O_3^+$ ion and the transfer of the acetyl ion are sterically hindered. The role of the steric effect is confirmed by the observation that the phenol



(in which the methyl groups are remote from the reaction centre) is readily acetylated[77]. Thus even in the ion–molecule collision of complex multi-atomic particles, which can be expected to produce a long-lived collision complex, the exothermic IMR may be found to be slow as a result of steric effects opposing the formation of an intermediate reactive complex with strong interactions between the degrees of freedom responsible for the chemical regrouping of the atoms.

These (and other similar) experimental results have led to the realisation that ion–molecule complexes must be classified into two distinct types. The collision between an ion and a molecule can give rise to a "soft" complex, in which the reactants are bound by relatively weak polarisation forces and remain relatively far apart, so that energy and mass exchange in the complex are hindered. Such a complex can either dissociate back into its initial reactants or be converted into a "hard" complex, characterised by a strong chemical bond between the reactants. The "hard" complex can be treated in terms of the statistical theory to calculate the relative probabilities of alternative decomposition paths.

The need to distinguish between two types of complex is evident also from the temperature dependence of the rate constants of IMR. Thus, a study[78,79] of the transfer of the

hydride ion from isobutane to s-$C_3H_7^+$ has revealed the existence of two temperature regions, with different temperature dependences of the rate constant. At high temperatures the rate constant has a negative temperature coefficient, and at low temperatures it becomes independent of temperature and equal to the Langevin limiting value. This temperature dependence can be explained by postulating the following scheme:

$$R_1^+ + R_2H \underset{k_b}{\overset{k_c}{\rightleftarrows}} [R_1^+ \ \ldots \ R_2H]_{soft} \xrightarrow{k_T} [R_1 \ \ldots \ R_2H]^+_{hard} \rightarrow \text{products} .$$

It is assumed[78,79] that the rate constants for the formation (k_C) and for the back dissociation (k_b) of the soft intermediate complex are independent of temperature whereas the rate constant of the transition from the soft to the hard complex (k_T) is a function of temperature. This dependence was calculated by the activated complex theory for bimolecular reactions, assuming that the activation energy is zero and that only the pre-exponential factor is temperature-dependent:

$$A(T) = \gamma T^{-(2+r/2)} \qquad (11)$$

where γ is temperature-independent and r is the number of internal rotators in the reacting molecules which are converted into oscillators in the activated complex (performing torsional vibrations). For example, from the temperature dependence of the rate constant of the reaction

$$t\text{-}C_4H^+_9 + \text{iso-}C_5H_{12} \rightarrow C_5H^+_{11} + C_4H_{10} \qquad (12)$$

we obtain (experimentally) $r = 2$. This means that the formation of the activated complex of reaction (12) is accompanied by the disappearance of two internal rotators (probably methyl groups, since the rotation of these groups can be strongly hindered in an activated complex). According to the structural formulae of the reactants the maximum number of rotators which may become hindered is six. Thus the model (in conjunction with experimental data on the temperature dependence of the rate constant) offers valuable information on the properties of the activated complex for IMR.

In some reactions the experimental temperature coefficient is even smaller than the value expected from the number of hindered rotators according to the above model. The temperature dependence of the rate constant for the reaction

$$CH_4D^+ + CH_4 \rightarrow CH_5^+ + CH_3D$$

has been explained[80] by postulating a model which assumes the existence of a soft and a hard complex but allows the rate constant of the backward decomposition of the soft complex into the initial reactants to be temperature-dependent. This model is free from the stringent limitations imposed on the temperature coefficient by the number of hindered rotators, but it includes some parameters which cannot easily be calculated theoretically (for example, the life time of the soft complex). The results of experiments under non-equilibrium conditions have also been explained by this qualitative model. For example, in IMR of s-$C_3H_7^+$ with iso-butane, normal butane, pentane, and hexane the rate constant for the exchange of a hydride ion is much lower in the pure vapours than in mixtures (which are diluted with molecules not involved in the interaction with the reactant ion[81]). This difference has been ascribed[81] to decrease in internal energy of the reactant ion resulting from the increased number of collisions with molecules of the buffer gas prior to the reaction. The characteristic time of the backward decomposition decreases as the excitation energy of the soft complex increases, and therefore the probability of the exchange reaction decreases: it is assumed that the rate constant for the conversion of the soft complex into a hard complex is weakly dependent on the excitation energy.

The rate constant for the formation of the soft complex is not always equal to the Langevin limit. According to measurements of the rate constant of associative IMR the high-pressure limit[82] for the formation of the soft complex can be much lower than the rate constant of the ion-molecule collisions. Collision may be followed by reflection or rapid back-dissociation of the complex into the reactants during a single vibration if the relative kinetic energy of the reactants cannot be accommodated in internal degrees of freedom of the ion-molecule complex during the collision. No theoretical calculations of the efficiency for the formation of soft complexes during ion-molecule collisions have yet been reported.

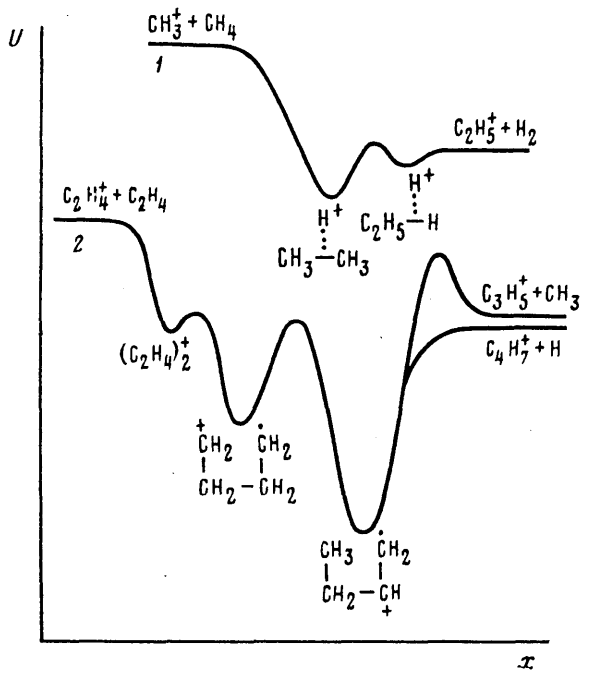


Figure 1. Profiles of the reaction paths $CH_3^+ + CH_4 \rightarrow C_2H_5 + H_2$ [85] (*1*) and $C_2H_4^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_3$ [86] (*2*); U is the potential energy, x is the reaction co-ordinate.

The potential curve for the formation of ion-molecule complexes of two types in processes such as

$$A^+ + B \rightleftarrows AB^+ \rightleftarrows CD^+ \rightarrow C + D^+ \qquad (13)$$

has two minima, separated by a small barrier. In the state AB^+ the system has enough energy to be converted into the state CD^+, or to decompose into the initial reactants. The potential barrier opposing the reverse dissociation into A^+ and B is high, but under these conditions the pre-exponential factor in the expression for the rate constant is also large, and the decomposition of the soft complex (AB^+) takes place through a soft transition state. On the other hand the potential barrier to the transition of AB^+ into the hard complex CD^+ is relatively small, but the transition takes

place through a hard transition state and therefore the pre-exponential factor is small[83]. This model accounts for the low efficiency and negative temperature coefficient of the rate constants of isotope exchange reactions of the type of

$$CD_3\overset{O}{\overset{\|}{C}}CD_2^- + CH_3\overset{O}{\overset{\|}{C}}CH_3 \rightarrow CH_3\overset{O}{\overset{\|}{C}}CH_2^- + CD_3\overset{O}{\overset{\|}{C}}CD_2H$$

$$^{37}Cl^- + CH_3^{35}Cl \rightarrow {}^{35}Cl^- + CH_3{}^{37}Cl$$

and allows us to calculate the height of the barrier separating the soft from the hard complex. The concept of a soft and a hard complex can also be used to explain the effect of temperature and pressure on the kinetics of IMR.[84]

Some ion-molecule systems can include several types of hard complex, or they may not have a complex of either type. Information on the form of the potential surface along the reaction co-ordinate can be obtained from data on ion-molecule equilibria[85] and from experiments on the photo-ionisation of the van der Waals molecular complexes[86]. Typical potential energy profiles are shown in Fig.1.

IV. PATH PROFILES AND KINETIC FEATURES OF IMR

Statistical methods of calculation assume a quasi-equilibrium distribution of the reaction products in excitation energy, but substantial departures from equilibrium are often observed in experiments. If the shape of the potential energy surface is known, both the reaction cross-section and the distribution functions of the products in excitation energy can be obtained from calculations by the dynamic method[87]. This method is usually applied to a linear reaction of the type of

$$A + BC \rightarrow AB + C$$

whose potential energy surfaces do not include deep potential wells. In this case the reaction takes place without the formation of a long-lived intermediate complex. The largest non-equilibrium effects can be expected in these direct reactions. The probability of the reaction can be calculated (for each trajectory) by the classical equations of motion. The energy distribution over the degrees of freedom of the products is very sensitive to the mass ratios of the atoms A, B, and C, and to the shape of the potential energy surface. For example, if the evolution of energy in an exothermic reaction takes place during the ejection of the products the energy of the reaction appears as kinetic energy of the products, but if the evolution of energy takes place during the approach of the reactants a higher proportion of the energy of the reaction will appear as vibrational energy of the product molecule AB.

Calculations by the dynamic method for the potential energy surfaces of exothermic reactions with a potential barrier show that the barrier can be surmounted by the kinetic energy of the reactants if it is located in the region of the reactants. On the other hand if the barrier is displaced towards the reaction products it is surmounted by the vibrational energy of the reactant.

Non-empirical calculations of the potential energy surface are extremely laborious even for the simplest systems, and they require a large number of approximations which can seriously degrade the precision of the result[55,87]. For this reason the most successful methods so far have been semi-empirical[55,87].

The simple and effective "bond order–bond energy" method[88,89] is now widely used for reactions between neutral species because it allows the profiles of reaction paths to be calculated precisely. It is based on empirical relationships between the order and the length of a bond, and between the bond energy D and the bond order n:

$$D = D_S n^p$$

where D_S is the energy of the simple bond and p is an empirical parameter termed the bond index.

The method can be applied to IMR without fundamental changes[90,91], though the bond index for an ion has to be calculated in a different way. In the case of neutral species this index is calculated from the parameters of diatomic complexes of the inert gases, whereas in the case of ions the parameters of "inert gas atom–alkali metal positive ion" complexes have to be used. This method makes some allowance for the specific properties of the bond between an ion and a neutral particle.

The method has been applied to about 20 proton or hydrogen atom transfer reactions of the type of

$$HeH^+ + He \rightarrow He + HeH^+$$
$$H_2^+ + He \rightarrow HeH^+ + H$$
$$NH_3^+ + H_2 \rightarrow NH_4^+ + H \quad .$$

Examples of complex exchange IMR involving the transfer of atoms from the second period of the Periodic Table will be given in the last section of the present review: the path profiles for these reactions were calculated by a modified "bond order–bond energy" method.

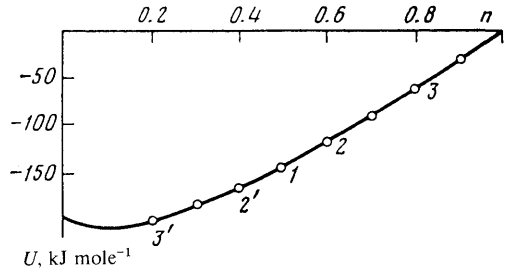


Figure 2. Profile of the reaction path $HeH^+ + Ar \rightarrow He + ArH^+$; U is the potential energy, n is the order of the He–H^+ bond. The distance R between the He and Ar atoms in the linear reactive complex He...H...Ar is 2.52 Å at point *1*, 2.54 Å at points *2* and *2'*, and 2.65 Å at points *3* and *3'*.[128]

The path profile of the reaction

$$HeH^+ + Ar \rightarrow He + ArH^+$$

is shown in Fig.2. Decreasing n from 1 to 1/2 causes a decrease in R due to the closer approach of the reactants, but if n is decreased still further the repulsion of the products causes R to increase. The energy of reaction is released mainly during the approach of the reactants. According to the Eyring–Polanyi rule in this case most of the reacton energy is localised in the vibrational degrees of freedom of the product (ArH^+). When $R \cong 2.8$ Å we find a small minimum in the potential energy, indicating the possibility of stable existence of the $[ArHHe]^+$ ion, with a dissociation energy of ~1.0 kcal mole^{-1}. There is no potential barrier in the reaction profile. These results (absence of activation energy and preferential evolution of the reaction energy in a vibrational form) are typical of all the proton transfer reactions so far examined.

In the case of the hydrogen atom transfer reaction

$$NH_3^+ + H_2 \rightarrow NH_4^+ + H \qquad (14)$$

the bond index was calculated by making the potential barrier in the path profile of the reaction equal to the experimentally measured activation energy. The barrier for this reaction was found to be displaced towards the reactants, showing that in this case the barrier is most effectively surmounted by the translational energy of the reactants.

The dependence of the cross-section of the reaction

$$NH_3^+ + D_2 \rightarrow NH_3D^+ + D \qquad (15)$$

on the translational energy of the ion and on the energy of its vibrational excitation has been studied experimentally[92], using a double mass spectrometer with coaxial primary and secondary ion beams[93]. The influence of vibrational excitation on the cross-section of the IMR (15) has been studied experimentally on a photo-ionisation mass spectrometer[22].

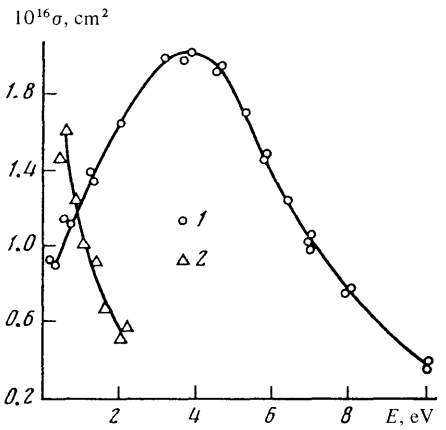


Figure 3. Cross-sections of the reactions $NH_3^+ + D_2 \rightarrow NH_3D^+ + D$ [92] (*1*) and $D_2^+ + H_2 \rightarrow D_2H^+ + H$ [94] (*2*) as a function of the relative kinetic energy of the reactants (the scale of curve *2* is a factor of 10 smaller).

The dependence of the reaction cross-section σ on the kinetic energy E_k of the NH_3^+ ions (assumed to be localised at the centre of gravity of the ion) is shown in Fig.3. When the energy is increased to ~4 eV the cross-section increases to 2×10^{-16} cm^2, but it begins to decrease if E_k is increased still further. This shows that the translational energy of the relative motion of the reacting species is effective in activating the reaction, in keeping with the theoretical calculation of the profile of the reaction path[91]. For comparison Fig.3 also shows the dependence[94] of σ upon E_k for the reaction

$$D_2^+ + H_2 \rightarrow D_2H^+ + H$$

which is typical of an exothermic reaction without activation energy.

The dependence of the cross-section of reaction (15) and of the reaction

$$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2 \qquad (16)$$

on the ionising photon energy (Fig.4) shows the effect of the vibrational excitation of the electronic ground state of the primary ions formed by electron removal from a non-bonding nitrogen orbital on the yield of secondary ions. An increase in photon energy raises the vibrational excitation energy of the NH_3^+ ions to ~1 eV. Under these conditions the cross-section of reaction (16) decreases slightly, according to Potapov[21], as expected for a fast exothermic reaction. The increase in the cross-section of reaction (15) with the vibrational excitation energy of the NH_3^+ ions shows that the vibrational energy of the ion plays an important part in surmounting the activation barrier of the IMR: in other words, it is incorrect to consider the kinematics of the reactants in reaction (15) merely in terms of a simpler linear model with a two-dimensional potential energy surface[91].

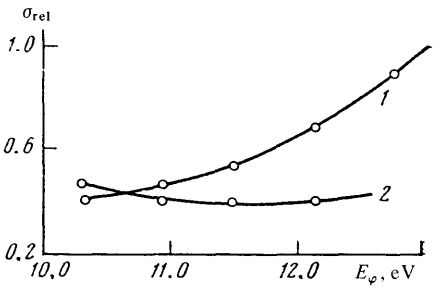


Figure 4. Dependence of the relative cross-sections of the reactions $NH_3^+ + D_2 \rightarrow NH_3D^+ + D$ (*1*) and $NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$ (*2*) on the photo-ionisation energy E_ϕ. [92]

The dependence of the IMR cross-section on the excitation energy of the ion has been studied in detail by the photoelectron–photo-ion coincidence method[25], but so far only for reaction (4). The results (Fig.5) for different kinetic energies of the relative motion of the reactants give a $\sigma(E)$ relationship consistent with the prediction from statistical theory: the cross-sections decrease as the excitation energy of the reactants increases, and the effect is most marked at the lower translational energies[62]. The application of the statistical theory is not entirely justified in this case, because molecular beam experiments have shown that even at low translational energies the life-time of the intermediate complex is less than the rotation period of the complex, i.e. the reaction takes place by a direct mechanism. The absence of a long-lived complex in reaction (4) has been confirmed by calculations[96] of the potential energy surface for H_4^+.

In addition to reaction (15), the following exothermic reactions have been shown[97] to be slow:

$$CH_3OH^+ + D_2 \rightarrow CH_3OHD^+ + D \ , \qquad (17)$$

$$C_2H_5OH^+ + D_2 \rightarrow C_2H_5OHD^+ + D \ , \qquad (18)$$

$$C_2H_5OH^+ + CD_4 \rightarrow C_2H_5OHD^+ + CD_3 \ , \qquad (19)$$

$$CH_3NH_2^+ + D_2 \rightarrow CH_3NH_2D + D \ , \qquad (20)$$

$$CH_3NH_2^+ + CD_4 \rightarrow CH_3NH_2D^+ + CD_3 \ . \qquad (21)$$

A possible explanation of the anomalous behaviour of the IMR (17)–(21) is suggested in Ref. 97. In all these reactions the recombination energy of the reactant ions is very different from the ionisation potential of the reactant molecules: the recombination energies of the NH_3^+, CH_3OH^+, $C_2H_5OH^+$, and $CH_3NH_2^+$ ions are 10.1, 10.8, 10.5, and 9 eV respectively, whereas the ionisation potential of H_2 is 15 eV. The molecular orbital diagram for the participants in these reactions is shown in Fig. 6*a*. The upper, half-filled orbital of the reacting ion A^+ lies at a large distance from both the occupied and the unoccupied orbital of D_2.

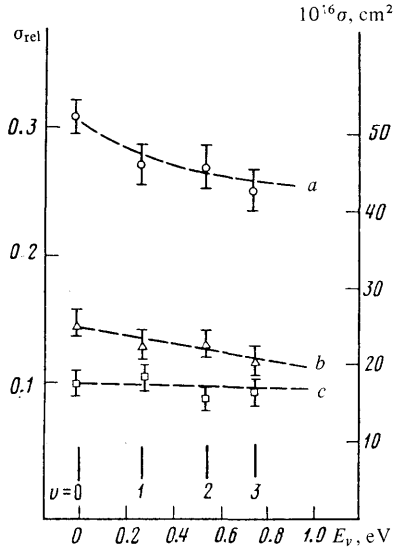


Figure 5. Cross-section of the reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$ as a function of the vibrational excitation energy of the H_2^+ ion for different energies of the relative motion of the reactants [25]: *a*) 0.11, *b*) 0.46, *c*) 0.93 eV; σ_{rel} [defined as $I_{H_3^+}/(I_{H_3^+} + I_{H_2^+})$] is the ratio of the H_3^+ and H_2^+ ion currents, E_v is the vibrational excitation energy, v is the vibrational quantum number.

According to perturbation theory[98–100] the attractive energy between particles at distances consistent with chemical re-grouping is inversely proportional to the difference in energy between the interacting orbitals. For example, in the simplest two-electron system the interaction between He^+ and H (which have very different orbital energies) leads to a net repulsion both in the $^3\Sigma$ and in the $^1\Sigma$ state[100]. In addition to the interaction of the lower unoccupied orbital of D_2 with the upper half-filled orbital of the A^+ ion, which can only cause weak attraction, we must also consider the interaction of the occupied D_2 orbital with the occupied A^+ orbital, which have similar energies. This interaction between occupied orbitals can lead to repulsion (similar to the repulsion between atoms with full electron shells). The overall effect of the interaction between these pairs of orbitals could be to create an energy barrier opposing the reaction. Reaction (16), like reaction (15), has a high rate constant[17] (10^{-9} cm^3 s^{-1}), typical of an exothermic IMR. This can be explained by the similarity of the energies for the upper molecular orbitals of the reactants NH_3^+ and NH_3, which leads to a net attraction, similar to the attraction observed in simpler systems with equal molecular orbital energies (H^+...H, H...H, He^+...He).

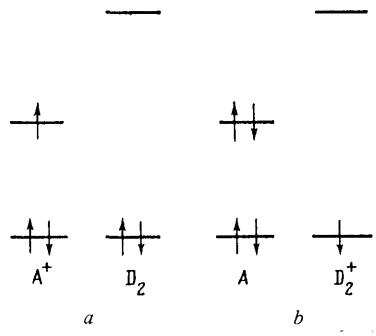


Figure 6. Molecular energy level diagram for the $A^+ + D_2$ (*a*) and $A + D_2^+$ systems (*b*).[97]

We shall now examine the reaction

$$NH_3^+ + CD_4 \rightarrow NH_3D^+ + CD_3 \cdot \qquad (22)$$

The upper energy level diagram for the reactants is qualitatively similar to the diagram of Fig. 6*a*, but the ionisation potential of CD_4 is 2.7 eV lower than the ionisation potential of H_2, and therefore the distance between the occupied upper orbitals of NH_3^+ and CD_4 is less than the corresponding distance for NH_3^+ and H_2. This is a case intermediate between reactions (15) and (16), and the attraction between the reactants NH_3^+ and CD_4 should be greater than the attraction between NH_3^+ and D_2. The methanol ion CH_3OH^+ also reacts more rapidly with CD_4 than with D_2. The rate constants of the reaction of the ethanol ion $C_2H_5OH^+$ with CD_4 and with D_2 are both small. Since the ionisation potential of alcohols decreases as the length of their hydrocarbon chain increases, the above considerations suggest that the molecular ions of all the $C_nH_{2n+1}OH^+$ alcohols with $n > 1$ should react very slowly with molecular hydrogen and deuterium.

Let us now consider the reaction

$$H_2^+ + NH_3 \rightarrow NH_4^+ + H \qquad (23)$$

analogous to (15) but with the opposite localisation of charge on the reactants. The configuration and occupancy of the energy levels of the reactants are similar to those shown in Fig. 6*b*. In this case the interaction between the half-filled orbital of H_2^+ and the inner filled orbital of A, which has a very similar energy, produces an attractive force between the particles at small distances. The rate constant of reaction (23) and that of the corresponding reaction involving D are high (10^{-9}–10^{-10} cm^3 s^{-1}),[17] as expected from the attraction between the reactants. We note that reaction (23) (like the analogous reaction with D_2^+) is strongly exothermic, and therefore the secondary ion can dissociate, with formation of NH_3^+ and NH_2^+ (or NH_2D^+ and NHD^+). Furthermore, the interaction between an ion with a high recombination energy and a complex molecule with a relatively low ionisation energy is usually accompanied by charge transfer[102], because of the ease with which resonance transitions can take

place in the closed-spaced system of energy levels of the complex molecule. Charge transfer by resonance process can take place at much greater distances than the transfer of heavy particles. This makes the rate constant of a reaction involving the transfer of a heavy particle lower than in the absence of competing charge transfer processes[103]. The competition between the charge transfer reaction

$$Ar^+ + CH_4 \rightarrow Ar + CH_3^+ + H$$

and the hydrogen atom transfer reaction

$$Ar^+ + CH_4 \rightarrow ArH^+ + CH_3 \qquad (24)$$

can account for the presence of an energy threshold[104] in the exothermic reaction (24). At low kinetic energies the charge transfer and the subsequent fast dissociation of the excited ion

$$(CH_4^+)^* \rightarrow CH_3^+ + H$$

take place while the reacting particles are relatively far apart, and the closer approach of Ar and CH_3^+ cannot lead to a re-grouping of the heavy particles because this process would be endothermic. As the kinetic energy of the reactants increases, the time during which they are in contact after the redistribution of charge becomes comparable to the dissociation time of the excited molecular ion, and the effectiveness of reaction (24) (with a re-grouping of heavy particles) increases.

A similar explanation can be suggested for the appearance of a potential barrier[105] in the reaction

$$N_2^+ + CH_4 \rightarrow N_2H^+ + CH_3 .$$

Other reactions between ions with a high recombination energy and complex molecules with a relatively low recombination coefficient can be expected to be slow, for the same reason: for example

$$Ar^+(N_2^+,\ H_2^+) + C_nH_{2n+2} \rightarrow ArH^+(N_2H^+,\ H_3^+) + C_2H_{2n+1} .$$

Exothermic reactions between an ion with a high recombination energy and simple molecules with a relatively low ionisation potential and a low density of energy levels may have low rate constants both for the charge rearrangement and for the transfer of heavy particles. A good example is the low efficiency of the reactions between ions with a high recombination energy (He^+ and Ne^+) and the simplest molecule (H_2).[106]

It has been assumed[107,108] that in collisions between particles with a low kinetic energy the electron, ion, and atom transfer processes are fully analogous and controlled by the "random resonance" condition $\tau_t \cong \tau_c$, where $\tau_t = h/|\Delta E|$ is the time of the transition between the electronic-vibrational-rotational energy levels of the reactants and the products separated by a distance ΔE (the energy defect), and $\tau_c = a/v$ is the collision time (a being the effective width of the collision region and v the relative velocity of the translational motion of the reactants). The reaction cross-sections were calculated by the semi-empirical formula

$$\sigma = \begin{cases} \sigma_m \exp\left[k'\left(1 - \dfrac{a|\Delta E|}{hv}\right)\right] & \text{for } v < \dfrac{a|\Delta E|}{h} \\ \sigma_m & \text{for } v \geqslant \dfrac{a|\Delta E|}{h} \end{cases} .$$

Here σ_m is the cross-section of the resonance process for $v = a|\Delta E|/h$, and k' is a parameter whose optimum value is 2. The optimum value of a for IMR is 100 Å. A large value of a corresponds to a spiral trajectory for the motion of the reactants at low kinetic energies. At thermal energies the rate constants were calculated by the formula

$$k = \sigma v .$$

The six lowest possible exothermic energy defects were determined, a cross-section was calculated for each of them, and the results were combined. The calculation included averaging over the rotational states and summing over the accessible electronic levels of the products.

The rate constants of approximately 20 charge transfer and exchange reactions during collisions between mono-atomic and diatomic particles have been calculated. For example, for the reaction

$$N^+(^3P_{0,2,1}) + O_2 \rightarrow NO^+(X^1\Sigma^+,\ a^3\Sigma^+) + O(^3P_2,\ ^1D_2,\ ^1S_0)$$

the calculated rate constant is $\sim 3 \times 10^{-10}$ cm^3 s^{-1}, and the experimental value is $\sim 4 \times 10^{-10}$ cm^3 s^{-1}. For the reaction

$$O^+(^4S_{3/2}) + N_2(^1\Sigma_g^+) \rightarrow NO^+(X^1\Sigma^+) + N(^4S_{3/2}) \qquad (25)$$

the calculated rate constant is $\sim 10^{-12}$ cm^3 s^{-1}, and the experimental values lie in the range $(1-3) \times 10^{-14}$ cm^3 s^{-1}. The agreement between calculation and experiment is always good, in spite of the fact that the energy defects are calculated for the isolated reactants and no allowance is made for the effect of Franck–Condon factors in the transition probabilities.

Though the calculations are simple (in principle), they require a knowledge of the energy levels, and therefore they rely on accurate spectroscopic data, which are not always available. We should also note that calculations by this method predict a positive temperature effect for slow IMR, whereas reactions such as (25) show a negative temperature effect at low kinetic energies.

V. LAW OF CORRELATION OF THE SYMMETRY OF STATES

A qualitative method of estimating the rates of chemical reactions is implicit in the law of conservation of state symmetry in reactions. Reactions are considered to be allowed if the symmetries of the wave functions and the total spin of the electronic ground state are the same for reactants and products. In reactions between an atom and a diatomic molecule or between two diatomic molecules under conditions leading to the formation of linear product molecules the symmetry type of the reactants and products is determined by the quantum number of the orbital angular momentum. In this case conservation of symmetry reduces to conservation of the resulting angular momentum of reactants and products.

Reactions which are forbidden in this sense can take place only if the reactants or the products are electronically excited.

The law of conservation of state symmetry has been used to explain[109] the anomalously low rate constant of the ion-molecule reaction (25), which is important in the chemistry of the Earth's ionosphere. It was pointed out[110] that under laboratory conditions and for a kinetic energy of the O^+ ion of a fraction of an electron-volt the rate constant of this reaction is $\sim 10^{-11}$ cm^3 s^{-1}, which is much lower than the Langevin limit. Reaction (25) was later studied in detail by different methods and over a wide range of kinetic energies of the ions (Fig. 7). Measurements in a drift tube at kinetic energies of 0.04–2 eV detected an initial decrease in the reaction cross-section, with a minimum of ~ 0.01 Å^2 at an energy of 0.3 eV, followed by an increase in cross-section with ion energy. In the high energy region the measurements were made with a double mass spectrometer. The highest cross-section (~ 5 Å^2) is reached for a kinetic energy of 8 eV, and beyond this point the cross-section falls off very steeply.

The ground states of the reactants are $^1\Sigma_g^+$ for N_2 and ^4S_u for O^+. The linear approach of N_2 and O^+ gives N_2O^+ in the $^4\Sigma^-$ excited state. Without allowance for the polarisation energy the potential energy curve for this state has no

minimum, and the energy increases monotonically as the particles move closer together. The potential curve for the reaction products $NO^+(^1\Sigma^+)$ and $N(^4S_u)$ has a similar shape. The potential surface calculated for $N_2O^+(^4\Sigma)$ has a potential barrier between the reactants and products of this exothermic IMR ~8 eV high, and the depth of the potential well due to the polarisation attraction between the reactants[111] is ~0.38 eV. Since the two branches of the energy curve for the $^4\Sigma^-$ state intersect the potential curve of the ion in the ground state $[N_2O^+(^2\Pi)]$ the reaction can follow a different path which avoids the high potential barrier. The low probability of reaction (25) at low kinetic energies can be ascribed to the low probability of non-adiabatic transitions from the $^4\Sigma^-$ curve (corresponding to the approach of the O^+ ion towards the N_2 molecule) to the curve for the ground state of $N_2O^+(^2\Pi)$, and of the backward transitions from the $N_2O^+(^2\Pi)$ curve to the $^4\Sigma^-$ curve, corresponding to the separation of the NO^+ and N products, since these transitions are forbidden for orbital angular momentum and for spin.

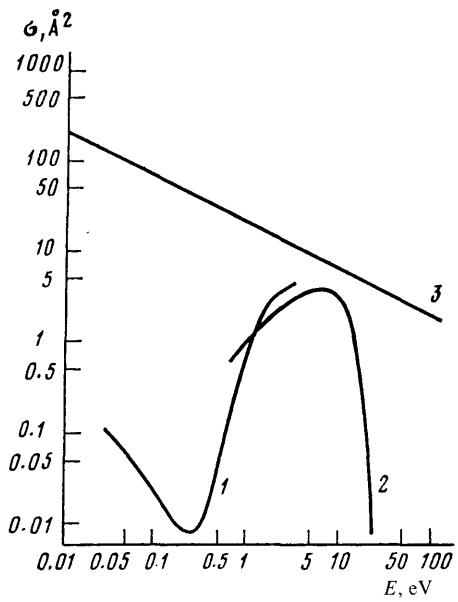


Figure 7. Cross-section of the reaction $O^+ + N_2 \rightarrow NO^+ + N$ against the kinetic energy of the O^+ ion. Cross-sections measured: *1*) by the drift tube method[18] and *2*) by using a double mass spectrometer[118]. Curve *3* denotes the cross-section of the ion–molecule collisions, calculated by formula (2).

The increase in reaction cross-section with kinetic energy of the ions arises from the increased probability of non adiabatic transitions, whereas the decrease in cross-section in the low-energy region can be explained by the decrease in life-time of the soft polarisation complex[112]. We note that the activated complex theory as used to explain the negative temperature dependence of the IMR rate in the case of the transfer of a hydride ion can also explain the change in sign of the effect of ion energy on the rate constant (because of the increased contribution from the vibrational partition functions when the complex has a high energy[113]).

The decreasing cross-section of reaction (25) at high ion energies has been explained[114] by the direct reaction mechanism (removal of a nitrogen atom followed by capture of the incident O^+ ion with formation of the molecular ion NO^+). The theory of these reactions[115] assumes that the system of particles remains on a fixed energy surface throughout the reaction, that the interaction potential V is of the pair type, and that the interaction between the ion and the bound nitrogen atom can be treated in the impulse approximation, i.e. that we can write

$$\omega a/v \ll 1$$

where ω is the vibrational frequency of the molecule. The calculated dependence of the cross-section on the ion energy correctly reflects the most striking feature of the experimental curve: a steep fall of σ with increasing energy of the colliding particles for $E > 12$ eV. The position and height of the maxima in the theoretical and the experimental curve are almost the same, and the position of the maximum in the theoretical curve corresponds to the largest phase volume defined by the capture conditions. Thus the complex energy dependence of the cross-section of reaction (25) is adequately explained by existing qualitative models.

The law of conservation of orbital momentum can also explain the difference between the rate constants of the isotope exchange reactions

$$^{15}N^+ + {}^{14}N_2 \rightarrow {}^{14}N^+ + {}^{14}N^{15}N \quad , \qquad (26)$$

$$^{18}O^+ + {}^{16}O_2 \rightarrow {}^{16}O^+ + {}^{16}O^{18}O \quad . \qquad (27)$$

The rate constant of reaction (26) is more than two orders of magnitude greater than that of reaction (27): this has been ascribed[116] to the symmetry- and spin-forbidden formation of a triatomic linear complex in the electronic ground state in the case of reaction (27) but not of reaction (26). It has been shown[117] that exothermic IMR with proton transfer of the type of

$$C^-(^4S) + XH \rightarrow X^- + CH(^2\Pi)$$

(where X is a radical of various types) are usually slow, but they become fast when the energy evolved by the reaction is sufficient to give $CH(^4\Sigma)$ as a product.

Some reactions involving relatively simple molecules are incompatible with the above law. For example, though the reaction

$$N^+(^3P) + O_2(^3\Sigma) \rightarrow NO_2^+(^1\Sigma) \rightarrow NO^+(^1\Sigma) + O(^3P) \qquad (28)$$

is forbidden for orbital angular momentum conservation, and the reaction

$$O^+(^4S) + CO_2(^1\Sigma) \rightarrow O_2^+(^2\Pi) + CO(^1\Sigma) \qquad (29)$$

is also spin-forbidden, their rate constants are close to the Langevin limit (5×10^{-10} and 11×10^{-10} $cm^3\ s^{-1}$ respectively[118]).

The removal of the restrictions on reaction (28) is due to the strong coupling between the rotational and the orbital momentum of the electron[119], and in the case of reaction (29) it is due to the strong coupling between the orbital and the spin momentum. The spin-orbital coupling in the intermediate complex of reaction (29) has been shown[119] to be due to the strong resonance interaction of the reactants, arising from the very similar values of the ionisation potential in O and CO_2.

Cases of symmetry-allowed yet slow reactions have also been reported. For example, the exothermic exchange reaction

$$CO^+(^2\Sigma^+) + O_2(^3\Sigma_g^-) = CO_2^+(^2\Pi_g) + O(^3P) \qquad (30)$$

is slow, whereas the competing (forbidden) exothermic charge transfer reaction

$$CO^+(^2\Sigma^+) + O_2(^3\Sigma_g^-) \rightarrow CO(^1\Sigma^+) + O_2^+(^2\Pi) \quad (31)$$

is fast[120].

We note that a theoretical explanation of the high rate of reactions (28) and (29) can be put forward. In the case of IMR of the type of

$$A^{\pm} + BC \rightarrow AB^{\pm} + C \quad (32)$$

(where A, B, and C can be carbon, oxygen, and nitrogen atoms) a simple method of calculating the rate constant can be based[121] on the assumption that the reaction will be fast if it does not involve a substantial redistribution of the charge density. This hypothesis leads to the rule that reaction (32) will have a large cross-section if atom A is less electronegative than atom B (in the case of IMR involving positive ions), since the positive charge in the reaction product AB^+ can then remain on the atom A.

In the case of reactions involving negative ions we can expect a large cross-section if the electronegativity of the A atom is greater than that of the B atom. If the electronegativities of A and B are similar, the reactions in which the redistribution of electron density in the product molecule C as compared with the reactant BC is least marked will be the fastest. This will be the case when the C molecule has the same dipole moment and the same geometry as the BC molecule. It has also been pointed out that the rate constants of slow IMR involving a rearrangement of the electron density increase with the internal energy of the reactants, whereas in fast IMR (with an unchanged electron density) the rate constants decrease as the internal energy increases.

Let us examine the application of the electronegativity rule to reaction (25). The oxygen is more electronegative than the nitrogen atom: we can therefore expect reaction (25) to have a low efficiency. In reaction (29) the CO_2 molecule has no net dipole moment, though the electron density is sharply divided between the oxygen atoms and the carbon: as a result, the oxygen atoms carry a negative charge and the carbon atom a positive charge. In the CO molecule the negative charge is also shifted towards the oxygen, i.e. reaction (29) can take place without a major redistribution in the electron density. According to the rule formulated above we can expect this reaction to be fast.

The rule was later extended[123] to IMR of the type of

$$AH_k^+ + BCH_l \rightarrow ABH_m^+ + CH_n$$
$$AH_k^+ + BH_l \rightarrow ABH_m^+ + p\,H_2 + q\,H$$
$$AH_k^+ + BCH_l \rightarrow ABCH_m^+ + p\,H_2 + q\,H$$

where A, B, and C are large central atoms, and k, l, m, n, p, and q are integers. To a first approximation the hydrogen atoms can be ignored, so that only the electronegativity of the large central atoms needs to be considered. A large number of IMR has been examined[121], and the validity of the rule has been demonstrated. For example, symmetrical exchange reactions with transfer of the electronegative O^+ ion are found to be slow[122,124,125]:

$$^{12}CO_2^+ + {}^{13}CO \rightarrow {}^{12}CO + {}^{13}CO_2^+ , \quad (33)$$

$$^{14}N_2O^+ + {}^{15}N_2 \rightarrow {}^{15}N_2O^+ + {}^{14}N_2 . \quad (34)$$

The slowness of these reactions can also be explained by the need for excitation of the reactants in the intermediate decomposition step of the primary ion, since the ground states of the linear CO_2^+ and N_2O^+ ions do not correlate with the ground states of the decomposition products $CO + O^+$ and $N_2 + O^+$.[124]

The fast IMR

$$C^+ + O_2 \rightarrow O^+ + CO \quad (35)$$

in which charge is transferred from the less electronegative C atom to the more electronegative O^+, is incompatible with the electronegativity rule[126]. The reaction

$$C^+ + O_2 \rightarrow CO^+ + O \quad (36)$$

in which the positive charge remains on the C atom, is slower[126] than reaction (35). In this case the contradiction can be explained by postulating a two-step elementary act: initially the intermediate complex has the structure $[O...CO^+]$, corresponding to the products of reaction (36), but in a time comparable to the dissociation time this complex undergoes an internal charge redistribution and is converted into the more stable $[O^+...CO]$ structure, corresponding to the products of reaction (35).

The following exothermic reactions were found to be slow:

$$N^+(^3P) + CO(^1\Sigma) \rightarrow NO^+(^1\Sigma) + C(^3P) \quad (37)$$

$$N^+(^3P) + CO_2(^1\Sigma_g) \rightarrow NO^+(^1\Sigma) + CO(^1\Sigma) \quad (38)$$

though the positive charge in the NO^+ ion is concentrated on the N atom[127–129]. Reaction (37) is symmetry allowed. It is interesting to note that the reactants in reactions (37) and (38) can undergo the fast non-dissociative charge transfer reactions:

$$N^+ + CO \rightarrow CO^+ + N . \quad (39)$$

$$N^+ + CO_2 \rightarrow CO_2^+ + N . \quad (40)$$

The dependence of the cross-sections of reactions (37) and (39) on the kinetic energy of the ions (E_i) is illustrated in the Table.

Cross-sections of reactions (37) and (39) as a function of the kinetic energy of the ions[128].

E, eV	0.2	0.5	1.0	2.5	5.5	10.0	20.0
σ_{37}, Å^2	2.6	1.3	0.6	0.4	1.0	0.9	0.17
σ_{39}, Å^2	28	10	4.8	2.4	2.0	2.6	3.3

When the kinetic energy is increased from 0.2 to 20 eV the cross-section of the IMR (37) initially decreases from 2.6 to 0.4 Å^2 (at 2.5 eV), then increases to ~1 Å^2 (at 5.5 eV), and finally falls off sharply, reaching 0.17 Å^2 at 20 eV. The cross-section of the charge transfer process (39) initially decreases from 28 to 2 Å^2 (at 5.5 eV), and then increases to 3.3 Å^2 at 20 eV. Thus the allowed reaction (37) has a low cross-section, whose dependence on the kinetic energy of the ion is similar to that of the forbidden reaction (25). The cross-section of reaction (38) at a kinetic energy of 2 eV is only 6% of the cross-section of the charge transfer reaction (40).[129]

The statistical theory, which allows for the formation of only one type of intermediate complex, predicts the opposite ratio of cross-sections for heavy particle transfer and charge transfer reactions, since in the examples considered the enthalpy of the heavy particle transfer reactions is greater than the enthalpy of charge transfer. The observed relative

cross-sections can be explained only if the initially formed soft complex has a short life-time (as a result of a fast exothermic charge rearrangement, which can take place at relatively long distances in a soft complex). This effect inhibits the formation of the hard complex, which must precede the regrouping of the chemical bonds. Thus the non-dissociative charge transfer processes (like the dissociative processes discussed above) can lower the cross-section of IMR involving the regrouping of heavy particles.

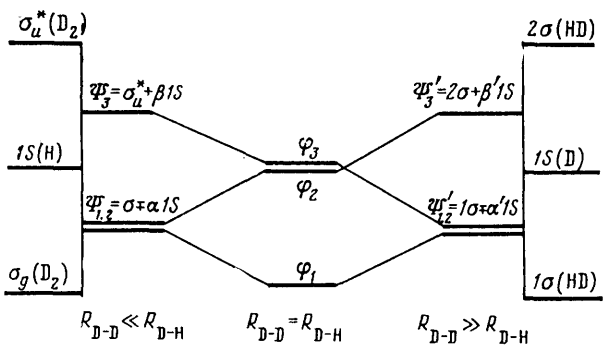


Figure 8. Correlation diagram of the molecular orbitals of the D...D...H system[130].

VI. LAW OF CONSERVATION OF ORBITAL SYMMETRY

The rate constants of IMR can be discussed qualitatively by drawing the correlation diagrams for the molecular orbitals, based on the law of conservation of the symmetry of molecular orbitals during a reaction. For the linear HD_2 system the correlation diagram of the molecular orbitals[130] is shown in Fig.8. The diagram explains the difference in probability of the reactions

$$H^+ + D_2 \rightarrow HD + D^+ \qquad (41)$$

$$H + D_2 \rightarrow HD + D \qquad (42)$$

$$H^- + D_2 \rightarrow HD^- + D \qquad (43)$$

in which the occupancy of the $1S(H)$ orbital is 0, 1, and 2 respectively. It is clear from the diagrams that the $\sigma_g(D_2)$ orbital correlates with the lowest orbital (ϕ_1) of the complex. In the course of the reaction two electrons are transferred from the $\sigma_g(D_2)$ orbital through the ϕ_1 orbital of the intermediate complex to the $1\sigma(HD)$ orbital of the product. For reaction (41), in which only two electrons take part, the close approach of the reactants lowers the potential energy, and should lead to a fast reaction. The electrons located on the $1S(H)$ orbital are transferred to the ϕ_2 orbital of the intermediate complex, which has a node, and therefore the potential energy increases as the reactants move closer together. The greater the number of electrons in the orbital, the stronger the repulsion. Therefore reaction (41) should be fast, and reaction (43) should be the slowest, though attractive polarisation forces between the ion and the molecule are present in both cases. This conclusion has been confirmed experimentally[131,132]. The recently discovered[132] activation energy for the exothermic proton transfer IMR

$$NH_2^- + H_2 \rightarrow H^- + NH_3$$

$$CH_2{=}CH{-}CH_2^- + C_6H_5CH_3 \rightarrow C_6H_5CH_2^- + CH_2{=}CH{-}CH_3$$

probably has a similar origin. Here, as in reaction (43), a negative ion interacts with a molecule which has no partially filled orbitals.

The correlation diagram shown in Fig.8 also explains the low efficiency of IMR of the type of

$$D_2^+ + H \rightarrow DH^+ + D$$

since in this case only one electron is found on the bonding orbital (ϕ_1) of the complex, whereas the second electron is transferred to the antibonding ϕ_2 orbital. Under these conditions the resulting interaction is repulsive, because the increase in energy of the antibonding orbitals caused by bringing the particles closer together is usually much greater than the corresponding decrease in energy of the bonding orbitals. Vibrational excitation of the D_2^+ ion raises the $\sigma_g(D_2)$ level, bringing it closer to the $1S(H)$ level, and thus facilitates electron transfer from the $1S(H)$ to the $\sigma_g(D_2)$ level. This opens a path for charge transfer and new paths for non-adiabatic exchange reactions involving the ground state and the first electronically excited state of the D_2H^+ complex. The calculation of the dependence of the cross-section of non-adiabatic IMR on the kinetic and internal energies of the ions requires a detailed knowledge of the potential energy surfaces of the ground and the excited state of the D_2H^+ system, and of the probabilities of transitions between these states[54,133].

The correlation diagram[106] for the reactions

$$He^+ + H_2 \rightarrow HeH^+ + H \qquad (44)$$

$$H_2^+ + He \rightarrow HeH^+ + H \qquad (45)$$

is similar to the diagram shown in Fig.8, differing from it only in the absence of resonance between the energy levels of reactants and products. In reaction (44) one electron is found on the $1S(He)$ orbital and two on the $\sigma_g(H_2)$ orbital. During the reaction the electron in the $1S(He)$ orbital is adiabatically transferred to the $1\sigma(HeH)$ orbital. The two electrons from the $\sigma_g(H_2)$ orbital are transferred to the antibonding orbital of the complex, from which they pass into the antibonding $2\sigma^*(HeH)$ orbital, giving the highly excited HeH* particle and a proton. Alternatively, the two electrons can be transferred to the $1S(H)$ level in the region of contracting orbital energies, giving HeH^{2+} and H^-. These two reaction channels are allowed for orbital symmetry, but they are strongly endothermic and therefore inaccessible at low kinetic energies. The exothermic channel giving $HeH^+ + H$ from the reactants He^+ and H_2 is forbidden, because it requires the transfer of an electron between potential surfaces of very different energy which nowhere approach each other sufficiently closely. A similar set of arguments shows that all reactions of the type of

$$He^+(Ne^+) + XH \rightarrow HeH^+(NeH^+) + X$$

must be slow (X is a radical with an ionisation potential a few eV lower than the ionisation potential of Ne).

In reaction (45) the $1S(He)$ orbital is occupied by two electrons, and the $\sigma_g(H_2)$ orbital by one electron. In this case the molecular orbitals of the ground states of reactants and products are correlated, and reaction (45) can be expected to be fast (as is found experimentally[106]). A reaction is facile when the orbitals of the reactants in their ground state

are correlated to those of the products in their ground state. If on the other hand the ground state orbitals are correlated to those of an excited state we can expect the reaction to be very ineffective (at low kinetic energies and low internal excitation energies) towards endothermic processes with formation of excited products.

The correlation diagrams for a large number of IMR involving complex atoms are given in Ref.106. Forbidden reactions include double decompositions by a planar four-centre cyclic transition state[134], such as

$$H_2 + D_2 \rightarrow 2HD \ . \qquad (46)$$

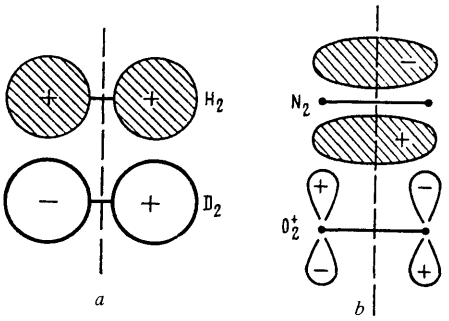


Figure 9. Molecular orbitals involved in the reactions $H_2 + D_2 \rightarrow 2HD$ (*a*) and $O_2^+ + N_2 \rightarrow NO^+ + NO$ (*b*).

In the case of the reaction

$$AB + CD \rightarrow AD + BC \qquad (47)$$

and assuming that the orbital energies are equal to the corresponding bond energies of the molecules, the correlation diagrams give the following expression for the activation energy[135]:

$$E_a = \frac{D(CD)\,[D(CD) + D(AB) + D(AD) - D(BC)]}{D(CD) + D(AD)} \qquad (48)$$

where D(AB) and D(CD) are the dissociation energies of the stronger and the weaker bond in the reactants, and D(AD) and D(BC) are the dissociation energies of the weaker and the stronger bond in the products. For example, for reaction (46) the activation energy calculated by this formula is 420 kJ mole^{-1}. In the case of molecules consisting of atoms with many electrons the orbital correlation diagrams become extremely complex, and in order to classify a reaction as forbidden or allowed we must use Pearson's method[136,137], in which only the highest occupied and the lowest unoccupied orbitals of the reactants are considered. Whereas in the Woodward and Hoffman method[134] the correlation between the molecular orbitals of reactants and products in their ground states is used as a criterion of whether the reaction is allowed or forbidden, in the Pearson approach the criterion is the positive overlapping of the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor. For the chemical reaction to have a low activation energy we require the HOMO of the donor to have the same symmetry as the LUMO of the acceptor, and the transfer of an electron from the donor to the acceptor must weaken the bonds being broken and strengthen those being created. In reactions involving positive ions the donor is always the reactant molecule, and in reactions with negative ions the molecule is always the acceptor.

The shape of the molecular orbitals taking part in reaction (46) is shown in Fig.9*a*. The occupied bonding orbital of H_2 is cross-hatched, and the unoccupied D_2 antibonding orbital is left blank. These orbitals have different symmetries, and the approach of the reactants leads to repulsion (and hence to a high activation energy for the reaction).

In the isotope exchange reactions

$$^{15}N_2^+ + {}^{14}N_2 \rightarrow {}^{15}N^{14}N^+ + {}^{15}N^{14}N$$
$$^{18}O_2^- + {}^{16}O_2 \rightarrow {}^{18}O^{16}O^- + {}^{18}O^{16}O$$

electrons are transferred from an N_2 bonding orbital to an N_2^+ bonding orbital, and from an O_2^- antibonding orbital to an O_2 antibonding orbital. The overlap of the orbitals is positive in both cases (the overlapping orbitals have the same sign), but the electron transfer weakens one of the existing bonds and strengthens the other. Therefore these reactions also are forbidden.

Another example of the application of Pearson's rule to IMR is the double decomposition reaction

$$N_2^+ + O_2 \rightarrow NO^+ + NO \qquad (49)$$

which has a very small cross-section[138]. In this case the acceptor is the N_2^+ ion, whose lowest unoccupied orbital is the $\sigma_g(2p_x)$ bonding orbital. The highest occupied orbital of O_2 is the antibonding Π_g^x orbital. Again, the orbitals of the reactants have different symmetries with respect to the plane normal to the axis of the molecule, and this accounts for the slowness of the reaction.

A reaction analogous to (49) but with the opposite charge distribution on the reactants

$$O_2^+ + N_2 \rightarrow NO^+ + NO \qquad (50)$$

is also forbidden, since in this case the electron has to be transferred from a bonding N_2 orbital to an antibonding O_2^+ orbital (Fig.9*b*).

An experimental study[139] of ion-molecule reactions caused by collisions between O_2^+ and N_2 has shown that if the kinetic energy of the O_2^+ ions is less than 15 eV the rate constant of the formation of NO^+ is less than 3×10^{-13} cm^3 s^{-1}. Under these conditions NO^+ can be formed by the reaction

$$O_2^+ + N_2 \rightarrow NO^+ + N + O \qquad (51)$$

as well as by reaction (50). It has also been reported[138] that the weakly endothermic reactions [analogous to (51)]

$$NF^+ + O_2 \rightarrow NO^+ + F + O \qquad (52)$$

$$N_2^+ + O_2 \rightarrow NO^+ + N + O \qquad (53)$$

have very small cross-sections (less than 10^{-17} cm^2 for ions with kinetic energies between 2 and 50 eV), whereas the cross-sections of the strongly endothermic dissociations

$$NF^+ + O_2 \rightarrow N^+ + F + O_2$$
$$N_2^+ + O_2 \rightarrow N^+ + N + O_2$$

are much higher.

The most likely reason for the lack of dependence of the rate of exchange reactions on the kinetic energy of the reactants is a displacement of the potential barrier towards the products for reactions (51)–(53) or towards the high-curvature region of the path for reactions (49) and (50). The profiles of the reaction paths for some symmetry-forbidden double decomposition reactions of the type of (50) and of exchange reactions with dissociation of the type of (51) have recently been calculated by a modified "bond order–bond energy" method[140,141].

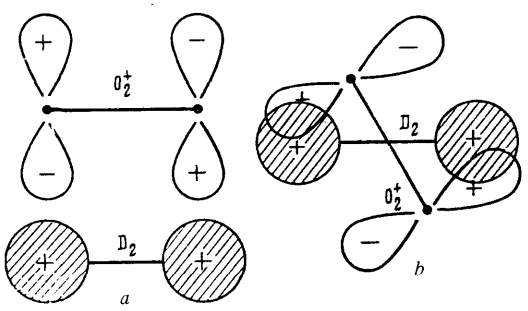


Figure 10. Molecular orbitals participating in the reaction $O_2^+ + D_2 \rightarrow OD^+ + OD$: *a*) is the planar complex, *b*) is a complex formed by the approach of the reactants in a non-parallel mutual configuration.

The approach of the reactants with formation of a non-planar complex can convert a reaction which is forbidden for a planar complex into an allowed reaction. For the reaction

$$O_2^+ + D_2 \rightarrow OD^+ + OD \quad (54)$$

the planar complex is shown in Fig.10*a* and the complex formed when the reactants approach each other along an axis perpendicular to the plane of the paper (with the molecular axes in a non-parallel configuration) is shown in Fig.10*b*. In the latter case reaction (58) is allowed, because the overlap of the orbitals is positive and the bond in the reactants is weakened by the electron transfer. The analogous reaction

$$D_2^+ + O_2 \rightarrow OD^+ + OD$$

is forbidden, because the bond in the reactants is strengthened by the electron transfer. These conclusions are consistent with experimental results[138]: the cross-section for the formation of OD^+ is higher for collisions between O_2^+ and D_2 than for collisions between D_2^+ and O_2.

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The examples discussed in this review show the importance of wide-ranging and detailed studies of the elementary reaction act in IMR in establishing the origin of the chemical reactivity and the mechanism of the elementary reaction acts in the chemical regrouping of particles, and in characterising the elementary acts of the energy redistribution processes.

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