



## MOLECULAR STRUCTURE AND CHEMICAL REACTIVITY. THE ROLE OF THE ACTIVATION ENERGY\*

*A semi-empirical intersecting-state-model allows the calculation of the energy barrier of elementary reactions in terms of the reaction energy, the force constants and the sum of the bond length of the reactive bonds, the bond order at the transition state and the so called «mixing entropy». Some of these parameters provide new mechanistic insights on gas phase reactions of hydrides and nonhydrides, and on electron transfer and nucleophilic substitution reactions in liquid solutions. The model is compared with current approaches which relate activation energies with molecular structure, namely linear free energy relationships, Marcus and BEBO theories, and Woodward-Hoffmann rules.*

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Ferreira da Silva, one of the most eminent portuguese analytical chemists of all times, and the founder of the Sociedade Portuguesa de Química was born in 1853. Chemical kinetics had just started, with the measurement of the rate of inversion of sucrose by Wilhemy [1] in 1850. Ferreira da Silva was thus able to follow the first developments of this discipline which stands, together with thermodynamics, as the most significant quantitative criterium for chemical reactivity. In 1889 Arrhenius [2] explained the effect of temperature on reaction rates, which was probably the most important advance in the understanding of chemical kinetics during the lifetime of Ferreira da Silva. According to Arrhenius, in a reacting system an equilibrium exists between ordinary and «active» molecules, and only the latter ones are rich enough energetically to undergo chemical reaction. The apparent activation energy is the difference between the average energy of the active molecules and the average energy of all the molecules. It is precisely the relationship between molecular structure and activation energy which is the topic of this lecture. It is thus my pleasure to bring here two eminent chemists whose lifes ran in parallel: Ferreira da Silva 1853-1923 and Arrhenius 1859-1927.

### STRUCTURE — REACTIVITY RELATIONSHIPS: AN HISTORICAL VIEW

The theoretical calculation of the absolute rates of chemical reactions is one of the most important, and at the same time one of the most difficult problems in chemistry today. The problem is particularly crucial with respect to prediction of the activation energy. It was first pointed out by Marcelin [3] in 1915, that the activation energy is conveniently treated from the point of view of the passage of a system over a potential energy surface. London [4] was the first to suggest, in 1928, that the properties of the activated complexes can be calculated by quantum mechanics, using the same methods that are used for

calculating the energies of stable molecules. Although a considerable progress has been made on the methods for the calculations of potential energy surfaces [5], the problem can only consider to be solved for the most simple chemical reactions. Furthermore the potential energy surfaces provide mainly a synthetic view of the role of the different molecular factors on the activation energy, in spite of some general qualitative insights, which have been provided for the topography of these surfaces [6]. Thus, it is no surprise that simpler methods, based on chemical analogies, have enjoyed a wide success in predicting reaction rates for the less simple chemical reactions.

Taylor in 1914 [7] was the first person to seek for a correlation between rate constants,  $k$ , and thermodynamic parameters (equilibrium constants  $K$ ), a suggestion which was developed in 1924 by Brönsted [8] for acid-base catalysis:  $k = GK^\alpha$  ( $G$  and  $\alpha$  are constants). The influence of substituents on the rates of organic reactions has been interpreted in terms of electrical effects by Robinson and Ingold and many other [9]. However probably the most successful approach was the one of Hammett [10], in 1940, based also on linear free-energy relationships.

The relation between the structure of the activated complexes and those of reactants and products was considered explicitly by Leffler in 1953 [11], by postulating that the slope of a rate-equilibrium relationship ( $(\partial \log k / \partial \log K) = \gamma$ ) (measures the position of the transition state along the reaction coordinate).

About the same time Hammond also considered this problem [12] by postulating that the position of the transition state is displaced toward the reactants as the reaction becomes more exergonic.

Explicit relationships between molecular parameters and activation energies,  $E_a$ , have also been studied. In 1938 Evans and Polanyi [13] found an empirical linear relationship between  $E_a$  and the enthalpies of several elementary reactions in the vapour

phase. In 1956 Marcus [14], based on an intersecting harmonic potential energy curve model, related the activation free energy,  $\Delta G^\ddagger$ , with the free energy of the reaction,  $\Delta G^\circ$

$$\Delta G^\ddagger = \Delta G^\ddagger(o) \left( 1 + \frac{\Delta G^\circ}{4\Delta G^\ddagger(o)} \right)^2$$

where  $\Delta G^\ddagger(o)$  is the activation free energy for the thermoneutral reaction. This theory, which was initially developed for outer sphere electron transfers, has been extended to other kinds of reactions [15]. Other energy barriers rather than the parabolic ones have been considered by Johnston and coworkers [16] and by Agmon and Levine [17], all of which include Leffler's interpretation of the transition state configuration [18]. The most famous method is that developed during the early sixties by Johnston: the BEBO method (bond-energy-bond-order) which was designed for hydrogen-atom transfer reactions. This method is based on the empirical rule of Pauling between bond length,  $R$ , and bond order,  $n$ ,

$$R - R_e = 0.26 \ln n$$

and on a relationship between energy and bond order

$$E = D_e n^p$$

where  $R_e$  is the bond length for a bond order of unity,  $p$  is the energy coefficient and  $D_e$  the dissociation energy. Furthermore the model assumes that the bond being formed is continuously replaced by the old one such as  $n_1 + n_2 = 1$ , for single chemical bonds. The influence of substituents on the rates of organic reactions has been interpreted in terms of electronic theories since very early times [9] and these ideas have been extended to the influence of substituents on the energy of activation (19,20). However such effects are mainly viewed as a perturbation on the reference reaction. In fact, most of

the models which we have considered so far only provide relationships between thermodynamic and kinetic parameters. The BEBO model is virtually the only case where the role of electronic factors is explicitly assumed via the bond order  $n$ . Woodward and Hoffmann [21], in 1965, have provided an important insight on the relationship between electronic structure and activation energy by proposing that during a concerted reaction molecular orbital symmetry is conserved. The application of this principle has revealed the existence of chemical processes where the bond order at the transition state is zero, the so called forbidden reactions, and which have very high activation energies. Since then the potentialities of molecular orbital methods to the study of the dynamic properties of the chemical systems has been extensively explored [22].

## A GENERAL INTERSECTING STATE MODEL FOR THE ACTIVATION ENERGY

### QUALITATIVE PREDICTIONS

It is well established that reactions of the type  $A + BC \rightarrow AB + C$  can be interpreted in terms of independent bond-forming and bond-breaking process [16]. The course of such reactions can be represented by plotting the energy for bond-breaking of BC or bond-forming of AB against a common reaction coordinate. The point where the states of BC and AB cross corresponds to the transition state. As Figure 1 shows the energy of the transition state relative to reactants (BC) is dependent on three parameters:

- I — the energy of the reaction,  $\Delta E$  ( $\Delta H$ ) or equivalent parameters such as  $\Delta G$ , if potential free energy curves are considered.
- II — The characteristics of the potential energy curves for the reactive bonds, BC and AB. For harmonic oscillators such curves are characterized

by their force constants,  $f$ , but for more realistic curves, e.g. Morse oscillators, the potential energy curves can be characterized in terms of force constants and dissociation energies,  $D_e$ .

- III — the distance,  $d$ , between the minima of the two potential energy curves in the nuclear configuration diagram of Figure 1.

Since  $\Delta E$ ,  $f$  and  $D_e$  can be obtained, in principle, from thermodynamic and spectroscopic data, the development of a general model for the calculation of  $E_a$  requires the establishment of relationships between  $d$  and molecular structure.

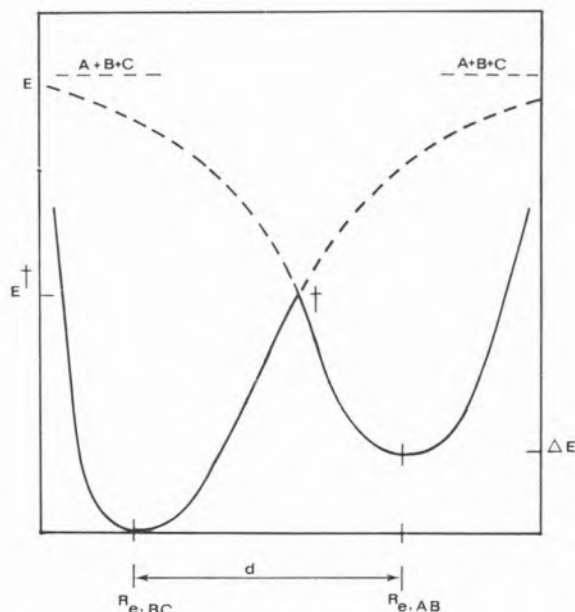


Fig. 1

*Intersecting Morse energy curve representation for the reaction  $A + BC \rightarrow AB + C$ .*

As Figure 1 reveals the horizontal displacement of the two oscillators,  $d$ , corresponds to the sum of the bond distortions of reactants and products at the transition state. Relationships between  $d$  and molecular structure have to be sought on such bond distortions.

If the equilibrium bond length  $R_{e,BC}$  of the reactant BC is small its distension at the transition state is also expected to be small. However if  $R_{e,BC}$  is large such a distension can also be large. The same is also valid for the product bond length  $R_{e,AB}$  and because  $d$  is the sum of the two bond distensions, we can predict that  $d$  is proportional to  $R_{e,AB} + R_{e,BC}$ .

At the transition state the energy of the reaction,  $\Delta E$ , has to be accommodated as internal energy of the activated complexes. This implies that a further distension of the bonds AB and BC will occur, and, consequently,  $d$  should also depend on  $\Delta E$ .

In addition to the dependence of  $d$  on geometric ( $R_{e,AB} + R_{e,BC}$ ) and thermodynamic ( $\Delta E$ ) parameters,  $d$  should be dependent on electronic parameters. According to the BEBO model during the whole course of the reaction the overall bond order is unity,  $n_{AB} + n_{BC} = 1$ . This is certainly true if in the reactants and products there are only occupied bonding molecular orbitals. However if in the reactants and/or products there are occupied nonbonding or antibonding orbitals which acquire a bonding character at the transition state, the overall bond order of the activated complexes can be higher than 1,  $n_{AB} + n_{BC} = m$  ( $m > 1$ ). This siphoning of electron density into the activated complexes would decrease its bond distensions. Consequently,  $d$  should depend also on the bond order,  $n^\ddagger$ , at the transition state.

### QUANTITATIVE MODEL

A quantitative model which introduces the concept of *variable bond order* along the reaction coordinate was developed recently in collaboration with Professor Varandas [23]. The model is based on the Pauling relationship [24] between bond length and bond order

$$R - R_e = a \ln n$$

where  $a$  is a constant, and on the concept of «entropy of mixing»,  $M$ , introduced by Agmon and Levine [17],

$$M = -n_{AB} \ln n_{AB} - n_{BC} \ln n_{BC}$$

The model defines the energy along the reaction coordinate as

$$E = n \Delta E - \lambda M$$

where  $n = n_{AB}$  is the variable for the reaction progress and  $\lambda$  a parameter which has the dimensions of energy. At the transition state  $E$  has a maximum, and we have shown [23] that

$$d = \frac{2a \ln 2}{m} + \frac{a}{2\lambda^2} \Delta E^2$$

However  $d$  should also depend on  $R_{e,AB} + R_{e,BC}$ . To have a normalized bond distension we have considered this in the Pauling relationship

$$a = a' (R_{e,AB} + R_{e,BC})$$

where  $a'$  is considered to be an universal parameter. The normalized bond distension is defined as

$$\eta = \frac{d}{R_{e,AB} + R_{e,BC}} \quad (1)$$

and consequently

$$\eta = \frac{a' \ln 2}{n^\ddagger} + \frac{a'}{2\lambda^2} \Delta E^2 \quad (2)$$

where  $n^\ddagger$  is the order of each bond at the transition state,  $n^\ddagger = m/2$ . Equation [2] is the expression which allows the establishment of a quantitative relationship between activation energy and molecular structure.

### CROSSING OF THE POTENTIAL ENERGY CURVES

In the crossing of the potential energy curves at the transition state we have so far

neglected any interaction between the electronic states which leads to a resonance splitting,  $\varepsilon$ , of the curves. As Figure 2 shows

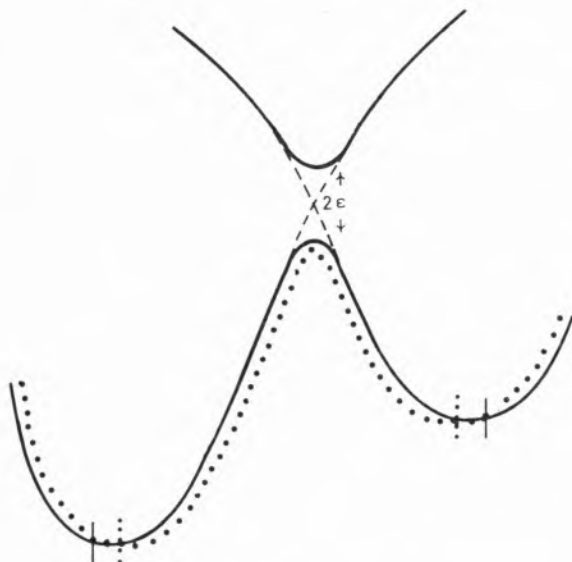


Fig. 2

Effect of the interaction energy on the parameter  $d$ .

the model can take care of such effect through a decrease in  $d$ , a decrease which is large if the resonance splitting is also large. However, in general,  $\varepsilon \ll E_a$  and the resonance splitting does not affect  $d$  in any significant manner. Its main effect is on the transmission coefficient of the rate constant, a factor which takes into account the fact that not every activated complex is converted into products [25].

## EXPERIMENTAL TESTS OF THE THEORY

The model has been tested with several reactions in the vapour phase [23] and in liquid solutions [26,27]. Here we will review briefly some of the most significant aspects of such studies, with the purpose of illustrating the role played by the different molecular parameters.

## GAS PHASE REACTIONS

### Hydrides

If the potential energy curves BC and AB are represented by Morse oscillators, the sum of bond extensions at the transition state is given by [23]

$$d = -\frac{1}{\beta_{AB}} \ln \left\{ 1 - \left( \frac{E^\ddagger - \Delta E}{D_{e,AB}} \right)^{1/2} \right\} - \frac{1}{\beta_{BC}} \ln \left\{ 1 - \left( \frac{E^\ddagger}{D_{e,BC}} \right)^{1/2} \right\} \quad (3)$$

where  $\beta$  are the Morse parameters and  $D_e$  the dissociation energies.  $E^\ddagger$  is the energy of the crossing point of the potential energy curves, considered to be equal to the activation energy. Equation [3] allows the evaluation of  $d$  for several elementary reactions of known activation energies [28]; spectroscopic data were taken from ref. [29]. The reduced bond distension  $\eta$  is calculated through eq. [1].

Figure 3 illustrates the test of eq. [2] for a selection of the reactions already studied [23]. A series of linear correlations of  $\eta$  and  $\Delta E^2$  is found. The slopes appear to be essentially of two types  $3.7 \times 10^{-6} \text{ kJ}^{-2} \text{ mol}^2$  and  $1.3 \times 10^{-5} \text{ kJ}^{-2} \text{ mol}^2$ . The intercepts obey the simple progression 1:1/2:1/3 (0.218; 0.108; 0.072). According to eq. [2] the slopes of the plots of Figure 3,  $a'/2\lambda^2$ , are related to the configurational entropy  $\lambda$ . For elementary gas phase reactions there appear to be essentially two types of slopes corresponding to  $|\lambda| = 77 \text{ kJ mol}^{-1}$  and  $|\lambda| = 145 \text{ kJ mol}^{-1}$ . The lowest entropy  $|\lambda|$  is found in cases where a light atom lies between two dynamically heavy atoms, and the highest entropy when there is no light atom in the middle. When we compare the two kinds of activated complexes  $\text{HHL}^\ddagger$  and  $\text{HLH}^\ddagger$  (H heavy and L light atoms) the first is the one with the highest stretching frequencies. If the entropy

associated with vibration is significant compared with that of rotation we can predict that  $S(HHL^\ddagger) > S(HLH^\ddagger)$ .

The more disordered the activated complexes are, the more states exist to accommodate the energy of the reaction without large bond distortions. Consequently the higher is  $\lambda$  the less is the effect of  $\Delta E^\ddagger$  on  $d$ .

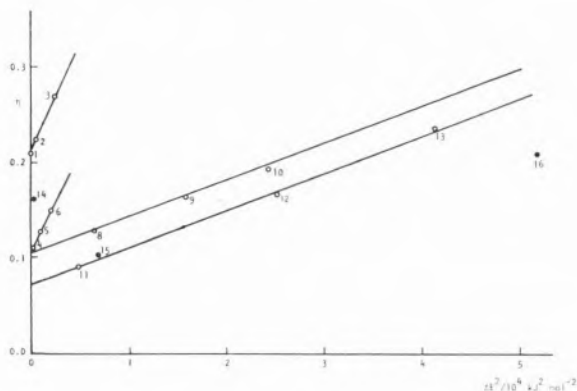


Fig. 3

Plot of the reduced bond distortion  $\eta$  as a function of  $\Delta E^\ddagger$ , for elementary gas phase reactions.

○ reactions with hydrides; 1  $H + H_2 \rightarrow H_2 + H$ ; 2  $CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$ ; 3  $H + C_2H_6 \rightarrow H_2 + C_2H_5$ ; 4  $Cl + CH_4 \rightarrow HCl + CH_3$ ; 5  $Cl + CH_2Cl_2 \rightarrow HCl + CHCl_2$ ; 6  $CH + CHCl_3 \rightarrow HCl + CCl_3$ ; 7  $Br + CH_4 \rightarrow HBr + CH_3$ ; 8  $Br + H_2 \rightarrow HBr + H$ ; 9  $I + CH_4 \rightarrow HI + CH_3$ ; 10  $F + CH_3 \rightarrow HF + CH_3$ ; 11  $I + C_2H_5I \rightarrow I_2 + C_2H_5$ ; 12  $H + I_2 \rightarrow HI + I$ ; 13  $H + Cl_2 \rightarrow HCl + Cl$  (data selected from ref. 23); ● reactions with nonhydrides; 14  $2NOCl \rightarrow 2NO + Cl_2$ ; 15  $NO + Cl_2 \rightarrow NOCl + Cl$ ; 16  $CO + NO_2 \rightarrow CO_2 + NO$ .

Equation [2] predicts the existence of distinct intercepts, depending on the bond order at the transition state,  $n^\ddagger$ . The intercepts,  $\eta^0$ , should have a reciprocal dependence on  $n^\ddagger$  and this is observed with the following bond orders:  $n^\ddagger = 1/2$ ,  $\eta^0 = 0.218$ ;  $n^\ddagger = 1$ ;  $\eta^0 = 0.108$ ;  $n^\ddagger = 3/2$ ,  $\eta^0 = 0.072$ . The constant  $a'$  is found to be  $a' = 0.156$ , and

$$\eta^0 n^\ddagger = 0.108 \quad (4)$$

The bond order  $n^\ddagger = 1/2$  corresponds to the situation considered in the BEBO model,

$n_{AB} + n_{BC} = 1$ . For a thermoneutral reaction, at the transition state,  $n_{AB} = n_{BC} = n^\ddagger$ ; and consequently  $n^\ddagger = 1/2$ . An example of such type of transition states is provided by reaction  $H + H_2 \rightarrow$  where there are no non-bonding or antibonding electrons in the reactants or the products. Figure 4 illustrates in qualitative terms an energy diagram for the three-center molecular orbitals of the linear activated complex  $H_3^\ddagger$ . The electron distribution leads to a total bond order of unity,  $m = 1$ , and for each of the Hbonds,  $n^\ddagger = 1/2$ .

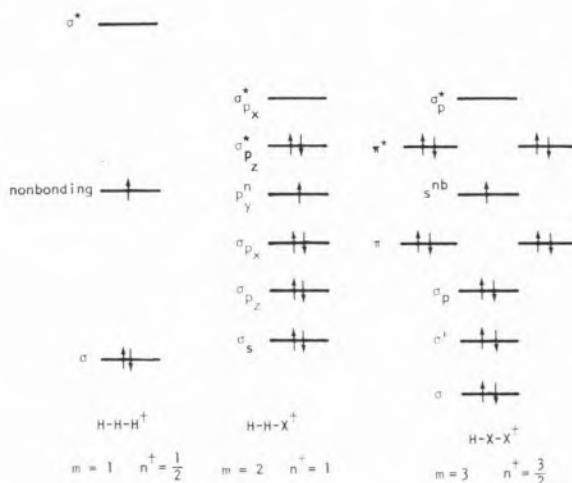


Fig. 4

Molecular orbital energy diagram for triatomic activated complexes (X is a halogen atom).

A representative reaction of the transition states  $n^\ddagger = 1$  is  $Br + H_2 \rightarrow HBr + H$ . Here there are nonbonding electrons in the bromine atom. If a pair of such electrons acquire a bonding character at the transition state, the overall bond order increases by 1, and, therefore,  $m = 2$ . Figure 4 illustrates the molecular energy diagram [30] for the angular activated complexes  $H_2Br^\ddagger$ , which has  $m = 2$  and average bond orders  $n^\ddagger = 1$ ; for a linear activated complex the maximum bond order would be  $m = 3/2$  and  $n^\ddagger = 3/4$ . This activated complex has features of an electronically excited molecule,

Table 1  
Reduced Oscillators displacement for Elementary Vapour Phase Reactions of Nonhydrides

Reaction	$E_a/\text{kJ mol}^{-1} a)$	$\Delta H/\text{kJ mol}^{-1}$	$f/10^3 \text{ kJ mol}^{-1} \text{ A}^{e-2}$	$(R_{e,AB} + R_{e,BC})/\text{A}^e$	$d/\text{A}^e$	$\eta$	$\eta_o$	$n^\dagger$
$\text{NO} + \text{Cl}_2 \rightarrow \text{NOCl} + \text{Cl}$	96.	83.5	1.95 (Cl—Cl)	2.3 (N—Cl)	0.415	0.105	$\approx 0.072$	$3 \frac{1}{2}$
$2\text{NOCl} \rightarrow 2\text{NO} + \text{Cl}_2$	98.6	- 14.8	2.3 (Cl—N)	1.95 (Cl—Cl)	0.634	0.160	0.160	$2 \frac{1}{3}$
$\text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}$	132	- 226	9.15 (C=O)	6.8 (N—O)	0.495	0.211	$\approx 0.062$	1.75

a) Data collected in K. J. Laidler, «Chemical Kinetics», McGraw-Hill, London, 2nd ed., 1965, p. 125.

because the electrons are not occupying all the lowest energy molecular orbitals.

The transition state  $n^\dagger=3/2$  is illustrated by the reaction  $\text{H} + \text{I}_2 \rightarrow \text{HI} + \text{I}$  where a pair of the antibonding electrons of  $\text{I}_2$  acquire a bonding character at the transition state. Figure 4 illustrates the corresponding molecular energy diagram which leads to an overall bond order  $m = 3$ .

### Nonhydrides

A few elementary reactions between nonhydride species can also be studied (see Table 1).

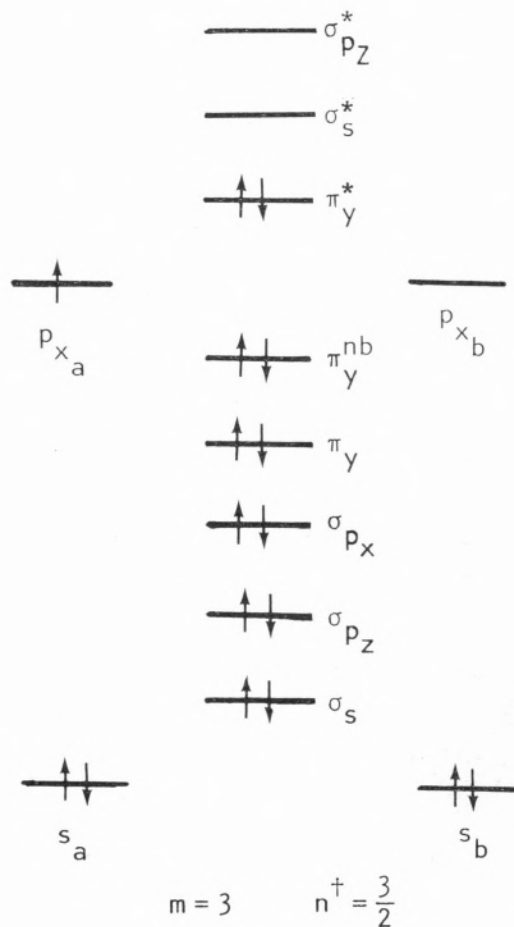


Fig. 5

Molecular orbital energy diagram for an angular  $\text{XY}_2^\dagger$  activated complex

Here, for reasons of simplicity we have considered the reactive bonds as harmonic oscillators. The present data conform with the previous findings, but illustrate other type of transition states.

The reaction  $\text{NO} + \text{Cl}_2 \rightarrow \text{NOCl} + \text{Cl}$  has an intercept close to 0.072, which corresponds to  $n^\ddagger = 3/2$ . Figure 5 illustrates the molecular energy diagram for an angular species  $\text{XY}_2$ , which for this reaction has 17 electrons (14 of  $\text{Cl}_2$  and 3 from O) in the transition state; the bond order at the transition state is  $n^\ddagger = 3/2$ .

For the reaction  $\text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}$  the number of electrons to be considered is 11 ( $2\text{C} + 6\text{O} + 3\text{N}$ ) which leads to  $m = 3.5$  and consequently to  $n^\ddagger = 1.75$ . With this bond order eq. [14] allows the estimation of  $\eta^0 = 0.062$ ; eq. [2] then gives  $|\lambda| = 163 \text{ kJ mol}^{-1}$  a value which compares well with  $145 \text{ kJ mol}^{-1}$  found for several other hydride reactions.

Finally the transition state of the reaction  $2\text{NOCl} \rightarrow 2\text{NO} + \text{Cl}_2$  can be understood in terms of an energy diagram for a tetratomic species  $\text{HAAH}$  (Figure 6) with the 14 electrons of the Cl atoms and more 2 electrons, one of each of the terminal atoms. In fact the diagrams of Figure 4 reveal that the conversion of a  $\text{X}_q$  system into  $\text{X}_{q-1}\text{H}$  can be obtained by subtracting 2 electrons to the total number of electrons of  $\text{X}_q$ : Since this transition state has 20 electrons ( $14 \text{ Cl} + 3\text{O} + 3\text{O}$ ) it is equivalent to 16 electrons in a  $\text{A}_2\text{H}_2$  diagram. As Figure 6 shows the total bond order is  $m = 2$  and since there are 3 bonds, the order per chemical bond is  $n^\ddagger = 2/3$ . Such a value corresponds to  $\eta^0 = 0.162$  a value in very good agreement with the experimental value (0.160).

These simple considerations on the electronic structure of the activated complexes allow one to interpret the observed bond

orders  $n^\ddagger$  for hydride and nonhydride molecules.

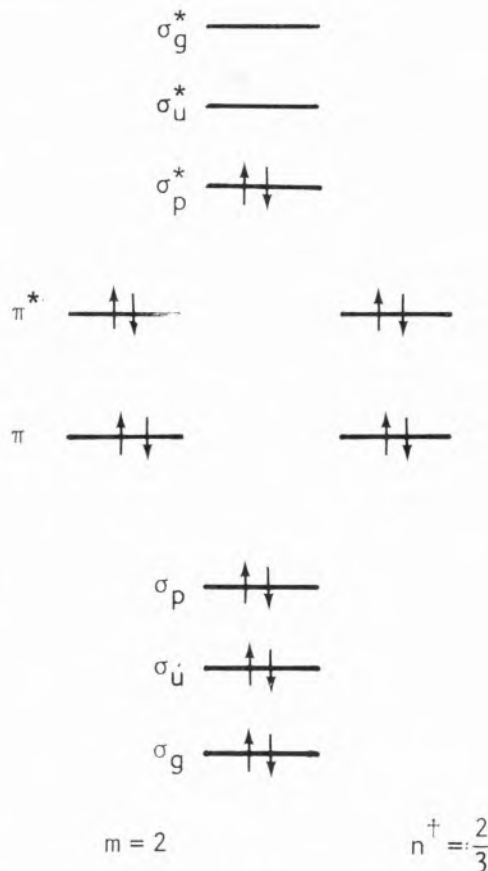


Fig. 6

Molecular orbital energy diagram for a tetratomic molecular species  $\text{HAAH}$ .

## ELECTRON TRANSFER REACTIONS

### Outer-sphere reactions

The present model is quite general and can be applied to the study of mechanisms of reactions in solution. Although this intersecting-state-model has been developed for bond-breaking bond-forming processes it encompasses reactions where there is no breaking of chemical bonds such as the outer-sphere electron transfer reactions [26]. The transfer of an electron between two reacting moieties occurs for a common configuration of reactants and products found

at the intersection of two potential free energy curves. Assuming that these curves can be represented by harmonic oscillators

$$\frac{1}{2} f_r x^2 = \frac{1}{2} f_p (d - x)^2 + \Delta G^\circ \quad (5)$$

where  $d$  is the horizontal displacement of the oscillators  $x$  is the bond distention in the reactants and  $\Delta G^\circ$  the free energy of the reaction. The activation energy due to the changes in lengths of the ion-ligand bonds is given by

$$\Delta G^\ddagger = \frac{1}{2} f_r x^2 \quad (6)$$

where  $x$  is estimated through eq. [5].

Instead of two separate potential energy curves for the reactants (or products) it is much more convenient to combine these curves into a single one, by averaging the corresponding force constants  $f_r = (f'_r + f''_r)/2$ . Since for the change in configuration of the coordination shell several ligands contribute through in-and out-phase motions, the force constant for the potential energy curve is  $f_r = \sqrt{m'}$  ( $f'_r + f''_r$ )/2 where  $m'$  is the coordination number of the metal ions [26,31].

Table 2 presents the distensions  $d$  and  $\eta$  which reproduce the experimental activation energies for some electron exchange reactions. The interesting result is that  $\eta^\circ \approx 0.108$ , implying a transition state bond order  $n^\ddagger = 1$ , because the ion-ligand bonds are single bonds and there is no chemical breaking during electron transfer.

Table 2

Bond distensions for Electron exchange Reactions \*

Reactants	$\Delta G^\ddagger$ / kJ mol <sup>-1</sup>	$\eta_o$	$d$ /nm
Fe <sup>2+</sup> /Fe <sup>3+</sup>	70.0	0.104	0.043
Cr <sup>2+</sup> /Cr <sup>3+</sup>	82.0	0.108	0.0464
V <sup>2+</sup> /V <sup>3+</sup>	86.3	0.109	0.0476
Mn <sup>2+</sup> /Mn <sup>3+</sup>	93.0	0.116	0.049

The effect of  $\Delta G^\circ$  on  $\Delta G^\ddagger$  can also be evaluated through eqs. [5] and [6] for exothermic reactions. A linear dependence of  $\eta$  and  $(\Delta G^\circ)^2$  was found for the reactions studied [26]. Here the interesting feature is that the observed parameters for the mixing entropy,  $\lambda$ , correlate very well with the entropy of

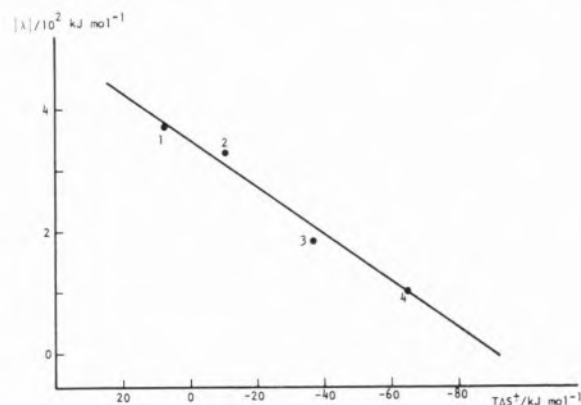


Fig. 7

Correlation of the mixing entropy  $\lambda$  with the entropy of activation ( $T = 298\text{K}$ ) for several outer-sphere electron transfer reactions: 1 Ce<sup>3+</sup>/V<sup>4+</sup>; 2 Cr<sup>2+</sup>/Co<sup>3+</sup>; 3 Eu<sup>2+</sup>/V<sup>3+</sup>; 4 Cr<sup>2+</sup>/Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>. Data selected from ref. 26.

activation,  $\Delta S^\ddagger$  (Figure 7). For  $T = 298\text{ K}$  the observed relationship is

$$|\lambda| / \text{kJ mol}^{-1} = 360 + 4 T\Delta S^\ddagger \quad (7)$$

with  $\Delta S^\ddagger > 0$  there is a small dependence of  $\eta$  on  $(\Delta G^\circ)^2$ ; with  $\Delta S^\ddagger < 0$  there is a large increase of  $\eta$  with an increase in  $|\Delta G^\circ|$ .

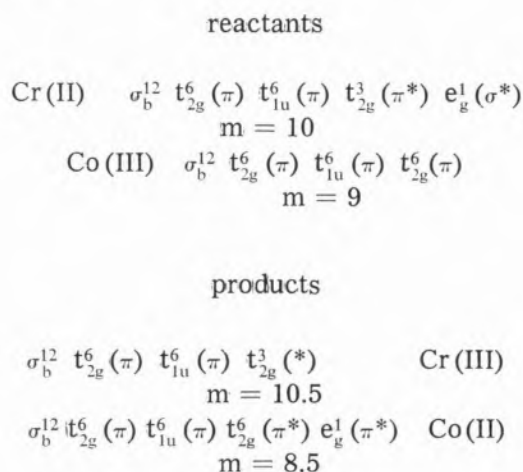
#### Inner-sphere reactions

The role of the bond order at the transition state is well illustrated in the case of inner-

\* Data selected from ref. 26.

\*\*  $\lambda(\lambda \text{ in } 2)$  is the intrinsic potential energy barrier of thermoneutral reactions and consequently has enthalpic and entropic contributions. The independent term takes into account the enthalpic contributions together with a term resulting from the conversion of an entropy of mixing in mole fractions into molar concentrations.

sphere reactions where the two reactant species share a common ligand in the activated complexes. Several reactions were studied [26] and all of them have a linear dependence  $\eta$  with  $(\Delta G^\circ)^2$  with an intercept  $\eta^\circ \approx 0.068$ . This value is close to the one found for vapour phase reactions with  $n^\dagger \approx 3/2$ . In order to understand these bond order values let us consider an example of an inner-sphere reaction:  $\text{Cr}^{2+}_{(\text{aq})}/\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ . The most convenient way to interpret these reactions is in terms of the molecular orbital theory. An interaction of  $nd(t_{2g})$  and  $(n+1)p$  orbitals with low-lying nonbonding  $\pi$  ligand orbitals causes changes in the ion coordination shells in the activated complexes and this can lead to electronic configurations such as:



which corresponds to an average total bond order of  $m = 9.5$  and, since there are 6 ion-ligand bonds,  $n^\dagger = 1.583$ . With this value eq. [4] gives  $\eta^\circ = 0.068$ , as found from the experimental data.

Electron transfer between  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Fe}(\text{CN})_6^{3-}$  is an outer-sphere process, because the inner coordination spheres are inert to substitution. However for this reaction  $\eta^\circ = 0.070$ , a value characteristic of an inner-sphere reaction [26]. Because the  $\pi$  orbitals of the  $\text{CN}^-$  ligands can interact with the metal ion orbitals, the metal ligand bonds already have a bond order higher than 1 in reactants and products. The bond order can be

estimated, for example by subtracting the antibonding effect of the d orbitals from the value of 2 for the metal-ligand bond. Thus, for  $d^5$  and  $d^6$  configurations of the metal ions, the antibonding effect per bond is  $(5+6)/4 \times 6 = 0.46$  and  $n^\dagger = 1.54$ . With this value the estimated reduced displacement is  $\eta^\circ = 0.070$ .

In 1960 Marcus [32] predicted that for very negative reaction free energies, the rates of electron transfer processes will decrease with a decrease in  $\Delta G^\circ$ . This region, the so called inverted region, has been searched for experimentally in several systems. Examples have been found of the predicted decrease, but

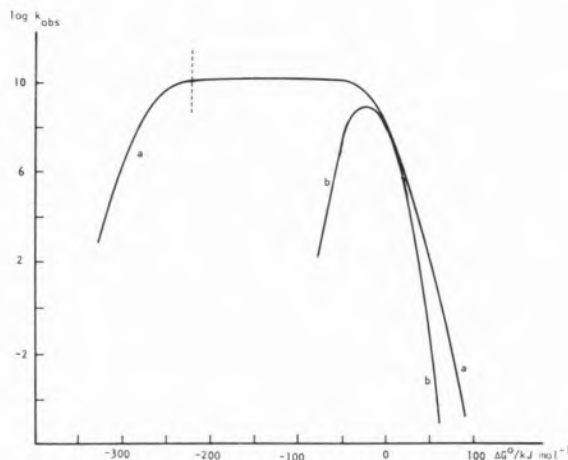


Fig. 8

Calculated rates of electron transfer,  $k_{obs}$ , for inner sphere reactions (--- limit of the region accessible experimentally);  $k_d = 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ;  $k_{-d} = 10^{10} \text{ s}^{-1}$ , frequency factor:  $10^{13} \text{ s}^{-1}$ ,  $\eta^\circ = 0.07$ ,  $f = 3 \times 10^3 \text{ kJ mol}^{-1} \text{ A}^{-2}$ ,  $l = 4 \text{ A}^\circ$ ; a)  $|\lambda| = 290 \text{ kJ mol}^{-1}$ ; b)  $|\lambda| = 90 \text{ kJ mol}^{-1}$ .

for other systems there is no inverted region, because only a diffusion controlled rate plateau has been found [33]. It has been a matter of controversy the kind of parameters which are responsible for the observation or the non-observation of the inverted region. The present model seems to solve such problem in terms of the entropy of mixing.

Figure 8 presents the calculated rates of electron transfer as a function of  $\Delta G^\circ$ , in a system controlled by diffusion, i.e.,

$$k_{\text{obs}} = \frac{k_d k_{\text{et}}}{k_{-d} + k_{\text{et}}}$$

where  $k_d$  is the rate of diffusion,  $k_{-d}$  the rate of separation of the two reacting moieties from the collision complex and  $k_{\text{et}}$  the rate of electron transfer within the collision complex. As the figure shows for a low  $|\lambda|$  the inverted region is observed experimentally, because it occurs at moderately  $\Delta G^\circ$ . However when  $|\lambda|$  is high the inverted region cannot be observed experimentally because it occurs at very negative energies, not experimentally available, even for electrochemically excited states.

## SUBSTITUTION REACTIONS

### *Diagnosis of Mechanisms in terms of Bond Order*

The molecular parameters of this intersecting-state-model can provide new insights on reaction mechanisms. A good example of this is the diagnosis of the mechanisms of nucleophilic reactions based on the bond order at the transition state [27].

Water exchange reactions of metal ions in aqueous solutions are convenient to illustrate this application because  $\Delta G^\circ = 0$ . The bond order  $n^\ddagger$  is calculated through the procedure already described for the electron transfer reactions. However, since only one bond is stretched along the reacting coordinate, the potential energy curves are calculated with the force constant of a single chemical bond. Two extreme situations can be considered for these reactions: one is an associative mechanism where the rate determining step is the formation of an intermediate of increased coordination number; the other is a dissociative mechanism where in the rate determining step there is the generation an intermediate of reduced coordination num-

ber. For an associative mechanism there is bond-forming and bond-breaking processes and if there is no intervention of nonbonding electrons, the total bond order is conserved and  $n^\ddagger = 1/2$ . For a dissociative mechanism with conservation, of bond order  $n^\ddagger = 1$ .

Table 3 illustrates the calculated  $n^\ddagger$  for several metal ions. The results reveal a continuum of  $n^\ddagger$  values, from 0.5 to values even higher than 1 for cases where some non-

Table 3

Bond Orders at the Transition State for Water Exchange Reactions of Metal Ions <sup>a)</sup>

Ion	$n^\ddagger$	Mechanism <sup>b)</sup>
Cr <sup>3+</sup>	0.51	A
Be <sup>2+</sup>	0.76	I <sub>a</sub>
Fe <sup>2+</sup>	0.85	I <sub>d</sub>
Co <sup>2+</sup>	1.00	D
Gd <sup>3+</sup>	1.30	D <sub>b</sub>

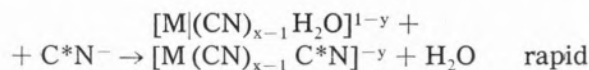
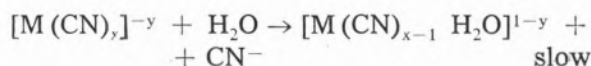
<sup>a)</sup> Data from ref. 27. <sup>b)</sup> A associative; I<sub>a</sub> associative interchange; I<sub>d</sub> dissociative interchange; D dissociative; D<sub>b</sub> dissociative bridging.

bonding electrons of the ligand acquire a bonding character at the transition state. The data reveal that the mechanisms of nucleophilic substitution in fact form a continuum between first and second order processes, where the usual subdivisions are somewhat arbitrary.

### $\Delta G^\circ$ as a driving force for reactions

Marcus has shown very convincingly that for moderately exothermic electron transfer

reactions  $\Delta G^\circ$  acts as a driving force for reactions (14,32,33). However this seems not to be valid for several nucleophilic substitutions. One example is provided by the exchange of cyanide which in fact is rate determined by the aquation process.



According to the present model the activation energy should depend on  $\Delta G^\circ$  of the aquation process, which should also vary with the stability of the cyanide complexes. However, as Table 4 reveals there no corre-

Table 4

Exchange rate and stability of some cyano complexes <sup>a)</sup>

Complex	Dissociation constant	Exchange rate
Fe(CN) <sub>6</sub> <sup>4-</sup>	10 <sup>-37</sup>	very slow
Ni(CN) <sub>4</sub> <sup>2-</sup>	10 <sup>-30</sup>	very fast
Mn(CN) <sub>6</sub> <sup>3-</sup>	10 <sup>-27</sup>	moderate
Ag(CN) <sub>2</sub> <sup>-</sup>	10 <sup>-21</sup>	very fast

<sup>a)</sup> Data from ref. 34

lation between the rates of reaction and the equilibrium constants.

Activation energy depends on several factors and a correlation between  $E_a$  and molecular parameters can only be established when the effect of one of the factors is dominant or when several factors work in the same direction. However when this is not the case, more profound analysis have to be carried out. Table 5 presents the calculated  $\eta^\circ$  for

Table 5

Reduced Displacements for Aquation of Cyanide Metal Complexes

Complexes	$\Delta G^\ddagger$ / kJ mol <sup>-1</sup>	f/kJ mol <sup>-1</sup> A <sup>e-2</sup> a)				$\Delta G^\circ$ /kJmol <sup>-1</sup>	$\lambda$ /kJ mol <sup>-1</sup> d	d/A° R <sub>e,AB</sub> + R <sub>e,BC</sub> /A°	$\eta^\circ$	Mechanisms				
		M—C	M—O	Bond order reactant product	Associative Dissociative									
					n <sup>‡</sup>					$\eta^\circ$	n <sup>‡</sup>	$\eta^\circ$		
Mn (CN) <sub>6</sub> <sup>3-</sup>	83 b)	2 × 10 <sup>3</sup>	1.6 × 10 <sup>3</sup>	18	1.7 × 10 <sup>2</sup> d)	0.576	4.06	0.141	1.67	1.0	0.667	0.16	1.67	0.065
Fe (CN) <sub>6</sub> <sup>4-</sup>	102 b)	2.8 × 10 <sup>3</sup>	9.6 × 10 <sup>2</sup>	26	1.7 × 10 <sup>2</sup> d)	0.677	4.0	0.168	1.50	1.0	0.625	0.173	1.50	0.072
	130 c)					1.1		0.216						
Ag (CN) <sub>2</sub> <sup>-</sup>	74.5	1.25 × 10 <sup>3</sup>	4 × 10 <sup>2</sup>	48	3 × 10 <sup>2</sup> e)	0.71	5.0	0.140	1.0	1.0	0.5	0.216	1.0	0.108
	60					0.55		0.108						

<sup>a)</sup> J. R. Ferraro «Low Frequency Vibrations of Inorganic and Coordination Compounds». Plenum Press, New York 1971, J. Burgess «Metal ions in Solution». Wiley, London, 1978, p. 85.

<sup>b)</sup> Experimental values of ref. 34

<sup>c)</sup> Calculated values; rates compared with the one of Mn(CN)<sub>6</sub><sup>3-</sup>;  $5 \times 10^{-9}$ ; 30;  $1 \times 10^4 (\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1})$ ;

<sup>d)</sup>  $T\Delta S^\ddagger = -47 \text{ kJ mol}^{-1}$  | 34 | and eq. (7);

<sup>e)</sup>  $T\Delta S^\ddagger = -16 \text{ kJ mol}^{-1}$ .

the aquation processes of  $\text{Mn}(\text{CN})_6^{3-}$  and  $\text{Fe}(\text{CN})_6^{4-}$ , taking into account the endothermicity of the reactions. As the results show the mechanisms are strongly associative. The relative order for the exchange rates is dominated by  $\Delta G^\circ$  and the force constants. Calculations with  $\text{Ag}(\text{CN})_2^-$  seem to show that a very fast exchange can only occur if the mechanism of aquation has a more dissociative character. For this complex the reaction free energy, on its own, would make the exchange process a very slow one.

An even more striking example of the apparent absence of correlation of rate and equilibrium constants has been reported by Taube [35] and concerns substitution reactions of ruthenium ammines complexes. Whereas the equilibrium constants vary ca.  $10^7$  times the rate constants only vary by a factor of 5 (Table 6). Since the rate of complex formation does not reflect the stability of the complex, Taube concluded that there was very little bond formation in the activated complexes.

We have applied our model to calculate  $d$  in order to reproduce  $\Delta G^\ddagger$ . These were estimated from  $k_1$  with a preexponential factor of  $10^{13} \text{ s}^{-1}$ . The force constant Ru-N and Ru-O is  $1.6 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$  [36] and  $R_{e,AB} + R_{e,BC} = 4.27 \text{ \AA}$ . Figure 9 presents the plot of  $\eta$  as a function of  $(\Delta G^\circ)^2$ . A good

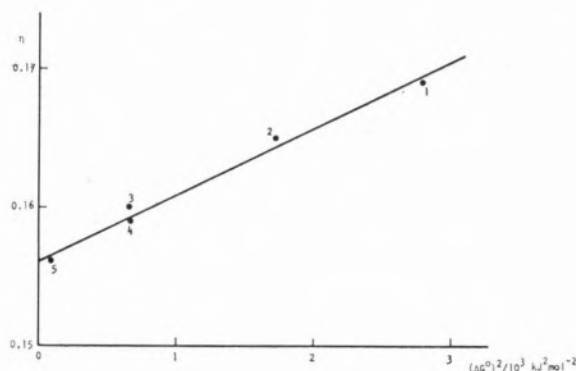


Fig. 9

Reduced displacement  $\eta$  as a function of  $(\Delta G^\circ)^2$  for ruthenium ligand exchange  $[\text{Ru}(\text{NH}_3)_5\text{OH}_2]^{2+} + \text{L} \rightarrow [\text{Ru}(\text{NH}_3)_5\text{L}]^{2+} + \text{H}_2\text{O}$ ; legend for ligands L in Table 6.

Table 6

Specific rates of ligation,  $k_1$ , in  $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$  as a function of stability <sup>a)</sup>.

	Ligand	$K_{\text{eq}}$	$k_1 / \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$	$-\Delta G^\circ / \text{kJ mol}^{-1}$	$\Delta G^\ddagger / \text{kJ mol}^{-1}$
1		$2 \times 10^9$	0.105	52.8	79.4
2		$2 \times 10^7$	0.093	41.5	79.0
3	$\text{NH}_3$	$3.5 \times 10^4$	0.055	25.8	81.0
4	$\text{N}_2$	$3.3 \times 10^4$	0.073	25.7	80.3
5	$\text{NH}(\text{CH}_3)\text{CH}_2\text{CO}_2\text{Et}$	50	0.021	9.7	83.3

<sup>a)</sup> Data from ref. 35;  $R_{e,AB} + R_{e,BC} = 4.27 \text{ \AA}$

linear relationship is observed with an intercept  $\eta^0 = 0.156$  and a slope which gives  $|\lambda| = 1.35 \times 10^2 \text{ kJ mol}^{-1}$ .

The first important conclusion is that  $\Delta G^0$  is a driving force for the reaction. However its effect is not significant because there is a considerable entropy of mixing. From eq. [7] an estimation can be made  $\Delta S^\ddagger = -188 \text{ J mol}^{-1} \text{ K}^{-1}$ . The intercept reveals that the mechanism can have a strong associative character,  $I_a$ , because  $n^\ddagger = 0.69$ . Such conclusion contrast with the conclusion of Taube [35] based only on the apparent lack of correlation between  $k$  and  $\Delta G^0$ .

## EPILOGUE

In contrast with the information provided by potential energy surfaces the present model can assess independently the role of several thermodynamic, geometric and electronic factors on the energy barrier ( $E_a$  or  $\Delta G^\ddagger$ ) of a chemical reaction. The relevant parameters are:

- i — the energy of the reaction,  $\Delta H$  or  $\Delta G$ .
- ii — the force constants,  $f$ , of the reactive bonds or other characteristics of the potential energy curves, such as the dissociation energy.
- iii — the sum of the lengths of the reactive bonds,  $R_{e,AB} + R_{e,BC}$ .
- iv — the bond order at the transition state,  $n^\ddagger$ .
- v — the entropy of mixing,  $\lambda$ , or its equivalent, i.e., the activation entropy,  $\Delta S^\ddagger$ .

This analytic feature of the model is very useful in teaching Chemical Kinetics, because it can help the students to assess, in a qualitative way, the effect of several molecular factors on reaction mechanisms. Within this

kind of model we have already used the parameters  $\Delta H$  ( $\Delta G$ ),  $f$ , and  $R_{e,AB} + R_{e,BC}$  to provide new insights in the teaching of chemical kinetics [37] and molecular reactivity [38]. The discover of the concept of a variable transition state bond order can also be incorporated in the teaching at an university level. The entropy of mixing is probably a more difficult concept to use for qualitative predictions.

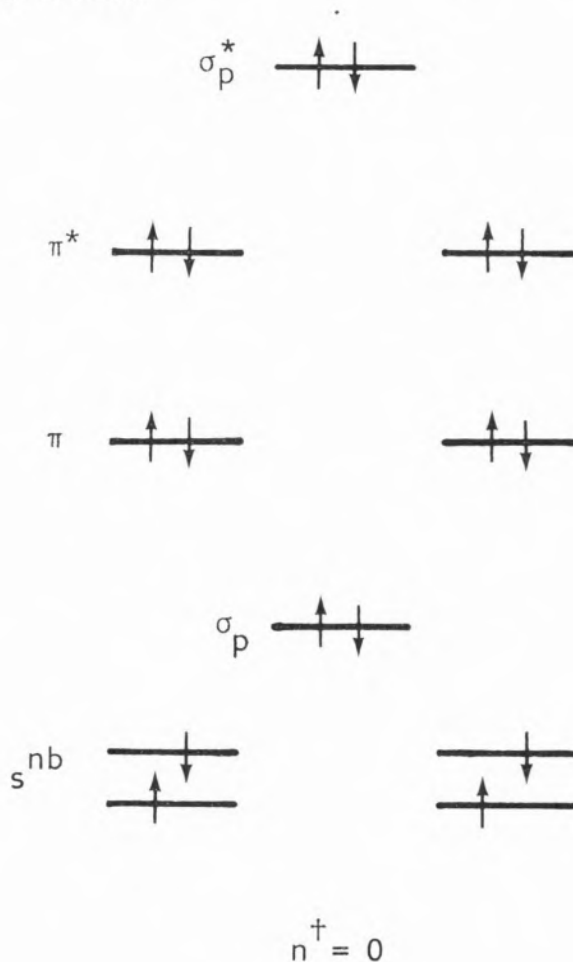


Fig. 10

Molecular orbital energy diagram for the hypothetical cyclic transition state  $H_2I_2^\ddagger$ .

However the scope of the model is considerably broader than the one of its pedagogical value, because it is a quantitative model which generalizes the previous approaches already mentioned including, as parti-

cular cases, the BEBO and Marcus theories. Recently Grunwald [39] has discussed the limitations of the Marcus theory on describing the reaction progress in terms of just one variable. To circumvent this difficulty Grunwald has proposed a new model where two «ad hoc» progress variables are defined. Here the present model virtually adds two independent variables,  $n^\ddagger$  and  $\lambda$ , to the theory of Marcus and is therefore even more flexible than the model of Grunwald.

The role of the electronic factors on the energy barrier for a chemical reaction is a quantification of the Woodward-Hoffmann principles [22]. The conservation of orbital symmetry divides the chemical reactions into allowed and forbidden processes. The latter ones have a bond order at the transition state equal to zero,  $n^\ddagger = 0$ , and therefore have an «infinite» energy barrier, such as the hypothetical elementary reaction  $H_2 + I_2$  (Figure 10). However the allowed processes have different degrees of electronic allowdness which can range from  $n^\ddagger = 1/2$  to  $n^\ddagger = 2$  or even higher values.

In conclusion, we hope to have revealed that the present model can provide new insights on the mechanisms of chemical reactions and can establish a more rigorous framework for the current theories of absolute rates.

On finishing this presentation I would like to refer to the title of Professor Ferreira da Silva lecture for the opening of the academic year at the University of Oporto in November 1911: «A importância e a dignidade da ciência». I and certainly all of you, share that same conviction. This is the best tribute which we can pay to the founder of the Sociedade Portuguesa de Química.

This work was developed through a collaboration of many years with my friend and colleague António Varandas. Our educational and scientific association has influenced in many ways the ideas presented here.

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## RESUMO

**Estrutura molecular e reactividade química. A importância da energia de activação.**

Apresenta-se um modelo semi-empírico de intersecção de curvas de energia potencial para o cálculo de energias de activação. O modelo mostra que a energia de activação depende de factores termodinâmicos e electrónicos: energia de reacção, constantes de força e soma dos comprimentos das ligações químicas reactivas, da ordem de ligação no estado de transição e da chamada «entropia de mistura». Alguns destes parâmetros moleculares são importantes na elucidação do mecanismo de reacções. Ilustra-se este facto com a aplicação do modelo a reacções de hidretos e não-hidretos em fase gasosa, e a reacções de transferência de electrões e substituição nucleofílica em soluções aquosas. Compara-se o modelo com outros formalismos teóricos que procuram relacionar energia de activação e estrutura molecular, nomeadamente as relações lineares de energia livre, as teorias de Marcus e BEBO e as regras de conservação de simetria de Woodward-Hoffmann.