



## A SIMPLE THEORETICAL MODEL FOR THE ENERGY BARRIER IN UNIMOLECULAR REACTIONS

A simple classical intersecting-state model, which estimates energy barriers in terms of thermodynamic, geometric and chemical bond order factors, is employed to calculate  $\Delta G^\ddagger$  for the isomerizations of cyclopropane and methyl isocyanide and the dissociation of cyclobutane. Within reasonable structural assumptions agreement between theory and experiment is obtained. The large difference in  $\Delta G^\ddagger$  for the two isomerization reactions is interpreted in terms of differences in the bond orders of the transition states.

## INTRODUCTION

The last decade brought a tremendous increase in a number of accurate *ab initio* and even simple MO theory calculations for chemical reactions. However, to unravel trends of reactivity within a family of related processes, theoretical models, which sacrifice rigour to gain simplicity and computational feasibility, are often better than such *ab initio* calculations [1]. They have also a heuristic value, an aspect which has been somewhat neglected in quantum chemistry. We have recently developed a simple model to estimate energy barriers of chemical reactions in terms of geometric, electronic and thermodynamic factors [2]. We can probably say that this model was designed more for viewing the wood rather than the individual trees. Nevertheless it presents a unified model for several empirical and semi-empirical relations between kinetics and thermodynamics, namely the Marcus and BEBO theory and Linear Free Energy Relationships [2, 3].

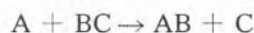
Although theories of absolute reaction rates offer expressions permitting calculations of the energy barrier of unimolecular reactions, virtually the only cases where reasonable predictions of the activation energy have been made by simple methods are simple bond-breaking bond-forming processes and a few elimination reactions [4, 5].

In view of the importance of unimolecular reactions in gas-phase kinetics, we have decided to test the applicability of our model to the estimation of energy barriers for three unimolecular reactions, namely the isomerization of cyclopropane and methyl isocyanide and the dissociation of cyclobutane. We aim also to assess the most important structural factors which determine the magnitude of the chemical energy barriers of these reactions.

## THEORETICAL MODEL

The intersecting-state model (ISM) has been described in detail elsewhere [2] and will

only be stated briefly here. The model estimates the energy barrier of the reaction



from the intersection of the potential energy curves of BC and AB. If one assumes that the potential energy curves can be represented by harmonic oscillators

$$\frac{1}{2} f_r x^2 = \frac{1}{2} f_p (d - x)^2 + \Delta E^0 \quad (1)$$

where  $f_r$  and  $f_p$  are the force constants of reactant and product, respectively,  $x$  the bond distension in the reactant and  $\Delta E^0$  the reaction energy. The parameter  $d$  is the sum of the bond distensions in reactant and product, and it has been shown [2] to be proportional to the sum of the equilibrium bond lengths of reactant and product

$$d = \eta (l_r + l_p) \quad (2)$$

The reduced bond distension  $\eta$  is given by

$$\eta = \frac{a' \ln 2}{n^\ddagger} + \frac{a'}{2} \left( \frac{\Delta E^0}{\lambda} \right)^2 \quad (3)$$

where  $a'$  is a constant ( $a' = 0.156$ ),  $n^\ddagger$  is the bond order of the transition state for the thermoneutral situation, and  $\lambda$ , which is the so called «configuration entropy» proposed by Agmon and Levine [6], is a measure the «energy capacity» of the activated complexes. When the bond-forming bond-breaking processes involve a single bond in reactant and another one in the product, the total bond order is assumed to be conserved along the reaction coordinate [7] and consequently  $n^\ddagger = 1/2$  [2]. However, the present model considers the possibility that the total bond order can be higher than unity. This can occur either for double or triple bonds, with conservation of total bond order, or for cases where the total bond order is not conserved. The latter case occurs when nonbonding or antibonding electrons acquire a bonding character in the transition state. These transition

state bond orders can be known from simple molecular orbital diagrams [3]. Consequently all the parameters of the model come from fields outside chemical kinetics, with the exception of  $\lambda$  which, in general, must be estimated empirically from kinetic data. However, for many reactions  $|\Delta E^0| \ll \lambda$  and we can neglect the dependence of  $\eta$  on  $\lambda$  and  $(\Delta E^0)^2$ .

Once  $d$  is known from eqs (2) and (3),  $x$  can be estimated from eq (1) and the energy barrier due to the distension of the reactant is

$$\Delta E^\ddagger = \frac{1}{2} f_r x^2 \quad (4)$$

For vapour phase reactions involving the breaking of one bond and the making of another one, ISM gives a good estimation of the activation energy [2]. However, for reactions in condensed media or for vapour phase reactions of complex molecules there are many other degrees of freedom rather than one stretching in reactant and another in product. To keep the model unidimensional, we have to treat such degrees of freedom on a statistical basis by employing free energies rather than internal energies. In fact, under such conditions the model provides good estimations of  $\Delta G^\ddagger$  for several types of reactions (2, 3, 8, 9).

Although temperature is not an explicit parameter of ISM,  $\Delta G^0$  and  $\lambda$  [3] are temperature dependent parameters.

Furthermore, when the chemical reaction involves bond-breaking bond-forming processes of more than one chemical bond in reactant and product, a judicious choice of the effective force constants along the reaction coordinate has to be made.

The energy barrier due to bending motions can also be estimated within the assumption of harmonic behaviour

$$\Delta G_b = \frac{1}{2} f_b (\theta - \theta^0)^2 \quad (5)$$

as long as the change in bond angle,  $\theta - \theta^0$ , is not very large.

## ISOMERIZATION OF CYCLOPROPANE

The rearrangement of cyclopropane into propylene is considered to be a simple unimolecular process [10]. In the high pressure region ( $> 10$  Torr) and in a temperature range of 469 to 519°C, the rate constants follow the expression

$$k/s^{-1} = 1.5 \times 10^{15} \exp(-272.0/RT \text{ kJ mol}^{-1})$$

The activation free energy of the reaction can be estimated from

$$k = \frac{k_B T}{h} c_0^{1-m} \exp(-\Delta G^\ddagger/RT)$$

where  $c_0$  is the standard concentration ( $c_0 = 1 \text{ mol dm}^{-3}$ ),  $m$  is the molecularity of the reaction and the other symbols have their usual meaning. Within the temperature range of the experimental studies,  $\Delta G_{792}^\ddagger = 242 \text{ kJ mol}^{-1}$  and  $\Delta G_{792}^0 = -57 \text{ kJ mol}^{-1}$ , estimated from the data collected by Benson *et al.* [11].

The following vibrational modes can be considered to be important for this reaction: in the bond-forming bond-breaking processes the stretching of one C-C and one C-H bond in the reactant and one C=C and one C-H bond in the products. The most significant changes in bond angles are the CCC and CCH. Assuming that such changes up to the transition state are one half of the overall change between reactant and product, the bond angle variations are  $30^\circ$  ( $90^\circ$ - $60^\circ$ ) for CCC and  $19.5^\circ$  ( $109.5^\circ$ - $90^\circ$ ) for CCH.

The stretching modes can be taken as independent diatomic oscillators and under this assumption the average stretching force constant of two independent modes is  $f = \sqrt{f_1^2 + f_2^2}$  [12]. The relevant data are  $f_{C-H} = 2.9 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$ ;  $f_{C-C} = 2.7 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$  and  $f_{C=C} = 5.77 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$  [13]. Consequently  $f_r = 4.0 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$  and  $f_p = 6.5 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$ . The bond length data  $l_{C-H} = 1.096 \text{ \AA}$ ,  $l_{C-C} = 1.537 \text{ \AA}$  and  $l_{C=C} = 1.335 \text{ \AA}$ , lead to  $l_r + l_p = (l_{C-H} + l_{C-C})/2 + (l_{C-H} + l_{C=C})/2 = 2.523 \text{ \AA}$ .

Now we can estimate the energy barrier due to the stretching of the chemical bonds, through eqs (1)-(4), for free energies rather than internal energies. The square dependence of  $\eta$  on  $(\Delta G^0)^2$  can be neglected because  $\lambda$  is expected to be high ( $\lambda \gg |\Delta G^0|$ ) for molecules with many degrees of freedom, particularly if the activation entropy is positive, as it is the case for the reactions under study (3). With  $n^\ddagger = 1/2$  the estimated energy barrier for stretching is  $\Delta G_{792}(\text{st}) = 164 \text{ kJ mol}^{-1}$ .

The bending force constants are  $f_{CCC} = 0.146 \text{ kJ mol}^{-1} \text{ deg}^{-2}$  and  $f_{CCH} = 0.10 \text{ kJ mol}^{-1} \text{ deg}^{-2}$  [13]. We can thus estimate the following energy contributions for the bending motions,  $\Delta G_b^\ddagger(\text{CCC}) = 66 \text{ kJ mol}^{-1}$  and  $\Delta G_b^\ddagger(\text{CCH}) = 20 \text{ kJ mol}^{-1}$ . The estimated overall free energy barrier is the sum of all these energy contributions, e.,  $\Delta G_{792}^\ddagger = 250 \text{ kJ mol}^{-1}$ . The calculated value is in good agreement with the experimental data ( $242 \text{ kJ mol}^{-1}$  [10]). The present calculation reveals also that the main contributions for the energy barrier can be attributed to the stretching of the chemical bonds (65 %).

Other motions could have been considered for the reaction coordinate, such as the in-phase motion of the two oscillators, in reactant and product. However for this case the effective force constant is  $f = f_1 + f_2$  and the estimated energy barrier is much higher than the experimental value.

## ISOMERIZATION OF METHYL ISOCYANIDE

The thermal unimolecular isomerization of methyl isocyanide  $\text{CH}_3\text{CN}$ , has been investigated by Schneider and Rabinovitch [14]. The activation free energy is  $\Delta G_{533}^\ddagger = 155 \text{ kJ mol}^{-1}$  at pressures  $> 5$  Torr and temperatures between 200°C and 260°C and  $\Delta G_{533}^0 = -68 \text{ kJ mol}^{-1}$  [11].

Two possible situations can be envisaged for the transition state. The first one considers

the only reactive bonds to be C-N in the reactant and a C-C bond in the product because the  $C\equiv N$  bond is unaffected by the reaction. With  $f_{C-N} = 2.95 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$ ,  $f_{C-C} = 2.7 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$ ,  $l_{C-N} = 1.47 \text{ \AA}$ ,  $l_{C-C} = 1.537 \text{ \AA}$  [13] and  $n^\ddagger = 1/2$ , the activation energy barrier for stretching is calculated to be  $\Delta G_{533}^\ddagger(\text{st}) = 117 \text{ kJ mol}^{-1}$ .

The second situation considers also the involvement of the  $C\equiv N$  bond in the bond-breaking bond-forming processes in the reactant and the product. The effective force constant is  $f_r \cong f_p = 1.1 \times 10^4 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$  because  $f_{C\equiv N} = 1.07 \times 10^4 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$  [13]. The average bond order in reactant and product is  $n = 2$ , and consequently, if the total bond order is conserved along the reaction coordinate, then  $n^\ddagger = 1$ . With these parameters and  $l = (l_{C-N} + l_{C-C} + 2 l_{C\equiv N})/4$  ( $l_{C\equiv N} = 1.157 \text{ \AA}$  [13]) eqs (1) to (4) lead to  $\Delta G_{533}^\ddagger(\text{st}) = 82 \text{ kJ mol}^{-1}$ . This value is considerably lower than in the previous case, because the transition state bond order is now considerably higher; the effect of an higher force constant on  $\Delta G^\ddagger$  is compensated by the effect of a shorter bond length.

Assuming a triangular transition state, the change in bond angle CNC is very large (ca.  $110^\circ$ ) and consequently the harmonic behaviour is no longer valid. The energy barrier owing to the bending motion can be approximately estimated from the «strain energy» of cyclopropane  $105 \text{ kJ mol}^{-1}$  [15]. The bending energy in the transition state can be attributed to the strain of only two bonds; the  $C\equiv N$  is assumed to cause no strain. Then the estimated energy barrier is ca.  $70 \text{ kJ mol}^{-1}$ . With the calculated energy barriers for stretching and bending, the energy barrier is estimated to be  $\Delta G_{533}^\ddagger = 152 \text{ kJ mol}^{-1}$  again close to the experimental value.

It is worth an emphasis on the role played by the  $C\equiv N$  bond in the transition state. Transition state bond orders higher than 0.5 have been found with molecular species with apparently nonreactive nonbonding and antibonding electrons [2, 3]. Here we have an example where bonding electrons can act in

a similar way by syphoning electronic density into the transition state. This seems to be one of the main reasons (accounts for  $35 \text{ kJ mol}^{-1}$ ) why the isomerization of methylisocyanide has an energy barrier  $87 \text{ kJ mol}^{-1}$  lower than that in the cyclopropane isomerization. The others are associated with equilibrium bond lengths and force constants which are smaller for the former reaction (account for  $30 \text{ kJ mol}^{-1}$ ). The difference in  $\Delta G^\circ$  accounts only for a difference of  $5 \text{ kJ mol}^{-1}$  in the energy barriers.

## DISSOCIATION OF CYCLOBUTANE

The dissociation of cyclobutane into two ethylene molecules has been studied experimentally by Walters and coworkers [16]. In the high pressure region the activation free energy of this unimolecular reaction is  $\Delta G^\ddagger = 228 \text{ kJ mol}^{-1}$  and  $\Delta G^\circ = 7.0 \text{ kJ mol}^{-1}$  at  $713 \text{ K}$ . A correction was applied in  $\Delta S^\circ$  for the change in the standard state from  $1 \text{ atm}$  to  $1 \text{ mol dm}^{-3}$ .

Several possible reaction coordinates can be considered. One is that the four C-C bonds of reactant and two  $C=C$  bonds of products act as independent oscillators. With  $l = l_{C-C} + l_{C=C}$  and  $n^\ddagger = 1/2$  this leads to a very high energy barrier ( $\Delta G^\ddagger = 310 \text{ kJ mol}^{-1}$ ). The alternative coordinate that we can define, a cyclic transition state with a common C-C stretch leads to a very low barrier ( $123 \text{ kJ mol}^{-1}$ ). However this is not surprising because the simultaneous stretch of four bonds in cyclobutane does not lead to the formation of two ethylene molecules. This requires the contraction of two CC bonds and the distension of the other two. A possible effective force constant is the one of a cyclic ring, common to reactant and product where there is the composition of these two kinds of motions;  $f = \sqrt{2} f_{C-C}$  and with  $l = 2 l_{C-C}$ , an energy barrier  $\Delta G_{713}^\ddagger \cong 248 \text{ kJ mol}^{-1}$  is estimated for harmonic oscillators. When one compares the energy barrier for the stretching motions of the dissociation of cyclobutane and the isomerization of cyclopropane, conc-



cludes that the higher energy barrier of the former process can be attributed to an higher  $\Delta G^\circ$  and 1.

## CONCLUSIONS

We have shown that within reasonable assumptions ISM can provide estimations of energy barriers for simple unimolecular reactions in fair agreement with experiment. In spite of the distorted picture that the model may provide, it has revealed some interesting mechanistic insights such as the role of  $C \equiv N$  bond order on decreasing the energy barrier of the isomerization of methyl isocyanide and the role of equilibrium bond lengths and stretching force constants in controlling reaction energy barriers.

Recebido 28.Junho.1986

## ACKNOWLEDGMENTS

We are grateful to Instituto Nacional de Investigação Científica for financial support.

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## RESUMO

Um modelo teórico simples para a barreira de energia de reacções unimoleculares

Aplica-se um modelo de intersecção de estados para o cálculo de barreiras de energia em termos de parâmetros termodinâmicos, geométricos e de ordem de ligação, ao cálculo de  $\Delta G^\ddagger$  na isomerização do ciclopropano, isocianeto de metilo e na dissociação do ciclobutano. Utilizando parâmetros estruturais razoáveis obtém-se acordo com os dados experimentais. O estudo revela alguns aspectos mecanísticos relevantes, tais como o do papel de ordens de ligação no estado de transição que explica em grande medida a diferença nas barreiras de energia das duas reacções de isomerização.