

RATE PROCESSES WITH ISOMERISM OF THE ACTIVATED COMPLEX*

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The rate processes have been studied which (when described on the level of the absolute reaction rates) exhibit several possible ways from reactants to products going through various activated complexes. Relations have been derived between activation parameters of the partial rate processes through the individual activated complexes and the rate characteristics determined experimentally for the overall process. The general formulas are illustrated numerically by the example of cyclohexane isomerization. Isomerism of the activated complex has been observed in the quantum-chemical calculations of the rate constants on the basis of the theory of absolute reaction rates.

Nowadays for theoretical treatment of rate processes the procedures are used which either are based on the equilibrium hypothesis (especially the theory of absolute reaction rates^{1,2}) or do not require this hypothesis (as the method of molecular dynamics³). The both treatments necessitate some knowledge of the potential energy hyper-surfaces as the input information. The concept of the activated complex requires only information about the course of the potential energy surface in close surroundings of some of its stationary points. However, solution of classical or quantum-mechanical equations of motion needs an analytical expression of the whole potential energy hyper-surface. Present state of numerical quantum chemistry allows to obtain the whole hyper-surfaces only in the simplest systems. On the other hand, the task of finding only the minima and saddle points of hyper-surfaces and describing their course in close surroundings of these points in the terms of the second derivatives of energy has been mastered at many methodical levels of quantum chemistry since the pioneering work of McIver and Komornicki⁴. This recent progress in numerical quantum chemistry arose an increased interest in the activated complex theory which represents the only description of rate processes where the data are available from quantum-chemical calculations even for chemically interesting systems. At the same time obtaining of the activated complex characteristics from reliable quantum-chemical calculations allows a more safe verification of the absolute reaction rates theory itself. The formerly found differences between calculated and experimental rate constant values could be caused, besides the presumptions involved in the theory itself, by an error in the activated complex characteristics obtained from empirical potential functions or from an assessment⁵.

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The original concept of theory of absolute reaction rates presumes^{1,2} that transformation of reactants into products goes through a single activated complex. However, recently it was possible to begin systematical investigation of energy hyper-surfaces generated by various quantum-chemical methods, and it turned out that they contain generally more than one stationary point fulfilling the requirements⁵ necessary for an activated complex of the studied rate process. Investigation of mechanism of N_2F_2 *cis-trans* isomerization⁷ by CNDO/2 method indicated a possible existence of two reaction ways with the activated complexes of different structures but with very close activation barriers. These two activated complexes are connected with twisting around the nitrogen-nitrogen bond and with inversion of one nitrogen atom, respectively. Another example of a rate process for which more than one activated complex were found is inversion of cyclohexane⁸. Komornicki and McIver⁸ found two activated complexes at the respective MINDO/2 energy hyper-surface of the chair to boat conversion, each of them belonging to a different symmetry point group, but practically equivalent in their energies.

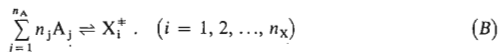
Whereas theoretical calculation allows separate evaluation of rate constants corresponding to transitions through individual activated complexes, in experiment such differentiation is usually impossible. Generally it must be expected that in the cases, where theory detects isomerism of the activated complex, experiment will give only an overall rate constant value involving contributions of all partial ways from reactants to products through individual activated complexes. The confrontation with this summary experimental value based only on theoretical characteristics of the energetically most favourable activated complex is justifiable only in the cases of the other activated complexes being energetically far higher. Generally the correct confrontation of theoretical and experimental values leads to the problem as to what is the contribution of any partial way through the particular activated complex to the effective values of activation parameters ΔH^\ddagger and ΔS^\ddagger obtained in experiment. This problem is close to that solved in ref.⁹ for the case of equilibrium processes with isomerism of reaction components. The present paper deals with the kinetic consequences of the activated complex isomerism.

Formulation of the Problem

Let us consider a rate process in ideal gas phase from reactants A_j to products B_j ; n_j , m_j being the stoichiometric factors:



Let us further consider n_X various ways from the reactants A_j to products B_j , each of them going through a single activated complex X_i^\ddagger ($i = 1, 2, \dots, n_X$). Each of the ways is (for the purposes of the theory of absolute reaction rates) sufficiently described, if the activated complex structure is known. No further data about the corresponding trajectory are requested. Hence, various ways from reactants to products mean the same as various activated complexes. In the sense of the activated complex theory, n_X equilibria are established between the reactants A_j and the respective activated complexes X_i^\ddagger :



For characterization of these n_x equilibria (B) a set of concentration equilibrium constants K_i^\ddagger (unit molarity standard state) are chosen:

$$K_i^\ddagger = \frac{c_{X_i^\ddagger}}{\prod_{j=1}^{n_A} c_{A_j}^{n_j}} \quad (1)$$

In literature there existed a certain confusion about the choice of equilibrium constants characterizing the process (B), which was exactly identified by Guggenheim¹⁰. His symbols and interpretation of the quantities K_i^\ddagger and $c_{X_i^\ddagger}$ will be used below. The energy ΔE_i^\ddagger in Eq. (2) giving the temperature change of the

$$RT^2 \frac{d \ln K_i^\ddagger}{dT} = \Delta E_i^\ddagger \quad (2)$$

constant K_i^\ddagger for the process (B) in ideal gas phase has the meaning¹⁰ of the excess energy of X_i^\ddagger over $n_j A_j$ ($j = 1, 2, \dots, n_A$), omitting the kinetic energy associated with the reaction coordinate. According to the theory of absolute reaction rates¹¹ Eq. (3) gives the relation between the rate constant k_i and equilibrium constant K_i^\ddagger of the process (A) going through the activated complex X_i^\ddagger

$$k_i = \frac{kT}{h} K_i^\ddagger \quad (3)$$

Let the rate process (A) be experimentally followed in such a way that all the paths going through the n_x activated complexes X_i^\ddagger contribute to the measured rate constant k , there being no other contributions. Then the experimentally measured rate constant k is the sum of the calculated partial constants k_i

$$k = \sum_{i=1}^{n_x} k_i \quad (4)$$

Temperature dependence¹² of measured rate constants is usually expressed either in the terms of the Arrhenius frequency factor A and activation energy E_a or in the terms of activation enthalpy and entropy, ΔH^\ddagger and ΔS^\ddagger , respectively. The alternative approach from quantum-chemical calculations gives characteristics of the partial rate processes ΔE_i^\ddagger (or ΔH_i^\ddagger) and ΔS_i^\ddagger . It is to be found how the mentioned partial quantities contribute to the summary ones.

General Relationships

Introduction of summary equilibrium constant K^\ddagger by Eq. (5) allows to make use

of the results of ref.⁹ concerning equilibrium processes with isomerism of reaction components.

$$K^{\ddagger} = \sum_{i=1}^{n_x} K_i^{\ddagger} \quad (5)$$

It must be, however, taken into account that concentration equilibrium constants are considered now. Using the procedure suggested in ref.⁹ we obtain Eq. (6) giving the relation between summary and partial energy changes, ΔE^{\ddagger} and ΔE_i^{\ddagger} , respectively

$$\Delta E^{\ddagger} = \sum_{i=1}^{n_x} \frac{K_i^{\ddagger}}{K^{\ddagger}} \Delta E_i^{\ddagger} . \quad (6)$$

If ideal behaviour is presumed for all components of the processes (B), then the equation of state of ideal gas can be used to express the summary enthalpy of the activation process, Δn^{\ddagger} being the change in number of mol during the activation process (B)

$$\Delta H^{\ddagger} = \Delta n^{\ddagger} RT + \sum_{i=1}^{n_x} \frac{K_i^{\ddagger}}{K^{\ddagger}} \Delta E_i^{\ddagger} . \quad (7)$$

Finally using the partial activation enthalpies ΔH_i^{\ddagger} , Eq. (7) is transformed to

$$\Delta H^{\ddagger} = \sum_{i=1}^{n_x} \frac{K_i^{\ddagger}}{K^{\ddagger}} \Delta H_i^{\ddagger} . \quad (8)$$

Using the results of ref.⁹ for entropy we get the summary term ΔS^{\ddagger}

$$\Delta S^{\ddagger} = \sum_{i=1}^{n_x} \frac{K_i^{\ddagger}}{K^{\ddagger}} \left(\Delta S_i^{\ddagger} + R \ln \frac{K_i^{\ddagger}}{K^{\ddagger}} \right) . \quad (9)$$

Expression for the Arrhenius activation energy is obtained from its definition

$$E_a = RT^2 \frac{d \ln k}{dT} \quad (10)$$

by carrying out the temperature derivative of (4) and (3)

$$E_a = RT(1 - \Delta n^{\ddagger}) + \sum_{i=1}^{n_x} \frac{K_i^{\ddagger}}{K^{\ddagger}} \Delta H_i^{\ddagger} . \quad (11)$$

The knowledge of expression of the Arrhenius activation energy gives immediately the value of frequency factor

$$A = \frac{kT}{h} \exp(1 - \Delta n^\ddagger) \exp(\Delta S^\ddagger/R) \quad (12)$$

where ΔS^\ddagger is given in terms of characteristics of partial processes by Eq. (9).

Illustrative Examples and Discussion

Eqs (8), (9), (11) and (12) give summary rate characteristics of the process (A) (i.e. ΔH^\ddagger , ΔS^\ddagger , E_a and A) as functions of the activation parameters ΔH_i^\ddagger and ΔS_i^\ddagger of the partial processes, and they represent the solution of the given problem. The formulae obtained give instructions for treatment of characteristics of the partial processes (from theoretical calculations) to give the summary quantities which are available experimentally. Comparison of experimental and theoretical values first at this level can be considered correct. If one of the isomeric activated complexes is fundamentally more favourable energetically than the other ones, then the summary characteristics ΔH^\ddagger and ΔS^\ddagger are practically identical with the corresponding characteristics of the respective dominant partial process. This partial process must have so favourable ΔE_i^\ddagger (or ΔH_i^\ddagger) value, that a possible compensation by the entropy term is out of question (such compensation is meant here, which would in terms of K_i^\ddagger lead to comparable stability of the activated complex favoured energetically and some other ones).

Nevertheless, not regarding the magnitude of individual partial equilibrium constants K_i^\ddagger , a useful assessment⁹ of magnitude of ΔH^\ddagger can be made in the terms of the minimum (ΔH_{\min}^\ddagger) and the maximum (ΔH_{\max}^\ddagger) values of the ΔH_i^\ddagger set, viz.

$$\Delta H_{\min}^\ddagger \leq \Delta H^\ddagger \leq \Delta H_{\max}^\ddagger . \quad (13)$$

For the entropy term ΔS^\ddagger it is impossible to make analogous assessment using minimum and maximum entropy values of partial processes (ΔS_{\min}^\ddagger , ΔS_{\max}^\ddagger). However, introduction of the ratio λ of the smallest and the greatest equilibrium constants from the set K_i^\ddagger (Eq. (14)) enables an assessment (Eq. (15)) of the summary activation entropy

$$\lambda = K_{\max}^\ddagger / K_{\min}^\ddagger , \quad (14)$$

$$\Delta S_{\min}^\ddagger + R(\ln n_X - \ln \lambda) \leq \Delta S^\ddagger \leq \Delta S_{\max}^\ddagger + R \ln n_X . \quad (15)$$

Equality in relation (13) holds for all the partial enthalpies being equal to one value. Equality in relation (15), in addition, necessitates the analogous equality of the partial

entropy terms. In the last case the summary entropy differs from the partial activation entropy value by the term $R \ln n_x$ (which is well known as the entropy of mixing of optical isomers to give equimolecular mixture¹³). For a special case of two various activated complexes which are mirror images of one another the summary rate constant is just twice as great as that of the partial process going through one of the activated complexes. Thus the result following organically from the above treatment is the same as that obtained previously by ascribing of $1/2$ to the symmetry number of the activated complex or by statistical factors³.

A useful result follows from the presumption of comparable thermodynamic stability of all the activated complexes

$$K_1^\ddagger \approx K_2^\ddagger \approx \dots \approx K_{n_x}^\ddagger. \quad (16)$$

With this presumption the weighted sum (Eq. (8)) gives the simple arithmetic mean

$$\Delta H^\ddagger \approx \frac{1}{n_x} \sum_{i=1}^{n_x} \Delta H_i^\ddagger. \quad (17)$$

Relation (17) (if presume the validity of relations (16)) allows to carry out correct confrontation between experimental and theoretical activation enthalpy without calculation of entropy terms, *i.e.* on the basis of the partial activation enthalpies only. Of course, it is obvious generally that even mere confrontation at the enthalpy level necessitates to know the respective entropy terms in the case of rate processes with isomerism of the activated complex.

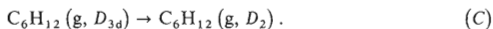
TABLE I

Comparison of Partial and Summary Activation Enthalpies and Entropies of Cyclohexane Isomerization $C_6H_{12} (g, D_{3d}) \rightarrow C_6H_{12} (g, D_2)$ at 298 K

Rate process	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J mol ⁻¹ K ⁻¹
Through the activated complex of C_s symmetry	26.36 ^a	25.02 ^a
Through the activated complex of C_2 symmetry	26.78 ^a	28.62 ^a
Overall process	26.60	32.75

^a Ref.⁸.

Table I summarizes the results for the chair to boat isomerization of cyclohexane



The partial activation parameters are taken from ref.⁸; they were calculated by the quantum-chemical method MINDO/2. The authors found two activated complexes with C_s and C_2 symmetry for the isomerization (C). Whereas the enthalpy terms do not reflect much the phenomenon of the activated complex isomerism, its influence on the activation entropy is significant.

Eqs (8) and (9) allow to calculate summary quantities from partial activation parameters and *vice versa*. The latter case is similar to the problem of equilibrium processes with isomerism of the reaction components dealt with in ref. 14. In the case of rate processes the solution would consist in finding of the terms ΔH_i^\ddagger from experimental temperature dependence of the rate constant k and by a suitably chosen optimization procedure, respectively. Of course, the ΔS_i^\ddagger values would have to be generated theoretically by some quantum-chemical method. This method would give molecular characteristics of the activated complexes for construction of their partition function. This inverse procedure would be important especially in the case when the problem is solvable only at the level of such quantum-chemical methods which afford the enthalpy term of no direct use, whereas the basis for entropy calculation is sufficiently reliable. Possibilities for analysis of experimental data would thus be extended, since the present treatment of experiment¹² gives, of course, only the summary quantity ΔH^\ddagger .

Recently Arnot¹⁵ suggested a new formula for the theory of absolute reaction rates, *viz.*

$$k = 2kTK^\ddagger/h \quad (18)$$

differing from the original Eyring equation¹¹ by the numerical factor 2. If correctness of the factor 2 had to be verified by confrontation of theoretical and experimental rate constants, it would have to be done with the reactions of safely known number of all the activated complexes. From above conclusions it follows that the presence of two energetically close activated complexes can lead to redoubling of the rate constant compared with the case having one activated complex. This effect on the rate constant value is the same as that caused by replacement of the original Eyring equation (3) by the formula suggested by Arnot. Also this case shows the necessity of systematic investigation of isomerism possibilities in the activated complex in connection with theoretical studies of rate processes by means of the theory of absolute reaction rates.

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