STUDIES ON ROTATIONAL BARRIERS IN ALKYL HALOGENIDES BY MEANS OF VIBRATIONAL SPECTROSCOPY

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A simple model describing the influence of the neighbouring molecules on the mechanism of the internal rotation in a given molecule has been proposed which allows the calculation of the barrier hindering the internal rotation in the ideal gaseous state from the temperature dependency of the infrared spectra. To ascertain its adequacy, the kinetics of conformational transitions in seven halogenated alkanes has been investigated, and values of the activation enthalpies accompanying the internal rotation in a solution as well as the rotational barriers in the ideal gaseous state have been determined.

Vibrational spectroscopy represents one of the important methods in studies of the kinetics of conformer transitions. The measurement of the temperature dependency of the intensity ratio of the bands belonging to different conformers (at the varying temperature) makes it possible to calculate the barrier hindering the internal rotation. In this case, the rotational barrier has been considered to be an analogy of the energy of activation pertaining to a chemical reaction[1−4]. In the condensed state, this barrier is influenced by the presence of other molecules. To take this circumstance into account, several interpretations have been proposed[3−5]. The aim of this paper is the construction of a simple model allowing the conversion of rotational barriers measured in the condensed state to the ideal gaseous state and an experimental verification of this model.

THEORETICAL

Kinetics of Conformer Transitions

The substance investigated here represents a system consisting of n conformers which undergo mutual transformations according to the scheme

$$1 \rightleftharpoons 2 \rightleftharpoons \ldots \rightleftharpoons n$$
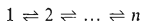
The kinetics of these transformations is described by a set of differential equations for the first-order reactions. The sum of the concentrations of the individual con-

formers is equal to the analytical concentration of the sample, *i.e.* to $\bar{x}$, which does not change with time (x denotes here and in the following text the mole fraction). In the experimental investigation of the kinetics of conformer transitions, the temperature changes with time; therefore, it is possible to choose the temperature as the independent variable. Taking this into account and introducing the equilibrium constants for the mutual conformer transitions, the kinetics of these transformations can be described by this set of differential equations

$$\frac{dx_i}{dT} = \sum_{j=1}^{n-1} a_{ij}x_j + b_i ; \quad i = 1, 2, \ldots, n-1 \tag{1}$$

with

$$a_{ij} = (k_{ji} - k_{ni})/\beta \quad \text{for} \quad i > j$$

$$a_{ij} = (K_{ij}k_{ji} - k_{ni})/\beta \quad \text{for} \quad i < j$$

$$n_{ii} = -\frac{1}{\beta}\left[\sum_{j=i+1}^{n-1} K_{i1}k_{1i} + \sum_{l=1}^{i-1} k_{1i} + k_{ni}(1 + K_{in})\right] \tag{2}$$

$$b_i = k_{ni}\bar{x}\beta^{-1} .$$

The symbol β denotes the velocity of the cooling of the sample, *i.e.* $dT/d\tau$, x_i stands for the mole fraction of the i-th conformer, k_{ij} denotes the rate constant, and K_{ij} the equilibrium constant of the transformation of the i-th to the j-th conformer.

The rate constants of the conformer transitions are given by the Eyring equation:

$$k_{ij} = \frac{kT}{h}\exp\left(\Delta S_{ij}^*/R - \Delta H_{ij}^*/RT\right), \tag{3}$$

where k stands for the Boltzmann constant and h for the Planck constant; the symbol $\neq$ refers to the eclipsed conformation which represents an analogy of the activated complex. The torsional vibration of the rotor about its axis can then be taken as an unstable mode of vibration.

Influence of Neighbouring Molecules on the Rate Constant of Conformer Transition

Because the mechanism of internal rotation in a given molecule is influenced by other molecules, the activation enthalpy ΔH_{ij}^* in Eq. (3) cannot be equalized with the poten-

tial barrier in the ideal gaseous state; the function ΔH_{ij}^{+} can, however, be expressed by means of the following relation

$$\Delta H^{+} = V_0 + \Delta H_{I}, \tag{4}$$

where V_0 denotes the potential barrier in an isolated molecule, and ΔH_{I} is the interaction enthalpy representing the influence of the environment upon the conformer transition.

To describe the influence of the surroundings upon the internal rotation, it is reasonable to consider interaction between a pair of molecules: molecule a, consisting of a nonpolar rotor (alkyl group) and a polar frame, and molecule b, which acts upon the rotor of the first molecule by means of dispersion and induction forces. This interaction is described by the potential U which depends on the mutual position of the two molecules and on the angle of internal rotation ω.

Let us assume that the forces acting upon the rotor can be derived from the potentials which are valid for dispersion and induction effect and which are independent of the mutual orientation of the two molecules[6]. The potential which is responsible for the forces acting on the rotor can then be written as $a(\omega)/r^6$, and the forces influencing the internal rotation, *i.e.* the transition from the position ω_1 to ω_2, are characterized by the potential

$$U(r) = \int_{\omega_1}^{\omega_2} \int_{\infty}^{r} \frac{\partial U(r, \omega)}{\partial r} \, d\omega \, dr = \frac{A}{r^6}. \tag{5}$$

The potential $U(r)$ makes it possible to calculate the internal energy of interaction, *i.e.* ΔU_{I} (see[7]):

$$\Delta U_{I} = \frac{2\pi N_{A}^{2}}{v} \int_{0}^{\infty} U(r) \, g(r; v, T) \, r^2 \, dr, \tag{6}$$

where g is the radial distribution function, N_{A} denotes the Avogadro constant, and v is the molar volume.

In the condensed state, ΔH_{I} is approximately equal to ΔU_{I}. To evaluate the integral in Eq. (6), it is necessary to make a proper choice of the radial distribution function. The most simple choice is $g = 1$ for the intermolecular distance $r \geq r_0$ and $g = 0$ for $r < r_0$; here r_0 denotes the molecular diameter:

$$r_0 = \left(\frac{3v}{4\pi N_{A}} \right)^{1/3}. \tag{7}$$

By substituting into Eq. (6) and integrating, we obtain

$$\Delta H_1^{(11)} = R\alpha_{11}/v_1^2 , \qquad (8)$$

where $\alpha_{11} = 8\pi_A^3 A_{11}/3R$.

Equation (8) holds for interactions between molecules of the same kind. However, the measurements are performed on a solution of the substance in question in a non-polar solvent. To arrive at an adequate description of the interaction between the molecules of the solvent and of the sample, it is necessary to take into account the mean molecular diameter for these two different kinds of molecules. Under the assumption that this mean diameter can be approximated by the arithmetical means of the diameters of the solvent and solute molecules, the contribution to the enthalpy arising from the interaction between the solvent and solute molecules becomes

$$\Delta H_1^{(12)} = 64R\alpha_{12}(v_1^{1/3} + v_2^{1/3})^{-6} , \qquad (9)$$

where α_{12} is defined in an analogous way as α_{11} in Eq. (8); the indices 1 and 2 denote the sample and the solvent, respectively.

Assuming that this system behaves as an ideal solution, the complete activation Gibbs energy of internal rotation is

$$\frac{\Delta G^\ddagger}{RT} = \frac{V_0}{RT} + \frac{\bar{x}\alpha_{11}}{Tv_1^2} + \frac{64(1 - \bar{x})\alpha_{12}}{T(v_1^{1/3} + v_2^{1/3})^6} - \Delta S^\ddagger/R . \qquad (10)$$

The application of Eq. (10) in the rate equations describing the internal rotation requires the knowledge of the temperature dependence of molar volumes. If it is possible to take these volumes to be constant over the experimental temperature range, then the activation enthalpy of conformational transition does not depend on temperature as well, and — at the same time — its dependence on the total concentration of the sample is linear.

A more realistic approach to the description of the influence of the surroundings upon the internal rotation requires to take into account the temperature dependence of molar volumes. When the activation entropy of internal rotation is known, Eq. (10) comprises three unknown parameters that do not depend on temperature and on composition, i.e.: 1) The barrier V_0 in a free molecule in the ideal gaseous state. 2) The interaction parameter α_{11}, characterizing the influence of condensation of the sample upon the internal rotation. 3) The interaction parameter α_{12}, characterizing the effect of solvation of the sample upon the internal rotation.

The simplified model contains only one unknown parameter, i.e. the concentration dependent activation enthalpy $\Delta H^\ddagger$. The combination of Eq. (10) with the rate equations (1) allows the calculation of these parameters from experimental data.

Calculation of Rotational Barriers from Experimental Data

For the measurement of concentration of individual conformers by means of infrared spectroscopy, the stretching vibrations of the carbon–halogen bond are suitable because their frequencies are conformationally sensitive. For all the conformers of a given substance, the absorbancies of the same kind were measured; because of very similar structure of individual conformers, it has been assumed that their absorbance coefficients are the same. This assumption was also used in another paper[3]. Under this assumption, the mole fraction of the i-th conformer is:

$$x_i = A_i \, \bar{x} / \sum_i A_i \,, \qquad (11)$$

where A denotes the absorbancy and $\bar{x}$ the analytical concentration of the sample in the solution which has a constant value.

For the calculation of rotational barriers, it is necessary to make an estimate of the activation entropy of internal rotation. The internal rotation, *i.e.* the transition between two stable conformers, represents an analogy with a monomolecular reaction, where no chemical bond is formed or destroyed. It is therefore possible to use the approximation, according to which the entropy of the unstable eclipsed conformation (analogy with the activated complex) is equal to the arithmetical mean of the entropies of stable conformers. Thus,

$$\Delta S_{ij}^{*} = 0.5 \, \Delta S_{ij}^{0} \,, \qquad (12)$$

where ΔS_{ij}^{*} denotes the activation entropy of internal rotation and ΔS_{ij}^{0} the experimentally accessible entropy change accompanying the conformational transition.

For the temperature dependency of molar volume of the liquid, the following relation has been used[8]:

$$v = \frac{RT_c}{P_c} \, z_c^{1+(1-T_r)^{2/7}} \,, \qquad (13)$$

where z_c denotes the critical value of the compressibility factor, T_c and P_c critical temperature and pressure, respectively; T_r is reduced temperature and R is the gas constant.

The dependence of the concentration on the parameters $(V_0, \alpha_{11}$ and α_{12}, and ΔH^{*}, respectively) is not linear. Therefore, the treatment of the experimental data requires the use of a non-linear regression; the method of calculation is given in the Appendix.

EXPERIMENTAL

Substances used. The barriers hindering internal rotation were measured in the following substances: 2-bromobutane, 2-iodobutane, 2-bromopentane, 2-iodopentane, 2-chlorohexane, 2-chloroheptane, and 2-chlorooctane. The secondary butyl halides have three stable conformers, the remaining substances only two. The wave numbers of the bands corresponding to the carbon––halogen stretching vibrations for the individual conformers were ascertained by measuring the spectra of pure substances. A summary of the wave numbers of the above-mentioned substances in the individual conformers of the above-mentioned substances is given in Table I. All these substances were prepared from the corresponding secondary alcohols. The purity of the substances used and/or prepared was checked by the refractive index and density.

Procedure. The samples for spectral measurements were prepared by weighing, using nujol as the solvent. The infrared spectra were measured on an instrument UR—10. For the low-temperature measurements, the sample cell described in ref.[15] was used. The sample in the cell was cooled by a stream of cold dry nitrogen evaporating from the liquid state in a Dewar vessel, using electrical resistance heating. The rate of the cooling of the sample during the measurement was controlled by the intensity of evaporation of the liquid nitrogen in the Dewar vessel; this cooling rate varied between -0.33 and -0.45 K s^{-1}. The temperature of the sample was measured with the help of a copper-constantan thermocouple and continuously registered on a EZ—10 recorder. The measured spectra were interpreted by the base-line method. The enthalpy and entropy changes accompanying the conformational transition were calculated by the least squares method, using the absorbancies measured at higher temperatures. In the temperature range down to approximately $-110°C$, the dependence of the logarithm of the absorbance ratio on reciprocal temperature is linear because the rate of conformational transition is by an order of magnitude higher than the cooling rate.

RESULTS AND DISCUSSION

First, the values of the activation enthalpy of internal rotation $\Delta H_{ij}^{\ddagger}$ were calculated, assuming that they were temperature independent. The following step included the calculation of the potential barriers V_0 hindering internal rotation in the ideal gaseous state, and of the interaction parameters α_{11} and α_{12}, characterizing the influence of the sample and solvent molecules, respectively, upon the internal rotation.

To get the initial guess of these quantities, Eq. (10) was used.

The plot of the dependence of the activation entropies of the transition between the conformers S_{HH} and S_{CH} on the mole fraction of the sample investigated for the chloro, bromo, and iodo derivatives is shown in Figs 1 to 3. In Fig. 4, the plot of the concentration dependence of $\Delta H_{ij}^{\ddagger}$ for 2-chlorobutane, 2-chloropentane and 3-chloroheptane taken from ref.[3] is shown for the sake of comparison with our values, assuming that the molecular weight of the solvent used (nujol) was nearly the same in both cases. From this figure it is evident that all the concentration dependencies of $\Delta H_{ij}^{\ddagger}$ are linear which complies with Eq. (10). When arriving at this equation, it was assumed that the system in question forms an ideal solution. Because of the nonpolar character of the solvent and only a slightly polar character of the solutes,

this assumption is very approximately fulfilled. The extrapolation of the concentration dependence of activation enthalpy to the value of the mole fraction $x = 1$ should give the value of the barrier, corresponding to the pure liquid state. The extrapolated values in the case of 2-chlorobutane, 2-bromobutane, and 2-iodobutane are 31·4 kJ/mol, 34·2 kJ/mol, and 35·7 kJ/mol, respectively. The barriers hindering internal rotation in these molecules, measured by the ultrasound technique in the liquid state[16], are 23·9 kJ/mol, 27·8 kJ/mol, and 26·4 kJ/mol, respectively. Moreover, from the graphs it is evident that the linear concentration dependencies of the activation enthalpies of internal rotation are very approximately parallel and equidistant. Nearly the same increment of the value of activation enthalpy of internal rotation, accompanying the prolongation of the carbon chain by the CH_2 group, is in accordance with the additivity rule which is valid for a variety of physico-chemical properties of substances.

The calculation of the barriers in the ideal gaseous state and of the interaction parameters α_{11} and α_{12} showed that the scatter of the calculated values in most cases did not exceed 5%. The average values of these quantities are given in Table II. From the data given in Table II, it is evident that the values of the barriers corresponding
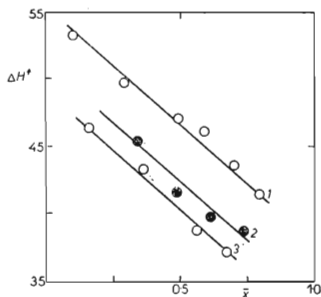

FIG. 1

Activation Enthalpy of Internal Rotation (kJ mol⁻¹) vs the Concentration for Secondary Alkyl Chlorides

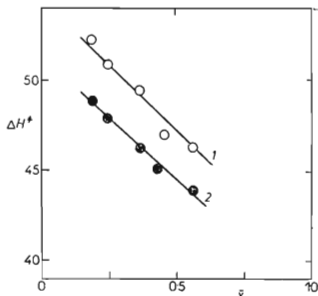*1* 2-Chlorooctane, *2* 2-chloroheptane, *3* 2-chlorohexane.

FIG. 2

Activation Enthalpy of Internal Rotation (kJ mol⁻¹) vs the Concentration for Secondary Alkyl Bromides

1 2-Bromopentane, *2* 2-bromobutane.

TABLE I

Wave Numbers of Carbon–Halogen Stretching Vibrations for Individual Conformers

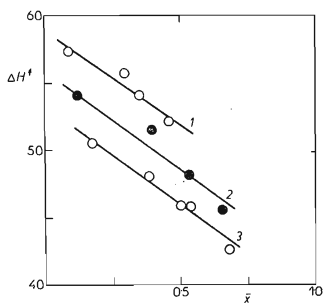| Compound	$\tilde{\nu}_{(exp.)}$			$\tilde{\nu}_{(ref.)}$			Ref.
	S_{HH}	$S_{HH'}$	S_{CH}	S_{HH}	$S_{HH'}$	S_{CH}	
2-Bromobutane	534	582	613	534	581	613	10, 11
2-Iodobutane	488	553	579	488	553	581	10, 11
2-Bromopentane	540		619	537		617	11, 12
2-Iodopentane	493		580	492		580	12
2-Chlorohexane	615		672	611		670	13
2-Chloroheptane	617		670	614		667	14
2-Chlorooctane	613		673	612		672	12, 13

FIG. 3

Activation Enthalpy of Internal Rotation (kJ mol^{-1}) vs the Concentration for Secondary Alkyl Iodides
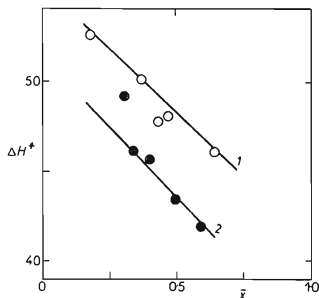
  1 2-Iodopentane, 2 2-iodobutane.

FIG. 4

Activation Energy of Internal Rotation (kJ mol^{-1}) vs the Concentration for the Chloroalkanes (according to Ref.[3])

  1 3-Chloroheptane, 2 2-chloropentane, 3 2-chlorobutane.

to the ideal gaseous state do not change significantly with the length of the carbon chain, especially in the case of molecules containing a greater number of carbon atoms. This fact supports the idea that the height of the barrier hindering internal rotation is, first of all, determined by the character of the groups directly joined to the axis of rotation. The independence of this barrier on the number of carbon atoms in the molecule can also be interpreted on the basis of torsional frequencies. In all the molecules investigated, the rotational barriers are higher than approximately 15 kJ/mol. It is therefore possible to use the torsional approximation, according to which a tor-

TABLE II

Average Values of Rotational Barriers and of Interaction Parameters

Compound	V_{12} kJ mol^{-1}	V_{23} kJ mol^{-1}	V_{13} kJ mol^{-1}	$\alpha_{11} \cdot 10^2$ dm^6 K mol^{-2}	α_{12} dm^6 K mol^{-2}
2-Bromobutane	16·23	16·46	16·14	2·062	0·193
2-Iodobutane	15·60	15·80	15·62	2·634	0·204
2-Bromopentane	16·70			3·454	0·239
2-Iodopentane	15·89			3·760	0·224
2-Chlorohexane	14·89			4·194	0·254
2-Chloroheptane	14·96			5·94	0·306
2-Chlorooctane	15·37			8·30	0·361

TABLE III

Ratio of Torsional and of Skeletal Frequencies

Compounds	Frequency ratio	
	torsional	skeletal
C_4H_9Cl/C_4H_9I	1·23	1·248
C_4H_9Cl/C_4H_9Br	1·16	1·14
C_4H_9Br/C_4H_9I	1·059	1·094
$C_5H_{11}Cl/C_5H_{11}I$	1·46	1·244
$C_5H_{11}Cl/C_5H_{11}Br$	1·242	1·14
$C_5H_{11}Br/C_5H_{11}I$	1·177	1·092

sional frequency is assigned to the hindered internal rotation; this frequency is given by the relation[17]

$$\tilde{v} = \frac{n}{2\pi c} \sqrt{\frac{V_0}{2I_r}}, \qquad (14)$$

where n denotes the symmetry number of internal rotation, c the velocity of light, and I_r the reduced moment of inertia of the internal rotor.

Torsional vibrations of the internal rotor belong to the characteristic molecular vibrations. The torsional frequencies allow the correlation of the measured values of potential barriers with the values estimated from thermodynamic similarity[18]. The torsional frequencies were calculated from Eq. (5), the reduced moments of inertia from the formula

$$1 - I_N \left(1 - \sum_{i=1}^{3} \cos^2 \lambda_i \frac{I_N}{I_i} \right), \qquad (15)$$

where I_N is the moment of inertia of the rotor itself, λ_i is the direction angle between the axis of the rotor and the i-th principal axis of the whole molecule, and I_i is the moment of inertia of the whole molecule about this axis. In the calculations, tetra-edric structure of the molecules was assumed, and for the internuclear distances the following average values were used: C—H 109·3, C—C 154, C—Cl 179·5, C—Br 194 C—I 213·5 pm.

As a reference skeletal vibration, the stretching vibration carbon–halogen was chosen. The corresponding wave numbers are given in Table I; the value for 2-chloro-butane was taken from ref.[10], for 2-chloropentane from ref.[11]. The results of these calculations are summarized in Table III.

The calculated values of the barriers in the ideal gaseous state are in line with the idea about the mechanism of internal rotation and — at the same time — with the values of the barriers measured in the gaseous state for simpler molecules. The model used here is subject to a number of simplifications; therefore, the values of the barriers in the ideal gaseous state should rather be considered to be an estimate.

The results obtained prove the suitability of the suggested model to the description of the influence of the condensed state on the mechanism of internal rotation; the number of the molecules investigated, however, does not allow to draw conclusions of general validity.

APPENDIX

Equation for the Calculation of Rotational Barriers from the Temperature Dependence of the Concentrations of Individual Conformers

The use of the Gauss–Newton iteration procedure requires the calculation of the values of the derivatives having the general formula $\partial y / \partial W_\alpha$, where y denotes the regression formula and W_α is the parameter. In the case of two conformers it holds:

$$x_1 = \exp\left[-\int_0^T Q(u)\,du\right]\left\{x_1^{(0)} \exp\int_0^{T^{(0)}} Q(u)\,du + \frac{\bar{x}}{\beta}\int_{T^{(0)}}^T k_{21}\exp\left[\int_0^u Q(h)\,dh\right]du\right\},$$

$$(A1)$$

where the symbol (O) denotes the values at the starting point of the integration interval; the function Q is given by the formula:

$$Q = k_{21}(1 + K_{12})\,\beta^{-1}.\qquad (A2)$$

For the derivatives of x_1 with respect to the unknown parameters, the following relation holds:

$$\frac{1}{R}\frac{\partial x_1}{\partial V_0} = -G(T)\,x_1 + e^{-F(T)}\left\{x_1^{(0)}e^{F(T^{(0)})}G(T^{(0)}) + \frac{\bar{x}}{\beta}\int_{T^{(0)}}^T e^{F(q)}k_{21}\left[G(q) - \frac{1}{q}\right]dq\right\}$$

and

$$(A3)$$

$$\frac{1}{R}\frac{\partial x_1}{\partial \alpha_1} = -H(T)\,x_1 + e^{-F(T)}\left\{x_1^{(0)}e^{F(T^{(0)})}H(T^{(0)}) + \right.$$

$$\left. + \frac{\bar{x}}{\beta}\int_{T^{(0)}}^T e^{F(q)}k_{21}[H_i(q) - Z_i(q)]\,dq\right\}\qquad (A4)$$

with

$$F(q) = \int_0^q Q(y)\,dy,$$

$$G(q) = -\int_0^q \left[\frac{Q(y)}{y}\right]dy,$$

$$H_i(q) = -\int_0^q Q(y)\,Z_i(y)\,dy,\qquad (A5)$$

$$Z_1(q) = \bar{x}(qv_1^2),$$

$$Z_2(q) = 64(1 - \bar{x})\,q^{-1}(v_1^{1/3} + v_2^{1/3})^{-6}.$$

In the case of a greater number of conformers, the situation is complicated by the fact that the solution of the set of differential equations (1) has to be obtained by a numerical integration. This set of equations can be rewritten in the form

$$\frac{dx_1}{dT} = f_i(x_j, W_\alpha, T), \quad i = 1, \ldots, n-1$$

$$j = 1, \ldots, n-1$$

$$\alpha = 1, \ldots, M\qquad (A6)$$

For the calculation of the derivatives of the mole fractions x_i with respect to the unknown parameters, i.e. W_α, it is advantageous to use the procedure described in the literature[9]. Introducing the notation

$$g_{\alpha i} = \frac{\partial x_i}{\partial W_\alpha}, \qquad (A7)$$

we get for the derivative of Eq. ($A7$) with respect to the temperature

$$\frac{\mathrm{d} g_{\alpha i}}{\mathrm{d} T} = \sum_{j=1}^{n-1} \frac{\partial f_i}{\partial x_j} g_{ij} + \frac{\partial f_i}{\partial W_\alpha} \qquad (A8)$$

the initial condition being $g_{\alpha i}(T^{(0)}) = 0$.

To obtain the gradients ($A7$), it is necessary to solve simultaneously the sets of equations ($A8$) and ($A6$) (M denotes here the number of the unknown parameters to be determined). Taking into account Eqs (1) and (2), we obtain the following relations for the individual partial derivatives

$$\frac{\partial f_i}{\partial x_j} = a_{ij} \qquad (A9)$$

$$\frac{1}{R} \frac{\partial f_i}{\partial V_{\alpha\beta}} = \sum_{j=1}^{n-1} \frac{\partial a_{ij}}{\partial V_{\alpha\beta}} x_j + \frac{\partial b_i}{\partial V_{\alpha\beta}} \qquad (A10)$$

$$\frac{1}{R} \frac{\partial f_i}{\partial \alpha^k} = -Z_k(T) \left[\sum_{j=1}^{n-1} a_{ij} x_j + b_i \right], \qquad (A11)$$

where the function $Z_k(T)$ is given by ($A5$); further it holds

$$\frac{\partial b_i}{\partial V_{\alpha\beta}} = -\frac{\bar{x}}{\beta T} k_{ni} \delta_{\alpha n} \delta_{\beta i} \qquad (A12)$$

$$\frac{\partial a_{ij}}{\partial V_{\alpha\beta}} = \frac{k_{ni} \delta_{\alpha n} \delta_{\beta i} - k_{ji} \delta_{\alpha j} \delta_{\beta i}}{\beta T} \quad \text{for} \quad i < j \qquad (A13)$$

$$\frac{\partial \alpha_{ij}}{\partial V_{\alpha\beta}} = \frac{k_{ni} \delta_{\alpha n} \delta_{\beta i} - K_{ij} k_{ji} \delta_{\alpha j} \delta_{\beta i}}{\beta T} \quad \text{for} \quad i > j$$

$$\frac{\partial \alpha_{ii}}{\partial V_{\alpha\beta}} = \frac{1}{\beta T} \left[\left(\sum_{l=i+1}^{n-1} K_{li} k_{li} + \sum_{l=1}^{i-1} k_{li} \right) \delta_{\alpha 1} \delta_{\beta i} + (1 + K_{1n}) k_{ni} \delta_{\alpha n} \delta_{\beta i} \right], \qquad (A14)$$

where the symbol δ_{ij} stands for the Kronecker delta.

When using the simplified version of the model which assumes the activation enthalpy $\Delta H^{\neq}$ to be temperature independent, the derivatives of the concentrations x_i and of the functions f_1, respectively, with respect to the parameter $\Delta H^{\neq}$, are identical with the derivatives with respect to the barrier V_0.

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