

CALCULATION OF THERMODYNAMIC AND KINETIC PARAMETERS OF DEHYDROCHLORINATION REACTIONS OF CHLORINATED HYDROCARBONS

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A kinetic evaluation is made of the elimination of hydrogen chloride from a large number of mono- and polychlorinated alkanes and alkenes. Activation energies were determined by an empirical method of additivity of dissociation energies of bonds in the ground and transition states. Dissociation energies of C—H, C—Cl, and C—C bonds in different structures were calculated by the Vedeneyev equation. Deviations between experimental and calculated values correspond to a mean uncertainty of ± 6.3 kJ mol⁻¹. Activation entropies were calculated according to an additive rule from entropic contributions of bonds and structural elements for the ground and transition states. Deviations between experimental and calculated frequency factors correspond to a mean uncertainty of ± 0.5 in log (A/s^{-1}). A statistical evaluation of calculated kinetic parameters is given in the conclusion.

In last years much attention has been given to dehydrohalogenation reactions of halogenated hydrocarbons and to addition reactions of halogenated hydrocarbons on π bonds in unsaturated hydrocarbons. Many authors have been trying to find definite procedures for calculating activation energies and activation entropies of these reactions which pass through a 4-centre transition state.

The first method of evaluation of activation energies of addition reactions was worked out by Noyes^{1,2}. His method is based on a simplifying assumption which states that the bond order among four centres of the activated complex is retained and, simultaneously, no charge separation occurs during the activation process. Pahari and Basu^{3,4} worked out a computational technique where partial (activated) bonds are evaluated by a procedure which differs from that used by Noyes. O'Neal and Benson⁵ elaborated a simple computational method for activation entropies which is based on an assignment of vibrational modes to one-electron bonds in a loose 4-centre activated complex. Besides that, Bose, Benson, and Haugen⁶⁻⁸ also developed a new variant of the method for calculating activation energies of addition reactions. In their semiionic model, the polarization of splitting bonds is considered and simultaneously it is assumed that all four interacting centres lie in one plane producing thus a sufficiently rigid quadrangle. Recently Maltman and Tschuikov-Roux^{9,10} have been trying to modify the Benson, Bose, and Haugen model by introducing a variable polarization of splitting bonds. In all the aforementioned methods however, the activation energy of HCl elimination can be found only from the activation energy of the addition reaction between HCl and the alkene double bond and from the reaction enthalpy of the reaction studied.

Presently there is no other direct method for calculating the activation energy of dehydrochlorination reactions except one due to Moin¹⁶ and we employed a modified form of this method in our work. In our earlier papers^{11,12} we evaluated the thermal stability of model polyvinylchloride-based substances according to the activation energy and activation entropy of dehydrohalogenation reactions proceeding through a rigid activated complex. The activation energy was calculated by the method of additivity of dissociation energies of bonds in the ground state and of activated bonds in the transition state. The activation entropy was calculated by a consistent method; we employed the method of additivity of entropies of bonds and entropic structural contributions from the ground and transition states. The additivity methods are equivalent to methods enumerated in the introduction but simultaneously they are more simple. In our work we applied methods of additivity of bond contributions to a larger number of mono- and polychlorinated hydrocarbons with different structural parameters denoting the position of tertiary hydrogen, chloride, and the double bond (inside and at the end of the chain). Computed thermodynamic and kinetic parameters of investigated reactions agree surprisingly well with observed values.

THEORETICAL

From the kinetic point of view the calculations are based on the theory of absolute reaction rates¹³, which gives the following expression for the rate constant characterizing investigated monomolecular elimination reactions

$$k(T) = \kappa e(k_B T/h) \exp(\Delta S^\ddagger/R) \exp(-E/RT), \quad (1)$$

where κ is the transmission coefficient (which is equal to unity in our calculations), $k_B T/h$ is the so called universal frequency factor which depends only on temperature but not on the reactant species or the reaction type, ΔS^\ddagger is the activation entropy and E activation energy. This equation shows that reaction rates of investigated reactions are determined by their activation energies and entropies. In the case of the comparison of calculated and experimental values of the activation entropy, we take calculated and experimental frequency factors, for which the theory of absolute reaction rates of monomolecular reactions gives the expression

$$A = e(k_B T/h) \exp(\Delta S^\ddagger/R). \quad (2)$$

The calculation of the standard heat of reaction was made by the method of group additivity of enthalpic contributions^{14,15}, which gave enthalpies of formation of reactants and products for the standard state at 298 K and 101.325 kPa.

Calculation of Activation Energies

The activation energy was being determined by additivity rules for bond contributions, which had been extended by Moin¹⁶ by the inclusion of the additivity of properties of so called "activated bonds" in the activated complex. According to this empirical method, the activation energy at the temperature of absolute zero is defined by

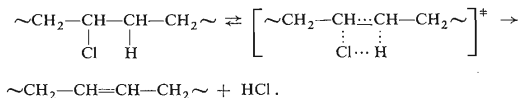
$$E = \sum_i Q_i - \sum_i Q_i^{\ddagger}, \quad (3)$$

where Q_i is the dissociation energy of the splitting bond and Q_i^{\ddagger} is the dissociation energy of the activated bond. Dissociation energies of splitting bonds were determined by a semiempirical method due to Vedeneyev¹⁷. This method yields the following expression for the dissociation energy Q_{R-X} of the bond in the molecule (R—X)

$$Q_{R-X} = E'_{R-X} - \left[\sum_{m,i} M_i \alpha_i \exp(-\omega m) + a E_{\text{conj}} \right] - \left[\sum_{n,j} N_j \alpha_j \exp(-\omega n) + b E_{\text{conj}} \right], \quad (4)$$

where E'_{R-X} is the so called specific energy for the given bond type (e.g. C—H, C—Cl, or C—C) and its value is determined from experimental dissociation energies of bonds of simple hydrocarbons. The second term in Eq. (4) represents the stabilization energy of radical R[•] and M_i is the number of bonds of type i which are connected with the m th carbon of the investigated bond, α_i is the specific stabilization parameter corresponding to the given bond type in the molecule, $\exp(-\omega)$ is a coefficient independent of the bond type in the molecule and equal to 0.4 and E_{conj} is the stabilization energy of conjugation of the free radical and the double bond, and a is the number of conjugated groups. The third term in Eq. (4) represents the stabilization energy of radical X[•] and the symbols used have the same meaning.

It is assumed in the calculation of thermodynamic and kinetic parameters considered that the mechanism of all elimination reactions investigated is monomolecular and can be schematically illustrated as



During the dehydrochlorination one C—H and C—Cl bonds are split and new C=C and H—Cl bonds are created. The activation energy of HCl elimination at absolute zero is then equal to

$$E = Q_{C-Cl} + Q_{C-H} - (Q_{C-Cl}^{\ddagger} + Q_{C-H}^{\ddagger} + Q_{H-Cl}^{\ddagger} + Q_{\pi-\pi}^{\ddagger} + \omega^{\ddagger}), \quad (5)$$

where ω^{\ddagger} is zero for saturated hydrocarbons and assumes different values for unsaturated hydrocarbons: a) with the double bond inside the chain $\omega^{\ddagger} = \beta_{C=C}^{\ddagger}$ and b) with the double bond at the end of the chain $\omega^{\ddagger} = \alpha_{C=C}^{\ddagger}$ ¹¹.

Values of E'_{R-X} , E_{conj} as well as values of parameters α_i are taken from¹¹. The mean uncertainty of dissociation energies of bonds determined by this method is $\pm 4.18 \cdot 10^3 \text{ J mol}^{-1}$. Dissociation energies of activated bonds which appear in investigated compounds were determined from a large number of experimental activation energies by Moin¹⁶ and in our work¹¹. Mean values of dissociation energies of activated bonds and values of parameters $\alpha_{C=C}^{\ddagger}$ and $\beta_{C=C}^{\ddagger}$ are taken again from¹¹. Activation energies of elimination of HCl from those compounds where cumulative double bonds appear during the reaction were determined from the parameter $\lambda_{C=C=C}^{\ddagger} = -74.1 \text{ kJ mol}^{-1}$, which includes the correction for the cumulation of arising double bonds and it was determined from experimental data^{15,20}. Values of activation energies are determined by this method with the mean uncertainty of $\pm 6.3 \cdot 10^3 \text{ J mol}^{-1}$ and they are given in Table I for all hydrocarbons studied.

Calculation of Activation Entropies

Activation entropies of elimination reactions investigated are calculated by the method of additivity of entropic contributions from bonds and taking into account corrections for the conjugation and cumulation of double bonds and for cycles as well as the effect of symmetry and optical activity of molecules according to Mulyava and Shevtchuk¹⁸.

The theory of absolute reaction rates¹³ yields the following definition for the activation entropy

$$\Delta S^{\ddagger} = S^{\ddagger} - S^0, \quad (6)$$

where S^{\ddagger} is the entropy of a molecule in the activated state and S^0 is its entropy in the ground state. The entropy of a simple molecule in the ground state can be calculated as the difference between the sum of entropies of free atoms S_{at}^0 constituting the molecule and the sum of entropic contributions S_{bond}^0 from bonds connecting individual atoms in this molecule diminished by the correction term for the molecular symmetry:

$$S^0 = \sum_{at} S_{at}^0 - \sum_{bond} S_{bond}^0 - R \ln \sigma, \quad (7)$$

where σ is the symmetry number of the molecule.

In the additivity method employed it is assumed that values of entropic contributions can be transferred from individual bonds to different molecules of chlorinat-

ed hydrocarbons. For the study of elimination reactions of more complicated molecules, however, corrections for the so called second order interactions must be included into the entropic scheme; they are corrections for the conjugation, ΔS_{conj}^0 , and cumulation of bonds, ΔS_{cum}^0 , and corrections for the presence of rings, ΔS_{ring}^0 . By including these corrections into Eq. (7) we obtain the following expression for the entropy of the molecule in the ground state

$$S^0 = \sum_k S_{\text{at},k}^0 - \sum_l S_{\text{bond},l}^0 + \sum_m \Delta S_{\text{ring},m}^0 - \sum_n \Delta S_{\text{conj},n}^0 - \sum_v \Delta S_{\text{cum},v}^0 + R \ln (ng_e/\sigma), \quad (8)$$

where n is the number of energetically equivalent 2^p optical isomers (p is the number of structurally different asymmetrical carbons in the molecule) and g_e is the electronic degeneration. The symmetry number σ is determined by the product of the symmetry number σ_e , which refers to the symmetry of the entire molecule, and symmetry numbers σ_d characterizing the symmetry of those parts of the molecule which can rotate around its single bonds¹².

A relation similar to Eq. (8) may be derived for the entropy S^* of the molecule in the activated state. To be able to obtain a fully general expression for S^* we will consider that in the transition state a part of the atoms are connected by generally γ activated bonds, a total of δ activated rings may arise, the conjugation of ε double bonds with newly developing activated double bonds appears, and there are η double bonds cumulated with activated double bonds. Then, according to the notation of Eq. (8), the rest of the molecule contains $l - \gamma$ nonactivated bonds, $m - \delta$ nonactivated rings, $n - \varepsilon$ conjugated double bonds, and $v - \eta$ cumulated double bonds. These considerations yield the following expression for the entropy of the molecule in the activated state:

$$S^* = \sum_k S_{\text{at},k}^0 - \sum_{p=\gamma+1}^l S_{\text{bond},p}^0 - \sum_{r=1}^{\gamma} S_{\text{bond},r}^* + \sum_{s=\delta+1}^m \Delta S_{\text{ring},s}^0 + \sum_{t=1}^{\delta} \Delta S_{\text{ring},t}^* - \sum_{u=\varepsilon+1}^n \Delta S_{\text{conj},u}^0 - \sum_{v=1}^{\varepsilon} \Delta S_{\text{conj},v}^* - \sum_{w=\eta+1}^v \Delta S_{\text{cum},w}^0 - \sum_{z=1}^{\eta} \Delta S_{\text{cum},z}^* + R \ln (n^* g_e^* / \sigma^*). \quad (9)$$

According to relation (6), the activation entropy is then given by

$$\Delta S^* = \sum_{r=1}^{\gamma} S_{\text{bond},r}^0 - \sum_{r=1}^{\gamma} S_{\text{bond},r}^* + \Delta \Delta S + R \ln (\sigma n^* g_e^* / \sigma^* n g_e), \quad (10)$$

TABLE I
 Activation Energies (kJ mol^{-1}), Activation Entropies ($\text{J mol}^{-1} \text{K}^{-1}$), Frequency Factors (s^{-1}), and Standard Enthalpies of Reaction (kJ mol^{-1})

α , β and γ denote the splitting of hydrogen from a primary carbon, secondary carbon, and a carbon at one end of a double bond, respectively

| Substance | Splitting | $E_{a,\text{calc}}$ | $E_{a,\text{exp}}$ | $\langle E \rangle$ | ΔS^\ddagger | $\log A_{\text{calc}}$ | $\log A_{\text{exp,corr}}$ | $\log \langle A \rangle$ | $\Delta_f H^0$ | Ref. | | |
|---------------------------|-----------|---------------------|--------------------|---------------------|---------------------|------------------------|----------------------------|--------------------------|----------------|------|----|----|
| 1-Chloroethane | α | 228.0 | 244.6 ± 6.3 | | 3.2 | 13.40 | 13.64 ± 0.44 | | 67.7 | 25 | | |
| | | | 237.1 ± 0.4 | | | | | 13.07 ± 0.03 | | | 26 | |
| | | | 237.0 | | | | | 13.14 | | | | 27 |
| | | | 249.1 | | | | | 13.82 | | | | 28 |
| | | | | 237.0 ± 0.6 | | | | 13.13 ± 0.05 | | | | 27 |
| 1,1-Dichloroethane | α | 228.9 | 224.0 ± 3.4 | | 3.2 | 13.40 | 13.09 ± 0.24 | | 64.1 | 29 | | |
| | | | 224.0 ± 5.0 | | | | | 13.14 ± 0.04 | | | 29 | |
| | | | 207.3 | | | | | 11.72 | | | | 28 |
| | | | 207.3 | | | | | 11.30 | | | | 30 |
| 1,1,1-Trichloroethane | α | 229.8 | 226.9 | | 21.5 | 14.35 | 13.72 | | 55.7 | 31 | | |
| 1,1,1,2-Pentachloroethane | α | 230.7 | 249.1 | | 3.23 | 13.40 | 13.82 | | 41.7 | 28 | | |
| | | 223.2 | 230.3 ± 5.0 | | | 6.8 | 13.58 | 13.07 ± 0.35 | | 56.0 | 21 | |
| 1-Chloropropane | β | | 230.6 ± 2.9 | | | | 13.13 ± 0.21 | | | 27 | | |
| 1,1-Dichloropropane | β | | 230.3 | | | | 13.44 | | | 32 | | |
| | | 224.1 | 214.4 | | 6.8 | 13.58 | 12.40 | | 52.4 | 33 | | |
| | | 212.0 | 146.1 | 212.4 | 1.7 | 13.32 | 13.42 | 13.40 | 71.4 | 22 | | |
| 1,2-Dichloropropane | β | 223.7 | | | 12.5 | 13.88 | | | 69.0 | | | |
| 2,2-Dichloropropane | α | 212.4 | 215.2 | | 10.8 | 13.79 | 14.20 | | 73.9 | 34 | | |
| 2-Methyl-1-chloropropane | β | 218.4 | 238.2 | | 5.3 | 13.51 | 11.57 | | 50.5 | 33 | | |
| | | | 321.5 | | | | 13.44 | | | | 27 | |
| 1-Chlorobutane | β | 221.3 | 238.7 ± 1.7 | | 6.8 | 13.58 | 13.62 ± 0.1 | | 56.0 | 21 | | |
| | | | 244.1 | | | | 14.24 | | | 35 | | |

| | | | | | | | | | | |
|--------------------------------|----------|-------|-----------------|-------|-------|-------|------------------|-------|-------|----|
| 2,2-Dichlorobutane | α | 208.8 | 230.9 ± 3.1 | 208.2 | 5.1 | 13.49 | 13.26 ± 0.23 | 13.88 | 73.9 | 27 |
| | β | 207.6 | 242.4 ± 2.5 | 210.2 | 8.6 | 13.68 | 14.13 | | 62.2 | 36 |
| 2-Chloro-2,3,3-trimethylbutane | α | 178.4 | 175.4 | | 10.1 | 13.75 | 13.54 | | 66.4 | 23 |
| 1-Chloropentane | β | 220.5 | 231.7 ± 1.5 | | 6.8 | 13.58 | 13.44 ± 0.11 | | 56.0 | 26 |
| 2-Chloropentane | α | 206.5 | 212.3 | 205.2 | 10.8 | 13.79 | 13.77 | 14.17 | 65.7 | 37 |
| | β | 204.8 | | | 14.4 | 13.98 | | | 54.0 | |
| 2,4-Dichloro-2-methylpentane | α | 183.9 | 184.9 | 182.7 | 10.1 | 13.75 | 13.60 | 14.13 | 69.7 | 37 |
| | β | 182.3 | | | 13.6 | 13.94 | | | 62.2 | |
| 1,2-Dichlorohexane | α | 206.4 | 209.3 | 204.6 | 1.7 | 13.32 | 13.08 | 14.05 | 71.4 | 24 |
| | β | 204.4 | | | 14.4 | 13.98 | | | 54.0 | |
| 1,6-Dichlorohexane | β | 220.2 | 242.8 | | 6.8 | 13.58 | 14.15 | | 56.0 | 24 |
| 2,2-Dichloroheptane | α | 206.6 | 188.4 | 205.1 | 5.1 | 13.49 | 12.49 | 13.87 | 73.9 | 24 |
| | β | 204.6 | | | 8.6 | 13.68 | | | 62.2 | |
| 2-Chlorooctane | α | 205.6 | 203.9 | 204.1 | 10.8 | 13.79 | 13.28 | 14.17 | 65.7 | 39 |
| | β | 203.6 | | | 14.4 | 13.98 | | | 54.0 | |
| 1,10-Dichlorodecane | β | 220.1 | 221.9 | | 6.8 | 13.58 | 13.01 | | 56.0 | 24 |
| 6,7-Dichlorodecane | β | 198.3 | 206.4 | 198.2 | 20.2 | 14.28 | 13.28 | 14.45 | 67.0 | 24 |
| | γ | 198.2 | | | 14.4 | 13.98 | | | 54.0 | |
| 1-Chlorododecane | β | 220.1 | 233.2 | | 6.8 | 13.58 | 13.75 | | 56.0 | 24 |
| 1,3-Dichloro-1-pentene | β | 198.6 | 203.1 ± 7.1 | 199.1 | 9.9 | 13.7 | 14.44 ± 0.14 | 13.88 | 54.0 | 39 |
| | γ | 203.4 | | | 7.6 | 13.6 | | | 104.5 | |
| 4-Chloro-1-hexene | β | 190.3 | 191.4 | 190.4 | 9.9 | 13.74 | 13.42 | 13.78 | 54.0 | 38 |
| | γ | 203.9 | | | 14.4 | 13.98 | | | 54.0 | |
| 2-Chloro-1-heptene | β | 236.4 | 230.3 | | 7.8 | 13.63 | 13.25 | | 91.5 | 24 |
| 3-Chloro-2-heptene | β | 235.8 | 233.3 | | 7.8 | 13.63 | 13.59 | | 91.6 | 23 |
| 4-Chloro-3-heptene | β | 232.5 | 238.7 | | 7.8 | 13.63 | 13.64 | | 91.5 | 24 |
| 5-Chloro-3-heptene | β | 141.2 | 183.8 ± 1.9 | 141.2 | -35.1 | 11.40 | 12.85 ± 0.16 | 11.40 | 54.0 | 27 |
| | γ | 200.5 | | | 7.6 | 13.62 | | | 91.5 | |

with

$$\Delta\Delta S = \sum_{t=1}^{\delta} (\Delta S_{ring,t}^{\ddagger} - \Delta S_{ring,t}^0) - \sum_{v=1}^{\epsilon} (\Delta S_{conj,v}^{\ddagger} - \Delta S_{conj,v}^0) - \sum_{z=1}^{\xi} (\Delta S_{cum,z}^{\ddagger} - \Delta S_{cum,z}^0). \quad (11)$$

The expression $(\sigma n^{\ddagger} g_e^{\ddagger} / \sigma^{\ddagger} n g_e)$ is equivalent to the "reaction path degeneracy"¹⁵. For each of the studied molecules, values of the electron degeneracy in the ground and activated states are identical ($g_e = g_e^{\ddagger}$), which makes the term $R \ln (g_e^{\ddagger} / g_e)$ equal to zero.

In the determination of activation entropies of elimination reactions of investigated molecules, the Badgasaryan classification of bonds has been used¹⁹. All C—C bonds are considered as equivalent in all the investigated molecules and the notation C₁—X, C₂—X, and C₃—X is employed for hydrogen or chlorine atoms (X = H or Cl) connected with a primary, secondary, and tertiary carbon, respectively. The following notation was used for unsaturated chlorinated hydrocarbons: C₂²—H and

C₂³—H for $\begin{array}{c} \text{H} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{H} \end{array}$ and $\begin{array}{c} \text{C} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{H} \end{array}$ groups and C₂²—Cl and C₂³—Cl for $\begin{array}{c} \text{H} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{Cl} \end{array}$

and $\begin{array}{c} \text{C} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{Cl} \end{array}$ groups. Values of most entropic contributions from bonds as well as corrections for the second order interactions are taken from¹². Similarly as in the case of activation energies, two $\Delta S_{conj}^{\ddagger}$ contributions were calculated also here: a) for the π bond at the end of the chain and b) for the π bond inside the molecular chain. Besides entropic contributions from¹² it was also necessary to determine some entropic contributions from bonds which are not given in the reported paper; their values are $S_{C_2-C_1}^0 = 124.7 \text{ J mol}^{-1} \text{ K}^{-1}$, $S_{C_3-C_1}^0 = 124.1 \text{ J mol}^{-1} \text{ K}^{-1}$. These entropic contributions were determined from experimental data²⁰.

For a comparison of calculated and experimental data, the frequency factor of dehydrochlorination reactions investigated was calculated by Eq. (2) from the activation entropy. In this comparison, the effect of temperature on the value of the activation energy must be considered, since our calculations of ΔS^{\ddagger} are performed for 298 K whereas experimental data for A were obtained at different temperatures. Calculations of the heat capacity of the molecule in its activated state by the Benson method¹⁵ showed that temperature corrections of the activation entropy at different temperatures do not exceed $0.25 \text{ J mol}^{-1} \text{ K}^{-1}$, which lies far beyond the uncertainty limit with which we are working and, consequently, our calculated activation entropies can be considered as temperature independent. For the comparison of experimental and calculated frequency factors we therefore recalculate experimental frequency factors according to Eq. (2) to the temperature of 298 K.

During dehydrochlorination reactions many chlorinated hydrocarbons can split off their hydrogen atoms either from their primary or secondary carbon atom, respectively from that carbon atom which is at one end of a double bond. We denote by α the splitting of hydrogen from a primary carbon and by β or γ the splitting of hydrogen from a secondary carbon or from a carbon which is at one end of a double bond. The mean uncertainty of calculated activation entropies is $\pm 6.3 \text{ J mol}^{-1} \text{ K}^{-1}$ and they are together with frequency factors given in Table I for all hydrocarbons investigated.

Mean Values of Activation Energies and Frequency Factors

Elimination reactions may generally proceed by several mechanisms. Experimental activation energies and frequency factors represent then certain mean values and therefore, for a correct comparison between experimental and calculated data, it is necessary to find statistical mean values of calculated activation energies and frequency factors corresponding to different elimination mechanisms. Let us assume that an elimination reaction may generally proceed by one of a definite number of mechanisms with different activation energies and frequency factors. In the case of a continuous distribution of activation energies we can define a distribution function $N(E)$ of individual mechanisms so that $N(E) dE$ is proportional to the number of mechanisms corresponding to activation energies from the range $(E, E + dE)$ and to the mean frequency factor $\langle A \rangle$ which characterizes these mechanisms. The rate constant of such an elimination reaction in the normalized form will be then expressed by

$$k_r = \int_0^{\infty} N(E) \exp(-E/RT) dE. \quad (12)$$

Since experimental values of E and A are determined from the dependence $\log k_r = f(1/T)$, we obtain the following relations for statistical mean values of the activation energy and frequency factor

$$\langle E \rangle = -R \left[\frac{\partial \ln k_r}{\partial (T^{-1})} \right]_p = \frac{\int_0^{\infty} EN(E) \exp(-E/RT) dE}{\int_0^{\infty} N(E) \exp(-E/RT) dE} \quad (13)$$

$$\langle A \rangle = k_r \exp(\langle E \rangle / RT) = \int_0^{\infty} N(E) \exp[(\langle E \rangle - E) / RT] dE. \quad (14)$$

In the case of dehydrochlorination reactions investigated, for 11 hydrocarbons only

two independent mechanisms are possible for the HCl elimination. Therefore we will use a discrete two-level distribution function of activation energies E_1 and E_2 . This yields the following expression for the mean value of the activation energy:

$$\langle E \rangle = \sum_m p_m E_m, \quad m = 1, 2, \quad (15)$$

and

$$p_m = k_m / \sum k_m, \quad (16)$$

where k_m is the rate constant of the given monomolecular reaction. Obviously it holds $\sum p_m = 1$. These assumptions together with the introduction of the Dirac δ -function into the derivation of the probability p_m lead to an expression for the mean value of the activation energy

$$\langle E \rangle = E_1 + RT r / (1 + r), \quad r = (A_2/A_1) \exp(-\varepsilon), \quad \varepsilon = (E_2 - E_1)/RT. \quad (17)$$

The mean value of the frequency factor is then given by

$$\begin{aligned} \langle A \rangle &= \sum_{i=1}^2 \int_0^{\infty} A_i \exp [(\langle E \rangle - E)/RT] \delta(E - E_i) dE = \\ &= A_1 (1 + r) \exp [\varepsilon r / (1 + r)]. \end{aligned} \quad (18)$$

Mean values of activation energies and frequency factors of the 11 hydrocarbons, a comparison between statistical mean values and experimental data and values of standard enthalpies of all studied reactions are given in Table I.

RESULTS AND DISCUSSION

Calculated values of activation energies and activation entropies of dehydrochlorination reactions of 28 mono- and polychlorinated hydrocarbons are given in Table I. It is obvious that the outlined methods for calculating activation energies and activation entropies of the HCl elimination, which are based on the principle of additivity of bond and structural contributions from both the ground and the activated state, are successful also in the prediction of the investigated kinetic parameters of polychlorinated hydrocarbons. A comparison between the other method discussed in the introduction into this work and our method cannot be performed since the former methods, as far as we know, were applied to calculations of thermodynamic and kinetic parameters of dehydrochlorination reactions of chlorinated hydrocarbons. However, there are results of Benson, Bose, and Haugen computations⁶⁻⁸ of these parameters for addition reactions between halogen hydrides and polar olefins, where these methods proved unsuccessful⁹.

Measured activation energies indicate a definite systematic substitution effect of chlorine atoms. It may be verified that, according to the position of the chlorine atom in the chain of the investigated molecule, highest activation energies are found for compounds with primary chlorine and they decrease during the transition to compounds with secondary chlorine. A significant decrease in activation energies is observed for compounds with tertiary chlorine (2-chloro-2,3,3-trimethylbutane and 2,4-dichloro-2-methylbutane). Experimental values also reveal the effect of the double bond inside the chain, which manifests itself in a decrease of the activation energy (5-chloro-3-heptane). Calculated values of the activation energy fully correspond with the indicated trend of experimental values.

For some of the hydrocarbons we may observe in Table I (1-chloroethane, 1,1-dichloroethane, 2,2-dichloropropane, 1-chlorobutane) a remarkable scatter in experimental values of activation energies, which can be ascribed to the absence of some experimental conditions necessary for the investigation of monomolecular dehydrochlorination reactions. Most important of these conditions are⁴⁰: a) the first-order kinetics at high pressures, b) the Lindemann "fall-off" effect at low pressures, c) the reaction proceeds without any induction period, and d) the absence of inhibitors and accelerators (atoms, radicals).

The method employed for the computation of activation energies does not take into account the change of the thermal energy (internal energy) which accompanies the activation process; due to this reason the computed activation energies must be related to absolute zero. A comparison between experimental and calculated activation energies would require an adjustment of these values to a common temperature, in our case to 298 K; this would again require the knowledge of the molar heat capacity of the transition state. Corrections obtained in this manner are never higher than $\pm 4 \text{ kJ mol}^{-1}$, which is fully covered by the uncertainty of this method and, consequently, in the case of activation energies the temperature corrections were neglected. It follows from Table I that most deviations between experimental and calculated activation energies lie in the range of the mean uncertainty of $\pm 6.3 \text{ kJ} \cdot \text{mol}^{-1}$, which amounts on the average to 4.3% of the absolute value of the activation energy. The maximum deviation between the experimental and calculated activation energy is 21 kJ mol^{-1} , which represents 10.7% of the absolute value of the activation energy. The observed agreement between experimental and calculated values is very good, especially if we consider the induction and mesomeric effects of chlorine atoms^{41,42} as well as the effect of conjugation of the π -bond at the end of or inside the substrate on the character of the transition state.

Table I also reports values of activation entropies and frequency factors of investigated dehydrochlorination reactions in the gaseous phase. The results only confirm the success of the method in the extension of the additivity principle of bond entropies and structural entropic contributions from molecules in the ground state to molecules in the activated state. Although the difference between calculated and

experimental frequency factors is for some compounds as large as 1.5 in $\log(A/s^{-1})$ units, most differences lie in the uncertainty range of ± 0.5 in $\log(A/s^{-1})$ units, which is considered in the literature as a good agreement between experimental and calculated deviations¹⁵. Higher deviations are observed for some experimental values of 1,1-dichloroethane and 2,2-dichloropropane, however, maximum deviations between calculated and experimental values of activation energies were also found here and even the experimental values for these substances exhibit a large scatter.

If we compare computed values of frequency factors with those determined by the O'Neal-Benson⁵ method, which is based on a suitable assignment of vibrational modes to structural units of the ground and transition states, we realize that the uncertainty of our results is fully within the uncertainty range of the O'Neal-Benson method.

It can be shown that frequency factors of many chlorinated hydrocarbons reach values of $10^{13} s^{-1}$. Therefrom we can deduce that changes in the rate of dehydrochlorination produced by changes in the substrate structure manifest themselves above all in values of activation energies and to a relatively lesser extent in values of activation entropies (Table I).

An estimate of the reliability of the employed methods may be found by analyzing the obtained results. Although the Vedeneyev relation for calculating dissociation energies of bonds takes into account the effect of structural factors on a values of the dissociation energy of a bond, the effect of different conformal substituents on this value is neglected. The uncertainty in values of activation parameters ω^\ddagger , which include the effect of the double bond inside and at the end of the chain, is somewhat higher since presently only few accurate experimental values of activation energies are available for unsaturated hydrocarbons. It would be also possible to include the effect of temperature into the parameter ω^\ddagger , because interactions between the π -bond in the chain and the partial π -bond in the activated complex change with changing temperature, which leads to changes in the torsion potential of the single C—C bond.

The uncertainty in computed frequency factors could be improved by determining force constants of bonds in the ground and activated states by the GF-analysis. It would be possible in this manner to take into account specific effects of structural properties of substrates, especially on relevant frequencies in the transition state.

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