On thermal dehydrochlorination of model compounds for poly(vinyl chloride)
V. Frequency factor calculations

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Dedicated to Professor Ing. RNDr. A. Tkáč, DrSc., in honour of his 60th birthday

This paper deals with the statistical thermodynamic method applied to calculation of activation entropies and determination of frequency factors for thermal dehydrochlorination of 49 model substances of PVC. The entropic contributions of stretching and bending vibrations, restricted internal rotations, and torsional vibrations have been determined. The degeneration of the reaction pathway has been also taken into account. The calculations have been carried out on the assumption that the investigated reactions follow the monomolecular mechanism through a four-centric, planar and polar activated complex. The calculated frequency factors are statistically averaged and compared with the experimental values obtained from literature. There is a good agreement of the measured and calculated frequency factors because the differences between these values vary in the interval $\Delta \log (A/\mathrm{s}^{-1}) = \pm 0.5$.

В работе применяется статистическо-термодинамический метод расчета энтропий активации для определения частотных факторов термического дегидрохлорирования 49 модельных соединений поливинилхлорида. Определены энтропические составляющие валентных и деформационных колебаний, ограниченного внутреннего вращения и крутильных колебаний, причем учитывается вырождение реакционного пути. Расчеты проводятся в предположении, что изучаемые реакции проходят по мономолекулярному механизму через четырехцентрический, плоский, полярный активированный комплекс. Рассчитанные частотные факторы статистически усреднены и сравнены с экспериментальными значениями, указанными в литературе. Было достигнуто хорошее согласие между измеренными и рассчитанными частотными факторами. Отклонения последних находятся в пределах $\Delta \log (A/\mathrm{c}^{-1}) = \pm 0,5$.

The reactions involving elimination of hydrogen halides from halogenated saturated and unsaturated hydrocarbons belong to the class of elimination reac-

tions which are in the limelight from the cognitional as well as technological viewpoint [1, 2]. The reactions studied in this paper belong to the group of monomolecular reactions which are by their character not so simple that the mechanism of their decomposition could be solved by means of *ab initio* methods and on the other hand, they are not so complicated that they could not be elucidated by means of semiempirical methods of chemical physics and statistical thermodynamics.

This class of elimination reactions has also been given attention from the standpoint of the RRKM theory [3, 4] which is much dependent on the estimation of distribution of the quantum states due to the collisions of the energized molecular systems. The pertinent quantities are the density of quantum states for a given energy and the number of quantum states with energies which are less than this value. The estimation of these quantities is a common source of difficulties in the application of the RRKM theory. Another approach to estimation of the activation parameters for hydrogen halide elimination is based on the theory of absolute reaction rates and the use of the laws of statistical mechanics.

The aim of this study is the calculation of frequency factors for hydrogen chloride elimination from 49 alkyl and alkenyl chlorides. Many of the valuated chlorinated hydrocarbons represent model substances for studying the thermal dehydrochlorination of PVC the elucidation of which as well as the destruction of some other technically important polymers, for instance poly(vinyl alcohol) [5], is a subject of the present interest of technologists [6]. The frequency factors are determined on the basis of the statistical thermodynamic procedure involving evaluation of the *Benson* four-centric planar model of activated complex [7]. The calculated values of frequency factors were statistically averaged by means of the activation energies determined by us earlier [8] and compared with the experimental data found in literature.

Specification of the model for the reaction of hydrogen chloride elimination

In calculating the frequency factors, we have started from the assumption that all investigated alkyl and alkenyl chlorides thermally decompose according to the monomolecular mechanism of the first-order reactions and the progress of reaction is affected neither by inhibitors nor accelerators. *O'Neal* and *Benson* [7] proposed the following model of planar four-centric activated complex (Scheme 1)
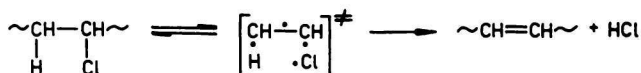
Scheme 1

This model of activated complex is characterized as the so-called "loose" activated complex which consists of two one-electron $C \cdot H$ and $C \cdot Cl$ bonds with the Pauling bond order 0.5 of the arising C—H and C—Cl bonds and a three-electron C—C bond with the order 1.5 which is the germ of the arising $C = C$ π bond. The interaction between the atoms H and Cl in the activated complex is considered to be very weak, the order being much less than 0.5.

Since the experimental data refer to the high-pressure region, the experimental high-pressure Arrhenius parameters are defined by the following equations

$$E_\infty = k_B T^2 \, \mathrm{d} \ln k_\infty / \mathrm{d}T \qquad (1)$$

$$E_\infty / k_B T = T(\mathrm{d} \ln k_\infty / \mathrm{d}T) \qquad (2)$$

where k_∞ is the high-pressure rate constant for the reaction under consideration.

The theory of absolute reaction rates of monomolecular reactions which is the basis for the calculation of frequency factors in this paper gives the subsequent expression for the value of high-pressure frequency factor [9]

$$A_\infty = (e k_B T / h) \exp(\Delta S^* / R) \qquad (3)$$

where k_B is the Boltzmann constant, h is the Planck constant, and ΔS^* stands for the activation entropy of the investigated dehydrochlorination reaction. The activation entropies have been calculated by systematic procedure involving attribution of bending, stretching, and torsional frequencies to activated complexes with respect to degeneration of the reaction pathway and to changes in internal rotations of a molecule.

Determination of contribution to activation entropy

From the standpoint of statistical thermodynamics, the entropy of a molecule may be determined as the sum of contributions of the translational, vibrational, and rotational motion as well as contributions due to internal rotation of particular groups, symmetry, electron degeneration, and optical activity of this molecule. For the dehydrochlorination reactions we assume that no significant changes in translational entropy take place in the course of reaction and small changes in total rotational entropy may be neglected. As the reactants and investigated transition states occur in the fundamental singlet electron state, the contribution of electron degeneration may be also omitted. Each of other contributions to the activation entropy is thus given as difference between the values of this contribution for a molecule in the transition state and in initial state. The activation entropy of the investigated reaction may be calculated as follows

$$\Delta S^* = \Delta S^*_{vib} + (- S^0_{hr} + S^*_{tors}) + \Delta S^*_{sym} \qquad (4)$$

where $\Delta S_{vib}^{\neq}$, S_{hr}^{0}, $S_{tors}^{\neq}$, and $\Delta S_{sym}^{\neq}$ are the contribution of vibrational activation entropy changes, the entropic contribution of hindered internal rotation in the initial state, the entropic contribution of torsional vibration about the arising double bond, and the entropic contribution including the changes in symmetry and optical activity.

Contribution of vibrational motion

The calculation of entropic vibrational contributions is based on the attribution of normal vibrations to the molecule in initial state and in transition state. The particular normal vibrations are transferable and for this reason, we may assign constant values of vibrational frequencies to particular normal vibrations and use them for determining the entropic vibrational contributions on the basis of statistical thermodynamic relations. A molecule consisting of N atoms displays $3N$-6 normal vibrations comprising N-1 stretching and $2N$-5 bending vibrations. The total number of bending vibrations includes internal and external bending vibrations, restricted internal rotations of groups about single bonds, and out of plane bending vibrations. The entropic vibrational contributions are determined for molecules in harmonic approximation.

It results from the quantum mechanics that the total vibrational energy of a molecule represented by the set of harmonic oscillators in the coordinate system of normal coordinates is given by the following expression

$$E = hc \sum_{i=1}^{3N-6} \bar{v}_i \left(v_i + \frac{1}{2} \right) \qquad v_i = 1, 2, \ldots \qquad (5)$$

where the wavenumbers $\bar{v}_i$ and vibrational quantum numbers v_i belong to particular normal vibrations. If we denote $u_i = hc\bar{v}_i / k_B T$, then we obtain from statistical physics for the vibrational partition function of polyatomic molecule [10]

$$Q_{vib} = \prod_i \sum_i \exp(-u_i v_i) \qquad (6)$$

By modifying this partition function for one normal vibration and inserting into the expression for entropy of the Gibbs canonical ensemble, we may obtain the entropic contribution of a mole of harmonic oscillators in the form [11]

$$S_{vib} = R[u/(e^u - 1) - \ln(1 - e^{-u})] \qquad (7)$$

The vibrational entropic contributions of stretching and bending vibrations of the investigated molecules were determined for the initial state by means of the vibrational frequencies presented in papers [7, 12, 13].

Because of the short life-time, we cannot experimentally ascertain the vibrational frequencies of the normal vibrations incidental to the activated bonds in

Table 1

Vibrational frequencies of normal vibrations and the corresponding entropic contributions of stretching and bending vibrations in the initial and transition state at 600 K

Type of vibration	$\bar{\nu}_i/\mathrm{cm}^{-1}$	$S_i/\mathrm{J\ mol}^{-1}\,\mathrm{K}^{-1}$
C—C	1000	2.76
C=C	1650	0.79
C—H	3000	0.04
C—Cl	650	5.40
C$\doteq$C	1300	1.59
C · H	2200	0.25
C$\diagup$C$\diagdown$C	420	8.58
H$\diagup$C$\diagdown$H ^{a}	1450	1.17
H$\diagup$C$\diagdown$C ^{a}	1150	2.09
Cl$\diagup$C$\diagdown$C	400	8.96
Cl$\diagup$C$\diagdown$H	700	4.90
Cl$\diagup$C$\diagdown$Cl	280	11.81
C$\diagup$C$\diagdown$C	420	8.58
H · C$\diagdown$C	800	4.06
H · C$\diagdown$H	1000	2.76
Cl · C$\diagdown$C	280	11.81
Cl · C$\diagdown$H	700	4.90
H$\diagup$C$\diagdown$C	1150	2.09
Cl · C$\diagdown$C	280	11.81
Cl$\diagup$C$\diagdown$C	400	8.96
Cl · C$\diagdown$Cl	280	11.81
H · C$\diagdown$Cl		

a) Bending vibrations of the wagging and twisting type.

activated complex. The activation vibrational frequencies of normal vibrations have been found in harmonic approximation from the force constants determined on the basis of the empirical *Badger* rule [14] according to which the force constant of a certain bond is given by the expression

$$k^{-(1/3)} = a_{ij}(d_n - b_{ij}) \qquad (8)$$

where d_n is the length of bond of the n-th order and a_{ij}, b_{ij} are constants depending on the pair of bonded atoms i and j [15]. The individual types of normal vibrations occurring in the investigated compounds as well as their vibrational frequencies and entropic contributions (for 600 K) are given in Table 1.

The influence of anharmonicity on the value of entropic vibrational contributions of linear anharmonic oscillator was also appreciated by solving the Schrödinger equation for the Morse potential. The obtained characteristic values of energy of anharmonic oscillator were used for formulating the anharmonic partition function and the expression for the entropic contribution of anharmonic vibration in the form [16]

$$S_{\text{vib, anh}} = R\{u/(e^u - 1) - \ln(1 - e^{-u}) + \ln[1 + 2x\ u/(e^u - 1)^2] +$$
$$+ [2u\ e^u/(e^u - 1) - 1]2x\ u/[(e^u - 1)^2 + 2x\ u]\} \qquad (9)$$

where $x = hv/4D$, v is the fundamental vibrational frequency, D is the dissociation energy of bond, and the meaning of u is like in eqn (6). By using eqn (9), the entropic contributions of some vibrations were calculated and it was revealed that the differences between harmonic and anharmonic entropic contributions were of decimal order 4×10^{-2} J mol^{-1} K^{-1} and thus occurred in the interval of the errors accompanying the determination of experimental frequency factor. On the basis of these facts, we consider the use of harmonic approximation to be justifiable.

Contribution of hindered internal rotations

As for the entropic scheme of polyatomic molecules, the greatest entropic contribution to activation entropy is the contribution of hindered internal rotations of the internal groups of molecule about the single C—C σ bonds. The hindered internal rotations take place if their potential barrier is comparable with the energy of the thermal vibration $k_B T$. The potential function of these rotations is a periodic function of the angle of rotation φ and may be written in the following form [17]

$$V = \frac{1}{2} V_0(1 - \cos \sigma' \varphi) \qquad (10)$$

where V_0 is the height of the potential barrier and σ' is the number of symmetry characterizing internal symmetry of the rotating groups. The entropic contributions

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of restricted internal rotations are to be determined by means of the partition function for free rotation

$$Q_{\text{rot}, t} = (\sqrt{\pi}/\sigma')(8\pi^2 I_r k_B T/h^2)^{1/2} \qquad (11)$$

which can be obtained by the use of the characteristic values of energy of free rotor. I_r is the reduced moment of inertia and other symbols have equal meaning as before. After determining the entropic contribution of free rotation on the basis of properties of the Gibbs canonical ensemble, we estimated the correction with respect to restricted internal rotation as a function of V_0/RT by using the procedure put forward by *Pitzer* [17]. We studied the hindered internal rotations in the investigated molecules by means of the data about the rotation of single model groups presented by *Benson* [7]. We approximated all cases of restricted internal rotation occurring in the investigated molecules by the entropic contributions of these model groups. The potential barriers, partition functions of free rotation and entropic contributions of free rotation (S_{fr}^0) and hindered internal rotation (S_{hr}^0) for individual model groups at 600 K are given in Table 2.

Owing to increasing polarity of the activated bonds, the potential barrier of the hindered internal rotations substantially rises during the formation of activated complex. Then these rotations turn into torsional vibrations. This type of vibrations was also valuated by means of the model compounds (methyl-substituted ethylenes) with three-electron bonds as proposed by *Benson* [7]. According to papers [7, 18], the half-values of torsional frequencies of the vibrations about the corresponding double bonds are regarded as torsional frequencies of the vibrations about the three-electron bonds. The model methyl-substituted ethylenes and torsional

Table 2
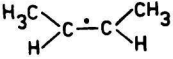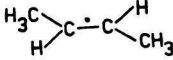
Potential barriers, partition functions of free rotation, and entropic contributions of free and hindered internal rotation at 600 K

Model group		Barrier V_0/kJ mol^{-1}	Partition function Q_t	S_{fr}^0/J mol^{-1} K^{-1}	S_{hr}^0/J mol^{-1} K^{-1}
Methyl:	CH_3-	12.56	15.6	27.21	24.28
Ethyl:	CH_3CH_2-	14.65	52.0	37.26	34.75
Isopropyl:	$(CH_3)_2C<$	16.75	65.0	38.94	34.65
tert-Butyl:	$(CH_3)_3C-$	18.84	72.0	39.77	36.34

frequencies of the vibrations about the $C = C$ π bonds and $C \dot{-} C$ bonds are given in Table 3.

Table 3

Wavenumbers of torsional vibrations in the methyl-substituted ethylenes

Compound		$\tilde{v}/cm^{-1}$ [a]	$\tilde{v}/cm^{-1}$ [b]
Ethene	$CH_2 \dot{-} CH_2$	1000	500
Propene	$CH_2 \dot{-} CHCH_3$	800	400
Isobutene	$(CH_3)_2C \dot{-} CH_2$	700	350
cis-2-Butene	$\begin{smallmatrix} H_3C \\ H \end{smallmatrix}>C \dot{-} C<\begin{smallmatrix} CH_3 \\ H \end{smallmatrix}$	400	200
trans-2-Butene	$\begin{smallmatrix} H_3C \\ H \end{smallmatrix}>C \dot{-} C<\begin{smallmatrix} H \\ CH_3 \end{smallmatrix}$	300	150
2-Methyl-2-butene	$(CH_3)_2C \dot{-} CHCH_3$	250	125
Tetramethylethene	$(CH_3)_2C \dot{-} C(CH_3)_2$	210	105

a) Wavenumber of torsional vibration about the double bond; *b*) wavenumber of torsional vibration about the three-electron bond.

Nevertheless, not only the methyl groups but also the chloromethyl groups bonded to the arising $C \dot{-} C$ bonds are present in the investigated molecules. *O'Neal* and *Benson* [7] have shown that the frequencies of the torsional vibrations about the three-electron bonds in the methyl-substituted ethylenes ($\tilde{v}_1$) and chlorosubstituted ethylenes ($\tilde{v}_2$) may be expressed within the accuracy $\pm 50 \times \times 10^2$ m^{-1} by the following expression

$$\tilde{v}_1/\tilde{v}_2 = (\mu_2/\mu_1)^{1/2} \qquad (12)$$

where μ_1 and μ_2 are reduced weights of the compared groups. Thus all torsional frequencies of the vibrations about the three-electron bonds in halogenated hydrocarbons were determined and their entropic contributions were subsequently calculated according to eqn (7).

Contribution of symmetry and optical activity

The value of activation entropy of elimination reactions is also influenced by the changes in overall symmetry and optical activity of molecule. As we have shown in paper [8], the contribution to activation entropy due to these changes may be expressed by the equation

$$\Delta S_{\text{sym}}^{+} = R \ln \left(\frac{\sigma n^{+}}{\sigma^{+} n} \right) \qquad (13)$$

where σ and σ^{+} are overall numbers of symmetry of molecule in initial state and transition state while n and n^{+} stand for overall numbers of energetically equivalent optical isomers in these states. These numbers are given by the formula 2^{p} where p is the number of structurally different asymmetric carbon atoms in a molecule. The determination of the quantities σ, σ^{+}, n, and n^{+} has been discussed in paper [8].

Results and discussion

After determining all discussed entropic contributions, we determined the activation entropies according to eqn (4) and calculated the frequency factors for HCl elimination from 49 model substances of PVC according to eqn (3). All calculations were made for the temperature of 600 K. This temperature is the mean temperature of the temperature intervals presented in literature for which the frequency factors were experimentally determined. We compared these values with our calculated results. In order to find out the error in the value of activation entropy due to the use of the mean temperature $\langle T \rangle = 600$ K, we determined the dependence of ΔS^{+} on temperature for $T \in \langle 400$ K, 700 K$\rangle$ by means of the experimental data of frequency factor using the method of calculation based on group additivity of heat capacities [19]. It has been revealed that the correction with respect to temperature for the value of ΔS^{+} in the investigated temperature interval is always less than 0.4 J mol^{-1} K^{-1} and thus it entirely fits in the interval of experimental reliability for the determination of frequency factor so that the use $\langle T \rangle = 600$ K may be regarded as justifiable.

Some of the investigated chlorinated hydrocarbons are able so eliminate HCl that they split off a hydrogen atom either from the primary or secondary carbon atom and casually from a carbon atom bonded to the carbon atom of a double bond. Therefore we adopted the denotation α for elimination of hydrogen atom from the primary carbon atom and the denotations β and γ for elimination of hydrogen atom from the secondary carbon atom or the carbon atom bonded to the carbon atom of a double bond. It results from these facts that the elimination of HCl from some compounds may proceed by two mechanisms, i.e. elimination of

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Table 4

Values of entropic contributions, activation entropies, and frequency factors
Comparison with experimental data

Compound	$\Delta S^{\ddagger}_{vib}$	$\Delta S^{\ddagger}_{sym}$	$S^{\ddagger}_{tors}$	S^{o}_{br}	$\Delta S^{\ddagger}$	$\log (A_{calc}/s^{-1})$	$\log (\langle A \rangle /s^{-1})$	$\log (A_{exp}/s^{-1})$	Ref.
	J mol^{-1} K^{-1}	J mol^{-1} K^{-1}	J mol^{-1} K^{-1}	J mol^{-1} K^{-1}	J mol^{-1} K^{-1}				
1-Chloroethane	7.33	9.13	5.53	24.28	−2.26	13.41		13.93 ± 0.44	[24]
								13.37 ± 0.03	[23]
								13.44	[22]
								14.13	[20, 21]
								13.43 ± 0.05	[25]
1,1-Dichloroethane	14.82	9.13	9.76	24.28	9.43	14.02		13.38 ± 0.24	[27]
								13.44 ± 0.40	[22]
								12.03	[20, 21]
								11.60	[26]
1,2-Dichloroethane	2.01	5.78	23.70	33.50	−2.01	13.42		11.90 ± 1.00	[28]
1,1,1-Trichloroethane	4.48	18.30	9.84	24.28	8.34	13.95		14.02	[29]
								13.91	[29]
1,1,1,2,2-Pentachloro-ethane	5.23	9.13	26.96	33.91	3.05	13.37		14.12	[20, 21]
1-Chloropropane	0.04	5.78	19.59	33.50	−8.09	13.11		13.37 ± 0.35	[30]
								13.43 ± 0.21	[25]
								13.70	[31]
2-Chloropropane	3.81	14.91	10.17	24.28	4.61	13.77		13.36	[20, 21]
1,1-Dichloropropane	2.38	11.51	19.64	33.49	0.04	13.54		12.70	[36]
2,2-Dichloropropane	0.96	14.91	10.26	24.28	1.85	13.63		14.50	[37]
								11.87	[38]

Table 4 (Continued)

Compound	$\Delta S_{vib}^{\neq}$	$\Delta S_{sym}^{\neq}$	$S_{tors}^{\neq}$	S_{hr}^{0}	$\Delta S^{\neq}$	$\log (A_{calc}/s^{-1})$	$\log (\langle A \rangle/s^{-1})$	$\log (A_{exp}/s^{-1})$	Ref.
	J mol^{-1} K^{-1}	J mol^{-1} K^{-1}	J mol^{-1} K^{-1}	J mol^{-1} K^{-1}	J mol^{-1} K^{-1}				
2-Methyl- -1-chloropropane	0.42	0	22.19	33.08	−10.47	12.99		13.96	[31]
								13.75	[25]
1,2-Dichloropropane	α 0.04	5.78	19.64	33.45	−7.99	13.11		13.73	[20, 21]
	β 0.42	0	22.19	33.08	−10.47	13.05			
1-Chlorobutane	0.04	5.78	19.59	33.50	−8.09	13.11		13.92 ± 0.10	[30]
								14.55	[38]
								13.57 ± 0.23	[25]
								14.44	[27]
2-Chlorobutane	α 3.81	9.13	10.17	24.28	−1.17	13.47		13.69	[39]
	β 2.89	5.78	19.64	34.75	−6.44	13.19	13.65	13.98 ± 0.25	[40]
								14.05 ± 0.13	[41]
2,2-Dichlorobutane	α 0.96	14.91	10.26	24.28	1.85	13.63		14.48	[37]
	β 0.04	11.56	20.26	34.75	−2.92	13.38	13.82		
1-Chloropentane	0.04	5.78	19.59	33.50	−8.09	13.11		13.75 ± 0.11	[25]
2-Chloropentane	α 3.81	9.13	10.17	24.28	−1.17	13.47		14.07	[32]
	β 2.89	5.78	19.64	34.75	−6.44	13.19	13.65		
3-Chloropentane	2.89	11.56	19.64	34.75	−0.66	13.50		12.28	[42]
								14.37	[32]
2,4-Dichloropentane	α 3.81	9.13	10.17	24.28	−1.17	13.47		13.37 ± 0.29	[32]
	β 2.89	5.78	19.64	34.75	−6.44	13.19	13.65	18.36	[42]
2,5-Dichlorohexane	α 3.81	9.13	10.17	24.28	−1.17	13.47		12.62	[42]
	β 2.89	5.78	19.64	34.75·	−6.44	13.19	13.65		
1,2-Dichlorohexane	α 4.86	5.78	24.24	33.08	1.80	13.62		13.39	[42]
	β 2.89	5.78	19.64	34.75	−6.44	13.19	13.75		
1,6-Dichlorohexane	0.04	5.78	19.59	33.49	−8.08	13.11		14.46	[42]

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Table 4 (Continued)

Compound	$\Delta S^{\ddagger}_{\text{vib.}}$ J mol⁻¹ K⁻¹	$\Delta S^{\ddagger}_{\text{sym}}$ J mol⁻¹ K⁻¹	$S^{\ddagger}_{\text{tors}}$ J mol⁻¹ K⁻¹	S^{0}_{hr} J mol⁻¹ K⁻¹	$\Delta S^{\ddagger}$ J mol⁻¹ K⁻¹	$\log(A_{\text{calc}}/\text{s}^{-1})$	$\log(\langle A\rangle/\text{s}^{-1})$	$\log(A_{\text{exp}}/\text{s}^{-1})$	Ref.
2,2-Dichloro-	α 0.96	14.91	10.26	24.28	1.85	13.63		12.80	[42]
heptane	β 0.04	11.56	20.26	34.75	−2.89	13.38	13.81		
1,4,7-Trichloro-	β 0.04	5.78	19.59	33.49	−8.08	13.11		12.28	[42]
heptane	γ 2.89	5.78	19.64	34.75	−6.44	13.19	13.22		
2,4,6-Trichloro-	α 3.81	9.13	10.17	24.28	−1.17	13.47		14.14 ± 0.27	[32]
heptane	β 2.89	5.78	19.64	34.75	−6.44	13.19	13.65		
2-Chlorooctane	α 3.81	9.13	10.17	24.28	−1.17	13.47		13.58	[43]
	β 2.89	5.78	19.64	34.75	−6.44	13.19	13.65		
1,10-Dichloro-	0.04	5.78	19.59	33.50	−8.09	13.11		13.31	[42]
dodecane									
1-Chlorododecane	0.04	5.78	19.59	33.50	−8.09	13.11		14.05	[42]
3-Chlorododecane	2.89	11.56	19.64	34.75	−0.66	13.49		12.27	[42]
4-Chlorododecane	2.89	11.56	19.64	34.75	−0.66	13.49		11.95	[42]
5,7-Dichloro-	2.89	11.56	19.64	34.75	−0.66	13.49		14.24	[42]
dodecane									
6,7-Dichloro-	β 0.46	0	24.66	33.91	−8.79	13.07		13.59	[42]
dodecane	γ 2.89	5.78	19.59	34.75	−6.49	13.19	13.44		
2-Methyl-2-chloro-	3.81	18.28	10.17	24.17	7.98	13.95		14.21	[44]
propane								13.78	[45]
								13.72	[46]
								13.78	[47]
								14.42	[48]
2-Methyl-2-chloro-	α 3.81	14.91	10.17	24.28	4.61	13.77		14.67	[44]
butane	β 3.27	5.78	19.64	33.45	−4.76	13.28	13.89	13.84	[45]
2,3-Dimethyl-	α 3.81	14.91	10.17	24.28	4.61	13.77		13.41	[45]
-2-chlorobutane	β 3.27	0	21.69	33.91	−8.95	13.06	13.84		

Table 4 (Continued)

Compound	ΔS_{vib}^{+}	ΔS_{sym}^{+}	S_{tors}^{+}	S_{hr}^{0}	ΔS^{+}	$\log(A_{calc}/s^{-1})$	$\log(\langle A \rangle/s^{-1})$	$\log(A_{exp}/s^{-1})$	Ref.
	$J\,mol^{-1}\,K^{-1}$	$J\,mol^{-1}\,K^{-1}$	$J\,mol^{-1}\,K^{-1}$	$J\,mol^{-1}\,K^{-1}$	$J\,mol^{-1}\,K^{-1}$				
2,3,3-Trimethyl--2-chlorobutane	3.81	14.91	10.17	24.28	4.61	13.77		13.84	[45]
3-Ethyl-3-chloro-pentane	2.89	14.91	19.64	34.33	3.11	13.69		13.19	[34, 35]
2-Methyl-2,4-di-chloropentane	α 3.81	14.91	10.17	24.28	4.61	13.37		13.90	[32]
	β 2.89	5.78	19.64	34.33	−6.02	13.21	13.87		
3-Methyl-3-chloro-heptane	α 3.81	9.13	10.17	24.28	−1.17	13.47		12.44	[42]
	β 2.89	11.56	19.64	34.33	−0.24	13.52	13.79		
3-Methyl-3-chloro-undecane	α 3.81	9.13	10.17	24.28	−1.17	13.47		11.35	[42]
	β 2.89	11.56	19.64	34.33	−0.24	13.52	13.80		
3-Chloro-1-butene	3.82	9.13	10.17	24.28	−1.16	13.47		13.26	[49]
2-Methyl-3-chloro--1-butene	3.81	9.13	10.17	24.28	−1.17	13.47		13.33	[49]
3-Methyl-3-chloro--1-butene	3.81	14.91	10.17	24.28	4.61	13.77		13.34	[50]
3-Chloro-1-pentene	2.89	5.78	19.64	34.75	−6.44	13.19		14.58 ± 0.19	[32]
								9.20	[34, 35]
1,3-Dichloro--1-pentene	2.89	5.78	19.64	34.75	−6.44	13.19		13.75 ± 0.14	[32]
4-Chloro-1-hexene	2.89	11.56	19.64	34.75	−0.66	13.50		13.65	[48]
4-Chloro-2-pentene	−12.06	9.13	0	24.28	−27.21	12.11		12.03 ± 0.19	[32]
4-Chloro-2-hexene	−12.98	5.78	0	34.75	−41.95	11.34		10.77	[42]
5-Chloro-3-heptene	−12.98	5.78	0	34.75	−41.95	11.34		13.15 ± 0.16	[32]
6-Chloro-2,4-hepta-diene	−12.06	9.13	0	24.28	−27.21	12.11		10.43 ± 0.41	[32]

the H atom by the way α or β and let us say γ. However, the experimental frequency factors are certain mean values and for this reason, the comparison of the calculated values with the experimental frequency factors necessitates a statistical averaging of the calculated frequency factors. In paper [8], we have described a method which enables us to determine the mean values of frequency factors $\langle A \rangle$ for either mechanism by means of activation energies and frequency factors. By using the activation energies presented for HCl elimination from the investigated compounds in paper [8], we statistically averaged the calculated frequency factors and the values of log $\langle A \rangle$ as well as the values of activation entropies and particular entropic contributions are listed in Table 4.

As evident from this table, we divided the investigated chlorinated hydrocarbons into the following groups: chloroalkanes with the primary, secondary, and tertiary C—X bond (X = H, Cl) and chloroalkenes with the π bond at the end or inside the molecule. It results from the comparison that the best agreement with the experimental data was obtained for chloroalkanes with the primary and secondary C—X bond. Greater differences were observed for dichloroalkanes.

The analysis of the contributions to activation energy shows that $\Delta S_{vib}^{\neq}$/ /J mol^{-1} K$^{-1} \in \langle -13, 15 \rangle$, S_{hr}^{0}/J mol^{-1} K$^{-1} \in \langle 24, 35 \rangle$, $S_{tors}^{\neq}$/J mol^{-1} K$^{-1} \in \langle 5, 27 \rangle$, and $\Delta S_{sym}^{\neq}$/J mol^{-1} K$^{-1} \in \langle 0, 15 \rangle$. It follows from these results that the entropic contributions of hindered internal rotations are major contributions to the value of activation entropy and the contributions of torsional vibrations are in the second place in the order of relevance.

The comparison with experimental data has been performed in the form log (A/s^{-1}) or log $(\langle A \rangle / s^{-1})$. Except the values found for 8-dichloro- or tri-chlorohydrocarbons, it holds for the differences Δ log (A/s^{-1}) = log (A_{exp}/s^{-1}) − − log (A_{calc}/s^{-1}) < ± 0.5, which is regarded in literature as a good agreement of the calculated frequency factors with the measured ones [6, 7]. The differences found for the quoted eight hydrocarbons also appear in the values of activation energies and frequency factors published in paper [8], which supports the view on unreliability of the experimental methods used for their determination.

These discrepancies may be also attributed to experimental conditions of the determination of kinetic data. This may be connected with measurement at low pressure owing to which a change in reaction order due to the process involving energy transfer between the molecules of reactants and the molecules of reaction products may appear [51]. Such situation manifests itself in the position of a fall of kinetic curves. However, the kinetic data presented in different papers do not enable us to accomplish their advisable analysis.

Individual theories of monomolecular reactions differ from each other in the manner in which they fully describe the process of transition of the energized molecules into the state of activated complex. The point at issue is the question whether all configurations of a molecule with a given total energy are freely

interconvertible by distributing the energy among individual degrees of freedom. Under these conditions, every energized molecule can get into the state of activated complex in the course of sufficiently long time.

From this point of view, the suggested model of transition state and the presented statistical thermodynamic method of investigation of frequency factors proved to be a relatively simple, reliable, and operational tool for investigating the kinetic stability of a great class of chlorinated hydrocarbons with very variable structure. This fact entitles us to believe that the method presented in this paper could be also used for investigating the mechanism of elimination of other hydrogen halides (HBr, HI), which is the topic of our subsequent paper [52].

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