Additivity methods of the calculation of thermodynamic-kinetic parameters of HBr elimination from brominated hydrocarbons

P. KOVAŘÍK, L. VALKO, and J. OREMUSOVÁ

*Department of Physical Chemistry, Faculty of Chemical Technology,
Slovak Technical University, CS-812 37 Bratislava*

Dedicated to Academician V Kellö, in honour of his 70th birthday

In this paper, the additivity methods have been applied to calculation of the activation parameters of the HBr elimination reactions of 15 saturated and unsaturated brominated hydrocarbons. The activation energies were determined by the additivity method of the bond energies in original and activated state. The mean deviation between experimental and calculated values is $\pm 6.25\,kJ\,mol^{-1}$ The frequency factors were calculated on the basis of the theory of absolute reaction rates by using the values of activation entropies obtained by application of the principle of additivity of the entropic contributions of bonds and structural elements to the original and to the activated state. The mean deviation between measured and calculated frequency factors is $\pm 0.5 \log(A/s^{-1})$ units. The calculated thermodynamic--kinetic parameters were statistically evaluated for some possible mechanisms of HBr elimination.

В работе демонстрируется применение аддитивных методов расчета активационных параметров реакции элиминирования НВг из 15 насыщенных и ненасыщенных бромпроизводных углеводородов. Величины энергий активации определяются с помощью метода аддитивности энергий химических связей в исходном и активированном состоянии. Среднее отклонение между экспериментальными и рассчитанными величинами равно $\pm 6,25$ кДж моль$^{-1}$. Частотные факторы были рассчитаны на основе теории абсолютных скоростей реакции с помощью величин энтропии активации, определенных путем приложения принципа аддитивности энтропийных вкладов химических связей и структурных элементов для исходного и активированного состояния. Среднее отклонение между измеренными и вычисленными значениями частотных факторов составляло $\pm 0,5$ единиц $\log(A/c^{-1})$. Для различных возможных механизмов элиминирования НВг была проведена статистическая оценка рассчитанных термодинамическо--кинетических параметров.

At present, great attention is paid to the study of mechanisms of monomolecular reactions with special regard to reactions in which small molecules are eliminated from low-molecular as well as macromolecular substances.

In our preceding studies [1—4] we investigated the kinetics of HCl elimination from chlorinated hydrocarbons and poly(vinyl chloride) (PVC) with the aim to elucidate the mechanism of thermal destruction of PVC. We proposed some methods of calculation for determining the thermodynamic-kinetic parameters of dehydrochlorination reactions. This paper is concerned with modification of a group of the methods of calculation for determining the activation energies and frequency factors of HBr elimination from brominated hydrocarbons which may serve as model substances for the retarders of burning.

The used methods of calculation belong to the group of empirical methods. On the basis of the ideas of the theory of absolute reaction rates, the activation parameters sought for have been determined by using the additivity of the dissociation energies of bonds in original and activated state as well as the additivity of the entropies of bonds and structural elements in original and activated state. When compared with the semiempirical [5—9] and quantum-chemical *ab initio* [10] methods, the additivity methods give the results on equal qualitative level which are consistent with experimental data and the practical application of them is much simpler than that of other methods.

Theoretical

The activation energies and frequency factors of the investigated elimination reactions may be determined on the basis of the theory of absolute reaction rates [11] according to which the rate constant of monomolecular reactions obeys the equation

$$k(T) = \varkappa(ek_B T/h) \exp (\Delta S^+/R) \exp (- E/RT) \qquad (1)$$

where $\varkappa$, k_B, ΔS^+, and E stand for transmission coefficient (here its value is put equal to 1), the Boltzmann constant, activation entropy, and activation energy, respectively. It holds for the value of frequency factor

$$A = (ek_B T/h) \exp (\Delta S^+/R) \qquad (2)$$

The experimental values of activation energies and frequency factors necessary for the comparison with the calculated values have been obtained from literature data by evaluating the experimental Arrhenius relationships $\ln k = f(1/T)$.

In calculating the activation parameters we have started from the idea of monomolecular mechanism of HBr elimination from brominated hydrocarbons according to which this reaction proceeds through a four-centric, planar, and polar activated complex
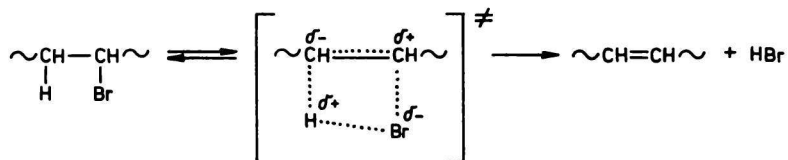
Calculation of activation energies

The calculation of activation energies based on application of the additivity rules was put forward by *Moin* [12]. According to his method, it follows for the activation energy of the above reaction

$$E = Q_{C-Br} + Q_{C-H} - (Q^{\ddagger}_{C\cdots Br} + Q^{\ddagger}_{C\cdots H} + Q^{\ddagger}_{H\cdots Br} + Q^{\ddagger}_{\pi-\pi} + \omega^{*}) \qquad (3)$$

Q_{C-Br} and Q_{C-H} are the dissociation energies of the breaking bonds, $Q^{\ddagger}_{C\cdots Br}$, $Q^{\ddagger}_{C\cdots H}$, $Q^{\ddagger}_{H\cdots Br}$, and $Q^{\ddagger}_{\pi-\pi}$ are the dissociation energies of the bonds in the activated complex, and ω^{*} is the parameter expressing the influence of the double bond that has zero value for saturated hydrocarbons. On the other hand, it holds $\omega^{*} = \beta^{*}$ for a double bond inside the chain of an unsaturated hydrocarbon and $\omega^{*} = \alpha^{*}$ for a double bond at the end of the chain.

The dissociation energies of the breaking bonds are to be determined by the semiempirical method of Vedeneev [13] according to which it holds

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

where E'_{R-X} is the so-called specific energy of a given kind of bond. The second term in eqn (4) expresses the stabilization energy of radical R• and the symbols M_i, a_i, $\exp(-\omega)$, E_{conj}, and a stand for number of the bonds of i-th type which are bonded to the m-th carbon atom starting from the investigated bond, specific stabilization parameter attributed to a given type of bond in a molecule, coefficient independent of the type of bond equal to 0.4, stabilization energy corresponding to conjugation of radical R• with a double bond, and number of the conjugated groups, respectively. The third term of eqn (4) expresses the stabilization energy of radical X• and the used symbols have analogous signification as the symbols specified for radical R•.

The values of E'_{R-X}, E_{conj}, parameters a_i, and dissociation energies of activated bonds determined by means of experimental data about the dissociation energies of simple hydrocarbons and about the activation energies of dehydrobromination reactions or of data taken from our preceding papers [2] are given in Table 1.

Table 1

Values (kJ mol^{-1}) of the constants for calculation of activation energies

Constant	Value	Constant	Value
α_{C-H}	41.87	$Q^{\neq}_{C_{prim}\cdots Br}$	66.99
α_{C-Br}	62.80	$Q^{\neq}_{C_{sec}\cdots}$	87.92
$\alpha_{\pi-\pi}$	46.05	$Q^{\neq}_{C_{tert}\cdots}$	108.86
E'_{C-H}	535.07	$Q^{\neq}_{C\cdots}$	117.23
E'_{C-Br}	406.12	$Q^{\neq}_{C\cdots C}$	71.18
E'_{C-C}	608.34	$Q^{\neq}_{H\cdots Br}$	138.86
E_{conj}	81.22	$\alpha^{\neq}_{C=C}$	-15.91
		$\beta^{\neq}_{C=C}$	-71.18

The presented method of calculation does not take into consideration the change in intrinsic energy due to temperature which takes place in the course of activation process and the calculated activation energies refer to the temperature of 0 K. A rigorous comparison of the experimental with the calculated activation energies requires application of temperature corrections, which necessitates the knowledge of heat capacity of the activated complex. However, the corrections of this kind are never greater than ± 4 kJ mol^{-1}, *i.e.* they are in the range of the mean error of determination of the activation energies (± 6.3 kJ mol^{-1}) and that is why they are not taken into account in confrontation of the experimental and calculated values.

Calculation of activation entropies

The activation entropies have been determined by the method of additivity of entropic contributions of bonds by using the corrections respecting the conjugation and cumulation of double bonds as well as the influence of symmetry and optical activity of molecules as formulated in paper [2]. It holds for the activation entropy of the investigated HBr elimination reactions

$$\Delta S^{\neq} = \sum_{a=1}^{\gamma} S^{\circ}_{\text{bond},a} - \sum_{a=1}^{\gamma} S^{\neq}_{\text{bond},a} - \sum_{b=1}^{\delta} (\Delta S^{\neq}_{\text{conj},b} - \Delta S^{\circ}_{\text{conj},b}) -$$

$$- \sum_{c=1}^{\varepsilon} (\Delta S^{\neq}_{\text{cum},c} - \Delta S^{\circ}_{\text{cum},c}) + R \ln (\sigma n^{\neq} g_{e}^{\neq} / \sigma^{\neq} n g_{e}) \quad (5)$$

S°_{bond} and $S^{\neq}_{\text{bond}}$ are the entropies of bonds in the original and the activated state and $\Delta S^{\circ}_{\text{conj}}$, $\Delta S^{\neq}_{\text{conj}}$, $\Delta S^{\circ}_{\text{cum}}$, and $\Delta S^{\neq}_{\text{cum}}$ are the entropic contributions due to

170

conjugation and cumulation of double bonds in the original and the activated state. σ and σ^+ are the symmetry numbers of molecule determined by the product of the symmetry number σ_c which expresses the symmetry of molecule as a whole and the symmetry numbers σ_d characterizing the symmetry of those parts of molecule which are able to rotate about simple bonds [2]. The symbols n and n^+ denote the number of the energetically equivalent 2^p optical isomers (p is the number of structurally different asymmetric carbons in a molecule). The symbol g_e expresses the electronic degeneration which is equal for the investigated molecules in the original and the activated state so that the term $R \ln (g_e^+/g_e)$ disappears in the course of calculations.

For classifying the individual types of bonds and their entropic contributions we have used the characterization put forward in paper [2]: The C—C bonds are considered to be equivalent in all investigated molecules; C_1—X, C_2—X, and C_3—X (X = H, Br) denote the bonding of X to the primary, secondary and tertiary carbon and the denotations C_2^2—H and C_2^3—H are used for the $\underset{\displaystyle C}{\overset{\displaystyle H}{\diagdown}}{=}C{-}H$

and $=C{-}H$ structures; $\Delta S^+_{\text{conj. term}}$ and $\Delta S^+_{\text{conj. int}}$ stand for the entropic contribution of conjugation of an arising double bond in the activated complex containing a terminal or internal double bond, respectively.

The values of entropic contributions necessary for determining activation entropies of the HBr elimination reactions are given in Table 2. The entropic contributions of bonds and structures containing the Br atom were determined by means of the experimental frequency factors of dehydrobromination reactions [9, 14, 15] and the values of other entropic contributions are taken from paper [2].

The entropic contributions used in this method correspond to the temperature of 298 K. For comparing the experimental frequency factors with the frequency factors calculated according to eqn (2), it was necessary to take into account their temperature dependence because the experimental data were obtained at different temperatures. By calculating the heat capacity of a molecule in the activated state by the *Benson* method of group additivity [16], we found that the correction of the value of activation entropy for temperature did not reach over the value $0.25 \, \text{J mol}^{-1} \text{K}^{-1}$, which was deeply below the value of the mean error of determination of activation entropy obtained by the presented method ($\pm 6.3 \, \text{J mol}^{-1} \text{K}^{-1}$). For this reason, we do not take into account the correction for temperature in the calculation of activation entropies and all experimental frequency factors compared with the corresponding calculated values are converted to the mean temperature of 298 K.

Table 2

Values of entropic contributions to activation entropy

Entropy of atoms, bonds, and structural elements in original state	Entropic contribution	Entropy of bonds and structural elements in activated state	Entropic contribution
	$J\ mol^{-1}\ K^{-1}$		$J\ mol^{-1}\ K^{-1}$
S_C°	158.10	$S_{C\cdots C}^{\ddagger}$	147.38
S_H°	114.69	$S_{C_1\cdots H}^{\ddagger}$	133.27
S_{Br}°	189.58	$S_{C_2\cdots H}^{\ddagger}$	118.57
S_{C-C}°	150.01	$S_{C_3\cdots H}^{\ddagger}$	114.01
$S_{C=C}^\circ$	113.21	$S_{C_1\cdots Br}^{\ddagger}$	136.49
$S_{C_1-H}^\circ$	100.61	$S_{C_2\cdots Br}^{\ddagger}$	131.97
$S_{C_2-H}^\circ$	98.60	$S_{C_3\cdots Br}^{\ddagger}$	125.90
$S_{C_3-H}^\circ$	92.57	$S_{H\cdots Br}^{\ddagger}$	97.97
$S_{C_2^2-H}^\circ$	107.64	$S_{C_2^3\cdots H}^{\ddagger}$	134.19
$S_{C_2^3-H}^\circ$	107.43	$\Delta S_{ring}^{\ddagger}$	136.07
$S_{C_1-Br}^\circ$	118.78	$\Delta S_{conj,term}^{\ddagger}$	4.44
$S_{C_2-Br}^\circ$	116.23	$\Delta S_{conj,int}^{\ddagger}$	49.45
$S_{C_3-Br}^\circ$	115.35		
$\Delta S_{conj,term}^\circ$	12.56		

Mean values of activation parameters

In general, the course of elimination reaction can follow a few mechanisms. For HBr elimination from the investigated hydrocarbons we may assume the abstraction of hydrogen atom from the primary or secondary carbon atom and eventually from the carbon atom with double bond. In this paper, the denotation α is used for the abstraction of hydrogen from the primary carbon atom while the denotation β corresponds to the abstraction from the secondary carbon atom.

In order to compare the experimental values with the calculated values of activation parameters we have to take into consideration that the experimental values are certain mean values for both possible mechanisms of elimination and therefore it is necessary to determine the mean values for these mechanisms from the calculated activation parameters as well. By the method put forward in paper [2] we derived the expressions for the mean values of activation energies and frequency factors in the form

$$\langle E \rangle = (E_1 + RTr)/(1 + r) \tag{6}$$

$$r = (A_2/A_1)\exp(-\varepsilon) \quad \text{and} \quad \varepsilon = (E_2 - E_1)/RT \tag{7}$$

$$\langle A \rangle = A_1 (1 + r) \exp \left[\varepsilon r / (1 + r) \right] \qquad (8)$$

where E_1, E_2 and A_1, A_2 are the activation energies and frequency factors for both possible mechanisms of HBr elimination.

This method was used for five brominated hydrocarbons in order to compare the experimental with the calculated activation parameters.

Calculation of the standard reaction enthalpies

In order to appreciate the course of HBr elimination reactions completely, we calculated the standard reaction enthalpies for which it is valid

$$\Delta_r H^{\ominus} = - \sum_i \nu_i \Delta H_{f,i}^{\ominus} \qquad (9)$$

where ν_i are stoichiometric coefficients of reactants and reaction products and $\Delta H_{f,i}^{\ominus}$ are the corresponding standard enthalpies of formation calculated by the *Benson* method of group additivity [16]. The standard reaction enthalpies as well as the standard formation enthalpies are defined for the standard state of components in pure state at the temperature of 298 K and at the pressure of 1.01325×10^5 Pa. This standard state is consistent with the conditions under which the activation parameters have been calculated so that all these quantities may be used for calculating other thermodynamic characteristics of the investigated elimination reactions.

Results and discussion

The calculated values of activation energies, activation entropies, and frequency factors as well as the comparison of them with the experimental data of about 15 saturated primary, secondary, tertiary and unsaturated brominated hydrocarbons are listed in Table 3.

A comparison of the experimental values with the calculated activation energies shows that the mean deviation between both the values is ± 6.25 kJ mol^{-1} and the only maximum deviation is 15.2 kJ mol^{-1} which indicates that the experimental and the calculated values are in good agreement. It also results from Table 3 that the presented method of calculation is able to seize the systematic substitution effect of bromine atoms affecting the values of activation energies of elimination reactions. In line with the trend of experimental values, the calculated activation energies decrease from the primary to the tertiary brominated hydrocarbons. Thus we may state in spite of a certain vagueness in getting the parameters for the calculation of activation energies that the presented method of additivity is able successfully to predict the values of activation energies of the HBr elimination reactions as well. The results are also

Table 3

Values of activation parameters of HBr elimination, comparison with experimental data

Compound	Type of abstraction	$E_{a,calc}$ kJ mol^{-1}	$E_{a,exp}$ kJ mol^{-1}	$\langle E \rangle$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J mol^{-1} K^{-1}	log (A_{calc}/s^{-1})	log (A_{exp}/s^{-1})	log ($\langle A \rangle$/s^{-1})	$\Delta_r H^{\ominus}$ kJ mol^{-1}	Ref.
1-Bromomethane		218.9	225.7		5.28	13.81	13.62		83.74	[16]
			218.5				13.04			[16]
			217.7				13.78			[16]
1-Bromopropane		214.2	212.3		8.83	13.99	12.85		71.64	[16]
			217.3				13.09			[17]
1-Bromobutane		213.1	213.1		8.83	13.99	13.37		71.64	[16]
1-Bromopentane		211.5	211.4		8.83	13.99	13.50		70.72	[16]
							13.28			[16]
1-Bromohexane		211.2	211.4		8.83	13.99	13.36		70.72	[16]
							13.50			[16]
2-Bromopropane		189.1	199.7		7.29	13.91	14.01		83.82	[16]
			200.1							[16]
			199.3							[17]
2-Bromobutane	α	185.5	183.4	184.7	7.29	13.91	13.77	14.31	83.82	[16]
	β	184.3	194.6		10.80	14.10			78.54	[16]
			190.5							[17]
2-Bromo-2-methyl-propane		159.2	169.6		12.43	14.18	13.50		76.49	[16]
			175.9							[16]
			171.7							[17]
2-Bromo-2-methyl-butane	α	154.9	169.5	154.1	12.43	14.18	13.63	14.58	76.53	[16]
	β	153.7			12.43	14.18			64.85	
1-Bromo-2-methyl-propane		209.4	211.0		2.51	13.40	13.24		66.95	[16]
4-Bromo-1-pentene	α	185.5	187.1	186.6	2.81	13.68	13.11	14.08	86.58	[16]
	β	186.6			6.36	13.86			56.94	
2-Bromo-2,3-di-methylbutane	α	152.1	163.3	151.1	12.43	14.18	13.95	14.31	78.59	[16]
	β	149.7			4.65	13.77			61.42	
2-Bromo-2-methylpentane	α	154.4	169.6	153.1	12.43	14.18	13.99	14.58	78.58	[17]
	β	152.5			15.99	14.37			66.86	
3-Bromopentane		180.7	190.1		10.80	14.10	13.75		70.72	[17]
1,1-Dibromomethane		196.6	207.2		5.28	13.81	13.75		78.56	[17]

P. KOVAŘÍK, L. VALKO, J. OREMUSOVÁ

important because of the fact that many in the introduction mentioned semiempirical methods did not appear to be applicable to elimination reactions [18, 19] and could be used only for addition reactions [20]. The activation energies calculated by us in connection with the determined values of the standard reaction enthalpies allow to determine the activation energies of HBr elimination and addition at the same time

$$E_{\text{elim}} = E_{\text{ad}} + \Delta_r H^\ominus \tag{10}$$

A comparison of the experimental frequency factors with the values calculated from the determined activation entropies also confirms the success of the method of additivity of entropic contributions in estimating the activation entropies of the HBr elimination reactions. The maximum deviation between the calculated and the experimental values of frequency factor is 0.9 log (A/s^{-1}) units. However, the great majority of deviations is in the interval of ± 0.5 log (A/s^{-1}) units, which is regarded in literature as a very good approximation of experimental and calculated values [7]. If we compare the calculated frequency factors with the values determined by the method presented by *O'Neal* and *Benson* [7] which is based on appropriate assignment of the vibration modes to structural units of original and activated state, we can see that the uncertainty of our results is thoroughly comparable with the uncertainty of the results obtained by the mentioned method.

As for frequency factors, we can observe a lesser influence of systematic substitution effect of the bromine atoms on the value of frequency factor. For this reason, we can state that the value of activation energy has major influence on the value of rate constant.

The obtained results confirm the usability of the additivity methods for determining the thermodynamic-kinetic parameters of the HBr elimination from brominated hydrocarbons and support the idea of monomolecular mechanism of these reactions.

References

1. Valko, L., Tvaroška, I., and Kovařík, P., *Eur. Polym. J. 11*, 411 (1975).
2. Valko, L. and Kovařík, P., *J. Phys. Chem. 80*, 19 (1976).
3. Kovařík, P., Valko, L., and Gatial, A., *Collect. Czechoslov. Chem. Commun. 42*, 3265 (1977).
4. Kovařík, P., Valko, L., and Gatial, A., *Chem. Zvesti 36*, 611 (1982).
5. Noyes, R. M., *J. Am. Chem. Soc. 88*, 4311 (1966).
6. Pai.ari, M. B. and Basu, R., *J. Chim. Phys. Physicochim. Biol. 68*, 753 (1971).
7. O'Neal, H. E. and Benson, S. W., *J. Phys. Chem. 71*, 2903 (1967).
8. Maltman, K. R., Tschuikow-Roux, E., and Jung, K. H., *J. Phys. Chem. 78*, 1035 (1974).
9. Tschuikow-Roux, E., *J. Phys. Chem. 91*, 3037 (1987).

10. Hiberty, P. C., *J. Am. Chem. Soc. 97,* 5975 (1975).
11. Glasstone, S., Laidler, K. J., and Eyring, H., *The Theory of Rate Processes.* McGraw-Hill, New York, 1941.
12. Moin, F. B., *Usp. Khim. 7,* 1223 (1967).
13. Semenov, N. N., *Some Problems in Chemical Kinetics and Reactivity.* Princeton University Press, New Jersey, 1958.
14. Tschuikow-Roux, E., Faraji, F., Paddison, S., Niedzielski, J., and Miokawa, K., *J. Phys. Chem. 92,* 1488 (1988).
15. Osamu Kondo and Benson, S. W., *Int. J. Chem. Kinet. 16,* 949 (1984).
16. Benson, S. W., *Thermochemical Kinetics.* J. Wiley and Sons, New York, 1968.
17. Robinson, P. T. and Holbrook, K. A., *Monomolekulyarnye reaktsii.* Izd. Mir, Moscow, 1975.
18. Benson, S. W. and Bose, A. N., *J. Chem. Phys. 39,* 3463 (1963).
19. Chuchani, G., Dominguez, R. M., and Rotinov, A., *Int. J. Chem. Kinet. 18,* 203 (1986).
20. Haugen, G. R. and Benson, S. W., *Int. J. Chem. Kinet. 2,* 235 (1970).

Translated by R. Domanský