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Abstract

Full Text

PHYSICAL CHEMISTRY

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CALCULATION OF ACTIVATION ENERGY BASED ON THE PRINCIPLE OF ADDITIVITY. HYDROCARBON REACTIONS

(Presented by Academician V. N. Kondrat' ev on 5 IX 1964)

As was shown earlier (1) using radical reactions as an example, the potential energy of the activated complex can be regarded as an additive quantity composed of the energies of bonds between individual atoms. The established regularity, as shown by an analysis of numerous experimental data on chemical kinetics, can also be extended to reactions of saturated molecules. This makes it possible to calculate the activation energies of the corresponding reactions. The equation derived in (1) for calculating the activation energy E can readily be generalized to the case of any chemical reaction. Omitting the derivation, we give only the final form of the generalized equation

$$E = \sum Q_{\text{break}} - \sum Q^{\neq}. \tag{1}$$

In other words, the activation energy is equal to the sum of the energies of the bonds being broken minus the sum of the bond energies of the atoms in the activated complex (activated bonds).

Fig. 1. Relationship between the bond energies of atoms in the molecule and in the activated complex (according to the data of Table 1)

As in the case of radical reactions, equation (1) is applicable both to the exo- and to the endothermic direction of a reaction, with the difference between the activation energies of the forward and reverse reactions being equal to the heat effect.

The quantities required for calculating the activation energy can be determined with the aid of reliable experimental data for certain reactions. The values obtained in this way for the energies of various bonds between C and H atoms in molecules and activated complexes are given in Table 1.

The mean values of the bonds in molecules listed in Table 1 were taken from (²). The quantity $Q_{1\pi}$ was determined as the difference between the C—C bond energies in olefins (140 kcal) and paraffins (79 kcal). The quantity $Q_{2\pi}$ was determined analogously, as the difference between the C—C bond energies in acetylene ($\sim$ 196 kcal) and olefins. The values of $Q^{\neq}$ were obtained from an analysis of experimental data on reaction kinetics. A linear relationship is observed between the quantities Q and $Q^{\neq}$, as is seen from Fig. 1. The existence of this relationship makes it possible to determine the value of the energy of an activated bond when the bond energy in the molecule differs appreciably from the mean value indicated in Table 1.

If the activated complex contains a system of conjugated double bonds, then the energy of each conjugated activated bond should be increased by the amount Q_{conj}, equal to 12 kcal.

Table 1

Bond energies in molecules and activated complexes

No.	Bond	Designation	Q, kcal	$Q^{\neq}$, kcal
1	H—H	Q_{HH}	103	48
2	C—H	Q_{CH}	99	45
3	σ-C—C in paraffins	Q_{σ}	79	27
4	π-C—C in olefins	$Q_{1\pi}$	61	17
5	π-C—C in acetylene	$Q_{2\pi}$	56	9
6	Correction for conjugation	Q_{conj}	–	12

Let us illustrate the calculation of the activation energy of hydrocarbon reactions with examples.

1. Cis-trans isomerization of ethylene derivatives.

$$\begin{array}{ccccc} \text{R}\backslash\quad/\text{R} & & \text{R}\backslash\quad/\text{R} & & \text{R}\backslash\quad/\text{H} \\ \text{C}=\text{C} & \rightarrow & \text{C}\cdots\text{C} & \rightarrow & \text{C}=\text{C} \\ \text{H}/\quad\backslash\text{H} & & \text{H}/\quad\backslash\text{H} & & \text{H}/\quad\backslash\text{R} \end{array} \tag{2}$$

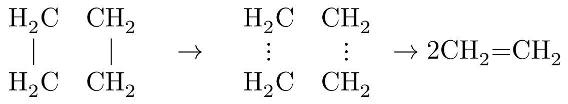
In this reaction, one π-bond is broken, in place of which the corresponding activated bond is formed, permitting free intramolecular rotation.

According to equation (1), the activation energy of reaction 2 is equal to

$$E = Q_{1\pi} - Q_{1\pi}^{\neq} = 61 - 17 = 44 \text{ kcal.}$$

According to literature data ($^{3-5}$), the experimental value of E for reactions (2) proceeding without a change in multiplicity varies within the range 41.6–46 kcal.

2. Decomposition of cyclobutane.



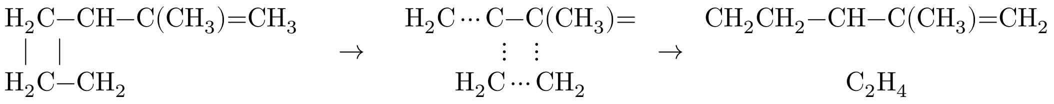
$$\begin{array}{cc} H_2C & CH_2 \\ | & | \\ H_2C & CH_2 \end{array} \rightarrow \begin{array}{cc} H_2C & CH_2 \\ \vdots & \vdots \\ H_2C & CH_2 \end{array} \rightarrow 2CH_2{=}CH_2 \qquad (3)$$

In this reaction two σ-C–C bonds are broken, and four activated bonds are formed: two $\sigma^{\neq}$ and two $\pi^{\neq}$. The energy of cleavage of the C–C bond in cyclobutane is 60 kcal (^{6}). From Fig. 1 we find the energy of the corresponding activated bond, equal to $\sim$ 12 kcal. The activation energy of reaction (3), according to equation (1), is

$$E = 2 \cdot 60 - (2 \cdot 12 + 2 \cdot 17) = 62 \text{ kcal}.$$

The experimental value is 62.5 kcal (^{7}).

3. Decomposition of isopropenylcyclobutane.



$$\begin{array}{l} H_2C{-}CH{-}C(CH_3){=}CH_3 \\ \;|\quad\; | \\ H_2C{-}CH_2 \end{array} \rightarrow \begin{array}{c} H_2C \cdots C{-}C(CH_3){=} \\ \vdots\;\; \vdots \\ H_2C \cdots CH_2 \end{array} \rightarrow \begin{array}{c} CH_2CH_2{-}CH{-}C(CH_3){=}CH_2 \\ \\ C_2H_4 \end{array}$$

The activated complex of this reaction differs from the preceding one only in that in it one activated double bond is conjugated; consequently, the energy of the activated complex must be increased by $Q_{\text{conj}} = 12$ kcal.

$$E = 2 \cdot 60 - (2 \cdot 12 + 2 \cdot 17 + 12) = 50 \text{ kcal}.$$

The experimental value of the activation energy for this reaction is 51 kcal (^{8}).

In a completely analogous manner, we calculated the activation energies of a number of different hydrocarbon reactions (see Table 2).

In calculations of the activation energy, the following values of the C–C bond energy in cycloparaffins were adopted (6): cyclopropane 50 kcal, cyclobutane 60 kcal, cyclopentane 72 kcal, cyclohexane 78 kcal. The corresponding values of the energies of the activated bonds were found for the indicated substances from Fig. 1.

As the data given in Table 2 show, the calculated values of E agree well with the experimental values for reactions of the most varied type with hydrocarbons of different structure.

Table 2

Activation energies of hydrocarbon reactions

Reaction	*E* calc., kcal	*E* exp., kcal	Literature source
cis-RHC=CRH → trans-RHC=CRH	44	45	(3)
Vinylcyclopropane → cyclopentene	51	50	(3)
α-Pinene → dipentene	43	43.7	(10)
Cyclobutane → $2C_2H_4$	62	62.5	(7)
Methylcyclobutane → $C_2H_4 + C_3H_6$	62	61.2	(11)
Isopropylcyclobutane → $C_2H_4 + C_5H_{10}$	62	62.5	(12)
Isopropenylcyclobutane → $C_2H_4 + C_5H_8$	50	51	(8)
Isopropenylcyclobutane → 1-methylcyclohexene	48	51	(8)
Cyclobutene → $CH_2{=}CH{-}CH{=}CH_2$	34	32.5	(13)
1-Methylcyclobutene → $CH_2{=}C(CH_3)CH{=}CH_2$	34	35.1	(14)
1,2-Dimethylcyclobutene → $CH_2{=}C(CH_3)C(CH_3){=}CH_2$	34	36	(15)
1,3-Butadiene → $C_2H_4 + C_2H_2$	52	50	(16)
$C_2H_4 \rightarrow C_2H_2 + H_2$	51	50	(17)
1,3-Butadiene $+C_2H_4$ → cyclohexene	25	26.7	(18)

Reaction	E calc., kcal	E exp., kcal	Literature source
2-[Butadiene] → vinylcyclohexene	25	23.1	(19)
2[1, 3-pentadiene] → dimer	25	25.4	(20)
Acetylcyclobutane → $C_2H_4 + CH_3COCH{=}CH_2$	50	54.5	(21)

The discrepancy does not exceed 2–3 kcal over a wide range of activation energies (25–62 kcal). This confirms the validity of the principle of additivity of the energy of the activated complex not only for radical reactions, but also in the general case.

The additive scheme for calculating activation energies directly relates the reactivity of various molecules to their structure. It is important that the principle of additivity makes it possible to give a simple and clear interpretation of the activation energy of very complex reactions, which at present is inaccessible to other theories.

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