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Abstract

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CALCULATION OF THE ACTIVATION ENERGY OF RADICAL REACTIONS ON THE BASIS OF THE ADDITIVITY PRINCIPLE

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The connection between the activation energy and the heat effect of radical reactions is most clearly manifested in Polanyi' s rule and the relation of N. N. Semenov (^{1,2}). Recently the idea has been expressed (^{3}) that the free energies of activation are additive quantities consisting of two increments: radical and molecular. Knowledge of these increments would make it possible to calculate readily the rate constants of radical reactions. However, the method for calculating the increments is not given in (^{3}). Nor is the physical meaning of the indicated increments entirely clear.

Analysis of numerous experimental data on the kinetics of radical reactions has led us to the conclusion that the additivity principle can be extended to the energies of bonds between atoms in the activated complex. This makes it possible to calculate easily the activation energies of radical reactions, and makes the calculation scheme clear and physically better justified.

For the radical reaction

$$\mathrm{R}\cdot + \mathrm{R'X} \rightarrow \mathrm{RX} + \mathrm{R'}\cdot . \tag{1}$$

the activated complex has the form $\mathrm{R} \ldots \mathrm{X} \ldots \mathrm{R'}$, where the dots denote the bonds of the radicals $\mathrm{R}\cdot$ and $\mathrm{R'}\cdot$ with the radical residue X in the activated complex (“activated bonds”). The role of X is most often played by atoms H, Cl, Br, J, and other elements.

The activation energy of the reaction is equal to the difference between the potential energies of the initial system and the activated complex. The potential energy of the initial system is an additive quantity consisting of the energies of the bonds between atoms in the radical $\mathrm{R}\cdot$ and the molecule $\mathrm{R'X}$:

$$E_1 = \sum_{\mathrm{R}\cdot} Q + \sum_{\mathrm{R'X}} Q.$$

We assume that the same additivity principle is also valid for the energy of the activated complex, so that the potential energy of the activated complex can be represented as the sum of the energies of bonds between atoms:

$$E_2 = \sum_{\mathrm{R\ldots X\ldots R'}} Q = \sum_{\mathrm{R\cdot}} Q + \sum_{\mathrm{R'\cdot}} Q + Q_{\mathrm{R\ldots X}} + Q_{\mathrm{R'\ldots X}}.$$

Hence, the activation energy of reaction (1) is equal to:

$$E = E_1 - E_2 = \sum_{\mathrm{R'X}} Q - \sum_{\mathrm{R'\cdot}} Q - \left(Q_{\mathrm{R\ldots X}} + Q_{\mathrm{R'\ldots X}}\right).$$

The difference between the potential energies of the molecule $\mathrm{R'X}$ and the radical $\mathrm{R'\cdot}$, obviously, is equal to the bond dissociation energy of $\mathrm{R'-X}$. Thus, finally we obtain:

$$E = Q_{\mathrm{R'-X}} - \left(Q_{\mathrm{R\ldots X}} + Q_{\mathrm{R'\ldots X}}\right). \tag{2}$$

Table 1

Activation energies of CH_3 and C_2H_5 reactions (2)

Reaction	E, kcal	Q, kcal	Reaction	E', kcal	Q', kcal	$E - E'$	$Q - Q'$
H + CH_4	13	101.5	H + C_2H_6	9.5	98	3.5	3.5
OH + CH_4	9.0	101.5	OH + C_2H_6	5.5	98	3.5	3.5
Na + CH_3Cl	10.2	80	Na + C_2H_5Cl	9.7	80	0.5	0
Na + CH_3Br	5	65	Na + C_2H_5Br	4.9	65	0.1	0
H + CH_3Cl	8	80	H + C_2H_5Cl	8	80	0.0	0

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

It is easy to see that equation (2) is applicable both to the exothermic and to the endothermic direction of the reaction, and the difference between the activation energies of the forward and reverse reactions is equal to the heat effect:

$$E_{\text{end}} - E_{\text{ex}} = Q_{R'-X} - Q_{R-X} = \Delta H.$$

The derivation of equation (2) is based on the assumptions that the energy of the activated bond $R \cdots X$ does not depend on the kind of radical $R'\cdot$, and that the bond energies of atoms in the radicals $R\cdot$ and $R'\cdot$ do not change upon activation. These assumptions, generally speaking, are valid only to a certain approximation.

Table 2

Bond energies of atoms in activated complexes and molecules

Bond	$Q_{H\ldots R}$, kcal	Q_{H-R}, kcal
$H \cdots H$	44.7	103.2
$H \cdots OH$	48.5	118.0
$H \cdots O$	52.5	103.0
$H \cdots NH_2$	50.2	104.0
$H \cdots CH_3CO$	34.4	85.0
$H \cdots CH_3$	43.8	101.5
$H \cdots C_2H_5$	43.8	98.0
$H \cdots CH_2CH_2R'$	41.2	95*
$H \cdots CH(R')(R'')$	37.1	89*
$H \cdots C(R')(R'')(R''')$	33.4	85*
$H \cdots CF_3$	46.7	101.0

* The bond energy of H with a primary carbon atom is taken to be 95 kcal; with a secondary, 89; with a tertiary, 85 kcal; R', R'', R''' are alkyl radicals.

As is known, the nature of substituents can influence the bond energy of atoms in a molecule. In the same way, the nature of the radical $R\cdot$ can change, within certain limits, the energy of an activated bond. However, we assume that this influence should be small and can be taken into account in an appropriate manner.

Equation (2) makes it easy to calculate the activation energy of reaction (1), if the energies of the activated bonds $R \cdots X$ and $R' \cdots X$ are known. The most rigorous way to determine these energies is a sequential quantum-mechanical calculation of the activated complex. At present, however, quantum chemistry does not make it possible to calculate the activated complex, except in a few of the simplest cases.

Another way consists in using reliable experimental data on the activation energies of certain reactions. The calculated energies of activated bonds make it possible to determine the activation energies for a whole series of other radical reactions.

Let us show how the energies of activated bonds can be found. The energy of an activated bond can be determined most simply if the radicals $R\cdot$ and $R'\cdot$ are identical. In this case, obviously,

$$Q_{R\ldots X} = {}^{1}/_{2}(Q_{R-X} - E).$$

Table 3

Activation energies of some radical reactions

Reaction	E_{exp}, kcal	E_{calc}, kcal	Literature source
$OH\cdot + CH_4 \rightarrow H_2O + CH_3\cdot$	9.0	–	(6)
$OH\cdot + CH_4 \rightarrow H_2O + CH_3\cdot$	8.5	9.2	(7)
$OH\cdot + C_2H_6 \rightarrow H_2O + C_2H_5\cdot$	5.5	5.7	(7)
$OH\cdot + CH_3CHO \rightarrow H_2O + CH_3CO\cdot$	4.0	2.1	(8)
$H\cdot + C_2H_6 \rightarrow H_2 + C_2H_5\cdot$	9.5	9.5	(2)
$H\cdot + C_3H_8 \rightarrow H_2 + \text{iso-}C_3H_7\cdot$	8.5	7.2	(2)
$H\cdot + C(CH_3)_4 \rightarrow H_2 + CH_2C(CH_3)_3$	9.3	9.1	(2)
$H\cdot + CH_3CHO \rightarrow H_2 + CH_3CO\cdot$	6.0	5.9	(2)
$CH_3\cdot + C_4H_{10} \rightarrow CH_4 + \text{iso-}C_4H_9\cdot$	8.1	8.1	(2)
$CH_3\cdot + C_5H_{12} \rightarrow CH_4 + \text{iso-}C_5H_{11}$	8.1	8.1	(2)
$CH_3\cdot + C_6H_{14} \rightarrow CH_4 + \text{iso-}C_6H_{13}$	8.1	8.1	(2)

Reaction	E_{exp}, kcal	E_{calc}, kcal	Literature source
$CH_3\cdot + CH_3-CH(CH_3)-CH(CH_3)-CH_3 \rightarrow CH_4 + CH_3-\dot{C}(CH_3)-CH(CH_3)-CH_3$	6.9–7.8	7.8	(2)
$CH_3\cdot + \text{iso-}C_4H_{10} \rightarrow CH_4 + (CH_3)_3C\cdot$	7.6	7.8	(2)
$CH_3\cdot + (CH_3)_3CC(CH_3)_3 \rightarrow CH_4 + (CH_3)_3CC(CH_3)_2CH_2\cdot$	9.5	10.0	(2)
$CH_3\cdot + (CH_3)_2CH-CH(CH_3)-CH(CH_3)_2 \rightarrow CH_4 + (CH_3)_2-\dot{C}(CH_3)-CH(CH_3)-CH(CH_3)_2$	7.9	7.8	(2)
$CH_3\cdot + (CH_3)_4C \rightarrow CH_4 + (CH_3)_3CCH_2\cdot$	10.0	10.0	(2)
$CH_3\cdot + C_3H_8 \rightarrow CH_4 + \text{iso-}C_3H_7\cdot$	8.0	8.1	(2)
$CH_3\cdot + CH_4 \rightarrow CH_4 + CH_3\cdot$	11.2	13.9	(4)
$CH_3\cdot + CH_4 \rightarrow CH_4 + CH_3\cdot$	14.3	13.9	(5)
$CF_3\cdot + CH_4 \rightarrow CF_3H + CH_3\cdot$	9.5–10.3	11.0	(2)
$CF_3\cdot + C_3H_8 \rightarrow CF_3H + \text{iso-}C_3H_7$	6.5	5.2	(2)

Reaction	E_{exp}, kcal	E_{calc}, kcal	Literature source
$CF_3 \cdot + C_4H_{10} \to CF_3H + \text{iso-}C_4H_9$	5.1	5.2	(2)
$CF_3 \cdot + \text{iso-}C_4H_{10} \to CF_3H + (CH_3)_3C\cdot$	4.7	4.9	(2)

Thus, for example, for the reaction $CH_3 \cdot + CH_4 \to CH_4 + CH_3\cdot$,

$$Q_{\text{CH3...H}} = \frac{1}{2}\left(Q_{\text{CH3−H}} - E\right).$$

However, for this reaction different values of E are given in the literature: 11.2 kcal (^{4}) and 14.3 kcal (^{5}). Therefore, in the present case one must proceed in a somewhat different way.

An analysis of the experimental data on the activation energies of reactions involving $CH_3\cdot$ and $C_2H_5\cdot$ radicals shows that the energies of the activated bonds $X \ldots CH_3$ and $X \ldots C_2H_5$ should be approximately equal ($X = H, Cl, Br$). This follows from the fact that the difference between the activation energies involving $CH_3\cdot$ and $C_2H_5\cdot$ is almost always equal to the difference between the bond energies of X with these radicals.

The corresponding data are given in Table 1.

As can be seen, the value $E - E'$, to within 0.5 kcal, coincides with the difference $Q - Q' = Q_{\text{CH3−X}} - Q_{\text{C2H}_5\text{−X}}$. The data of Table 1 in themselves confirm the principle of bond additivity in the activated complex.

Taking $Q_{\text{CH3...H}} = Q_{\text{C2H}_5\text{...H}}$, from the reaction $CH_3 \cdot + C_2H_6 \to CH_4 + C_2H_5$, $E = 10.4$ kcal (^{2}), we find:

$$Q_{\text{CH3...H}} = \frac{1}{2}(98.0 - 10.4) = 43.8 \text{ kcal}.$$

Now, from the reaction $H \cdot + CH_4 \to H_2 + CH_3$, $E = 13$ kcal (^{2}), which has the activated complex $H \ldots H \ldots CH_3$, it is not difficult to find $Q_{\text{H...H}} = 101.5 - 13.0 - 43.8 = 44.7$ kcal. In a completely analogous way we found the energies of several other activated bonds. The data are given in Table 2.

The calculated values of the energies of activated bonds make it possible to determine the activation energies of a number of reactions. To calculate E, it is recommended to use the bond-energy values of atoms in molecules adopted in Table 2.

The activation energies of a number of reactions, calculated from equation (2) using the data of Table 2, are given in Table 3. The corresponding literature data are also given there. As can be seen, the calculated activation energies in most cases agree with the experimental values to within 0.5–0.7 kcal. If one takes into account that the accuracy of the experimental determination of activation energies of radical reactions is relatively low (1–2 kcal), the approximation obtained should be regarded as good.

The additivity rule is obeyed by reactions of the most diverse radicals with different molecules. Exceptions are the reactions of halogen atoms and reactions of the type $H\cdot + H_2 \rightarrow H_2 + H\cdot$ involving H and D atoms. It is noteworthy that these same reactions also do not obey Semenov' s relation. Clarification of the reasons for this circumstance will contribute to a deeper understanding of the nature of the elementary act of a chemical reaction.

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