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Abstract

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A SEMIEMPIRICAL METHOD FOR CALCULATING THE HEATS OF FORMATION OF HYDROPEROXIDES AND THE CONJUGATION ENERGIES OF SOME PEROXIDE RADICALS

(Presented by Academician V. N. Kondrat' ev, March 21, 1960)

In the oxidation processes of a broad range of organic substances in the gas, liquid, and solid phases, hydroperoxides play an essential role as branching agents. To calculate the energetics of reactions involving hydroperoxides, it is necessary to have information on the heats of formation of these compounds. However, the experimental data presently available are few in number and do not cover the compounds of greatest interest.

There exist various semiempirical methods for calculating the heats of formation of molecules ([1,2]). The inadequacy of experimental data on ΔH of hydroperoxides and, in particular, the practically complete absence of such data for the initial members of homologous series do not permit these methods to be used with any reliability for calculating the heats of formation of organic hydroperoxides.

The method we propose is based on the following considerations. According to the ideas developed by N. N. Semenov ([3,4]), the magnitude of the bond energy X—Y (Q_{XY}) may be represented in the following form: $Q_{XY} = E_{XY} - B_X - B_Y$, where E_{XY} is the energy of rupture of the X and Y bond under the assumption that the electronic configurations of the free X and Y remain the same as in the original molecule; B_X and B_Y are the conjugation energies of radicals X and Y. Thus, for compounds of the type $XOOX$ and $XOO\cdot$ one may write the equalities:

$$Q_{X—OOX} = E_{OX} - B_X - A_1; \tag{1}$$

$$Q_{X—O_2^{\cdot}} = E_{OX} - B_X - A_2; \tag{2}$$

$$Q_{XO—O^{\cdot}} = E_{OO} - B_{OX} + A_1, \tag{3}$$

where A_1 is the conjugation energy of the $XO_2\cdot$ radical, and A_2 is the transition energy of the O_2 molecule, obtained upon detachment of X from $XO_2\cdot$, into the real stable state. From the law of conservation of energy it follows that, independently of the nature of X, the identity

$$A_1 + A_2 = A_1^0 + A_2^0 = \text{const}, \tag{4}$$

must hold, where $A_1^0 + A_2^0$ is the sum of the energies of the two three-electron bonds in the oxygen molecule.

Indeed, the transition from the state $XOOX$ to the state $2X+O_2$ can be carried out in two ways: a) by simultaneous rupture of both OX bonds with expenditure of energy

$$q = 2E_{OX} - (A_1^0 + A_2^0) - 2B_X \tag{5}$$

and b) by successive detachment of X from XOOX and XO_2, with expenditure of energy

$$q = Q_{X-O_2X} + Q_{X-O_2}. \tag{6}$$

The combination of equations (1), (2), (5), and (6) gives equality (4), which may be regarded as a thermodynamic criterion that all the compounds under consideration correspond to the chemical formulas assigned to them, are thermochemically consistent, and obey the rule of additivity.

The numerical calculation of A_1 and A_2 from equations (1), (2), and (3) was carried out for cases in which $X = H,\ Cl,\ ClO,\ R,\ F^*$, where R is a hydrocarbon radical. The data used in the calculations ([3,8]) are given in Table 1.

From Fig. 1 it is seen that the quantity

$$A_1 + A_2 = A_1^0 + A_2^0 = 82 \pm 2 \text{ kcal} \tag{4'}$$

does not depend on the nature of X.

Equation (4′) makes it possible to approach the calculation of the heats of formation of hydroperoxides. Expressing the heat effects of the reactions

$$\text{RH} + O_2 \rightarrow \text{ROOH} + Q_1;$$

$$\text{RH} + \tfrac{1}{2}O_2 \rightarrow \text{ROH} + Q_2$$

through the energies of the corresponding bonds, one may write:

$$Q_1 = \{E_{CO} + E_{OH} - E_{CH}\} + \{B_{R(H)} - B_{R(O)}\} - (A_1 + A_2); \qquad (7)$$

$$Q_2 = \{E_{CO} + E_{OH} - E_{CH}\} + \{B_{R(H)} - B'_{R(O)}\} - \tfrac{1}{2}(A_1 + A_2 + E_{00}), \qquad (8)$$

where $B_{R(H)}$, $B_{R(O)}$, and $B'_{R(O)}$ are the conjugation energies of the radical R obtained from RH, ROOH, and ROH.

Combining (7) and (8) and assuming $B_{R(O)}$ and $B'_{R(O)}$ to be equal, we obtain the expression:

$$\Delta H_{\mathrm{ROOH}} = \Delta H_{\mathrm{ROH}} + \tfrac{1}{2}(A_1 + A_2 - E_{00}) = \Delta H_{\mathrm{ROH}} + 23 \text{ kcal}. \qquad (9)$$

Fig. 1. Dependence of A_1, A_2, and $A_1 + A_2$ on the electronegativity of the atom directly attached to oxygen

Table 1

Bond energies in compounds of the type XOOX and $XO_2^{\cdot}$ (kcal)

Compound	Q_{X-OOX}	Q_{X-O_2}	$Q_{XO-O^{\cdot}}$	Method of selecting E
HOOH	89.5	47	62	$E_{OH} = \frac{1}{2}(Q_{H-OH} + Q_{OH})$
ClOO	–	4.3	63.7	$E_{OO} = Q_{HO-OH} - 2B_{OH}$
$ClOO_2$	–	−6	48.8	$E_{Ocl} = \frac{1}{2}(Q_{Cl-OCl} + Q_{O-Cl})$
RO_2	–	14	–	1) $E_{CO} = Q_{R-OH} + B_R + B_{OH}2$) From the activity of OH in reactions at the C–C and C–H bonds

Fig. 2. Dependence of ΔH_{ROOH} on ΔH_{ROH}. AB –theoretical straight line; experimental points for R: 1 –tetrahydrofuryl-1, 2 –cyclohexyl, 3 –methylcyclohexyl, 4 –tert-butyl, 5 –n-hexyl, 6 –decalinyl, 7 –n-heptyl.

Figure 1: Fig. 2. Dependence of ΔH_{ROOH} on ΔH_{ROH}. AB –theoretical straight line; experimental points for R: 1 –tetrahydrofuryl-1, 2 –cyclohexyl, 3 –methylcyclohexyl, 4 –tert-butyl, 5 –n-hexyl, 6 –decalinyl, 7 –n-heptyl.

$*$ For the compound ClO_2F, the quantity $A_1 + A_2$ was calculated from kinetic data.

As shown in Fig. 2, the points corresponding to the experimental data ([5,6]) fit well on the straight line calculated from this equation.

The constancy of the quantities $A_1 + A_2$ for different compounds and the applicability of relation (9) to hydroperoxides of different classes make it possible to calculate, with sufficient reliability, the heats of formation of hydroperoxides for which experimental data are lacking, by comparison with the known heats of formation of the corresponding alcohols. This, in turn, makes it possible to calculate the energies of rupture of the O–O bonds in hydroperoxides, since at present the heats of formation of a number of alkoxyl radicals are known ([5]).

Fig. 2. Dependence of ΔH_{ROOH} on ΔH_{ROH}. AB –theoretical straight line; experimental points for R: 1 –tetrahydrofuryl-1, 2 –cyclohexyl, 3 –methylcyclohexyl, 4 –tert-butyl, 5 –*n*-hexyl, 6 –decalinyl, 7 –*n*-heptyl.

The calculation shows that, with increasing length and increasing branching of the hydrocarbon chain, $Q_{\mathrm{RO-OH}}$ regularly increases from 32 kcal for CH_3OOH to 39 kcal for tert-$C_5H_{11}OOH$. It follows from Fig. 1 that the conjugation energy of peroxide radicals decreases as the electronegativity of the atom directly bonded to oxygen decreases, according to the equation

$$A_1 = -27 + 22.5\rho.$$

Apparently, when the electronegativity of X decreases, the mobility of the neighboring σ-bond increases and, consequently, so does its ability to enter into conjugation with the unpaired electron, which leads to destabilization of the three-electron bond in the peroxide radical.

It is interesting to note that expression $(4')$ makes it possible to calculate the conjugation energies of peroxide radicals in cases where A_2 can be determined from the heat of the reaction $R + O_2 \rightarrow RO_2 + q$. Such a calculation was carried out for the peroxide radical formed after irradiation of Teflon with γ-rays in the presence of oxygen, according to the data of work ([7]). The conjugation energy of such a radical proved to be 25 ± 2.5 kcal.

Equation (4′) also makes it possible to analyze the structure of a number of polyoxygen compounds.

In particular, it is easy to show that neither the biradical form nor the form of a three-membered ring corresponds to the true structure of ozone, since in these cases criterion (4′) is not satisfied.

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Note: Figure translations are in progress. See original paper for figures.