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Abstract

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Specific Properties of Oxidation Catalysts and Their Bond Energies with Oxygen, Hydrogen, and Carbon Atoms

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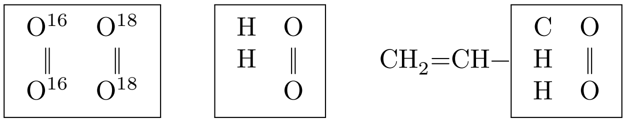
At the present time, a widely accepted view is that the specificity of the action of catalysts and their activity are determined by the bond energies of the catalyst with the reacting groups of atoms in the molecules (1). Balandin and co-workers (2,3), on the basis of kinetic data, proposed methods of calculation, and for a number of processes (hydrogenation, dehydration, etc.) calculated the bond energies of catalysts with the principal atoms (C, H, O, N) comprising molecules of organic substances. Similar calculations for catalysts for the oxidation of organic compounds have not been carried out. This is apparently due to the fact that, before the development of the flow-circulation method for studying the kinetics of catalytic reactions, there were no sufficiently reliable data on the activation energies of exothermic reactions. This gap has now been substantially filled by the works of Boreskov and co-workers (4,5), who studied, by the flow-circulation method, the kinetics of a number of processes on typical oxidation catalysts. A number of authors (6–8) have also studied in sufficient detail the kinetics of propylene oxidation to acrolein on copper oxides, the same process (9) and a number of others (10) on vanadium pentoxide, as well as the kinetics of ethylene oxidation to ethylene oxide on a silver catalyst (11). In the opinion of Belousov, Gorokhovatskii, and Rubanik (6), when studying kinetics under the conditions of a flow-circulation apparatus with the use of the method of freezing out the reaction products, activation energies close to the true values can be determined, since the heats of adsorption of the reaction products are excluded from them.

On the basis of the method for calculating bond energies proposed by Kiperman and Balandin (3), as applied to oxidation processes, the following principal catalytic reactions are proposed for determining the bond energies of catalysts with the elements of organic molecules: homomolecular oxygen exchange, hydrogen oxidation, and propylene oxidation to acrolein. When these reactions are used, the principal reacting groups of atoms will be:



$$\boxed{\begin{array}{cc} O^{16} & O^{18} \\ \| & \| \\ O^{16} & O^{18} \end{array}} \qquad \boxed{\begin{array}{cc} H & O \\ H & \| \\ & O \end{array}} \qquad CH_2{=}CH{-}\boxed{\begin{array}{cc} C & O \\ H & \| \\ H & O \end{array}}$$

According to the energetic aspect of the multiplet theory $^{(1)}$:

$$E' = -Q_{\mathrm{AB}} - Q_{\mathrm{CD}} + (Q_{\mathrm{AK}} + Q_{\mathrm{BK}} + Q_{\mathrm{CK}} + Q_{\mathrm{DK}}),$$

$$E'' = Q_{\mathrm{AD}} + Q_{\mathrm{BC}} - (Q_{\mathrm{AK}} + Q_{\mathrm{BK}} + Q_{\mathrm{CK}} + Q_{\mathrm{DK}}),$$

where E' is the heat of formation of the intermediate complex, and E'' is the heat of its decomposition.

For the reaction of homomolecular oxygen exchange:

$$E' = -Q_{\mathrm{O_2}^{16}} - Q_{\mathrm{O_2}^{18}} + 2Q_{\mathrm{O^{16}K}} + 2Q_{\mathrm{O^{18}K}}.$$

Since the dissociation energy of $\mathrm{O_2}^{18}$ has not yet been determined, it may be assumed that $Q_{\mathrm{O_2}^{16}}$ and $Q_{\mathrm{O_2}^{18}}$ are close; then $Q_{\mathrm{O_2}^{16}} \approx Q_{\mathrm{O_2}^{18}}$ and $Q_{\mathrm{O^{16}K}} \approx Q_{\mathrm{O^{18}K}}$. According to $^{(12)}$, $\varepsilon = 11.75 - \gamma E'$, where ε is the activation energy of the process; moreover, for exothermic reactions $\gamma = 0.25$. $Q_{\mathrm{O_2}^{16}} = 119.2$ kcal/mol $^{(13)}$. After transformations we obtain:

$$Q_{\mathrm{O-K}} = 71.35 - \varepsilon_1, \tag{I}$$

where ε_1 is the activation energy of the reaction of homomolecular oxygen exchange on the given oxide.

For hydrogen oxidation reactions:

$$E' = -Q_{\mathrm{H-H}} - Q_{\mathrm{O=O}} + 2Q_{\mathrm{H-K}} + 2Q_{\mathrm{O-K}},$$

since $Q_{\mathrm{H=H}} = 104.2$ kcal/mole (^{13});

$$Q_{\mathrm{H-K}} = 135.20 - Q_{\mathrm{O-K}} - 2\varepsilon_2, \tag{II}$$

where ε_2 is the activation energy of hydrogen oxidation on the given oxide.

For the reaction of propylene oxidation to acrolein:

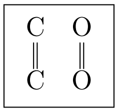
$$E_1 = -Q_{\mathrm{C-H}} - Q_{\mathrm{O=O}} + Q_{\mathrm{H-K}} + Q_{\mathrm{C-K}} + 2Q_{\mathrm{O-K}}.$$

According to (^{13}), in the methyl group of propylene $Q_{\mathrm{C-H}} = 77$ kcal/mole; hence:

$$Q_{\mathrm{C-K}} = 243.2 - Q_{\mathrm{H-K}} - 2Q_{\mathrm{O-K}} - 4\varepsilon_3, \tag{III}$$

where ε_3 is the activation energy of the reaction of propylene oxidation to acrolein.

With respect to the reaction of complete oxidation of olefins, it has been suggested (14) that this process proceeds not through adsorption at the methyl group, but at the $C = C$ bond, followed by its complete destruction. In this case the reacting group of atoms will be:



$$\boxed{\begin{array}{cc} \mathrm{C} & \mathrm{O} \\ \| & \| \\ \mathrm{C} & \mathrm{O} \end{array}}$$

$$E' = -Q_{\mathrm{C=C}} - Q_{\mathrm{O=O}} + 2Q_{\mathrm{C-K}} + 2Q_{\mathrm{O-K}}; \quad Q_{\mathrm{C=C}} = 120 \text{ kcal/mole } (^{13});$$

Then

$$Q_{\mathrm{C-K}} = 143.1 - Q_{\mathrm{O-K}} - 2\varepsilon_4, \qquad \text{(IV)}$$

where ε_4 is the activation energy of complete oxidation of an olefin to CO_2 and H_2O.

Table 1

Bond energies of oxidation catalysts with elements of organic molecules

Catalyst	ε_1	ε_2	ε_3	ε_4	$Q_{\mathrm{O-K}}$	$Q_{\mathrm{H-K}}$	$Q_{\mathrm{C-K}}$	$Q_{\mathrm{=C-K}}$	Source
CuO	26	13	18	26	45.3	63.8	16.6	35.7	(4,5,6,8)
V_2O_5	33	21	12	21	38.3	54.8	63.6	62.7	(4,5,9)
$V_2O_3^*$	–	–	–	–	42.6	56.4	26.7	–	(16)
Cr_2O_3	30	18	–	–	41.3	57.8	–	–	(4,5)
$Cr_2O_3^*$	–	–	–	–	51.8	60.9	22.7	–	(16)
MnO_2	22	14	–	–	49.3	57.8	–	–	(5)
Co_3O_4	16	11	–	–	55.3	57.8	–	–	(4,5)
NiO	24	14	–	–	47.3	59.8	–	–	(4,5)
Ni^*	–	–	–	–	48.5	55.0	6.0	–	(15)
ZnO^*	–	–	–	–	61.7	48.6	23.1	–	(16)
ZnO	30	24	–	–	41.3	45.8	–	–	(4,5)
MoO_3^*	–	–	–	–	42.9	61.3	27.7	–	(11)
WO_3^*	–	–	–	–	43.5	53.2	27.6	–	(16)
Ag^{**}	13	–	15	20	58.3	–	24.8	44.8	(11,17)
Pt^{**}	36	7.5	–	–	35.3	49.6	–	–	(11,18)
Pt^{**}	–	–	–	–	34.1	54.2	6.9	–	(16)

* The bond energies for these catalysts are taken from Balandin' s data ([15,16]). From ε_1 for U_2O_5, Cr_2O_3, and ZnO the heats of adsorption of oxygen on these oxides ([4]) have been excluded.

** For Ag and Pt, $Q_{\mathrm{O-K}}$ was calculated from data on isotopic oxygen exchange, and $Q_{\mathrm{C-K}}$ and $Q_{\mathrm{C-K}}$ for Ag—from the activation energies of ethylene oxidation to oxide (ε_3) and CO_2 and H_2O (ε_4) on silver.

Table 1 gives the values of $\varepsilon_1, \varepsilon_2, \varepsilon_3$, and ε_4 from literature data and the bond energies calculated by formulas I, II, III, and IV for a series of metal oxides and some metals.

It should be noted that, in view of the fact that homomolecular exchange proceeds chiefly on the most active regions of catalysts ([4]), the bond energies with oxygen given in the table characterize only these regions.

For less active sites, ε_1 will be higher, and $Q_{\mathrm{O-k}}$ lower, than those indicated in Table 1. In addition, it must be taken into account that in the process of hydrocarbon oxidation partial reduction of oxides occurs, and the values $Q_{\mathrm{C-k}}$ have been determined precisely for such partially reduced oxides.

The data of Table 1 agree well with the known experimental material characterizing the specific properties of individual oxidation catalysts. Thus, for example, copper oxide (partially reduced) is a typical catalyst for the oxidation of propylene and other olefins to unsaturated carbonyl compounds. This property of the given oxide can readily be explained by the especially high value of the bond energy with hydrogen ($Q_{\mathrm{H-Cu}}$), owing to which the weakest C—H bond in the methyl group of the olefin is readily cleaved, with the formation of unsaturated carbonyl compounds in the presence of oxygen. A competing parallel reaction in the oxidation of olefins on copper oxides is the reaction of complete oxidation of the olefin to CO_2 and H_2O ([14]), which, apparently, is caused by the rather high affinity of this catalyst for the double C=C bond ($Q_{\mathrm{=C-Cu}}$), leading to easier destruction of the molecule on the catalyst and further oxidation to CO_2 and H_2O.

In the case of vanadium oxide, the bond energies $Q_{\mathrm{C-V}}$ and $Q_{\mathrm{=C-V}}$ are higher than $Q_{\mathrm{H-V}}$. This indicates that vanadium pentoxide should carry out oxidation reactions with destruction of organic molecules along carbon–carbon bonds considerably more actively than with cleavage of C—H bonds. Indeed, V_2O_5 catalyzes the oxidation of propylene chiefly with rupture of double bonds; it readily oxidizes aromatic hydrocarbons with destruction of the aromatic ring and formation of maleic and phthalic acids. It should be noted that for V_2O_5 the activation energies for the formation of acrolein and CO_2 are not sufficiently reliable, since they were determined only by the flow method. This characterizes $Q_{\mathrm{C-V}}$ and $Q_{\mathrm{=C-V}}$ as somewhat less accurate quantities than those given in Table 1 for the other catalysts.

The high value of $Q_{\mathrm{=C-Ag}}$ is noteworthy; it indicates that a silver catalyst has an especially high affinity for the double bond. This is a highly specific catalyst for the oxidation of olefins to oxides. It is interesting that silver—a typical oxidation catalyst—has a considerably higher bond energy with oxygen than platinum, which is better known as a hydrogenation catalyst. Platinum, moreover, is also a catalyst for deep oxidation of hydrocarbons. However, the process of complete oxidation on platinum proceeds heterogeneously-homogeneously ([18]). Apparently, owing to the high affinity of platinum for hydrogen, hydrocarbon radicals are formed upon detachment of the H atom on the catalyst; because of the low value of the bond energy ($Q_{\mathrm{C-Pt}} = 6.9$ kcal/mol), these radicals are readily desorbed from the catalyst and are then oxidized, in the presence of oxygen, to CO_2 and H_2O by a chain mechanism in the volume. On silver, however, owing to the comparatively higher affinity of silver for carbon, the process of complete oxidation of hydrocarbons proceeds heterogeneously ([19]).

As can be seen from the data of Table 1, for all oxides used as typical oxidation catalysts (except ZnO) the values of $Q_{\mathrm{H-k}}$ are fairly large, and these quantities vary comparatively little, whereas the values of $Q_{\mathrm{O-k}}$ change within considerably wider limits.

It is interesting that the $Q_{\mathrm{H-k}}$ values calculated in the present work and those determined by Balandin and co-workers ([15,16]) from activation-energy values for endothermic reactions are fairly close.

Patent data on the oxidation of propylene to acrolein indicate that, as catalysts for this process, oxides of all the metals (except ZnO) listed in Table 1 are used. Thus,

the catalysts for this reaction must therefore possess good dehydrogenating properties. According to the hypothesis of Bretton and Dodge [20], the role of oxidation catalysts in the first stage of the reaction is reduced to the abstraction of a hydrogen atom from the hydrocarbon molecule with the formation of hydrocarbon radicals.

Subsequently, probably depending on the magnitude of the $Q_{\mathrm{C-K}}$ bonds, the process proceeds either on the catalyst, with the formation mainly of products of mild oxidation of hydrocarbons, or, when this quantity is small, with escape into the bulk and the formation of products of complete combustion, which is characteristic of a number of deep-oxidation catalysts. Apparently, in order to carry out processes of mild oxidation of hydrocarbons, it is necessary that the $Q_{\mathrm{C-K}}$ and $Q_{\mathrm{=C-K}}$ bonds have comparatively high values.

Table 2

Sum of the energies of bonds formed with the catalyst (q), and half-sums of the breaking and forming bonds ($s/2$) for several reactions on copper oxide

Reactions	$s/2$, kcal/mol	q, kcal/mol
$H_2 + O_2 \to H_2O$	214.04	218.40

Reactions	$s/2$, kcal/mol	q, kcal/mol
$C_3H_8 + O_2 \rightarrow CO_2 + H_2O$	209.60	162.20
$O_2^{18} + O_2 \rightarrow 2O^{18}O^{18}$	238.40	181.40
$C_3H_6 + O_2 \rightarrow CH_2{=}CH{-}CHO$	199.27	124.20

In Table 2 are given the sums of the energies of bonds formed with the catalyst (q), and the half-sums of the breaking and forming bonds ($s/2$) for four reactions proceeding on copper oxide.

As is seen from the data of Table 2, a copper-oxide catalyst can be considered optimal in activity [1] only for the reaction of hydrogen oxidation, since only in this case is the sum of the energies of bonds formed with the catalyst (q) close to the half-sum of the breaking and forming bonds ($s/2$).

It is known that the rate of oxidation of propylene to acrolein is considerably higher on a catalyst reduced to cuprous oxide, whereas the reaction of complete oxidation proceeds at a higher rate on copper oxide [21]. Apparently, cuprous oxide is a more favorable catalyst for this process.

Thus, the values of the bond energies of oxidation catalysts with the elements of organic molecules explain rather well their specific properties in oxidation reactions.

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