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Abstract

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ON THE BOND ENERGIES OF ORGANOGENIC ELEMENTS WITH THE SURFACE OF OXIDE CATALYSTS

Previously ([1]) it was indicated that the multiplet theory implies the possibility of decomposing the activation energies ε of heterogeneous catalytic reactions into separate components—the bond energies Q. Such a decomposition was first carried out experimentally in ([2]). This additivity underlies the kinetic method ([3]) for the experimental determination of the bond energies of reacting atoms with the catalyst surface, Q_{AK}. The problem of determining Q_{AK} is important for the theory of catalyst selection, since knowledge of Q_{AK} makes it possible, from a small amount of data, to calculate ε for a series of reactions. As indicated by one of the authors ([4]), the catalytic properties of elements are related to their position in the Mendeleev system, and this should also apply to Q_{AK}. Work in this direction is being carried out systematically in our laboratory.

In the case of oxide catalysts there arises a question that does not occur for pure metals, namely: are the reacting atoms attracted to the atoms of the metal or of the oxygen? The active center may also consist of atoms of both kinds. A priori all these cases are possible, which complicates the interpretation of the data obtained. However, the information currently available indicates that, apparently, the matter is simpler and the first of the possibilities mentioned is realized. This question has already been partly discussed earlier ([5–7]). The following facts speak in favor of the bonding of molecules with the metal.

1) The observed Q_{AK} values for metals and for oxides do not differ greatly from one another, as has already been noted in the cases of Ni and Cr_2O_3 ([2]).

2) In the dehydrogenation and dehydration of alcohols, oxygen in the initial molecule participates in the reaction; if it were to bind to the oxygen of the catalyst oxide, a peroxide bond would have to form, which is chemically quite improbable ([6]). This is confirmed by the fact that in peroxides $Q_{\mathrm{O-O}} \simeq 35$ kcal—less than the observed values of $Q_{\mathrm{O-K}}$, which in the case of oxides sometimes exceed 60 kcal (see Table 1).

3) If the organogen were bonded to the oxygen of the oxide, then Q_{OK} should change comparatively little on passing from one oxide catalyst to another. In fact, however, Q_{OK} is precisely the quantity most strongly subject to changes depending on the nature and method of preparation of the catalyst (from 72.0 for Pr_2O_3 to 29.8 kcal for ZrO_2, see Table 1) ([2]).

4) If an organogen were bonded to the oxygen of an oxide, then replacing the oxide catalyst by the sulfide of the same metal should have led to a strong change in Q_{AK}. In reality, Q_{AK} values for oxides and sulfides are close to one another; for example, for MoO_{3-x} and for MoS_2: Q_{HK} 61.3 and 60.3; Q_{CK} 27.7 and 26.8; Q_{OK} 42.9 and 52.5 kcal, respectively; and similarly for WO_{3-x} and for WS_2: Q_{HK} 51.0 and 58.0; Q_{CK} 29.6 and 26.8; Q_{OK} 61.3 and 54.2 kcal ([8]). This indicates that the organogens are bonded to metal atoms.

5) The bond energies found, Q_{HK} and Q_{OK}, with catalysts—rare earths—change sympathetically, while Q_{CK} changes antibatically with the magnetic moment of the metal ion ([9]). Consequently, the decisive role is played by the nature of the metal, not of the oxygen, and this indicates that it is precisely with the metal, and not with the oxygen, that the reacting atoms in the catalytic complex are connected. This is an especially convincing proof.

All that has been said above permits the following general conclusion to be drawn: the bond energies of organogens with the surface of oxide catalysts, as determined by the kinetic method, characterize organogen—metal bonds. This conclusion can probably

Table 1

Heats of formation ΔH_f^0 according to [11], kinetic Q^K and thermochemical Q^T bond energies for oxides; dissociation energies D according to [12] (all quantities in kcal)

Atomic number of element	Oxide	ΔH_f^{0*}	$Q^K_{H-Me_nO_m}$ mean	$Q^K_{H-Me_nO_m}$ standard	$Q^K_{C-Me_nO_m}$ mean	$Q^K_{C-Me_nO_m}$ standard	$Q^K_{O-Me_nO_m}$ mean	$Q^K_{O-Me_nO_m}$ standard	Q^T_{O-Me}	D_{O-Me}	Source
4	BeO	146	49.8	49.8	19.6	19.6	66.8	66.8	102.5	124	(14)
22	TiO_2	218	59.0	60.5	30.2	28.6	44.9	46.3	84.0	160	(15)
23	V_2O_3	290	56.5	56.4	26.5	26.7	43.6	42.5	78.0	147	(16)
24	Cr_2O_3	270	61.0	60.9	22.5	22.7	48.8	51.8	74.4	97	(17)
25	MnO	92	50.8	50.7	26.7	26.7	38.8	38.8	75.5	—	(18)
30	ZnO	83.2	48.6	48.6	23.1	23.1	61.7	61.7	71.1	92	(7)
31	Ga_2O_3	258	53.5	53.5	23.8	23.8	67.6	67.6	72.5	—	(19)
39	Y_2O_3	—	53.6	53.6	22.0	22.1	56.5	58.8	—	160	(20)
40	ZrO_2	—	59.9	61.3	13.1	11.8	31.5	29.8	—	150	(21)
42	MoO_3	180	60.5	61.3	28.5	27.7	43.6	42.9	59.5	—	(22)
57	La_2O_3	458	47.5	47.5	17.2	17.2	64.9	64.9	106.0	188	(9)
58	CeO_2	233	56.2	57.6	21.2	19.8	49.0	49.9	87.8	150	(25)
59	Pr_2O_3	444	52.9	52.9	11.4	11.4	72.0	72.0	103.6	—	(9)

Atomic number of element	Oxide	ΔH_f^{0*}	$Q^{K}_{H-Me_{nO}m}$ mean	$Q^{K}_{H-Me_{nO}m}$ standard	$Q^{K}_{C-Me_{nO}m}$ mean	$Q^{K}_{C-Me_{nO}m}$ standard	$Q^{K}_{O-Me_{nO}m}$ mean	$Q^{K}_{O-Me_{nO}m}$ standard	Q^{T}_{O-Me}	D_{O-Me}	Source
60	Nd_2O_3	442	52.8	52.8	16.0	16.0	64.7	64.7	103.0	–	(9)
64	Gd_2O_3	–	54.8	54.8	15.0	15.0	65.2	65.2	–	139	(9)
74	WO_3	201	53.2	52.6	27.7	27.6	42.9	43.5	63.0	–	(26)
90	ThO_2	292	56.3	52.3	17.7	21.6	48.8	61.3	102.5	–	(23)
92	U_3O_8	898	48.9	48.9	25.6	25.6	40.3	40.3	85.7	–	(24)

* Data of [11].

be extended also to sulfides, selenides, nitrides, borides, and hydrides of metals.

In the next approximation, it is necessary to take into account the valence of the metal and the influence of the nature, number, and arrangement of the atoms surrounding the active center. Thus, in the case of chromium oxides, Q_{OCr} decreases somewhat [3] with increasing valence of Cr. The influence of the environment is described [1] by the sublimation term λ. As was shown, the use of apparent activation energies instead of true ones for dehydrogenation and dehydration has little effect [10] on the values found for Q_{AK}. According to [5], the reacting atoms in catalysis are adsorbed in hollows between neighboring atoms of the catalyst and, consequently, in the present case, between metal atoms. Even if, in complex active centers, oxygen atoms in small numbers also enter into the active center, then, as is clear from the foregoing, their influence cannot be decisive.

From the conclusion that the atoms of reacting molecules are bound to the metal atoms of oxide catalysts, further consequences follow. If this conclusion is correct, one may expect the existence of parallelism between the bond energies of the oxygen of the reacting molecule with the surface of the catalyst–oxide $Me_{nO}m$, determined by the kinetic method, $Q^{K}_{O-Me_{nO}m}$, on the one hand, and the energies of bonds of the metal with oxygen in the oxide, determined thermochemically, Q^{T}_{O-Me}, on the other hand. Indeed, $Q^{K}_{O-Me_{nO}m}$ and Q^{T}_{O-Me} measure one and the same quantity–the affinity of the metal for oxygen, but only on

surface and in the bulk, respectively, and therefore they should also differ by the magnitude of the sublimation term λ.

Table 1 compares various relevant data. Column 1 gives the atomic number of the element N, column 2 the formula of the oxide catalyst, column 3 the heat of formation of this oxide from the elements ΔH_f^0 according to [11], and the next six columns collect Q values for oxides obtained up to the present time in our laboratory. In order to reduce the differences in λ, data are given for

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

catalysts (without supports) prepared, as far as possible, by the same method—by precipitation with ammonia from a nitrate solution. As a rule, tetralin and alcohols were passed over the catalysts. Column 4 gives the mean $Q^{\text{k}}_{\text{H}-\text{Me}_n\text{O}_m}$ values found from the activation energies ε for the dehydrogenation of tetralin and the mean ε values for the dehydrogenation and dehydration of various alcohols; column 5 gives analogous values, but standard ones—differing in that, besides ε for tetralin, ε for one alcohol, isopropyl alcohol, was taken. In some

Fig. 1

Fig. 2

cases the experiments, apart from tetralin, were carried out only with the latter; then the mean and standard values in Table 1 coincide. Columns 6 and 7 give analogous data for $Q^{\text{k}}_{\text{C}-\text{Me}_n\text{O}_m}$, and columns 8 and 9 the same for $Q^{\text{k}}_{\text{O}-\text{Me}_n\text{O}_m}$. Wherever necessary, bond energies were recalculated using the data ([12]) for Q_{OH}, Q_{CO}, and Q_{CH}. Column 10 contains $Q^{\text{T}}_{\text{O}-\text{Me}}$, calculated from ΔH^0_f ([11]), taking into account the dissociation energy of O_2 (for example, for $\text{O}-\text{Be}$ from $\text{Be} + \frac{1}{2}\text{O}_2 = \text{BeO} + 146$; $\text{O} = \frac{1}{2}\text{O}_2 + 59.1$; $\text{Be} + \text{O} = \text{Be} = \text{O} + 205.1$; whence $Q^{\text{T}}_{\text{O}-\text{Be}} = 102.5$ kcal).

Column 11 gives the dissociation energies of the $D_{\text{O}-\text{Me}}$ bonds according to ([13]). Finally, column 12 gives references to the literature on standard kinetic bond energies. Comparison of columns 4 and 5 of Table 1 shows that the bond energies in them are close to one another, and the same applies to columns 5 and 7, as well as 8 and 9; this indicates the same orientation of the alcohols by the reacting group toward the catalyst, in agreement with multiplet theory.

A comparison of the numbers in columns 9 and 10 is made in Fig. 1, where the atomic number of the metal in the oxide is plotted on the abscissa, and $Q^{\text{k}}_{\text{O}-\text{Me}_n\text{O}_m}$ and $Q^{\text{T}}_{\text{O}-\text{Me}}$ on the ordinate. It can be seen that the expected parallelism between these quantities is indeed observed. Such parallelism, first, confirms that in catalysis the atoms of the reacting molecules are adsorbed on the metal and not on the oxygen, and, second, indicates

because $Q^{\text{k}}_{\text{O}—\text{Me}n\text{O}_m}$ is a periodic function of the atomic number, since it is known that $Q^{\text{t}}_{\text{O}—\text{Me}}$ is a periodic function of N.

In Fig. 1 the line for $Q^{\text{t}}_{\text{O}—\text{Me}}$ is located higher than the line for $Q^{\text{k}}_{\text{O}—\text{Me}n\text{O}_m}$, and there are certain deviations from complete parallelism that exceed the limits of experimental error. This is due to the influence of the sublimation term and is

also in agreement with the multiplet theory.

From Table 1 one more, semiempirical dependence follows. Fig. 2 is constructed similarly to Fig. 1, but in it, instead of $Q^{t}_{O—Me}$, the values $D_{O—Me}$—the numbers in column 10 divided by the valence v—are plotted. In Fig. 2 the parallelism is expressed even more clearly than in Fig. 1. This can be explained by the smaller influence of λ; however, the reason why division by v is necessary is still unclear.

The regularity found (Fig. 1) also makes it possible to improve the calculation of the activation energy of dehydrogenation of hydrocarbons ε_1, if these quantities are known for the dehydrogenation of alcohols (ε_2) and the dehydration of the latter (ε_3). In (6) the formula was derived

$$\varepsilon_1 = {}^{2}/_{3}(\varepsilon_2 + \varepsilon_3) + Q_{OK} - 48.6.$$

Owing to the absence of other data, in (6) the value $Q^{t}_{O—Me}$ was adopted for Q_{OK}. However, according to the meaning of the calculation, here Q_{OK} is $Q^{k}_{O—MenO_m}$; the latter quantity is smaller than $Q^{t}_{O—Me}$ (see Fig. 1). Taking this circumstance into account leads to an improvement of the results obtained in (6).

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