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Abstract

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ON THE MAGNITUDES OF THE BOND ENERGY OF NICKEL CATALYSTS WITH ELEMENTS OF ORGANIC COMPOUNDS

In solving the problem of the scientific selection of catalysts, it is of substantial importance to find the magnitudes of the bond energies of catalysts with various elements. Among the methods that may be used for this purpose, we shall mention the thermochemical, adsorption-chemical ([1]), and kinetic ([2]) methods. The kinetic method had previously been applied only to oxide catalysts ([3,4]). Below an attempt is made to apply this method to calculations of the bond energies of nickel catalysts with elements of organic compounds, using reactions that had not previously been employed.

The bond energy of a nickel catalyst with hydrogen $Q_{\mathrm{H-Ni}}$ and deuterium $Q_{\mathrm{D-Ni}}$. We shall use the reactions of the para-ortho conversion of hydrogen (1) and the isotopic exchange of hydrogen with deuterium (2), studied under identical conditions by Fajans ([5]), at 36-100°C on nickel gauze activated by alternating oxidation and reduction. The mechanism of these reactions is still under discussion ([6]). Assuming that the indicated reactions are limited by the surface interaction of the adsorbed components (the adsorption stage), let us represent both reactions by the doublet scheme of the multiplet theory ([7]), and write expressions for the heights of the energy barriers E of reactions ([2]):

$$-2Q_{\mathrm{H-H}}^{\mathrm{para}} + 4Q_{\mathrm{H-Ni}} = E_1, \tag{1}$$

$$-Q_{\mathrm{H-H}} - Q_{\mathrm{D-D}} + 2Q_{\mathrm{H-Ni}} + 2Q_{\mathrm{D-Ni}} = E_2. \tag{2}$$

($Q_{\mathrm{H-H}}^{\mathrm{para}}, Q_{\mathrm{D-D}}$, and $Q_{\mathrm{H-H}}$ are the corresponding energies of rupture of molecular bonds.) Hence, taking into account the relation $\varepsilon = -(3/4)E$ ([2]), we have:

$$Q_{\mathrm{H-Ni}} = \frac{1}{2}Q_{\mathrm{H-H}}^{\mathrm{para}} - \frac{1}{3}\varepsilon_1, \tag{3}$$

$$Q_{\mathrm{D-Ni}} = \frac{1}{2}\left(Q_{\mathrm{D-D}} + Q_{\mathrm{H-H}} - Q_{\mathrm{H-H}}^{\mathrm{para}}\right) - \frac{1}{3}(2\varepsilon_2 - \varepsilon_1), \tag{4}$$

where ε_1 and ε_2 are, respectively, the activation energies of reactions (1) and (2). Substituting $Q_{\text{H–H}} = 104.2$ kcal ([8]), $Q_{\text{D–D}} = 105.96$ kcal ([9]) (the difference between $Q_{\text{H–H}}$ for hydrogen of normal composition at 298.1°K and $Q_{\text{H–H}}^{\text{para}}$ is insignificant ([12])), $\varepsilon_1 = 5910$ cal/mol, $\varepsilon_2 = 7290$ cal/mol ([5]), we obtain $Q_{\text{H–Ni}} = 50.1$ kcal, $Q_{\text{D–Ni}} = 50.1$ kcal. According to an estimate ([10]) from thermochemical data, $Q_{\text{H–Ni}} = 55$ kcal; Eley ([11]), from the Pauling equation, estimates $Q_{\text{H–Ni}} = 60.2$ kcal.

Using the values $\varepsilon_1 = 7600$ cal/mol and $\varepsilon_2 = 9500$ cal/mol, obtained in ([5]) after a decrease in the activity of the catalyst, we arrive at $Q_{\text{H–Ni}} = 49.6$ kcal and $Q_{\text{D–Ni}} = 49.5$ kcal, i.e., a change in the activity of the catalyst has only a small effect on $Q_{\text{H–Ni}}$ and $Q_{\text{D–Ni}}$.

If, however, the reactions under consideration are limited by the desorption stage (the Bonhoeffer and Farkas mechanism ([16])), then from the expressions for the two-stage process ([2]) we obtain $Q_{\text{H–Ni}} = 54.1$ kcal and $Q_{\text{D–Ni}} = 55.9$ kcal.

We shall use the obtained values of $Q_{\text{H–Ni}}$ and $Q_{\text{D–Ni}}$ for approximate calculations of the bond energies of nickel catalysts with other elements, using other hydrogen activation reactions, assuming that the transition to other Ni samples will not introduce appreciable changes in $Q_{\text{H–Ni}}$ and $Q_{\text{D–Ni}}$.

Bond energy of a nickel catalyst with carbon at a double bond $Q_{=C-\text{Ni}}$. Let us use Twigg' s data ([13]) on the hydrogenation of ethylene at 70-100°C on nickel wire activated by alternate oxidation and reduction. Here:

$$Q_{=C-\text{Ni}} = \frac{1}{2}(Q_{C=C} + Q_{H-H}) - Q_{H-\text{Ni}} - \frac{2}{3}\varepsilon_3, \tag{5}$$

where ε_3 is the activation energy, and $Q_{C=C}$ is the energy of rupture of one of the $C = C$ bonds. Substituting $\varepsilon_3 = 8200$ cal/mol ([13]), $Q_{C=C} = 46.7$ kcal, $Q_{H-H} = 104.2$ kcal ([8]), and $Q_{H-\text{Ni}} = 50.1$ kcal, we obtain $Q_{=C-\text{Ni}} = 19.9$ kcal. According to an estimate of the ease of occurrence of various organic reactions ([10]), $Q_{=C-\text{Ni}} = 19$ kcal.

For the same reaction at 20-160°C on a nickel film, according to the data of Jenkins and Rideal ([14]), $\varepsilon_3 = 10200$ cal/mol, whence $Q_{=C-\text{Ni}} = 18.6$ kcal; i.e., on passing to another Ni sample, $Q_{=C-\text{Ni}}$ changes little.

For the isotope exchange $C_2H_4 + D_2$ ([13]) under the same conditions as in ([14]), the activation energy is $\varepsilon_4 = 17200$ cal/mol; in this case we have:

$$Q_{=C-\text{Ni}} = Q_{D-D} + Q_{C-H} - 2Q_{D-\text{Ni}} - Q_{H-\text{Ni}} - \frac{4}{3}\varepsilon_4, \tag{6}$$

where Q_{C-H} is the energy of rupture of the $C - H$ bond, equal to 90.5 kcal ([8]). Substituting $Q_{H-\text{Ni}} = Q_{D-\text{Ni}} = 50.1$ kcal and the other quantities given above, we obtain $Q_{=C-\text{Ni}} = 23.2$ kcal. Elley ([11]), by the method already mentioned,

obtained for adsorption (and not for the reaction) a considerably larger value, $Q_{=C-\mathrm{Ni}} = 50.6$ kcal.

Bond energy of a nickel catalyst with carbon $Q_{C-\mathrm{Ni}}$ (with an ordinary bond at carbon). This quantity can be calculated from the data of Morikawa, Benedict, and Taylor ([15]) on the hydrogenolysis of ethane $C_2H_6 + H_2 = 2CH_4$ in the range 100-130°C on a nickel catalyst supported on kieselguhr. For this reaction

$$Q_{C-\mathrm{Ni}} = \frac{1}{2}(Q_{C-C} + Q_{H-H}) - Q_{H-\mathrm{Ni}} - \frac{2}{3}\varepsilon_5, \tag{7}$$

where the activation energy $\varepsilon_5 = 43000$ cal/mol ([15]). Substituting $Q_{C-C} = 66.3$ kcal ([8]), $Q_{H-\mathrm{Ni}} = 50.1$ kcal, and the remaining quantities given above, we obtain $Q_{C-\mathrm{Ni}} = 6.5$ kcal. According to the estimate ([10]), $Q_{C-\mathrm{Ni}} = 6$ kcal.

For the isotope exchange $CH_4 + D_2$, studied in ([15]), at 110-184°C:

$$Q_{C-\mathrm{Ni}} = Q_{C-H} + Q_{D-D} - Q_{H-\mathrm{Ni}} - 2Q_{D-\mathrm{Ni}} - \frac{4}{3}\varepsilon_6. \tag{8}$$

Substituting the value of the activation energy $\varepsilon_6 = 28000$ cal/mol ([15]), $Q_{H-\mathrm{Ni}} = Q_{D-\mathrm{Ni}} = 50.1$ kcal, and the other quantities given above, we obtain $Q_{C-\mathrm{Ni}} = 8.9$ kcal. The average $Q_{C-\mathrm{Ni}} = 7.7$ kcal.

For the same isotope-exchange reaction on a more active catalyst—nickel films—and at higher temperatures (206-255°C), according to ([22]), $\varepsilon_6 = 23800$ cal/mol, whence $Q_{C-\mathrm{Ni}} = 14.5$ kcal.

Bond energy of a nickel catalyst with oxygen $Q_{O-\mathrm{Ni}}$. We use the data of van Mechelen and Jungers ([18]), who studied the hydrogenation of acetone in an autoclave at temperatures of 106-150°C on skeleton nickel. The activation energy is $\varepsilon_7 = 9500$ cal/mol (for other aliphatic ketones, similar values were obtained). For this reaction:

$$Q_{O-\mathrm{Ni}} = Q_{C=O} + Q_{H-H} - Q_{=C-\mathrm{Ni}} - 2Q_{H-\mathrm{Ni}} - \frac{4}{3}\varepsilon_7 \tag{9}$$

($Q_{C=O}$ is the energy of rupture of one of the $C=O$ bonds, equal to 83.4 kcal ([8]).) Substituting $Q_{=C-\mathrm{Ni}} = 19.9$ kcal, $Q_{H-\mathrm{Ni}} = 50.1$ kcal, and the other quantities given above, we obtain $Q_{O-\mathrm{Ni}} = 54.8$ kcal. According to the estimate ([10]), $Q_{O-\mathrm{Ni}} = 48.5$ kcal. The thermochemical value is $Q_{O-\mathrm{Ni}} = 59$ kcal ([10]).

For the isotope-exchange reaction $CH_3OH + D_2 = CH_3OD + HD$ we have

$$Q_{O-\mathrm{Ni}} = Q_{O-H} + Q_{D-D} - Q_{H-\mathrm{Ni}} - 2Q_{D-\mathrm{Ni}} - \frac{4}{3}\varepsilon_8. \tag{10}$$

(Q_{O-H} is the energy of rupture of the O–H bond, equal to 110.6 kcal ([8]).) Substituting the value of the activation energy $\varepsilon_8 = 6600$ cal/mole ([19]), for nickel films in the interval 0-41.5°C, $Q_{H-Ni} = 50.1$ kcal, $Q_{D-Ni} = 50.1$ kcal, and the other quantities given above, we obtain $Q_{O-Ni} = 57.5$ kcal. In studying the adsorption-chemical equilibrium of oxygen on a nickel catalyst by the method of ([1]), we obtained, for average coverages of the surface by oxygen, the value $Q_{O-Ni} = 56.1$ kcal.

The bond energy of a nickel catalyst with nitrogen, Q_{N-Ni}. We use the reaction of isotopic exchange of ammonia with deuterium, studied on nickel films. For this reaction:

$$Q_{N-Ni} = Q_{N-H} + Q_{D-D} - Q_{H-Ni} - 2Q_{D-Ni} - {}^4/_3\varepsilon_9, \tag{11}$$

where Q_{N-H} is the energy of rupture of the N–H bond, equal to 84.3 kcal ([8]); ε_9 is the activation energy. In various studies, depending on the activity of the film, the values of ε_9 vary from 8700-9300 cal/mole ([20]) to 14,700-16,100 cal/mole ([21]). On the least active films, the values of ε_9, although obtained in the interval 200-300°C, corresponded, as the authors indicate ([21]), to the activity of the catalyst in the initial experiments at room temperature. Substituting into equation (11) $\varepsilon_9 = 16,100$ cal/mole for the least active films ([21]), $Q_{H-Ni} = 50.1$ kcal, $Q_{D-Ni} = 50.1$ kcal, and the other quantities given above, we obtain $Q_{N-Ni} = 18.6$ kcal. According to the estimate ([10]) (from comparison of the ease of the reactions), $Q_{N-Ni} = 18$ kcal. A change in the activity of the same catalyst ($\varepsilon_9 = 14,700$ cal/mole ([21])) leads to $Q_{N-Ni} = 20.4$ kcal. For more active films ($\varepsilon_9 = 9300$-8700 cal/mole ([20])) we obtain $Q_{N-Ni} = 27.6$-28.4 kcal.

As is seen from the data presented, the kinetic method can be applied to finding the values of bond energies of nickel catalysts with various elements, using such reactions as the para-ortho conversion of hydrogen, isotopic exchange, hydrogenation, and hydrogenolysis. The values obtained in most cases agree with those calculated by an entirely different route ([10]). The bond energy Q_{D-Ni} practically does not differ from Q_{H-Ni} (the difference in zero-point energies for Ni–H and Ni–D, equal to 0.7 kcal ([17]), lies within the sensitivity of the method).

Fluctuations in the activity of the catalyst, leading to a change in ε by several thousand cal/mole, have little effect on the values of Q and in a number of cases have little influence on the transition to other catalyst samples; however, a twofold change in ε_9 leads to a change in Q_{N-Ni} by 50%. In almost all cases, Q for films is higher than for other catalyst samples.

It is significant that, using different reactions to calculate one and the same Q, we obtain close, and sometimes practically coincident, values. As a first approximation, the method can be used for calculations of bond energies on different catalyst samples.

In some cases the values obtained are smaller than the thermochemical ones (cf. ([2],[10])). This means that the corresponding surface compounds are less

stable than the bulk compounds.

Let us use the found values of the bond energies to calculate the adsorption potential q (i.e., the sum of the bond energies of the reacting atoms with the catalyst) for the dehydrogenation of formic acid on Ni:

$$q = Q_{=\mathrm{C-Ni}} + Q_{\mathrm{O-Ni}} + 2Q_{\mathrm{H-Ni}}; \tag{12}$$

substituting $Q_{=\mathrm{C-Ni}} = 19.9$ kcal, $Q_{\mathrm{H-Ni}} = 50.1$ kcal, $Q_{\mathrm{O-Ni}} = 54.8$ kcal, we obtain $q = 174.9$ kcal. On the other hand, we have:

$$q = Q_{\mathrm{C-H}} + Q_{\mathrm{O-H}} - {}^{4}/_{3}\varepsilon_{10}, \tag{13}$$

where ε_{10} is the activation energy. From tabulated values we can, taking $Q_{\mathrm{C-H}} = 90.5$ kcal, $Q_{\mathrm{O-H}} = 110.6$ kcal ([8]), and the experimental value $\varepsilon_{10} = 19700$ cal/mol according to Toyama and Kubokawa ([23]), who worked at 143-160°C, calculate q from equation (13); this gives $q = 174.8$ kcal—in excellent agreement with the value found above by an independent route.

In the present work the following values of Q (in kcal) have been obtained for the one-stage mechanism of reactions proceeding on nickel wire, foil, low-activity films, or porous catalysts: $Q_{\mathrm{H-Ni}} = 50.1$; $Q_{\mathrm{D-Ni}} = 50.1$; $Q_{=\mathrm{C-Ni}} = 19.9$; $Q_{\mathrm{C-Ni}} = 7.7$; $Q_{\mathrm{O-Ni}} = 54.8$; $Q_{\mathrm{N-Ni}} = 18.6$.

In conclusion, we shall calculate from these Q values the adsorption potentials q, as well as the energy barriers E for the reactions considered, using the values of the heats of reaction u and the sums of the energies of the bonds formed and broken s from the relation $q - s/2 + u/2 = E$ ([2]) (Table 1).

Table 1

Adsorption potentials q and energy barriers E on Ni (in kcal)

Reaction	$u/2$	$s/2$	q	$-E$
I. n-H_2 = o-H_2	0	208.4	200.4	8.0
II. $H_2 + D_2 = 2HD$	0	210.2	200.4	9.8
III. $C_2H_4 + H_2 = C_2H_6$	15.0	165.9	140.0	10.9

Reaction	$u/2$	$s/2$	q	$-E$
IV. $CH_3OH + D_2 = CH_3OD + HD$	0	216.6	205.1	11.5
V. $CH_3COCH_3 + H_2 = CH_3CH(OH)CH_3$	6.8	194.4	174.9	12.7
VI. $NH_3 + D_2 = NH_2D + HD$	0	190.3	168.9	21.4
VII. $C_2H_4 + D_2 = C_2H_3D + HD$	0	196.5	170.2	26.3
VIII. $HCOOH = H_2 + CO_2$	−6.8	194.4	174.9	26.3
IX. $CH_4 + D_2 = CH_3D + HD$	0	196.5	158.0	38.5
X. $C_2H_6 + H_2 = 2CH_4$	5.3	175.7	115.6	54.8

It follows from it that, for most of the reactions considered on a nickel catalyst, q is close to $s/2$, i.e., to the optimum. Reaction X should proceed with the greatest difficulty.

It is of particular note that the application of the kinetic method for determining bond energies to simple reactions proceeding on metallic nickel gives results close to those previously calculated from thermochemical data and from comparison of the ease with which reactions of more complex organic compounds proceed.

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REFERENCES CITED

1. A. E. Romanushkina, S. L. Kiperman, M. I. Temkin, ZhFKh, **27**, 1181 (1953).

2. A. A. Balandin, ZhOKh, **16**, 793 (1946).

3. A. A. Balandin, Izv. AN SSSR, OKhN, 1955, No. 4, 624.

4. A. A. Balandin, A. A. Tolstopyatova, ZhFKh, **30**, 1367, 1636 (1956); A. A. Balandin, A. A. Tolstopyatova, V. A. Ferapontov, DAN, **103**, 611 (1955).

5. E. Fajans, Zs. phys. Chem., **B28**, 239 (1935).

6. B. M. W. Trapnell, article in the collection *Catalysis*. Ed. P. H. Emmett, N. Y., 3, 1955, p. 1.

7. A. A. Balandin, ZhRKhO, **61**, 909 (1929); DAN, **94**, 667 (1954).

8. P. Kotrell, *Strength of Chemical Bonds*, IL, 1956.

9. Bureau of Stand., Circ. 500, Wash., 1952.

10. A. A. Balandin, DAN, **107**, 85 (1956).

11. D. Elley, Disc. Farad. Soc., **8**, 34 (1950).

12. A. Farkas, *Orthohydrogen, Parahydrogen and Heavy Hydrogen*, M., 1936.

13. G. H. Twigg, Trans. Farad. Soc., **35**, 935 (1939).

14. G. Jenkins, E. K. Rideal, J. Chem. Soc., 1955, 2490.

15. K. Morikawa, W. S. Benedict, H. S. Taylor, J. Am. Chem. Soc., **58**, 1445, 1795 (1936).

16. K. F. Bonhoeffer, A. Farkas, Zs. phys. Chem., **B12**, 231 (1933).

17. H. Eyring, A. Sherman, J. Chem. Phys., **1**, 345 (1933).

18. C. van Mechelen, J. C. Jungers, Bull. Soc. Chim. Belg., **59**, 597 (1950).

19. J. R. Anderson, C. Kemball, Trans. Farad. Soc., **51**, 966 (1955).

20. C. Kemball, Trans. Farad. Soc., **48**, 254 (1952); Proc. Roy. Soc., **A214**,

413 (1952).

21. J. H. Singleton, E. R. Roberts, E. R. Winter, Trans. Farad. Soc., **47**, 1318 (1951).

22. C. Kemball, Proc. Roy. Soc., **A217**, 356 (1953).

23. O. Toyama, Y. Kubokawa, J. Chem. Soc. Japan, **74**, 283 (1953).

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