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Abstract

Full Text

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Analysis of the Experimental Entropy of Activation of the Hydrogenation Processes of Carbon Oxides on a Nickel Catalyst

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Hydrogenation of carbon monoxide in a large excess of hydrogen on a nickel-chromium catalyst, whose active component is nickel, leads to the formation of methane and is practically not accompanied by side processes or changes in the composition of the catalyst. At CO concentrations up to 0.3 vol.% and temperatures of 135-175° in the kinetic region, zero order with respect to CO is observed; the reaction products do not affect the rate (1). Special experiments established that, under these same conditions, the order with respect to hydrogen is also zero. Thus, the kinetic equation has the form:

$$W = kP^0_{\mathrm{CO}}P^0_{\mathrm{H2}}.$$

Let us calculate, from the experimental kinetic data, the value of the effective entropy of activation $\Delta S^*_{\mathrm{eff}}$. According to transition-state theory (2,3),

$$\Delta S^*_{\mathrm{eff}} = \frac{E}{T} - R + 4.575\lg\frac{k}{\chi\frac{kT}{h}}, \qquad (1)$$

where E is the experimental heat of activation, determined from the Arrhenius equation, R is the gas constant, k is the Boltzmann constant, h is the Planck constant, T is the absolute temperature, and χ is the transmission coefficient. According to the data of work (1), at 160° $W = k = 1.58 \cdot 10^{-7}$ mol/sec per 1 cm^3 of catalyst; $E = 16.2$ kcal/mol. The nickel surface is 32.2 m^2/cm^3 of catalyst. At 80-150° hydrogen removes from the catalyst surface the entire CO monolayer previously adsorbed on Ni and bound by a linear form of bonding (4), which indicates the participation in catalysis of practically the entire nickel surface. This is also confirmed by data (5). Expressing the rate in molecules per gL per second (L is the number of elementary areas per 1 cm^2 of nickel surface, equal on average for its three main crystallographic planes to $1.54 \cdot 10^{15}$ (6); g is the number of possible positions of the active complex when one of the areas occupied by it is fixed (equal on average to 4)), we obtain:

$$k = \frac{1.58 \cdot 10^{-7} \cdot 6.02 \cdot 10^{23}}{32.2 \cdot 10^{4} \cdot 4 \cdot 1.54 \cdot 10^{15}} = 4.8 \cdot 10^{-5} \text{ molecules}/gL \cdot \text{sec.}$$

The only unknown quantity needed to calculate $\Delta S^{*}_{\text{eff}}$ by equation (1)—the transmission coefficient χ—we take equal to unity. Then we obtain $\Delta S^{*}_{\text{eff}} = -43.6$ e.u.

On the other hand, the zero order of the reaction with respect to both components entering into the active complex indicates (3) that the effective entropy of activation is the difference between the absolute entropy of the active complex S^{*} and the sum of the entropies of the adsorbed initial substances—carbon monoxide $\left(S^{0}_{[\text{CO}]}\right)$ and hydrogen $\left(S^{0}_{[\text{B}]}\right)$:

$$\Delta S^{*}_{\text{eff}} = S^{*} - S^{0}_{[\text{CO}]} - S^{0}_{[\text{B}]}.$$

Square brackets here and below refer to the adsorbed state, $*$ to the activated complex; 0 denotes the standard state.

Since CO is part of the activated complex, and in the initial state is adsorbed on nickel in localized fashion (7), it is obvious that $S^{*} > S^{0}_{[\text{CO}]}$. Then

$$\Delta S^{*}_{\text{eff}} > -S^{0}_{[\text{H}]}$$

The value of $S^{0}_{[\text{H}]}$ depends, first, on how many hydrogen molecules (atoms) take part in the formation of the activated complex and, second, on the mobility of adsorbed hydrogen, on the nature of the degrees of freedom of its motion.

The high negative value of $\Delta S^{*}_{\text{eff}}$ could be explained by assuming that:

1) the activated complex contains 3 molecules (6 atoms) of hydrogen—in accordance with the stoichiometry of the overall reaction of hydrogenation of CO to methane;

2) hydrogen adsorbed on nickel is a layer of atoms possessing complete two-dimensional mobility (a two-dimensional atomic gas). Calculation of the molar (i.e., per mole H_2) entropy of hydrogen for such a model gives a value of 18.7 entropy units at 160° (6); in calculating $\Delta S^{*}_{\text{eff}}$, the standard state for adsorbed molecules is taken to be a surface coverage $\theta = 0.5$ (8). Then $S^{0}_{[\text{H}]} = 3 \cdot 18.7 = 56.1$ entropy units and $\Delta S^{*}_{\text{eff}} > -56.1$ entropy units, in agreement with the value $\Delta S^{*}_{\text{eff}} = -43.6$ entropy units calculated above from kinetic data, since the difference of 12.5 entropy units could be attributed to the inequality $S^{*} > S^{0}_{[\text{CO}]}$ (the greater complexity and looseness of the activated complex compared with adsorbed CO).

However, both assumptions on which the model considered is based are too exaggerated. First, participation of as many as 6 hydrogen atoms in the activated complex is allowed; second, hydrogen adsorbed on nickel is in reality only partially mobile. The experimental value of its molar entropy at 25° and $\theta = 0.5$ is 7 entropy units (6); the temperature correction, calculated for a mobile layer, is 0.7 entropy unit, i.e., at 160° the value of $S^0_{[\mathrm{H}]}$ does not exceed $7.7 \cdot 3 = 23.1$ entropy units. Therefore, even assuming participation of 6 hydrogen atoms in the activated complex, the value of $\Delta S^*_{\mathrm{eff}}$ cannot be lower than -23.1 entropy units, which is 20.5 entropy units greater than the value -43.6 entropy units calculated from experimental kinetic data. The fact that $S^* > S^0_{[\mathrm{CO}]}$ and that the number of hydrogen atoms in the activated complex may be < 6 further strengthens this discrepancy.

The only way to remove it is to abandon, in calculating $\Delta S^*_{\mathrm{eff}}$ from equation (1), the assumption that the transmission coefficient is equal to unity. If the true $\Delta S^*_{\mathrm{eff}}$ is taken to be -23.1 entropy units, then in equation (1) one should substitute $\chi = 3 \cdot 10^{-5}$ (upper limit); if, however, $\Delta S^*_{\mathrm{eff}} \approx 0$ is taken, as is often the case for zero-order reactions, then $\chi \approx 3 \cdot 10^{-10}$ (lower limit).

Reactions with a low value of χ (most often these are nonadiabatic reactions) are known among homogeneous processes, although their fraction of the total number of reactions is small (9). Zolbakken has carried out an analysis of χ for certain adsorption and desorption processes. For adsorption of NO on alumogel ($-92 \div 0°$), according to this author' s estimate, $\chi \approx 6 \cdot 10^{-9}$—$3 \cdot 10^{-8}$ (10). It is possible that hydrogenation of carbon monoxide on a nickel catalyst is an example of a nonadiabatic heterogeneous catalytic process.

It is interesting that problems of this kind do not arise in analyzing the activation entropy of the process of hydrogenation of carbon dioxide, proceeding under identical conditions.

Hydrogenation of CO_2 to methane in an excess of hydrogen on the same catalyst is likewise not complicated by side processes. In the kinetic region at 125-175° and with a CO_2 content in the nitrogen-hydrogen mixture of up to 0.4 vol.%, first order with respect to CO_2 is observed, and the products do not affect the rate (11). It was specially shown that under these conditions the order with respect to hydrogen is zero; i.e., finally the kinetic equation has the form:

$$W = k \cdot P^1_{\mathrm{CO}_2} \cdot P^0_{\mathrm{H}_2}. \tag{2}$$

According to (11), the limiting stage of the process is the interaction of atomic hydrogen adsorbed on the surface with a CO_2 molecule from the gas phase, and the most probable composition of the active complex is $[\mathrm{HCOOH}]^*$. The kinetic equation (2) and the indicated composition of the active complex correspond (3) to the following effective equilibrium for formation of the active complex from the initial substances:

$$\mathrm{CO}_2 + 2[\mathrm{H}] \rightleftharpoons [\mathrm{HCOOH}]^*,$$

whence

$$\Delta S^*_{\text{eff}} = S^* - S^0_{CO_2} - 2S^0_{[H]}. \tag{3}$$

Obviously, the value of S^* is close to the magnitude of the absolute entropy of the active complex of the formic-acid dehydration reaction. According to (12), this value is 26 e.u. The entropy of gaseous CO_2 at 160° (the temperature of our calculation) and 1 atm is $\sim$ 55 e.u. (13). The molar entropy of atomic hydrogen adsorbed on nickel at a degree of coverage of 0.5 and 160° is $\sim$ 8 e.u. (6). Substituting all these quantities into (3), we obtain the expected value of the effective entropy of activation in the chosen standard state:

$$\Delta S^*_{\text{eff}} = 26 - 55 - 8 = -37 \text{ e.u.} \tag{4}$$

Let us now calculate ΔS^*_{eff} from the experimental kinetic data. At 160° $k = 2.1$ cm^3/sec $\cdot$ cm^3 of catalyst $= 2.9 \cdot 10^{-2}$ molecules/gL sec $\cdot$ atm; $E = 13.9$ kcal/mole (11). Participation of practically the entire nickel surface in catalysis was shown in (14).

If one takes $\varkappa = 1$, then from equation (1) we obtain $\Delta S^*_{\text{eff}} = -36$ e.u., in good agreement with the expected value (4). Hence it follows that, in the case of CO_2 hydrogenation on a nickel catalyst, the transmission coefficient is close to unity. The calculation carried out also confirms the adopted assumption concerning the composition of the active complex.

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CITED LITERATURE

1. V. M. Vlasenko, G. E. Yuzefovich, M. T. Rusov, *Kinetika i kataliz*, **6** (1965).
2. S. Glasstone, K. Laidler, G. Eyring, *Theory of Absolute Reaction Rates*, IL, 1948, p. 198.
3. G. I. Golodets, V. A. Roiter, *Kinetika i kataliz*, **4**, 177 (1963).
4. V. M. Vlasenko, L. A. Kutsar' et al., *Kinetika i kataliz*, **5**, 337 (1964).

5. V. M. Vlasenko, G. K. Boreskov, G. E. Braude, *Khim. prom.*, No. 4, 200 (1958).

6. G. Sweet, E. Rideal, *Actes du II congrès intern. de catalyse*, **1**, Technip, Paris, 1961, 175.

7. B. Trepnell, *Chemisorption*, IL, 1958, p. 268.

8. M. I. Temkin, *ZhFKh*, **14**, 1054 (1940).

9. M. I. Temkin, On the method of the activated complex. Appendix to the book: N. N. Semenov, *On Certain Problems of Chemical Kinetics and Reactivity*, Publishing House of the Academy of Sciences of the USSR, 1958, p. 651.

10. A. Sollbakken, *Actes du II congrès intern. de catalyse*, **1**, Technip, Paris, 1961, 341.

11. V. M. Vlasenko, M. T. Rusov, G. E. Yuzefovich, *Kinetika i kataliz*, **2**, 525 (1961).

12. W. Sachtler, J. Fahrenfort, *Actes du II congrès intern. de catalyse*, **1**, Technip, Paris, 1961, 831.

13. L. V. Gurvich et al., *Thermodynamic Properties of Individual Substances. Handbook*, **2**, Publishing House of the Academy of Sciences of the USSR, 1962, p. 336.

14. V. M. Vlasenko, M. T. Rusov, G. E. Yuzefovich, *Kinetika i kataliz*, **2**, 394 (1961).

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