PHYSICAL CHEMISTRY

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1960

SovietRxiv

Abstract

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ON THE CATALYTIC ACTIVITY OF TUNGSTEN PENTOXIDE

The kinetics of the reaction of dehydration of alcohols–ethyl, isopropyl, *n*-butyl, tert-butyl, cyclohexanol–and of the dehydrogenation of methyl alcohol and tetralin on W_2O_5 under isothermal conditions was studied in this work. The catalyst–blue tungsten oxide W_2O_5–was obtained from tungstic acid by calcination at 350—400° in a stream of air to WO_3; the latter was reduced to W_2O_5 during the reaction with alcohols at the experimental temperature 200—300°. The apparatus was an ordinary flow unit with automatic feeding of the initial liquid substances. Gas was supplied and gaseous products were collected with the aid of an automatic Patrikeev gas meter. The experiments were carried out at low conversions, not more than 30%, in the kinetic region. The gaseous catalyzate was analyzed on a VTI apparatus and by chromatography. In the liquid catalyzate the amount of dissolved unsaturated hydrocarbons was determined by the Kauffman-Halpern method. After careful purification the initial substances had constants coinciding with those in the literature.

Table 1

Apparent activation energies for the dehydration of alcohols on tungsten oxide under isothermal conditions

Alcohol	Amount of alcohol in mixture, mol. %	Temperature interval, °C	ε, kcal/mol
Ethyl	65	269–303	29.8
Ethyl	80	269–301	29.0 29.4
Isopropyl	65	168–199	23.7
Isopropyl	80	168–200	23.7 23.8
n-Butyl	50	168–200	23.9
n-Butyl	65	230–262	29.5
n-Butyl	80	230–262	29.9 29.9
n-Butyl	54	230–262	29.9
Tert.-butyl	65	230–262	30.5
Tert.-butyl	65	92–113	17.8
Cyclohexanol	65*	180–204	21.9

* A mixture of cyclohexanol with cyclohexene was passed.

In carrying out experiments on W_2O_5 it was observed that the thermal effect of the endothermic reaction of alcohol dehydration strongly affects the results of kinetic measurements. To eliminate this phenomenon, the catalyst, 2 g (2 ml) (2 parts), was diluted with pieces of quartz (3 parts), whose size corresponded to the size of the catalyst grains. The alcohol was diluted with the reaction product —water or the corresponding unsaturated hydrocarbon. Thus, for example, in determining the relative adsorption coefficients of water, three aqueous solutions with molar alcohol contents of 80, 65, and 54% were prepared. Such dilution of the catalyst and alcohol ensured practical isothermicity of the process. By this method, under isothermal conditions, the apparent activation energies of the dehydration of the alcohols ethyl, isopropyl, tertiary butyl, and cyclohexanol were determined, Table 1. A regularity is observed in the values of the apparent activation energies as a function of the structure of the alcohol. Primary alcohols, ethyl and *n*-butyl, are dehydrated with the same activation energy, equal to ~ 30 kcal/mol. The activation energy of the secondary alcohol (isopropyl) is ~ 6 kcal/mol lower than that of the primary, and the activation energy of tertiary butyl alcohol is ~ 6 kcal/mol lower than that of the secondary. The difference in the activation energies of dehydration of primary, secondary, and tertiary alcohols on W_2O_5 amounts to···

is approximately 6 kcal/mol. The regularity obtained by us is close to that obtained by Adadurov and Krainii [^2], who, in studying the dehydration of alcohols on blue tungsten oxide in a flow system, observed that a methyl group in the α-position lowers the activation energy of alcohol dehydration by 5.5 kcal/mol.

To calculate the true rate constants of the reactions, K, equation (1) was used, following from the general kinetic equation of A. A. Balandin [^3] for monomolecular heterogeneous-catalytic reactions in a flow. For the case of binary mixtures alcohol—reaction product, this equation has the form:

$$K = (z_2 N + z_3 A_1) \ln \frac{A_1}{A_1 - m} - (z_2 + z_3 - 1)m, \tag{1}$$

where A_1 is the volumetric rate of the alcohol (in ml/min, recalculated to gas at NTP), N is the total amount of alcohol and reaction products in the initial mixture (in ml/min, recalculated to gas at NTP), m is the amount of evolved unsaturated hydrocarbons in experiments with binary mixtures (in ml/min); z_2 and z_3 are the relative adsorption coefficients of water and unsaturated hydrocarbons, respectively, i.e., the ratio of the adsorption coefficient of the reaction product to the adsorption coefficient of the initial alcohol; z_2 and z_3 were calculated by formula (2), also following from the general kinetic equation of A. A. Balandin [^3]

$$z = \left(\frac{m_0}{m} - 1\right) \Big/ \left(\frac{100}{P} - 1\right), \tag{2}$$

where m is the amount of unsaturated hydrocarbons evolved per unit time in experiments with a binary mixture (alcohol—water, alcohol—unsaturated hydrocarbon); m_0 is the calculated value of m for the pure alcohol; P is the molar percentage of alcohol in the binary mixture.

For the calculation of z_2 and z_3 by formula (2), not the experimental but the computed m_0 was substituted. Using the fact that z is a constant quantity at a given temperature and does not depend on the percentage composition of the mixture, we substitute into formula (2) the value P_1 and m_1, found from experiment, for one mixture and then P_2 and the corresponding m_2 for another mixture and, solving both equations simultaneously with respect to m_0, obtain the following formula for calculation:

$$m_0 = (1-a)\Big/\left(\frac{1}{m_1} - \frac{a}{m_2}\right), \quad \text{where } a = \left(\frac{100}{P_1} - 1\right)\Big/\left(\frac{100}{P_2} - 1\right). \qquad (3)$$

Since the work was carried out with three mixtures of each reaction product with the alcohol, a total of three equations of type (3) could be compiled,

Table 2

Relative adsorption coefficients z_2 and z_3 of the products of alcohol dehydration under isothermal conditions

n-Butyl alcohol	*n*-Butyl alcohol	*n*-Butyl alcohol	Isopropyl alcohol	Isopropyl alcohol	Isopropyl alcohol
Temp., °C	z_2	z_3	Temp., °C	z_2	z_3
262	0.58	0.58	200	0.48	0.42
255	0.53	0.60	192	0.55	–
245	0.37	0.71	184	0.49	0.39
230	0.76	–	173	–	0.54
235	–	0.70	176	0.50	–
	av. 0.56	av. 0.65		av. 0.50	av. 0.45

Table 3

Verification of the applicability of kinetic equation (1) to the reaction of alcohol dehydration

Amount of iso-C_3H_7OH in the aqueous mixture, mol. %	Temp., °C	m, ml/min	K
80	194	20.1	27.2
65	194	18.1	28.2
50	194	15.0	28.0

Amount of iso-C_3H_7OH in the aqueous mixture, mol. %	Temp., °C	m, ml/min	K
80	181.3	9.9	12.1
65	181.3	8.8	12.3
50	181.3	7.3	12.0

which made it possible to calculate the mean value of m_0 for each temperature. Table 2 presents the found values of the relative adsorption coefficients of the reaction products of the dehydration of isopropyl and n-butyl alcohols under isothermal conditions. The relative adsorp-

tion coefficients of water, propylene, and butylene in the temperature interval studied do not depend on temperature. The applicability of equation (1) to the reaction of dehydration of alcohols is confirmed by the fact that, when the experimental values of m obtained at a given temperature for mixtures of different percentage composition at constant catalyst activity were substituted into it, the calculated values of the rate constants of the dehydration reaction proved to be practically identical (Table 3). Table 4

Table 4

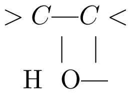
Dehydration of alcohols on tungsten oxide under isothermal conditions

Alcohol	Temp. interval, °C	z_2	z_3	ε_{app}, kcal/mol	$\varepsilon_{\text{true}}$, kcal/mol	K_0	$\frac{\varepsilon}{\lg K_0}$
n-Butyl	230–262	0.56	0.65	29.9	33.4	$1.88 \cdot 10^{15}$	2.19
Isopropyl	168–200	0.50	0.45	23.7	26.1	$4.29 \cdot 10^{13}$	1.91

gives the main results of kinetic determinations for the dehydration of isopropyl and n-butyl alcohols. From the data of Table 4 it is seen that the true activation energy exceeds the apparent one by approximately 3 kcal/mol.

The relative adsorption coefficients z are equilibrium constants of the process of adsorption displacement of the initial substance by the products of its conversion from the catalytically active part of the surface. In the case of dehydration of alcohols, these are processes of displacement of the alcohol by water and the corresponding unsaturated hydrocarbon. Therefore, by the usual thermodynamic formulas it is easy to calculate for this process the change in free energy ΔF, entropy ΔS, and heat content ΔH (i.e., the heats of adsorption displacement with the opposite sign).

From the independence of the relative adsorption coefficients of water and unsaturated hydrocarbons from temperature, which is observed in our case, it follows that the corresponding values of ΔH for them will be equal to zero. Since the heats of adsorption displacement of the alcohol by water are identical (equal to zero), the values of the heats of adsorption of the alcohols themselves must be equal to one another. Hence it follows that both alcohols, different in their structure, during dehydration are oriented toward the catalytically active part of the surface of W_2O_5 identically, by the common group for each alcohol



$$\begin{array}{c} > C\text{—}C < \\ \;\;|\quad | \\ \mathrm{H}\;\; \mathrm{O}\text{—} \end{array}$$

so that each of these atoms proves to be bound by adsorption forces to the catalytically active surface of W_2O_5.

Determination of the bond energies of the reacting atoms C, H, and O of molecules with the catalytically active surface of W_2O_5. The bond energies were determined by the kinetic method of Balandin (^{4}). For this purpose, on W_2O_5 the activation energy of dehydrogenation of tetralin, $\varepsilon_1 = 26.8$ kcal/mol, was determined in the interval 449—491°, and the activation energy of dehydrogenation of methyl alcohol, $\varepsilon_2 = 24.4$ kcal/mol, in the interval 380—420°C. For calculation of the bond energies (^{5,6}) Q_{HK}, Q_{OK}, Q_{CK} according to

Table 5

Bond energies of the reacting atoms and molecules with the surface of the catalyst W_2O_5

Name of alcohol	Activation energy of dehydration of alcohols	Values of bond energies		
Name of alcohol	Activation energy of dehydration of alcohols	Q_{HK}	Q_{CK}	Q_{OK}
n-Butyl	29.9	56.7	15.9	39.2
Ethyl	29.4	56.4	16.3	39.5
Isopropyl	23.7	52.6	19.4	43.3
Cyclohexanol	21.9	51.5	21.3	44.4
tert-Butyl	17.8	48.7	24.0	47.3

in formulas (4), in addition to the quantities ε_1 and ε_2, the values of the activation energies of dehydration ε_3 of primary, secondary, and tertiary alcohols were also used, Table 1. This made it possible to study the influence of the structure of the dehydrating alcohols on the values of the bond energies (the bond energies between the atoms $Q_{\mathrm{CH}}, Q_{\mathrm{CO}}, Q_{\mathrm{OH}}$ were taken from Cottrell' s data (^{7}))

$$Q_{\mathrm{HK}} = \frac{1}{3}(-\varepsilon_1 - 2\varepsilon_2 + 2\varepsilon_3) + 62;$$

$$Q_{\mathrm{CK}} = \frac{1}{3}(-\varepsilon_1 + 2\varepsilon_2 - 2\varepsilon_3) + 28.5; \qquad (4)$$

$$Q_{\mathrm{OK}} = \frac{1}{3}(3\varepsilon_1 - 2\varepsilon_2 - 2\varepsilon_3) + 48.6.$$

It turned out that, upon successive replacement by methyl radicals of the hydrogen atoms at the carbon atom bonded to the hydroxyl group of the alcohol, the quantities Q_{OK} and Q_{CK} increase, while Q_{HK} decreases (Table 5: ethyl, isopropyl, tert-butyl alcohols). It should be noted that both hydrogen atoms and the methyl groups replacing them do not participate directly in the reaction, i.e., here there is an influence of remote substituents (^{8}) on the magnitudes of the bond energies of C, H, and O with the catalyst,

(Figure: schematic structural fragment)

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Received
17 V 1960

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