CONCLUSIONS

1. On the alumina–rhodium catalyst obtained by decomposition of $[(CH_3)_2S]_3RhBr_3$, heterogenized on Al_2O_3, reactions that are typical for platinum-group metals take place: C_5-dehydrocyclization, skeletal isomerization, dehydroisomerization, and others.

2. The catalytic, structural, and adsorption properties of the alumina–rhodium catalysts that we have investigated are determined by their genesis.

LITERATURE CITED

1. O. V. Bragin, D. B. Furman, N. V. Volchkov, M. L. Khidekel', and I. P. Lavrent'ev, Kinet. Katal., 21, 1351 (1980).
2. B. A. Kazanskii, Research in the Field of Organic Catalysis [in Russian], Nauka, Moscow (1977), pp. 57-95.
3. I. V. Gostunskaya, N. S. Goryachev, V. S. Gladkov, and B. A. Kazanskii, Dokl. Akad. Nauk SSSR, 203, 103 (1972).
4. Z. Karpinski and J. K. A. Clarke, J. Chem. Soc., Faraday Trans. 1, 71, 893 (1975).
5. A. Peter and J. K. A. Clarke, J. Chem. Soc., Faraday Trans. 1, 72, 1201 (1976).
6. J. R. Anderson and D. E. Mainwaring, Ind. Eng. Chem., Prod. Res. Devel., 17, 202 (1973).
7. O. V. Bragin, V. G. Tovmasyan, D. B. Furman, and A. L. Liberman, Izv. Akad. Nauk SSSR, Ser. Khim., 32 (1976).
8. N. E. Buyanova, A. P. Karnaukhov, N. G. Koroleva, N. T. Kulishkin, V. T. Rybak, and V. B. Fenelonov, Kinet. Katal., 16, 741 (1975).
9. O. M. Poltorak and V. S. Boronin, Zh. Fiz. Khim., 40, 2671 (1966).
10. H. Matsumoto, Y. Saito, and Y. Yoneda, J. Catal., 22, 182 (1971).
11. J. A. Carter, J. A. Cusumano, and J. H. Sinfelt, J. Catal., 20, 223 (1971).

CONVERSIONS OF ETHERS ON DEHYDRATING CATALYSTS.

4.[†] KINETICS OF DISPROPORTIONATION REACTION

A. A. Silakova, N. V. Nekrasov,
and M. M. Kostyukovskii

UDC 541.127:542.97:547.27

In the present work, for an elucidation of the possible mechanism of disproportionation of ethers, we carried out a study of the kinetic relationships of this reaction in the presence of Al_2O_3 alone and Al_2O_3 treated with HCl (9.3%). We investigated the conversion of a mixture of diethyl and dipropyl ethers to ethyl propyl ether,

$$Et_2O + Pr_2O \rightleftarrows 2EtOPr$$

The kinetic experiments were performed at 200°C on Al_2O_3, and at 175°C, 185°C, and 200°C on Al_2O_3–HCl.

EXPERIMENTAL

The reaction was carried out in a completely sealed flow-circulating unit at atmospheric pressure; the original mixture was diluted with nitrogen. Cylinder nitrogen was purified by passing successively through a column with nickel–chromium catalyst and a trap with zeolite, chilled by a mixture of dry ice and acetone. The catalyst was regenerated in a stream of air at 450°C. In all experiments, the catalyst charge was 4 cm^3 (2.4 g), and the catalyst particle size was 1-2 mm. The original mixture of ethers, from thermostated saturators, was passed through the reactor, and the products were analyzed chromatographically every 10-15 min. After establishing steady-state operation, the experiment was continued for 45-120 min, with the activity remaining unchanged. The constancy of catalyst activity was checked in control

---

[†] For communication 3, see [1].

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 996-1000, May, 1982. Original article submitted July 20, 1981.

TABLE 1. Kinetic Data on Disproportionation of Ethers on Al_2O_3 with Various Initial Conditions, at 200°C

U, liters/h	C_1^0	C_3^0	C_1	C_2	C_3	r, mmoles/(h·g cat)		Degree of dehydration, %
	mmoles/liter					experiment	calculation	
3,16	1,07	1,10	0,94	0,25	0,74	0,36	0,43	21,4
5,26			0,97	0,20	0,87	0,47	0,45	11,8
10,52			1,01	0,12	0,94	0,53	0,49	9,1
15,79			1,03	0,08	1,00	0,53	0,50	5,4
21,05			1,04	0,06	1,05	0,51	0,51	1,8
5,13	0,55	0,54	0,47	0,15	0,34	0,38	0,40	22,2
10,26			0,50	0,10	0,36	0,48	0,45	24,1
15,39			0,51	0,08	0,41	0,54	0,47	16,7
20,53	0,55	1,09	0,52	0,06	0,44	0,55	0,49	13,0
10,40			0,51	0,08	1,04	0,34	0,36	1,0
20,79			0,53	0,04	1,08	0,39	0,37	0,0
10,40			1,04	0,11	0,40	0,48	0,49	16,4
20,79	1,09	0,55	1,06	0,07	0,46	0,58	0,54	9,1
5,10	0,28	0,54	0,22	0,11	0,38	0,28	0,31	18,5
10,40	1,39	0,25	1,35	0,07	0,19	0,33	0,35	8,0
10,40	0,29	1,36	0,26	0,05	1,17	0,21	0,21	12,5

experiments under selected standard conditions. The original concentrations of Et_2O ($C_1°$) and Pr_2O ($C_3°$) were varied from 0.25 to 1.4 mmoles/liter. The feedstock space velocity was varied from 800 to 5260 h^{-1}. The highest rate of reactant feed was 20 liters/h, and the circulation rate was 500 liters/h, giving gradientless conditions [2].

DISCUSSION OF RESULTS

A test for possible influence of internal diffusion was performed by calculating the Weiss number [3] from the formula

$$W = r^*R^2/3D^*C \tag{I}$$

where r* is the reaction rate, moles/cm^3 catalyst·sec; R is the mean radius of a catalyst particle, cm; D* is the effective diffusion coefficient, cm^2/sec; C is the concentration of the original substance, moles/cm^3. The value of D* for EtOPr was taken as 10^{-2} cm^2/sec, corresponding to the extremal value of the effective diffusion coefficient for the system under consideration [4]. The value of the Weiss number calculated by the use of Eq. (I) was 0.08, i.e., $W \ll 1$, indicating that there is no internal-diffusion retardation under the conditions we have selected and that the reaction proceeds in the kinetic region.

The rate of accumulation of the mixed ether was calculated from the formula

$$r = UC_2/G \tag{II}$$

where U is the flow rate, liters/h; C_2 is the concentration of the mixed ether, mmoles/liter; G is the quantity of catalyst, g.

In order to account for the reverse reaction, we introduced a correction factor γ [5]. The value of the equilibrium constant, which is needed to calculate γ, was assumed as unity [6]. In calculating the disproportionation rate, we took into account the occurrence of the ether dehydration reaction. According to [7], the rate of Pr_2O dehydration at 360°C is five times the rate of dehydration of Et_2O or EtOPr. On the basis of these data, it was considered that it is mainly the Pr_2O that is subject to dehydration. And in fact, as can be seen from Tables 1 and 2, the original concentration ratio Pr_2O/Et_2O in all cases was greater than the ratio of instantaneous concentrations of these substances. In order to determine the influence of the H_2O (formed by dehydration of the ethers) on the disproportionation reaction rate, we performed experiments in which water vapor was present (C = 0.27-1.10 mmoles/liter). It was established that the addition of water to the reaction mixture in an amount more than 10 times the maximum concentration of H_2O formed in the course of the experiments did not change the disproportionation rate.

A preliminary analysis of the experimental data showed that the dependence of the

TABLE 2. Kinetic Data on Disproportionation of Ethers on Al_2O_3–HCl with Various Initial Conditions and Different Temperatures

U, liters/h	C_1^0	C_3^0	C_1	C_2	C_3	r, mmoles/(h·g cat)		Degreee of dehydration, %
	mmoles/liter					experiment	calculation	
175°								
5,20	1,39	0,25	1,32	0,14	0,19	0,32	0,29	0
10,40			1,35	0,08	0,23	0,38	0.35	0
5,20	1,09	0,55	1,01	0,17	0,46	0,39	0,31	0
5,26	1,07	1,10	1,02	0,11	1,03	0,24	0,27	1,4
10,52			1,03	0,08	1,06	0,34	0,28	0,9
5,20	0,55	1,09	0,51	0,08	1,04	0,17	0,18	1,0
5,20	0,29	1,36	0,26	0,05	1,28	0,11	0.09	4,0
10,40			0,27	0,03	1,33	0,12	0,09	1,1
185°								
10,52	1,07	1,10	1,02	0,10	1,02	0,46	0,53	2,7
10,40	1,09	0,55	1,03	0,11	0,47	0,51	0,62	4,5
5,20	1,39	0,25	1,30	0,18	0,16	0,47	0,39	0
10,40			1,34	0,11	0,20	0,49	0,51	0
5,20	0,55	1,09	0,49	0,12	1,00	0,27	0,34	2,7
10,40			0,51	0,08	1,02	0,34	0,36	2,7
5,20	0,29	1,36	0,25	0,08	1,29	0,17	0,17	2,2
10,40			0,26	0,04	1,31	0,18	0,19	2,2
200°								
5,26	1,07	1,10	0,88	0,37	0,70	1,04	0,97	19,5
10,52			0,94	0,25	0,78	1,22	1,13	17,7
10,40	0,55	1,09	0,44	0,22	0,86	1,10	0,79	11,0
20,79			0,50	0,11	0,95	0,94	0,94	7,8
10,40	1,39	0.25	1,32	0,13	0,13	0,62	0,66	22,0
20,79			1,34	0.09	0,15	0,86	0,78	22,0
10,40	0,29	1,36	0.23	0,11	1,08	0,52	0,49	16,5
20,79			0.25	0,07	1,24	0,59	0,51	6,2

disproportionation reaction rate on the concentration of reactants can be expressed by an equation of the fractional-rational form. An overall kinetic equation of the following type was analyzed:

$$r = \frac{k_1 C_1^m C_3^n}{(C_1 + k_2 C_2 + k_3 C_3)^q} \qquad \text{(III)}$$

where k_1, k_2, k_3, m, n, and q are constants (m, n, and q were varied from 0 to 2).

The calculations were performed in a BÉSM-6 computer with a program given in [8]. A comparison of the results calculated by the use of Eq. (III) with different values of the exponents showed that the experimental results are best described by this equation with m = n = 1 and q = 2. The following values of the constants were obtained:

Al_2O_3, 200°	Al_2O_3–HCl, 200°	
$k_1=4{,}54$ mmoles/(h·g)	$k_1=11{,}8$ mmoles/(h·g)	$E_1=40{,}1$ kJ/mole
$k_2=1{,}50$	$k_2=1{,}55$,	$E_2=-47{,}0$
$k_3=1{,}90$	$k_3=1{,}95$,	$E_3=-46{,}3$

The experimental and calculated data are presented in Tables 1 and 2. The standard deviation was 7.9% for the Al_2O_3 and 13.0% for the Al_2O_3–HCl.

On the basis of the experimental results we have obtained and certain literature data on the intermediate compounds in the reaction of alcohol and ether dehydration on oxide catalysts [9-11], we can represent the course of the ether disproportionation reaction by the following scheme:

1. $PrOPr \rightleftarrows (PrOPr)_{ads}$
2. $EtOEt \rightleftarrows (EtOEt)_{ads}$
3. $(PrOPr)_{ads} \rightarrow (PrO)_{ads} + (Pr)_{ads}$ — Chain initiation
4. $(PrO)_{ads} + (EtOEt)_{ads} \rightleftarrows (PrOEt)_{ads} + (EtO)_{ads}$ } Chain growth
5. $(EtO)_{ads} + (PrOPr)_{ads} \rightleftarrows (EtOPr)_{ads} + (PrO)_{ads}$
6. $(PrO)_{ads} + (H)Z \rightarrow C_3H_6 + H_2O + Z$ — Chain breaking
7. $(PrOEt)_{ads} \rightleftarrows PrOEt$
8. $(Pr)_{ads} + Z \rightarrow C_3H_6 + (H)Z$

where Z is a center of the catalyst surface.

In this scheme it is postulated that the reaction proceeds through a chain mechanism. In stage 3, a chain is initiated, forming alkoxide radicals, the participation of which in conversions of alcohols and ethers is postulated in [9-11]. Chain breaking takes place as a result of the interaction of an adsorbed active particle $(\mathrm{PrO})_{\mathrm{ads}}$ with an acidic center of the catalyst, leading to the formation of dehydration products (C_3H_6 and H_2O). Interaction of alkoxide radicals with surface-adsorbed molecules of the original substances in stages 4 and 5 leads to the formation of the reaction product.

It is assumed that the surface concentrations of $(\mathrm{PrO})_{\mathrm{ads}}$, $(\mathrm{Pr})_{\mathrm{ads}}$, $(\mathrm{EtO})_{\mathrm{ads}}$, and $(\mathrm{Et})_{\mathrm{ads}}$ are far smaller than the concentration of adsorbed molecules of PrOPr and EtOEt. Therefore, there is a very low probability that the mixed ether will be formed through a reaction such as $(\mathrm{Pr})_{\mathrm{ads}} + (\mathrm{EtO})_{\mathrm{ads}} \rightleftarrows \mathrm{PrOEt}$.

With a stationary course of the reaction, the rates of generation and destruction of active species are equal: $r_3 = r_6 = k_3[\mathrm{PrOPr}]_{\mathrm{ads}} = k_6[\mathrm{PrO}]_{\mathrm{ads}}[\mathrm{H}]\mathrm{Z}$. For each catalyst at a given temperature, $[\mathrm{H}]\mathrm{Z} = \mathrm{const}$ and $r_6 = k_6'[\mathrm{PrO}]_{\mathrm{ads}}$, where $k_6' = k_6[\mathrm{H}]\mathrm{Z}$. Whence, $[\mathrm{PrO}]_{\mathrm{ads}} = k_3[\mathrm{PrOPr}]_{\mathrm{ads}}/k_6'$. The rate of accumulation of the mixed ether is equal to the rate of stage 4.

$$r = r_4 = k_4[\mathrm{PrO}]_{\mathrm{ads}}[\mathrm{EtOEt}]_{\mathrm{ads}}$$

Expressing the concentrations of reacting species adsorbed on the surface in terms of their concentrations in the gas phase, we can obtain an equation analogous to Eq. (III),

$$r = k_4 \frac{k_3\,[\mathrm{PrOPr}]_{\mathrm{ads}}[\mathrm{EtOEt}]_{\mathrm{ads}}}{k_6'} = \frac{k_4k_3\alpha_1C_1\alpha_2C_2}{k_6'\,(\alpha_1C_1+\alpha_2C_2+\alpha_3C_3)^2}$$

or

$$r = k\frac{C_1C_3}{(C_1+k_1'C_2+k_2'C_3)^2}$$

Let us note that the kinetic equation we have found does give a satisfactory description of the experimental results obtained previously [1] in a static circulating system with reactant partial pressures 0.05 MPa ($C_1^\circ = C_3^\circ = 12.9$ mmoles/liter), which is almost an order of magnitude greater than the concentrations of these substances under the conditions of the present studies in the flow-circulating system. For example, with the Al_2O_3–HCl catalyst at 200°C, the experimentally determined reaction rate is 4.5×10^{-7} mole/sec·g, and the value calculated by the use of Eq. (III) is 3.9×10^{-7} mole/sec·g.

In [1] we advanced the hypothesis that dissociative adsorption of ethers, leading to rupture of a C–O bond, takes place on both Lewis and Brønsted centers of the catalyst (stages 1-3). On the basis of the proposed scheme, the interaction of the active species $(\mathrm{PrO})_{\mathrm{ads}}$ with a molecule of a symmetrical ether adsorbed on a Lewis acid center leads to the formation of a molecule of the mixed ether (stages 4 and 5). In contrast, the interaction of adsorbed surface species with a Brønsted acid center will lead to the formation of dehydration products (stage 6).

Moreover, a decrease in the original concentrations of the reacting ethers should lead to a decrease in their surface concentrations and correspondingly to an increase in the number of Brønsted acid centers on the catalyst surface that are free of adsorbed substances. As a result, the fraction of ether dehydration relative to the overall process should increase with decreasing reactant concentrations, and this is indeed observed in the experiment (Tables 1 and 2).

Thus, the kinetic equation that we have obtained and the disproportionation reaction scheme based on this equation are consistent with our previous hypothesis on the influence of Lewis and Brønsted acidity on the course of the ether disproportionation and dehydration reactions.

CONCLUSIONS

1. On the basis of a kinetic study of the disproportionation reaction for diethyl and dipropyl ethers in the presence of Al_2O_3 and Al_2O_3–HCl, a kinetic equation has been obtained,

giving a good description of the experimental data.

2. A staged reaction scheme is proposed on the assumption that the reaction is a chain process; this scheme takes into account the interaction of the original substances and the intermediate species with the acidic centers of the catalyst. This scheme leads to a kinetic equation that coincides with the experimentally determined equation.

LITERATURE CITED

1. A. A. Silakova, G. I. Levi, and V. É. Vasserberg, Izv. Akad. Nauk SSSR, Ser. Khim., 855 (1982).
2. M. I. Temkin, S. L. Kiperman, and L. I. Luk'yanova, Dokl. Akad. Nauk SSSR, 74, 763 (1950).
3. S. L. Kiperman, Introduction to the Kinetics of Heterogeneous Catalytic Reactions [in Russian], Nauka, Moscow (1964).
4. C. N. Satterfield, Mass Transfer in Heterogeneous Catalysis, MIT Press, Cambridge, Mass. (1969).
5. S. L. Kiperman and V. S. Gadzhi-Kasumov, Izv. Akad. Nauk SSSR, Ser. Khim., 1110 (1965).
6. A. A. Silakova, G. I. Levi, and V. É. Vasserberg, Izv. Akad. Nauk SSSR, Ser. Khim., 2352 (1974).
7. B. Imai, Bull. Chem. Soc. Jpn., 49, 2802 (1976).
8. S. N. Sokolov and I. N. Silin, "Finding the minima of functionals by the linearization method," OIYáI [United Institute of Nuclear Research], Preprint D-810, Dubna (1961).
9. B. Notari, Chem. Ind., 51, 1200 (1969).
10. V. I. Yakerson, Dissertation (1971).
11. J. Caillod and J. C. Lavalley, J. Chim. Phys., 77, 379 (1980).

KINETIC RELATIONSHIPS IN FORMATION OF ISOPRENE FROM EQUILIBRIUM MIXTURE OF 3-METHYL-1-BUTEN-3-OL AND 3-METHYL-2-BUTEN-1-OL IN AQUEOUS PERCHLORIC ACID SOLUTIONS

G. F. Osipova, R. S. Ryabova,
and M. I. Vinnik

UDC 541.127:542.91:547.315.2

3-Methyl-1-buten-3-ol (or dimethylvinylcarbinol, DMVC) and 3-methyl-2-buten-1-ol (or dimethylallyl alcohol, DMAA), which are obtained in the synthesis of 4,4-dimethyl-1,3-dioxane from isobutylene and formaldehyde [1], are readily dehydrated in acidic media forming isoprene i-C_5H_8 [2, 3].

The reversible isomerization of DMVC to DMAA proceeds in an acidic medium much more rapidly than the dehydration of the equilibrium mixture of DMVC and DMAA to i-C_5H_8 [3-6]. When the DMVC is heated in 4-7%[†] aqueous H_2SO_4 solutions at 70-90°C, the main reaction product is i-C_5H_8 [3]. The DMVC is also dehydrated when subjected to the catalytic action of KU-2 ion-exchange resin [7].

In [8], the kinetics and mechanism of i-C_5H_8 formation from an equilibrium mixture of DMVC and DMAA were investigated in 4.3-35.0% aqueous H_2SO_4 solutions at 25°C in a homogeneous reaction mixture. The initial DMVC concentrations ranged from 10^{-5} to 10^{-4} mole/liter. It was shown that under these conditions, the DMVC and DMAA dehydration is an equilibrium reaction, and the equilibrium concentration of isoprene depends on the concentration of H_2SO_4 in the solution. The ratio of the sum of the equilibrium concentrations of DMVC and DMAA (C_b^{∞}) to the equilibrium concentration of i-C_5H_8 (C_i^{∞}) decreases from 15.8 to 7.2 as the H_2SO_4 concentration is raised from 4.3% to 39.2%.

[†] All concentrations are given in % by weight.

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow.

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1001-1005, May, 1982. Original article submitted June 19, 1981.

0568-5230/82/3105-0885$07.50