Heterogeneous catalytic transformation of isobutyl benzoate by the inverse Tishchenko reaction

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Using the catalytic transformation of isobutyl benzoate at 663 K in the presence of 12 % MnO_2/γ-Al_2O_3 in a He atmosphere as an example, it has been shown that the inverse Tishchenko reaction can take place at a temperature above 600 K. Isobutyl benzoate gives isobutanal and benzaldehyde as well as products of their transformation, *i.e.*, benzyl isobutyrate, isobutanol, benzyl alcohol, and toluene.

Key words: reversibility of the Tishchenko reaction, esters, aldehydes, heterogeneous catalysis, MnO_2/γ-Al_2O_3 catalyst.

The known catalytic methods for aldehyde preparation are based on oxidation, alcohol dehydrogenation, and olefin hydroformylation and play an important role in organic chemistry.[1] The use of organic compounds in which the number of carbon atoms in a molecule is equal to the number of carbon atoms in the aldehyde (alcohols) or is one C-atom less (olefins) is a typical feature of these methods. The ability of aldehydes to enter various condensation reactions makes it possible for the products of these reactions to be used as potential synthons for the preparation of aldehydes. The number of carbon atoms in these products is usually equal to the total number of them in the molecules of the aldehydes that form them.

From this standpoint the Tishchenko reaction can be of certain interest in terms of developing new preparative methods of the preparation of aldehydes. The Tishchenko reaction (1), the irreversible condensation of two aldehyde molecules in the presence of aluminum alkoxides, is usually performed in the liquid phase at 300 K:[2,3]

$$2\,\mathrm{MeCHO} \xrightarrow{\mathrm{Al(OR)_3}} \mathrm{MeCOOCH_2Me}. \qquad (1)$$

The thermodynamic equilibrium of reaction (1) has been calculated for R = R^1 = Me in order to elucidate the temperature range in which the Tishchenko reaction may become reversible. The acetaldehyde—ethyl acetate system was chosen because of the existence of reliable experimental values of $\lg K_r$[4] for this system. The results of the thermodynamic calculation are presented below.

T/K	300	400	500	600	700
$\lg K_r$	10.53	5.75	2.89	1.00	−0.34

It can be seen that the Tishchenko reaction is almost irreversible at 300 K. Increasing the temperature results in a decrease in $\lg K_r$, and the inverse Tishchenko reaction becomes thermodynamically possible within the temperature range from 600 to 700 K.

We tried to experimentally elucidate the possibility of the inverse Tishchenko reaction in the temperature range from 600 to 700 K using the transformation of isobutyl benzoate (IB) as an example. IB was chosen because the use of an unsymmetrical ester allows one to follow both the forward and reverse Tishchenko reactions by the products of its transformation. It is evident that the existence of benzaldehyde (BA) and isobutyral (IBA) in an equimolar ratio should indicate the occurrence of reaction (2) and that of benzyl isobutyrate (BIB) should indicate reaction (3).

$$\mathrm{PhCOOCH_2CH(CH_3)CH_3} \rightarrow \mathrm{PhCHO} + \mathrm{CH_3CH(CH_3)CHO} \quad (2)$$

$$\mathrm{PhCHO} + \mathrm{CH_3CH(CH_3)CHO} \rightarrow \mathrm{CH_3(CH_3)CHCOOCH_2Ph} \quad (3)$$

Experimental

The experiments were performed in a flow-type reactor of 1Kh18N9T steel with a stationary layer of catalyst and without it in a He flow (helium pressure was 0.5 MPa) at 663 K; 12 % MnO_2/γ-Al_2O_3 with 1—2 mm grains was used as the catalyst. The initial IB (~99.9 % purity) was introduced into the reactor with a specific velocity of 1.0—1.5 mol L_{Cat}^{-1} h^{-1}. At the

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output of the reactor the reaction products were collected in a water-cooled trap ($\approx$10 °C) and analyzed by GLC on a "Chrom-5" chromatograph (FID, N_2 50 ml/min, 2000 × 3 mm column, 5 % Carbowax 20M + 3 % KOH + 0.5 % Apiezon M on Chromosorb G, 60—80 mesh at 60—230 °C, 10—20 deg/min). The reaction products were identified on a Kratos MS-25RF/DS-90 JC-MS instrument using standard spectra of chromatographically pure compounds: isobutyral, isobutanol, benzaldehyde, benzyl alcohol, toluene, and benzyl isobutyrate. The conditions of the mass spectral analysis: energy of ionizing electrons was 70 eV, emission current was 50 μA, and the temperature of the ion source and the molecular separator was 200 °C.

Results and Discussion

The results of the transformation of IB on 12 % $MnO_2/\gamma\text{-}Al_2O_3$ at 663 K in a He atmosphere are presented in Table 1, and the mass spectra of the main reaction products are presented in Table 2.

As can be seen from the data obtained, the composition of the product of the catalytic transformation of IB is complicated, and benzaldehyde (BA) and isobutyral (IBA) do not exist in an equimolar ratio, as would be expected for the stoichiometric occurrence of reaction (2). Large amounts of products of deep transformations of BA and IBA are observed in addition to the latter, which are the products of the inverse Tishchenko reaction. This is not surprising because it is unlikely that such labile reaction products as aldehydes could remain in a completely unchanged state at such a high reaction temperature. BA (2—3 %) and IBA (0.5—1 %) are not completely transformed into more stable products. This fact is of principal significance and provides some prospects for the development of a direct preparative method for the preparation of aldehydes from esters.

Before considering possible means of forming other reaction products let us note that IB practically does not undergo any thermal transformations in the absence of the catalyst (conversion of IB is $\sim$1 %), *i.e.*, the inverse Tishchenko reaction is catalytic. The data on the influence of the specific velocity of IB introduction (see

Table 1. Transformation of isobutyl benzoate on 12 % $MnO_2/\gamma\text{-}Al_2O_3$ (663 K, He pressure is 0.5 MPa, Volume velocity of He is 750 h^{-1})

Experiment	Specific velocity of IB introduction, mol L_{Cat}^{-1} h^{-1}	Conversion (%)	Content of products (%)							Yield** (%)	
			IBA	IA	BA	BnA	T	BIB	Unidentified products	IBA+IA	BA+BnA+T
1	1.0	47	1	15	3	2	5	3	18	84	36
2	1.5	35	0.5	10	2	1	4	2	15	74	34
3*	1.0	1	0.03	0.23	0.26	0.18	—	—	0.3	64	56

*Without a catalyst.

**Of theoretical yield.

Table 2. Mass spectra of products of the transformation of isobutyl benzoate on 12 % $MnO_2/\gamma\text{-}Al_2O_3$

Component of the product of isobutyl benzoate transformation	Characteristic ions in mass spectra, *m/z* (intensity in % of the maximum peak)*
Benzyl isobutyrate $(CH_3)_2CHC(O)OCH_2Ph$	39 (10); 41 (11); 43 (40); 44 (9); 51 (7); 57 (8); 65 (16); 71 (21); 76 (9); 79 (12); 89 (6); 90 (14); 91 (100); 92 (9); 107 (7); 108 (48); 178 M^+ (14).
Isobutanal	27 (47); 29 (25); 38 (5); 39 (30); 41 (84); 42 (10); 43 (100); 72 M^+ (46).
Isobutanol	27 (43); 28 (8); 29 (18); 31 (72); 33 (73); 39 (17); 41 (66); 42 (60); 43 (100); 74 M^+ (6).
Benzaldehyde	39 (6); 50 (19); 51 (38); 52 (9); 74 (6); 77 (100); 78 (14); 104 (5); 105 (94); 106 M^+ (94); 107 (7).
Benzyl alcohol	39 (16); 50 (17); 51 (35); 52 (10); 53 (10); 63 (6); 65 (8); 75 (5); 77 (74); 78 (16); 79 (100); 80 (9); 89 (6); 90 (9); 91 (15); 105 (23); 106 (22); 107 (66); 108 $M^{+\cdot}$(83); 109 (6).
Toluene	39 (20); 50 (7); 51 (11); 62 (5); 63 (11); 65 (14); 91 (100); 92 $M^{+\cdot}$(73); 93 (5).
Isobutyl benzoate $(CH_3)_2CHCH_2OC(O)Ph$	27 (12); 29 (10); 39 (8); 41 (12); 50 (6); 51 (20); 56 (26); 77 (42); 105 (100); 106 (8); 123 (45); 178 M^+ (0).

*Peaks with intensity less than 5 % (except molecular M^+) are not presented.

experiments 1 and 2, Table 2) agree well with the results of experiment 3. Increasing the specific velocity of IB introduction from 1 to 1.5 mol L_{Cat}^{-1} h^{-1} (by the corresponding 1.5-fold decrease in the conventional contact time) results in a decrease in its conversion from 47 to 35 %, which is normal for heterogeneous catalytic reactions in a flow-type reactor.

The preparation of benzyl isobutyrate (BIB) from BA and IB *via* reaction (3) together with the data on reaction (2) indicates that the Tishchenko reaction is reversible under the chosen conditions.

The formation of other reaction products in addition to BA and IBA can be easily explained if one takes into account the possibility of the occurrence of their hydrogenation. It can be assumed that hydrogen, which is necessary for hydrogenation transformations, can be formed through the processes of condensation of aromatic compounds, resulting in the formation of high-molecular unidentified products (15—18 %). If this is taken into account, then isobutyl (IA) and benzyl (BnA) alcohols are products of the hydrogenation of IBA and BA, respectively. At the same time, toluene (T) can be considered to result from the hydrodeoxygenation of IA and BnA. The considerable divergence between the theoretical yields of the aliphatic (IBA+IA) and aromatic (BA+BnA+T) products of the catalytic transformation of IB points to the predominant contribution of aromatic compounds to the preparation of high-molecular products.

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Catalysis of the transfer of hydrogen from 2-propanol to cyclohexanone by immobilized ruthenium tetrasulfate

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Heterogenized metal complex systems prepared by immobilization of ruthenium tetrasulfate on the surface of silica gel containing γ-aminopropyl groups or on the surface of modified styrene-divinylbenzene copolymer catalyze the transfer of hydrogen from 2-propanol to cyclohexanone in both Ar and air. It has been shown that the activity and stability of the obtained catalysts depend on the concentration of the promoting alkali and on the nature of the support.

Key words: catalysis, ruthenium, modified silica gel, modified polymers, hydrogen transfer, cyclohexanone.

In this work, it has been shown that it is possible for the C=O-group of ketone to be reduced by chemically bound hydrogen (2-propanol) in the presence of a binuclear ruthenium sulfate complex immobilized on silica gel containing γ-aminopropyl groups and styrene-divinylbenzene copolymers modified by 3(5)-methylpyrazole and imidazole groups.

Experimental

Binuclear sulfate $[Ru_2(\mu-SO_4)_4(H_2O)_2]$ was prepared according to the method described in Ref. 1. The synthesized complex was immobilized on silica gel containing γ-aminopropyl groups (γ-AMPS) (Silochrom, S_{sp} = 120 m^2/g, concentration of NH_2-groups is 7.10^{-4} mol/g), sample **1**, and on modified

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