LIQUID-PHASE CATALYTIC HYDROGENATION OF UNSATURATED ETHERS

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Catalytic hydrogenations of 3-phenyloxy-1-propene, 3-phenyl-3-methoxy-1-propene, and 1-phenyl-3-methoxy-1-propene were studied at normal conditions, in substance, in methanol, and in cyclohexane on platinum and palladium carrier catalysts. The hydrogenations were usually accompanied by hydrogenolysis of the ether bond. The effects of the substance structure, solvent, and catalyst type on the course of the hydrogenation and hydrogenolysis were examined. Reaction schemes were suggested, described in some cases by power 1st order kinetic equations.

Catalytic hydrogenations of unsaturated ethers are frequently accompanied by side reactions, usually hydrogenolysis of the ether bond with the formation of an alcohol and a hydrocarbon. The selectivity of hydrogenation is governed principally by the reaction conditions, but it depends also on the structure of the ethers hydrogenated. Hydrogenations of unsaturated ethers were studied most frequently at high temperatures and pressures. In mild reaction conditions, palladium and nickel were employed as the catalysts. For instance, hydrogenation of simple vinyl ethers in normal conditions led to alkyl ethers in high yields[1]. Hydrogenation of diallyl ether, allyl benzyl ether, and dibenzyl ether in ethanol on palladium afforded in addition to the corresponding saturated products also products of cleavage of the ether bond[2]. Hydrogenolysis of the saturated dibenzyl ether proceeded very slowly[2,3].

Hydrogenation of 3-phenyl-3-methoxy-1-propene and 1-phenyl-3-methoxy-1-propene has not been reported. The two isomeric ethers are relatively easily available, their structure has a pronounced effect upon the course of the hydrogenation and hydrogenolysis reactions, and the hydrogenation products, as well as the starting materials, are interestingly smelling and can find use in perfume industry. 3-Phenyloxy-1-propene has been used in this work to arrive at some general conclusions concerning the effect of structure of unsaturated ethers on the course of catalytic hydrogenation.

EXPERIMENTAL

Chemicals. 3-Phenyloxy-1-propene was a commercial chemical of Koch-Light (Great Britain). Mixture of 3-phenyl-3-methoxy-1-propene with 1-phenyl-3-methoxy-1-propene was prepared[4] by sodium carbonate catalyzed reaction[5] of 1-phenyl-3-chloro-1-propene with methanol. 1-Phenyl-3-chloro-1-propene was obtained[5] by reaction of 4-phenyl-1,3-dioxane with hydrochloric

acid, 4-phenyl-1,3-dioxane by acid-catalyzed reaction of styrene with formaldehyde[6−8]. The ether mixture was distilled to give[9] 65% wt. 3-phenyl-3-methoxy-1-propene (b.p. 75—75·5°C/1·87 kPa) and 35% wt. 1-phenyl-3-methoxy-1-propene (104—105°C/1·87 kPa). The total ether yield was 56% with respect to 4-phenyl-1,3-dioxane and 85·4% with respect to 1-phenyl-3-chloro-1-propene. All ethers were distilled prior to use and were chromatographically pure. Cyclohexane and methanol *p.a.* (Lachema, Brno) freshly distilled served as the solvents. The catalysts were 10% Pt on silica gel, prepared according to[10], and 10% Pd on activated carbon, prepared analogously as in the patent[11]. The supports were silica gel 100/250 for chromatography (Lachema, Brno) and Supersorbon Degussa HB—3 (FRG), catalyst grain size below 0·063 mm.

Apparatus and techniques. The hydrogenations were conducted in a standard apparatus[12] at 20°C and atmospheric pressure of hydrogen. The work was carried out with 0·03—0·05 g of the catalyst, 1 ml of the substrate, and 10 ml of the solvent, or — for the solvent -free systems — with 0·1 g of the catalyst and 2 ml of the substrate. Samples of the reaction mixture were taken in suitable intervals for chromatographic analysis.
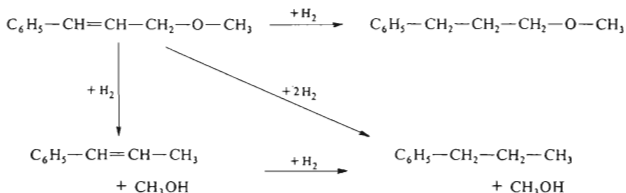
Analytical methods. The analyses were performed on a Chrom 4 chromatograph with flame ionization detection at 170°C. Glass packing columns 2·5 m long, i.d. 2·5 mm, were used, packed with 15% Carbowax 20 M on Chromatom NAW-HMDS and 15% Reoplex 400 on Chromatom NAW. The molar responses of the substances evaluated were considered equal, with regard to the lack of standards.

RESULTS AND DISCUSSION

All measurements were carried out under conditions of vigorous stirring, eliminating the effect of external diffusion on the reaction rate. The effect of inner diffusion, which might occur, was limited by using fine fractions of the catalysts.

The time variations of the concentrations were established for hydrogenation of 1-phenyl-3-methoxy-1-propene, 3-phenyl-3-methoxy-1-propene, and 3-phenyl-oxy-1-propene on palladium and platinum catalysts, always in substance and in methanol and cyclohexane solutions.

The hydrogenation of 1-phenyl-3-methoxy-1-propene proceeded under all conditions according to the Scheme 1. The initial rates of the reactions were read from the dependences measured, and the rate constants were calculated from them as-

$$C_6H_5-CH=CH-CH_2-O-CH_3 \xrightarrow{+H_2} C_6H_5-CH_2-CH_2-CH_2-O-CH_3$$

$$\downarrow +H_2 \qquad \searrow +2H_2$$

$$C_6H_5-CH=CH-CH_3 \xrightarrow{+H_2} C_6H_5-CH_2-CH_2-CH_3$$
$$+ CH_3OH \qquad\qquad\qquad\qquad + CH_3OH$$

SCHEME 1

suming the reaction to be first order with respect to the concentration of the starting substance. Since 1-phenyl-1-propene was not formed in quantities exceeding 10%, its amount was added to that of 1-phenylpropane, and the simplified reaction scheme of side reactions of 1-phenyl-3-methoxy-1-propene to-1-phenyl-3-methoxypropane (k_1) and to 1-phenylpropane (k_2) was considered. The corresponding system of first order differential equations was integrated numerically on a Tesla 200 computer by using the Runge–Kutta–Merson procedure[13]; the values obtained from the initial reaction rates served as the starting approximations. The first estimates of the rate constants were refined if the necessity appeared from a visual comparison of the calculation with the experimental data, and the calculations were repeated until an optical agreement between the calculated course and the experimental points was achieved in all cases tested. The same procedure was applied to the data of hydrogenation of the other unsaturated ethers. The rate constants obtained are given in Table I. The refined constants (a) did not differ from the initial estimates more than by 20%.

TABLE I

Rate Constants of the Reactions

A = 1-phenyl-3-methoxy-1-propene, B = 1-phenyl-3-methoxypropane, C = 3-phenyl-3-methoxy-1-propene, D = 1-phenyl-1-methoxypropane, E = 3-phenyloxy-1-propene, F = 1-phenyloxypropane, P. 1-phenylpropane.

Reaction scheme	Catalyst	Rate constant	Rate constant value, min^{-1} g$_{cat}^{-1}$		
			substance	methanol	cyclohexane
A $\xrightarrow{k_1}$ B, $\xrightarrow{k_2}$ P	Pt	k_1	0·005	0·300^a	—
		k_2	0·012	0·400^a	—
	Pd	k_1	0·009	4·733^a	0·734^a
		k_2	0·017	1·433^a	0·867^a
C $\xrightarrow{k_1}$ D $\xrightarrow{k_2}$ P	Pt	k_1	0·050	3·800^a	1·100^a
		k_2	0·012	0·062^a	0·040^a
C $\xrightarrow{k_1}$ D, $\downarrow k_3$, $\xrightarrow{k_2}$ P	Pd	k_1	0·079	5·867	2·265
		k_2	0·009	0·933	0·500
		k_3	0·008	0·098	0·057
E $\xrightarrow{k_1}$ F	Pt	k_1	0·032	1·33	0·750
	Pd	k_1	0·070	6·400	1·100

^{a} Refined value based on numerical integration of 1st order equation system.

As can be seen from Table I, the catalyst type and the solvent have a pronounced effect on the overall rate of conversion of the starting ether as well as on the selectivity of formation of 1-phenyl-3-methoxypropane. On both catalysts, the hydrogenations in substance were considerably slower than in the presence of solvents. 1-Phenyl-3-methoxy-1-propene reacted fastest on the palladium catalyst; in this case the selectivity of formation of 1-phenyl-3-methoxypropane was also highest. On the platinum catalyst in cyclohexane the reaction proceeded slowly. Practically the only products were 1-phenylpropane and methanol, which dissolved only slightly in the solvent used, so that a second liquid phase formed in the system and the reaction came to a standstill at approximately 40% conversion. Also during the hydrogenation in substance, the reaction ceased to proceed after 760 min because of the formation of the second liquid phase.

While the saturated ether formed on hydrogenation of 1-phenyl-3-methoxy-1-propene (Fig. 1) did not undergo further changes in the conditions applied, in the case of hydrogenation of 3-phenyl-3-methoxy-1-propene the saturated ether formed was consecutively hydrogenolyzed to 1-phenylpropane and methanol. On platinum catalyst, these products were created only by this consecutive reaction, whereas on palladium they formed also by simultaneous side reaction directly from 3-phenyl-3-methoxy-1-propene, as is shown in Figs 2 and 3. The starting estimates of the rate constants k_2 and k_3 characterizing the rate of conversion of 1-phenyl-1-methoxypropane in the system of the consecutive and parallel-consecutive reactions were obtained from the slopes of the tangents to the descending parts of the curves portraying the time dependence of concentration of 1-phenyl-1-methoxypropane.
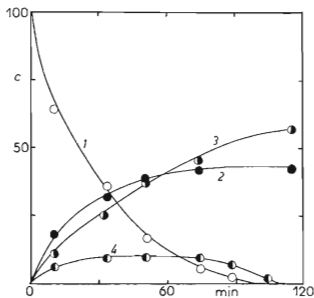

Fig. 1

Hydrogenation of 1-Phenyl-3-methoxy-1-propene on Pt Catalyst (0·05 g) in Methanol

1 1-Phenyl-3-methoxy-1-propene, 2 3-phenyl-3-methoxypropane, 3 1-phenylpropane, 4 1-phenyl-1-propene. c Dimensionless conc. instantaneous conc./init. conc. of hydrogenated substrates (%).

The tangents were constructed in points where their slopes were highest. In the case in question the catalyst affected even the type of the reaction scheme. Here, too, the hydrogenations in solvents were considerably faster than in substance; the fastest was the reaction of 3-phenyl-3-methoxy-1-propene again on palladium catalyst in methanol. The reaction in methanol on platinum catalyst proceeded slightly more slowly, but it was highly selective as concerns the formation of 1-phenyl--1-methoxypropane. Hydrogenation of 3-phenyloxy-1-propene proceeded selectively in all conditions. Similarly as in the preceding cases, it was faster on palladium catalyst, and on both catalysts it was fastest in methanol and slowest in substance. On palladium catalyst, a small amount (max. 6%) of an intermediate product apperaed during the hydrogenation in both solvents; this was obviously 1-phenyloxy-1-propene, formed as a result of displacement of the 3-phenyloxy-1-propene double bond to the thermodynamically more stable position. The reaction order approached zero (the reaction rate decreased only slightly with proceeding conversion); for a better mutual comparison, however, the rate constants were obtained in this case, too, by dividing the initial reaction rates by the initial concentrations, which were the same as in the preceding cases.

Of the ethers examined, 3-phenyl-3-methoxy-1-propene was most reactive practically in all conditions, followed by the other ether with a polysubstituted double bond —
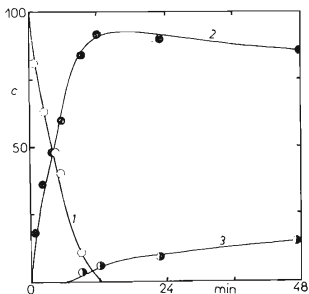

FIG. 2

Hydrogenation of 3-Phenyl-3-methoxy-1-propene on Pt Catalyst (0·05 g) in Methanol
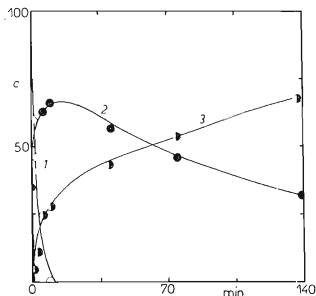*1* 3-Phenyl-3-methoxy-1-propene, *2* 1-phenyl-1-methoxypropane, *3* 1-phenylpropane.

FIG. 3

Hydrogenation of 3-Phenyl-3-methoxy-1-propene on Pd Catalyst (0·05 g) in Methanol
1 3-Phenyl-3-methoxy-1-propene, *2* 1-phenyl-1-methoxypropane, *3* 1-phenylpropane.

3-phenyloxy-1-propene. Lest reactive was the ether with double bond inside the chain − 1-phenyl-3-methoxy-1-propene. This is in a good agreement with the results of hydrogenation of other unsaturated substrates concerning the double bond position in the molecule[14].

Of interest is the effect of structure of the unsaturated ethers on the selectivity of their hydrogenation, which can be so far discussed only qualitatively. Hydrogenation of 3-phenyloxy-1-propene proceeded quantitatively in all circumstances, and the hydrogenated product, 1-phenyloxypropane, was resistant to hydrogenolysis similarly as the starting substance. The stability is obviously due to the conjugation of the aromatic ring π-system with the electron pairs of the oxygen.

Hydrogenation of 1-phenyl-3-methoxy-1-propene was accompanied by a side reaction of hydrogenolysis to 1-phenylpropane or 1-phenyl-1-propene and methanol; hydrogenolysis of the second ether bond to 3-phenyl-1-propanol and methane did not occur. The saturated product, with the methoxy group bonded at the primary carbon, was stable in the hydrogenation conditions. Hydrogenation of 3-phenyl-3-methoxy-1-propene on palladium catalyst was also accompanied by hydrogenolytic side reaction to 1-phenylpropane and methanol. On both catalysts, the hydrogenation product − 1-phenyl-1-methoxypropane − was unstable and underwent consecutive hydrogenolysis to 1-phenylpropane and methanol. The instability is obviously accounted for by the fact that in this case the methoxy group is bonded at the secondary carbon, a substituent of which is a phenyl group.

For synthesis of 1-phenyl-3-methoxypropane on a preparatory scale, it is most convenient to conduct the hydrogenation of 1-phenyl-3-methoxy-1-propene in alcohol on palladium catalyst (yield 76%) 1-phenyl-1-methoxypropane is best prepared by hydrogenation of 3-phenyl-3-methoxy-1-propene in alcohol on platinum catalyst (yield 92%). These conditions seem to be promising also for the preparation of other 1- and 3-alkoxy-1-phenylpropanes by hydrogenation of 3-alkoxy-3-phenyl- and 3-alkoxy-1-phenyl-1-propenes.

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