

A KINETICS OF HYDROGENOLYSIS OF ALIPHATIC ESTERS ON RHODIUM

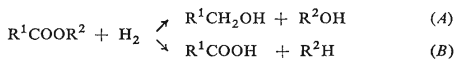
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Kinetics of hydrogenolysis of aliphatic esters to an acid and a hydrocarbon catalysed by rhodium was studied in a gaseous phase at 300°C. Initial reaction rates were well correlated by kinetic equations of the Langmuir-Hinshelwood type assuming a surface reaction as the rate determining step of the conversion. Constants of kinetic equations were compared for four esters measured.

Simple aliphatic esters of organic acids undergo hydrogenolysis in two ways¹. The site of the cleavage of their molecule and final products of the reaction depend on a catalyst and temperature. The reaction according to equation (A) was studied by a number of authors. It is catalysed by some mixed catalysts, mostly consisting of copper and chromium oxides at a temperature ranging from 200–300°C and under an increased pressure of hydrogen². The reaction according to equation (B) proceeds on some platinum metals. Reaction of benzyl esters, which are hydrogenolysed easily at a temperature below 100°C in a liquid phase, was studied in more detail³. Aliphatic esters are much less reactive, and the kinetics of the reaction and the effect of their structure on the reactivity have not yet been determined. Experiments of preparative character were made by Šujkin and coworkers¹ who hydrogenolysed pentyl and hexyl acetates and butyl butyrate in a gaseous phase at 300°C under atmospheric pressure. The authors employed platinum or palladium on activated carbon as catalysts, obtained nearly 100% conversion, and did not observe formation of side products.



In this work we were concerned with a kinetics of hydrogenolysis of four esters at 300°C, catalysed by rhodium. The study was limited to the esters of primary alcohols, since with the esters of secondary, and especially tertiary alcohols, a complicating thermal⁴ or catalytic⁵ elimination of the olefin from the ester could be expected.

EXPERIMENTAL

Catalyst. Technical grade activated carbon (Supersorbon, produced by Chema, Chvaly) of a 0.32–0.50 mm particle size was refluxed with conc. HCl and washed with distilled water.

A solution of $\text{RhCl}_3 \cdot 3 \text{H}_2\text{O}$, containing calculated amount of the metal (3% of the weight of the carbon) was added and after standing for 24 h, the solvent water was evaporated and the catalyst was dried at $100^\circ\text{C}/10$ Torr. Samples of the catalyst (0.02–0.5 g) were mixed with the same volume of glass balls (0.5–0.8 mm) and reduced directly in the reactor prior to the experiments. The catalyst was always heated to 200°C in a stream of nitrogen over a period of 30 min, and at this temperature the nitrogen was being replaced by hydrogen during 30 min. In another 30 min the temperature was raised to 300°C , and the reduction was completed in another 1 h.

Compounds used. The gases, nitrogen and hydrogen, were of the same provenience as in a previous work⁶ and were also purified in a similar manner. Organic acids and butyl acetate were commercial preparations (Lachema, Brno). Other esters were prepared by reported procedures⁷. All organic compounds were dried over a molecular sieve and purified by fractional distillation. Their purity was checked by gas chromatography. Methyl acetate, b.p. 58°C (ref.⁷ 56°C), butyl acetate, b.p. 125°C (ref.⁷ 125°C), methyl propionate, b.p. 98°C (ref.⁷ 99°C), and methyl butyrate, b.p. 104°C (ref.⁷ 103°C).

Apparatus and the analysis of products. Kinetic data were obtained in a flow apparatus with one pass of the reaction mixture. The apparatus was similar to the instrument described in a previous work⁶, with the exception that gaseous mixture leaving the reactor was directly fed to a gas chromatograph by means of a six-way valve. Porapak Q (a 0.15–0.18 mm particle size, 220°C oven temperature) or poly(cyanoethyl) methacrylate⁸ (a 0.1–0.2 mm particle size, a 165°C oven temperature) was used as a stationary phase for all four esters. The chromatographic column was 0.5 m long (5 mm i.d.), a hydrogen flow rate was 36 ml per min. A thermal conductivity detector and a sampling valve were maintained at a temperature of 150°C . The products other than corresponding acid and hydrocarbon (hydrocarbon fraction was not analysed in detail) were not detected. Conversion was calculated from the amounts of the acid and ester in the reaction mixture.

Procedure. Initial activity of catalyst was not reproducible and its activity further decreased during its using. The activity was therefore intermittently tested under standard conditions and the results of experiments were calculated to an arbitrarily chosen level of activity⁶, i.e. about 75% of the average initial activity. The catalyst was being used till its activity has decreased to a 50 to 60% initial activity. Initial rates r^0 were determined as a slope to the curves $x = f(W/F)$ at the origin (W is the amount of the catalyst and F is the feed of an ester). Conversions were 2–15%, and the above-mentioned dependences were not linear in this region. With each ester, 20 values of r^0 for varying initial partial pressure of an ester, p_E^0 , and hydrogen, p_H^0 , were obtained. The reaction mixture was diluted with nitrogen. Initial rates were correlated by a set of Langmuir–Hinshelwood equations and by equations of "redox model" (altogether 25 equations) in the way used previously in this laboratory⁹. From the same results obtained with the catalysts having particle size of 0.32–0.50 mm and of 0.08–0.20 mm it was concluded that under given experimental conditions the rate of the reaction is not influenced by transport phenomena.

RESULTS AND DISCUSSION

The reaction heat of hydrogenolysis of ethyl acetate is -27 kcal/mol, as estimated from heats of combustion¹⁰. In spite of the fact that the reaction is strongly exothermic, we succeeded in maintaining the reaction temperature constant by diluting the catalyst by glass balls. It cannot be excluded, however, that a local overheating of catalyst surface is one of the reasons why the activity of the catalyst gradually

decreases. As mentioned in Experimental part, this phenomenon was compensated by calculating obtained conversions to an arbitrarily chosen standard activity, using the procedure suggested by Hájek and coworkers⁶. This procedure, from the point of view of the errors, was favourably considered by Šlemrová and Kraus¹¹. We further calculated the change of the free reaction enthalpy by the method of group contributions¹² and found it to be -10 kcal/mol for hydrogenolysis of all the esters studied at 300°C . Under the conditions used the reaction can be therefore regarded irreversible. This conclusion is supported by the analysis of the products obtained by competitive reactions of several couples of esters (*e.g.* methyl butyrate-butyl acetate). Other esters than the starting ones were not found even at high conversions, so that, in agreement with irreversibility of the reaction, an exchange of alkyls of the esters does not proceed. The hydrogenolysis under study likely proceeds directly *via* the interaction of the ester with hydrogen on catalyst surface. The possibility of the elimination of an olefin from an ester and its subsequent hydrogenation

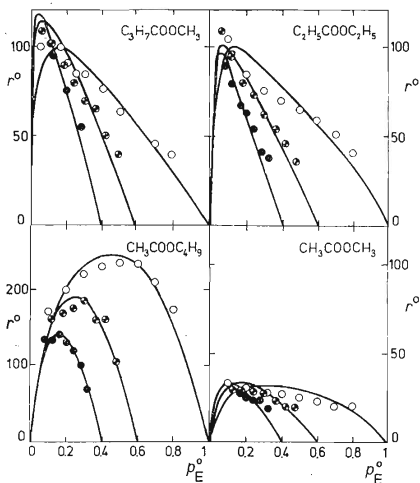


FIG. 1

Experimental Initial Reaction Rates r^0 (mol/h kg_{cat})

Curves were calculated according to Eq. (2). \circ $p_{\text{H}}^0 + p_{\text{E}}^0 = 1.0$ atm; \oplus $p_{\text{H}}^0 + p_{\text{E}}^0 = 0.6$ atm; \bullet $p_{\text{H}}^0 + p_{\text{E}}^0 = 0.4$ atm; p_{H}^0 and p_{E}^0 denote partial pressures of hydrogen and ester in the feed.

to give the observed products was already excluded by Šujkin and coworkers¹. Furthermore, we did not observe any decomposition when passing vapours of the esters over the catalyst at 300°C. The support was catalytically inactive.

Experimental initial reaction rates for the four esters studied in their dependence on the ratio of the components and on the total partial pressure of the reaction mixture are graphically represented in Fig. 1. As follows from the curves, reaction rate depends rather significantly on the structure of esters and increases with the size of both acid and alcohol part of the ester. The curve for butyl acetate differs in its form from the curves for the other three esters. The maximum is located in another region and it shifts much faster to left-hand side with decreasing pressure. Also the height of the maximum undergoes different changes with decreasing pressure. From the foregoing it follows that butyl acetate differs in its kinetic behaviour from the other esters, which has appeared also in the choice of kinetic equation.

Mathematical treatment⁹ of data from Fig. 1 by a combination of linear and non-linear regression and the choice of the best equations on the basis of the sums of squared deviations of the experimental from calculated rates Q resulted in elimination of all equations considered but Eqs (1) and (2).

$$r^0 = \frac{kK_H p_H^0 \sqrt{(K_E p_E^0)}}{[1 + K_H p_H^0 + \sqrt{(K_E p_E^0)}]^3}, \quad (1)$$

$$r^0 = \frac{kK_H p_H^0 K_E p_E^0}{[1 + K_H p_H^0 + \sqrt{(K_E p_E^0)}]^4}. \quad (2)$$

In these equations k denotes rate constants, K_H and K_E are equilibrium adsorption coefficients of hydrogen and the ester. Values of the constants for individual substances are summarized in Table I. The critical values, Q_{crit} , calculated for 95% level of significance⁹ indicate (Table I) that for methyl butyrate, ethyl propionate, and methyl acetate both equations are valid, while for butyl acetate the data fit only Eq. (1). The most important formal difference between Eqs (1) and (2) is the occurrence of the square root at the term for the ester in the numerator of Eq. (1). These equations can be distinguished by the method of competitive experiments suggested by us earlier¹³. The method confirmed that in this case the only suitable equation is Eq. (2).

The values of K_H (Table I) also correspond to the above-mentioned similarities in the form of graphical dependences for methyl acetate, methyl propionate, and methyl butyrate. Values of K_E exhibit a similar trend as reaction rates and reaction constants k . On the contrary, K_H , and especially K_E , for butyl acetate are significantly smaller; the value of k corresponds, however, to the expectation. The reason of the different behaviour of butyl acetate is not yet clear. Our attempts at finding whether the starting compounds contains a catalytic poison or other admixture have failed.

TABLE I
Parameters of Eqs (1) and (2) Obtained by Nonlinear Regression of Rate Data

Ester	CH ₃ COOC ₄ H ₉	C ₃ H ₇ COOCH ₃	C ₂ H ₅ COOC ₂ H ₅	CH ₃ COOCH ₃
	Eq. (1)			
$k, \text{mol h}^{-1} \text{kg}_{\text{cat}}^{-1}$	8 748	3 281	2 773	885
$K_{\text{H}}, \text{atm}^{-1}$	0.9	3.1	2.3	2.7
$K_{\text{E}}, \text{atm}^{-1}$	0.3	36	19	9.6
$Q, \text{mol}^2 \text{h}^{-2} \text{kg}_{\text{cat}}^{-2}$	1 300	872	1 061	224
$Q_{\text{crit}}, \text{mol}^2 \text{h}^{-2} \text{kg}_{\text{cat}}^{-2}$	1 930	1 340	1 550	350
	Eq. (2)			
$k, \text{mol h}^{-1} \text{kg}_{\text{cat}}^{-1}$	19 340	7 809	6 546	2 218
$K_{\text{H}}, \text{atm}^{-1}$	0.9	2.9	2.3	3.1
$K_{\text{E}}, \text{atm}^{-1}$	2.4	105	61	43
$Q, \text{mol}^2 \text{h}^{-2} \text{kg}_{\text{cat}}^{-2}$	3 597	1 511	1 515	317

Other systematic errors are also improbable. We also attempted to find whether for all esters such combinations of constants k , K_{H} , and K_{E} could be found in which butyl acetate has not such extreme value of the adsorption coefficient, and for which $Q < Q_{\text{crit}}$. We calculated the values of a function $Q = f(k, K_{\text{H}}, K_{\text{E}})$. However, we found that this function has sharp minima, so that the combinations of the values of the constants, which would give for all the esters, inclusive butyl acetate, a satisfactory agreement of the K_{H} values and of the trend of K_{E} 's, have Q much higher than Q_{crit} .

The effect of the structure of esters on their reactivity is evident from both Fig. 1 and the values of k for both rate equations. Logarithms of r_{max}^0 and k are roughly linearly dependent on the number of carbon atoms in the molecule of esters. As the study of only four esters did not allow to draw general conclusions, we measured hydrogenolysis of a broad series of esters. As already mentioned, in this work the attempt at separating the rate and adsorption constants on the basis of the Langmuir-Hinshelwood model has met only with a partial success. For that reason we compared reactivity on the basis of competitive experiments. The results and their interpretation will be the subject of a subsequent communication¹⁴.

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