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Isomerization and Hydrogenolysis of 1,2-Epoxybutane on Platinum

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The transformation of 1,2-epoxybutane on Pt/C and Pt/Cr_2O_3 catalysts in the presence of hydrogen has been studied in a flow apparatus at atmospheric pressure and in the temperature range 160–190°C. Parallel formation of butanal, 2-butanone, 1-butanol, and 2-butanol has been observed. The selectivities of ring opening to 1- and 2-butane derivatives were independent of the reaction conditions but the ratio of isomerization to hydrogenolysis changed with the partial pressure of the epoxide and of hydrogen. Rate equations were found which satisfactorily described both reactions. The rate of isomerization depended also on the partial pressure of hydrogen, increasing linearly with it.

INTRODUCTION

The reactions of epoxyalkanes (oxiranes) with hydrogen in the presence of metallic catalysts have been studied mostly from the point of view of preparation of primary and secondary alcohols and of factors influencing this (presumably) hydrogenolytic opening of the ring (for a review of the literature, see (*1*)). However, some authors have observed that isomerization of epoxyalkanes to aldehydes and ketones can be achieved on metals, similarly as on acidic catalysts, even in the presence of hydrogen, as a competitive reaction to hydrogenolysis (*2–8*). Cornet *et al.* (*5–7*) have found that isomerization and hydrogenolysis of the ring are parallel reactions and that their ratio depends on the nature of the metal. They also studied the role of hydrogen in the isomerization by means of experiments in the presence of deuterium. Until now, no kinetic analysis of the complex interaction of an epoxy compound with hydrogen over a metallic catalyst has been published.

In the present work, 1,2-epoxybutane has been chosen as the model compound, and supported platinum as the catalyst, for the study of the kinetics of parallel isomerization and hydrogenolysis.

EXPERIMENTAL

Materials

1,2-Epoxybutane was a commercial preparation (Fluka AG) used without further purification, except for drying by a molecular sieve.

Pt/C catalyst was prepared by impregnation of 50 g of granulated (0.25–0.31 mm) active carbon by a solution of 4.2 g of hexachloroplatinic acid hexahydrate in 300 ml of water. When the yellow color of the solution disappeared, the solids were filtered off and dried at 120°C. The surface area (BET) was 980 m^2/g, and the pore volume (7.5–7500 nm) was 0.21 cm^3/g; the pore size distribution in the same range had two maxima, a smaller one at 10 nm and a larger one at 70 nm.

Pt/Cr_2O_3 catalyst was prepared by evaporation of water from a suspension of 18 g of granulated chromium oxide in a solution of 1.5 g of hexachloroplatinic acid hexahydrate in 200 ml of water. Chromium oxide was prepared by precipitation of chromium hydroxide from a solution of chromium nitrate by ammonia, decantation, washing, filtering off, drying at 120°C, and calcination at 600°C. The fraction 0.25–0.31 mm was

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used for impregnation. The surface area of the catalyst was 15 m^2/g, pore volume (7.5–7500 nm) was 0.22 cm^3/g; the pore size distribution in the same range had one maximum at 40 nm.

Hydrogen and nitrogen from pressure flasks were purified by removing water and oxygen (to approximately 10 ppm).

Apparatus and Procedure

A glass flow system was used which consisted of a feeding device with a syringe, an evaporator, a small tube reactor with a thermocouple well, and a condenser. The gases were measured by capillary flowmeters and the temperature in the reactor was automatically regulated to ±0.5°C. In kinetic experiments, the weight of the catalyst was 0.3 g and the catalyst bed was reduced at 200°C every day, first with a hydrogen-nitrogen mixture (1 : 5) for 30 min and then with pure hydrogen for 90 min. All kinetic measurements were conducted with the same catalyst bed. However, as its activity fell slightly during the day, periodic tests (two or three times in a day) were made at standard conditions in order to determine the actual activity and the factor for the correction of the found conversions to the standard (by definition) activity of the catalyst. In kinetic runs, the conversion of the 1,2-epoxybutane was kept under 0.1 and because the conversion curves were almost linear (see Fig. 1) initial reaction rates for the formation of individual products were calculated by the relation $r^0 = x/(W/F)$, where x is conversion and F/W the space velocity. The range of space velocities was 0.1 to 0.3 mol h^{-1} g_{cat}^{-1}. For every set of partial pressures of reactants, three determinations of r^0 at different F/W were made and the average value was used for the estimation of the rate equation.

The reaction products were analyzed by glc, using a 2.5-m-long column with 10% poly(ethyleneglycol adipate) on Rysorb (Lachema, Brno) at 59°C, with hydrogen as the carrier gas (33 ml/min) and with thermal conductivity detection. Quantitative evaluation of the chromatograms was based on calibration graphs for individual compounds.

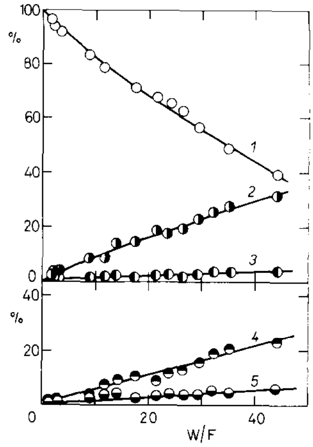


FIG. 1. Conversion curves for the reaction of 1,2-epoxybutane (curve *1*) on Pt/C catalyst at 190°C. p_A^0 = 0.03 MPa, p_H^0 = 0.07 MPa, reciprocal space velocity W/F in g_{cat} h mol^{-1}. Curve (*2*) butanal, (*3*) 2-butanone, (*4*) 1-butanol, (*5*) 2-butanol.

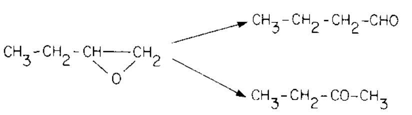
Treatment of Data

The kinetic data in the form $r^0 = f(p_i^0)$ were fitted to the supposed rate equations by the Marquardt nonlinear estimation method. The best equation was selected on the basis of the smallest value of the sum of squared deviations between the experimental and calculated data, other criteria being the sign of the estimated constants (equations which had negative values of rate or adsorption coefficients were discarded) and the possibility to correlate linearly the logarithm of the constants against $1/T$.

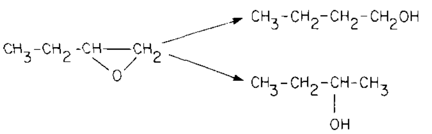
RESULTS

Reaction Scheme

The products of the interaction of 1,2-epoxybutane (ethyloxirane) with hydrogen over platinum on carriers such as active carbon, silica, and chromium oxide consist of butanal, 2-butanone, 1-butanol, and 2-butanol. With active carbon and silica, the carbonyl compounds predominate over the alcohols. This shows that with these catalysts, the isomerization of the oxirane ring


(1)
(2)

is more important than the hydrogenolytic splitting of one of the C–O bonds.


(3)
(4)

The question arises as to whether hydrogenolysis occurs at all; the formation of the alcohols might be a consecutive process consisting of isomerization of the oxirane and hydrogenation of the formed carbonyl compounds. Our results presented in Fig. 1 show that this is not the case. Up to 60% conversion, the formation of all four products seems to proceed in parallel processes. Even at very low conversions, the alcohols are present in the reaction products and no maxima or inflections, typical of consecutive reactions, appear on the conversion curves. This is in agreement with the findings of Sénéchal and Cornet (*6*) who, however, have found practically no butanal in their products of the reaction of 1,2-epoxybutane on platinum films or on platinum/pumice.

The negligible extent of the carbonyl group hydrogenation is a surprising fact as ketones and aldehydes are readily hydrogenated over platinum under these conditions (e.g., (*9*)). This may be caused by a very strong adsorption of the 1,2-epoxybutane in comparison with the reaction products. The form of the conversion curves in Fig. 1 supports this assumption. They are linear or almost linear, corresponding to apparent zero-order kinetics which is obtained when the surface is practically fully covered by the molecules of the starting compound.

Also the hydrogen transfer reactions between a carbonyl compound and an alcohol seem to be absent.

Figure 1 also demonstrates the preferential formation of the compounds with the functional groups in the 1-position (butanal and 1-butanol) in comparison to the 2-substituted butane derivatives (2-butanone and 2-butanol). This disagrees with the data of Sénéchal and Cornet (*6*) who have found more ketone and secondary alcohol than primary alcohol and aldehyde on their platinum catalysts, but agrees with the experience obtained with other compounds on most catalysts (cf. (*1*)).

In our kinetic experiments with the Pt/C catalyst, the ratio of the opening of the ring in the directions to 1-substituted and to 2-substituted compounds was, within experimental error, independent of the partial pressures of the reactants and of the temperature, for both the carbonyl compounds and the alcohols, showing only random variation. Table 1 summarizes the average values of these selectivities, calculated as the ratios of rates $S_c = r_1^0/r_2^0$ and $S_a = r_3^0/r_4^0$ (subscripts 1 to 4 correspond to the numbering of chemical equations), together with standard deviations.

This independence of the ring-opening selectivities on reaction conditions allowed us to treat the kinetics of the two isomerization pathways (Eqs. (1) and (2)) and of the two hydrogenolytic pathways (Eqs. (3) and (4)) as the kinetics of only two independent single reactions. For this simplification, isomerization and hydrogenolysis reaction rates were calculated as the sums $r_i^0 = r_1^0 + r_2^0$ and $r_h^0 = r_3^0 + r_4^0$, respectively. However, as Fig. 2 demonstrates, the dependence of r_i^0 and r_h^0 on the composition of the reaction mixture is quite different.

TABLE 1

Average Values of Selectivities for the Isomerization and Hydrogenolysis of 1,2-Epoxybutane in the Direction toward the 1- and 2-Substituted Compounds

Temperature (°C)	Number of r^0 values	S_c	S_a
160	10	3.32 ± 0.62	6.5 ± 2.6
175	18	3.57 ± 0.16	7.0 ± 2.8
190	10	3.46 ± 0.34	4.9 ± 1.1
160–190	38	3.48 ± 0.44	6.3 ± 2.0

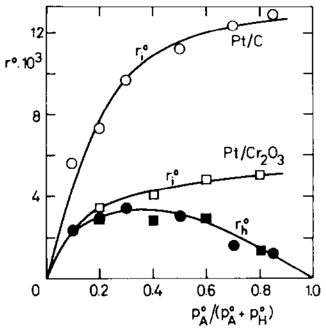


FIG. 2. Dependence of the initial reaction rates for isomerization r_i^0 and for hydrogenolysis r_h^0 (in mol h^{-1} g_{cat}^{-1}) on the composition of the reaction mixture at total atmospheric pressure.

Kinetics of Isomerization

The selection of a suitable rate equation for the isomerization on Pt/C was based on the data for 175°C which were most precise with the applied experimental setup. The data consisted of r_i^0 values measured at different initial partial pressures of 1,2-epoxybutane, p_A^0, hydrogen, p_H^0, and nitrogen, p_N^0, their sum totaling to atmospheric pressure. The initial reaction rates showed a dependence on p_H^0 although hydrogen is not a reactant in the isomerization. Figure 3 shows the increase of r_i^0 with the partial pressure of hydrogen at different p_A^0. For this reason, the rate equation must include a term describing this influence of hydrogen which seems to be linear. Extrapolation to $p_H^0 = 0$ suggests a nonnegative rate with a pure 1,2-epoxybutane feed and the term for the influence of hydrogen in the form of $(1 + C_H p_H^0)$. However, we were not able to measure the rates without hydrogen being present in the feed because the conversion fell very rapidly under these conditions and no steady state of catalyst activity could be obtained.

The rate also showed a dependence upon the partial pressure of 1,2-epoxybutane which was satisfactorily described by a simple Langmuir–Hinshelwood type of term. The resulting rate equation thus had the form

$$r_i^0 = \frac{k_i K_A^i p_A^0 \, (1 + C_H p_H^0)}{1 + K_A^i p_A^0} . \qquad (5)$$

With other equations, e.g., those containing square roots of p_H^0 and p_A^0 and higher powers of the binomial terms in the denominator or numerator, the fit was worse. The lines in Fig. 3 have been calculated using Eq. (5) and the numerical values of K_A^i and C_H are given in Table 2.

The data for 160 and 190°C have also been successfully correlated by means of Eq. (5). However, the influence of hydrogen on r_i^0 at 160°C was quite small and the relative error high so that, in consequence, the value of C_H could not be determined with certainty. The values found are given in Table 2. The activation energy for isomerization, calculated by means of the apparent Arrhenius equation from k_i values, was 107 kJ/mol.

The form of Eq. (5) indicates two parallel isomerization processes, the first being hydrogen independent, the second requiring the presence of hydrogen. The rate constant k_i describes the hydrogen-independent reaction; the constant C_H is probably a composite parameter including the rate constant of the hydrogen-dependent process.

Kinetics of Hydrogenolysis

The hydrogenolytic reaction, as Fig. 2 also indicates, obeyed the expected depen-

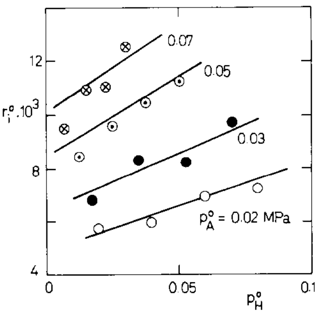


FIG. 3. Initial reaction rate r_i^0 (in mol h^{-1} g_{cat}^{-1}) for isomerization of 1,2-epoxybutane on Pt/C catalyst in dependence on the partial pressure of hydrogen (in MPa). Points are experimental; lines are calculated by means of Eq. (5).

TABLE 2

Values of the Constants of Equations (5) and (6) for the Reactions of 1,2-Epoxybutane

Temperature (°C)	Isomerization			Hydrogenolysis		
	k_i (mol h^{-1} g^{-1})	$K_A{}^i$ (MPa^{-1})	C_H (MPa^{-1})	k_H (mol h^{-1} g^{-1})	$K_A{}^h$ (MPa^{-1})	K_H (MPa^{-1})
160	4.41	84	1.0	92	62	34
175	17.96	17	3.9	149	14	17
190	29.6	12	6.6	652	10	1.2

dence on the partial pressures of both reactants. Several Langmuir–Hinshelwood types of equations and the power law rate equation were tested for the correlation of the $r_h{}^0$ data and the best fit was obtained, also with respect to the temperature dependence of the constants, with the equation

$$r_h{}^0 = \frac{k_h K_A{}^h p_A{}^0 K_H{}^h p_H{}^0}{(1 + K_A{}^h p_A{}^0 + K_H{}^h p_H{}^0)^3}. \tag{6}$$

Other equations, with square roots in $K_A{}^h p_A{}^0$ and $K_H{}^h p_H{}^0$ terms, or with other values of the exponent in the denominator, fitted the data badly or their constants could not be correlated by means of the Arrhenius and van't Hoff equations. The values of the constants of Eq. (6) are given in Table 2. The fit of the data by means of the power law rate equation

$$r_h{}^0 = k'(p_A{}^0)^a(p_H{}^0)^b \tag{7}$$

was also very good but the dependence of a and b values on temperature was large and irregular (for 160, 175, and 190°C, we found $a = -0.173$, 0.0014, and 0.206, respectively, and $b = 0.285$, 0.082, and 0.889, respectively). The k' values showed an expected trend with the temperature: $k' = 2.47$, 4.13, and 187.5 mol h^{-1} g^{-1} MPa$^{-(a+b)}$, respectively.

The Langmuir–Hinshelwood model, on which the rate equations (5) and (6) are based, requires equal values of the adsorption coefficients $K_A{}^i$ and $K_A{}^h$ when adsorption on the same sites as the first step of both isomerization and hydrogenolysis is assumed. As the values in Table 2 show, this seems to be the case within the limits of uncertainty which were calculated to be in the range ±30 to 50%.

The activation energy for the hydrogenolysis, described by Eq. (6), was 178 kJ/mol and the adsorption heat of ethyloxirane, calculated from the common dependence of $K_A{}^i$ and $K_A{}^h$ on $1/T$, was 120 kJ/mol.

Influence of Carrier

In preliminary experiments for this work, a suitable catalyst was sought and various metals and carriers were compared with respect to activity and selectivity. With platinum as the active component a great difference was found in selectivity when this metal was deposited on active carbon and silica or on chromia. In the case of Pt/Cr_2O_3, the formation of 2-butanone and 2-butanol predominated over that of butanal and 1-butanol, in contrast to the observations reported here for the Pt/C catalyst.

However, further experiments, prolonged over several days, showed a gradual change in selectivity with a parallel decrease in activity. When a stationary state was achieved the average selectivity ratios were $S_c = 3.1 \pm 1.0$ and $S_a = 4.0 \pm 1.3$, which are the same, within experimental error, as those for Pt/C (cf. Table 1).

The carrier also influenced the ratio of isomerization to hydrogenolysis. Detailed kinetic measurements revealed that this change is caused by a relative decrease in activity for isomerization whereas the hydrogenolytic activity remained the same as with the Pt/C catalyst. Figure 2 demonstrates this effect. The points for the hydrogenolysis on both catalysts lie on the same curve but, with respect to isomerization, the catalysts differ appreciably in activity.

The kinetic data on isomerization for Pt/Cr_2O_3, obtained at 175°C, were again worked up by means of Eq. (5), giving k_i = 7.2 mol h^{-1} g^{-1}, $K_A{}^i$ = 19 mPa^{-1} and C_H = 4.0 mPa^{-1}. Comparison with the values in Table 2 shows that the carrier influences only the rate constant k_i.

All carriers were inactive for the hydrogenolysis and isomerization, as separate experiments without platinum showed.

DISCUSSION

Catalytic isomerization reactions on platinum group metals requiring the presence of hydrogen have been observed previously in this laboratory. Šimoník and Beránek (*10*) have found that the isomerization of 2-buten-1-ol to butanal, catalyzed by platinum on silica, proceeds by a monomolecular and a bimolecular mechanism simultaneously, the latter depending on hydrogen concentration. Kraus (*11*) and Beránek and Kraus (*12*) studied in detail the isomerization of unsaturated alcohols to aldehydes on palladium on active carbon which does not proceed in the absence of hydrogen. The conclusion of this work, based on treatment of kinetic data and on experiments with deuterium, was that hydrogen maintains the surface of the metal in a state active for the catalytic reaction, but does not participate otherwise in the reaction mechanism.

The work of Sénéchal and Cornet (*6*) on the reactions of 1,2-epoxybutane and 2,3-epoxybutane in the presence of deuterium on several platinum group metals and on nickel indicated the participation of hydrogen (or deuterium) in the formation of 2-butanone from these oxirane derivatives. However, they did not observe the formation of butanal in significant quantities, and 1-butanol was a minor product in comparison to 2-butanol and 2-butanone. This large difference in the selectivity pattern of their reaction system and ours may be due to the temperature because they (*6*) measured at 90°C and the activation energies of isomerization and hydrogenolysis are different. Also the state of the surface may be temperature dependent.

The positive influence of hydrogen's presence on the activity of various catalysts has been observed by a number of authors (for a review see Bartók (*13*), and also e.g., Tamaka *et al.* (*14*)). This synergetic or cocatalytic effect of hydrogen seems to be well proven, but in spite of several suggested explanations its mechanism is not clear and further work is necessary.

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