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NOTES

Mono and Bimolecular Mechanisms in the Catalytic Isomerization of Crotyl Alcohol to Butyraldehyde

In the course of examination of the kinetics of a heterogeneously catalyzed complex reaction system, namely the parallel-consecutive hydrogenation of crotonaldehyde via butyraldehyde or via crotyl alcohol to butanol (*1*), we found that along with hydrogenation of the formed reaction intermediate (crotyl alcohol) its isomerization to butyraldehyde occurred to a large extent:

$$\underset{(N)}{CH_3{-}CH{=}CH{-}CH_2OH} \rightarrow \underset{(M)}{CH_3{-}CH_2{-}CH_2{-}CH{=}O}$$

The catalyst consisted of platinum (1%) and iron (0.7%) supported on silica gel (alkalized with 2% NaOH in order to minimize the side reactions). The reaction was carried out in the gas phase at atmospheric pressure and 160°C. As for the kinetic description of the transformation of crotonaldehyde to butanol a knowledge of the kinetics of crotyl alcohol isomerization is necessary, we have studied this reaction separately as the same reaction conditions. In this note we wish to report the results which show some special features.

Isomerization of unsaturated alcohols to corresponding saturated aldehydes or ketones has already been reported to proceed on oxides (*2, 3*), especially on aluminium oxide, or on metals (*3–9*), of which particularly copper, nickel, and palladium were studied. A systematic investigation of the isomerization of unsaturated alcohols on platinum group metals was recently carried out by Kraus (*10, 11*). However, there is no report on the kinetics of this isomerization reaction.

We examined the kinetics of the isomerization of crotyl alcohol in a flow system both in the presence and in the absence of hydrogen. In the presence of hydrogen, hydrogenation of crotyl alcohol to butanol was also taking place. However, by using the method of initial reaction rates, we were able to measure the rates of isomerization and hydrogenation separately. We first determined 30 values of initial reaction rates in the presence of hydrogen, using four different total pressures of the reactants (1, 0.75, 0.5, and 0.25 atm; the pressure was reduced by diluting the reactants with nitrogen) and varying hydrogen to crotyl alcohol ratios. The results are represented by points in Fig. 1 which shows two different regions. At lower partial pressures of crotyl alcohol (around 0.05 atm) and in excess of hydrogen a distinct maximum in reaction rate is attained, the height of the maximum being dependent on the partial pressure of hydrogen. With increasing partial pressure of crotyl alcohol, the reaction rate decreases. In the following region (at $p_N^0 > 0.4$ atm) the reaction rate again increases, even though the amount of hydrogen in the reaction mixture decreases. In order to explain this dependence we measured the initial reaction rates in the absence of hydrogen. In these measurements the partial pressure of crotyl alcohol was decreased by addition of nitrogen. The results (Fig. 2) show that the reaction takes place even in the absence of hydrogen, and its rate increases with increasing partial

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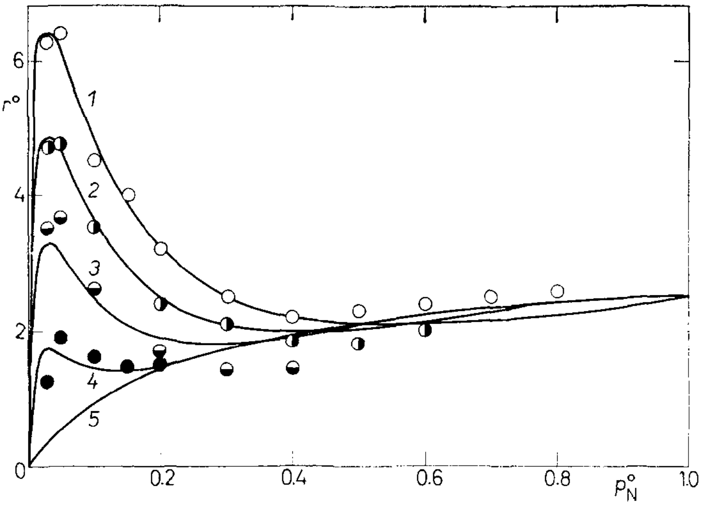

FIG. 1. Dependence of initial rate of isomerization of crotyl alcohol in the presence of hydrogen r^0 (mole hr^{-1} kg^{-1}) on partial pressure of crotyl alcohol p_N^0 (atm) at different total pressures of the reaction mixture hydrogen + crotyl alcohol.

Solid curves represent the dependences calculated from Eq. (5) for different P[(1) — 1 atm; (2) — 0.75 atm; (3) — 0.5 atm; (4) — 0.25 atm]. Points are experimental data (○:1 atm; ◑:0.75 atm; ◒ 0.5 atm; ●: 0.25 atm). Curve 5 represents the calculated dependence $r_1^0 = f(p_N^0)$ for the monomolecular process in the absence of hydrogen from Fig. 2.

pressure of crotyl alcohol. The righthand side of this dependence (from $p_N^0 = 0.4$ atm) resembles that illustrated in the right-hand side of Fig. 1. It seems likely that in this region the reaction proceeds via a monomolecular mechanism, i.e., without participation of hydrogen in the rate-determining step, because its effect on reaction rate is weak. In the region between $p_N^0 = 0.3$ and 0.6 atm the effect of hydrogen seems even to be negative (the points for $P = 0.75$ and 0.5 atm in Fig. 1 lie below the curve obtained in the absence of hydrogen). However, in the left-hand side of Fig. 1 (up to $p_N^0 = 0.4$ atm) the effect of hydrogen partial pressure is strong and

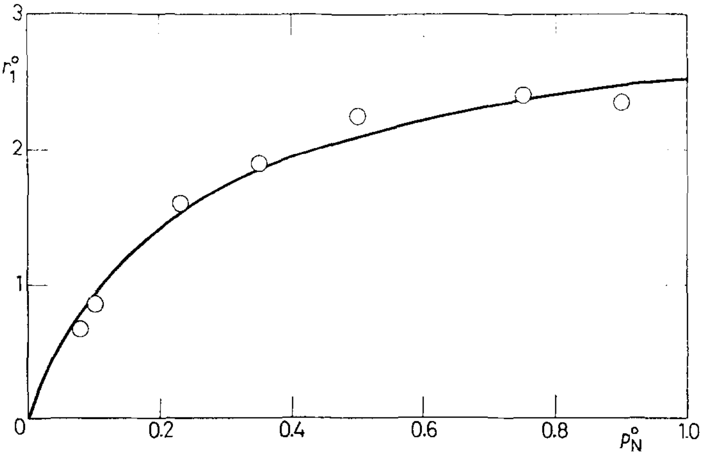

FIG. 2. Dependence of initial rate of isomerization of crotyl alcohol in the absence of hydrogen r_1^0 (mole hr^{-1} kg^{-1}) on partial pressure of crotyl alcohol p_N^0 (atm).

The curve was calculated from Eq. (1) using $n = s = 1$ and $k_1 = 3.14$ mole hr^{-1} kg^{-1}, $K_{N,1} = 4.15$ atm^{-1}. Points represent the experimental data.

the reaction seems to be bimolecular (i.e., with hydrogen participating). This is indicated by the occurrence of maxima in the dependence of the reaction rate on the composition of the reaction mixture hydrogen–crotyl alcohol and by the effect of hydrogen partial pressure on the height of these maxima.

In order to describe the kinetics of the reaction quantitatively, we treated the data on a Langmuir–Hinshelwood basis. We considered only such kinetic models in which a surface reaction becomes the rate-determining step; the possibility that the adsorption of crotyl alcohol or hydrogen or the desorption of butyraldehyde would be rate-determining seemed improbable on the basis of a previous study (*1*) as well as of analysis of the influence of slow adsorption or desorption on the course of heterogeneously catalyzed complex reactions (*12, 13*). For isomerization rates in the absence of hydrogen, we used equations of the type

$$r_1{}^0 = k_1 K_{N,1} p_N{}^0/[1 + (K_{N,1} p_N{}^0)^n]^s, \quad (1)$$

where $n = 0.5$ or 1, depending on whether the adsorption of crotyl alcohol is regarded as taking place with or without dissociation, and $s = 1$–4, along with equations of the type (where $s = 2$ or 3)

$$r_1{}^0 = k_1[(1 + 8K_{N,1} p_N{}^0)^{1/2} - 1]^s/4(4K_{N,1} p_N{}^0)^{s-1}, \quad (2)$$

which describe cases in which crotyl alcohol is adsorbed on two centers, however without dissociation (*14*) (r^0 is the initial reaction rate, k is the rate constant, K_N is the adsorption coefficient, and $p_N{}^0$ is the initial partial pressure of crotyl alcohol; the monomolecular process is denoted by index 1). Treatment of the experimental rate data by nonlinear regression (*15*) by means of nine equations of the types (1) and (2) showed that the monomolecular isomerization is better described by Eq. (1) with $n = 1$. (Fig. 2).

For isomerization in the presence of hydrogen, we assumed that the reaction rate is the sum of the rates of the monomolecular and bimolecular process $r^0 = r_1{}^0 + r_2{}^0$. In the corresponding rate equations, we expressed the term $r_1{}^0$ by one of the equations of the type (1) and (2). For the bimolecular process, we tried to use equations of the type

$$r_2{}^0 = \frac{k_2 K_{N,2} K_{B,2} p_N{}^0 p_B{}^0}{[1 + (K_{N,2} p_N{}^0)^n + (K_{B,2} p_B{}^0)^b]^s} \quad (3)$$

(where n and b equals 0.5 or 1, depending on whether the adsorption is assumed to occur with or without dissociation, and $s = 1$ to 4) or, for adsorption of crotyl alcohol occurring on two centers without dissociation (*14*), by equations of the type

$$\begin{aligned} r_2{}^0 &= k_2 K_{B,2} p_B{}^0 \\ &\times (\{[1 + (K_{B,2} p_B{}^0)^b]^2 + 8K_{N,2} p_N{}^0\}^{1/2} \\ &- [1 + (K_{B,2} p_B{}^0)^b])^{s+1}/4(4K_{N,2} p_N{}^0)^s, \quad (4) \end{aligned}$$

where b is again 0.5 or 1, and $s = 2$ or 3. K_B is the adsorption coefficient, and $p_B{}^0$ is the initial partial pressure of hydrogen; the bimolecular process is denoted by the index 2. The obtained combinations of the expressions for mono and bimolecular process (a total of 24) were treated by nonlinear regression. The best equations turned out to be the three which consisted of the combinations of the relations (1) and (3) with n and $b = 1$ and $s = 1$ for the monomolecular process and 2 to 4 for the bimolecular process. Fig. 1 shows the dependence of r^0 on $p_N{}^0$ for the reaction in hydrogen calculated for different total pressures from the relation

$$r = \frac{k_1 K_{N,1} p_N{}^0}{[1 + K_{N,1} p_N{}^0 + K_{B,1} p_B{}^0]} + \frac{k_2 K_{N,2} K_{B,2} p_N{}^0 p_B{}^0}{[1 + K_{N,2} p_N{}^0 + K_{B,2} p_B{}^0]^2}, \quad (5)$$

using $k_1 = 3.14$ mole hr^{-1} kg^{-1}, $k_2 = 647$ mole hr^{-1} kg^{-1}, $K_{N,1} = 4.15$ atm^{-1}, $K_{B,1} = 3.7$ atm^{-1}, $K_{N,2} = 29.5$ atm^{-1}, $K_{B,2} = 0.042$ atm^{-1}. It is evident that this equation describes the whole experimental region, i.e., from the predominant bimolecular to the prevailing monomolecular process.

From the mechanistic viewpoint, Eq. (5) is compatible with assumption that both reaction components, crotyl alcohol and hydrogen, are adsorbed during reaction, probably as molecules. The different values of adsorption coefficients for the mono and bimolecular isomerization ($K_{N,1} \neq K_{N,2}$ and $K_{B,1} \neq K_{B,2}$) show that both processes probably take place on different sites; the reverse model ($K_{N,1} = K_{N,2}$ and $K_{B,1} = K_{B,2}$) correlates the data worse (the sum of squared deviations is more than doubled). From Eq. (5), it follows further that hydrogen is adsorbed also on sites on which monomolecular isomerization is taking place, and consequently, at sufficiently high p_B^0, it retards the reaction and thus decreases the contribution of this mechanism to the total reaction rate. In this way, the already mentioned negative effect of hydrogen on the total reaction rate, observed at medium partial pressures of crotyl alcohol can be explained (except for two points which deviate significantly from the computed curve for an unknown reason). In case of bimolecular mechanism, hydrogen is adsorbed much more weakly than crotyl alcohol, which causes that maxima in Fig. 1 to occur in the region of very low partial pressures of crotyl alcohol.

Concerning the nature of active sites for mono and bimolecular isomerizations, the possibility cannot be ruled out that the monomolecular process occurs on the surface of the oxide carrier while the bimolecular process takes place on the metal component of the catalyst (similarly as in accompanying parallel hydrogenation (*1*), active centers for isomerization and hydrogenation not being necessarily the same). The catalytic activity of the carrier for the isomerization could not be checked directly, as it itself undergoes changes during addition of the metal components Pt and Fe, due to the action of anions of the salts of these metals and of the added alkali. The unmodified carrier was found to be catalytically active. By the addition of NaCl, Na_2SO_4 and NaOH in amounts corresponding to the added H_2PtCl_6, $FeSO_4$ and NaOH, the carrier became inactive: no doubt, in this way, its state after deposition of the metal components Pt and Fe is not accurately simulated.

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