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n-Butene Isomerization on Acidic Ion-Exchange Resin

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The selectivity during the *n*-butene interconversion depends neither on the fouling of a commercial silica-alumina cracking catalyst with a heterogeneous active surface, nor on the pressure between 32 and 750 torr over a SO_3H resin (Amberlyst 15). These observations confirm the assumption of a common surface intermediate which presumably is the *sec*-butyl carbonium ion. Nevertheless, the selectivity can phenomenologically be given with high accuracy by the differential equations for a triangle reaction scheme involving first order steps. Formally identical equations can be derived on the assumption of a *common* intermediate. The rate constants for adsorption and desorption have been calculated from the kinetic equations. The activation energies are 13 kcal/mole for 1-butene adsorption, and 22 kcal/mole for desorption into 1-butene. The surface coverages can be determined, too, provided the sites of the resin are of the same activity. The values are between 0.1 and 0.9.

The mechanism of hydrocarbon reactions in the gas phase, catalyzed by acidic oxides, has been studied very extensively in the last decades. No generally valid correlation has been found, however, between catalytic activity and acid strength. The preparation methods and pretreatment of the samples yield catalysts with different acid strength distributions of Brönsted and Lewis type acidic sites. Therefore, the application of cation-exchange resins as catalysts in these reactions may be of great importance, in view of the well-known nature and the homogeneous distribution of their acidic groups (*1*).

In this short communication the catalytic *n*-butene isomerization is discussed. First, the catalytic properties of a silica-alumina and those of an ion-exchange resin will be compared. A reaction mechanism consistent with the observed kinetics on the resin catalyst is given.

EXPERIMENTAL

The silica-alumina was a commercial cracking catalyst manufactured in the USSR with the following characteristics: specific surface area 357 m^2/g; Al_2O_3 11.0%; SiO_2 77.6%; Fe_2O_3 3.6%; MgO 4.8%; CaO 1.9%; Na_2O 0.3%; K_2O 0.2%.

The cation-exchange resin used in acidic form was Amberlyst 15 (Serva, Heidelberg) with SO_3H as its active group. Further data for this catalyst are as follows: grain size, 0.3–1 mm; diameter of the elementary globular polymer particles, 600–800 Å; specific surface area from krypton adsorption isotherm at $-196°C$, 45 m^2/g, from butane adsorption isotherm at 0°C, 47.5 m^2/g; acidity, 4.5 meq/g; water content, 10 wt%.

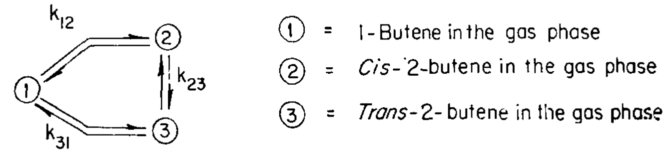
The experiments were carried out in a closed apparatus with gas circulation. The reaction conditions were as follows: pressure, 1 atm; catalyst bed temperatures ranging from 70° to 150°C for silica-alumina; pressures from 32 to 750 torr and temperatures from 35° to 150°C in the case of the resin catalyst.

In both cases 1-butene was fed. Initial rates of 1-butene conversion to 2-butene isomers over fresh catalysts, and selectivity curves [e.g., $x_2 = f(x_1)$, where x_2 is the mole fraction of the *cis* isomer and x_1, that of 1-butene] both on fresh, and fouled catalyst samples were determined.

Results and Discussion

Activity and Selectivity on Silica-Alumina and on Ion-Exchange Resin

The catalytic activity of the resin proved to be much higher than that of silica-alumina, the initial rates of 1-butene isomerization being 185×10^{-12} and 3.9×10^{-12} moles $\mathrm{cm}_{\mathrm{cat}}^{-2}\ \mathrm{sec}^{-1}$, respectively, at atmospheric pressure and at 100°C. Moreover, the selectivities of the two catalysts differ considerably, too. If the phenomenological triangle scheme for the isomerization of the n-butenes is accepted, where all the conversions are reversible and of first order (*2*, *4*), the differential equation of the selectivity [e.g., $dx_2/dx_1 = f'(x_1,x_2)$] can be derived and the rate constants relative to k_{12} can be calculated, assuming different values for them and solving the differential equation by numerical integration. The values which best fitted the experimental selectivity curves are at 100°C: for the resin, $k_{23}/k_{12} = 1.5 \pm 0.1$, $k_{31}/k_{12} = 0.17 \pm 0.01$; for the silica-alumina, $k_{23}/k_{12} = 0.56 \pm 0.04$, $k_{31}/k_{12} = 0.066 \pm 0.004$. The relative rate constants for the resin are in good agreement with those calculated from the data given by Manassen and Khalif (*1*). Before examining the differences in the selectivity between the two types of catalyst, the course of the catalytic reaction is to be analyzed in detail.



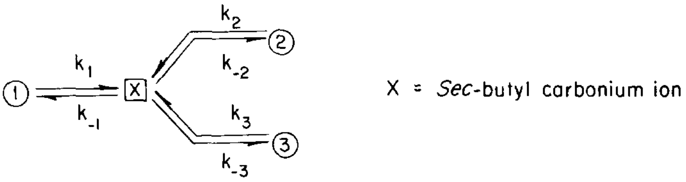
The Mechanism of the Catalytic Isomerization

To have any conception about the path of the catalytic reaction, some experimental observations should be reviewed.

In addition to isomerization, polymerization also takes place as a side reaction on the resin, as well as on the silica-alumina. The adsorption of polymer formed during the experiments results in a decrease of the catalytic activity but does not influence the above-mentioned selectivity. This means that the adsorption species for the n-butene isomers are *identical.* It seems very unlikely that the heterogeneity of the silica-alumina surface is not affected by polymer adsorption. The change in heterogeneity is not expected to influence the adsorption state of the three n-butene isomers in an identical way to result in unaltered selectivity.

Similarly, no change in selectivity can be observed on the ion-exchange resin between 32 and 750 torr. The lack of a pressure dependence excludes the possibility that more than one adsorbed species of the three isomers exist on the quasihomogeneous surface of catalyst.

These facts confirm the assumption that a common surface intermediate, presumably the *sec*-butyl carbonium ion suggested by several authors (*3*, *4*), is responsible for catalytic butene isomerization.



Nevertheless, the experimental selectivity curve could be interpreted with high accuracy on the basis of kinetic equations derived for the triangle scheme consisting of reversible first order reactions. If instead of the triangle scheme, the isomerization is represented by a "star" or Y mechanism with a common intermediate, the differential equation for the selectivity function, e.g., $dx_2/dx_1 = f'(x_1,x_2)$ will formally be identical with that for the triangle scheme (*5*), provided that the rates of adsorption are taken proportional to the corresponding partial pressures and to the number of uncovered active sites, and those of desorption proportional to the surface coverage by the intermediate. The correspondence of the experimental rate equations to rate equations derived for a catalytic reaction mechanism, in principle, reminds of the treatment of kinetics in a phenomenological triangle scheme by de Boer and van der Borg (*6*). They discuss irreversible conversions through three adsorbed intermediates, whereas all the steps in the Y scheme mentioned above are reversible, and a single intermediate participates in the catalytic reactions. The formal identity means in our case that each rate constant in the triangle scheme corresponds to a product of an adsorption and a desorption rate constant [see, e.g., Eq. (1)] and, therefore, no rate-determining step can be supposed (*5*), as was possible for the conversions discussed by de Boer and van der Borg (*6*). In this way, the calculation of the relative rate constants for adsorption and the determination of the desorption probabilities is made possible using the empirical rate constants in the triangle scheme (*5*). These values are listed at 100°C in Table 1.

TABLE 1

Adsorption and Desorption of n-Butenes during the Isomerization[a]

	Relative adsorption rates of—			Probabilities of desorption into—		
	1-Butene, k_1/k_1	*cis*-2-Butene, k_2/k_1	*trans*-2-Butene, k_3/k_1	1-Butene, k_{-1}/k_X	*cis*-2-Butene, k_{-2}/k_X	*trans*-2-Butene, k_{-3}/k_X
Over Amberlyst 15	1	0.95 ± 0.1	0.70 ± 0.1	0.085 ± 0.01	0.36 ± 0.03	0.56 ± 0.04
Over silica-alumina	1	0.85 ± 0.07	0.23 ± 0.02	0.15 ± 0.01	0.51 ± 0.04	0.34 ± 0.03

[a] $k_X \equiv (k_{-1} + k_{-2} + k_{-3})$.

However, disregarding the temperature dependence of the values in Table 1, some qualitative conclusions can be arrived at which are roughly in accordance with the hypothesis of Hightower and Hall (*4*):

(a) If the n-butenes are adsorbed in protonated form and only steric factors are taken into account, the adsorption rates of the isomers should be in the order: 1-butene > *cis*-2-butene > *trans*-2-butene. The highest adsorption rate for 1-butene is also expected from the fact that the protonation of the primary carbon atom is energetically the most favorable. Since the ground energy level of the *cis* isomer is higher than that of the *trans* isomer, a greater adsorption ability of the former seems likely.

(b) The desorption into *cis* and *trans* isomers must have a greater probability than that into 1-butene because in the latter case a proton is removed from a primary and not from a secondary carbon atom, as is required in the formation of 2-butene.

The initial rates (r) of the conversion for 1-butene were measured at different pressures on Amberlyst 15. The higher the partial pressure of 1-butene (p_1), the lower the rate constant ($k_{1,\mathrm{expt}}$) determined from the following simple equation (p_2 and p_3 being zero)

$$r[\text{moles cm}_{\text{cat}}^{-2}\ \text{sec}^{-1}] = (k_{31} + k_{12})p_1 = (k_{1,\mathrm{exp}}k_{-2}/k_X + k_{1,\mathrm{exp}}k_{-3}/k_X)c_0p_1 \quad (1)$$

where c_0 is the concentration of SO_3H groups [moles $\text{cm}_{\text{cat}}^{-2}$], and k_X, the desorption rate constant (see Table 1).

The dependence of $k_{1,\mathrm{expt}}$ on the pressure p_1, as derived on the basis of the Y scheme, is (*5, 7*)

$$k_{1,\mathrm{expt}} = k_1\left[1 - \frac{k_1p_1}{k_1p_1 + k_X}\right], \quad (2)$$

if $p_2 = p_3 = 0$.

Applying Eq. (2), the adsorption rate constant for 1-butene (k_1) and the desorption rate constant (k_X) can be calculated, if $k_{1,\mathrm{expt}}$ is known at different pressures p_1.

The approximate values of the coverages (θ) of the active SO_3H groups can be determined from k_1, k_X, p_1 at the beginning of the 1-butene isomerization (*7*) because of the homogeneity of the active sites. This calculation leads to values ranging from 0.1 to 0.9, depending on the pressure and temperature, in agreement with the results of adsorption measurements.

From the temperature dependence of the rate constants, the following activation energies were determined: for the adsorption of 1-butene, 13 ± 1 kcal/mole, and for the desorption of the *sec*-butyl carbonium ion into 1-butene, 22 ± 1 kcal/mole. Accordingly, the exothermic heat of 1-butene adsorption is about 9 kcal/mole.

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