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The Isomerization of Butenes over KC_8

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The isomerization of butenes over KC_8 has been investigated. The double-bond-migration and the cis-trans isomerization took place over KC_8, but the skeletal isomerization could not be observed. From the rates of reactions and the selectivity ratios, all six of the relative rate constants and the activation energies of reaction were determined. The reaction paths on the triangular graph calculated from the rates constants show the *cis*-convex-type profile, which suggests one of the catalytic characteristics of KC_8.

It is well known that graphite reacts with alkali metals to form a variety of intercalation compounds with a transition metal-like nature.[1] In these substances, the alkali metal atoms are not merely distributed randomly between the layers of the graphite structure, but have an ordered layer-lattice of their own. The corresponding intercalation compounds exhibit well-defined stoichiometric compounds, *e.g.*, KC_8.

Although the intercalation compounds of graphite have been known for at least fifty years, their catalytic and surface properties have only recently begun to be explored. In the present work, the interest has centered on the catalytic characteristics of KC_8, the isomerization of butenes being employed as a model reaction.

Experimental

Materials. The KC_8 samples used as catalysts were prepared *in vacuo* in the apparatus shown in Fig. 1. The graphite (1.25 g of Union Carbide Spectroscopic-grade powder) in the vessel, G, was first degassed for 3 h at 540 K. The bulb, K, containing potassium metal was then heated by applying a soft flame, so that the metal ran into the preparation vessel, P, the wall of which was covered with potassium film, leaving the dross behind. The weight ratio, potassium/graphite, was set as 0.60. K was then removed at the seal-off. After the stopcock, III, had been closed, this apparatus was removed from the vacuum line and inclined in order to transfer the graphite powder from the vessel, G, to P. After G had been removed from the seal-off, the apparatus was again connected to the vacuum line. P was heated in a electric heater for 24 h at 540 K to form KC_8, and then it was evacuated for 30 min. The excess potassium on KC_8 was separated by the evacuation. The intercalation compound thus formed was kept for another 24 h at the same temperature. The apparatus was then removed from the vacuum line at the seal-off point and inclined so as to transfer the KC_8 powder from P to the reactor, R. A capillary tube sampler connected to the apparatus was used for X-ray analysis *in vacuo* to identify the intercalation compound. The X-ray diffraction data of the KC_8 samples prepared thus agreed quite well with those reported by Rudroff and Schulze.[2] The color of the KC_8 obtained was gold.

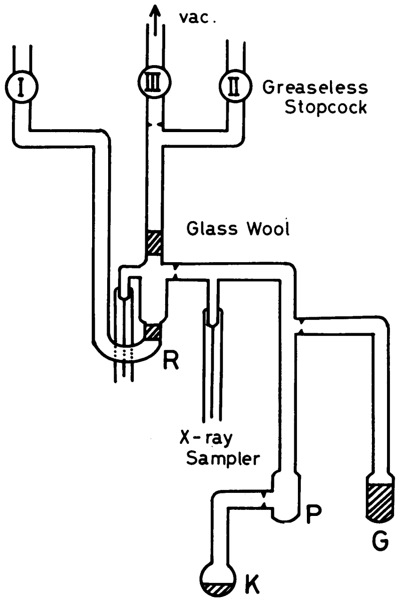


Fig. 1. Apparatus for preparation of KC_8.

The 1-butene, *cis*-2-, and *trans*-2-butene used as the reactants were obtained from the Tokyo Kasei Kogyo Co., Ltd., and were purified by repeated distillation *in vacuo*, the purity was confirmed by gas chromatography to be more than 99%.

Procedure. The apparatus used for the present study was essentially the same as that used previously.[3] A closed circulating system with a U-shaped reactor and with greaseless stopcocks, connected to a conventional vacuum line and a gas chromatograph, was used to follow the reaction. The volume of the reaction system corresponded to about 288 cm^3 at the reaction temperature of 373 K. The reaction mixtures were occasionally analyzed by means of the gas chromatograph with a column of dimethylsulfolane on Celite-545.

Before each run, the catalyst was evacuated for 2 h at 470 K, after which helium was introduced into the reactor. The reactor was then cooled to the reaction temperature and evacuated for a few minutes.

Results and Discussion

The double-bond-migration and the *cis-trans* isomerization of butenes took place over KC_8. The graphite does not show any catalytic activity for a reaction under the same experimental conditions. The skeletal isomerization could not be observed. No gaseous hydrocarbon other than butenes could be detected in the reaction mixtures under the present experimental conditions.

Figure 2 shows how the composition of the butenes changes with the time over KC_8 at 373 K when 1-butene is the reactant; *cis*-2-butene is predominantly formed. The ambient pressure of 1-butene at the initial state was 2.80×10^3 Pa in this reaction. When potassium metal was employed as the catalyst, *trans*-2-butene was predominantly formed as this temperature.[4] The results suggest that the KC_8 used as the catalyst is different in catalytic nature from potassium metal. The active sites of the catalyst are attributed to KC_8, and not to potassium atoms, which might be randomly present

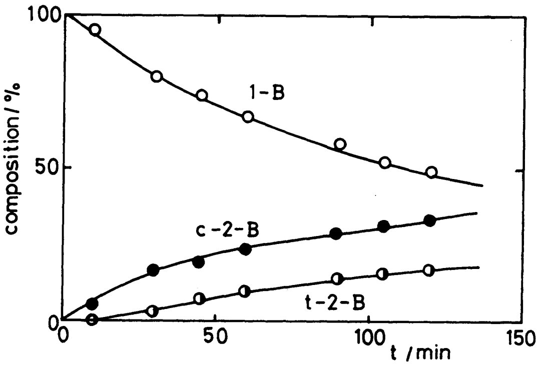


Fig. 2. Isomerization of 1-butene over KC_8 at 373 K.

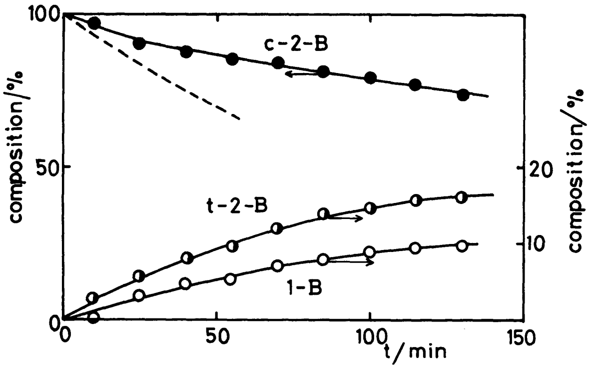


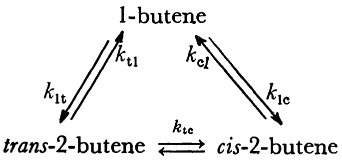
Fig. 3. Isomerization of *cis*-2-butene over KC_8 at 373 K.

between the layers of the graphite structure.

The equilibrium composition of butenes at 373 K, as calculated from the thermodynamical data,[5] is $x_{1e} : x_{ce} : x_{te} = 0.052 : 0.288 : 0.660$, where x_{1e}, x_{ce}, and x_{te} are the mole fractions of 1-butene, *cis*-2-butene, and *trans*-2-butene respectively at equilibrium. The amount of *cis*-2-butene formed at a later time becomes more than that at the equilibrium.

Figure 3 shows how composition of the butenes changes with the time at 373 K when *cis*-2-butene is the reactant. The ambient pressure of *cis*-2-butene at the initial state was 2.80×10^3 Pa in the reaction. The rate of the isomerization reaction of *cis*-2-butene is lower than that of 1-butene; the dotted line represents the time course of 1-butene shown in Fig. 2. The amount of 1-butene at the later time also exceeds that at equilibrium.

The isomerization reaction of butenes was almost first-order with respect to the pressure of reactants, ranging from 2.0×10^3 to 1.4×10^4 Pa. From the rates of reaction and the selectivity ratios, all six of the relative rate constants expressed by Scheme 1 and the activation energies of reaction were determined. The relative rate constants at 373 K and the activation energies (bracketed) are shown in Fig. 4.



Scheme 1.

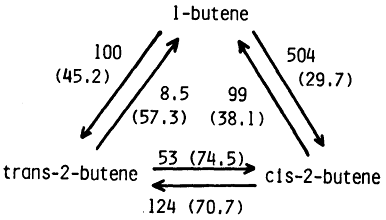


Fig. 4. Relative rate constants at 373 K and activation energies (kJ/mol) bracketed.

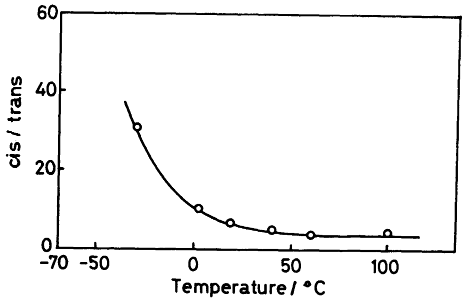


Fig. 5. Temperature dependence of selectivity ratio, *cis*/*trans*, for isomerization of 1-butene.

Figure 5 shows the temperature dependence of the *cis*/*trans* selectivity ratio, 1-butene being the reactant. The ratio became extremely high (more than 30) at a lower temperature.

Since the isomerization of butenes has been the subject of many detailed investigations, three mechanisms have been proposed for different catalytic systems:[6]

(a) A hydride-addition mechanism for metals and organometallic systems;

(b) a carbenium-ion mechanism for acid catalysts, and

(c) an allylic (carbanion) mechanism which is operative over basic catalysts. Each of these mechanisms has certain characteristic features. When the isomerization takes place with the allylic mechanism, the initial *cis*/*trans* ratio is more than unity and the initial 1/*trans* ratio is larger than the 1/*cis* ratio.[6,7]

The relative initial rates of isomerization are also similar to those for the carbanion mechanism; *i.e.*, the rate of the isomerization of 1-butene>that of *cis*-2> that of *trans*-2-butene. The data obtained in the present study are in agreement with an allylic mechanism. A further discussion of the reaction mechanism must await a new result which might be obtained from a rather sophisticated experiment.

Wei and Prater[8] developed an interesting method for evaluating the kinetic parameters of a monomolecular, or pseudomonomolecular, first-order multicomoponent system, triangular diagrams being employed. An extension of the Wei and Prater method was devised by Lombardo and Hall[9] to reduce the required work. Haag and Pines,[10] on the other hand, had proposed a method to estimate the relative values of six rate constants for the interconversion of butenes; they had shown that the reaction path could be calculated from the first-order rate equation by using the relative rate constants. The concentrations of 1- and of *cis*-2-butene were plotted against that of *trans*-2-butene. Kagawa[11] kinetically analyzed the reaction path in a system consisting of a Langmuir-Hinshelwood-type reaction.

In the Haag and Pines analysis, mixtures of butenes were not used as the reactants; the differential equation employed was applied only for a pure reactant. In the present paper, the isomerization of butenes, is dealt with in a more general way.

Since there is no change in the total number of moles with the extent of reaction:

$$x_l + x_c + x_t = 1, \tag{1}$$

where x_l, x_c, and x_t are the mole fractions of 1-butene, *cis*-2-butene, and *trans*-2-butene respectively. The overall reaction rates can be accordingly expressed by Eq. 2:

$$\frac{dx_l}{dt} = -(k_{lc}+k_{lt})x_l + k_{cl}x_c + k_{tl}x_t \tag{2-l}$$

$$\frac{dx_c}{dt} = k_{lc}x_l - (k_{ct}+k_{cl})x_c + k_{tc}x_t \tag{2-c}$$

$$\frac{dx_t}{dt} = k_{lt}x_l + k_{ct}x_c - (k_{tl}+k_{tc})x_t \tag{2-t}$$

The particular solution of Eq. 2 satisfying the boundary conditions of the initial composition, x_{i0} (i=l, c, t), at $t=0$ and the equilibrium composition, x_{ie}, at $t=\infty$ is:

$$\begin{aligned}
x_l = {} & (1/\sqrt{m^2-4n})[(k_{cl}-k_{tl})x_{c0} + k_{tl} \\
& - \{k_{lc}+k_{lt}+k_{tl}-(m+\sqrt{m^2-4n})/2\}x_{l0} \\
& - \{(m+\sqrt{m^2-4n})/2\}x_{le}]\exp[-\{(m-\sqrt{m^2-4n})/2\}t] \\
& - (1/\sqrt{m^2-4n})[(k_{cl}-k_{tl})x_{c0} + k_{tl} \\
& - \{k_{lc}+k_{lt}+k_{tl}-(m-\sqrt{m^2-4n})/2\}x_{l0} \\
& - \{(m-\sqrt{m^2-4n})/2\}x_{le}] \times \\
& \exp[-\{(m+\sqrt{m^2-4n})/2\}t] + x_{le},
\end{aligned} \tag{3-l}$$

$$\begin{aligned}
x_c = {} & (1/\sqrt{m^2-4n})[(k_{lc}-k_{tc})x_{l0} + k_{tc} \\
& - \{k_{ct}+k_{cl}+k_{tc}-(m+\sqrt{m^2-4n})/2\}x_{c0} \\
& - \{(m+\sqrt{m^2-4n})/2\}x_{ce}]\exp[-\{(m-\sqrt{m^2-4n})/2\}t] \\
& - (1/\sqrt{m^2-4n})[(k_{lc}-k_{tc})x_{l0} + k_{tc} \\
& - \{k_{ct}+k_{cl}+k_{tc}-(m-\sqrt{m^2-4n})/2\}x_{co} \\
& - \{(m-\sqrt{m^2-4n})/2\}x_{ce}] \times \\
& \exp[-\{(m+\sqrt{m^2-4n})/2\}t] + x_{ce},
\end{aligned} \tag{3-c}$$

$$\begin{aligned}
x_t = {} & (1/\sqrt{m^2-4n})[\{k_{lt}+k_{tl}+k_{tc}-(m+\sqrt{m^2-4n})/2\}x_{l0} \\
& + \{k_{ct}+k_{tl}+k_{tc}-(m+\sqrt{m^2-4n})/2\}x_{co} \\
& - \{k_{tl}+k_{tc}-(m+\sqrt{m^2-4n})/2+x_{te}(m+\sqrt{m^2-4n})/2\}] \times \\
& \exp[-\{(m-\sqrt{m^2-4n})/2\}t], \\
& - (1/\sqrt{m^2-4n})[\{k_{lt}+k_{tl}+k_{tc}-(m-\sqrt{m^2-4n})/2\}x_{l0} \\
& + \{k_{ct}+k_{tl}+k_{tc}-(m-\sqrt{m^2-4n})/2\}x_{c0} \\
& - \{k_{tl}+k_{tc}-(m-\sqrt{m^2-4n})/2+x_{te}(m-\sqrt{m^2-4n})/2\}] \times \\
& \exp[-\{(m+\sqrt{m^2-4n})/2\}t] + x_{te},
\end{aligned} \tag{3-t}$$

where

$$m = k_{lt} + k_{tc} + k_{cl} + k_{tl} + k_{lc} + k_{ct} \tag{4}$$

$$\begin{aligned}
n = {} & k_{tl}k_{cl} + k_{lt}k_{tc} + k_{lt}k_{ct} + k_{tl}k_{lc} + k_{tl}k_{cl} \\
& + k_{tl}k_{ct} + k_{cl}k_{tc} + k_{lc}k_{ct} + k_{cl}k_{tc}.
\end{aligned} \tag{5}$$

When the isomerization of butenes proceeds, the composition of butenes in the gas phase varies with the time. The values of x_l, x_c, and x_t corresponding to the reaction time, t, can be calculated from Eqs. 3, k_{ij}, x_{i0}, and x_{ie} being given. Figure 6 shows the reaction paths calculated at 373 K and at 293 K respectively. These triangular graphs thus represent one of the catalytic characteristics of KC_8 for the isomerization of butenes. The curves, which originate from the left side of the triangle, bend convexly to the left. The profile may be named the *cis*-convex type. The *cis*-convexity became higher at a lower temperature, as is shown in Fig. 6b.

The mole fraction of *cis*-2-butene, x_c, seemingly increases with the time at the earlier period, as is shown in Fig. 6b, when mixtures of 1- and *cis*-2-butene are

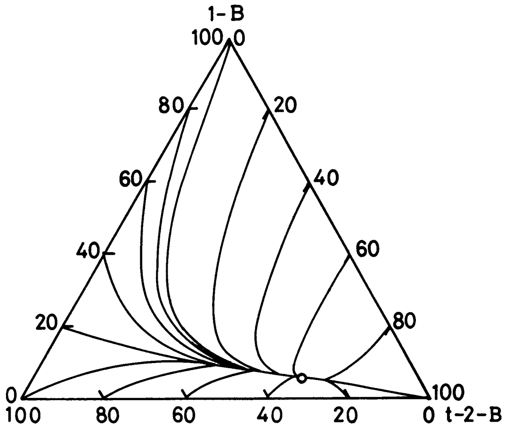


Fig. 6a. Reaction profile of isomerization of butenes over KC_8 at 373 K.

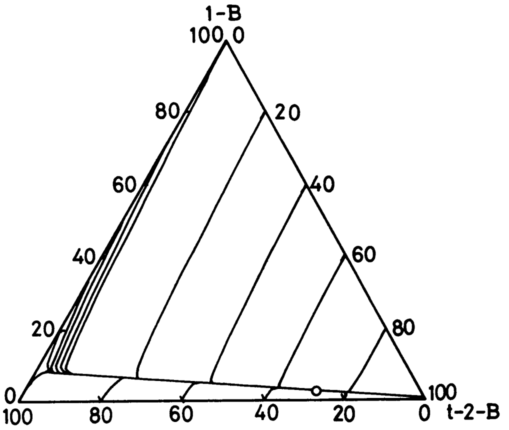


Fig. 6b. Reaction profile of isomerization of butenes over KC_8 at 292 K.

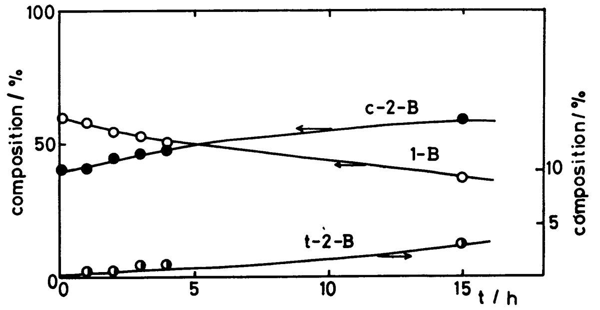


Fig. 7. Composition change with time, when the mixture of 0.6 1-butene/0.4 *cis*-2-butene reacted over KC_8 at 292 K.

employed as the reactants. The tendency is typically shown in Fig. 7; the time course of the 0.6/0.4 mixture is shown. The ambient pressures of 1-butene and of *cis*-2-butene at the initial state were 4.20×10^3 and 2.80×10^3 Pa respectively. The solid lines represent the curves calculated, while the points are the experimental results. The mole fraction of *cis*-2-butene, x_c, increased with the time and exceeded the equilibrium value, x_{ce} (0.288), although that at the initial state, x_{c0} (0.400), was higher than that at equilibrium. The curve of x_c, of course, will show its maximum and go downwards later. These results can be explained kinetically on the basis that k_{1c} (20.31) is much larger than k_{1t} (1.00) and k_{ct} (0.013) at 292 K.

Conclusion

The catalytic selectivity of KC_8 is different from that of potassium metal for the isomerization of butenes. The reaction may proceed by means of an allylic mechanism. One of the catalytic characteristics is thus shown in Fig. 6. The *cis*-convex type profile is due to the fact that the rate constant of the isomerization of 1-butene to *cis*-2-butene is higher than that to *trans*-2-butene and that of *cis*-2-butene to *trans*-2-butene.

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