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LETTERS TO THE EDITORS

Isomerization of *n*-Butenes Catalyzed by Anhydrous Magnesium Perchlorate

Rooney and Hathaway (*1*) have recently observed that anhydrous magnesium perchlorate chemisorbs triphenylmethane and triphenylmethanol at room temperature, the triphenylmethyl cation being formed. The presence of such surface activity indicated that the salt might catalyze some carbonium ion reactions of hydrocarbons at moderate temperatures. We now wish to report preliminary results on the isomerization of *n*-butenes.

Two samples of salt, each of 7 g (Hopkins and Williams, Ltd.), were used, and reactions carried out in a static system employing a Pyrex glass vessel (80 ml). In order to ensure that the surfaces of the crystals were completely anhydrous, each sample was evacuated at 250°C (*2*) for 3 hr and then cooled to reaction temperature. In each experiment reactant was admitted to a pressure of 50 mm of Hg, the products extracted after a suitable interval, and analyzed by gas-liquid chromatography.

Conversion of *cis*-but-2-ene to the isomeric *n*-butenes occurred readily at 150°C. At low conversions isobutene was the only other product but with increasing conversion, formation of isobutane became important. Thus, when conversion to equilibrium had reached 78%, the ratio of isobutane to isobutene was 2.4. Conversion to equilibrium was defined as $100(1-x)/(1-x_e)$ where x is the fraction of reactant remaining with respect to the total *n*-butenes, and x_e is the fraction at equilibrium. This expression was originally used by Brouwer (*3*) and we have also used his values for x_e (0.10, 0.30, and 0.60 for but-1-ene, *cis*-but-2-ene, and *trans*-but-2-ene, respectively). Ratios of but-1-ene to *trans*-but-2-ene are plotted as a function of conversion to equilibrium in Fig. 1, which shows that but-1-ene is formed initially in less than equilibrium amounts with respect to the *trans* isomer.

A continuous decline in catalytic activity was also noted but the rate of decline decreased rapidly in the first three experiments. The yields of isomeric *n*-butenes and total iso compounds were 27% and 15%, respectively, after a contact time of 30 min in the initial experiment. When the total reaction time had amounted to 4 hr, a further experiment of 30 min duration showed a decrease in these values to 14% and 4%, respectively.

Isomerization of but-1-ene on a second sample of catalyst at 150°C gave preferential formation of the less stable *cis* isomer and ratios of *cis*-but-2-ene to *trans*-but-2-ene are recorded in Fig. 2. In contrast to *cis*-but-2-ene, reactions of but-1-ene also gave *n*-butane in addition to isobutene and isobutane. However, yields of *n*-butane were less than those of isobutane by at least a factor of 10. A similar falloff in catalytic activity as a function of time of exposure to the olefin was also noted.

After completing this series of experiments, isomerization of *cis*-but-2-ene was again investigated at 150°C, using the second sample of salt. Preferential formation of but-1-ene was now observed in the first few experiments and no trace of isobutene or isobutane could be detected. Product ratios are also plotted in Fig. 1. In subse-

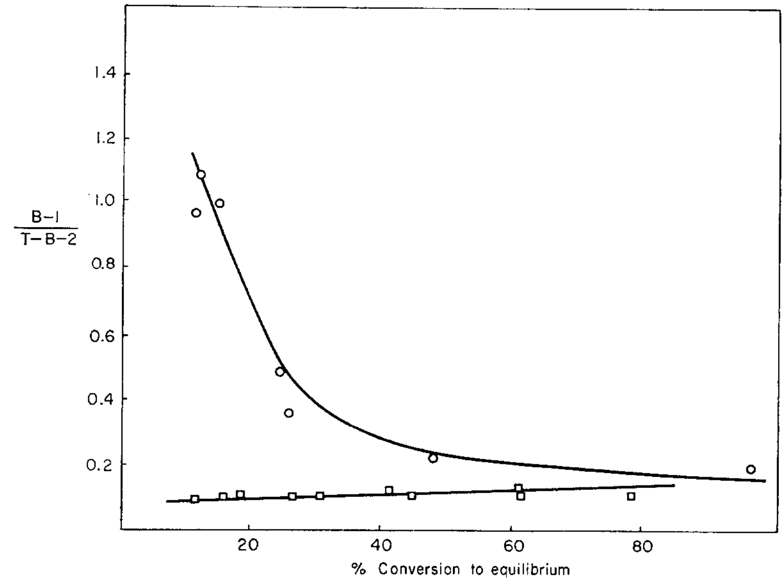


FIG. 1. Product ratios from isomerization of *cis*-but-2-ene on anhydrous magnesium perchlorate: □, first sample; ○, second sample of salt.

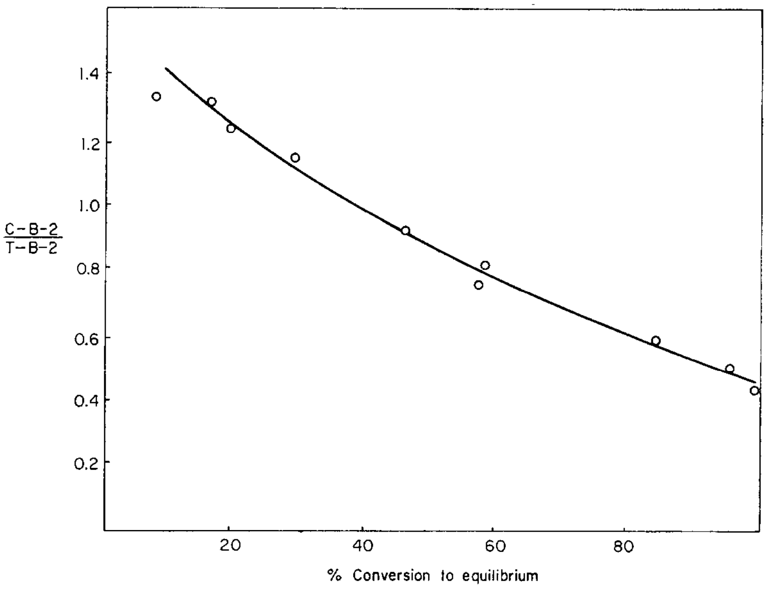
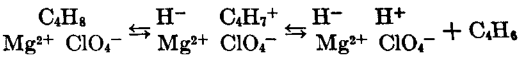


FIG. 2. Product ratios from isomerization of but-1-ene on anhydrous magnesium perchlorate.

quent experiments the catalytic properties gradually changed until they were identical with those of the first sample of salt. Examination of both samples of salt after completion of all experiments revealed that carbonaceous residues had been deposited on the crystal surfaces.

Mechanisms for these reactions are briefly summarized in the following equations:



$$\begin{matrix} C_4H_8 & \\ Mg^{2+} & ClO_4^- \end{matrix} \rightleftarrows \begin{matrix} H^- & C_4H_7^+ \\ Mg^{2+} & ClO_4^- \end{matrix} \rightleftarrows \begin{matrix} H^- & H^+ \\ Mg^{2+} & ClO_4^- \end{matrix} + C_4H_6 \qquad (I)$$

$$\begin{matrix} H^- & H^+ \\ Mg^{2+} & ClO_4^- \end{matrix} + C_4H_8 \leftrightarrows \begin{matrix} H^- & C_4H_9^+ \\ Mg^{2+} & ClO_4^- \end{matrix} \rightarrow \begin{matrix} & C_4H_{10} \\ Mg^{2+} & ClO_4^- \end{matrix} \quad \text{(II)}$$

Butenyl carbonium ions are formed initially and reversal of these reactions may result in isomerized olefin. However, some of these ions must dissociate further to butadiene, which presumably participates in polymerization processes leading to deposition of surface residues. In effect, dehydrogenation in these reactions produces perchloric acid as part of the surface structure, and these newly created Bronsted sites may then react with additional olefin to give butyl carbonium ions. Further addition of hydride ions results in complete saturation.

According to Leftin and Hobson (*4*) mechanism (I) accounts for preferential formation of *cis*-but-2-ene in isomerization of but-1-ene on acidic oxide catalysts. Examination of the two possible structures of the butenyl ions shows that *cis*-but-2-ene and *trans*-but-2-ene are not readily interconverted by mechanism I, which is therefore expected to give selective double-bond shift. However, Holbrook and Rooney (*5*) have recently obtained conclusive evidence that mechanism (II) may also give preferential formation of *cis*-but-2-ene from but-1-ene. At the moment therefore, it is not possible to say which mechanism is the more important during reaction of but-1-ene on anhydrous magnesium perchlorate. An important aspect of mechanism (II) is that conversion of the various butyl carbonium ions to π-complexes between olefins and protons may be necessary before the olefins desorb (*5, 6*). These π complexes appear to decrease in stability in the following order (*7*):

cis-but-2-ene > *trans*-but-2-ene >> but-1-ene

This sequence explains why mechanism (II) gives preferential formation of *cis*-but-2-ene from but-1-ene and results in such low yields of but-1-ene in isomerization of but-2-enes (*3*) and in elimination reactions (*5*) where ionic intermediates are involved.

The present results from reactions of *cis*-but-2-ene provide good support for the above theories. Formation of isobutane and isobutene during interconversion of the *n*-butenes clearly shows that mechanism (II) is important and consequently there is preferential *cis–trans* isomerization. When the iso compounds are absent from the products, mechanism (I) is responsible for isomerization and selective double-bond shift is observed (Fig. 1). An explanation of the gradual change in catalytic properties of the second sample of salt during reactions of *cis*-but-2-ene, which resulted in mechanism (II) largely replacing mechanism (I), must await further work. However, it is likely, as in similar catalytic systems (*3*) involving carbonium ions, that the history of the surface with respect to the formation of carbonaceous deposits has an important influence on the activity and selectivity of the salt for these reactions.

We have concluded that these results support the belief that magnesium ions are the initial centers of catalytic activity. Evidence of this kind is of interest in view of the theory that divalent cations in zeolitic materials are also sources of catalytic activity for carbonium ion reactions of hydrocarbons (*8*).

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