

ISOMERIZATION OF 1-BUTENE OVER SODIUM OXIDE AND POTASSIUM OXIDE

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The isomerization of 1-butene took place over sodium oxide and potassium oxide; cis-2-butene and trans-2-butene are formed. The ratio, cis/trans, was dependent upon the reaction temperature, and became less than unity in the reaction over the potassium oxide higher than 380 K.

The catalytic isomerization of n-butenes over solid acids and bases has extensively been investigated.¹⁾ However, the catalytic activity of alkali metal oxides for the reaction has not been reported so far, although that of alkaline earth metal oxides was reported.²⁾ In the present work, we investigated the isomerization of 1-butene over sodium oxide and potassium oxide in order to obtain more information on the base-catalysis.

A closed circulating system connected to a conventional vacuum line, and to a gas chromatograph was used to follow the reaction. The reaction mixtures were occasionally analyzed by the gas chromatograph with a column of dimethyl-sulfolane on Celite-545.

The sodium oxide and potassium oxide used as a catalyst were prepared by in situ oxidation, for which a U-shaped glass tube with a side-arm containing alkali metal was employed. The metal was purified by repeated vacuum-distillation to remove hydrogen and carbohydrates, under a pressure lower than 10^{-3} Pa. The alkali metal oxide was first evaporated on the wall of reactor in vacuo, and was then exposed to oxygen at 298 K to form alkali metal oxide until no more oxygen was taken up. The oxide was heated at 420 K with evacuation for 12 h.

1-Butene obtained from Tokyo Kasei Kogyo Co., Ltd., was purified by gas chromatography until the purity became more than 99 %.

The isomerization of 1-butene took place over sodium oxide and potassium oxide. No other gaseous hydrocarbon than n-butenes could be detected in the reaction mixtures; the skeletal isomerization could not be observed. The reaction was almost first order with respect to the pressure of 1-butene.

Figure 1 shows some results for the isomerization of 1-butene over sodium oxide and potassium oxide at various temperatures; the ratios, cis/trans, obtained by the extrapolation of the products ratios to zero conversion, are shown as a function of the reaction temperatures. The temperature dependence

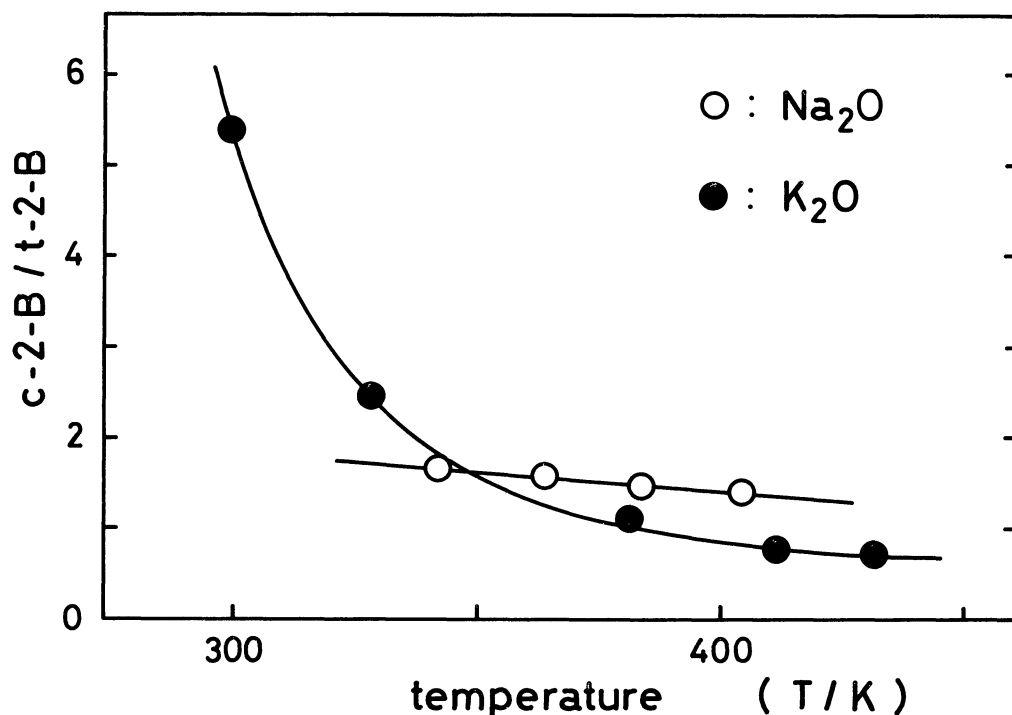


Fig. 1. Temperature dependence of selectivity ratios.

of the selectivity ratios is shown in both oxides. It is of interest that the ratio became less than unity in the reaction over potassium oxide at higher temperature.

Figure 2 shows how the composition of the butenes changes with time over potassium oxide at 413 K; trans-2-butene is predominantly formed. The potassium oxide probably has basic catalytic properties, and the result seemingly does not agree with the usual tendency that cis-2-butene is predominantly formed from

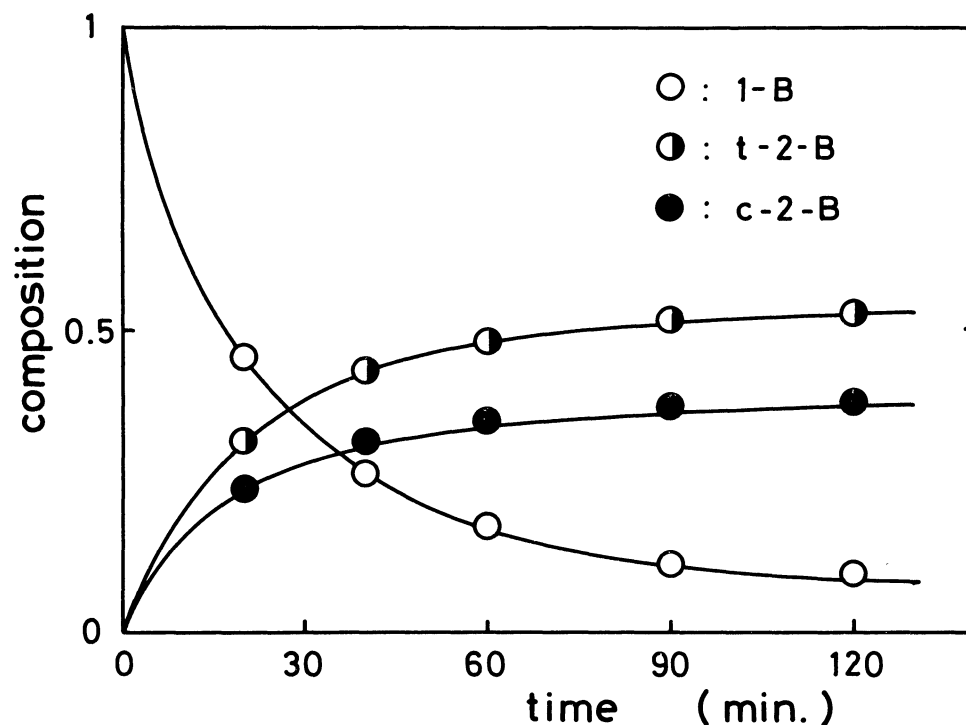


Fig. 2. Isomerization of 1-butene over potassium oxide at 413 K.

1-butene over a solid-base catalyst.³⁾

The stereoselectivity in the isomerization of 1-butene over a base-catalyst has reasonably been explained on the basis of the stability of the reaction intermediates;⁴⁾ two types of the intermediates, *cis*-intermediate and *trans*-intermediate, are considered, and the *cis*-intermediate is more stable than the *trans*-intermediate in the base-catalysis. The stability may be due to dipole-dipole interactions. However, the stereoselectivity observed in the present work can be tentatively explained on the basis of the difference in the chemisorption strength. If the *cis*-intermediate molecules are much more strongly chemisorbed on the potassium oxide at higher temperature than the *trans*-intermediate molecules, the weakly chemisorbed *trans*-intermediate molecules may be more easily desorbed from the surface; the reaction path to *cis*-2-butene becomes relatively narrow in practice, and the isomerization to *trans*-2-butene took place predominantly. At the lower temperature, the *trans*-intermediate may be more strongly chemisorbed than *cis*-intermediate, and the *cis*-2-butene is predominantly formed. The relative strength in the chemisorption of the reaction intermediates may

be differently dependent upon the temperature, and the temperature dependence of the selectivity ratio is observed. In order to confirm the tentative explanation further investigations are certainly necessary.

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(Received February 24, 1978)