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ISOMERIZATION OF 1-BUTENE OVER POTASSIUM

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The isomerization of 1-butene takes place over potassium; trans-2-butene and cis-2-butene are formed. The ratio, trans/cis, was 0.1 - 0.2 in the temperature range 20 - 40 °C, and was about unity in the range 90 - 140 °C.

The catalytic isomerization of 1-butene over solid acids and bases has extensively been investigated.[1] However, the catalytic activity for the reaction of potassium metal has not so far been reported, although that of sodium metal on active alumina was found long time ago.[2] In the present work, we investigated the isomerization of 1-butene over potassium metal to obtain further informations on the base-catalysis, eliminating the effect of a support.

A continuous flow system with a by-pass at atmospheric pressure was used to follow the reaction, helium being used as diluent. The reactor was a U-shaped glass tube with a side-arm containing potassium metal. The potassium was purified by repeated vacuum-distillation to remove hydrogen and carbohydrates, leaving the dross behind, under a pressure lower than 10^{-5} torr. The potassium was evaporated on the wall of reactor beforehand in a vacuum system, and the reactor was brought to be fixed in the flow system. The helium stream with 1-butene, which had been flowing in the meantime only through the by-pass, was diverted to flow through the reactor. The reaction mixtures were analyzed by g. c. with a column of dimethylsulfolane on Celite-545.

Figure 1 shows some results for the isomerization of 1-butene over potassium at various temperatures; the ratios, trans/cis, are shown as a function of conversion. The rate of reaction increased with increasing the reaction temperature as usual, the conversions being larger at higher temperature. No other gaseous hydrocarbon than butenes could be detected in the helium stream. The He/1-butene was 325 (mol/mol), and W/F, the contact time parameter, was varied in the range 7 - 4500 ($g/mol \cdot hr^{-1}$) to change the conversion. The W/F and the conversion were defined as: W/F = (weight of catalyst, g)/(feed rate of 1-butene and helium, $mol \cdot hr^{-1}$), and conversion = (mol of 2-butenes formed)/(mol of butenes remaining and formed) X 100.

It is of interest that ratio, trans/cis, is markedly different, depending upon the reaction temperature; the ratio was less than unity at lower temperature, and was almost unity at higher temperature. The order of runs in the present work was at random, and the ratios are suggestively independent of the preceding run, even if the reaction temperature is different. The result that the ratio, trans/cis, was about unity, seemingly does not agree with the usual tendency that

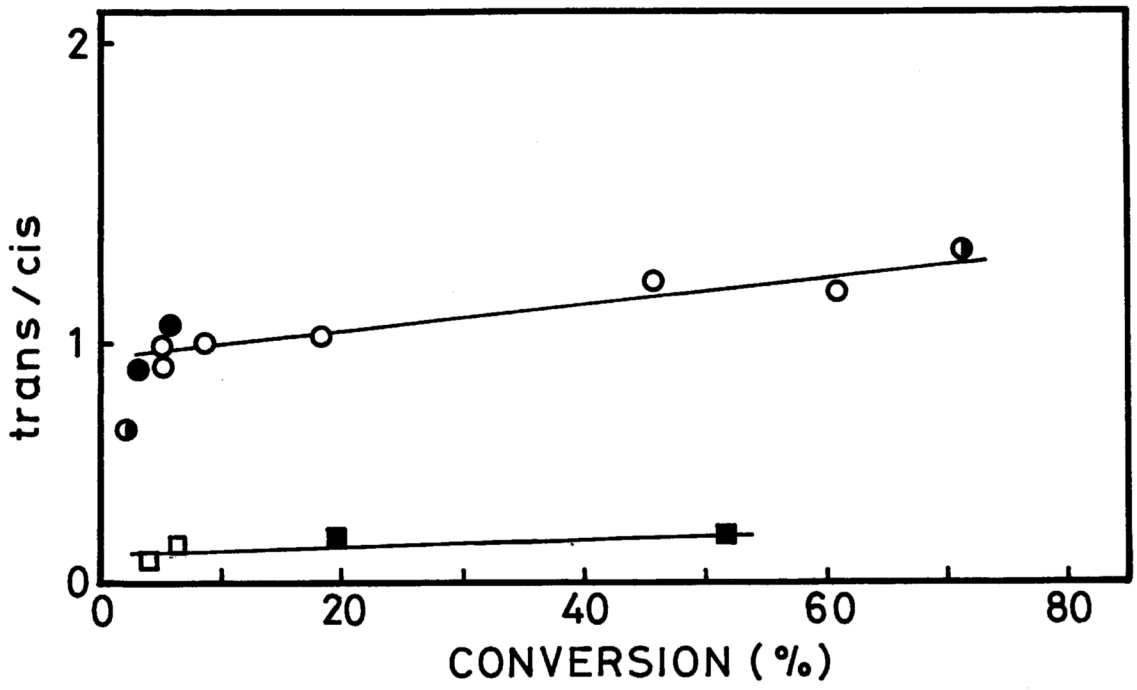

Fig. 1. Isomerization of 1-butene over potassium.
Reaction temp., □: 20°C, ■: 40°C, ◑: 90°C, ○: 120°C, ●: 140°C.

cis-2-butene is predominantly formed from 1-butene over a solid-base-catalyst.[3] At the higher temperature in the present work, however, potassium is liquid, and the selectivity may accordingly be different, base-catalytic properties being lost. On the point, a further investigation is certainly necessary in view of the catalysis by molten metals.

References

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