

THE ISOMERIZATION OF 1 BUTENE ON $TiCl_3$
AN EXAMPLE OF KINETICALLY CONTROLLED ISOMERIZATION

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During the last few years several communications¹⁻³ have reported isomerizations of 1-butene which have exhibited a degree of stereoselectivity in that the isomerization reaction initially produces more of the thermodynamically less favoured cis-2-butene than trans-2-butene.

While studying the reaction of certain gaseous hydrocarbons on the surface of the alpha form of titanium trichloride at room temperature we have observed an isomerization of 1-butene in which the reaction comes under kinetic control and for which the initial cis-2-butene:trans-2-butene ratio is markedly different from the normal equilibrium condition.

¹ A. Schriesheim and C.A. Rowe, Jr. Tetrahedron Letters No. 10, 405, (1962).

² A. Schriesheim, J.E. Hofman and C.A. Rowe, Jr., J. Amer. Chem. Soc. 83, 3731, (1961)

³ W.O. Haag and Herman Pines, J. Amer. Chem. Soc. 82, 387, (1960).

The titanium trichloride used in the system was formed on the spherical surface of a thermostated glass reaction vessel of a high vacuum system by the reaction of redistilled titanium tetrachloride and hydrogen at a hot tungsten filament. The 1-butene was of a chemically pure grade free of isomers and was contacted with the $TiCl_3$ surface at pressures of the order of ten centimeters of mercury. Analysis of the reaction products was carried out by gas chromatography using a 21 ft. column of dimethylsulfolane on firebrick. Samples were removed at half hour intervals by means of an automatic sampling system designed to operate at subatmospheric conditions.⁴

If one plots the log of the olefine concentration as a function of time the resulting curve is linear and indicative of the fact that the isomerization reaction is first order.

Plotting the cis/trans ratio as a function of time and extrapolating to zero time³ one obtains a cis/trans ratio of 2.2 which is about nine times the cis/trans equilibrium value of 0.25 determined by Schriesheim and Rowe¹. The value of the cis/trans ratio which we have determined is similar to the values obtained by Haag and Pines for the sodium systems which they have studied but is considerably lower than the figure obtained for the potassium-t-butoxide in dimethylsulfoxide system of Schriesheim and Rowe¹.

An experiment was performed in which cis-2-butene was

⁴ K. Casey, F.H.C. Edgecombe and D.A. Jardine, The Analyst in the press.

contacted with $TiCl_3$. Trans-2-butene slowly formed and no 1-butene production was observed.

The mechanism of the isomerization on a $TiCl_3$ surface is currently under study and when such has been completed details will be released.