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Bull. Chem. Soc. Jpn., 56, 1539—1540 (1983)

The Catalytic Isomerization of Butenes over a Sulfuric Acid-Graphite Intercalation Compound

Susumu Tsuchiya,* Masao Hara, and Hayao Imamura
Department of Industrial Chemistry, Faculty of Engineering, Yamaguchi University, Ube, Yamaguchi 755

(Received August 23, 1982)

Synopsis. The relative rate constants and the activation energies of the isomerization of butenes over sulfuric acid-graphite intercalation compound have been measured. *cis*-2-Butene is more reactive than 1-butene. The reaction profile shown on the triangular graph is of the *trans*-convex type.

Much attention has been paid to all the characteristic properties of graphite intercalation compounds, and the catalytic properties of the compounds have been extensively investigated in various reaction systems.[1-2] In this study, the interest has centered on the catalytic characteristics of the sulfuric acid-graphite intercalation compound (H_2SO_4-GIC), the isomerization of butenes being employed as a model reaction.

Experimental

A usual flow-type system with a by-pass at atmospheric pressure was employed to follow the reaction, nitrogen being used as the diluent. The H_2SO_4-GIC, the catalyst, prepared beforehand in a vacuum system similar to that described previously,[3] was fixed in the system.

The nitrogen stream with butene as a reactant was flowing only through the by-pass in the meantime; then it was diverted to flow through the reactor. The flowing rate of the nitrogen was *ca.* 40 cm^3/min, the amount of catalyst used being 0.10 g for each run. The reaction mixtures were analyzed by means of gas chromatography with a column packing of 2,4-dimethylsulfolane on Uniport C.

The butenes were obtained from the Tokyo Kasei Kogyo Co., Ltd.; their purity was confirmed by gas chromatography to be more than 99%. Before each run, the catalyst was treated with a nitrogen stream at 373 K for 2 h, and the experimental results were well reproducible.

Results and Discussion

The double-bond migration and the *cis-trans* isomerization of butenes took place over H_2SO_4-GIC. The graphite does not show any catalytic activity for the reaction under the same experimental conditions. The skeletal isomerization could not be observed, as was reported previously.[3] No gaseous hydrocarbon other than butenes could be detected in the reaction mixtures under the present experimental conditions.

The rate of the isomerization of butenes was almost proportional to the pressure of the reactant. From the rates of reaction and the selectivity ratios, all six of the relative rate constants and the activation energies of reaction were determined in a manner similar to that described previously.[4] The results are shown in Fig. 1. It is of much interest that *cis*-2-butene is more reactive than 1-butene.

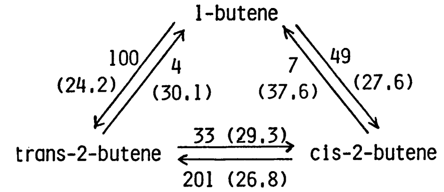

Fig. 1. Relative rate constants at 300 K and activation energies (kJ/mol) bracketed.

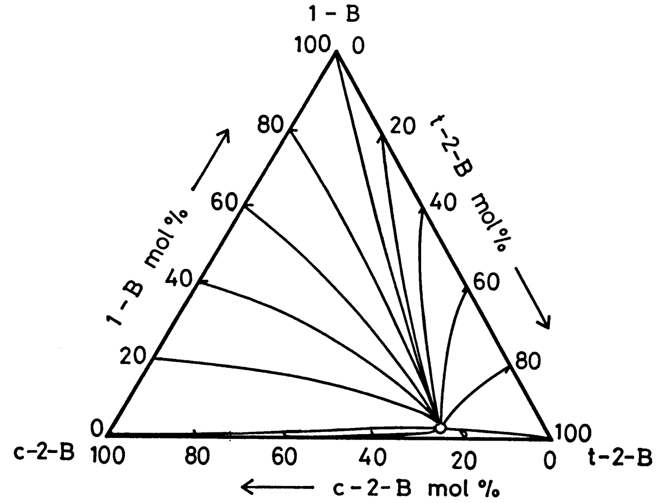

Fig. 2. Reaction profile of isomerization of butenes over H_2SO_4-GIC at 300 K.

Figure 2 shows the reaction paths calculated at 300 K. The triangular graph thus represents one of the catalytic characteristics of H_2SO_4-GIC for the isomerization of butenes. Since the rate equations employed are expressed on the basis of the sum of the forwards and backwards reactions, and since the time variable, *t*, is eliminated in the graph, the compositions of butenes can be shown from the initial to the equilibrium state. The curves, which originate from the left side of the triangle, bend convexly to the right. The profile may be named the "*trans*-convex type," which is entirely different from that obtained in the isomerization over KC_8.[4]

The following mechanisms for the isomerization of butenes have been proposed for different catalytic systems.[5] (1) A hydride-addition mechanism for metals, (2) a carbenium-ion mechanism for acid catalysts, and (3) an allylic mechanism for basic catalysts. When the isomerization takes place with a carbenium-ion mechanism, the selectivity ratio, *cis*/*trans*, is about unity, while 1/*cis* and 1/*trans* are less than 3.0, usually less than 1.0. The selectivity ratios obtained in the present may be in agreement with a carbenium-ion mechanism.

The observed order of the relative rate constants of isomerization, *cis*-2-butene>1-butene>*trans*-2-butene, however, does not agree with what would be expected from a carbenium-ion mechanism. Accordingly, it can not necessarily be concluded that the active sites of H_2SO_4–GIC have same kind of acidic properties as hitherto reported.[6] The further discussion on the points will have to await new results, which may clarify the reaction mechanism.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture for which the authors' thanks are due.

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