Pentane Isomerization Activity of Halogenated Rare Earth Intermetallics

Hayao Imamura,* Yuzo Kato, and Susumu Tsuchiya
Department of Industrial Chemistry, Faculty of Engineering, Yamaguchi University, 2557 Tokiwadai, Ube 755

(Received November 19, 1983)

Synopsis. Binary halides formed by treating $ErAl_3$ with halogen elements were subjected to an characterization as skeletal isomerization catalysts for pentane. Halogenation of $ErAl_3$ in the presence of CH_2Cl_2 or CCl_4 gives rise to superacidic binary halides as a result of formation of V-center-type sites due to excess of halogen species.

There have been various studies published of catalytic properties of solid superacids.[1–5] Recently, we have found that in the presence of halogens X_2 (X_2= Cl_2, Br_2, and I_2), rare earth- or Th-group IIIB intermetallics are readily converted into binary halides which are characterized as superacids.[6] These halogenated intermetallic compounds are exceptionally active as skeletal isomerization catalysts for pentane under mild conditions. We believe that the extreme activity is due to superacidity, but their catalytic behavior markedly varies with preparative conditions for the binary halides. To obtain information about the isomerization activity of the binary halide catalysts formed by direct halogenation of rare earth intermetallics, the present study was undertaken.

In a standard procedure for preparing the catalyst, X_2 is added to finely ground intermetallics suspended in dichloromethane (CH_2Cl_2) solvent, and the mixture is stirred to obtain the binary halide in a slurry form in dry argon under anhydrous conditions.[6] Pentane is injected to initiate the isomerization. When 2 ml of pentane was added to an $ErAl_3$ (1 mmol)–I_2 (6 mmol) system in CH_2Cl_2, the activity at 0°C was evaluated from the pentane conversion in 30 min as 61% (Table 1). On the other hand, when the isomerization was conducted without CH_2Cl_2 solvent, the catalytic activity was significantly decreased for $ErAl_3$–Cl_2 and $ErAl_3$–I_2. As shown in Table 1, however, the activity was restored to some extent by addition of a small amount of CH_2Cl_2. These observations indicate that CH_2Cl_2 used as a solvent plays an important role in the development of superacidity in the present system. NMR and element analyses for $ErAl_3$–X_2 in the presence of CH_2Cl_2 revealed that metathetic halogen exchange takes place between the halogenated $ErAl_3$ and CH_2Cl_2 along with the formation of CH_2XCl. It is supposed that this promoting action of CH_2Cl_2 on the isomerization of pentane is ascribed in part to the halogen exchange. To check this, the isomerization reaction was examined by adding Cl_2 or Br_2 to $ErAl_3$–I_2, because changes in Gibbs energy at 25°C are favorable for the halogen exchange between metal iodides and Cl_2 (or Br_2). The reaction between the iodinated $ErAl_3$ and Cl_2 could be followed gravimetrically to find $ErAl_3I_{11.6}Cl_{0.4}$, which is actually active for the isomerization (Table 1).

Table 1. Results of the isomerization of pentane

Catalyst	Solvent	Additive$^{a)}$	Conversion of pentane/%
$ErAl_3$–Cl_2	CH_2Cl_2	—	$25^{c)}$
	CCl_4	—	$25^{c)}$
	—$^{b)}$	—	$1.8^{d)}$
	—$^{b)}$	CH_2Cl_2	$7.6^{d)}$
$ErAl_3$–Br_2	CH_2Cl_2	—	$58^{c)}$
	—$^{b)}$	—	$5.6^{d)}$
$ErAl_3$–I_2	CH_2Cl_2	—	$61^{c)}$
	—$^{b)}$	—	none$^{d)}$
	—$^{b)}$	CH_2Cl_2	$9.0^{d)}$
	—$^{b)}$	CCl_4	$6.3^{d)}$
	—$^{b)}$	Cl_2	$1.2^{d)}$
	—$^{b)}$	Br_2	$5.3^{d)}$

a) CH_2Cl_2: 0.5 ml, CCl_4: 0.5 ml, Br_2: 3 mmol. b) Direct contact between $ErAl_3$ and X_2 was conducted *in situ* in pentane. c) The conversion (1 mmol $ErAl_3$–6 mmol X_2, solvent: 8 ml, pentane: 2 ml) was measured at 0 °C and 30 min. d) The conversion (0.5 mmol $ErAl_3$-3 mmol X_2, pentane: 10 ml) was measured at 23 °C and 6 h.

In addition, it can be presumed from Table 1 that the action of CH_2Cl_2 on $ErAl_3$–Cl_2 brings about another synergism for improving the catalytic activity, besides the halogen exchange. To understand this better, the chlorination of $ErAl_3$ was examined by using gravimetric techniques: after $ErAl_3$ was allowed to react at 23°C with the stoichiometric amount of chlorine required to chlorinate the Er and Al present in the alloy, CH_2Cl_2 (190 Torr) (1 Torr=133.322 Pa) was introduced into the system in place of chlorine gas. There was a further occurrence of the reaction between the chlorinated $ErAl_3$ and CH_2Cl_2 in which a large excess of chlorine species was taken up by the resulting binary halide. Carbon tetrachloride (CCl_4) behaved quite similarly to CH_2Cl_2. As shown in Table 1, for example, $ErAl_3$–I_2 exhibited an enhancement in activity to some extent when treated with CCl_4. For $ErAl_3$–Cl_2 in CCl_4 the active catalyst was such that the binary chloride formed contains chlorine species to an extent exceeding the stoichiometric amount by a factor of 1.3.

These results lead to speculations on the generation of active sites in terms of V-center-like effects which are induced by an excess of halogen. It is recognized that for alkali halides color centers formed in the crystal structure are often associated with catalytic activities.[7] ESR studies indicated that a strong ESR signal with a g value of 2.0059 and an overall width of *ca.* 60 G is formed at room temperature when CH_2Cl_2 or CCl_4 is added to the chlorinated $ErAl_3$. The siganl intensity remained unchanged over a period of 24 h. In view of

Table 2. Relative intensities of ESR signals measured for various catalyst systems

Catalyst system	Relative intensity of ESR signal
$ErAl_3$–Cl_2 in CH_2Cl_2	142
$ErAl_3$–Cl_2 in CCl_4	95
$AlCl_3$ in CH_2Cl_2 (or CCl_4)	3 (2)
$ErCl_3$ in CH_2Cl_2 (or CCl_4)	0.3 (0.5)
$ErCl_3$–$AlCl_3$(1:3) in CH_2Cl_2	1

the fact that the enhancing action of CH_2Cl_2 or CCl_4 on the isomerization activity was not noticeable for a 1:3 mixture of $ErCl_3$ and $AlCl_3$ or the individual compounds, a good correlation between the ESR signal intensity and the activity may be taken to have been observed for $ErAl_3$–Cl_2 in CH_2Cl_2 or CCl_4 (Table 2). Accordingly, it is concluded for the present system that CH_2Cl_2 or CCl_4-treated $ErAl_3$–X_2, possessing V-centers due to an excess of halogen species, shows superacidity.

Experimental

The rare earth intermetallic compound $ErAl_3$ used was obtained as a commercial product from Nippon Yttrium Co. Pentane was thoroughly dehydrated with sodium wires and subsequently distilled in dry argon. Dichloromethane and carbon tetrachloride were purified by distillation in the presence of phosphorus pentaoxide. The isomerization of pentane was investigated in the liquid phase over binary halides, which had been prepared *via* reaction of $ErAl_3$ with X_2 before each run. Special care was taken to exclude water and oxygen from the system. Further details regarding the procedure for the isomerization reaction have been described elsewhere.6)

This research was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Culture and Science. We are grateful to Mr. Toyoharu Saito, Tokyo Institute of Technology, for carrying out the elemental analyses.

References

1) G. A. Olah, K. Laali, and A. K. Mehrotra, *J. Org. Chem.*, **48**, 3360 (1983).

2) M. Hino, S. Kobayashi, and K. Arata, *J. Am. Chem. Soc.*, **101**, 6439 (1979).

3) H. Hattori, O. Takahashi, M. Takagi, and T. Tanabe, *J. Catal.*, **68**, 132 (1981).

4) Y. Ono, N. Kitajima, T. Nakajima, and T. Keii, "Proceedings of the 7th International Congress of Catalysis," ed by T. Seiyama and K. Tanabe, Kodansha Ltd., Tokyo (1980), p. 1006.

5) A. Krzywicki and M. Marczewski, *J. Chem. Soc., Faraday Trans. 1*, **76**, 1311 (1980).

6) H. Imamura and W. E. Wallace, *J. Catal.*, **64**, 238 (1980); H. Imamura, W. E. Wallace, and K. Soga, *ibid.*, **67**, 244 (1981); *Chem Lett.*, **1980**, 957.

7) E. H. Taylor, *Adv. Catal.*, **18**, 111 (1968).