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n-Pentane Isomerization with Catalysts Formed from Brominated Intermetallic Compounds

In earlier studies from this laboratory it has been shown that intermetallic compounds when oxidized with oxygen form materials that are very active synthesis gas conversion catalysts (*1–3*). In the present work these studies have been extended by studying the catalytic activity of systems formed when selected intermetallic compounds are oxidized with Br_2. The reaction studied was the isomerization of *n*-pentane to isopentane. Conversion of straight-chain hydrocarbons to branched-chain materials is of significance for octane number upgrading. It has been known for many years that Lewis acids combined with promoters such as hydrogen halide, alkyl halide, or water effectively catlayze isomerization reactions (*4, 5*). This and the earlier work on synthesis gas reactions suggested that the products formed by brominating appropriate intermetallic compounds might be catalytically interesting, particularly in the context indicated, i.e., isomerization reactions.

The intermetallic compounds used were $LaAl_2$, $CeAl_2$, $PrAl_2$, $ErAl_2$, SmAl, and $ThAl_2$. They were prepared by techniques that are standard in this laboratory—induction melting of the component metals in a water-cooled copper boat under an atmosphere of purified argon. *n*-Pentane obtained from Aldrich Chemical Company was distilled and stored on a molecular sieve. Bromine, which was an analytical-grade reagent obtained from Mallickrodt, was used without further purification. Methylene chloride as a solvent was reagent grade. Purification was accomplished by passing CH_2Cl_2 through a column of active alumina to remove dissolved HCl and then distilling in the presence of phosphorous pentoxide.

The reactions were conducted under a purified helium atmosphere to avoid the influence of water. The procedure used was as follows: Br_2 was admitted in a 50-ml flask with three necks, which contained finely ground intermetallics (1 mmol) suspended in Ch_2Cl_2 (8 ml). The mixture was vigorously stirred at room temperature. Reaction of the intermetallic compound with Br_2 readily occurred at room temperature to produce a suspended mixture, the nature of which was dependent upon the compounds employed. After disappearance of bromine's color in the solution, *n*-pentane (2 ml) was immediately injected into this mixture to initiate the reaction. The extent of the conversion was established by periodically taking an aliquot of the reacting solution and analyzing it by a Gow Mac gas chromatograph with a Durapak *n*-octane/Porasil C column.

A representative time course of the reaction over the $ThAl_2$ (1 mmol)–Br_2 (3 mmol) system is depicted in Fig. 1. The reaction readily progressed at 0°C. The only reaction product was isopentane at the initial stage of the conversion. During the reaction isobutane was found to be formed in a significant amount along with small amounts of C_6 hydrocarbon products. The results obtained for all of the systems stud-

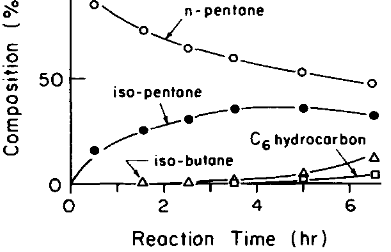

FIG. 1. Time course of the isomerization over the $ThAl_2$–Br_2 system. The reaction was performed at 0°C using $ThAl_2$ (1 mmol) and Br_2 (3 mmol).

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ied are summarized in Table 1. Since the selectivity of the products is considered to be very dependent upon the extent of the conversion owing to a subsequent secondary reaction such as cracking, the product distribution was recorded as the conversion after 0.5 hr. For most of the systems the selectivity for isopentane was more than 90%. However, it is to be noted that the selectivity decreased about up to one-half during the reaction. For the $ThAl_2$–Br_2 system the effect of Br_2 addition on the reaction activity and selectivity was examined, keeping other conditions constant. The results obtained are shown in Table 2. The activity was conveniently represented by the conversion after 0.5 hr. Increasing Br_2 addition tended to cause a rise in the activity, but conversely a drop in the selectivity for isopentane.

It is informative to note that neither intermetallics nor Br_2 alone exhibited any activity and that addition of 5 mmol of Br_2, giving rise to a maximal activity, corresponds to formation of $AlBr_3$–$ThBr_4$ based on a stoichiometric reaction. It has been reported that combined mixtures of aluminum chloride (*6–8*) or bromide (*9*) with metal salts, e.g., $CuCl_2$ or $MnSO_4$, are effective catalysts for the isomerization of *n*-pentane to isopentane. The present catalysts derived from halogenation of the intermetallic compound may closely resemble those just mentioned. However, it is presumed that using the intermetallics as a starting material involves the possibility of producing some special kind of solid, which is active as an isomerization catalyst, as opposed to a mere mixture of the component salts. Further studies are under way to establish the character of these catalysts.

TABLE 1

Activity of Intermetallics–Br_2 Systems[a]

Inter-metallics	Conversion[b] (%)	Product distribution[b] (%)			
		n-C_4	iso-C_4	iso-C_5	C_6
$LaAl_2$	6.0	—	10.0	90.0	—
$CeAl_2$	27.2	0.4	4.8	94.8	—
$PrAl_2$	8.9	—	14.7	85.3	—
$ErAl_2$	16.2	—	7.4	92.6	Tr
SmAl[c]	3.6	—	8.7	91.3	—
$ThAl_2$	16.7	—	3.0	97.0	—

[a] The reaction was carried out at 0°C in the presence of the mixture of the intermetallics (1 mmol) and Br_2 (3 mmol).

[b] The conversion and product distribution were evaluated after 0.5 hr.

[c] For this system SmAl (1 mmol) and Br_2 (1.5 mmol) were used.

TABLE 2

Effect of Various Br_2 Additions on Activity and Selectivity

$ThAl_2$–Br_2 system (mmol)	Activity (%)	Selectivity (%)
1–1	10	86.9
1–2	14.2	92.3
1–3	16.7	97.0
1–4	19.7	90.9
1–5	25.5	59.6

[a] The reaction was performed at 0°C over various $ThAl_2$–Br_2 systems.

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