

## Hydrocarbon Conversion Reactions Using Halogenated Intermetallic Systems

It is known (1) that many rare earth (or actinide) intermetallic compounds combined with 3d transition metals such as Mn, Fe, Co, and Ni reversibly absorb large amounts of hydrogen under mild conditions. Because of the excellent ability to activate hydrogen attempts have been made to apply these intermetallics as hydrogenation catalysts (2). Recently, it has been reported that the rare earth intermetallics modified with appropriate treatments yield effective catalysts for the synthesis gas conversion (3, 4) and hydrogenation reactions (5, 6). More recently, it has been found (7) that certain intermetallic compounds containing aluminum metal readily react with bromine to form active isomerization catalysts of *n*-pentane to isopentane. Skeletal isomerization of hydrocarbons is of significance for octane number upgrading. It is well known (8,10) that Lewis acid catalysts promoted with hydrogen halides, alkyl halides, or water effectively catalyze isomerization reactions.

The present study was undertaken to investigate catalytic behavior of the isomerization catalysts, which were prepared by the halogenation of rare earth (or Th) intermetallics involving elements of Group III of the Periodic Table.

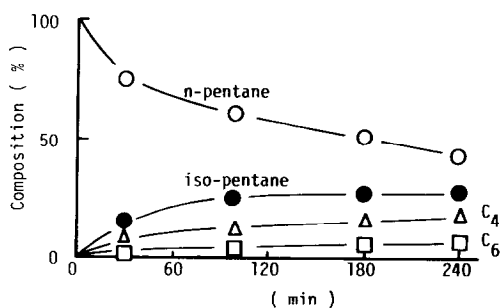
In this study the intermetallic compounds  $R_xM_y$  ( $R = \text{La, Ce, Pr, Er, and Th}; M = \text{Al, Ga, In, and Tl}$ ) were utilized. These compounds were prepared by induction melting of the metal components in a water-cooled copper boat under a purified argon atmosphere. To ensure homogeneity the compounds were remelted several times or, moreover, subjected to annealing treatments at a given temperature if required.

The desired structure of the intermetallics was confirmed by powder X-ray diffraction analysis. *n*-Pentane was thoroughly dehydrated by sodium wire and then distilled. Bromine and iodine, which were analytical-grade reagents commercially obtained from Mallinckrodt Inc., were used without further purification. Chlorine purchased from Matheson Gas Products was purified by bubbling through water and concentrated sulfuric acid before reacting with the intermetallic compounds. Reagent-grade methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) was purified by passing through a column of active alumina to remove dissolved HCl followed by distillation in the presence of phosphorous pentoxide.

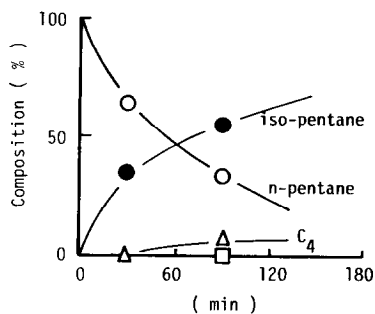
The reaction was studied in a 50-ml three-necked flask with stirring equipment. Each alloy sample (1 mmol) which had previously been powdered by a mortar and pestle was placed in the flask replaced with ultrahigh-purity helium. The prescribed  $\text{Br}_2$  or  $\text{I}_2$  (1– 6.5 mmol) was added to finely ground intermetallics suspended in a  $\text{CH}_2\text{Cl}_2$  solvent (8 ml) with stirring. The reactions of the alloys with halogens occurred readily at room temperature to produce binary halide catalysts. The chlorination of intermetallics was also smoothly achieved by bubbling purified chlorine gas through the reaction solution. After the disappearance of halogen's color in the solution, indicating that halogenation was complete, the reactor was held at reaction temperature and *n*-pentane (2 ml) was immediately injected into this mixture to initiate the reaction. The extent of the reaction 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 6 ft  $\times$   $\frac{1}{8}$  in.

The *n*-pentane conversion reaction was examined at 0 or 23°C using various intermetallic compound-halogen systems. The reaction took place without difficulty to form isopentane along with secondary reactions to some extent. Representative time courses of the reaction are illustrated in Figs. 1a and b. As shown in Fig. 1a, in the case of the ThAl<sub>2</sub>(1 mmol)-Br<sub>2</sub>(5 mmol) system, considerable amounts of C<sub>4</sub> and C<sub>6</sub> hydrocarbons were formed from the initial stage of the reaction, indicating the simultaneous occurrence of cracking or disproportionation reactions other than skeletal isomerization. (The C<sub>4</sub> hydrocarbon product was found to be entirely isobutane.) On the



(a)



(b)

FIG. 1. (a) Time course of conversion reaction using the ThAl<sub>2</sub>(1 mmol)-Br<sub>2</sub>(5 mmol) system. (b) Time course of conversion reaction using the ThAl<sub>2</sub>(1 mmol)-I<sub>2</sub>(5 mmol) system. Both conversion reactions of *n*-pentane (2 ml) were conducted at 0°C in a CH<sub>2</sub>Cl<sub>2</sub> solvent (8 ml).

TABLE I

Activity and Selectivity of Various Alloy-Halogen Systems

Alloy <sup>a</sup>	Catalyst system -Halogen(mmol)	Conversion (%)	Selectivity (%)
LaAl <sub>2</sub>	Cl <sub>2</sub>	5.2*	50*
LaAl <sub>2</sub>	Br <sub>2</sub> (4.5)	28.8*	73*
CeAl <sub>2</sub>	Cl <sub>2</sub>	15.0*	62*
CeAl <sub>2</sub>	Br <sub>2</sub> (5)	31.7*	58*
CeAl <sub>2</sub>	I <sub>2</sub> (5)	42.3*	96*
PrAl <sub>2</sub>	Cl <sub>2</sub>	8.3*	56*
PrAl <sub>2</sub>	Br <sub>2</sub> (4.5)	39.8*	96*
PrAl <sub>2</sub>	I <sub>2</sub> (4.5)	37.1*	97*
ErAl <sub>2</sub>	Cl <sub>2</sub>	25.2*	60*
ErAl <sub>2</sub>	Br <sub>2</sub> (4.5)	39.4*	61*
ErAl <sub>2</sub>	I <sub>2</sub> (4.5)	35.0*	93*
ThAl <sub>2</sub>	Br <sub>2</sub> (5)	25.5*	60*
ThAl <sub>2</sub>	I <sub>2</sub> (5)	39.1*	95*
PrGa <sub>2</sub>	Cl <sub>2</sub>	10.0**	72**
PrGa <sub>2</sub>	Br <sub>2</sub> (4.5)	6.0**	77**
ThGa <sub>2</sub>	Cl <sub>2</sub>	24.7***	60***
ThGa <sub>2</sub>	Br <sub>2</sub> (5)	46.0***	50***
CeIn <sub>3</sub>	Br <sub>2</sub> (6.5)	trace**	—
CeIn <sub>3</sub>	I <sub>2</sub> (6.5)	trace**	—
CeTl <sub>3</sub>	Br <sub>2</sub> (6.5)	—	—

Note. The conversion reaction of *n*-pentane (2 ml) was performed over the above catalysts in CH<sub>2</sub>Cl<sub>2</sub> (8 ml). (\*) Results obtained at 0°C after  $\frac{1}{2}$  hr. (\*\*, \*\*\*) Data measured at 23°C after 20 and 3 hr, respectively.

<sup>a</sup> The amount of alloy used was 1 mmol.

other hand, Fig. 1b for the ThAl<sub>2</sub>(1 mmol)-I<sub>2</sub>(5 mmol) system shows high selectivity for isopentane. Selectivity near 90% was observed up to over 80% *n*-pentane conversion. The isomerization rate of *n*-pentane to isopentane was found to be first order in the concentration of *n*-pentane. Temperature dependence of the first-order rate constant gave 12.4 kcal/mol for the apparent activation energy.

Date obtained for series of intermetallic compound-halogen systems are summarized in Table 1. Owing to the accompanying secondary reactions to some extent, the activity was conveniently expressed as the extent of *n*-pentane total conversion after  $\frac{1}{2}$  hr. The selectivity for iso-pentane was

also computed at the same reaction time. It should be noted that most binary halide catalysts were heterogeneous in the reaction solution.  $\text{ThAl}_3$  and  $\text{ErAl}_3$  systems listed later, however, produced homogeneous catalysts. It appears that the relationship between conversion activity and selectivity is intimately dependent upon combinations of the intermetallics with halogen species. The catalyst systems treated with iodine yielded higher selectivity than chlorinated or brominated catalysts in most cases. On the other hand, the activity increased in the order  $\text{Cl}_2 < \text{Br}_2 = \text{I}_2$ , which agrees with the previous finding (7, 8) that the reactivity sequence of aluminum halides for the isomerization of hydrocarbons is  $\text{AlCl}_3 < \text{AlBr}_3 < \text{AlI}_3$ . Among the elements of Group III of the Periodic Table in the precursor intermetallics aluminum showed a maximum activity. The result is also consistent with that found by Russell (11) in the methylcyclopentane-cyclohexane isomerization study using aluminum halides and gallium halides as catalysts, although the presence of cocatalysts should be taken into consideration.

TABLE 2

Effect of Halogen Addition on Reaction Behavior

Amount (mmol)		Conversion <sup>a</sup> (%)	Selectivity (%)
Alloy ( $\text{ErAl}_2$ )	Halogen ( $\text{Br}_2$ or $\text{I}_2$ )		
1	1	4.4(3.2) <sup>b</sup>	93(84)
1	2	10.3(9.8)	92(78)
1	3	16.2(15.7)	93(75)
1	4.5	39.4(35.0)	61(93)
( $\text{ThAl}_2$ )	( $\text{Br}_2$ or $\text{I}_2$ )		
1	1	10.0(4.6)	87(89)
1	2	14.2(12.6)	92(82)
1	3	16.7(21.0)	97(84)
1	4	19.7(21.7)	91(74)
1	5	25.5(39.1)	60(95)

Note. The conversion reaction of *n*-pentane(2 ml) was conducted at 0°C in  $\text{CH}_2\text{Cl}_2$ (8 ml).

<sup>a</sup> *n*-Pentane conversion measured after  $\frac{1}{2}$  hr.

<sup>b</sup> The values in parentheses represent the results on  $\text{I}_2$  addition.

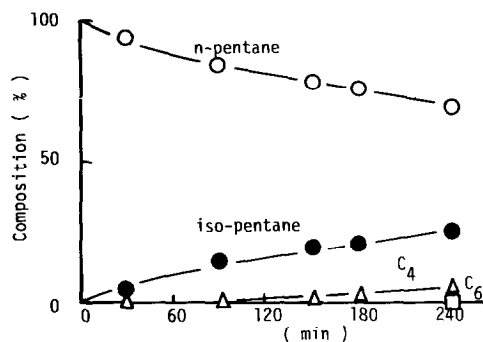


FIG. 2. Time course of conversion reaction using combined mixture of  $\text{ThI}_4$ (1 mmol) and  $\text{AlI}_3$ (2.1 mmol). The conversion reaction of *n*-pentane (2 ml) was carried out at 0°C in a  $\text{CH}_2\text{Cl}_2$  solvent (8 ml).

The effect of halogen addition on the reaction behavior is shown in Table 2. The activity increased with an increase in the extent of cocatalyst (halogen) regardless of the halogen species used. However, addition of halogen in large excess generally led to poor selectivity. To examine the question as to whether the binary halide catalyst prepared, for example, from the reaction of  $\text{ThAl}_2$ (1 mmol) with  $\text{I}_2$ (5 mmol) is similar to a mere 2:1 mixture of  $\text{AlI}_3$  and  $\text{ThI}_4$ , the *n*-pentane conversion reaction was carried out over the combined mixture of  $\text{AlI}_3$ (2.1 mmol) and  $\text{ThI}_4$ (1 mmol), keeping other conditions constant. Reaearch-grade  $\text{ThI}_4$  (99.9%) obtained from Cerac Inc., was outgassed around 220°C for 4 hr.  $\text{AlI}_3$ , purchased from Ventron, was purified by sublimation techniques at 200°C under reduced pressure. After these compounds were sufficiently mixed using a mortar and pestle without exposure to air, the resultant mixture was used as catalyst. The reaction was undertaken at 0°C in a  $\text{CH}_2\text{Cl}_2$  solvent (8 ml). The results obtained are depicted in Fig. 2 which clearly indicates that the activity is much lower compared to that of the  $\text{ThAl}_2$ - $\text{I}_2$  system. Accordingly, the present results strongly suggest that the intermetallic compounds form some special kinds of complexes by halogenation, which clearly differ from a mere mixture of aluminum halides and rare earth (or Th) halides.

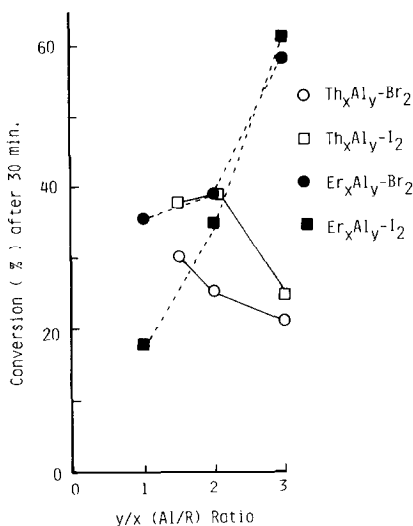


FIG. 3. Effect of component ratio ( $y/x$ ) in  $R_xAl_y$  on activity. The conversion reaction of  $n$ -pentane (2 ml) was carried out at  $0^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$  (8 ml) with the following catalyst systems:  $\text{Th}_2\text{Al}_3$  (0.5 mmol)-halogen (4.25 mmol),  $\text{ThAl}_2$  (1 mmol)-halogen (5 mmol),  $\text{ThAl}_3$  (1 mmol)-halogen (6.5 mmol),  $\text{ErAl}$  (1 mmol)-halogen (3 mmol),  $\text{ErAl}_2$  (1 mmol)-halogen (4.5 mmol), and  $\text{ErAl}_3$  (1 mmol)-halogen (6 mmol). Activity is expressed as the  $n$ -pentane conversion measured after  $\frac{1}{2}$  hr.

The influence of the component ratio in  $R_xAl_y$  on the present reaction was further studied (Fig. 3). The number on the abscissa represents the Al/R molar ratio in the starting material. For the  $\text{Er}_x\text{Al}_y\text{-Br}_2$  (or  $\text{I}_2$ ) systems, increasing the Al/R molar ratio brought about a rise in the activity, but  $\text{Th}_x\text{Al}_y$  systems showed the reverse tendency. The different behavior of  $\text{Er}_x\text{Al}_y$  and  $\text{Th}_x\text{Al}_y$  systems appears to be the origin in important physicochemical properties, which are significantly responsible for the resulting materials after the halogenation treatment.

The isolation of such special complexes is now in progress using the homogeneous  $\text{Er}_x\text{Al}_y\text{-I}_2$  systems, and the precise results will be reported in another paper.

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