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Olefin Hydrogenation Using Electron Donor–Acceptor Complexes Derived from Rare Earth Intermetallic Compound $SmMg_3$

It has been shown that alkali metals react readily with condensed-ring compounds to form complexes (*1–3*). For example, addition of sodium to anthracene produced the complex in 1 : 1 or 2 : 1 component ratio. The products obtained were characterized as electron donor–acceptor (EDA) complexes, in which charge transfer occurred, capable of hydrogen activation. Recently, formation of EDA complexes has been found from the reaction of rare earth intermetallics with the condensed-ring compounds (*4*). We have presented the first EDA study on the rare earth intermetallic compound. In an earlier publication, we reported on hydrogen uptake by the material formed when $SmMg_3$ was treated with anthracene. It was found that the product absorbed significant amounts of hydrogen at room temperature under atmospheric pressure, but there was no indication of hydrogen absorption by $SmMg_3$ alone under similar conditions. The source of the exceptional ability for hydrogen uptake is presumed to be due to complexation of $SmMg_3$ with anthracene. The results strongly imply that the treatment with the condensed-ring materials provides a novel way of promoting the ability of hydrogen uptake by rare earth intermetallic compounds. In the work reported here there were some important measurements made. Specifically, the present complex was characterized by spectrophotometer to establish the electronic nature. Moreover, we studied behavior of the complex as a hydrogenation catalyst to extend the earlier study.

The intermetallic compound $SmMg_3$ employed was prepared by melting together stoichiometric amounts of high-purity constituent elements in a water-cooled copper boat using induction heating techniques, a continuous flow of purified argon being maintained over the sample during melting (*5*). To confirm formation of the desired structure the sample was subjected to X-ray powder diffraction analysis.

Preparation of the complexes from $SmMg_3$ and the condensed-ring compounds was conducted as follows: The sample $SmMg_3$, which had been powdered with mortar and pestle, was placed in a 50-ml Schlenk reactor flushed thoroughly with dry nitrogen. The reaction of $SmMg_3$ with the aromatic compounds was carried out in the presence of trace amounts of C_2H_5Br in an anhydrous tetrahydrofuran (THF) solvent (10 cm^3) at room temperature and the products were dried *in vacuo* to provide the complexes as green powder. Ethylene hydrogenation was studied in a gas-recirculation reactor using 0.5 g of the catalyst thus

TABLE 1

Activity of Various Catalysts Derived from $SmMg_3$

Catalyst system	Activity[a] (mmol-C_2H_6/h · g-cat.)
$SmMg_3$–naphthalene (1 : 2)[b]	9.0×10^{-2}
$SmMg_3$–anthracene (1 : 1)[b]	2.1×10^{-2}
$SmMg_3$–anthracene (1 : 2)[b]	4.2×10^{-2}
$SmMg_3$–phenanthrene (1 : 1)[b]	5.2×10^{-2}
$SmMg_3$–chrysene (1 : 1)[b]	5.5×10^{-2}
$SmMg_3$–perylene (1 : 1)[b]	1.5×10^{-3}
$SmMg_3$	—[c]

[a] Initial rate of C_2H_6 formation.

[b] The ratio in parentheses represents the mixture ratio in which $SmMg_3$ reacted with the aromatic compound.

[c] The activity at 18°C was zero within detection limits.

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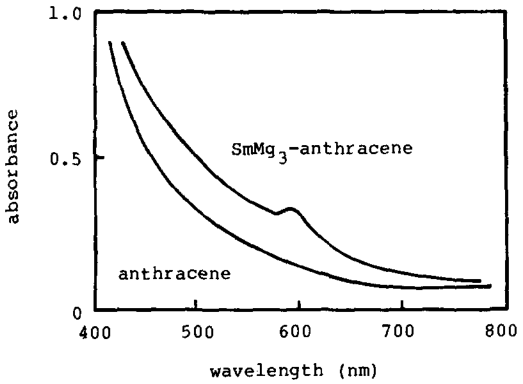

FIG. 1. Electronic spectra of $SmMg_3$–anthracene and anthracene in THF.

prepared. The extent of conversion was established by sampling the reactant gas from the reaction system and analyzing it by gas chromatography. Electronic spectra were recorded on a Shimadzu UV-200 spectrophotometer using as a source a W or D_2 lamp. The spectrophotometer was operated in double beam with a slitwidth of 1 nm.

The hydrogenation reactions were conducted by introducing a mixture of hydrogen (100 mm Hg) and ethylene (50 mm Hg). The reaction occurred readily at 18°C to form ethane and was first order in hydrogen pressure. The activities of the catalysts are indicated in Table 1. Results for $SmMg_3$ alone are included for comparison. $SmMg_3$ gave rise to the capability of catalyzing the present reaction upon complexing. In the earlier studies it was observed that the complexation led to activation of hydrogen (*4*). The activity varied considerably among the complexing systems with change in the partner compounds. It is evident that the catalyst derived from $SmMg_3$ and naphthalene exhibited the exceptional activity. The nature of the aromatic compound with which $SmMg_3$ is combined is important in determination of the catalytic activity. We believe that the difference is a consequence of variation of electronic interaction between $SmMg_3$ and the condensed-ring material. For the $SmMg_3$–anthracene system isolated as a dark-green complex, for example, attempts were made to perform electronic spectrum measurements. The spectrum is depicted in Fig. 1 together with that of anthracene for comparison. Anthracene has three peaks at 220, 251, and 357 nm with the fine structures. After complexing, however, visible absorption study showed that an additional EDA spectrum due to interaction appeared at 598 nm.

The precise explanation for the relationship between activity and electronic influence is unknown at the present time. Further study is under way to understand the properties of the complexes based on rare earth intermetallic compounds.

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