Kinetics and Catalysis, Vol. 44, No. 4, 2003, pp. 552–554. Translated from Kinetika i Kataliz, Vol. 44, No. 4, 2003, pp. 604–606.
Original Russian Text Copyright © 2003 by Tyurina, Smirnov, Potapov.

HIGHLY ORGANIZED CATALYTIC SYSTEMS

Catalytic Self-Hydrogenation of Anthracene in the Presence of a Magnesium–Anthracene Adduct

L. A. Tyurina, V. V. Smirnov, and D. A. Potapov
Faculty of Chemistry, Moscow State University, Moscow, 119899 Russia

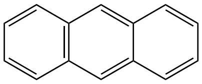
Received September 10, 2002

Abstract—The catalytic properties of cluster magnesium derivatives were studied using the self-hydrogenation reaction of unsaturated compounds as an example. In the presence of a cluster magnesium–anthracene adduct at 150–298 K, the self-hydrogenation of anthracene occurred with yields of up to 40 molecules per atom of magnesium.

INTRODUCTION

The self-hydrogenation of unsaturated compounds is a reaction typical of catalysis with the derivatives of transition metals, in particular, Group VIII metals [1]. The oxidative addition of an organic molecule to a metal atom in a low oxidation state with the formation of hydride intermediates plays a key role in this process. Until recently, processes of this kind were unknown for nontransition metals. In recent years, we found that cluster magnesium derivatives RMg_nX (R is an organic radical, and X is a halogen or hydrogen), which were prepared by metal vapor synthesis (MVS) [2, 3], exhibited catalytic properties in the reactions of halogen exchange [4] and allyl isomerization of olefins [5]; these properties are unusual for nontransition metals.

The appearance of properties that are typical of transition metals in the cluster derivatives of nontransition metals is of considerable interest; in our opinion, it deserves thorough investigation. This study was based on the hypothesis that reactions that are similar to the self-hydrogenation of olefins can be performed not only on transition metals but also in the presence of the cluster derivatives of nontransition metals, in particular, magnesium. The aim of this work was to test this hypothesis using as an example the self-hydrogenation of anthracene



I

in the presence of recently discovered [6] organomagnesium cluster adducts, which were prepared using MVS. These adducts contain tetrameric Mg_4 clusters inserted into one or two C–H bonds at the 9,10-positions of the starting hydrocarbon. The cluster adducts are stable at both low and room temperatures. The presence of RMg_4H groups, which are structurally similar to intermediates in the self-hydrogenation of unsaturated compounds on Group VIII metals (R–M–H, where M is Pd or Ni [1]), and our previous data on catalysis by organomagnesium cluster derivatives [4, 5] allowed us to assume that catalytic self-hydrogenation can occur in this system.

EXPERIMENTAL

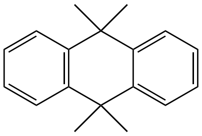
Magnesium (turnings; 99.5%; Fluka) was used in the syntheses without additional treatment. Anthracene (for scintillation; 99%) was purified by vacuum sublimation before the syntheses.

The samples containing magnesium–anthracene cluster adducts were prepared by the solid-phase reaction of magnesium with anthracene in cocondensed reactant vapors deposited onto the surface of a special evacuated reactor cooled with liquid nitrogen. The design of reactors for the cocondensation of metals with organic reactants was described in detail elsewhere [7, 8]. Magnesium was resistively evaporated at ~700 K. The temperature of anthracene evaporation was 400–450 K, and it was chosen to provide an anthracene-to-magnesium ratio in the range 50–500 : 1 during the cocondensation of the reactants. The cocondensation surface area was 200 cm^2, and the cocondensation time was 1–2 h. Upon completion of the cocondensation, the solid condensate film was heated to 150–298 K in a vacuum and thermostated at a given temperature within the above range for 0.2–24 h. Thereafter, the mixture was hydrolyzed at 150 or 298 K by the condensation of water vapor from a gas phase onto the mixture; water vapor was taken in excess with respect to magnesium. Organic products were analyzed by chromatography–mass spectrometry with the use of a Finnigan MAT-212 instrument and a Varian 3740 chromatograph. The reproducibility of analysis was ±3% rel. %. The scatter of experimental product yields (10–15 rel. %) was due to reactant-beam geometry fluctuations during condensation in the course of cryosynthesis. The magnesium content was determined by chelatometric titration with Eriochrome Black T.

RESULTS AND DISCUSSION

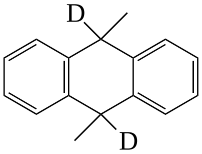
The cocondensates of Mg with **I** prepared by MVS at 80 K were dark brown. The films were decolorized in the range 100–130 K; this fact is indicative of the formation of magnesium–anthracene adducts. The formation of these adducts under the specified conditions and the presence of magnesium clusters and Mg–H bonds in the adducts were first found by Barkovskii *et al.* [9]. The chemical formula $C_{14}H_{10}Mg_4$ of this adduct was established by Tyurina *et al.* [6] with the use of MALDI–TOF mass spectrometry.

Simultaneously with adduct formation, the self-hydrogenation of **I** occurred in the sample to result in dihydroanthracene



II

If hydrolysis was performed immediately after heating the condensate to 150 K, the yield of **II** was ~50% on a magnesium basis regardless of the initial ratio between the components (see Table 1). Undoubtedly, the formation of **II** took place by the disproportionation of **I** with the participation of cluster adducts. The only alternative might be the formation of this compound in the course of hydrolysis of another magnesium derivative of anthracene, anthracenylmagnesium $C_{14}H_{10}Mg$, which is identical to a well-known adduct formed from magnesium and anthracene in a THF solution [10]. These two reaction paths can be distinguished using data on deuterolysis. It is well known that the deuterolysis of anthracenylmagnesium gives dideuteriodihydroanthracene



III

However, along with small amounts of **III**, the formation of **II** and monodeuteriodihydroanthracene was detected in our case (Table 2). In this case, the yield of **II** was 50% or higher, whereas the yield of **III** at 150 K was no higher than 2% on a magnesium basis. This result demonstrates that hydrogen released from water on the hydrolysis of the cluster nucleus of the magnesium–anthracene adduct did not participate in the formation of hydrogenated anthracenes. Thus, the process consists in the disproportionation of **I** with the formation of **II** and an unidentified polymer substance, which is likely the product of condensation of dehydrogenated anthracene molecules. This substance remained as a residue, which is insoluble in organic solvents, after the removal of magnesium by washing with hydrochloric acid and the removal of anthracene and its hydrogenated derivatives by dissolving in hot toluene.

Table 1. Yields of dihydroanthracene (**II**/Mg, molecule/atom Mg) in the hydrolysis of anthracene–Mg mixtures of different composition (**I**/Mg, molecule/atom Mg) heated to 150 K

[**I**]/Mg	53	85	136	250
[**II**]/Mg	0.50	0.43	0.46	0.54

Note: The cocondensation time was 1.5 h; the heating time was 15 min; the hydrolysis was performed immediately after heating at 150 K.

Table 2. Yields of dideuteriodihydroanthracene **III** and dihydroanthracene (**II**) (molecule/atom Mg) in the deuterolysis of anthracene mixtures with the magnesium–anthracene adduct prepared at different anthracene/Mg ratios ([**I**]/Mg, molecule/atom Mg**)**

[**I**]/Mg	58	93	146	215
[**III**]/Mg	0.018	0.020	0.016	0.015
[**II**]/Mg	0.515	0.502	0.514	0.586

Note: The deuterolysis temperature was 150 K; the other experimental conditions are specified in Table 1.

Table 3. Yields of dideuteriodihydroanthracene **III** and dihydroanthracene (**II**) (molecule/atom Mg) in the deuterolysis of anthracene mixtures with the magnesium–anthracene adduct prepared at different anthracene/Mg ratios (**I**/Mg, molecule/atom Mg)

[**I**]/Mg	47	79	112	194
[**III**]/Mg	0.02	0.02	0.02	0.02
[**II**]/Mg	21.60	35.40	43.70	38.80

Note: The condensation conditions are specified in Table 1; the deuterolysis temperature was 298 K; the exposure time at this temperature was 24 h.

The most interesting results were obtained in the analysis of samples subjected to hydrolysis after keeping at room temperature (Tables 3, 4). In this case, as can be seen in Tables 3 and 4, the yield of **II** was higher than the initial amount of magnesium by a factor of tens; that is, the process is undoubtedly catalytic. Note that the yield of **III** (Table 3) in the deuterolysis remained low.

Thus, the catalytic self-hydrogenation of anthracene really occurred in the presence of organomagnesium cluster adducts. The yields on a magnesium basis were as high as 40 molecules per atom; with consideration for the fact that magnesium occurred as Mg_4 aggregates in the system, ~160 product molecules per cluster were really formed. These data suggest an analogy between the catalytic properties of cluster magnesium derivatives and transition metal compounds. It is likely that

Table 4. Yields of dihydroanthracene (**II**/Mg) determined after the hydrolysis of mixtures with different anthracene/Mg ratios (**I**/Mg) at 298 K (molecule/atom Mg)

[**I**]/Mg	53	85	136	250
[**II**]/Mg	17.4	38.4	46.5	42.1

the cluster magnesium derivatives, similarly to the hydride derivatives of Group VIII metals, are capable of β-cleavage with the formation of unstable dehydrogenated C_{14} hydrocarbons and active cluster hydrides, which can hydrogenate anthracene. The naked magnesium clusters formed at this step inserted into the C–H bonds of anthracene, which was present in excess, with the regeneration of the initial cluster adduct.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (grant nos. 01-03-32784 and 03-03-32314).

REFERENCES

1. Gorelik, V.M., Kop’eva, I.A., Oreshkin, P.A., and Dolgoplosk, B.A., *Kinet. Katal.*, 1992, vol. 33, no. 1, p. 121.
2. Tjurina, L.A., Smirnov, V.V., and Beletskaya, I.P., *Grignard Reagents. New Developments*, New York: Wiley, 2000.
3. Tjurina, L.A., Smirnov, V.V., Barkovskii, G.B., Nikolaev, E.N., Esipov, S.E., and Beletskaya, I.P., *Organometallics*, 2001, vol. 20, p. 2449.
4. Tjurina, L.A., Smirnov, V.V., and Beletskaya, I.P., *J. Mol. Catal.*, 2002, nos. 182–183, p. 395.
5. Smirnov, V.V., Beletskaya, I.P., Tyurina, L.A., Barkovskii, G.B., Kashin, A.N., and Tarkhanova, I.G., *Kinet. Katal.*, 1998, vol. 39, no. 6, p. 885.
6. Tyurina, L.A., Smirnov, V.V., Esipov, S.E., and Beletskaya, I.P., *Mendeleev Commun.*, 2002, vol. 12, no. 3, p. 108.
7. Sergeev, G.B., Smirnov, V.V., Zagorskaya, O.V., Zagorskii, V.V., and Popov, A.V., *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1982, vol. 23, p. 232.
8. Sergeev, G.B., Smirnov, V.V., and Zagorsky, V.V., *J. Organomet. Chem.*, 1980, vol. 201, p. 9.
9. Barkovskii, G.B., Tyurina, L.A., and Smirnov, V.V., *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1993, vol. 34, p. 56.
10. Bogdanovic, B., Janke, N., Kinzelmann, H.-G., Seevogel, K., and Treber, J., *Chem. Ber.*, 1990, vol. 123, pp. 1517–1528.