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Catalytic isomerization of allylbenzene on organomagnesium clusters

D. A. Potapov, L. A. Tjurina, and V. V. Smirnov★

Department of Chemistry, M. V. Lomonosov Moscow State University,
1 Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (095) 932 8846. E-mail: smirnov@kinet.chem.msu.ru, tyurina@kinet.chem.msu.ru

Catalytic isomerization of allylbenzene to form *trans*-β-methylstyrene quantitatively occurs on the magnesium—anthracene cluster adduct under mild conditions. A low-stability organomagnesium compound, presumably of the cluster nature and active in catalytic allylbenzene isomerization, is formed by cocondensation of magnesium and allylbenzene vapors at the liquid nitrogen temperature. The products of low-temperature solid-phase reactions of magnesium with hydrocarbons containing aromatic rings exhibit high catalytic activity in the allyl isomerization of allylbenzene.

Key words: catalysis, isomerization, allylbenzene, magnesium, metal vapor synthesis, magnesium—anthracene adduct.

Magnesium compounds exhibit no catalytic activity in hydrocarbon transformations under conventional conditions, although some data indicate the activity of magnesium-containing products of metal vapor synthesis (MVS) in hydrocarbon conversion. For instance, the study of the magnesium cocondensates with propylene[1,2] revealed deuterio-hydrogen exchange. On heating the magnesium cocondensates with hexene, anthracene, indene, and 1-methylindene the isomerization of the starting olefins and products of their autohydrogenation occurs.[3,4] In many cases, the product : magnesium ratio is higher than unity, indicating the catalytic character of the processes. The catalytic isomerization and hydrogenation of unsaturated hydrocarbons are characteristic of strong acids or systems based on transition metals. It was assumed[4,5] that the catalytic activity of samples containing only magnesium and hydrocarbon is caused by the formation of active magnesium clusters.

It has previously[6—8] been shown that the Grignard reagent cluster containing the Mg_4 core can be formed in magnesium—halohydrocarbon systems at low temperatures. The quantum-chemical calculations[9,10] show that Mg_4 is the most stable of the small magnesium clusters. It has recently been shown that cluster compounds are also formed by the reactions of magnesium with some hydrocarbons. For instance, derivatives containing the Mg_4 cluster appear in the magnesium—anthracene system. Their formation was proved by MALDI TOF-MS mass spectrometry.[11]

All these data agree with our previous[4,5] supposition that the catalytic activity of the MVS products involving magnesium is caused by the presence of magnesium clusters with unsaturated coordination sites. At the same time, catalytic conversion of hydrocarbons in the presence of preliminarily prepared individual organomagnesium cluster derivatives has not been proved reliably to date.

The purpose of the present work is to carry out the catalytic isomerization of olefins (using allylbenzene as an example) in the presence of the preliminarily prepared organomagnesium cluster adduct and to reveal conditions for the reaction to proceed quantitatively.

Experimental

Cocondensates of magnesium with organic compounds were obtained by the simultaneous precipitation of magnesium and organic reactant vapors on a vacuum-activated reactor surface cooled from outside with liquid nitrogen. Reactors of two types were used: "immerse" (*A*) and "spectral" (*B*). In reactor *A*, condensation is conducted on the internal surface of the vacuum reactor cooled from outside with liquid nitrogen. Reactor *B* is a glass vacuum vessel applied for IR spectroscopic studies of the cocondensates. The vessel has a potassium bromide window, and a polished copper unit cooled with liquid nitrogen is placed into the reactor. Reagents are condensed on this unit. When IR spectra are recorded, a beam from a spectrometer is directed by a system of mirrors through the KBr window and a condensate film onto the copper unit, reflected, again passed through the KBr window, and directed to the spectrometer detector.[12] Cocondensation was carried out under a pressure of $\sim 10^{-4}$ Torr inside the reactors. Magnesium was evaporated from a quartz evaporator at 400—450 °C. The evaporation temperatures of anthracene (AN) and allylbenzene (AB) were selected to ensure the AN/Mg ratio of 50—200 and AB/Mg ratio of 10—110 during condensation. Reagents Mg, AN, and AB were condensed with rates of $(1.6-4.0) \cdot 10^{-5}$, $(0.9-8.5) \cdot 10^{-3}$, and $(0.1-3.8) \cdot 10^{-3}$ mol h^{-1}, respectively. The condensation duration in reactors *A* and *B* was 0.5—1.5 h and 10—30 min, respectively.

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When cocondensation of Mg and AN vapor was completed, reactor *A* was warmed to room temperature to form a magnesium—anthracene adduct. The moment of reaction cessation was determined from the time necessary for the complete decoloration of the condensate.[11] After the end of the reaction, a certain amount of allylbenzene was introduced into the condensate. The liquid phase was stored for 0.5—2 h, recondensed into an ampule, and analyzed by GC-MS and GLC.

IR spectra were recorded with an Infralyum FT-801 spectrometer (Lyumeks-Sibir´). GC-MS spectra were obtained on a Finnigan MAT-212 spectrometer. A Kristall Lyuks 4000 instrument was used for GLC.

The cocondensation of Mg and AB vapors was carried out in the reactors of both types. When reactor *A* was used, after cocondensation to 80 K, the reactor was heated to a specified temperature within 200—298 K, and this temperature was maintained constant for 5—100 min. To stop the reaction, excess (over magnesium) water amount was introduced into the system, the reactor was warmed to room temperature, and the liquid phase was recondensed into an ampule and analyzed by GC-MS and GLC. When Mg and AB vapors were condensed in reactor *B*, the IR spectra of the cocondensate film were recorded at specified temperatures in an interval of 80—160 K. Special testing experiments showed that olefins are not transformed in the absence of Mg and in the presence of the preliminarily obtained film of "bulk" metal.

The Mg content in the obtained samples was analyzed by complexonometric titration with EDTA in the presence of the indicator Eriochrome black T.

Results and Discussion

The Mg—AN adduct is stable *in vacuo* at room temperature.[11] This adduct catalyzes the transformation of AB at room temperature, and the complete conversion occurs within several minutes. The main product is the most thermodynamically stable AB isomer *trans*-β-methylstyrene; in addition, two by-products, *viz.*, *cis*-β-methylstyrene and *n*-propylbenzene, are formed in small quantities (0.1—3.0%). The latter is the product of autohydrogenation of the starting olefin. Nonvolatile products of olefin condensation, which are formed, most likely, in parallel, remain in the precipitate along with the metal when organic compounds are evaporated.

Dihydroanthracene is formed along with the allylbenzene conversion in the catalytic autohydrogenation of excess anthracene on the adduct.[4] The yields of the products at different ratios of AB, AN, and Mg—AN adduct are presented in Table 1. The yield of *trans*-β-methylstyrene is controlled only by excess AB introduced into the reaction and, most likely, can be much higher than that presented in Table 1. Since the reaction ceases within 2—3 min, a very high catalytic activity of the Mg—AN adduct in isomerization under mild conditions can be implied. The activity in autohydrogenation is much lower, and the complete anthracene conversion is not achieved. Note that the yield of 9,10-dihydroanthracene calculated for magnesium increases with an increase in the AN/Mg ratio.

It was of interest to find out whether isomerization can occur directly in the cocondensate of Mg and AB. Available published data suggest that the cocondensation of magnesium with substituted benzenes produces unstable cluster adducts similar in nature to the anthracene adducts.[13] These adducts are also active, most likely, in isomerization.

The cocondensation of the magnesium and AB vapors at 80 K produces a brown film. The analysis of the liquid phase obtained after melting of the film shows that it contains 89—95% *trans*-β-methylstyrene and small amounts (2—5%) of *n*-propylbenzene and *cis*-β-methylstyrene.

Thus, the complete conversion of AB to thermodynamically more stable isomers and autohydrogenation products occurs in the Mg—AB system. It can be assumed that, as in the case of the Mg—AN adduct, the catalysts of this reaction are the magnesium cluster derivatives formed by the reaction of small magnesium clusters with AB.

Table 1. Composition of the reaction products of allylbenzene (AB) with the preliminarily prepared magnesium—anthracene adduct (MAA) at 300 K

AB : AN* : Mg	AB : AN : MAA**	Conversion (%)		Yield/mol (mol Mg)$^{-1}$ (in parentheses, mol (mol MAA)$^{-1}$)		
		AB	AN	*trans*-β-Methylstyrene	*cis*-β-Methylstyrene***	9,10-Dihydroanthracene
17.2 : 95 : 1	68 : 379 : 1	100	17	17 (68)	0.2 (0.8)	16 (64)
46.3 : 70 : 1	184 : 279 : 1	100	31.5	45.8 (183)	0.5 (2)	22 (88)
145.7 : 50 : 1	584 : 199 : 1	100	54	143.3 (580)	2.4 (9.6)	27 (108)
317.5 : 200 : 1	1272 : 799 : 1	100	16	315.8 (1263)	1.7 (6.8)	32 (128)
483 : 120 : 1	1932 : 479 : 1	100	32	480 (1920)	3 (12)	39 (156)

* Anthracene.

** Calculated from the empirical formula of MAA $C_{14}H_{10}Mg_4$ (see Ref. 4).

*** Along with *n*-propylbenzene.

The Mg—AB system was studied by IR spectroscopy at 80—160 K. The spectrum of the condensate at 80—120 K is almost identical to the spectrum of AB. No new distinct bands that could be ascribed to the organomagnesium compound were observed. This is probably related to the fact that the adduct is formed in the presence of excess AB. The strong bands in the IR spectra of AB prevent recording the spectra of the adduct. At 120 K, bands characteristic of *trans*-β-methylstyrene appear in the IR spectra at 2733, 1490—1480, and 1284 cm^{-1} *i.e.*, isomerization starts already at this temperature long before melting of the solid sample.

The stepwise curve describing the kinetics of β-methylstyrene accumulation is observed in the temperature range from 150 to 160 K. The typical kinetic curve is presented in Fig. 1. It is seen that the AB conversion is ~0.5% within the 7-min reaction in the Mg—AB mixture at 120 K. The subsequent warming of the sample to 150 K increases the conversion to 3.0—3.8% within 2—3 min. The further storage of the reaction mixture does not increase the yield of the product. A similar time dependence of the product yield at 150—160 K was obtained in all experiments. Therefore, this reaction proceeds in the stepwise kinetic regime typical of solid-phase processes. Unfortunately, the cocondensate films become nontransparent on further warming to temperatures above 160 K, which prevents recording the IR spectra. This did not allow us to obtain a set of several "steps" in the kinetic curve and determine the activity distribution of reaction sites of the solid-phase process. However, there remains nearly no doubt about the stepwise character of catalytic isomerization in the solid phase. The reason for this behavior can lie in the environmental and structural differences between intermediate compounds (precursors of the reaction products) stabilized in the solid matrix.[14] Isomerization is accompanied by a change in the geometry of molecules and, therefore, requires a certain rotational (and, perhaps, some translational) mobility of molecules. As the temperature increases, the mobility of some AB molecules increases and their reactivity enhances. At the same time, species, which exist in less favorable configurations or are more rigidly fixed by surrounding molecules, do not react.[12]

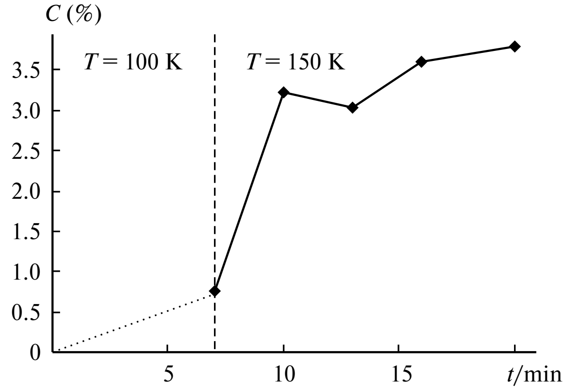

Fig. 1. Conversion of allylbenzene (*C*) in the cocondensate with magnesium *vs*. reaction duration. Ratio allylbenzene : magnesium = 21.5 : 1.

The studies at temperatures higher than 160 K were carried out in an immersion-type reactor (Table 2). The reaction during allylbenzene matrix melting (at 230—235 K) occurs with quantitative yield. Under these conditions, as in the case of the process in the presence of the magnesium—anthracene adduct, the yield calculated for magnesium is determined only by excess AB. The addition of AB to the cocondensate warmed above 240 K when its melting was completed provides no additional quantities of *trans*-β-methylstyrene. This indicates the decay of a catalytically active compound. A reason for the decay is, most likely, the aggregation of magnesium clusters to a compact metal. The formation of organomagnesium compounds unstable in solution at room tem-

Table 2. Conversion of allylbenzene (AB) and the yield of *trans*-β-methylstyrene for the Mg—AB systems

Reaction temperature/K	Conversion of allylbenzene (%)	Allylbenzene/Mg ratio	Yield of *trans*-β-methylstyrene /mol (mol Mg)$^{-1}$
80	0	25, 52, 110	0
120	<1	47	<0.1
130	1.5	34	0.5
150	3.8	21.5	0.8
210	13	52	6.8
220	15	58.5	8.9
230—235	100	11	9.4
		54	52.2
		81	78.4
		109	103.2
230—235*	0	—	0

* Magnesium is absent from the condensate film.

perature has previously been observed for the magnesium cocondensates with alkylbenzenes.[13] It is most likely that catalytically active organomagnesium clusters are formed by the reactions of magnesium with all derivatives containing aromatic rings. However, unlike the magnesium—anthracene cluster adduct,[11] the magnesium adducts with alkylbenzenes and AB are less stable and decay when the matrix melts. Nevertheless, due to their high catalytic activity, they induce the complete conversion of AB, which is present in the system in excess, even within the short lifetime under the conditions of high mobility of the reactants.

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