Conversions of hydrocarbons treated with neodymium metal under the conditions of mechanochemical activation at room temperature

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The conversions of cyclohexene and 1,3- and 1,4-cyclohexadienes treated with neodymium metal under the conditions of mechanochemical activation at 20 °C have been studied. A complicated cycle of conversions, including isomerization, disproportionation, and polymerization, occurs under the reaction conditions. A mechanism for the conversion of the hydrocarbons involving organometallic intermediates is proposed.

Key words: lanthanides, neodymium, hydrocarbons, cyclohexene, cyclohexadienes; mechanochemical activation, conversion.

At present a great number of works have been published on the conversion of hydrocarbons at low temperatures involving either isolated atoms or ions of transition metals (see, for example, Ref. 1). Such reactions proceed *via* oxidative addition of hydrocarbons to a metal at C—H or C—C bonds followed by conversions of organometallic intermediates.[2,3] Active centers that are close in their reactivity to isolated metal atoms can appear after mechanical deformation of metal. Specifically, nickel carbonyl was successfully synthesized from the metal and carbon oxide under mild conditions using mechanochemical activation.[4] Studies of the conversions of various compounds with metallic chromium and nickel in a ball-mill made it possible to conclude that polymer products are formed from benzene and toluene in 0.014 and 0.094 % yields, respectively, after 384 h under continuous mechanical treatment;[5] the polymer products were similar to polystyrene according to their IR spectra. Earlier it was shown that in the case of mechanochemical activation of neodymium and praseodymium in benzene and toluene, cleavage of the aromatic ring occurs to form carbene active centers resulting in polyconjugated linear polymers, and cleavage of C—H and C—C bonds to give organometallic intermediates.[6] In this work we present the results of studying conversions of cyclohexene and 1,3- and 1,4-cyclohexadienes treated with neodymium metal under the conditions of mechanochemical activation at 20 °C.

Experimental

Starting hydrocarbons of commercially pure or reagent-grade were dried over calcined aluminum oxide, allowed to stand with neophyl- or oligodienyl lithium, and recondensated *in vacuo*. Neodymium containing less than 0.3 % impurities of other lanthanides was used in the form of filings (particle size 0.1—0.5 mm). The reactions of the hydrocarbons with metals were carried out at 20 °C under conditions of mechanochemical activation in a powered vibrator mill (frequency 50 Hz, amplitude 4 mm) fitted with a temperature-controlled stainless steel working chamber with a volume of 105 mL. A weight of metal filings (1—2 g) was placed in the reaction chamber filled one/third full with steel balls 3 mm in diameter under argon dried and purified from oxygen; a vacuum was applied to the chamber for 2 h, the chamber was filled with argon, and a vacuum applied again. The hydrocarbon to be tested was placed in the chamber, hexane was added if necessary,* and the chamber was then filled with argon and placed in the vibrator mill. Prior to mechanical action, the metal filings collected at the bottom of the vessel within a fraction of second after they had been stirred up in the hydrocarbon. After completion of the mechanical treatment the reaction mixture was a dark colored (almost black) suspension, that took tens of hours to separate completely. Samples for GLC-analysis were taken by a syringe directly from the working chamber of the mill using a special self-sealing rubber membrane prior to mechanical action and just after its completion. In some experiments the engine of the mill was switched off between activation periods. In these cases the samples of the reaction mixture were taken from the working chamber just after the engine was switched off and before it was switched on, as well as during the exposure of the mixture with no activation. GLC-analysis was carried out on a LKhM-80 chromatograph with a flame-ionization detector (stainless steel column 200 cm×3 mm, 10 % Reoplex-400 on Chromaton N, carrier gas, nitrogen). After completion of the reaction the suspension from the working chamber of the mill was transferred into a glass tube under an argon atmosphere, and the chamber was

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[†] Deceased.

* The conversion of hexane under the conditions used for the reactions with cyclohexene and cyclohexadienes varies only slightly, which makes it possible to use hexane as the internal standard.

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washed with a fresh portion of hexane, which was then combined with the main bulk of the reaction mixture. To isolate polymer products all volatiles were initially distilled off *in vacuo* from the reaction mixture, benzene (containing a small amount of methanol) was added to the dry residue, and the mixture was stirred. The benzene became brown. The colored solution was allowed to stand, the precipitate was decanted, and a polymer material remained after the benzene was distilled off *in vacuo*. The content of metal in the isolated polymer did not exceed 1—2 %. The polymers were investigated by IR and NMR spectroscopy and elemental analysis. A polymer film, prepared by drying from a benzene solution on a KBr plate was used to record IR spectra. The spectra were measured on a Specord M-82 instrument within a range 600 to 4000 cm^{-1}. The assignments of absorption bands were performed by a well known procedure.[7] The NMR spectra were recorded in CCl_4 or $CDCl_3$ on a Bruker MSL-300 instrument.

Results and Discussion

The reaction of cyclohexane with neodymium was carried out both in the presence and in the absence of hexane at a cyclohexene/neodymium molar ratio equal to 13.0—16.2. The experimental data presented in Table 1 demonstrate that after a relatively short period of mechanochemical activation (5—8 h) cyclohexene is consumed with no formation any liquid products determinable by GLC. All consumed cyclohexene is converted to polymer (oligomer) products. More prolonged mechanochemical activation results in a significant amount of cyclohexane in the conversion products (see Table 1).

Cyclohexane units were recorded by NMR spectroscopy in the polymers isolated after a short activation time. The polymers contained sequences of methylene units (absorption bands at 1465, 2840, and 2960 cm^{-1}), but virtually no double bonds. The data obtained indicate that additive polymerization of cyclohexene occurs to yield a saturated polymer in the presence of lanthanides after a short activation time. We found isolated double bonds and moieties with polyconjugated double bonds along with cyclohexane units in the polymer isolated after prolonged activation (~40 h). Elemental analysis of this polymer demonstrated that the atomic ratio (H : C) in it is lower than the theoretical value for polycyclohexene, and is equal to 1.53, instead of 1.67. Taken as a whole, these data indicates that the polymer is formed from cyclohexane as well as from cyclohexadiene and benzene; the latter is supported by the presence of polyconjugated double bonds in the polymer.

As a rule, the reaction of cyclohexadienes with neodymium was carried out in the presence of C_6H_{14} (Table 2). Table 2 (experiments *1* and *2*) presents the data on the composition of the end products of the reaction carried out under conditions of continuous activation. These data indicate that the main liquid products of cyclohexadiene conversion are cyclohexene and benzene. Additionally, we found cyclohexane and cyclohexadiene (isomer of the starting compound) in the reaction mixture, but other hydrocarbons up to and including C_{12} were not found. The total yield of liquid products was significantly lower than the amount of cyclohexadiene reacted. This difference went to polymer (olygomer) products.

The IR spectra of the polymers isolated in the case of more than 90 % conversion of cyclohexadiene are very

Table 1. Conversion of cyclohexene with neodymium metal under conditions of mechanochemical activation at 20 °C (solvent — hexane)

Run	Cyclohexene/Nd, mol. ratio	C_6H_{14}/cyclohexene, vol. ratio	Reaction time/h	Conversion of cyclohexene (%)	Reaction products (% of reacted cyclohexene)	
					Cyclohexane	Polymer
1	13.0	2/3	5	20.8	0	100
2	16.2	1/1	8	25.3	0	100
3	14.3	2/3	25	66.5	19.3	80.7
4	13.4	0	23	45.4	20.7	79.3

Table 2. Composition of the products of cyclohexadiene conversion with Nd^0 under conditions of continuous (experiments *1* and *3*) and periodic (experiments *2* and *4*) mechanochemical activation at 20 °C

Run	Starting cyclohexadiene	Cyclohexadiene/Nd, mol. ratio	Reaction time*/h	Conversion of cyclohexadiene (%)	Reaction products (% of reacted cyclohexadiene)				
					Cyclohexadiene- 1,3	Cyclohexadiene- 1,4	Cyclohexene	Benzene	Polymer
1	1,3	12.5	8.0	97.0	—	2.0	38.0	37.0	23.0
2	1,3	10.5	3.4 (7.0)	98.5	—	3.3	32.4	38.6	25.7
3	1,4	12.6	9.0	86.7	0.8	—	22.8	37.4	39.0
4	1,4	8.4	5.4 (48.2)	90.7	1.2	—	24.7	25.7	48.4

* The first figure defines the time of mechanochemical activation, figure in parenthesis defines the total duration of the reaction including the exposure time with no activation.

Table 3. Composition of the products of cyclohexadiene conversion with Nd^0 under conditions of periodic mechanochemical activation at 20 °C

Reaction (activation) time/h	Initial cyclohexadiene	Cyclohexadiene conversion (%)	Yield of the reaction products (% of reacted cyclohexadiene)				
			cyclohexadiene-		Cyclohexene	Benzene	Polymer
			1,3	1,4			
0.8 (0.5)	1,3	15.5	—	8.5	2.3	6.8	82.4
4.3 (1.0)	1,3	25.7	—	28.7	6.1	10.2	55.0
27.0 (1.9)	1,3	63.3	—	28.9	15.8	23.1	32.2
50.0 (3.4)	1,3	87.6	—	10.7	30.8	30.6	27.9
73.0 (3.4)	1,3	98.5	—	3.3	32.4	38.6	25.7
0.5 (0.5)	1,4	11.2	47.0	—	16.2	14.7	22.1
2.9 (0.5)	1,4	27.8	45.0	—	7.1	20.6	27.3
4.9 (1.3)	1,4	43.0	38.4	—	10.6	26.2	24.8
5.7 (1.3)	1,4	46.6	40.3	—	11.6	23.5	24.6
21.7 (1.3)	1,4	73.0	26.4	—	17.0	20.8	35.8
26.5 (3.2)	1,4	80.7	18.0	—	21.2	24.3	36.5
46.2 (3.2)	1,4	81.1	11.2	—	23.8	27.2	37.8
48.2 (5.4)	1,4	90.7	1.2	—	24.7	25.7	48.4

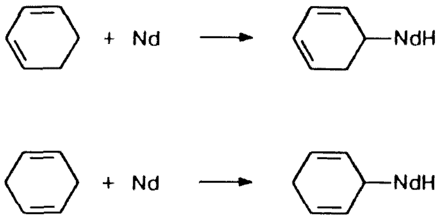
complicated. They contain bands assigned to vibrations of the double bond in the cyclohexene unit: 1650 cm^{-1} (ν(C=C)), 3025 cm^{-1} (ν(=CH)), 750 cm^{-1} (δ(=CH)), indicating that additive polymerization of cyclohexadiene occurs. In addition, the IR spectra contain the absorption bands that characterize sequences of methylene units (1465, 2840 and 2960 cm^{-1}); the band at 1370 cm^{-1} assigned to methyl groups, very slightly pronounced absorption bands of polyconjugated double bonds (1020, 1605—1620 cm^{-1}), absorption bands of a monosubstituted aromatic ring at 700, 740, 1500, and 1600 cm^{-1}, and a band at 888 cm^{-1}, which can be assigned to the absorption of $>C=CH_2$ groups. These data suggest that a mixture containing cyclohexadiene and cyclohexene polymers was obtained in the course of the reaction. Evidently, benzene is also involved in the formation of polymers, which is supported by the presence of polyconjugated double bonds. The elemental analysis data also indicate the formation of a polymer mixture: the (H : C) atomic ratio in them is 1.58, which is higher that the corresponding theoretical value for a homopolymer of cyclohexadiene (H : C = 1.33).

We found that the conversion of cyclohexadiene on Nd that occurs with mechanochemical activation, also occurs with no activation, although at the lower rate. A series of experiments was carried out in which short periods of activation were alternated with more prolonged periods of quiet. This way of performing the reactions allowed us to reveal some differences in the reactions of 1,3- and 1,4-cyclohexadienes, which are the most pronounced at the first step of the process. Thus, 30 min after beginning the activation the major amount of consumed 1,3-cyclohexadiene is converted to polymer, whereas the main product of the conversion of 1,4-cyclohexadiene is 1,3-cyclohexadiene (Table 3).

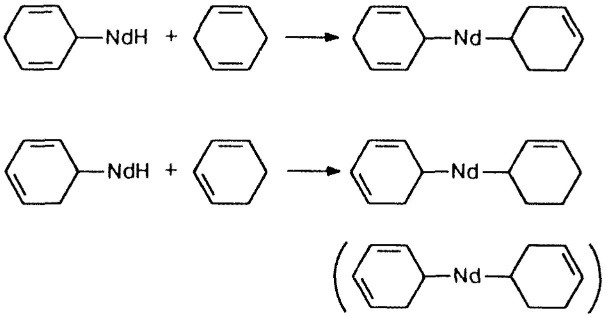
Later in the course of the reaction the quantitative composition of the products of cyclohexadiene conversion remained unchanged, but their ratio was changed. In particular, the content of polymer sharply decreased in the products of 1,3-cyclohexadiene, cyclohexene and benzene were gradually accumulated in the products of the reaction of 1,3- and 1,4-cyclohexadienes, and, as a rule, the quantity of benzene surpassed the quantity of cyclohexene. The date presented in Table 2 indicate that the composition and the ratio of end products of 1,3-cyclohexadiene conversion under conditions of periodic (experiments *2* and *4*) and continuous (experiments *1* and *3*) activation are almost identical. In the case of complete conversion of 1,4-cyclohexadiene the yield of polymer under conditions of periodic activation is somewhat higher than that under continuous activation. Under continuous activation of 1,4-cyclohexadiene the content of benzene is approximately 1.6 times higher than the content of cyclohexene, whereas under periodic activation this difference is not so big. Cyclohexane appears if 1,3- and 1,4-cyclohexadienes contact neodymium under the activation conditions for a prolonged period.

These data indicate that cyclohexadiene conversion by the action of neodymium with mechanochemical activation proceeds in three directions: polymerization, isomerization of 1,3- and 1,4-cyclohexadienes, and disproportionation leading to benzene and cyclohexene. The reaction mixtures obtained in the reactions of cyclohexene and cyclohexadienes with neodymium are effective catalysts for polymerization of butadiene and isoprene with no additives.[8] The polymers formed contain to 98 % 1,4-*cis*-units, which directly indicates the coordination mechanism of polymerization involving organometallic neodymium compounds.

Thus, the interaction of cyclohexadiene with neodymium results in the formation of organometallic compounds, as is the case of reactions of hydrocarbons with isolated metal atoms obtained by vaporization.[2] Obviously, formation of organometallic intermediates occurs *via* oxidative addition of hydrocarbons to the metal with cleavage of the C—H:

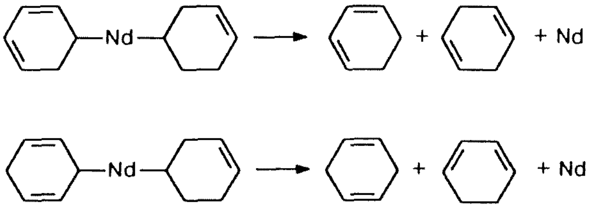


The cyclohexadienylneodymium hydrides formed are capable of reacting with the starting cyclohexadiene at the Nd—H bond according to the following scheme:

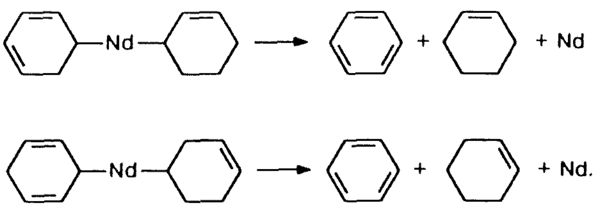


Apparently, the further direction of the reaction is determined by the stability and reactivity of the organometallic intermediates formed, the reactivity of the hydrocarbons in interaction with the C—Nd bond, and other factors. Specifically, in the course of the reaction (especially under continuous mechanochemical activation) the number of active centers increases, which can significantly affect the direction of the reactions.

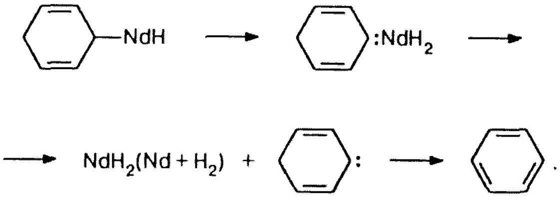
Isomeric cyclohexadienes can be formed as a result of β-elimination of the hydrogen atom from the cyclohexenyl group by the scheme:

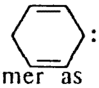


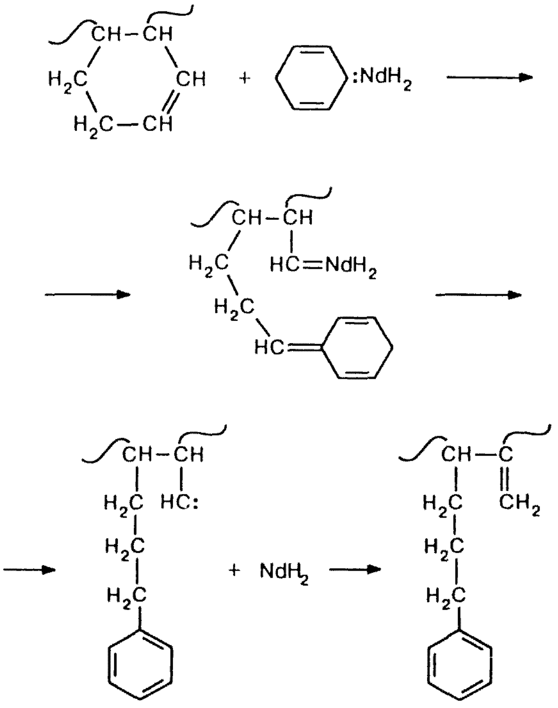
Disproportionation leading to cyclohexene and benzene proceeds by β(α)-elimination of the hydrogen from the cyclohexadienyl group of the organometallic intermediate:



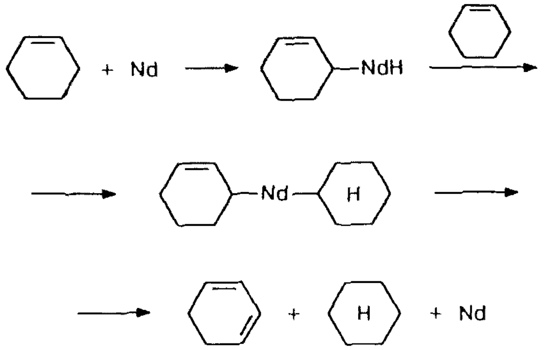
The fact that more benzene formed than cyclohexene can be explained, on the one hand, by the more facile polymerization of cyclohexene and, on the other hand, by decomposition of the cyclohexadienylneodymium hydrides formed in the oxidative addition of cyclohexadiene to Nd. In the case of 1,3-cyclohexadiene there is decomposition with elimination of the β-hydrogen atom of the cyclohexadienyl group and direct formation of benzene. Decomposition (which is typical of many transition metals and lanthanides) involving the α-hydrogen atom, with intermediate formation of a carbene complex stabilized by conjugation with two double bonds, followed by isomerization of carbene to benzene, is possible in the case of 1,4-cyclohexadiene:



The presence of $>C=CH_2$ and Ph groups in the polymer can also be explained by formation of a carbene complex  $:NdH_2$. These groups may appear in the polymer as a result of the reaction of carbene complex  $:NdH_2$ with the double bond of the polymeric chain according to a metathesis mechanism followed by isomerization:



The disproportionation of cyclohexene can be presented similarly to the conversion of cyclohexadiene:



Obviously, the polymer (oligomer) products are formed in the course of the successive addition of unsaturated hydrocarbons to the Nd—C bonds of organometallic intermediates.

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