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CHEMISTRY

1965

SovietRxiv

Abstract

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UDC 66.095.26+678.762

CHEMISTRY

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POLYMERIZATION OF BUTADIENE BY CATALYSTS BASED ON CARBONYLS OF GROUP VIII METALS OF THE PERIODIC SYSTEM OF ELEMENTS

(Presented by Academician B. A. Dolgoplosk, 29 III 1965)

Depending on the nature of the metal and of the ligands bound to it, complexes of Group VIII metals are by themselves catalysts for the stereospecific polymerization of butadiene, as is indicated by the catalytic activity of compounds of rhodium, ruthenium, palladium, and iridium (1). In our opinion, this circumstance is explained by the fact that compounds of Group VIII metals contain metals in a valence state lower than the maximum (corresponding to their position in the periodic system), and they have a very pronounced tendency to form π-complexes with unsaturated hydrocarbons (dienes, olefins, etc.).

In polymerization with the participation of Group VIII metals, the macromolecule may be "anchored" on the active center through formation of the corresponding π-complex, for example, a π-allyl complex (2,3).

For the creation of stereospecific catalysts, carbonyls of transition metals are of great interest. These compounds are distinguished by high reactivity in complex-formation processes. It is interesting to note that in the carbonyl complexes of iron and cobalt with butadiene, the latter is present in the cis conformation (4,5).

It is also known that nickel carbonyl complexes are active catalysts for the polymerization of acetylenic hydrocarbons (6,7).

In the present communication we give the results obtained in the polymerization of butadiene in the presence of catalysts based on nickel and cobalt carbonyls. By themselves, these compounds, under the conditions we studied, are not catalysts for the polymerization of butadiene, whereas the products of their interaction with Lewis acids do polymerize butadiene. The polymerization data are given in Table 1.

The polymerization was carried out in a hydrocarbon solvent (benzene or heptane) at a temperature of 50° for 17 h. At lower temperatures the yield of polymers decreased sharply. The concentration of butadiene in the solution was 2.5 mol/l; the concentration of Lewis acids was $5 \cdot 10^{-3}$ mol/l. The polymers were isolated from the solution by precipitation with ethyl alcohol.

The interaction of carbonyls with Lewis acids is accompanied by liberation of carbon monoxide and precipitation of sediments insoluble in hydrocarbons. The rate and stoichiometry of the interaction are determined by the nature of the Lewis acid: vanadium and tungsten compounds react most vigorously with nickel carbonyl. The rates of interaction of titanium halides with $Ni(CO)_4$, as well as the activity of the catalytic systems, decrease in the series: $TiCl_4 > TiBr_4 > TiJ_4$. It should be noted that tetrabutoxytitanium and dicyclopentadienyltitanium dichloride do not react with $Ni(CO)_4$.

Special experiments established that changing the temperature of interaction of the components within the range 20—55° does not affect the activity of the catalysts. Complete removal of the evolved carbon monoxide promotes the formation of more active catalytic systems.

The maximum conversion depth of butadiene is observed when catalysts $Ni(CO)_4$—VCl_4 and $Ni(CO)_4$—WCl_6 are used. The microstructure of the polybutadienes formed is determined mainly by the nature of the metal in the carbonyl and is practically independent of the Lewis acid used and of the ratio of the catalyst components.

Table 1

Catalytic systems based on metal carbonyls

Carbonyl compound	Lewis acid	Carbonyl / Lewis acid (mol.)	Polymer yield, %	Microstructure of polymer (unit content, %): 1,2	Microstructure of polymer (unit content, %): 1,4-trans	Microstructure of polymer (unit content, %): 1,4-cis	T_g, °C
$Ni(CO)_4$	$AlCl_3$	*	40	3	10	87	−104
$Ni(CO)_4$	$AlBr_3$	1	30	3	8	89	–
$Ni(CO)_4$	$AlBr_3$	2	100	2	8	90	–
$Ni(CO)_4$	$TiCl_4$	1	50	3	10	87	−105
$Ni(CO)_4$	$TiCl_4$	2	60	3	11	86	−106
$Ni(CO)_4$	$TiCl_4$	6	45	3	11	86	−103
$Ni(CO)_4$	$TiBr_4$	2	5	3	13	84	–
$Ni(CO)_4$	TiJ_4	2	1	–	–	–	–
$Ni(CO)_4$	VCl_4	1	50	3	4	93	−107
$Ni(CO)_4$	VCl_4	2	80	3	5	92	−108
$Ni(CO)_4$	VCl_4	3	70	4	5	91	−108
$Ni(CO)_4$	$VOCl_3$	2	65	3	5	92	−109
$Ni(CO)_4$	$MoCl_5$	1	45	–	–	–	–

Carbonyl compound	Lewis acid	Carbonyl / Lewis acid (mol.)	Polymer yield, %	Microstructure of polymer (unit content, %): 1,2	Microstructure of polymer (unit content, %): 1,4-trans	Microstructure of polymer (unit content, %): 1,4-cis	T_g, °C
$Ni(CO)_4$	$MoCl_5$	2	65	–	–	85(15)	–
$Ni(CO)_4$	WCl_6	1	6	4	6	90	–
$Ni(CO)_4$	WCl_6	2	80	3	5	92	−108
$Ni(CO)_4$	WCl_6	4	50	3	5	92	−108
$Co_2(CO)_8$	$MoCl_5$	1	40	96–100	–	–	−15
$Co_2(CO)_8$	$MoCl_5$	2	30	96–100	–	–	−16.5
$(C_5H_5NiCO)_2$	$TiCl_4$	1	8				−108
$(C_5H_5NiCO)_2$	$TiCl_4$	0.5	100	3	6	91	−109
$(C_5H_5NiCO)_2$	$TiCl_4$	0.25	25				−109
$(C_5H_5NiCO)_2$	$VOCl_3$	1	7	2	4	94	−106
$(C_5H_5NiCO)_2$	$VOCl_3$	0.5	10	3	5	92	−105

* The catalyst was prepared with an excess of aluminum chloride. The soluble part was used for polymerization.

In the case of nickel carbonyl, the polymers contain 96-98% 1,4-units, including 86-92% cis-1,4-units. The cobalt carbonyl—molybdenum pentachloride system leads to 1,2-polybutadiene. It was not possible to obtain active catalysts based on $Co_2(CO)_8$ and other Lewis acids ($TiCl_4$, $AlBr_3$, VCl_4, etc.), which to some extent is consistent with the absence of catalytic activity in the products of the interaction of bis(π-cyclopentadienyl)cobalt with Lewis acids ([8]). The products of the interaction of iron carbonyl with $VOCl_3$ and WCl_6 likewise had no catalytic activity in the polymerization of butadiene.

Dicyclopentadienyldinickel dicarbonyl, in a mixture with $TiCl_4$ and $VOCl_3$, behaves similarly to nickel carbonyl. For the system $(C_5H_5NiCO)_2$—$TiCl_4$, the maximum activity is attained at the ratio Ni/Ti = 1.

The nature of the solvent has a noticeable effect on the rate of butadiene polymerization. The greatest efficiency is observed in the case of aromatic solvents (benzene, toluene). For the $Ni(CO)_4$—WCl_6 system in *n*-heptane, the conversion depth did not exceed 25-30%, and the polymers obtained were characterized by low molecular weight. In microstructure these polymers did not differ from polymers synthesized in benzene solution.

Replacement of even one carbonyl group in the $Ni(CO)_4$ molecule by a triphenylphosphine molecule leads to complete loss of activity of the products of interaction of this complex with $TiCl_4$, VCl_4, and $VOCl_3$ in the polymerization of butadiene. At the same time, $Ni(CO)_3P(C_6H_5)_3$ is a catalyst for the polymerization of acetylenic hydrocarbons (^{7}).

According to Wilke (^{9}), complexes of zero-valent nickel with phosphine ligands, $[(C_6H_5)_3P]_4Ni^0$ and $[(C_6H_5)_3P]_2Ni^0$, cause cyclic ···

oligomerization of butadiene. However, the precipitates formed in the reaction of phosphine complexes of Ni^0 with Lewis acids do not initiate the polymerization of butadiene.

The products of the interaction of Lewis acids with π-allyltricarbonyl cobalt are likewise inactive. A distinctive feature of the catalysts described in the present work is the absence of an organometallic component in their composition. The catalytic activity of these systems is due to their π-complex nature.

Catalysts obtained by the interaction of nickel carbonyl with Lewis acids in aromatic hydrocarbons are arene complexes of transition metals

$$Ni(CO)_4 + AlCl_3 \to Ni^0(Arene)_2(AlCl_3)_n \quad (^{10}).$$

The reaction of cobalt carbonyl with $AlBr_3$ leads to the formation of mixed arene-cobalt carbonyls

$$Co_2(CO)_8 + AlBr_3 + C_6H_6 \to [Co_3(Arene)_3(CO)_2]Br \quad (^{11}).$$

To obtain active catalysts of the "arene" type, it is not necessary to start from metal carbonyls. In the present case the carbonyls prove to be merely convenient starting materials, readily exchanging carbon monoxide for aromatic ligands.

We have shown that arene complexes of nickel, obtained by Müller' s method [^{12}] from Raney nickel, aluminum chloride, and benzene, are also catalysts for the stereospecific polymerization of butadiene. Instead of Ni (Raney), nickel boride, obtained by reduction of nickel chloride with sodium borohydride, may be used.

The catalytic activity of the products of the interaction $TiCl_4 + AlCl_3 + Al + C_6H_6$ in processes of polymerization and cyclic oligomerization of butadiene was investigated by Fowinkel (^{13}). As this author showed, the catalyst in this case is an arene complex of titanium of composition $Al_2Cl_8Ti(C_6H_6)$ (^{14}).

Analysis of data on the catalytic activity of arene complexes of transition metals in the polymerization of butadiene leads to the conclusion that two metals must be present in the catalyst composition. In studying a catalytically active precipitate obtained by the reaction of $Ni(CO)_4$ with VCl_4, the presence in it of nickel and vanadium in a ratio of $1:1$ (mol.) was established. All of the initial chlorine was also found in the precipitate.

At present it is still impossible to draw reliable schemes for the reactions of nickel carbonyl with various Lewis acids. However, studies being carried out in our laboratory on the composition and nature of the complexes $Ni(CO)_4$+ Lewis acid compel us to suppose that this interaction is accompanied by a change in the valence states of the metals, at least in those cases where halides of transition metals are used as Lewis acids.

As noted earlier (2), the catalytic activity of arene complexes in the polymerization process is determined by the ease of displacement of the aromatic ligand by butadiene. It seems beyond doubt that, in the most general case, π-complexes of transition metals in which the strength of the ligand–metal bond is comparable with that in benzene complexes should possess the ability to initiate the polymerization of butadiene. Such ligands should include, first of all, carbon monoxide, since, on the one hand, numerous cases are known of mutual transitions

$$\text{arene} \underset{C_6H_6}{\overset{CO}{\rightleftarrows}} \text{carbonyl}$$

and, on the other hand, carbon monoxide in carbonyls is rather readily displaced by dienes.

This is confirmed by data on the catalytic activity of the products of the interaction of nickel carbonyl with Lewis acids in aliphatic hydrocarbons.

The catalytic systems described in the present work are undoubtedly genetically related to catalysts we have previously described based on π-allyl and π-cyclopentadienyl nickel complexes (3, 8). A detailed study of the reactions underlying the formation of these catalysts and of the mechanism of their action may be of fundamental importance for understanding the nature of ionic-coordination polymerization as a whole.

The authors express their gratitude to I. A. Zarova for her participation in the work.

All-Union Scientific Research Institute
of Synthetic Rubber
named after S. V. Lebedev

Received
23 III 1965

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Note: Figure translations are in progress. See original paper for figures.