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Final Report

THE POLYMERIZATION OF ISOPRENE IN THE PRESENCE OF COORDINATION COMPLEXES OF COBALT

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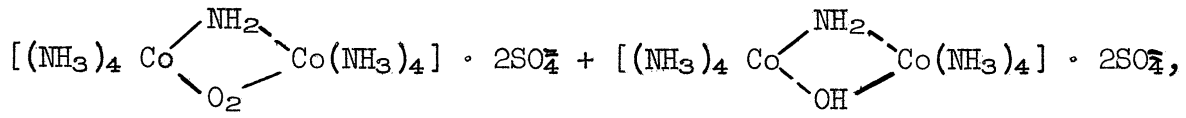
ABSTRACT

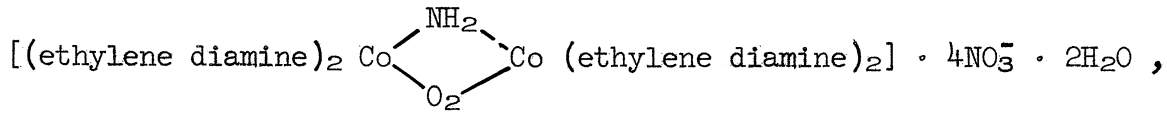
Coordination compounds of cobalt with organic diamines and ammonia and double salts of some of these complexes with cobaltous chloride ($CoCl_2$) were tried as catalysts for the steriospecific polymerization of isoprene. Reactions were carried out in the temperature range of 25-100°C in solvents such as n-pentane, and in aqueous emulsion in the presence of anionic carboxylic or nonionic soaps. Several redox combinations which are known to be effective in aqueous emulsion were tried as catalysts in hydrocarbon solvents.

Small amounts of polymer were formed in the presence of $[Co^{3+}(\text{ethylene diamine})_3] \cdot 3Cl^- \cdot CoCl_2 \cdot 4H_2O$ in n-pentane at 50-75°C during 40-60 hours; however, only traces of polymer were produced in hydrocarbon solvents in the presence of the other compositions.

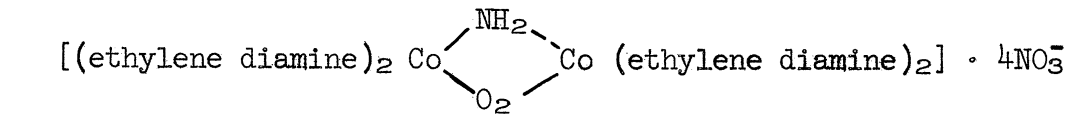
In aqueous emulsion, the salt $[Co^{3+}(\text{ethylene diamine})_3] \cdot 3Cl^-$ showed high catalytic activity. Polymer was formed in 90-100% yield at 50-75°C during 19-45 hours. Two compounds, Vortman's salt,



and the compound,



showed moderated activity in aqueous emulsion; low molecular weight polymer was formed in 20-50% yield. These further compounds: $[Co^{3+}(\text{o-phenylene diamine})_3] \cdot 3Cl^-$, $[Co^{3+}(\text{ethylene diamine})_3] \cdot 3Cl^- \cdot CoCl_2 \cdot 4H_2O$, and



exhibited limited catalytic activity.

Substantially larger amounts of polymer were formed in the aqueous systems in the presence of the anionic soap than in the presence of the nonionic surface active agent. Infrared analysis of the products of two of the aqueous polymerizations indicated that their structures were similar to those of polyisoperene formed in the presence of free radical initiators. Thus a new group of polymerization catalysts has been found which appears to be of the free radical type.

OBJECTIVE

The purpose of the study was to examine certain complex compounds of cobalt as catalysts for the polymerization of isoprene.

INTRODUCTION

The discovery and development of steriospecific catalysts which yield isotactic polymers has stimulated interest in gaining better understanding of heterogeneous catalysis. A number of catalytic systems have now been identified which yield polymers possessing high regularity of the spatial arrangement of the chain substituents. Some of the important steriospecific catalysts for diene polymerization are: alfin, Ziegler, metallic lithium, supported CrO_3 in oxidized condition, supported MoO_3 in a reduced condition, and lithium alkyl adsorbed on lithium.

While the details of the mechanism of isotactic polymerization have not been worked out it appears that the various steriospecific catalysts have in common 1) the ability to adsorb and activate the monomer in an oriented state, 2) to accept an incoming monomer in an oriented way, and 3) to accomodate a reaction between the two and then allow the more saturated portion of the product to be desorbed.

A calculation of the atomic distances in crystalline lithium indicated that the distance between the body-centered atom and a corner atom is similar to the carbon-1-to-the-carbon-4 distance of the isoprene molecule, whereas the distance between two adjacent corner atoms is dissimilar to the isoprene dimension. It appears that the actual topography of the adsorbing surface has a bearing on the effectiveness of the material as a catalyst.

In laying the basis for this study, it was assumed that activation resulted from some kind of electronic push-pull, or redox condition on the adsorbing surface. Such an assumption is not conventional for catalysts such as the alfin, Ziegler, and lithium systems; however, it may well apply to the chromic oxide (incompletely oxidized) and molybdenum (incompletely reduced) surfaces.

It was decided to combine these points of view in the trial of complex cobalt salts as steriospecific catalysts with the aim of incorporating an oxidation-reduction system within the inorganic molecule and selecting the molecule to be large enough to be able to maintain the isoprene molecule in the adsorbed condition. A further long range hope was that eventually a homogeneous soluble system could be developed that would be effective for the steriospecific synthesis of cis-1,4 polydienes in aqueous emulsion.

Complex cobalt salts of the Werner type were prepared by standard procedures with Co^{3+} as the oxidant and Co^{2+} and/or ethylene diamine or phenylene diamine as the reductant. In n-pentane suspensions these compounds gave

very little polymer. In aqueous emulsion in the presence of soap, however, some of them gave polyisoprene in high yield; the structures of the products are apparently similar to those formed by free radical polymerization.

In the process several of the well known redox combinations that are effective in aqueous emulsion polymerizations were tried in n-pentane and were found in all cases to be ineffective.

Thus, while the first application of the ideas has not led to the formation of isotactic polymer, new catalytic materials have been found apparently of the free radical type which are of interest in their own right.

The purpose of this report is to summarize the results of this study.

EXPERIMENTAL PART

CATALYST PREPARATION

The cobalt complex salts were prepared by the procedures described in the literature cited in Table I and briefly outlined below.

Compounds A and B were prepared by similar methods. o-Phenylene diamine (32.5 g) or ethylene diamine (21.5 g) were dissolved in 42 ml of H_2O. The solutions were neutralized with 17-20 ml of 6N HCl, and 25 g of $CoCl_2 \cdot 6H_2O$ were added. The solutions were vigorously areated and stirred at 50°C for 3 hours. The solutions were then heated on a steam bath until crusts formed. Concentrated HCl (15-20 ml) and ethanol (30-35 ml) were added and the solutions cooled to 20°C. The crystals which formed were separated and washed with cold ethanol.

Compounds C and D were prepared from Compounds A and B, respectively. To 5 g of compound A or B, 0.7 g of $CoCl_2 \cdot 6H_2O$ and 30 ml of concentrated HCl were added, and the resulting solutions were heated to 50°C. When crystals started to form, the mixtures were cooled. The crystals were separated, washed with cold ethanol several times, and finally with ether.

Compound E, Vortman's cobaltic fuscosulfate, and the remaining compounds which were prepared from it were synthesized according to the following procedure. One hundred grams of cobaltous nitrate, $Co(NO_3)_2 \cdot 6H_2O$, in 100 ml of H_2O, 850 ml of 23% NH_4OH, and 150 ml of H_2O were mixed and held at 30°C for 8 hours during which the solution was aerated by means of a slow stream of air. The reaction mixture was allowed to stand for 14 hours after which it was neutralized at 10°C (by cooling in an ice bath) with H_2SO_4. About 4.5 hours were required for the neutralization at 10°C. Vortman's salt precipitated on standing, and was separated and washed with H_2O.

TABLE I

IDENTIFICATION OF INORGANIC SALTS

Designation	Formula	Melting Point, °C		Color		Preparation Reference
		Obs.	Lit.	Obs.	Lit.	
A	$[Co^{3+}(o\text{-phen})_3] \cdot 3Cl^-$ [a]	252-4	--	purple-brown	--	1,2
B	$[Co^{3+}(en)_3] \cdot 3Cl^-$ [b]	250-4	256	orange	orange-yellow	2,3
C	$[Co^{3+}(o\text{-phen})_3] \cdot 3Cl^- \cdot Co^{2+}Cl_2 \cdot 4H_2O$	245-7	--	red-purple	--	4
D	$[Co^{3+}(en)_3] \cdot 3Cl^- \cdot Co^{2+}Cl_2 \cdot 4H_2O$	240-3	245	yellow-green	green	4
E	$[(NH_3)_4 Co(NH_2)_2Co(NH_3)_4] \cdot 2SO_4^=$				green	
	+	> 265	--	purple		5
	$[(NH_3)_4 Co(NH_2)(OH)Co(NH_3)_4] \cdot 2SO_4^=$				red	
F	$[(NH_3)_4 Co(NH_2)_2Co(NH_3)_4] \cdot 4NO_3^-$	> 265	--	green	green	6
G	$[(NH_3)_4 Co(NH_2)_2Co(NH_3)_4] \cdot 4NO_3^- \cdot 2H_2O$	> 265	--	red	red	6,7
H	$[(en)_2 Co(NH_2)_2Co(en)_2] \cdot 4NO_3^-$	> 265	--	green	green	6,7
I	$[(en)_2 Co(NH_2)_2Co(en)_2] \cdot 4NO_3^- \cdot 2H_2O$	> 265	--	red	red	6,7
X	Decomposition of reaction of F to H [c]	> 265 [d]	--	orange	--	--

a. "o-phen" = ortho phenylene diamine.

b. "en" = ethylene diamine.

c. probably trisethylene diamine salts.

d. color change at 250°C.

Compounds F and G were prepared directly from Compound E. Ten grams of E were dissolved in 40 ml of H_2O, and 250 ml of concentrated HNO_3 were added. A purple precipitate formed; the mixture was cooled to 2°C and the crystals were separated and washed with distilled H_2O until the washings were pink. The filtrate was evaporated to dryness, concentrated HNO_3 was added, and the mixture cooled to 0°C upon which green crystals, Compound F, were formed and separated. Compound G was obtained from the residual purple crystals mentioned above by washing with concentrated HNO_3 until the washings became slightly brown. The washings were collected and evaporated to yield red crystals, Compound G, which were separated.

Compounds H and I were obtained from Compounds F and G, respectively. To 6 g of Compound H or I, 90 ml of H_2O and 38 ml of 10% solution of ethylene diamine in water were added. The mixture was heated on a water bath until the evolution of NH_3 was complete. The remaining solution was neutralized with HNO_3, and cooled to 0°C, at which temperature precipitates F and G formed. These were separated and dried.

In addition to the above materials, several conventional redox combinations were tried as catalysts. The compounds, listed in Table II, were not synthesized in this study but were obtained from usual commercial sources.

PURIFICATION OF MATERIALS

Phillips "Pure Grade" isoprene was treated just prior to use by passing through a column packed with NaOH, Drierite, and anhydrous alumina, under an atmosphere of dry nitrogen. The solvents n-pentane and n-heptane, were treated with successive portions of concentrated H_2SO_4 until color ceased to develop in the acid layer. The acid was removed by further washings with distilled water and dilute $NaHCO_3$ solution. The solvents were dried by passing over Drierite, silica gel, and alumina, and were stored over freshly extruded sodium ribbon.

POLYMERIZATION PROCEDURES

The reactions were carried out at 25, 50, 70, and 100°C. The reaction vessels for the 25, 50, and 70°C experiments were 4-oz glass bottles sealed with the "self-sealing" butyl-nitrile rubber sandwich gasket frequently used in bottle polymerization work. The reaction at 100°C was performed in a Magna-Dash autoclave fitted with stirrer. The bottles were rotated on ball mill rolls located near a window for the 25°C experiments. In most cases the bottles were painted to exclude light. In the 50 and 70°C experiments, the bottles were rotated end over end in the dark in a conventional polymerization bath. In all cases great care was exercised to exclude oxygen from the reaction mixtures and the reaction vessels were flushed with either nitrogen or helium.

TABLE II

SUMMARY OF POLYMERIZATION EXPERIMENTS

Expt. No.	Catalyst, g	Solvent[a]	Soap		Reaction Conditions					Product
			K-ORR	Igepal	Temp., °C	Press., atm	Time, hr			
							Bath	Rollers	Autoclave	
1	0.5A	X			25	~1	60	1		none
2	0.5A[b]		X		25	~1	67	1		none
3	0.5A		X		25	~1	29			trace
4	0.5A	X			54	~2	57			trace
5	0.5A		X		72	~3	19			~1 g
6	0.5A			X	72	~3	45			~0.1 g
7	0.5B	X			25	~1	92	70		none
8	0.5B		X		25	~1	92			trace
9	0.5B		X		25	~1		29		trace
10	0.5B	X			54	~2	57			trace
11	0.5B		X		72	~3	19			~ 20 g
12	0.5B			X	70	~3	45			~0.3 g
13	0.4C		X		25	~1		29		trace
14	0.3D		X		25	~1	67			none
15[c]	0.4D		X		25	~1		29		~1 g
16	0.5D	X			25	~1	67	48		none
17	0.5D	X			54	~2	57			~0.05 g
18	0.5D	X			72	~3	45			~0.2 g
19	0.5D		X		72	~3	19			trace
20	0.5D			X	70	~3	45			none
21[d]	0.5D				100	~5			48	viscous liquid
22	0.5D	X			100	~5			48	slight viscosity increase
23	0.5D	X[e]			100	~5			48	slight viscosity increase
24[d]	none				100	~5			48	viscous liquid
25	0.3E	X			25	~1	50			none
26	0.5E		X		25	~1	65			trace
27	0.5E	X			54	~2	57			trace
28	0.5E		X		72	~3	16			4 g (low mol. wt.)
29	0.5E			X	70	~3	45			trace
30	0.3F	X			25	~1	50			none
31	0.4F		X		25	~1	65			trace
32	0.3F	X			54	~2	57			trace
33	0.4F		X		72	~3	19			0.5 g
34	0.1G	X			25	~1	50			none
35	0.1H	X			25	~1	50			none
36	0.18H			X	70	~3	45			~0.3 g
37	0.1I	X			25	~1	50			none
38	0.2I	X			54	~2	57			trace
39	0.2I		X		72	~3	19			10-15 g low mol. wt. material
40	0.3X	X			25	~1	50			none
41	0.5X		X		25	~1	65			trace
42	none		X		70	~3	24			trace
43	none			X	70	~3	24			trace
44	$Fe^{+2} \cdot Fe_2^{+3}(SO_4)_4$	X			25	~1	24			none
45	$Fe^{+2} \cdot Fe_2^{+3}(SO_4)_4$	X			50	~2	24			none
46	$Fe^{+2} \cdot Fe_2^{+3}(SO_4)_4$ + CPH[b]	X			25	~1	24			trace
47	$Na_4Fe^{+2}(CN)_6$ + CPH[f] + t-dodecylmercaptan	X			25	~1	24			none
48	$K_3Fe^{+3}(CN)_6$ + n-dodecylmercaptan	X[e]			25	~1	24			none
49	$K_3Fe^{+3}(CN)_6$ + n-dodecylmercaptan	X[e]			77	~3	72			none

a. n-pentane was used unless indicated.
b. 0.18 g of $CoCl_2$ added.
c. The reaction bottle was exposed to light throughout the polymerization reaction.
d. No solvent or emulsion was used.
e. n-heptane was used as the solvent.
f. CPH = cumene hydroperoxide.

For the experiments carried out in solvents, the material to be tried as the catalyst, 50 ml of solvent, 30 ml of isoprene, and the amounts of catalyst indicated in Table II were mixed in the absence of air. For the emulsion systems, 30 ml of isoprene were emulsified in 80 ml of water by use of either 2 g of the anionic potassium carboxylic soap, K-ORR, or the nonionic alkyl phenol ethylene oxide condensate, Igepal CO-430. For the trials of conventional redox systems in solvents, an organic peroxide or mercaptan was selected in combination with an inorganic reducing or oxidizing agent so that in each case one member of the couple was soluble.

The effects of pressure were not studied separately. The pressures recorded in Table II were those produced by heating the reaction mixtures to the indicated temperatures.

ISOLATION OF POLYMER

For the emulsion systems, after completion of the reaction period, the unreacted monomer was removed by addition of dry steam. Sodium chloride and sulfuric acid were used to "break" the suspension, the precipitated polymer was separated and washed with isopropanol. The polymer was then dissolved in benzene. (Frequently a long time was required for solution, presumably because of gel formation. In future experiments it would be desirable to add an anti-oxidant to the suspension immediately after completion of the reaction.) After filtration of the benzene solution, the polymer was precipitated by addition of isopropanol. Further purification was accomplished by redissolving in benzene and removing the benzene by sublimation at 0°C and reduced pressure.

The products from the polymerizations carried out in solvents were precipitated by the addition of isopropanol and further purified in the manner described above.

The results of the experiments are identified in Table II and the results discussed in the following paragraphs.

DISCUSSION OF RESULTS

In the hydrocarbon solvent systems none of these materials, either the cobalt compounds or the conventional redox combinations, were effective polymerization catalysts. The compound D, $[Co^{3+}(\text{ethylene diamine})_3] \cdot 3Cl^- \cdot CoCl_2 \cdot 4H_2O$, showed the greatest activity, but still less product was obtained than was needed for structural analysis. If further work on these systems is contemplated, it might be well to try this material on a catalyst support such as alumina.

In the aqueous emulsion systems, several of the cobalt complexes exhibited catalytic activity. In the presence of compound B, $[Co^{3+}(\text{ethylene diamine})_3] \cdot 3Cl^-$, 90-100% conversion was obtained (Expt. No. 11). Compounds E and I catalyzed the formation of moderate amounts of low molecular weight polymer (20-50% yield) and compounds A, D, and H showed more limited catalytic activity.

In the aqueous systems the nature of the surface active agent had a marked effect on the yield of product. Usually about ten times more polymer was formed in the presence of the anionic K-ORR than in the presence of the nonionic Igepal CO-430. From the information at hand it is not possible to decide whether this difference is due to a colloidal charge effect or to the catalytic activity of a decomposition product of the original cobalt complex.

At the higher temperatures the rates of polymerization were the greater.

The infrared spectra of the products of Expts. Nos. 11 and 15 (catalysts B and D in aqueous emulsion) were obtained and analyzed by Dr. S. D. Gehman. He reported that the molecular structures of these products were similar to those of polyisoprenes produced by free radical polymerization.

Thus it appears that these new catalysts function through a free radical type process.

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