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Specific Catalysis with Iron Coordination Complexes

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A novel three-component catalyst system has been found which is very active for the polymerization of isoprene. The catalyst consists of iron(III)acetylacetonate-triethylaluminum and specific bidentate ligands. The three bidentate ligands found which greatly promote the polymerization are in order of decreasing promoting ability: phenyl-2-pyridylacetonitrile, 2-cyanopyridine, and 2-pyridinealdoxime. The ligand must contain certain functionalities to result in an active catalyst. The polymerization of isoprene proceeds best at low temperatures, such as −23°C, and the rate and polymer yield decreases with increasing temperature. This unusual temperature effect is probably due to a greater catalyst stability at lower temperatures. This catalyst produces a polyisoprene which consists of approximately equal amounts of *cis*-1,4 and 3,4 linkages.

INTRODUCTION

Several complex catalyst systems have been reported for the selective polymerization, dimerization, alkylation, and cyclooligomerization of diolefins. In most of the catalyst systems a transition metal salt or compound is reduced by an organometallic compound. In many cases it is also desirable to add a third component, which will complex with the low valence transition metal. This third component or complexing agent can result in a more active catalyst system, impart stability to the catalyst or selectively direct the course of the reaction. Examples of three-component catalyst systems which have been reported are: cobaltous chloride-ditertiary phosphine complex and an organoaluminum compound for the selective preparation of 1,4-hexadiene by the reaction of butadiene with ethylene (*1*), and iron(III)acetylacetonate-2,2′-dipyridyl-triethylaluminum for the preparation of dimethyl-1,5-cyclooctadienes from isoprene (*2*).

This paper reports a novel three-component catalyst system which is very active for the polymerization of isoprene. The catalyst consists of iron(III)acetylacetonate-triethylaluminum and specific bidentate ligands. The three bidentate ligands found which greatly promote the polymerization are in order of decreasing promoting ability: phenyl-2-pyridylacetonitrile, 2-cyanopyridine, and 2-pyridinealdoxime. Without any one of these ligands, there is no polymerization.

EXPERIMENTAL

The metal acetylacetonates and most of the iron salts used in this study were obtained from the K & K Laboratories, Inc. Before use, they were dried in vacuum at 50°–60°C for 16 hr, then stored in a nitrogen atmosphere. The iron carbonyls and dicyclopentadienyl iron were obtained from Alfa Inorganic, Inc.

The nitrogen compounds were obtained from the Aldrich Chemical Company. The 2-cyanopyridine was vacuum distilled and stored under nitrogen. The other compounds were dried in vacuum at room temperature for 16 hr and stored under nitrogen.

Benzene (B & A), hexane (Phillips), *o*-dichlorobenzene, and 1,2-dichloroethane (both Eastman) were distilled under nitrogen and stored over molecular sieves in a nitrogen atmosphere. Isoprene (either Eastman or J. T. Baker) was distilled under nitrogen and stored in a nitrogen atmosphere. Butadiene (Matheson C. P. Grade) was dried by passing it through activated molecular sieves. Other monomers were treated the same way. Triethylaluminum (TEA) (Texas Alkyls) and other aluminum alkyls were used as received.

The small scale polymerizations were carried out in 200-ml pressure bottles obtained from the Fisher Scientific Company. The procedure for a polymerization run is as follows:

To a pressure bottle was added 1 mmole of iron acetylacetonate Fe(acac)$_3$, 1 mmole of ligand, 50 ml of benzene, 20 ml of isoprene, and 3 mmoles of TEA. All reactants and apparatus were kept in a dry, nitrogen atmosphere. The bottle was sealed and the reaction carried out for the desired time. The jelly-like product was dissolved in sufficient benzene to make it free-flowing, then poured into methyl alcohol containing a little hydrochloric acid to destroy the catalyst and 0.5 wt % (based on isoprene) 2,6-di-tert-butyl-*p*-cresol as antioxidant. The polymer was recovered and dried under vacuum at room temperature overnight.

The large scale polymerization experiments were carried out in a 1-liter resin kettle equipped with a pressure equalizing addition tube, a nitrogen inlet tube, and a stirrer. The kettle was dried overnight at 110°C and cooled to room temperature with a stream of dry, prepurified nitrogen flowing through it. Reactants and solvent had been previously weighed into bottles in a dry box and were kept under a nitrogen atmosphere until ready for use. The procedure for a typical experiment is as follows:

Into a resin kettle, through which a stream of nitrogen was flowing, was added a solution of 4 mmoles of Fe(acac)$_3$, 4 mmoles of 2-cyanopyridine, 80 ml of isoprene, and 130 ml of benzene. The stirrer was started and a solution of 12 mmoles of TEA in 30 ml benzene was quickly added. The kettle was sealed and the nitrogen flow was stopped. When the reaction mixture became so viscous that it adhered to the stirrer, an additional 250 ml of benzene was added to reduce the viscosity. After the desired time the kettle was opened and sufficient benzene was added to form a free-flowing solution. Usually, 1000–1500 ml of benzene was required. The benzene-polymer solution was transferred to a buret and slowly added to about 6000 ml of methyl alcohol containing a few milliliters of hydrochloric acid to destroy the catalyst and 0.5 wt % (based on isoprene charged) 2,6-di-tert-butyl-*p*-cresol as antioxidant. The precipitated polymer was filtered, washed with methanol, and dried under vacuum at room temperature for 24 hr.

The polymerization of isoprene at various temperatures was carried out by immersing the reaction bottle in a bath kept at the desired temperature. The following bath compositions were used: for −23°C, CCl_4 + dry ice; 0°C, ice + water; 25°C, none; 60°C and higher, oil.

The data for the conversion versus time plot (Fig. 3) at various temperatures were obtained by opening the bottle after the desired reaction time had elapsed, adding sufficient benzene (200–500 ml) to make a free flowing solution, and precipitating the polymer in methanol (containing a few milliliters concentrated HCl and about 1 wt % antioxidant). The yield of solid polymer was obtained after it had been washed with methanol and dried in vacuum overnight at room temperature.

Integrated NMR spectra of the polyisoprene were obtained at room temperature on a Varian HA-60-IL. Benzene-d$_6$ and carbon disulfide were used as solvents with a few percent benzene added to provide a lock signal. Samples of appropriate concentration were prepared by trial and error dilution of viscous solutions. Analysis was made for the ratio of (1,2-):(3,4-):*cis/trans*(1,4-) polyisoprene using the procedure developed by Chen (*3*). It was assumed that the polymer consisted of straight-chain structures. The procedure used for the structural determination of polybutadiene was that reported by Binder and Ransaw (*4*).

Samples were run as CS_2 solutions in matched cells, with CS_2 in the reference beam. Since standard samples were not available, accurate molar absorptivities and baseline positions could not be calculated and all values may be in error by as much as 20%. Gel content, dilute solution viscosity, and molecular weight data were obtained from Ameripol, Inc.

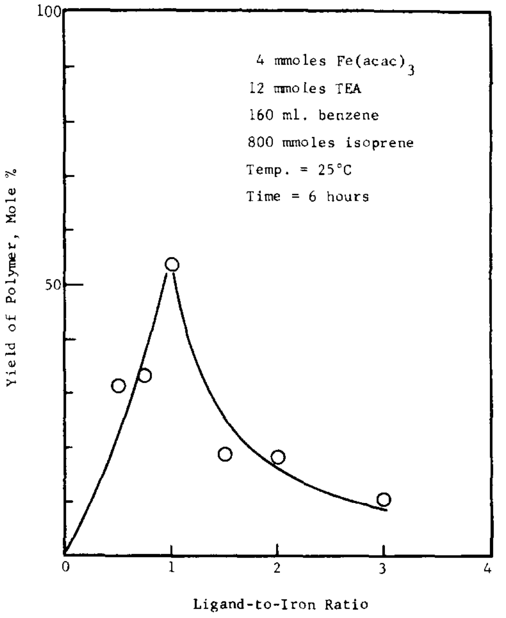


FIG. 1. Effect of ligand-to-iron mole ratio on the yield of polyisoprene.

RESULTS

Catalyst System

The basic catalyst system studied consisted of Fe(acac)$_3$, TEA, and a ligand containing nitrogen donor atoms. Without ligand, an Fe(acac)$_3$-TEA mixture exhibited very low activity for the conversion of isoprene to cyclic dimers. However, by adding the ligand 2-cyanopyridine to Fe(acac)$_3$ and TEA, a catalyst system was formed which resulted in the rapid polymerization of isoprene to a high molecular weight polymer. With this catalyst system, it is critical to use a ligand-to-iron mole ratio of 1 and an aluminum-to-iron mole ratio of 3, as shown by Figs. 1 and 2, respectively. Phenyl-2-pyridylacetonitrile, 2-pyridinealdoxime, 2-cyano-6-methylpyridine, and 2-cyano-6-methoxyquinoline were the other ligands found to be active promoters for the polymerization. The most active catalyst system was formed when phenyl-2-pyridylacetonitrile was used. These catalyst systems were all homogeneous. The data obtained during these

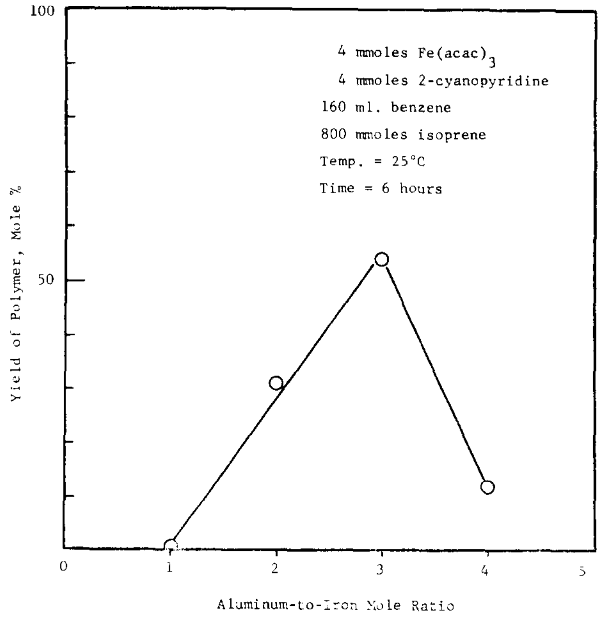


FIG. 2. Effect of aluminum-to-iron mole ratio on the yield of polyisoprene.

TABLE 1
CONVERSION DATA FOR VARIOUS MONOMERS

Monomer	Process	Ligand	% Conversion	Time (hr)
Isoprene	A[a]	phenyl-2-pyridylacetonitrile	65	6
Isoprene	A	2-cyanopyridine	54	6
Isoprene	A	2-pyridinealdoxime	33	6
Isoprene	A	2-cyano-6-methylpyridine	18	6
Isoprene	A	2-cyano-6-methoxyquinoline	15	6
Isoprene	B[b]	2-cyanopyridine	50	20
Butadiene	B	2-cyanopyridine	50	20
Chloroprene	B	2-cyanopyridine	7	4

[a] Type A—Prepared in a resin kettle as described in the experimental section, temperature 25°C.

[b] Type B—Experiments carried out in pressure bottles as described in the experimental section.

ligands are given in Table 1. The use of the following ligands with $Fe(acac)_3$ and TEA resulted in inactive polymerization, catalyst systems: 2-aminomethylpyridine 3-cyanopyridine, 4-cyanopyridine, 2-vinylpyridine, 2,2′-bipyridyl, 2-pyridinealdazine, 1,2-bis-(2-pyridyl)-ethylene, di-2-pyridyl ketone, 2-cyanoaniline, 2-acetylpyridine, 2,2′-biquinoline, 5,5′-bis-(8-hydroxyquinolyl)-methane, acetonitrile, and benzonitrile.

Ferric naphthenate and ferric octoate could be substituted for $Fe(acac)_3$ with no loss of activity for isoprene polymerization. However, ferric chloride, iron pentacarbonyl, diiron nonacarbonyl, and dicyclopentadienyl iron resulted in inactive systems.

The following other transition metal acetylacetonates were tested in the general catalyst system $M(acac)_X$-TEA-2-cyanopyridine: $Ni(acac)_2$, $Co(acac)_2$, $Co(acac)_3$, $V(acac)_3$, $Mn(acac)_2$, $Zr(acac)_4$, $Ce(acac)_3$, $Cd(acac)_2$, and $Zn(acac)_2$. Of these, only $Co(acac)_2$ exhibited activity, giving a 48% isoprene conversion with selectivity values of 81% and 19% to dimers and trimers, respectively. No higher molecular weight material was obtained.

Diethylaluminum chloride, ethylaluminum dichloride, phenylmagnesium chloride, di-sec-butylmagnesium, and triethylboron did not yield active catalysts when substituted for TEA. Triisobutylaluminum did result in an active catalyst system when substituted for TEA.

Reaction Conditions

Figure 3 shows a plot of the yield of polymer as a function of time at various temperatures. It is interesting to note the decline in catalytic activity with increasing reaction temperature. The rate of isoprene polymerization obeyed first-order kinetics at —23, 0, and 25°C for the first hour of reaction. However at 60°C, the rate of polymerization did not follow simple first order kinetics. The first-order rate constants obtained at these temperatures are given in Table 2. Using these data, an activation energy was determined to be —5.1 kcal/mole.

TABLE 2
FIRST ORDER RATE CONSTANTS AND ACTIVATION ENERGY FOR THE POLYMERIZATION OF ISOPRENE

Temperature (°C)	$k \times 10^3$, minutes^{-1}
−23	25.2
0	10.9
25	7.14

[a] $\Delta E = -5.1$ kcal/mole

Figure 4 shows the relationship between the polymer yield (mole % of isoprene converted to polymer) and the isoprene-to-iron mole ratio. These data were obtained from experiments carried out at —23°C for 4 hr. This figure also shows the relationship between the grams of polymer produced per

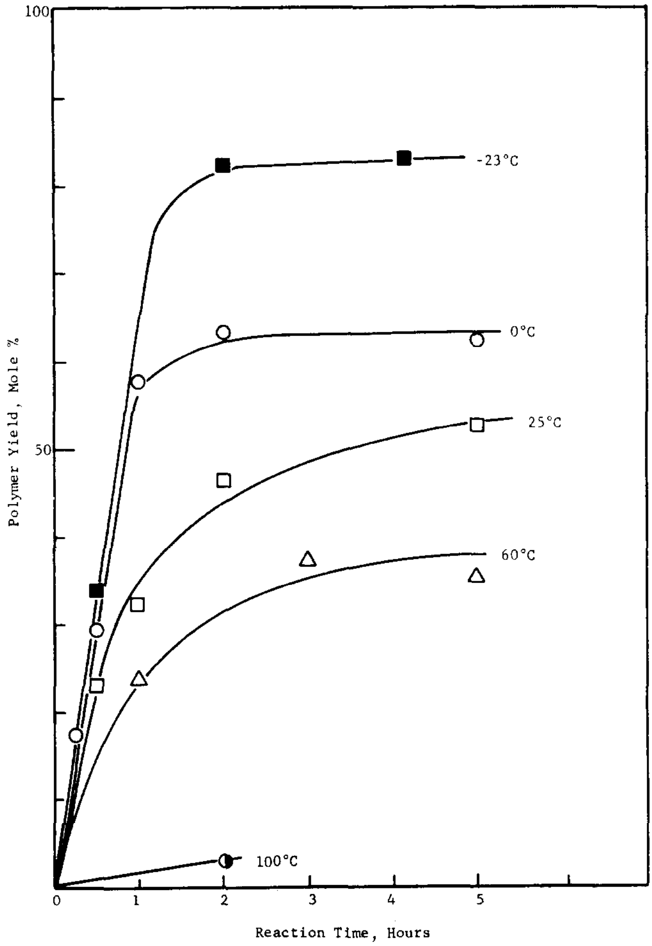


FIG. 3. Polymer yield as a function of time and temperature.

gram of $Fe(acac)_3$ as a function of the isoprene-to-iron mole ratio over this 4-hr period. The amount of polymer produced more than doubled in going from an isoprene-to-iron ratio of 200 to 700. For a given monomer-to-iron ratio, the initial rate of polymerization was fast but then the rate declined. However, addition of more isoprene increased the rate of polymerization (or the yield of polymer) and then it gradually declined again.

Table 3 gives the data obtained on aging the catalyst in the absence of isoprene. These data show that the catalyst rapidly loses activity at 25°C upon aging. At —23°C, catalyst deactivation due to aging is much slower.

TABLE 3
EFFECT OF CATALYST AGING ON ACTIVITY[a]

Aging and Reaction Temperature (°C)	Aging Time (Min)	Polymer Yield (Mole %)
25	0	45
25	15	12.5
25	60	9
−23	0	80
−23	15	80
−23	60	73

[a] 1 mmole $Fe(acac)_3$, 3 mmoles TEA, 1 mmole 2-cyanopyridine, 200 mmoles isoprene, 2 hr reaction time, for experiments carried out at 25°C. 50 ml of benzene was used, whereas for the −23°C experiments 50 ml of toluene was used.

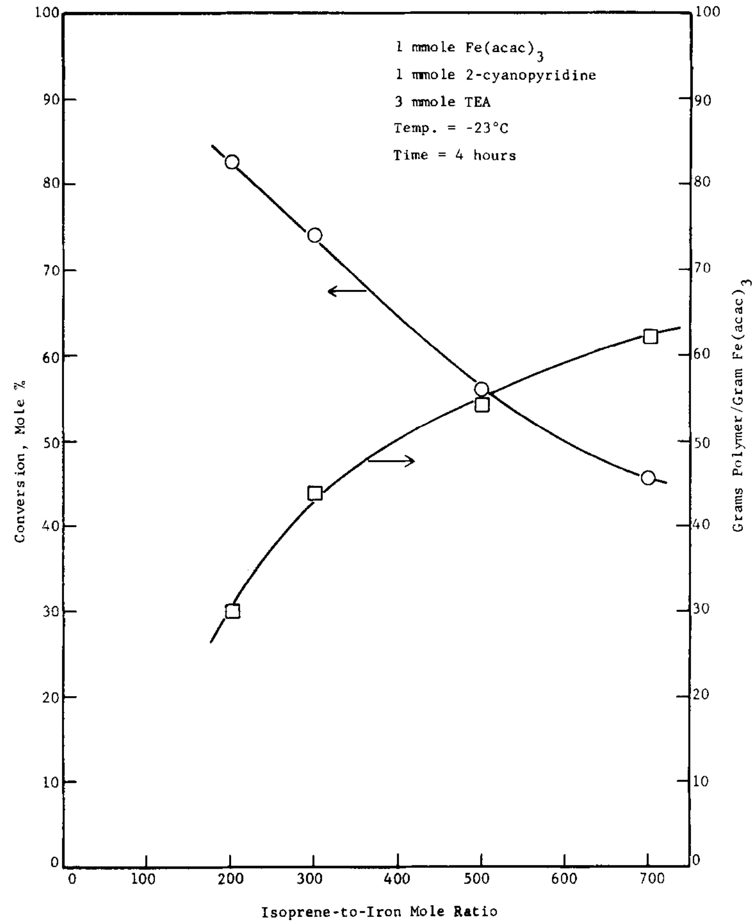


FIG. 4. Isoprene conversion as a function of the isoprene-to-iron mole ratio.

Comparable polyisoprene yields were obtained by carrying out the polymerization in benzene, dichlorobenzene, and hexane. The polymer yield decreased approximately 50% when 1,2-dichloroethane was used as the solvent.

Use of Other Monomers

The Fe(acac)$_3$-TEA-2-cyanopyridine catalyst system will homopolymerize butadiene, 1,3-pentadiene, and chloroprene. The results of some of these screening experiments are given in Table 1. This catalyst system will not homopolymerize isobutylene, 1-hexene, and styrene. It will catalyze the copolymerization of isoprene with butadiene, pentadiene, chloroprene, and styrene. The isoprene-styrene co-polymer contained approximately 18.6 mole % or 26 wt % styrene.

Nature of the Polyisoprene

Based on NMR experiments carried out at 100 MC., it was determined that the structure of the polyisoprene formed with the iron catalyst consisted of approximately 50% 3,4, 2%-3% 1,2, and the remainder *cis*-1,4. From infrared experiments, the structure of polybutadiene consisted of approximately 50% 1,2 and 50% *cis*-1,4. The number average molecular weight of the polyisoprene was determined to be 99,000 based on osmometry using toluene as the solvent. The gel percentage and dilute solution viscosity values were determined in toluene; the values were 5.2% and 1.22%, respectively.

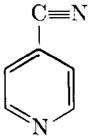
Discussion

In recent years, a considerable number of reports have been made on three-component catalyst systems for chemical synthesis (*5*). These three-component systems consist of a transition metal, reducing agent, and a complexing agent.

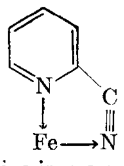
The transition metal is the most important component, for it is here that the catalysis takes place. The organic substrate coordinates with the metal via *d*-*p*π bonding and the catalytic action takes place in the coordination sphere. The metal can serve as an electron sink and/or to bring the substituents together with matched symmetry functions.

The reducing agent (such as an aluminum alkyl) functions mainly to reduce the transition metal to a lower valence state where *d*-*p*π bonding is more favorable. The aluminum alkyl or other reducing agents can also function as a polar scavenger or to alkylate the transition metal to form a metal-carbon sigma bond.

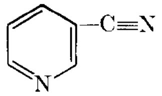
There are three major functions of a complexing agent or ligand. First, the ligand can help stabilize the transition metal in a lower valence state where *d*-*p*π bonding is highly favored. Second, the ligand is very important in directing traffic in the coordination sphere. This can be done by physically blocking one or more coordination sites and/or by changing the electron density in the *d*-orbitals which are available for bonding with an incoming substrate. Third, many ligands are better leaving groups than others and can facilitate the substitution on the transition metal of olefin or diolefin reactants.



4-cyanopyridine, inactive



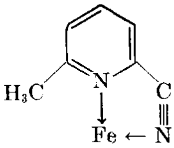
2-cyanopyridine-iron complex, active



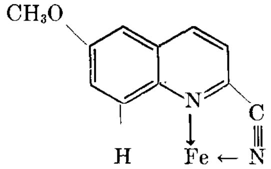
3-cyanopyridine, inactive

In this work, ligands capable of forming both sigma and pi bonds with the transition metal were investigated. An example of such a ligand is 2-cyanopyridine, with the nitrogen atom of the pyridine ring participating in mainly sigma bonding and the electronic system of the nitrile group participating in π bonding with the *d*-orbitals of the transition metal.

The first requirement for a ligand to form an active isoprene polymerization catalyst is that it must be capable of coordinating with reduced iron in two positions or function as a bidentate ligand. With 3- and 4-cyanopyridine, chelate rings cannot form and using these compounds results in inactive systems. In the structures of the iron complexes only one coordinated ligand is shown, this is reasonable because the highest activity was observed at a ligand-to-iron mole ratio of one. At higher ratios there is a sharp drop in activity (see Fig. 1). This is most likely due to coordination of another ligand at a site where isoprene would coordinate or the ligand could sterically hinder the coordination of isoprene with the desired orbitals. The low activity of the Fe(acac)$_3$-TEA-2-cyano-6-methylpyridine and Fe(acac)$_3$-TEA-2-cyano-6-methoxyquinoline systems strongly suggests a steric hindrance effect. The steric hindrance could be

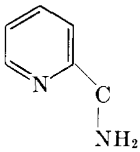


2-cyano-6 methylpyridine-iron complex, low activity

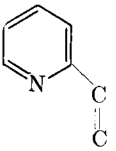


2-cyano-6-methoxyquinoline-iron complex, low activity a physical blocking or interference of the incoming isoprene.

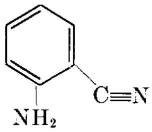
The fact that 2-aminomethylpyridine formed an inactive polymerization catalyst complex illustrates the second requirement: that side chain unsaturation is essential. However, side chain unsaturation is not the only critical part, there has to be a coordinating donor atom in the side chain since 2-vinylpyridine was not an active promoter. The necessity of having the nitrogen donor atom in the aromatic ring was verified by the fact that 2-cyanoaniline did not promote activity.



2-aminomethylpyridine, inactive

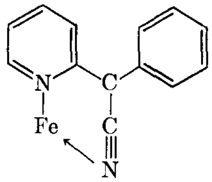


2-vinylpyridine, inactive



2-cyanoaniline, inactive

The greatest effect was accomplished with the phenyl-2-pyridylacetonitrile-iron complex, which forms a six-membered chelate ring. This shows that both six and five-membered chelate ring complexes can form active catalysts.



phenyl-2-pyridylacetonitrile-iron complex, active e

When ligands are used that are capable of mainly sigma bonding, i.e., where there is no side chain unsaturation such as 2,2′-bipyridyl and 2-aminomethylpyridine, only isoprene dimers and trimers are formed in low yields. It is known that TEA reacts with molecules containing donor atoms, such as pyridine, to form coordination complexes (*6*). Such a reaction cannot be responsible for the promoting effect reported in this paper, since molecules such as 2-vinylpyridine could coordinate with TEA as well as 2-cyanopyridine.

In this system, the ligand must have side chain unsaturation to participate in d-$p\pi$ bonding with the iron orbitals and stabilize the reduced valence state of iron. But yet the ligand has to have a donor atom in the side chain and in the aromatic ring to participate in mainly sigma bonding. Thus, it is necessary to have a critical balance of π and σ bonding in conjunction with stringent steric factors to have an active catalyst. The active center or catalyst site is probably closely approached by the iron-chelate structures shown. It has been recognized that slight changes in the structure of the ligand can have pronounced effects on the catalytic activity. For example, it has been reported (*7*) that nitrocyclic compounds having one or two methyl groups alpha to the nitrogen atom results in active catalyst systems with $TiCl_3$ for propylene polymerization; whereas, the nitrogen ligands which have no alpha methyl groups are inactive.

Saltman *et al.* (*7*) reported a mechanism for the polymerization of isoprene using $TiCl_3$-triisobutylaluminum as the catalyst. The reaction was reported to be first order in monomer concentration, with an activation energy of about 14.4 kcal/mole, at a constant Al/Ti mole ratio of 1.2, and at a constant catalyst concentration. A detailed kinetic study by Gaylord and coworkers (*8*) on the polymerization of butadiene with the same catalyst system confirmed the finding of earlier reports that the rate of polymerization on monomer disappearance can be represented by the equation

$$-dM/dt = k\,[M]^{n}\,[C]^{m}$$

where $[M]$ is the monomer concentration, $[C]$ is the active catalyst concentration with n = 1 or 2 and m = 1 and higher. The rate of monomer disappearance was found to be first order with respect to butadiene pressure when the Al/Ti mole ratio was between 1.0 and 1.6. When the Al/Ti mole ratio exceeded 2.0, the rate of monomer disappearance was found to be proportional to the square of butadiene pressure.

The polymerization of isoprene with the present iron coordination complex catalyst is first order with respect to monomer at −23, 0, and 25°C, agreeing with the previous reports. However, at 60°C the polymerization did not follow a simple kinetic order. It was quite interesting to find an anomalous temperature dependency with this catalyst system in that the rate of polymerization decreased with increasing temperature. From an Arrhenius plot, an activation energy of −5 kcal/mole was obtained. This is in contrast with reported values of 12.7 kcal for butadiene (*10*), 14.4 kcal for isoprene (*9*), and 17 kcal for propylene (*11*) using Ziegler catalyst systems. In an attempt to explain this inverse temperature effect the possible reactions with this catalyst system have to be examined.

First the $Fe(acac)_3$ is reduced and alkylated with TEA

$$Fe(acac)_3 + Al(C_2H_5)_3 \rightarrow Fe(C_2H_5)(acac) + Al(C_2H_5)(acac)_2 + C_2H_5\cdot \quad (1)$$

$$C_2H_5\cdot \rightarrow \tfrac{1}{2}C_2H_4 + \tfrac{1}{2}C_2H_6\,.$$

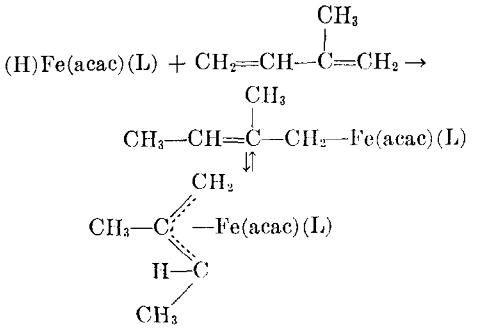
The reduced state of iron is immediately complexed with the bidentate nitrogen ligand (L), such as 2-cyanopyridine, to give a five coordinate complex

$$Fe(C_2H_5)(acac) + L \rightleftarrows Fe(C_2H_5)(acac)(L). \quad (2)$$

The five coordinate alkylated iron complex can then convert to a hydrido complex.

$$Fe(C_2H_5)(acac)(L) \rightleftarrows Fe(H)(acac)(L) + C_2H_4 \quad (3)$$

This hydrido complex can add butadiene or isoprene to form the σ complex which is in equilibrium with the corresponding π-allyl complex.



$$(H)Fe(acac)(L) + CH_2{=}CH{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2 \rightarrow CH_3{-}CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_2{-}Fe(acac)(L) \quad (4)$$

$$\rightleftarrows \quad CH_3{-}C(CH_2)(HC{-}CH_3){-}Fe(acac)(L)$$

The decrease in the rate of polymerization with increasing temperature is most likely due to a decrease in the active concentration [C]. This could happen two possible ways: first, further reduction of the iron catalyst species with TEA or any other aluminum species to form inactive lower valence iron species; or, the stability of the nitrogen ligand-iron complex could decrease with increasing temperature. The data obtained from the aging experiments shows that the active catalyst species is much more stable at lower temperatures.

The catalyst system reported in this paper gives a polymer containing approximately equal amounts of *cis*-1,4 and 3,4 structures. The *cis*-1,4 product can arise by the 1,4 addition of isoprene to the σ complex shown in (4) and both *cis*-1,4 and 3,4 additions can be obtained by the insertion of isoprene to the π-allyl complex shown in (4) at 1 and 3 positions.

The initial rate of isoprene conversion is very fast; however, the rate declines as the conversion increases. Adding more isoprene results in rate increase yielding more polymer. Again, the rate of isoprene conversion declines. This suggests that an equilibrium exists between the isoprene, catalyst and polymer. A similar phenomena has been reported by Gaylor and coworkers (*12*).

One final point of interest about this iron catalyst system is that it contains no halogen atoms. The vast majority of Ziegler-type catalysts contain halogen atoms in either the transition metal or in the organometallic part of the catalyst.

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