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Mechanism Studies of Isoprene Polymerization with the Aluminum Triisobutyl–Titanium Tetrachloride Catalyst[1]

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Analysis of the catalyst complex formed on mixing aluminum triisobutyl and $TiCl_4$ indicates that practically all the Ti is in the solid precipitate in a reduced valence state. As the amount of aluminum alkyl used increases, the solid changes from a brown $TiCl_3$ by a partial substitution of chlorine by alkyl groups. The rate of isoprene polymerization is strongly dependent on the Al/Ti mole ratio and shows a maximum rate at equimolar Al/Ti to give a rubbery product and a secondary maximum at 0.33 Al/Ti which produces a resinous polymer. The reaction is first order in monomer concentration with an activation energy of about 14,400 cal./g. mole at constant Al/Ti ratio and constant catalyst level. The over-all reaction appears to be proportional to [monomer] [Al alkyl] [$TiCl_4$] which is in agreement with a Langmuir–Hinshelwood type of mechanism.

Introduction

Since the first introduction of the aluminum alkyl–titanium tetrachloride catalysts for the low pressure polymerization of ethylene,[2] an extensive literature has appeared on the preparation of various linear and stereospecific polymers, and there is now a large and continually growing list of catalysts which are suitable for polymerization of α-olefins. The number of catalysts suitable for dienes is somewhat smaller. Of these, many give olefin-like, *i.e.*, 1,2-addition; only three systems have been disclosed which claim to result in a high *cis*-1,4 content with isoprene: Li,[3] LiR,[4] AlR_3 plus $TiCl_4$.[5] As a *cis*-1,4-polyisoprene is the counterpart of natural Hevea rubber, much of our interest has centered on its preparation. This report concerns an investigation into the nature of the aluminum alkyl–$TiCl_4$ catalyst and kinetic studies of the mechanism of isoprene polymerization using this catalyst system.

There appear to be several differences between the AlR_3–$TiCl_4$ system as applied to olefins and as applied to isoprene. For example, reference is often made to mole ratios of AlR_3 to $TiCl_4$ of anywhere from 2 to 10 for use in olefin polymerization. We find this area quite unrewarding. Natta in his careful studies[6] on the kinetics of propylene polymerization with $TiCl_3$ and triethylaluminum (TEA) showed the rate of polymerization to be dependent on temperature, monomer and $TiCl_3$ but independent of the TEA concentration. With $TiCl_4$ and isoprene we do find such a dependence. Using the $TiCl_3$–AlR_3 system and high purity isoprene we have been unsuccessful in obtaining satisfactory *cis*-1,4 polymer, and Natta[7] has reported preparation of a *trans*-1,4-polyisoprene from technical (80%) isoprene. Few kinetic data have been reported for the catalyst combination of $TiCl_4$ and AlR_3. Yields reported by Ziegler[8] with ethylene imply low rates at low Al/Ti mole ratios which increase and level off at mole ratios of 0.5 and higher. McGowan and Ford,[9] using $TiCl_4$ and butyllithium (or dibutylzinc), found the rate of polymerization to be proportional to the $TiCl_4$ concentration and to the square of the ethylene pressure. Above a certain concentration of alkyl the rate was independent of the alkyl concentration. Ludlum and co-workers,[10] using $TiCl_4$ and two aluminum alkyls, found the rate to be first order in ethylene and $TiCl_4$ but obtained a maximum in the rate on varying the Al/Ti mole ratio. Adams and co-workers[11] reported on the isoprene–AlR_3–$TiCl_4$ system and showed a similar maximum. The nature of the active species in the catalyst system has been examined by several investigators. Ziegler[12] has remarked that the solid precipitate formed when $TiCl_4$ and TEA are mixed contained equal amounts of Ti(II) and Ti(III). Mackey[13] found variable liquid and solid analyses for equimolar mixtures of TEA and $TiCl_4$. The brown precipitate is only slightly paramagnetic indicating its difference from the violet $TiCl_3$ which is paramagnetic. Natta[14] has reported that the solid formed at 60° varies in composition as the TEA/$TiCl_4$ ratio varies. As this ratio increases, the Cl/Ti ratio in the solid decreases while the Al/Ti ratio increases. Ludlum reports a decrease in the average Ti valence state as the Al/Ti ratio increases.

Friedlander[15] was able to polymerize ethylene with the reaction product of $TiCl_4$ and ethyllithium. Based on the gases evolved in the catalyst reaction (equivalent amounts of ethane and ethylene), he postulated a reaction scheme which produced $TiCl_3$. Several other active catalyst species besides $TiCl_3$ also have been proposed[16] which involve reaction schemes and unstable intermediates of alkyl substituted di-, tri- or tetravalent titanium halides or complexes of titanium halides and the

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[1] A portion of this paper was presented at the Gordon Research Conference on Elastomers, August 1, 1957.

[2] K. Ziegler, E. Holzcamp, H. Breil and H. Martin, *Angew. Chem.*, **67**, 541 (1955); K. Ziegler, Belgium Patent 533,362 (Nov. 16, 1954).

[3] F. W. Stavely and co-workers, *Ind. Eng. Chem.*, **48**, 778 (1956).

[4] H. Hsieh and A. V. Tobolsky, *J. Polymer Sci.*, **25**, 245 (1957); Italian Patent 559,704 (Sept. 18, 1956) to Firestone Tire & Rubber Co.

[5] Belgium Patent 543,292 (Dec. 2, 1955) to Goodrich-Gulf Chemicals Co.

[6] G. Natta, I. Pasquon and E. Giachetta, *Angew. Chem.*, **69**, 213 (1957); *Makromol. Chem.*, **24**, 258 (1957).

[7] G. Natta, L. Porri and G. Mazzanti, Belgium Patent 545,952 (Sept. 10, 1956).

[8] K. Ziegler, Belgium Patent 540,459 (Feb. 9, 1956).

[9] J. C. McGowan and B. M. Ford, *J. Chem. Soc.*, 1149 (1958).

[10] D. B. Ludlum, A. W. Anderson and C. E. Ashby, This Journal, **80**, 1380 (1958).

[11] H. E. Adams, R. S. Stearns, W. A. Smith and J. L. Binder, paper presented before the Division of Rubber Chemistry at the 132nd National Meeting of the American Chemical Society, New York, N. Y., October 13, 1957.

[12] K. Ziegler, *Angew. Chem.*, **68**, 581 (1956).

[13] J. C. Mackey, paper presented before the Akron Polymer Lecture Group, November 1, 1957.

[14] G. Natta, International Meeting on Chemistry of Coördination Compounds, Rome, September 15–21, 1957.

[15] H. N. Friedlander and K. Oita, *Ind. Eng. Chem.*, **49**, 1885 (1957).

[16] C. D. Nenitzescu, C. Huch and A. Huch, *Angew. Chem.*, **68**, 438, 581 (1956); K. Ziegler, Belgium Patent 543,259 (Nov., 1955).

aluminum alkyl. Natta[17] has prepared a stable, soluble and recrystallizable cyclopentadienyl–titanium–aluminum compound but was successful only in polymerizing ethylene with it.

The kinetics of the $TiCl_4$–triisobutylaluminum (TIBA) reaction was reported by Feldman and co-workers.[18] They showed that the titanium present is reduced to the trivalent state quite rapidly. Depending on the starting molar ratio of the components, more than one isobutyl group may be involved in the reduction. With an Al/Ti mole ratio of 1.2, the reduction to Ti(III) was over 90% complete in 20 minutes. On the basis of their results, Feldman proposed the reaction scheme

$$AlR_3 + TiCl_4 \longrightarrow TiCl_3 + AlR_2Cl + R\cdot$$
$$AlR_2Cl + TiCl_4 \longrightarrow TiCl_3 + AlRCl_2 + R\cdot$$
$$AlRCl_2 + TiCl_4 \longrightarrow TiCl_3 + AlCl_3 + R\cdot$$

Experimental data on the fate of R· have been reported by Friedlander and Oita[15] and Ludlum and co-workers.[10] The reduction of titanium is so rapid that any quadrivalent intermediates such as $TiCl_3R$ must be too short lived to serve as an active catalyst species.

Ziegler[2] has reported that when the liquid and the brown solid portions of the TEA–$TiCl_4$ mixture are separated, the solid (of undefined composition) will not polymerize ethylene. When we separated the solid and liquid portions of the 1:1 Al/Ti reaction, neither solid nor liquid is catalytically active with isoprene. When recombined, however, isoprene polymerization proceeds normally. Thus neither portion alone is active and both components are required.

Early in our work we observed that a number of ethers, notably dimethoxyethane, when injected into a AlR_3–$TiCl_4$ catalyst suspension caused an immediate agglomeration of the solid precipitate. On analysis of the filtered solid, evidence for the formation of an ether complex with the titanium halide was obtained. Since etherate complexes of the titanium tetrahalides were studied by Sisler and his co-workers,[19] the analysis of these solids appeared to be an alternate method for studying the composition of the catalyst formed at various Al/Ti ratios.

Experimental

Preparation of Materials.—There are very high purity requirements for reproducible experimental work with this catalyst system. Traces of water, air, polar and many unsaturated compounds affect the activity of the catalyst and the consequent rates of isoprene polymerization. In this study the solvents used were Phillips Pure grade (or better) heptane and pentane. The isoprene was also Phillips Pure grade (99%+). The TIBA, from Hercules Powder Co., analyzed 13.7% Al, corresponding to >98% TIBA, the remainder being the diisobutyl hydride. The $TiCl_4$ was 99.5% material from the Matheson Co. Both catalyst components were used without further purification. The nitrogen was lamp-grade.

The solvents were washed with sulfuric acid, then water, dried over calcium sulfate and distilled. They were stored over sodium until needed. The isoprene was distilled, passed through a column containing potassium hydroxide, calcium sulfate and silica gel and 0.02% wt. of *t*-butylcatechol added. It was thus stored until required and redistilled just prior to use.

The catalyst components were diluted in a dry-box with the appropriate nitrogen-flushed solvent to make about 0.3 molar solutions and stored in sealed bottles until used.

Catalyst Analyses.—Enough of the catalyst slurry was prepared to make about 1–2 g. of the brown solid by mixing various amounts of pentane solutions of TIBA and $TiCl_4$ in mole ratios of 0.33 to 3.0. The mixtures were periodically shaken while standing at room temperature from 5 to 33 days. They were filtered and the precipitates washed five times with pentane, dried under a stream of nitrogen and under vacuum. All operations and transfers were under nitrogen. The solid and liquid were analyzed for Ti (*via* Jones reductor) and Cl (as AgCl). The Ti analyses are thus for total Ti regardless of valence. The results given (Table I) are the average for two samples. There was no apparent correlation between variations in analyses and the sample age.

In most cases the precipitates may be handled satisfactorily on a medium frit filter, indicating precipitate agglomerates larger than 10–15 μ. At Al/Ti ratios higher than 3 the particle size becomes finer and more and more solid passes through the filter. Thus, above 3.0 Al/Ti we were unable to obtain complete separation of the solid and liquid portions.

Etherates.—Mixtures of TIBA and $TiCl_4$ were prepared at mole ratios of Al/Ti from 1 to 4 and allowed to age for about 48 hours. An excess of 1,2-dimethoxyethane or dioxane was injected and the entire mixture allowed to age for an additional 72 hours. The solid was filtered, washed several times with pentane and dried under vacuum. The filtrate and solid were then analyzed separately for titanium and chloride. Practically all of the titanium was in the solid; the amount in the filtrate was 1% or less of that charged. The yield of solid decreased as the Al/Ti ratio used in catalyst formation increased. It is noteworthy that the dried complexes obtained at Al/Ti ratio of 3 or 4, particularly the latter, decompose vigorously in water with evolution of gas indicating the possible presence of divalent titanium. At the same time a significant amount of black material, probably titanium metal, was found which dissolved slowly in dilute sulfuric acid.

Bottle Polymerizations.—These were carried out in 4 or 8 oz. screw-cap bottles with isoprene and solvent flushed thoroughly with nitrogen before sealing the bottle. The appropriate amounts of the catalysts were then added through the perforated bottle caps which had been backed with self-sealing rubber gaskets. Indicative of the effect of trace impurities was our early difficulty in reproducing polymerization results finally traced to extractable matter in these gaskets. After tumbling in a constant temperature bath for the desired time, the reaction was stopped by adding the bottle contents to a large excess of 2-propanol. The solid polymer was then dried under vacuum and weighed.

Analyses of the solvent–isoprene mixtures used in this way generally showed less than 10 p.p.m. of water and 5 p.p.m. of oxygen. This was satisfactory for the catalyst analyses and for polymerizations at high conversions and long reaction times. For short reaction time work (2 hours or less) the induction periods (15–60 min.) were still variable enough with this technique to constitute an appreciable fraction of the reaction time. This made the variability in apparent rate great enough so as to be unsatisfactory for obtaining low conversion kinetic data. To obtain such data it was necessary to use a completely sealed system.

Catalyst mixtures for analysis and mixtures with ethers were prepared as for the bottle polymerizations except that the monomer was omitted.

Kinetic Measurements.—These polymerizations were carried out in 500-ml., three necked, round bottom flasks fitted with a stirrer, through an air-tight seal, an inlet-sampling tube and an outlet tube. All equipment coming into contact with the reactants was thoroughly cleaned, rinsed with distilled water and dried 24–48 hr. at 120° before use. The equipment was removed from the oven hot, assembled and allowed to cool in a nitrogen atmosphere. The desired quantities of heptane and isoprene (prepurified

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[17] G. Natta, P. Pino, G. Mazzanti, H. Giannini, E. Mantica and M. Peroldo, *Chim. e ind.*, **39**, 19 (1957); G. Natta, P. Pino, G. Mazzanti and U. Giannini, THIS JOURNAL, **79**, 2975 (1957).

[18] C. F. Feldman, L. C. Arnold and D. W. McDonald, paper presented at the 131st National Meeting of the American Chemical Society, Miami, Florida, April, 1957.

[19] P. M. Hamilton, R. McBeth, W. Bekebrede and H. H. Sisler, THIS JOURNAL, **75**, 2881 (1953); R. F. Rolsten and H. H. Sisler, *ibid.*, **79**, 1068 (1957).

as above) were distilled directly into the flask while maintaining the nitrogen atmosphere. The flask was then capped and removed to a thermostated water-glycerol bath maintained at the desired temperature ±0.05°. After temperature equilibrium had been established, *n*-heptane solutions of the catalyst components were added. Sufficient agitation was used to effect adequate heat transfer between the reactants and the bath medium. Sampling was accomplished through use of a stainless steel tube which could slide in and out of the reaction solution through an air-tight seal. A hypodermic syringe was fitted to this tube so that samples of the solution could be removed. The course of the reaction was followed by the gain in solids after evaporation of monomer and solvent and correcting for the catalyst residue. This method of sampling gave quite reproducible data provided large enough samples were withdrawn (*ca.* 5 ml.) and provided also that the solution was not too viscous. At higher conversions (*e.g.*, >35%) and high monomer/solvent ratios (>0.3) this method did not give accurate data. Consequently, the range in concentration and extent of reaction in this study is bounded by these limits. The range studied in temperature and concentration of reactants was: temperature, from 0 to 20°; monomer concentration, from 0.25 to 2.00 moles/l.; catalyst concentration, from 3.50 × 10^{-3} to 2.80 × 10^{-2} mole/l. The catalyst mole ratio was held constant at 1.20 Al/Ti.

Discussion and Results

Catalyst Composition.—The yield of precipitate obtained per mole of $TiCl_4$ charged depends on the Al/Ti mole ratio as shown in the lower curve of Fig. 1. The filtrate still contains titanium in minor amounts which qualitatively correspond to the expected lower rate of Ti reduction with lesser amounts of aluminum alkyl. Assuming this titanium is simply *as yet unreacted* titanium, the calculated yield of solid per mole of $TiCl_4$ consumed is shown in the upper curve of Fig. 1. This assumption appears valid since, at 0.33 Al/Ti, the Cl/Ti ratio in the filtrate is 3.97.

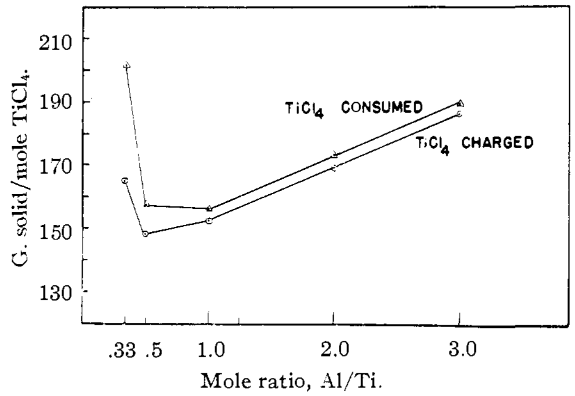

Fig. 1.—Variation in yield of solid per mole $TiCl_4$ obtained from catalysts formed from different Al/Ti charge ratios. Lower curve shown is per mole $TiCl_4$ charged; upper curve per mole $TiCl_4$ consumed. Average deviation of yield for duplicate samples, ±2%.

In view of the high yield of solid even at low Al/Ti ratios, the reaction must be one that can consume three moles of $TiCl_4$ per mole of TIBA. From that aspect our results appear consistent with Feldman's[18] proposed reaction scheme given above. The soluble mono- and dichloroaluminum alkyls will not appear in the precipitate but the insoluble $AlCl_3$ will. Thus the weight of solid obtained at 0.33 Al/Ti is higher than at the higher ratios. At 0.33 Al/Ti we obtain 202 g. of solid/mole $TiCl_4$ consumed (theory, 198.5 for $AlCl_3 \cdot 3TiCl_3$), which analyzes as $AlCl_3 \cdot 3Ti_{0.97}Cl_{2.68}$. At 0.5 and 1.0 Al/Ti the yield drops to 156, 157 g./mole $TiCl_4$ (theory, 154 for $TiCl_3$).

At still higher Al/Ti ratios (above 1.0), the yield of solid again increases but the fraction accountable as Ti and Cl decreases because heavier isobutyl groups are being substituted for chlorine.[20] This substitution is also confirmed by the decrease in the Cl/Ti mole ratio with increasing Al/Ti ratios shown in Fig. 2. There may be reduction to Ti(II) but no evidence for it was found.

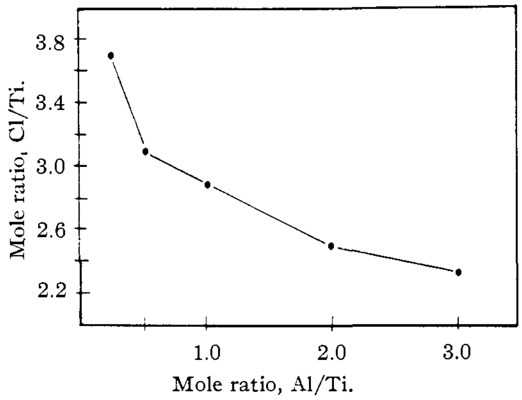

Fig. 2.—Variation in Cl/Ti mole ratio in the solid portion of catalysts formed from different Al/Ti charge ratios. Points represent average of duplicate samples; average deviation, ±0.1 Cl/Ti unit.

Natta's data[14] indicate that at higher temperatures this displacement of chlorine takes place more completely than we find for the room temperature reaction. At 2.0 Al/Ti, he finds the solid Cl/Ti ratio to be 2 while at 3.0 Al/Ti the Cl/Ti ratio is about 1. We do not, however, confirm the finding of appreciable amounts of aluminum in the precipitate (see Table I).

TABLE I

ANALYTICAL DATA ON SOLID FROM TIBA–$TiCl_4$ REACTION[a]

Al/Ti mole ratio	Ti, %	Cl, %	Al,[c] %	C,[c] %	H,[c] %
0.33	23.7	65.3	4.4	...	...
0.50[b]	30.4	69.7	...	...	...
1.0	30.0	64.0	42 p.p.m.	5.12	1.18
2.0	27.4	50.8	700 p.p.m.	8.35	1.53
3.0	25.2	42.1	700 p.p.m.	12.20	3.29

[a] Results are averages of duplicate samples. Average (±) deviations: Ti, 0.4%; Cl, 1.2%. [b] Theory for $TiCl_3$: Ti, 31.0%; Cl, 69.0%. [c] Analysis by U. S. Testing Co., Hoboken, N. J.

Thus, for Al/Ti ratios above 1.0 we favor the reaction sequence

$$TiCl_4 + AlR_3 \longrightarrow TiCl_3 + AlR_2Cl + R\cdot$$
$$TiCl_3 + AlR_3 \longrightarrow TiCl_2R + AlR_2Cl$$
$$TiCl_2R + AlR_3 \longrightarrow TiClR_2 + AlR_2Cl, \text{ etc.}$$

More than one of these reactions may occur simultaneously once the solid phase is formed due to

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(20) This is indicated by the Al, C and H analyses in Table I. Unfortunately the analyses were delayed some time and some decomposition appears to have occurred. They are quoted to indicate that the increase in yield is due to alkyl substitution rather than to complexing with any aluminum compound. Any complexes of the solid with TIBA apparently may be broken readily by complete washing of the solid.

local variations in concentration in the now-heterogeneous system. Thus, it is likely that some $TiCl_2R$ begins to form even below Al/Ti ratios of 1.0 and that the reactions at higher ratios proceed incompletely and mainly on the surface of the solids. The reaction apparently is not slow but nevertheless superficial, since on addition of TIBA to the isolated 1.0 Al/Ti solid (brown in color) the color immediately becomes black, the normal color found with the solids formed at higher Al/Ti ratios.

Although the solid formed at 0.5 Al/Ti corresponds well in analysis to $TiCl_3$, it apparently is a labile or higher energy form than the normal commercial violet product. Although Bock and Moser[21] in 1914 prepared a brown $TiCl_3$ in a silent electric discharge, no further work seems to have been published on the product prepared in this way. Mackey[13] recently has reported on other remarkable differences between the properties of the violet $TiCl_3$ and the brown solid formed by the TIBA–$TiCl_4$ reaction.

In the presence of dimethoxyethane (DME), the solid isolated from the AlR_3–$TiCl_4$ reaction is a green complex which (at 1.0 Al/Ti) appears to be a mixture of $TiCl_3$·DME and $TiCl_3$·2DME. The complexes obtained at higher Al/Ti ratios are difficult to assess because of the variety of species which are possible. The indications are, however, that the ether not only complexes with the solid but facilitates further reaction or reduction of the titanium alkyl halide with the excess AlR_3. Dioxane appears to act in an analagous fashion. When $TiCl_3$ (violet) was treated with DME, a blue complex was obtained which also appeared to be a mixture of $TiCl_3$·DME and $TiCl_3$·2DME. With $TiCl_2$, there was only a slight change in composition which could have resulted from the presence of small amounts of $TiCl_3$ or $TiCl_4$ in the dichloride. It appears reasonable to assume that $TiCl_2$ does not form an etherate under these conditions.

Polymerization

Effect on the Al/Ti Ratio.—When isoprene is polymerized in heptane using constant amounts of $TiCl_4$ and varying amounts of TIBA, the yield of solid polymer obtained varies as shown in Fig. 3.

In both series shown, with no TIBA present no solid polymer was obtained under these conditions. However, at higher temperatures and longer reaction times some resinous product may be formed. At Al/Ti ratios of about 0.2 to 0.3, the polymerization product is a powdery cross-linked material mainly insoluble in benzene. Infrared examination indicates a mixed micro-structure similar to that obtained by Richardson,[22] although our rates are appreciably slower.[23] The smaller maximum in the yield curve at the 0.33 Al/Ti mark doubtless is due to the presence of $AlCl_3$ in the catalyst solid.

As the Al/Ti ratio increases past 0.33, the extent of polymerization drops again. It is only in the neighborhood of 1.0 Al/Ti ratio that appreciable yields of solid, rubbery polymer are obtained. As the Al/Ti ratio increases toward 1.0, the amount of benzene insoluble material decreases. Infrared investigation of the materials formed in this region show an increasing *cis*-1,4-content in the polymer, to the point that at equimolar ratios of Al and Ti, the product is essentially a *cis*-1,4-polyisoprene.

At still higher Al/Ti ratios the yield of solid polymer again decreases. There is, however, a small yield of low molecular weight oil formed under these conditions. For example, at 2.5 Al/Ti where practically no solid product is formed, distillation of the reaction mixture indicates that about 24% of the isoprene monomer has been converted to high boiling liquids. The remainder was recovered as unreacted isoprene. At Al/Ti ratios of the order of 1.0, only minor amounts of liquid products can be formed, since almost quantitative yields of solid polymer readily are obtained. Thus, although the drop in total yield is not quite as sharp as shown in Fig. 3, the decrease in yield with increasing Al/Ti ratios is nevertheless confirmed.

Effect of Monomer Concentration.—The change in micro-structure of polyisoprene as a function of the variation in monomer and catalyst concentrations and temperature were not studied rigorously as a part of the program. Other studies in our laboratories, however, have not shown a dependence of micro-structure on the concentrations of either monomer or catalyst. The Al/Ti ratio in the catalyst does affect the micro-structure and, as mentioned above, a particular molar ratio of 1.20 was used for all catalyst formulations. Adams, *et al.*,[11] working with a system similar to this, have shown only a slight change in micro-structure with temperature, within the temperature range studied here. It will be assumed that the stereospecific nature of the reaction is independent of these variables (aside from the Al/Ti ratio) within the ranges studied and that the rates measured in each case refer to essentially the same processes.

Figure 4 represents a typical reaction curve obtained in this work. The degree of reproducibility between experiments is indicated by the fit of points from replicate runs. At a given catalyst concentration and temperature, the rate of reaction, in % conversion per minute at any time, was found to be independent of the initial monomer concentration. This, together with the fact that the plots in Fig. 5 are linear, indicates that the reaction is first order in monomer. In order to compare the relative velocities of the reaction at either constant catalyst concentration or temperature, it is convenient to introduce a parameter r_{m}, the index for the disappearance of monomer. This parameter, calculated from the slope of the monomer disappearance curve, is analogous to a rate constant for the reaction at constant temperature and catalyst level. Comparisons of the rate dependency on the variation in these latter two variables then can be

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(21) F. Bock and L. Moser, *Monatsh.*, **33**, 1407 (1913); **34**, 1825 (1914).

(22) W. S. Richardson, *J. Poly. Sci.*, **13**, 325 (1954).

(23) The yield of resin from equivalent amounts of synthetic mixtures of catalysts are in the order: $AlCl_3$ + brown (1.0 Al/Ti) solid > $AlCl_3$ + $TiCl_3$ (violet) > $AlCl_3$ > brown solid > $TiCl_3$ (violet). These results show agreement with the behavior expected at the smaller maximum found in Fig. 3, at the 0.33 Al/Ti ratio. The higher rates obtained by Richardson may be attributed to the solubilization of the $AlCl_3$ due to the presence of ethyl bromide or other polar solvents in his reaction mixtures.

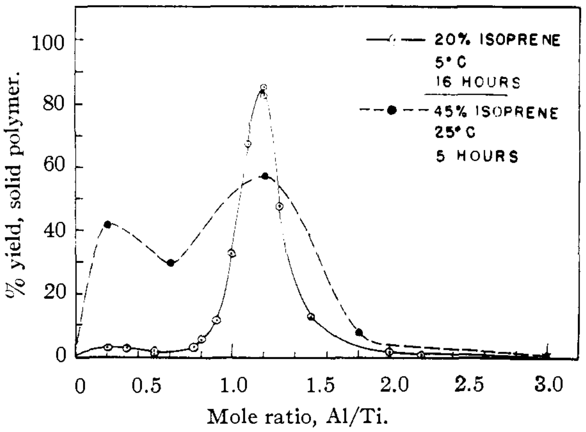

Fig. 3.—Yield of solid polyisoprene obtained from catalysts formed at different Al/Ti ratios; TiCl$_4$ concentration held constant while varying TIBA concentration.

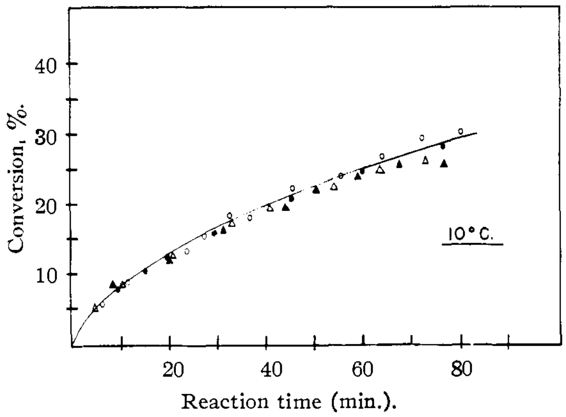

Fig. 4.—Typical reaction rate curve at 10°. Monomer concentration 1.00 mole/l., TIBA concentration 7.96 × 10^{-3} mole/l., TiCl$_4$ concentration 6.64 × 10^{-3} mole/l. Different symbols represent replicate runs.

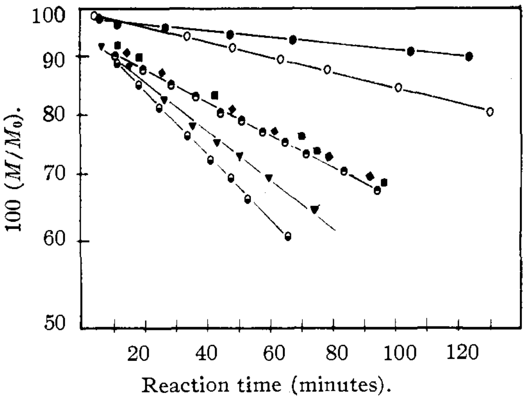

Fig. 5.—Monomer disappearance curves at various temperatures and initial monomer levels. TIBA concentration 7.96 × 10^{-3} mole/l., TiCl$_4$ concentration 6.64 × 10^{-3} mole/l: ●, 0°; ○, 5°; ■, ◆ and ◓, 10°; ▼, 15°, ◒, 20°. Reactions at 10° show effect of varying initial monomer concentration from 0.50 to 2.00 moles/l. For runs at other temperatures monomer concentration is 1.00 mole/liter.

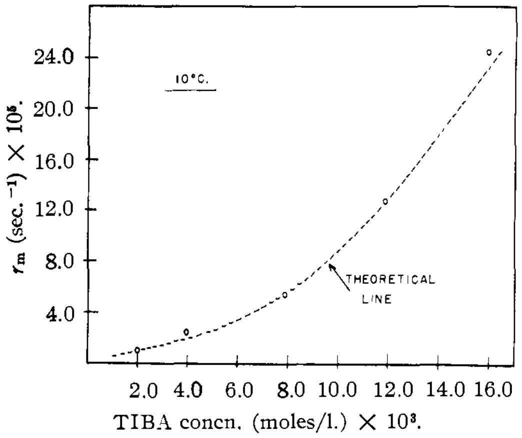

Fig. 6.—Monomer disappearance index *versus* TIBA concentration at 10°. Monomer concentration = 1.00 mole/l., Al/Ti molar ratio = 1.20. Values of r_m were calculated from the slopes of the monomer disappearance curves described in the text. The broken line is the curve drawn for r_m = 0.760[M][TIBA][TiCl$_4$].

made from variations in r_m with temperature or catalyst level.

In general, it was found that the semi-log plots shown in Fig. 5 did not extrapolate back through the 100% monomer mark at zero time. There generally appeared to be a residual reaction amounting to 2–5% conversion. This is thought to be due to initial heat effects caused by the addition of catalyst components.

Effect of Catalyst Concentration.—Polymerizations carried out at 10° using constant initial monomer levels and differing initial catalyst levels show a strong dependency of reaction velocity on the concentration of catalyst. The monomer disappearance curves, plotted as above for each initial catalyst level, are linear with time. Values of r_m calculated from these curves appear in Table II. The rate appears to be a function of the product of the two initial catalyst concentrations.[24] This dependency on the product of the catalysts level is demonstrated in Fig. 6, where the index for monomer disappearance, r_m, is plotted for several different initial catalyst levels. The data at 10° may be represented adequately by

$$r_m = 0.760\ [M][Al][Ti]$$

All of the reactions were carried out with the catalyst formed *in situ* (*i.e.*, the solutions of TIBA and TiCl$_4$ were added separately to the isoprene–heptane mixtures). Some data have been presented by other authors indicating that *in situ* preparations may be significantly higher in activity than preformed catalysts. Mackey[13] has reported that in the polymerization of α-olefins with AlR$_3$ and TiCl$_4$, *in situ* preparations are up to five times more active than the corresponding preformed catalysts. Relatively little is known concerning specific surface values for these two types of catalysts, but the possibility of forming larger particle size catalyst dispersion with the preformed types seems quite likely. Some microscopic observations of preformed catalysts at our laboratories indicated particles in the order of 0.1 to 1.0 μ in

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[24] The necessity for carrying out these reactions at a fixed Al/Ti ratio of 1.20 does not allow differentiation between the product of [Al][Ti] and [Al]^2 or [Ti]^2. However, theory indicates the product [Al][Ti].

diameter which formed clumps or aggregates about 15 to 20 μ in diameter. This would of course result in a significant decrease in specific surface. The reproducibility of our rates indicates that the catalysts formed *in situ* were not subject to significant variations in specific surface within the concentration ranges studied here.

Effect of Temperature.—Polymerizations were run at various constant temperatures to determine the over-all activation energy for the reaction at a constant initial catalyst level. From the monomer disappearance curves at these temperatures (Fig. 5), values of the index r_m were calculated. The logarithms of these indices were then plotted *versus* the reciprocal absolute temperature and from the slope the activation energy for the over-all process (at a constant catalyst level) was found to be 14.4 kcal./mole. This value is quite in keeping with the value reported by Natta[6] of 12.0 to 14.0 kcal./mole for propylene polymerization. Since the free radical polymerization of isoprene has an activation energy probably in the order of 20 to 30 kcal./mole, this is another indication of the ionic nature of the AlR_3–$TiCl_4$ catalyst system. A summary of our kinetic data is shown in Table II.

Molecular Weight.—A thorough study of the variation in the molecular weight of polyisoprene with the reaction variables was not attempted, due primarily to the formation of small amounts of crosslinked or gelled polymer under most conditions.

This, in addition to the fact that the nature of the cross-linking reaction is as yet unknown, precludes at this time more than qualitative observations of the system. Figure 7 shows the general variation in ln η_r/c (inherent viscosity) with conversion. The inherent viscosity increases with conversion to a point, then appears to level off. Diem, *et al.*,[25] have reported for the lithium catalyzed polymerization of isoprene, that the molecular weight of the polymer increases linearly with conversion to the point that the viscosity of the system affects the monomer diffusion rate. Adams *et al.*,[11] report further that in the AlR_3–$TiCl_4$ catalyzed polymerization of isoprene higher molecular weights are obtained at lower polymerization temperatures.[26]

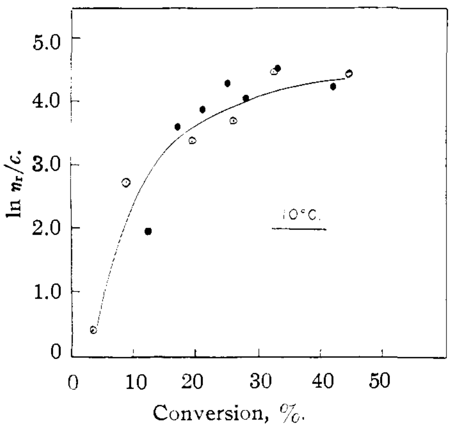


Fig. 7.—Increase in inherent viscosity with conversion at 10°. The inherent viscosities were measured at sufficiently low concentrations so as to give a reasonable approximation of the intrinsic viscosity. Monomer concentration 2.00 moles/l.; TIBA concentration 7.96 × 10^{-3} mole/l.; Al/Ti molar ratio = 1.20.

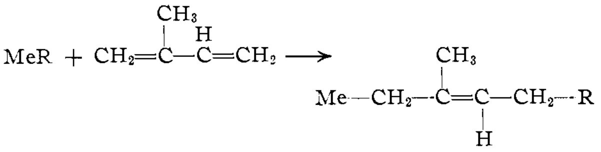
TABLE II

SUMMARY OF KINETIC DATA ON TIBA–$TiCl_4$–ISOPRENE SYSTEM

Monomer concn. (moles/l.)	TIBA[a] concn. (moles/l.) × 10^3	Temp. (°C.)	r_m (sec.$^{-1}$)[b] × 10^6
1.00	7.96	0	2.90
1.00	7.96	5	3.70
1.00	7.96	10	5.50
1.00	7.96	15	8.90
1.00	7.96	19	11.80
1.00	7.96	20	13.2
1.00	1.99	10	1.20
1.00	3.98	10	2.50
1.00	11.9	10	12.8
1.00	15.9	10	24.6
2.00	7.96	10	4.8
0.25	7.96	10	5.6

[a] All reactions were carried out at an Al/Ti molar ratio of 1.20. [b] r_m values shown are the average values of at least 3 and generally several runs. Experimental error is in the order of ±10%.

Reaction Mechanism.—The only reaction mechanism for polymerization proposed in any detail is that originally due to Natta.[27] His mechanism is anionic with attack of the monomer on one of the several metal alkyls described above. Natta has not described a mechanism for dienes, but the Natta mechanism as adapted for isoprene is shown (MeR is metal alkyl)



$$MeR + CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}\overset{H}{C}{=}CH_2 \longrightarrow Me{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}{=}\underset{\underset{H}{|}}{C}{-}CH_2{-}R$$

Since $-CH_3$ is electron donating, it is likely that the isoprene heads in as shown rather than with the $-CH_3$ on the third carbon. Hyperconjugation should lead to electron shifts assisting its entry in this fashion.

Sterically, this entry is also favored since the methyl group might be expected to find more room near the small metal ion rather than near the alkyl group attached to the metal. Having started in that way, it is apparently very difficult to react as an olefin, since there is little room for 1,2-addition. In polymerizing isobutylene with the Ziegler system, the same difficulty arises and only low molecular weight products (with possible rearrangement) are obtained.[28] In the *cis*-polyisoprene system *no* 1,2-addition is found, whereas there does appear to be 2–4% of 3,4-polymer formed. This may arise out of the reverse presentation of the monomer to the catalyst. When the opposite end of the isoprene unit attaches to the metal, the addition is olefin like (*i.e.*, 3,4) rather than 1,4. Since

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(25) H. E. Diem, Harold Tucker and C. F. Gibbs, paper presented before the Division of Rubber Chemistry at the 132nd National Meeting of The American Chemical Society, New York, N. Y., October 13, 1957.

(26) See also ref. 5.

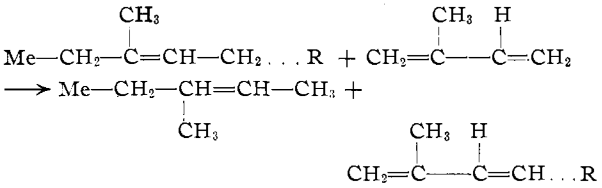
(27) G. Natta, *Angew. Chem.*, **68**, 393 (1956).

(28) A. Topchiev, *Doklady Acad. Nauk, SSSR*, **111**, 121 (1956).

this approach is not favored, only a few per cent. of 3,4 is formed.

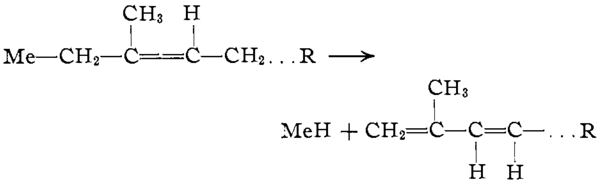
The polymerization continues with each new monomer unit inserting itself between the metal carbon bond. Termination is either by internal or external transfer of *hydride* ion

Transfer: (External)



$$\mathrm{Me{-}CH_2{-}\underset{|}{\overset{CH_3}{C}}{=}CH{-}CH_2\ldots R + CH_2{=}\overset{CH_3}{C}{-}\overset{H}{C}{=}CH_2 \longrightarrow Me{-}CH_2{-}\underset{CH_3}{CH}{=}CH{-}CH_3 + CH_2{=}\overset{CH_3}{C}{-}\overset{H}{C}{=}CH\ldots R}$$

Hydride formation: (Internal)



$$\mathrm{Me{-}CH_2{-}\overset{CH_3}{C}{=}\overset{H}{C}{-}CH_2\ldots R \longrightarrow MeH + CH_2{=}\overset{CH_3}{C}{-}\underset{H}{C}{=}\underset{H}{C}{-}\ldots R}$$

In both termination reactions a substituted conjugated diene is formed which could conceivably re-enter a new active chain or other reaction. Also, either a new chain is started or catalyst is regenerated.

Eirich and Mark, in a theoretical paper,[29] have derived several equations for the polymerization reaction rates depending on the strength of the monomer adsorption, nature of the catalyst complex, etc. For the case of weak monomer adsorption and strong complex formation, their results indicate a dependence of the rate on the square of the total surface available for catalyst complex formation.

In showing above that the isoprene reaction was first order in monomer, we have assembled all the possible catalyst concentration factors into the rate parameter, r_m. If we assume the total surface (*i.e.*, of brown $TiCl_3$) available is proportional to the $[TiCl_4]$ present, then a plot of these first-order rate parameters against the $TiCl_4$ concentration squared should fit the experimental points. As may be seen in Fig. 6 the fit is satisfactory.[24]

The Eirich and Mark results do not account for the maximum in the polymerization rate as the Al/Ti ratio is varied as described here and by Adams[11] for isoprene and for ethylene[10] and butadiene.[30] Their results also require a strong complex between alkyl and solid surface.

If we consider the polymerization as a series of surface reactions, then a simple Langmuir–Hinshelwood type of mechanism can be derived. Let us assume that propagation occurs *only* when both monomer and alkyl are adsorbed on the solid surface formed from the reaction of TIBA and $TiCl_4$. It should be noted that the total quantity of organoaluminum compounds is not reduced by this reaction but only changed from TIBA to an aluminum alkyl halide. If the fraction of surface covered by monomer is θ and the fraction of surface covered by alkyl is θ', then one may write the expressions for θ and θ' in terms of the concentrations and ratios of rate constants for adsorption and desorption[31]

$$\theta = \frac{K(\mathrm{M})}{1 + K(\mathrm{M}) + K'(\mathrm{A})} \qquad \text{(I)}$$

and

$$\theta' = \frac{K'(\mathrm{A})}{1 + K(\mathrm{M}) + K'(\mathrm{A})} \qquad \text{(II)}$$

where (M) and (A) are monomer and alkyl concentrations, respectively, and K and K' are the ratio of the rate constants for adsorption and desorption for M and A, respectively. For a given concentration of active centers, the rate of reaction is then $v = k'\theta\theta'$. Where the concentration of active centers (S) varies, we write for the propagation reaction

$$\begin{aligned} v &= k(\mathrm{S})\theta\theta' \\ &= \frac{kKK'(\mathrm{M})(\mathrm{A})(\mathrm{S})}{[1 + K(\mathrm{M}) + K'(\mathrm{A})]^2} \qquad \text{(III)} \end{aligned}$$

If either the (M) or (A) concentration is kept constant and the other concentration varied the rate will first increase, pass through a maximum and then decrease as the more strongly adsorbed reactant displaces the other. For the special case where monomer is weakly adsorbed, the rate of propagation is

$$v = \frac{kKK'(\mathrm{M})(\mathrm{A})(\mathrm{S})}{[1 + K'(\mathrm{A})]^2} \qquad \text{(IV)}$$

Here the reaction will show a maximum in the rate as the concentration of (A) increases but will be simply first order in monomer. If the reaction is between *unadsorbed* monomer and adsorbed alkyl, instead of equation III we have

$$\begin{aligned} v &= k(\mathrm{S})(\mathrm{M})(\theta') \\ &= \frac{kK'(\mathrm{M})(\mathrm{A})(\mathrm{S})}{1 + K'(\mathrm{A})} \qquad \text{(V)} \end{aligned}$$

Now the rate varies in a manner such that there is no maximum in the rate. Instead, as the concentration of (A) increases the rate increases and then levels off, *i.e.*, becomes independent of (A).

Thus for isoprene and the TIBA–$TiCl_4$ system, if we measure the number of active centers (S) by the $TiCl_4$ concentration and assume $K'(\mathrm{A})$ is small, the kinetics follow equation IV.

With propylene and $TiCl_3$ the kinetics probably follow the rate given by equation V. Natta's data[6] for this system extend down to 0.5 Al/Ti and do not show the drop in rate predicted at low Al/Ti by our mechanism. However, Mark[32] recently has reported that the initial rate of propylene conversion to polymer was proportional to the amount of alkyl as long as the alkyl concentration was low.

The inability to form satisfactory polymer with isoprene in the TIBA–$TiCl_3$ system apparently is connected with the inability of $TiCl_3$(violet) to adsorb this monomer.

Obviously, even equation IV represents an oversimplified picture for the isoprene system, since when varying amounts of alkyl are added to the isolated solid its composition changes and almost cer-

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[29] F. Eirich and H. Mark, "Kunstoffe Plastics" (International Zeitschrift fur das gesamte Kunstoff gebeit), **2**, 1 (1956).

[30] Belgium Patent 551,851, Phillips Petroleum Co. (Example 14).

[31] See, *e.g.*, P. H. Emmett, "Catalysis," Vol. I, Reinhold Publ. Corp., New York, N. Y., 1954, p. 154, *et seq.*

[32] H. Mark, "Progress in Plastics," Philosophical Library, New York, N. Y., 1957, p. 2.

tainly its activity changes as well. In the original mixture of TIBA and $TiCl_4$ there are probably present more than one species of alkyl. Thus it is only by holding the Al/Ti ratio constant that one can obtain a consistent solid surface and soluble fraction and thereby determine the over-all propagation rate. Even though our mechanism predicts a maximum in the rate, we cannot exclude that the changes in the solid surface also play an important role in determining the shape and location of the maximum.

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[CONTRIBUTION FROM THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS, AND THE LABORATORY FOR NUCLEAR SCIENCE, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Anion-exchange Studies. IV. Nature of the Adsorbed Species in the System Co(II)-HCl[1]

BY ROLFE H. HERBER[2] AND JOHN W. IRVINE, JR.

RECEIVED FEBRUARY 5, 1958

The spectra of Co(II) solutions in the presence of LiCl, HCl and $HClO_4$ have been re-examined in the region from 325 to 650 mμ. The optical absorbancy data have been correlated with the known adsorption behavior of Co(II) on strong-base (quaternary ammonium) anion-exchange resins, and the principal species adsorbed on the resin is shown to be the neutral complex $CoCl_2 \cdot aq$. The equilibrium constant for the reaction $Co^{++} \cdot aq + 2Cl^- \rightleftarrows CoCl_2 \cdot aq$ is calculated to be $5.3 \times 10^{-2}\ F^{-2}$. These data appear to support the suggestion that at least two distinct anion adsorption processes may occur in transition metal ion retentions.

In the preceding paper[3] of this series, it was suggested that a necessary condition for adsorption of the metal by an anion exchanger is that *an anion complex of single or higher negative charge be formed or be present within the resin,* without implying a concomitant presence of anionic complexes in the aqueous phase. Two processes by which this condition can be met are

$$MA_\nu + RA \rightleftarrows RMA_{\nu+1} \qquad (1)$$

$$MA^-_{\nu+1} + RA \rightleftarrows RMA_{\nu+1} + A^- \qquad (2)$$

where MA_ν represents the ν^{th} complex of the metal ion $M^{+\nu}$ with anion A^- and RA represents the resin in the A^- form. In the case of the systems Ni(II)-HCl and Ni(II)-LiCl, a distinction between these two possibilities could not be made due to the absence of chloro-complexes higher than $NiCl^+$, even in concentrated chloride media. The system Co(II)-HCl offers the possibility of yielding data, on the basis of which a choice can be made between these adsorption processes. The ion-exchange behavior of Co(II) has been investigated with HCl,[4] LiCl[5] and HBr[6] present as additional electrolytes, and the adsorption spectra of Co(II) solutions in chloride media are known to undergo marked changes as the anion concentration increases.[7,8] With a view to correlating the spectral absorbancy of a particular complex with the ion exchange behavior of Co(II) in HCl, the spectra of these solutions have been reexamined in the present investigation.

Experimental

The cobalt chloride salt employed was J. T. Baker A.R. grade containing 0.001% copper, 0.001% iron and 0.06% nickel as the only possibly interfering impurities, and was used without further purification. The $CoCl_2$ stock solutions were made up to a concentration of $4.22 \times 10^{-2}\ F$. Reagent grade hydrochloric acid was standardized against Na_2CO_3 within 4 hours prior to use. All titrations were carried out at 25° to a replicate error of less than ±0.4%. J. T. Baker A.R. grade lithium chloride and G. F. Smith perchloric acid were used without further purification. The solutions examined spectrophotometrically were prepared from the Co(II) stock solution and appropriate amounts of hydrochloric acid, perchloric acid or lithium chloride solutions in demineralized water to give a final metal concentration of $3.4 \times 10^{-3}\ F$. The final solutions were stored in subdued light until just prior to spectrophotometric analysis.

Spectrophotometric measurements were made in the region from 325 to 650 mμ with a Cary recording double beam spectrophotometer, Model 14M, using as a blank a solution of Co(II) in water at the same concentration as the test solutions.

Results and Discussion

Inasmuch as all of the spectra of the present work were measured against a blank containing Co(aq)$^{++}$ and an equivalent amount of chloride ion, any absorption observed can be ascribed to species other than the hydrated Co(II) ion.

The Co(II) spectrum in 10.7 F $HClO_4$ showed an optical absorption identical to that of the blank and no evidence for the existence of species with a hydration number differing from that of Co(II) in water was found, although the absence of such species is not necessarily implied by these data. Three spectra of Co(II) in lithium chloride solution (0.05 F in HCl to avoid possible hydrolysis effects) were obtained. At 3.86 F LiCl, no absorption peaks were noted, while at concentrations of 7.95 and 10.8 F a strong absorption at 624 mμ and very much weaker absorptions at 530 and 350 mμ were observed. The weak absorption at 530 mμ, which is not sensitive to changes in the chloride ion concentration, corresponds to only 2% of the absorption at the 624 mμ peak. For the 7.95 and 10.8 F LiCl solutions, the absorption curve at 530 mμ

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(1) This work supported in part by the U. S. Atomic Energy Commission.

(2) To whom correspondence should be addressed.

(3) R. H. Herber and J. W. Irvine, Jr., THIS JOURNAL, **78**, 905 (1956).

(4) K. A. Kraus, *et al.*, *ibid.*, **74**, 843 (1952); **75**, 1460 (1953).

(5) K. A. Kraus, F. Nelson, F. B. Clough and R. C. Carlson, *ibid.*, **77**, 1391 (1955).

(6) R. H. Herber and J. W. Irvine, Jr., *ibid.*, **77**, 5840 (1955).

(7) A. V. Kiss and M. Gerendas, *Z. physik. Chem.*, **180**, 117 (1937).

(8) L. I. Katzin and E. Gebert, THIS JOURNAL, **72**, 5464 (1950).