

CONTRIBUTION FROM THE PENNSALT CHEMICALS CORPORATION,
TECHNOLOGICAL CENTER, KING OF PRUSSIA, PENNSYLVANIA**Inorganic Coordination Polymers. VI. Linear Double-Bridged Chromium(III) Phosphinate Polymers with Inorganic Side Groups¹**

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The air oxidation of chromium(II) phosphinates under appropriate conditions yields polymers with the general formula $[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OPR}_2\text{O})_2]_x$ where R represents C_6H_5 , CH_3 , or $1/2(\text{CH}_3)(\text{C}_6\text{H}_5)$. Although they do not melt, these polymers are soluble in various solvents. The intrinsic viscosities in these solutions are large enough to show that linear polymers are present. Infrared spectra support the formulation given and indicate that polymerization occurs *via* double phosphinate bridges. Although thermogravimetric analysis gives 375° for the decomposition of $[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$ in nitrogen, an isothermal study gives first evidences of change in 6 hr. at 265°. The methylphenyl and dimethyl species appear to have approximately the same thermal stability. The intrinsic viscosity of solutions of the diphenyl form increases with time.

In a preliminary communication² we reported our initial findings on a new class of double-bridged coordination polymers which have the general formula $[\text{M}(\text{a})(\text{b})\text{X}_2]_x$. Subsequently, Podall and Iapalucci presented some evidence that metal carbonyls react with phosphinic acids to yield related polymers.³ In this paper we wish to give a more detailed presentation of the synthesis and properties of the polymers $[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OPR}_1\text{R}_2\text{O})_2]_x$ where R_1 and R_2 are phenyl and/or methyl groups.

These polymers are of particular interest because we have been able to synthesize samples with molecular weights which appear to be considerably higher than the values observed for related systems.^{4,5} Furthermore, these polymers display properties typical of linear polymers, even though an octahedral metal is involved in the backbone and no chelate rings are present as blocking groups. Finally, they are representative of a rather large number of polymers currently being studied in our laboratories.

Experimental

All chemicals and solvents were reagent grade or better and were used without further purification unless otherwise indicated.

Starting Materials.—Diphenylphosphinic acid, $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{OH}$, was prepared by the treatment of $(\text{C}_6\text{H}_5)_2\text{PCl}$ (technical grade, Victor Division of Stauffer Chemical Co.) with hydrogen peroxide.⁶ The product was recrystallized twice from absolute methanol; m.p. 194–195°.

Anal. Calcd. for $\text{C}_{12}\text{H}_{10}\text{O}_2\text{P}$: C, 66.05; H, 5.08; P, 14.20; neut. equiv., 218.2. Found: C, 66.23; H, 4.92; P, 14.07; neut. equiv., 217.5.

Methylphenylphosphinic acid, $\text{CH}_3(\text{C}_6\text{H}_5)\text{P}(\text{O})\text{OH}$, was prepared according to the method of Arbuzov⁷; m.p. 134.5–135.5°.

Anal. Calcd. for $\text{C}_7\text{H}_8\text{O}_2\text{P}$: C, 53.85; H, 5.81; P, 19.84; neut. equiv., 156.1. Found: C, 54.02; H, 5.78; P, 19.46; neut. equiv., 155.4.

(1) Part V: B. P. Block and J. Simkin, *Inorg. Chem.*, **2**, 688 (1963).(2) A. J. Saraceno and B. P. Block, *J. Am. Chem. Soc.*, **85**, 2018 (1963).(3) H. E. Podall and T. L. Iapalucci, *J. Polymer Sci.*, **B1**, 457 (1963).(4) B. P. Block, J. Simkin, and L. R. Ocone, *J. Am. Chem. Soc.*, **84**, 1749 (1962).(5) B. P. Block, S. H. Rose, C. W. Schauman, E. S. Roth, and J. Simkin, *ibid.*, **84**, 3200 (1962).(6) For details see B. P. Block, E. S. Roth, C. W. Schaumann, and L. R. Ocone, *Inorg. Chem.*, **1**, 860 (1962).(7) A. E. Arbuzov, *J. Gen. Chem. USSR*, **4**, 898 (1934); *Chem. Abstr.*, **29**, 2146 (1936).

Dimethylphosphinic acid, $(\text{CH}_3)_2\text{P}(\text{O})\text{OH}$, was prepared by the procedure of Reinhardt, Bianchi, and Mölle⁸; m.p. 90–93°.

Anal. Calcd. for $\text{C}_2\text{H}_7\text{O}_2\text{P}$: C, 25.54; H, 7.50; P, 32.93. Found: C, 25.23; H, 7.57; P, 33.34.

The monohydrate of chromium(II) acetate, $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$, was prepared by a modification⁹ of the usual technique.

$[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$.—A suspension of 2.3–2.5 g. of freshly prepared, moist $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ in 250 ml. of deoxygenated water was refluxed for 1 hr. under a continuous flow of nitrogen while being stirred magnetically. Solid particles were washed down occasionally by manually shaking the flask. A solution of $\text{KOP}(\text{C}_6\text{H}_5)_2\text{O}$, prepared by exact neutralization of 7.5 g. of $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{OH}$ with 1 M KOH, was purged with nitrogen for 45 min. and then added to the hot suspension at a rate such as not to cause violent foaming or excessive thickening of the reaction mixture. The reaction mixture, containing a very pale-colored precipitate, was heated with stirring at reflux for 5 min., cooled, and stirred an additional hour at room temperature. The reaction mixture was then filtered and washed with four 100-ml. portions of deoxygenated water with absolute exclusion of oxygen. The solid was then oxidized by dispersing it in 250 ml. of water and stirring the suspension while exposing it to air or passing a stream of air through the suspension maintained at 90°. After the oxidized product was filtered off, washed with water, and dried at 100°, it was added to 300 ml. of benzene and stirred. Most of the product slowly dissolved. The insolubles (usually 0.4 g. or less) were then removed by filtration, and the resulting solution was evaporated at room temperature in a stream of nitrogen. The brittle resinous film thus produced was dried at 120° to give a yield of 4.5 g. of polymer with an intrinsic viscosity of 0.3 to 0.7 in freshly prepared chloroform solution. The viscosities generally increased to 0.8 to 1.1 when a 1% solution was held at 54° for 10 days, although values ranging from 0.5 to 1.5 have been observed.

Anal. Calcd. for $\text{C}_{24}\text{H}_{20}\text{CrO}_6\text{P}_2$: C, 55.29; H, 4.45; Cr, 9.97; P, 11.88. Found: C, 55.93; H, 4.65; Cr, 9.7; P, 11.78.

As with many polymer syntheses the quality of the product, as gauged by intrinsic viscosity, is dependent on the details of the preparation. Thus, if the $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ is suspended in 100 ml. of deoxygenated water and the suspension is not refluxed, whereas the reaction mixture is refluxed for 22 hr. after addition of the $\text{KOP}(\text{C}_6\text{H}_5)_2\text{O}$ solution, cooled, and exposed to the atmosphere, a product is obtained which, after washing with water, drying, and work-up with chloroform, has intrinsic viscosities in chloroform in the range between 0.15 and 0.25 and only increases to values up to 0.4.

Anal. Calcd. for $\text{C}_{24}\text{H}_{20}\text{CrO}_6\text{P}_2$: C, 55.29; H, 4.45; Cr, 9.97; P, 11.88. Found: C, 55.52; H, 4.22; Cr, 9.6; P, 11.91.

(8) H. Reinhardt, D. Bianchi, and D. Mölle, *Chem. Ber.*, **90**, 1656 (1957).(9) L. R. Ocone and B. P. Block, *Inorg. Syn.*, **8**, in press.

Two important factors determining the characteristics of the product appear to be how the $\text{Cr}(\text{C}_6\text{H}_5\text{O}_2)_2 \cdot \text{H}_2\text{O}$ is treated prior to its use and how many times the intermediate chromium(II) phosphinate is washed prior to oxidation.

$[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$.—Solubility differences in the chromium(II) intermediate necessitated a different procedure for the synthesis of this polymer. The freshly prepared moist 2.3–2.5-g. sample of $\text{Cr}(\text{C}_6\text{H}_5\text{O}_2)_2 \cdot \text{H}_2\text{O}$ was washed with a 50-ml. portion of deoxygenated 99% ethanol. To it was added a solution of 4.15 g. of $\text{CH}_3(\text{C}_6\text{H}_5)\text{P}(\text{O})\text{OH}$ in 75 ml. of ethanol, and the resulting mixture was stirred magnetically at room temperature for 3 hr. Ethanol and acetic acid were then distilled into a large-capacity liquid-nitrogen trap at room temperature and reduced pressure. Air was diffused slowly into the reaction mixture after most of the ethanol had been removed, and the solid reaction product became dark green. The contents of the flask were dried at 100° and atmospheric pressure; during this time evolution of traces of acetic acid continued. The product was removed, washed with water, and further dried at 139° in an Abderhalden drying apparatus at reduced pressure.

Anal. Calcd. for $\text{C}_{14}\text{H}_{13}\text{CrO}_6\text{P}_2$: C, 42.33; H, 4.82; Cr, 13.1. Found: C, 42.43; H, 4.64; Cr, 13.6.

The intrinsic viscosity of the polymer ranges from 0.2 to 0.3 in chloroform solutions. Infrared indicates that the product as prepared in this manner contains traces of acetate (presumably present as end groups).

$[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$.—This polymer was prepared in essentially the same fashion as was the methylphenyl analog. A deoxygenated solution of 2.6 g. of $(\text{CH}_3)_2\text{P}(\text{O})\text{OH}$ in 50 ml. of ethanol was used, and the mixture was stirred magnetically for 20 hr. During the vacuum drying of the chromium(II) intermediate prior to oxidation there was apparently some oxidation to chromium(III) because the surface of the solid turned green. While it is possible that traces of air were responsible, it is more likely that oxidation occurred *via* H^+ from acetic acid. The slow, but continuous evolution of acetic acid during the drying operation indicates that this by-product is difficult to remove.

The product swells and dissolves easily in water and, after long standing in contact with chloroform, it partially dissolves to give chloroform solutions having an intrinsic viscosity of 0.13. The presence of acetate as potential end groups is indicated by elemental analysis and confirmed by infrared.

Anal. Calcd. for $\text{C}_8\text{H}_{15}\text{CrO}_6\text{P}_2$: C, 17.59; H, 5.54; Cr, 19.04; P, 22.68. Found: C, 19.5; H, 5.11; Cr, 19.2; P, 20.11.

Intrinsic Viscosity Measurements.—Apparent intrinsic viscosities were determined in chloroform at $30.0 \pm 0.1^\circ$ with a Cannon-Ubbelohde dilution viscometer (Cannon Instrument Co.) by standard procedures.¹⁰ Values of η_{sp}/c were plotted as a function of c to obtain the intrinsic viscosity, $[\eta]$, at the ordinate intercept (*i.e.*, infinite dilution) in units of dl./g. In some cases $(\ln \eta_{rel})/c$ was also plotted *vs.* c on the same graph to give $[\eta]$ at $c = 0$. Values obtained by the latter procedure agreed very well with the former method.

Solution Stability Studies.—The effects of several variables on the changes in intrinsic viscosity for solutions of $[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$ were examined by means of a statistically designed sequence of 24 experiments. The variables tested were temperature, concentration, exposure to visible light, agitation, solvent, exposure to atmosphere (two-level variables), and the presence or absence of trace quantities of phenol and pyridine (three-level variable). The time factor was maintained constant.

All runs in the statistical study were made with portions of a single sample of polymer which had an initial viscosity of 0.186, and the entire amount of each solvent employed came from a single stock bottle.

Deuteration of $[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$ was accomplished by exchange of D_2O with $[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$ in benzene. Benzene, dried overnight over sodium wire, was

distilled and stored under dry nitrogen. Excess D_2O (99.5 mole % min., Matheson Coleman and Bell) was added to the benzene in a flask in a dry bag and sufficient $[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$, previously heated at 90–100° under vacuum for 18 hr., was added to give a 1% solution. The two-phase mixture was shaken mechanically for 3 hr., and the benzene was removed under reduced pressure at room temperature. The flask containing the polymer residue was then returned to the dry bag, and fresh D_2O -containing benzene was added and the mixture allowed to stand 3 days. For infrared examination the benzene was removed as before and the polymer was milled in a dry bag with hexachlorobutadiene which had first been dried over molecular sieves (Linde, Type 4A) for 5 hr. and equilibrated overnight with nitrogen saturated with D_2O vapor at 26°. The infrared spectrum of hexachlorobutadiene alone was not changed by this treatment.

Infrared Spectra.—Infrared spectra were measured with a Perkin-Elmer Model 221 instrument employing a sodium chloride prism in the 2–15 μ region and a Perkin-Elmer Model 337 grating spectrometer in the 2–25 μ region. Spectra were obtained for solid powders in Nujol and hexachlorobutadiene mulls.

Thermal Stability.—The thermal stability of the polymers was determined dynamically by visual observation, differential thermal analysis, and thermogravimetric analysis. A detailed description of the latter procedure can be found elsewhere,¹¹ and only the general experimental conditions will be given here. For visual examination the polymers were heated in a capillary tube in air at 10°/min. for preliminary observation and at 1 to 3°/min. over narrower temperature ranges of interest. Differential thermal analysis was carried out at a heating rate of 5°/min. in a nitrogen atmosphere, thermogravimetric analysis at a heating rate of 5°/min. in either a nitrogen, dry air, or moist oxygen atmosphere.

The thermal stability of $[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$ was also determined isothermally at temperatures ranging from 100° to approximately 380° at a pressure of 2 to 10 μ . The apparatus essentially consisted of a closed, capped Pyrex glass tube surrounded by heating tape. The system was insulated with glass wool and asbestos tape, and the temperature was maintained to $\pm 5^\circ$ by means of a Wheelco indicating controller connected to the heating element *via* a Powerstat transformer. Temperature was measured with an iron-constantan thermocouple in a thermowell in contact with the sample and monitored with a Leeds & Northrup Speedomax G to obtain limits of temperature fluctuation during the runs. Approximately 0.5 to 1.0 g. of unpulverized polymer was placed in the Pyrex tube, and the system was evacuated for 24 hr. at reduced pressure (1–10 μ). A portion of the polymer was removed, allowed to equilibrate with the atmosphere for at least 1 hr., and checked for changes in solubility, infrared spectra, intrinsic viscosity fusion effects, and related solution behavior. The remainder of the polymer was re-evacuated and heated at 122° for 6 hr. Successive treatments at 169, 215, 265, 313, 340, 360, and 380° were thus cumulative. In general 1–2-hr. thermal equilibration times were allowed, and the system was cooled for 1 hr. prior to sample removal. For this study a single batch of polymer sample (intrinsic viscosity of 0.85 after the 10-day equilibration described previously) was used.

Discussion

All our evidence indicates that the products corresponding to $[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$ are polymers and that their polymeric properties are retained in either chloroform or benzene solutions. Thus vapor pressure osmometry in benzene or chloroform and ebulliometry in chloroform indicate molecular weights greater than 10,000 for all samples investigated, light scattering by a chloroform solution is consistent with a high molecular weight, and the intrinsic viscosities

(10) W. R. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, pp. 34–42.

(11) J. R. Soulen and I. Mockrin, *Anal. Chem.*, **33**, 1900 (1961).

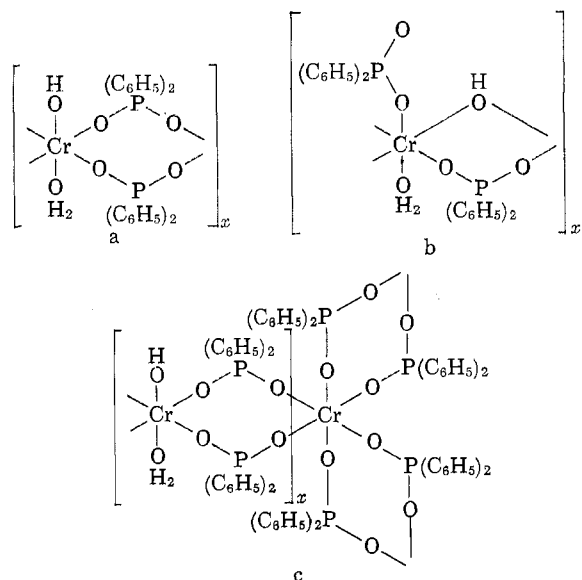
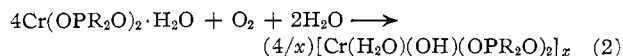
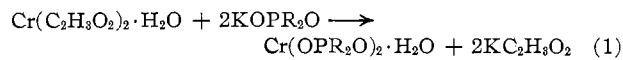


Fig. 1.—Some structural possibilities for $[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$.

measured all exceed 0.1 and are hence in the polymer range. Similar data for the methylphenyl and dimethyl analogs indicate that they are also polymeric.

The stoichiometry of the two steps in the synthesis is given in eq. 1 and 2. Although the intermediates written as $\text{Cr}(\text{OPR}_2\text{O})_2 \cdot \text{H}_2\text{O}$ have not been fully



characterized, it seems reasonable to assume that they are chromium(II) phosphinates. A detailed investigation of the polymerization is now underway in an attempt to determine the mechanism.

The diphenyl polymer appears to be essentially linear based on its solubility, extensive swelling prior to dissolving, and high intrinsic viscosity. Figure 1 illustrates some possibilities involving double-bridged structures, including systems in which a slight deficiency of water or a slight excess of diphenylphosphinate over hydroxyl groups could result in branching and/or cross linking.

Infrared absorption peaks characteristic of the diphenylphosphinate group in $[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$ are almost identical with those observed for $[\text{Cr}(\text{CH}_3\text{COCHCOCH}_3)(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$. In the latter the presence of the chelating ligand requires that the phosphinate anions function as bridging groups in order to explain the polymeric properties of the material.⁴ In the OH stretching region (Fig. 2) a sharp band and a broad band are observed at 3610 and 3300–3450 cm^{-1} , respectively, for $[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$. Neither of these bands is observed in $[\text{Cr}(\text{CH}_3\text{COCHCOCH}_3)(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$ or $[\text{Zn}(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$, and deuteration of $[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$ reduces the intensity of both bands and results in the appearance of an OD stretching at 2640 cm^{-1} , in excellent agreement with the expected isotopic shift. The two bands

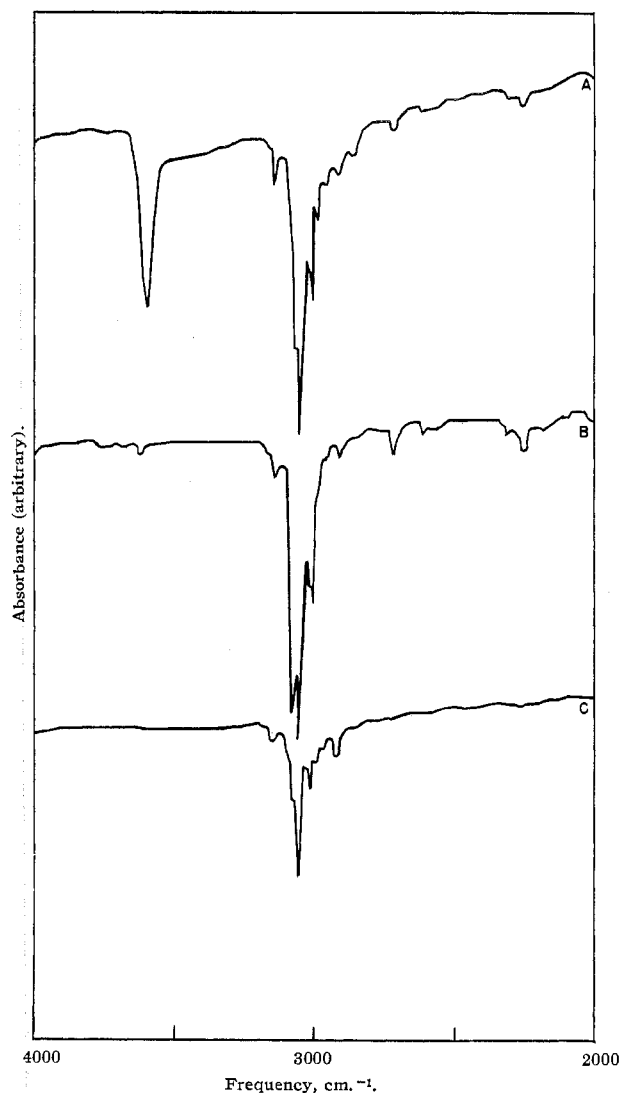


Fig. 2.—Infrared spectra of hexachlorobutadiene mulls of $[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$ (A), $[\text{Zn}(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$ (B), and $[\text{Cr}(\text{CH}_3\text{COCHCOCH}_3)(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$ (C) in the 4000–2000 cm^{-1} region.

in question are thus certainly to be assigned to OH groups. The sharp band is probably due to a coordinated hydroxyl group relatively free of hydrogen bonding, whereas the broad band is reasonably attributed to a strongly coordinated water molecule or to a strongly hydrogen-bonded hydroxyl group. The repeat unit of the polymer consequently appears to contain coordinated OH^- groups and H_2O , and the structure appears to be predominantly that shown in Fig. 1a. It is interesting to note that this same combination of sharp and broad bands has been observed for $\text{LiOH} \cdot \text{H}_2\text{O}$ at 3570 and around 3200 cm^{-1} , respectively.¹²

The methylphenyl and dimethyl polymers also exhibited at least two bands in the 3600–3400 cm^{-1} region directly attributable to OH stretching vibrations, hence the presence of hydroxyl groups in these systems is also confirmed.

Solutions of the diphenyl polymer in chloroform or benzene increase in intrinsic viscosity upon standing.

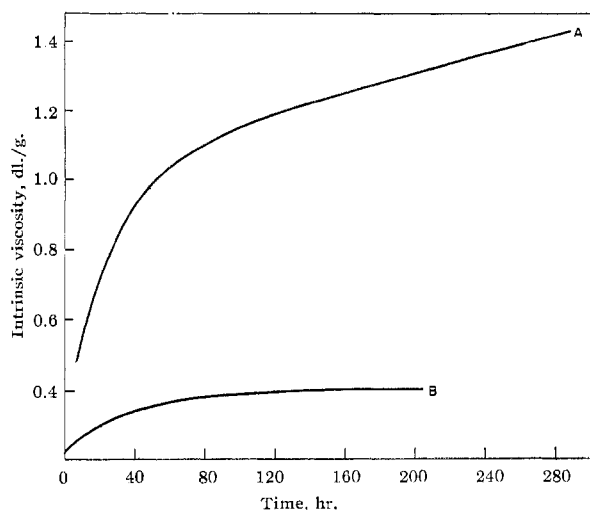


Fig. 3.—Increase of intrinsic viscosity of $[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$ as a function of time when stored as a 1% solution in CHCl_3 at 54° . Curve A is for a sample for which the $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ suspension was preheated and the chromium(II) phosphinate was washed with water. Curve B is for a sample made without these treatments.

The material recovered, however, has the same elemental analysis and infrared spectrum as the polymer initially placed in solution. This phenomenon appears then to be due to a change in the molecular weight of the polymer in solution. Preliminary examination of chloroform solutions of the polymer by light scattering confirms this conclusion¹³ and indicates in addition that the change is most likely an increase in chain length.

At present no specific mechanism can be given for the increase in molecular weight; however, the rate of increase and the limiting value of the intrinsic viscosity at constant temperature and concentration are sensitive functions of the preliminary treatment of the intermediates $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ and chromium(II) phosphinate. Figure 3 depicts the changes for selected samples for which the only variables were preheating of the $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ suspension and the extent to which the chromium(II) phosphinate was washed with water. It appears that the by-product $\text{KC}_2\text{H}_3\text{O}_2$ markedly inhibits the increase in molecular weight and consequently that the acetate ion functions primarily either as an end group or as a weak bridging agent in this system. The washing operation on the intermediate phosphinate thus serves to remove the end-group-terminating and stoichiometry-unbalancing acetate ion and permits growth to high molecular weights.

The statistical study showed that three variables affected the rate of change for the sample used: temperature, concentration, and solvent. There was also an interaction of higher temperatures and greater polymer concentrations leading to a significant additional increase in intrinsic viscosity. The role of solvent while appreciable was not as important as the effects of temperature and concentration. No effect was noted due to the presence or absence of air, moisture, or visible radiation. Finally, pyridine either decreased

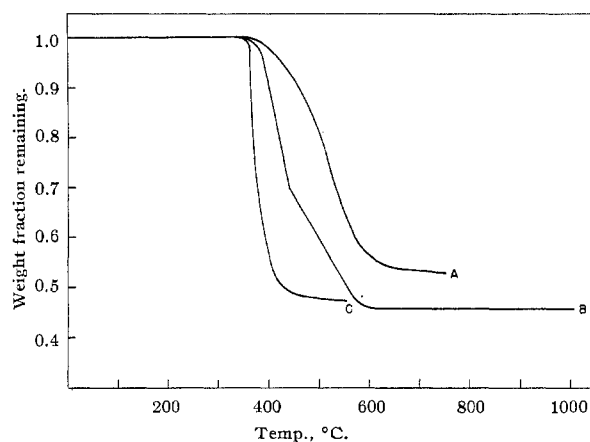


Fig. 4.—Thermogravimetric analysis of $[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$ in dry N_2 at $2.5^\circ/\text{min}$. (A), in dry air at $5^\circ/\text{min}$. (B), and in moist O_2 at $5^\circ/\text{min}$. (C).

the rate or in some cases even reversed the direction of change, in contrast to phenol which had no effect.

None of the polymers appears to melt at temperatures well above their decomposition points. Figure 4 summarizes the TGA results for $[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$. Initial weight losses due to polymer decomposition occur at about 375° in dry nitrogen, 355° in dry air, and 335° in moist oxygen. In the latter case decomposition proceeds very slowly up to about 360° and then accelerates greatly.

A more detailed study of isothermal stability in terms of changes in intrinsic viscosity, infrared spectra, and solubility is summarized in Table I. It is evident

TABLE I
RESULTS OF HEATING $[\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2]_x$
ISOTHERMALLY^a

Temp., °C.	Time, hr.	Solubility, %	Initial int. visc. in CHCl_3 , dl./g.	Int. visc. after aging in CHCl_3 , dl./g.
26	24	>98	0.16	0.83
120	6	>98	0.22	0.84
165	6	>98	0.30	0.88
215	6	>98	0.30	0.83
265	6	>98	0.30	0.75
313	6	>98	0.20	0.40
340	6	78 ^b	0.20	... ^e
365	6	5 ^c	... ^e	... ^e
380	6	0 ^d	... ^e	... ^e

^a Visual examination of each product showed no fusion or melting point effects. ^b Remainder of polymer consisted of swollen gel (22%). ^c Remainder (95%) consisted of partially swollen insolubles. ^d Completely unswollen insolubles. ^e Measurement not possible due to insufficient solubility and/or quantity.

that changes in the polymer are occurring at temperatures as low as 265° , although even up to 340° the samples still exhibit polymeric behavior after being heated for the intervals indicated. Infrared spectra show little or no change in the specimens up to 340° . At 365° an abrupt decrease in the intensity of the sharp OH band and an increase in intensity of the broad OH peak occur. This spectral change, which may be explained by a permanent alteration in the nature of the

(13) G. C. Berry and T. G. Fox, Mellon Institute, private communication.

hydroxyl groups, parallels the onset of essentially complete intractability of the polymer and occurs at approximately the decomposition temperature observed by TGA in dry nitrogen. No infrared evidence could be found to indicate any decomposition of the $OP(C_6H_5)_2O$ bridges up to temperatures of 380° at pressures of 0.01–0.02 mm. Differential thermal analysis of the polymer showed no major heat effects but only ill-defined deviations from the base line in the temperature region 335 – 520° . Minor exothermic effects apparently occurred at 370 and 420° . The former value corresponds closely to the thermogravimetric decomposition temperature.

TGA and DTA results for the methylphenyl and dimethyl polymer systems are complicated by the presence of acetate impurities, volatilization of which might not represent true decomposition of the polymer. Nevertheless major weight loss for the methylphenyl

polymer does occur at about 365° , a value not too different from that for the diphenyl analog. Low-temperature heating results in small weight losses and a simultaneous increase in intrinsic viscosity. For the dimethylphosphinate analog only a visual examination of stability has been made, and no change was observed up to 350° .

Acknowledgments.—This investigation was supported in part by the Office of Naval Research. We are indebted to G. Mincarelli for assistance with many of the experiments and to our Analytical Department, which performed the elemental analyses and obtained the molecular weight and infrared results. We are grateful to Dr. A. Kivnick of our Process Development Department for the design of the statistical study and the analysis of the results and to W. H. Chappell for the TGA and DTA studies.

CONTRIBUTION FROM THE CENTRAL BASIC RESEARCH LABORATORY,
ESSO RESEARCH AND ENGINEERING COMPANY, LINDEN, NEW JERSEY

Hexacarbonylbis(phenyl isocyanate) Diiron(0) and Related Compounds

By T. A. MANUEL

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The treatment of dodecacarbonyltriiron with phenyl isocyanate yielded hexacarbonylbis(phenyl isocyanate)diiron(0), which was also obtained from the treatment of dodecacarbonyltriiron with azidobenzene. Hexacarbonylbis(butyl isocyanate)diiron(0) was also prepared. Carbonyl(phenyl isocyanide) complexes of iron and molybdenum were formed by treatment of the metal carbonyl with phenyl isocyanate or phenyl isothiocyanate.

The reactions between organic isocyanides and metal carbonyls have been extensively investigated.^{1a,b} However, organic isocyanates have not been utilized as ligands in transition metal complexes, although the multiple bonding in the functional group suggests the possibility of forming bonds to suitable atoms. This paper describes the results of treatment of certain metal carbonyls with organic isocyanates and isothiocyanates.

Experimental

General.—The phenyl isocyanate, phenyl isothiocyanate, butyl isocyanate, 4-methyl-1,3-phenylene diisocyanate, and ethylcyclohexane were Matheson Coleman and Bell products, used without further purification, as was Fisher Spectroanalyzed cyclohexane. The purity of the phenyl isocyanate was verified by mass spectrometric analysis. The azidobenzene solution was obtained from K and K Laboratories, Inc. Triiron dodecacarbonyl was prepared according to the literature.² Reactions and chromatography (on 3×50 cm. alumina columns) were carried out under nitrogen without pretreatment of solvents or substrates.

Microanalyses and molecular weight determinations (osmometric, in benzene or chloroform) were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and the Analytical Re-

search Division of this company. The 2200–1600 and 700–400 cm^{-1} regions of the infrared spectrum were studied in cyclohexane solution on a Perkin-Elmer Model 421 instrument, with a resolution of $1\ cm^{-1}$.³ Nuclear magnetic resonance spectra³ were recorded on a Varian A-60 instrument for carbon disulfide solutions with tetramethylsilane as internal standard.

The Reaction between Phenyl Isocyanate and Dodecacarbonyltriiron.—A mixture of 5.0 g. (10 mmoles) of dodecacarbonyltriiron and 3.3 g. (27 mmoles) of phenyl isocyanate in 100 ml. of cyclohexane was heated in an oil bath at 85° for 68 hr. The mixture was cooled and filtered. The filtrate was chromatographed. Elution with pentane and evaporation of the eluate yielded 200 mg. of red-brown tar, with a complex infrared spectrum in the carbonyl stretching region. This tar was sublimed at 120° (0.1 mm.) and the sublimate was crystallized (pentane) to give 15 mg. of yellow crystals, m.p. 54 – 56° , with carbonyl stretching bands in the infrared spectrum identical with those of the tetracarbonyl(phenyl isocyanide)iron(0) $[Fe(CO)_4(CNC_6H_5)]^4$ prepared from phenyl isothiocyanate (see below).

Subsequent elution with a 2:1 pentane:dichloromethane mixture and evaporation of the eluate yielded 500 mg. of orange crystals. Crystallization (pentane) yielded 400 mg. of red-orange needles, m.p. 129 – 130° dec. (yield, 6%). Higher yields (24%) were obtained with shorter reaction times and excess iron carbonyl. Recrystallization of a portion yielded an analyti-

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(3) We gratefully acknowledge the help of Dr. J. J. Elliott in obtaining infrared spectra, of Mr. J. J. Waters in obtaining n.m.r. spectra, and of Dr. P. E. Butler in obtaining and interpreting mass spectrometric data.

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