indicated by the results of polarographic and gravimetric experiments and amperometric titrations.

The precipitate obtained from dilute acetate buffer contains cobalt and reagent in the molecular ratio 1:4.00. After extraction with 40% acetic acid this ratio becomes 1:3.00 ($\mathrm{Co(III)R_3}$). The extracted reagent requires only 3 electrons per molecule in its reduction, while HR requires 4 electrons. This is strong evidence that the extra molecule of reagent is a free radical, denoted as $\mathrm{H_2R}\cdot$, which is an intermediate and stable product formed in the reduction of HR

$$\mathrm{HR} + \mathrm{H^+} + \mathrm{e^-} \longrightarrow \mathrm{H_2R}\cdot$$

It is not plausible to assume that the precipitate in dilute acetate buffer is formed by the sequence of reactions

$$\mathrm{Co(II)} + \mathrm{HR} \longrightarrow \mathrm{Co(III)} + \mathrm{H_2R}\cdot \tag{1}$$

$$\mathrm{Co(III)} + 3\mathrm{HR} \longrightarrow \mathrm{Co(III)R_3} + 3\mathrm{H^+} \tag{2}$$

$$\mathrm{Co(III)R_3} + \mathrm{H_2R}\cdot \longrightarrow \mathrm{CoR_3{\cdot}H_2R}\cdot \tag{3}$$

In amperometric titrations of cobalt(II) with the reagent in acetate buffer and in the reverse titration it was found that at any stage of the titration before and after the end-point the over-all composition of the precipitate corresponded to 1:4.00. In 40% acetic acid the reaction ratio in both types of titration also was at any stage 1:4.00, although the precipitate had the composition $\mathrm{Co(III)R_3}$. Finally, from the identical polarographic behavior in AN of the precipitate formed from dilute acetate buffer and of the reaction product obtained by mixing cobalt(II) and HR in AN, and also from amperometric titrations in AN it appears impossible that the formation of the final reaction product occurs by the sequence of reactions 1 and 2. It is postulated that this sequence of reactions accounts for the observed results

$$\mathrm{Co(II)} + 2\mathrm{HR} \longrightarrow \mathrm{Co(II)R_2} + 2\mathrm{H^+} \tag{4}$$

$$2\mathrm{Co(II)R_2} \longrightarrow \mathrm{Co(III)R_3} + \mathrm{H_2R}\cdot + \mathrm{Co(II)} \tag{5}$$

The cobalt(II) complex formed according to eq. 4 is transformed rapidly in acid medium. In dilute acetate buffer $\mathrm{H_2R}\cdot$ is insoluble and coprecipitates with $\mathrm{Co(III)R_3}$. In 40% acetic acid $\mathrm{H_2R}\cdot$ is soluble and only $\mathrm{Co(III)R_3}$ precipitates. In AN both $\mathrm{Co(III)R_3}$ and $\mathrm{H_2R}\cdot$ are soluble.

As stated by Ilinski and v. Knorre[1] and confirmed in this Laboratory $\mathrm{Co(II)R_2}$ precipitates on mixing cobalt(II) with the sodium salt of the reagent in neutral or slightly alkaline medium. When such a precipitate is dissolved in AN containing acetic acid, it should disproportionate according to eq. 5. Qualitatively the polarogram should be and is found similar to that of curve 1 in Fig. 6. The ratio of the prewave to that of the total reagent wave minus the prewave was found 1:4, as required by eq. 5. The ratio of i_{d2} (cobalt wave, in this case Co(III) and Co(II)) to i_{d1} (total reagent wave) should be 1:3.00. Actually in several experiments a ratio of 1:2.97 ± 0.03 was found, in excellent agreement with the postulated interpretation.

The gravimetric data (Table II) and Fig. 5 indicate that coprecipitated $\mathrm{H_2R}\cdot$ can be volatilized more or less completely in a vacuum oven at 110°. The reason why Mayer and Feigl[4] could obtain such good results is not because they first oxidized cobalt from the divalent to trivalent state, but because they carried out the precipitation in fairly concentrated acetic acid medium in which $\mathrm{H_2R}\cdot$ is soluble.

Acknowledgment.—Appreciation is expressed to the Graduate School of the University of Minnesota for a grant in support of this research.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM RESEARCH AND DEVELOPMENT DEPARTMENT, WESTVACO CHLOR-ALKALI DIVISION, FOOD MACHINERY AND CHEMICAL CORPORATION]

The Synthesis of Tetrakis-(dichloromethylphosphine)-nickel from Methyldichlorophosphine and Nickel[1a]

BY LOUIS D. QUIN[1b]

RECEIVED FEBRUARY 23, 1957

The reaction of bulk nickel with methyldichlorophosphine was found to proceed readily to give high yields of tetrakis-(dichloromethylphosphine)-nickel. This represents the first synthesis of this type of compound by the direct reaction of nickel and a trivalent phosphorus compound. A small amount of a black unidentified solid adhering to the residual nickel is also formed. Similar conditions were not effective for causing phosphorus trichloride or phenyldichlorophosphine to react with nickel. The properties of tetrakis-(dichloromethylphosphine)-nickel were in general similar to those of related compounds.

Several compounds of the type $\mathrm{Ni(PY_3)_4}$ have been prepared in recent years by the reaction of nickel tetracarbonyl[2-5] or other $\mathrm{Ni(PY_3)_4}$ compounds[2,3] with trivalent phosphorus compounds. Their preparation by the direct reaction of nickel with phosphorus compounds has not yet been successful, although evidence of a reaction has been obtained with phosphorus trichloride.[2] Phosphorus trifluoride showed no reaction with nickel.[3,6] We now wish to report the facile synthesis of the new compound tetrakis-(dichloromethylphosphine)-nickel, $\mathrm{Ni(CH_3PCl_2)_4}$ (I), by the reaction of methyldichlorophosphine and elemental nickel.

The reaction has been affected by several tech-

---

(1) (a) Portions of this paper report work done under contract with the Chemical Corps, U. S. Army, Washington 25, D. C. (b) Department of Chemistry, Duke University, Durham, N. C.

(2) J. W. Irvine, Jr., and G. Wilkinson, *Science*, **113**, 742 (1951).

(3) G. Wilkinson, THIS JOURNAL, **73**, 5501 (1951).

(4) G. Wilkinson, *Z. Naturforsch.*, **9b**, 446 (1954).

(5) L. Malatesta and A. Sacco, *Ann. chim.*, **44**, 134 (1954).

(6) J. Chatt and A. A. Williams, *J. Chem. Soc.*, 3061 (1951).

niques, the best of which involves refluxing methyldichlorophosphine through a column packed with bulk nickel as turnings or wire. Under these conditions, the reaction proceeds relatively rapidly, as large surface area of nickel can be exposed to the methyldichlorophosphine. The product is very soluble in methyldichlorophosphine and accumulates in the pot; it is isolated by vacuum distillation of the unreacted methyldichlorophosphine and recrystallization of the residue. The pot temperature provides a good indication of the extent of reaction; the operation has generally been stopped when the temperature has risen from the boiling point of pure methyldichlorophosphine (81–82°) to 102–104°. Beyond this point, the solution becomes so concentrated in I that its crystallization commences; any material deposited on the walls of the flask is decomposed on continued heating. The conversion of methyldichlorophosphine to I at the usual stopping point is about 60–70%; the yields based on either consumed methyldichlorophosphine or nickel exceed 90%. With equipment properly sized for a charge of 250 g. of methyldichlorophosphine, a production rate of I of 40–50 g. per hour has been obtained. This rate is dependent primarily on the amount of nickel in the column.

Another technique for conducting this reaction involves merely refluxing methyldichlorophosphine in a flask containing nickel. In this case the reaction of a given amount of methyldichlorophosphine is considerably slower than that in the column. The product of this reaction appears to be less pure than that obtained by the column reaction. We have also found that Raney nickel will react with methyldichlorophosphine at room temperature to produce I, but this method of preparation has not been explored in detail.

In the preparation of I, bulk nickel slowly acquired a light powdery coating of an unidentified black by-product II which contains Ni, Cl and P (and probably C and H). There was no evidence of this coating decreasing the rate of production of I. That II was not an intermediate in the formation of I was shown by the fact that a small residue of II remained when a sample of nickel was completely consumed by prolonged refluxing with methyldichlorophosphine.

Compound I was found to be attacked readily by oxygen. When solutions of I were exposed to air or oxygen, precipitation of tan solids commenced immediately. These solids have not yet been sufficiently investigated to permit their identification. A report[2] on $Ni(PCl_3)_4$ implies instability of its solutions on exposure to air also.

Compound I reacted readily with phenyldichlorophosphine to affect replacement of all CH_3PCl_2 groups. The $Ni(C_6H_5PCl_2)_4$ so produced was of high purity; it melted at a temperature slightly higher than that previously reported.[5] In general other properties of I were similar to those of related compounds and are described in the Experimental section.

Attempts were made to apply the most favorable conditions for preparing I to the direct synthesis of $Ni(PCl_3)_4$ and $Ni(C_6H_5PCl_2)_4$. After prolonged refluxing of phosphorus trichloride and phenyldichlorophosphine through nickel-packed columns, there was no indication of a reaction and not a trace of the corresponding nickel complex could be isolated. The reduced availability of the electron pair on the phosphorus atom in these cases may be of importance in interpreting their lack of reactivity. Further study of the structural requirements of trivalent phosphorus compounds for undergoing the reaction with elemental nickel is contemplated.

Experimental[7]

Preparation of $Ni(CH_3PCl_2)_4$ (I).—A 1.8 cm. i.d. heated column with a 37-cm. section packed with 258 g. of chopped nickel turnings of average size 0.4 mm. × 5 mm. × 6 mm. was attached to a flask containing 274 g. (2.34 moles) of CH_3PCl_2. The top of the column was fitted with a reflux condenser. The system was flushed with nitrogen before the reaction and protected from the atmosphere thereafter. The CH_3PCl_2 was then boiled (81–82°) at a rate slightly below that causing flooding in the column. A yellow color developed in the pot after a few minutes; the nickel was noticeably blackened after 1–2 hr. operation. The pot temperature rose slowly at first and then rapidly as the relative change in content of solute (I) with respect to solvent (CH_3PCl_2) became greater. After 6 hr., the pot temperature had reached 100° and the reaction was stopped. On cooling, large crystals of I formed in the pot. The residual CH_3PCl_2 was removed by vacuum distillation. The crude I so obtained weighed 198 g. (0.376 mole). The conversion from CH_3PCl_2 charged was 64.3%. In the distillation there was recovered 88.2 g. (0.754 mole) of CH_3PCl_2; the yield of I from CH_3PCl_2 consumed was therefore 94.6%. The nickel packing was found to have lost 24.5 g. (0.417 mole); the yield of I based on this value was 90%. The crude I was recrystallized from dry diethyl ether or *n*-pentane at about −50° in the absence of air.

Anal. Calcd. for $C_4H_{12}Cl_8NiP_4$: C, 9.13; H, 2.30; Cl, 53.89; Ni, 11.2; P, 23.5. Found: C, 8.77; H, 2.35; Cl, 54.46; Ni, 11.2; P, 23.7.

Isolation and Properties of Black Ni–CH_3PCl_2 Product (II).—The nickel from an experiment such as that above was washed twice with dry, air-free *n*-pentane to remove residual I and CH_3PCl_2. The nickel was dried in a stream of nitrogen and transferred to a bottle. The bottle was shaken vigorously to cause detachment of the black coating on the nickel. The powder so obtained was removed through a sieve. Analysis of two different samples of II gave the following inconclusive data: Cl, 26.0 and 33.1; Ni, 49.1 and 33.8; P, 12.9 and 18.0, respectively. II was insoluble in all solvents investigated. It had no melting point but released a small amount of a volatile substance above 100°. No attempt has yet been made to identify this substance other than to ascertain that it is not CH_3PCl_2. II did not react with CH_3PCl_2 on prolonged refluxing in the presence or absence of nickel, indicating it not to be an intermediate in the formation of I. II has occasionally shown ferromagnetic properties, but this is possibly due to the presence of some elemental nickel.

Properties of $Ni(CH_3PCl_2)_4$. (a) **Thermal Stability.**—At room temperature, I appeared relatively stable when protected from the atmosphere, although it developed a strong CH_3PCl_2 odor. In a capillary, I slowly blackened over the range 170–185°; no melting point was observed. A 6.8-g. sample of I was heated to 240° in 15 minutes. There distilled 4.5 g. of dark blue liquid, which was redistilled to remove the trace of colored impurities. The liquid was found to be almost pure CH_3PCl_2 (74% yield) by its infrared spectrum. The pyrolysis flask was partially mirrored with nickel. The rest of the residue was a black powder, partly soluble in water.

(b) **Solubility.**—I was very soluble in organic solvents. The solutions were relatively stable at room temperature when protected from the atmosphere; at elevated temperatures, decomposition generally occurred to give dark brown or green mixtures. I was insoluble in cold water, though a slow reaction occurred over a period of several days to give a green solution. With boiling water, a green

---

(7) Melting points are uncorrected.

solution rapidly resulted; no solid separated on cooling. Similarly, the lower alcohols appeared to dissolve I with reaction on boiling. Hot sodium hydroxide (2 *N*) and ammonium hydroxide (concd.) rapidly gave dark brown mixtures with I.

(c) **Reaction with Oxygen.**—Most solutions of I deposited a light tan solid unless carefully protected from oxygen. When air was purposely passed for one hour through a solution of 1.49 g. of I in 25 ml. of *n*-pentane at room temperature, precipitation of the solid commenced immediately and a thick slurry resulted. The solid was recovered by filtration and washed with benzene. It weighed 0.30 g. Reliable analytical data have not yet been obtained for this compound. It was soluble in water (solution strongly acid) and alcohols and insoluble in organic solvents. It did not melt but darkened at a high temperature. Pentane-soluble products of the oxidation were not examined. Exposure of solid I to the atmosphere results in partial conversion to a pentane-insoluble solid which may be similar to the material described above.

(d) **Reaction with Phenyldichlorophosphine.**—A solution of 6.0 g. (0.0114 mole) of I in 40 g. (0.22 mole) of phenyldichlorophosphine was agitated at 70–80° at 35 mm. for 3 hr. CH_3PCl_2 replaced and volatilized was collected in a trap chilled by a bath of Dry Ice and trichloroethylene. The trap was found to contain 5.1 g. of pure CH_3PCl_2. This recovery represented 96% of theory. Excess phenyldichlorophosphine was removed by vacuum distillation of the orange reaction product, leaving an oil which readily crystallized. This residue was washed with *n*-pentane to remove residual phenyldichlorophosphine and then recrystallized from diethyl ether. The recovery of bright yellow product was rather low (57% yield) due to its great solubility in the solvent. It is believed the true yield of $Ni(C_6H_5PCl_2)_4$ was nearly quantitative. The product melted at 91–94°; since the reported value is 86.5°,[5] the solid was recrystallized again. It then melted at 93–94° after sintering at 91–92°. Analysis indicated it to be high purity $Ni(C_6H_5PCl_2)_4$.

Anal. Calcd. for $C_{24}H_{20}Cl_8NiP_4$: Cl, 36.6; Ni, 7.58; P, 16.0. Found: Cl, 36.4; Ni, 7.40; P, 15.9.

Acknowledgment.—The assistance of Donald C. Frokjer and Charles H. Rolston in performing some of the experimental work is acknowledged. Analyses were performed by Dr. Raymond Annino and his associates, of this Laboratory, and by the Schwarzkopf Microanalytical Laboratory, Woodside, New York.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Kinetic Studies of Thiourea Derivatives. II. The Dimethylthioureas[1]

BY WILLIAM H. R. SHAW AND DAVID G. WALKER

RECEIVED FEBRUARY 11, 1957

unsym-Dimethylthiourea isomerizes in aqueous solutions at elevated temperatures to form dimethylammonium thiocyanate. Experimental first-order rate constants for this reaction under a variety of conditions have been obtained. The isomerization is *p*H independent over a wide range and no effect of ionic strength was observed. At high *p*H, however, a complicating parallel reaction takes place. The behavior of *sym*-dimethylthiourea also has been examined. This compound decomposes to form methylamine and methyl isothiocyanate as primary products. Additional reactions by the product species occur. Rate constants and Arrhenius parameters for the isomerization of *unsym*-dimethylthiourea and for the decomposition of the symmetrical derivative are reported. All of the findings are discussed in terms of a possible mechanism.

Introduction

A few papers[2,3] on the chemistry of the dimethylthioureas have recently become available, but no work concerned with the kinetic behavior of these compounds could be found in the literature. Since data on both symmetrical and unsymmetrical dimethylthiourea would be of obvious value in any theoretical interpretation of the relative reactivity of thiourea derivatives, the present[4–7] study was undertaken.

Experimental

Apparatus and Technique.—The apparatus and technique used in the kinetic runs have been described in detail in earlier publications.[5–7]

Analytical Methods.—Ammonium, methylammonium and dimethylammonium ions were separated from the reaction mixture by passing the experimental solution through a cation-exchange column as previously described. Elution was effected by 20 ml. of 0.1 *N* NaOH, at the usual flow rate. This slight modification was necessary to ensure quantitative elution of the dimethylamine. After elution aliquots of the neutralized elutriate were used to determine ammonia,[5] methylamine[7] and dimethylamine[8] by spectrophotometric analyses described in detail elsewhere.

The ammonia analysis was not affected by dimethylamine in the concentrations encountered. As previously reported, however, methylamine exerted a moderate interference but suitable corrections could be made.

The methylamine analysis was unaffected by the ammonia and dimethylamine concentrations prevailing in the reaction mixtures. The dimethylamine analysis was similarly uninfluenced by ammonia and methylamine.

Thiocyanate ion was determined spectrophotometrically as before.[6] No significant interference by ammonia, methylamine, dimethylamine or the dimethylthioureas was encountered.

The average deviation of a set of 12 analyses of 0.3 m*M* dimethylamine was 7.0%. The average deviations for the other analyses have been reported in earlier work.

Compounds.—*sym*-Dimethylthiourea (1,3-dimethyl-2-thiourea) was prepared by the addition of methylamine to methyl isothiocyanate.[9] The product was separated as an oil from water solution twice and then finally crystallized, m.p. 64° (lit.[10] 61°) from benzene which had been partially distilled to remove the last traces of moisture.

Anal. Calcd. for $C_3H_8N_2S$: C, 34.6; H, 7.79; N, 26.9. Found: C, 34.8; H, 7.78; N, 27.0.

unsym-Dimethylthiourea (1,1-dimethyl-2-thiourea) was prepared by the addition of H_2S to dimethylcyanamide.[11]

---

[1] Presented before the Division of Physical and Inorganic Chemistry, 131st National Meeting of the American Chemical Society held in Miami, Florida, April, 1957.

[2] R. Singh, *J. Indian Chem. Soc.*, **31**, 355 (1954).

[3] R. H. Sahasrabudhey and R. Singh, *ibid.*, **30**, 695 (1953).

[4] Related work from this Laboratory on urea (ref. 5), thiourea (ref. 6) and methylthiourea (ref. 7) has been reported previously.

[5] W. H. R. Shaw and J. J. Bordeaux, THIS JOURNAL, **77**, 4729 (1955).

[6] W. H. R. Shaw and D. G. Walker, *ibid.*, **78**, 5769 (1956).

[7] W. H. R. Shaw and D. G. Walker, *ibid.*, **79** 2681 (1957).

[8] F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," 3rd ed., Vol. IV, D. Van Nostrand Co., Inc., New York, N. Y., 1954, pp. 37–39.

[9] E. C. Horning, Ed., "Organic Syntheses," Coll. Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 617–618.

[10] M. Freund and E. Asbrand, *Ann. Chem. Justus Liebigs*, **285**, 170 (1895).

[11] O. Wallach, *Ber.*, **32**, 1874 (1899).