a special procedure it is possible to show that the alcoholysis of $(CF_3P)_5$ produces the previously unknown and even less stable tetraphosphine $H_2(CF_3P)_4$.

Methanolysis of the Tetramer.—A mixture of 1.085 mmoles of $(CF_3P)_4$ and 3.15 mmoles of CH_3OH, in a vertical tube attached to a high-vacuum manifold, showed effervescence below 0°. After 12 hr at 25°, the mixture was resolved into the following fractions:

1. CF_3PH_2...0.029 mmole (47 mm at $-78°$)
2. "$CF_3PH(OCH_3)$"...0.134 mmole (166 mm at 0°; mol wt 130.5 *vs.* calcd 132; basic hydrolysis gave $0.51HCF_3$ per mole, as expected in view of $2.5HCF_3$ per mole of the CF_3P pentamer[2])
3. $\begin{cases} (CF_3PH)_2...0.176 \text{ mmole} \\ CH_3OH...0.167 \text{ mmole} \end{cases}$ inseparable but proved by analysis
4. $\begin{cases} \text{"}CF_3HP-PCF_3(OCH_3)\text{"}...35\% \\ CH_3P(OCH_3)_2............54\% \\ CH_3OH.................11\% \end{cases}$
   (Roughly one-third of the whole mixture; mole per cents estimated from average molecular weight and HCF_3 yield from basic hydrolysis)
5. $H_2(CF_3P)_3$...roughly 0.5 mmole (3.5 mm at 0°)
6. Products nonvolatile at 25°

Thus, the recoverable yield of the triphosphine was almost 50%, even though some of it may have been attacked by the excess methanol. The new compound "$CF_3PH(OCH_3)$" was well indicated but not further characterized, while the new diphosphine "$CF_3HP-PCF_3(OCH_3)$" is only reasonably postulated.

The Tetramer with Ethylene Glycol.—A solution of 1.860 mmoles of $(CF_3P)_4$ and 1.875 mmoles of $C_2H_4-(OH)_2$ in tetralin was heated for 15 hr at 100° (required temperature) under 225 mm of dry nitrogen, with delivery of volatiles at intervals through the reflux region of the vertical reaction tube. The effluent was resolved into 0.02 mmole of HCF_3, 0.103 mmole of CF_3PH_2, 0.031 mmole of $(CF_3PH)_2$, 0.70 mmole of $H_2-(CF_3P)_3$ (50% yield, based upon consumed tetramer), 1.4 mmoles of a fraction seeming to be mostly $C_2H_4O_2-PCF_3$,[3] and 0.176 mg (24% recovery) of $(CF_3P)_4$.

The glycol ester stood some 5 weeks at or below 25°, converting almost wholly to a nonvolatile viscous liquid which could represent more than one possible kind of polymerization.

Characterization of the Triphosphine.—The above alcoholyses led to pure samples of $H_2(CF_3P)_3$, for which the volatility data of Table I were obtained.

TABLE I
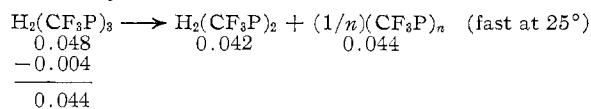VAPOR TENSIONS OF LIQUID $H_2(CF_3P)_3$[a]

Temp, °C	0.0	16.9	22.6	29.9	36.4	42.9
P_{obsd}, mm	3.5	10.3	14.5	21.5	30.1	41.3
P_{calcd}, mm	3.6	10.4	14.4	21.5	30.04	41.3

[a] $\text{Log } P = 6.4627 + 1.75 \log T - 0.0054T - 2375/T$; $t_{760} = 187.7°$; Trouton constant = 21.3 eu.

This triphosphine is appreciably unstable in the presence of mercury, tending to form $(CF_3P)_n$ and the diphosphine $(CF_3PH)_2$. It decomposes far more rap-

[3] A. B. Burg and J. E. Griffiths, *J. Am. Chem. Soc.*, **83**, 4333 (1961).

idly in the presence of a phosphine base. Thus, with a 10% admixture of $(CH_3)_3P$, the following millimolar stoichiometry was observed.

$$H_2(CF_3P)_3 \longrightarrow H_2(CF_3P)_2 + (1/n)(CF_3P)_n \quad \text{(fast at 25°)}$$

$$\begin{array}{ccc} 0.048 & 0.042 & 0.044 \\ -0.004 & & \\ \hline 0.044 & & \end{array}$$

Such catalysis correlates with the formation of the monomer complex $(CH_3)_3PPCF_3$.[4]

Alcoholysis of the Pentamer.—The instability of $H_2(CF_3P)_3$ relative to $H_2(CF_3P)_2$ suggested that the similar tetraphosphine would be even less stable. In order to obtain it directly in pure form, it seemed well to attack $(CF_3P)_5$ with a long-chain alcohol, so that both this alcohol and any alkoxyphosphine by-products would be less volatile than the desired tetraphosphine; then this product could be obtained as a certain fraction in a distillation process. In fact, exploratory experiments had shown that methyl, *t*-butyl, and *n*-heptyl alcohols all attacked $(CF_3P)_5$ well enough but formed mixtures from which the desired tetraphosphine could not be isolated; however, the problem was solved by the use of *n*-dodecyl alcohol (lauryl alcohol). This attacked $(CF_3P)_5$ at 30–40° (during 6 hr) in the boiler bulb of a small fractionating column (operating *in vacuo* with reflux at $-15°$), delivering a fraction which passed through a U tube at $-23°$ and condensed in a second trap at $-45°$—through which the more volatile products were removed. The vacuum-line stopcocks were halocarbon-greased to minimize catalytic effects.

The volatility of the $-45°$ condensate was 5 mm at 25°, reasonably higher than that of the solid $(CF_3P)_4$ or liquid $(CF_3P)_5$. The apparent molecular weight of the nearly saturated vapor was 424 (calcd for the chain tetraphosphine, 402); and subsequent measurements showed lower and lower results as decomposition increased the number of molecules. A long process of catalytic decomposition of a 25.6-mg repurified sample (from which the chain triphosphine might not have been quite absent) gave 0.054 mmole of CF_3PH_2, 0.151 mmole of CF_3P as tetramer and pentamer, and 0.018 mmole of $(CF_3PH)_2$. Thus, the formula could be written empirically as $H_{2.15}(CF_3P)_{3.78}$, representing a reasonable confirmation of the formula $H_2(CF_3P)_4$.

[4] A. B. Burg and W. Mahler, *ibid.*, **83**, 2388 (1961).

Preparation of Cobalt(III) Complexes by Continuous Anodic Oxidation

BY W. J. BLAEDEL AND M. A. EVENSON

Complexes of Co(III) have been prepared from aqueous Co(II) solutions in various ways. Most fre-

quently, an oxidizing gas was bubbled through a concentrated solution of Co(II). Walton[1] has described a typical preparation of hexaamminecobalt(III) chloride with air as the oxidant. Hill[2] used ozone while Brintzinger[3] bubbled chlorine through a cobalt(II) acetate solution for 24 hr to give a cobalt(III) acetate complex. Oxidation with nongaseous oxidants such as hydrogen peroxide,[4] sodium perborate,[5] and ferricyanide[6] has also been reported.

Several authors[7-12] offer methods for the production of Co(III) compounds by electrolytic oxidation, but there has been little work on the nature of the Co(III) complexes that result from electrolytic oxidation. Cobalt(III) sulfate resulted from the electrolysis of saturated cobalt(II) sulfate in 10 N sulfuric acid.[9] Cobalt(III) acetate was obtained with a platinum anode[10-12] in glacial acetic acid saturated with cobalt-(II) acetate. To date, most of the electrolytic oxidations reported in the literature were preparative in nature and were followed by crystallizations for isolation and purification of the Co(III) compound. In general, the oxidations were slow, most of them requiring at least a few hours, and yields often were not quantitative. High salt concentrations in solutions of high ionic strength were usually used.

The literature survey revealed no quantitatively electrochemical oxidations that were performed rapidly, in dilute solutions, and under closely controlled conditions, even though such oxidations should be possible. The advantages of such a method for the preparation and study of the less stable complexes might be considerable.

A flow-through electrode has been reported for performing electrolysis on a flowing stream[13] and has been used to convert alanine to the 1:1 Co(III) complex,[14] starting with a solution of alanine in an excess of Co-(III). Yields were quantitative in a number of supporting media and over a considerable range of applied potentials. In the following work, the similar preparation of a number of additional Co(III) complexes is described.

Experimental Section

The Oxidation Cells.—One type of flow-through electrode was a 4.5-cm length of 5-mm i.d. porous-glass tubing mounted concentrically with rubber stoppers inside a 4-cm length of 20-mm i.d. borosilicate-glass tubing. The anode was a bed of 60–100

(1) H. F. Walton, "Inorganic Preparations," Prentice-Hall, Inc., New York, N. Y., 1948.

(2) G. H. Hill, *J. Am. Chem. Soc.*, **71**, 2434 (1949).

(3) H. Brintzinger and F. John, *Z. Anorg. Allgem. Chem.*, **230**, 176 (1936).

(4) H. A. Laitinen and L. W. Burdett, *Anal. Chem.*, **23**, 1268 (1951).

(5) L. C. W. Baker and T. P. McCutcheon, *ibid.*, **22**, 944 (1950).

(6) H. Diehl and J. P. Butler, *ibid.*, **27**, 777 (1955).

(7) S. Glasstone and A. Hickling, "Electrolytic Oxidation and Reduction," Chapman and Hall, London, 1935.

(8) W. L. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J. 1960.

(9) C. E. Bricker and L. J. Loeffler, *Anal. Chem.*, **27**, 1419 (1955).

(10) J. A. Sharp and A. G. White, *J. Chem. Soc.*, 110 (1952).

(11) C. Schall and H. Markgraf, *Trans. Am. Electrochem. Soc.*, **45**, 164 (1924).

(12) H. Copaux, *Ann. Chim. Phys.*, **6**, 548 (1905).

(13) W. J. Blaedel and J. H. Strohl, *Anal. Chem.*, **36**, 1245 (1964).

(14) W. J. Blaedel and M. A. Evenson, *Radiochem. Methods Anal., Proc. Symp., Salzburg, Austria, 1964*, **2**, 371 (1965).

mesh crushed carbon (or 1–2 mm lengths of 24-gauge platinum wire) packed inside the porous-glass tube. The cathode was a similar bed of carbon or platinum in the annular space between the porous glass and the outer borosilicate-glass jacket. The cathodic solution was usually made to about the same composition as the anodic, but without Co(II), and was kept renewed during an oxidation run by pumping it through the cathode compartment at about 1.2 ml/min. The porous glass acted as the bridge between the two electrode compartments. Leads from the packed column beds to the outside permitted application of the desired voltages. Because of the low impedance of the system, applied voltages could be read from a panel voltmeter. Currents drawn were read from a panel milliammeter.

For the production of cobalt(III) sulfate complexes, higher yields were obtained with another type of cell, in which an anion-exchange membrane (Series 100, American Machine and Foundry Co., Springdale, Conn.) replaced the porous glass. The cell consisted of mirror-image slots (10 cm long × 2.4 mm wide × 3 mm deep) machined into Plexiglas blocks, which in turn were clamped together to sandwich the membrane film. Inlets and outlets for solutions and electrical leads were drilled into the slots from the sides and backs of the blocks. The electrodes consisted of 24-gauge platinum wire packed into the slots.

Oxidations were performed by pumping solutions of known Co(II) concentrations in various media through the anodic compartment with an appropriate applied potential. Pumping was performed at a constant rate (around 1 ml/min) with a peristaltic pump.

Analyses.—Oxidation yields were measured polarographically by passing the oxidizing cell effluent at steady state continuously through a deaerator which removed oxygen with a concurrent stream of nitrogen, and then through a flow-through dropping-mercury electrode. The half-wave potential for Co(II) reduction in most media was around −1.3 v against an Ag–AgCl electrode in 6 M NaCl, while that for Co(III) reduction was around −0.2 v.

For some oxidation runs, additional studies were made—spectrophotometric analyses, complex stability as a function of time, ion-exchange separations, and activity determinations when the complexes were prepared from $Co^{58}(II)$ or labeled ligands. All such studies were made on portions of the oxidizing cell effluent accumulated after steady state was reached.

Results and Discussion

Ammoniacal Systems.—Co(III) was quantitatively oxidized in 0.5 M NH₃–0.5 M NH₄Cl buffer (pH 9.5), but spectrophotometric studies showed that a mixture of 80% pentaammine and 20% hexaammine was obtained when carbon was used as the electrode material. To estimate the amounts of each complex in the mixture, absorbances were measured at 450 and 520 mμ. Spectrophotometric absorption curves in the buffer solution of pure aquopentaamminecobalt(III) chloride (pink, absorption peaks at 368 and 506 mμ) and of pure hexaamminecobalt(III) nitrate (yellow, peaks at 346 and 491 mμ) permitted estimation of the molar absorptivities of the two complexes at 450 and 525 mμ and consequent estimation of the percentage of each complex in the mixture.

Quantitative yields of cobalt(III) ammines were obtained using carbon and platinum packing in ammonia-ammonium salt buffers of chloride, nitrate, perchlorate, acetate, carbonate, and sulfate. Oxidation was easiest in chloride and most difficult in perchlorate as measured by the applied potential necessary to obtain 100% Co-(III). Polarograms of the oxidizing cell effluents in

ammonia–ammonium salt buffers containing various anions were not significantly different. The half-wave potentials for Co(III) to Co(II) and for Co(II) to Co(0) were similar in all of the solutions, and only trivial differences in the polarographic maxima were observed.

Sulfate Systems.—Oxidation of Co(II) in sulfate media required use of the membrane cell. The oxidation was not quantitative (yields up to 30%) and current efficiencies were low (around 20%).

Different Co(III) complexes were indicated spectrophotometrically. In all of the sulfate solutions, Co(II) showed a single absorption peak at 510 mμ. After electrolytic oxidation of 0.01 M CoSO$_4$ in 0.1 M H$_2$SO$_4$–0.01 to 1 M Na$_2$SO$_4$, two other peaks were observed at 610 mμ (previously reported for cobalt(III) sulfate) and at 406 mμ (unreported). The Co(III) was not very stable, because both polarographic current at −0.6 v and absorbances at 406 and 610 mμ decreased similarly with time. Half-times for Co(III) decay at room temperature were highly dependent upon the composition of the medium: 100 min in 0.1 M H$_2$SO$_4$–1 M Na$_2$SO$_4$; 75 min in 0.1 M H$_2$SO$_4$; 20 min in 0.1 M Na$_2$SO$_4$; and 12 min in 0.01 M Na$_2$SO$_4$. When 0.01 M cobalt(II) sulfate alone was oxidized without any supporting electrolyte, the half-time for decay was only about 3 min, long enough to observe polarographically, but not long enough to permit collection for absorbance measurements.

When prepared in 0.1 M H$_2$SO$_4$ alone, without any Na$_2$SO$_4$, the short-wavelength peak occurred at 387 mμ, which decreased and shifted to 406 mμ as decay occurred, indicating the existence of still another Co(III) complex.

Acetate Systems.—Quantitative oxidation of Co(II) in acetate solutions was obtained with the porous glass cell, giving a green Co(III) complex with a small absorption peak at 600 mμ and a larger peak at 344 mμ. When prepared by oxidation of 0.002 M Co(NO$_3$)$_2$ in 0.2 M HOAc–0.5 M NaOAc (pH 4.88), polarographic measurement showed the green Co(III) complex to be quite stable: only 50% reduction was observed after 48 hr.

Partial reduction of the green complex was catalyzed by passage through Dowex 50W or through Dowex 1, but that part of the green complex that was not reduced was not retained on either resin, in accord with previous observations.[10] Some workers have proposed a neutral trisacetate complex,[11] while others have proposed a polymeric hydroxy-bridged acetate complex.[10] In an unsuccessful attempt to determine the ratio of cobalt to acetate in the green complex, it was interestingly found that a mixed bed of Dowex 50W and Dowex 1 catalyzed the exchange of free C^{14}-labeled acetate in solution with acetate bound in the complex even more rapidly than the reduction.

Other Co(III) complexes were also obtained in acetate media. Electrolytic oxidation of 0.002 M Co(NO$_3$)$_2$ in 0.5 M NaOAc (pH 6.22) gave a fine brown precipitate, but the colorless supernate contained Co(III) (measured polarographically) which was strongly held on

Dowex 1, indicating an anionic species. After elution with 1 M NaCl, the cobalt was shown polarographically to be still in the trivalent state. Electrolytic oxidation of 0.002 M Co(NO$_3$)$_2$ in 0.003 M HOAc–0.008 M NaOAc (pH 3.58) also gave a colorless Co(III) complex, but no precipitate. The complex was retained on Dowex 1, but not strongly at all; it was eluted with only slight tailing by the dilute acetate buffer, and 1 M NaCl was not required for elution.

Acid Systems.—Co(III) species could be prepared even in 0.1 M HClO$_4$ and 0.1 M HNO$_3$ although the yields were quite small (around 15%), even with the membrane cell. The Co(III) was detected with the flow-through dropping-mercury electrode located about 20 sec downstream from the oxidizing cell. Further characterization of the Co(III) species was not attempted; their instability did not permit collection of the oxidizing cell effluent for batch spectrophotometric or polarographic analysis.

Conclusions

Continuous electrolysis cells are described in which Co(II) may be rapidly oxidized to Co(III) complexes at controlled potential, and in solutions of controlled composition, at concentrations sufficient to permit separation, characterization, and quantitation by conventional ion-exchange, spectrophotometric, and polarographic methods. Oxidation times are about 1 min. Co(III) complexes (some hitherto unreported) can be prepared in acid (HClO$_4$, H$_2$SO$_4$, HNO$_3$) and in buffered (acetate, ammonia) solutions. Anodic oxidation in flowing systems with continuous sensing devices should permit study of relatively short-lived Co(III) complexes.

The Chemistry of Bis(monofluorocarbonyl) Peroxide: Generation of the Fluoroformyl Radical and Synthesis of Fluoroformylsulfuryl Fluoride

BY W. B. FOX AND G. FRANZ

Arvia, *et al.*, recently reported that the reaction of fluorine, carbon monoxide, and excess oxygen affords a novel compound C$_2$F$_2$O$_4$, to which the structure corre-