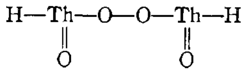
oxidizing agent. Permanganate also yellows the residue, but the color becomes obscured by deposition of (probably) MnO_2. Even with boiling, Ce^{4+} evolves no gas from the residue. The yellow material formed with nitric acid oxidation was found to retain no nitrogen. Karabash[4] also found yellowing with hydrogen peroxide, and on the basis of this reaction postulated that the yellow form corresponds to the species



$$\mathrm{H{-}\underset{\underset{O}{\|}}{Th}{-}O{-}O{-}\underset{\underset{O}{\|}}{Th}{-}H}$$

To form this peroxide by oxidation from HTh(O)-OH requires one equivalent of oxidizing agent per thorium. With the stable oxidizing agent Ce^{4+}, reaction at room temperature or with slight warming produced yellow residue with the consumption of only 10–20% of the expected amount of oxidant. More cerium could be consumed by prolonged boiling, but this further consumption might be due to residual chloride, etc. Only small volumes of permanent gas (in many cases, none) could be evolved under these conditions, in contrast with the claims of Karabash for permanganate oxidation. As noted above, permanganate in our hands could give the yellowing reaction. It may be that the yellowing reaction is limited primarily to surface layers, but the nature of the reaction and its product must still be classed as uncertain.

Experimental

One g. of cast thorium metal was dissolved in 5 *N* DCl. The mixture was heated under reflux to complete reaction. After cooling, the residue was separated by centrifugation. This residue then was washed four times with 2 *N* HCl, separating each wash liquid by centrifugation.

The washed residue was transferred to a two-neck flask. To one neck was attached a bent-necked flask containing 6 *N* HCl with the usual catalytic amounts of fluorosilicic acid. The second neck of the reaction vessel was attached to a vacuum line. The solution was frozen down and degassed, and the stopcock to the vacuum line was closed. The solution was added to the thorium residue by rotating the flask about its joint, and the mixture was heated until reaction was complete and the residue dissolved. The gas was transferred to a gas sample tube by means of a Toepler pump, and analyzed mass spectrometrically. (The instrument used was a Consolidated Engineering Corp. Model 21-620. We thank C. E. Plucinski for the analysis.) The gas contained only hydrogen, the isotopic composition of which was HD, 87%; H_2 12%; and D_2, 1%.

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A Novel Synthesis of the Hexafluorophosphate of the Cyclopentadienyliron Tricarbonyl Cation

BY R. B. KING

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The cation $[C_5H_5Fe(CO)_3]^+$, a member of the isoelectronic series which includes the species $C_5H_5Mn(CO)_3$,[1] $[C_5H_5Cr(CO)_3]^-$,[2] and $[C_5H_5V(CO)_3]^{-2}$,[3] was unknown until recently when two syntheses of this cation were reported. One method was based on the reaction of a cyclopentadienyliron dicarbonyl halide with carbon monoxide in an inert solvent in the presence of an aluminum halide as a catalyst.[4] The other method was based on the reaction of a cyclopentadienyliron dicarbonyl halide with carbon monoxide in acetone solution[5] in the presence of sodium tetraphenylborate. A substituted cyclopentadienyliron tricarbonyl cation also has been prepared by the protonation of fulveneiron tricarbonyl derivatives.[6]

This note describes a new method for the synthesis of the hexafluorophosphate of this cation involving the carbonylation of cyclopentadienyliron dicarbonyl iodide in the presence of a mixture of aqueous 65% hexafluorophosphoric acid and propionic anhydride. This method has the advantage that analytically pure $[C_5H_5Fe(CO)_3][PF_6]$ may be isolated directly from the reaction mixture and is suited for the convenient preparation of this salt in quantities of 20 g. and greater.

This hexafluorophosphoric acid–propionic anhydride mixture is also of use in the synthesis of stable salts of other substituted iron tricarbonyl cations. Treatment of cycloheptatrieneiron tricarbonyl and cyclooctatetraeneiron tricarbonyl with a hexafluorophosphoric acid–propionic anhydride mixture at room temperature yields the stable salts $[C_7H_9Fe(CO)_3][PF_6]$ and $[C_8H_9Fe(CO)_3][PF_6]$, respectively. Other salts of these

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[1] E. O. Fischer and R. Jira, *Z. Naturforsch.*, **9b**, 618 (1954).

[2] E. O. Fischer and W. Hafner, *ibid.*, **10b**, 140 (1955).

[3] E. O. Fischer and S. Vigoureux, *Ber.*, **91**, 2205 (1958).

[4] E. O. Fischer and K. Fichtel, *ibid.*, **94**, 1200 (1961).

[5] A. Davison, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.*, 3172 (1961).

[6] E. Weiss and W. Hübel, *Angew. Chem.*, **73**, 298 (1961).

cations such as the tetrafluoroborates have been reported previously.[7–9]

Experimental

Hexafluorophosphoric acid in 65% aqueous solution was purchased from the Ozark-Mahoning Company. The propionic anhydride was Eastman White Label grade used without further purification. Cyclopentadienyliron dicarbonyl iodide was prepared by a published method[10] which can be scaled up without difficulty to produce the material in pound quantities in nearly quantitative yields.

Cyclopentadienyliron Tricarbonyl Hexafluorophosphate.—A mixture of 13 ml. of 65% aqueous hexafluorophosphoric acid and 50 ml. of propionic anhydride was prepared by very slow addition with stirring since much heat is generated. After cooling to room temperature, this mixture and 10 g. (32.9 mmoles) of cyclopentadienyliron dicarbonyl iodide were charged into a shaker tube of 300 ml. capacity. The tube was pressurized with 5350 p.s.i. carbon monoxide and heated to 150–151° for 2 hr., the pressure dropping from 7100 to 7025 p.s.i. The tube then was cooled to room temperature and vented. The solid was separated by filtration. Unreacted $C_5H_5Fe(CO)_2I$ was removed by washing with four 100-ml. portions of dichloromethane, and white water-soluble impurities (possibly formed by corrosion of the bomb) then were removed by washing with four 100-ml. portions of water. After further washing with ethanol and dichloromethane, the yellow air-stable, water-insoluble crystals of $[C_5H_5Fe(CO)_3][PF_6]$ weighed 6.9 g. (60% yield).

This reaction can be scaled up to give more than 20 g. of product.

Anal. Calcd. for $C_8H_5O_3F_6PFe$: C, 27.4; H, 1.4; F, 32.5; P, 8.9; Fe, 16.0. Found (two independent preparations): C, 27.4, 27.4; H, 1.5, 1.6; F, 32.3, 31.9; P, 8.9, 8.8; Fe, 15.6, 15.7.

Infrared Spectrum.—C–H at 3160 (w) cm.$^{-1}$; carbonyl bands at 2090 (s) and 2150 (s) cm.$^{-1}$; P–F band at 835 (vs) cm.$^{-1}$; other bands at 1440 (w) and 880 (m) cm.$^{-1}$.

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(7) H. J. Dauben and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 497 (1961).

(8) R. Burton, L. Pratt, and G. Wilkinson. *J. Chem. Soc.*, 594 (1961).

(9) G. N. Schrauzer, *J. Am. Chem. Soc.*, **83**, 2966 (1961).

(10) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).

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Mercury and Sodium Tetracarbonylcobaltate(−I)

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The standard procedure[1] for the preparation of sodium tetracarbonylcobaltate(−I), $NaCo(CO)_4$, consists of treating an ether solution of dicobalt octacarbonyl with 1% sodium amalgam. In searching for alternate solvents, we noted that solutions of $Co_2(CO)_8$ in hexane, when treated with amalgam, became yellow before turning colorless. Investigation revealed that the yellow color was due to mercury(II) tetracarbonylcobaltate(−I), $Hg[Co(CO)_4]_2$. Isolation of the mercury compound and subsequent treatment of its ether solution with amalgam resulted in rapid conversion to $NaCo(CO)_4$. Apparently, therefore, in the ether (as well as in the hexane) preparation of $NaCo(CO)_4$ from dicobalt octacarbonyl and sodium amalgam, $Hg[Co(CO)_4]_2$ is an intermediate. Indeed it was possible to isolate a small amount of the mercury compound during the ether preparation.

We also wish to report that treating a hexane solution of dicobalt octacarbonyl with mercury alone at room conditions under carbon monoxide gives a quantitative yield of $Hg[Co(CO)_4]_2$. Since this carbonyl precipitates elemental mercury when warmed with pyridine,[2] a novel purification of mercury thus is available.

Experimental

A mixture of 45 g. of 1% Na–Hg was stirred under carbon monoxide with a solution of 1.80 g. of dicobalt octacarbonyl in 100 ml. of hexane. After 24 hr. of stirring, the conversion to sodium tetracarbonylcobaltate(−I) was complete. However, after only 1.5 hr., the solution contained approximately 1 mmole each of dicobalt octacarbonyl and mercury(II) tetracarbonylcobaltate(−I). Analysis was made by treating aliquots with pyridine, which reacts only slowly[2] with the mercury compound but very rapidly[3] with the cobalt carbonyl to liberate 8/3 moles of carbon monoxide per mole of $Co_2(CO)_8$. Addition of water to the mixture, followed by separation and evaporation of the hexane layer, gave pure $Hg[Co(CO)_4]_2$, m.p. 81–82°, identical with an authentic sample[4] prepared from ammonia, cobalt carbonyl, and mercuric chloride.

In a similar preparation, at 0° with ether as a solvent, an aliquot was withdrawn after 45 min. and evaporated to dryness. The residue was taken up in hexane; pyridine and then water were added. Separation and evaporation of the hexane layer gave a small quantity of $Hg[Co(CO)_4]_2$, m.p. 80–81°.

A solution of 0.130 g. of $Hg[Co(CO)_4]_2$ in dry ether was added to 20 g. of 1% Na–Hg under carbon monoxide. The yellow color of the solution disappeared completely after 15 min. The presence of $NaCo(CO)_4$ was confirmed by addition of methyl iodide followed by triphenylphos-

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(4) W. Hieber and H. Schulten, *Z. anorg. allgem. Chem.*, **232**, 17 (1937).