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Organometallic Difluorodithiophosphates

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A variety of organometallic difluorodithiophosphates have been prepared by the reaction of difluorodithiophosphoric acid, HPS_2F_2, or its cesium salt, $CsPS_2F_2$, with organometal halides and also by the reaction of this acid with organometal hydrides. The tertiary and ditertiary phosphine adducts $Mn(CO)_3P(C_6H_5)_3S_2PF_2$ and $Mn(CO)_3[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]SP(S)F_2$ have been synthesized. Some spectral properties of these new compounds are included.

A number of transition metal difluorodithiophosphate compounds have been reported by the reaction between HPS_2F_2 and transition metal halides.[1] An extension of this procedure has now led to a variety of nonsaline organometallic difluorodithiophosphates. Examples of the synthesis of these compounds from HPS_2F_2 and organometallic hydrides are also provided and these are summarized in the equations

$$\left.\begin{array}{l} HPS_2F_2 + \pi\text{-}C_5H_5M(CO)_xX \longrightarrow \\ \qquad\qquad \pi\text{-}C_5H_5M(CO)_{x-1}S_2PF_2 + HX + CO \\ \qquad M'(CO)_yX \longrightarrow M'(CO)_{y-1}S_2PF_2 + HX + CO \end{array}\right\} \quad (1)$$

$$\begin{array}{l} HPS_2F_2 + \pi\text{-}C_5H_5M(CO)_xH \longrightarrow \\ \qquad\qquad \pi\text{-}C_5H_5M(CO)_xSP(S)F_2 + H_2 \end{array} \quad (2)$$

where M = Fe [in (1) only], Mo, W; M′ = Mn; X = Cl, Br; x = 2, 3; y = 5. The cesium salt, too, can be used in such preparations,[2] and precedent has been established for the reactions of the latter with metal carbonyls and carbonyl halides.[3,4]

Experimental Part

Reagents.—The intermediates $\pi\text{-}C_5H_5Fe(CO)_2Cl$,[5] $\pi\text{-}C_5H_5Mo(CO)_3Cl$,[6] $\pi\text{-}C_5H_5Mo(CO)_3H$,[7] $\pi\text{-}C_5H_5W(CO)_3H$,[7] and $Mn(CO)_5Br$[7] were prepared and purified by previously elaborated methods. The 1,2-bis(diphenylphosphino)ethane, diphos, was obtained by the method of Chatt and Hart.[8] Difluorodithiophosphoric acid, HPS_2F_2, is synthesized by literature procedures.[9,10]

Apparatus and General Method.—Volatile substances were handled in a standard Pyrex-glass vacuum apparatus. Otherwise, all manipulations were executed within a dry nitrogen atmosphere. The reactors were Pyrex glass bulbs equipped with stopcocks or Fischer-Porter Teflon valves and Teflon-coated bar magnets for stirring. A measured quantity of the organometallic compound was placed into the reactor and an excess of HPS_2F_2 (sufficient to give a liquid phase under the reaction conditions) was distilled into the bulb at −196°. The reactor was allowed to warm slowly to the reaction temperature. Volatile substances were fractionated by distillation and identified by their infrared and/or mass spectra. Substances of low volatility were dissolved in suitable solvents and passed through chromatographic columns packed with Florisil, 60–100 mesh, and finally purified by crystallization or distillation in the manner described below. The quantities in parentheses are millimoles.

Analytical and Spectral Data.—Microanalyses were obtained from Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Carbon, hydrogen, and fluorine analyses were performed by combustion with V_2O_5, and phosphorus was measured gravimetrically. The infrared spectra of the organometallic difluorodithiophosphates were taken in the 2200–700-cm^{-1} region with a Perkin-Elmer Model 621 spectrometer. A 10-cm gas cell with NaCl windows was used for volatile compounds. The compounds which were the subject of this research were examined in solution or Nujol mulls. The results are given in Table I. Fluorine-19 nmr spectra were taken with a Varian Model V4310 spectrometer operating at 40 Mc and the ^{1}H spectra with an HA-60 instrument. Samples were measured in 5-mm o.d. Pyrex tubes using CCl_3F and TMS as internal standards for the fluorine and proton spectra, respectively. Methylene chloride was used as the solvent for the ^{19}F spectra and $CDCl_3$ for the proton.

Synthesis of $\pi\text{-}C_5H_5Fe(CO)_2SP(S)F_2$. A. Using $CsPS_2F_2$.—Twenty-five milliliters of solutions containing 1.6 mmol of each reactant, $\pi\text{-}C_5H_5Fe(CO)_2Cl$ and $CsPS_2F_2$, in acetone were combined in a 100-ml Pyrex reactor with a Fischer-Porter Teflon valve. The mixture was stirred for 48 hr. The CsCl was removed by filtration and the acetone was evaporated in a nitrogen stream. The solid was taken up with 15 ml of benzene and precipitated with petroleum ether (bp 30–60°). A yellow-brown amorphous solid, 0.65 mmol (40% recovery), was obtained, dec pt 95°. *Anal.* Calcd for $\pi\text{-}C_5H_5Fe(CO)_2SP(S)F_2$: C, 27.12; H, 1.63; F, 12.25; P, 9.99. Found: C, 27.01; H, 2.01; F, 12.75; P, 10.31.

B. Using HPS_2F_2.—Alternately, the reactants, $\pi\text{-}C_5H_5Fe(CO)_2Cl$ (4.3) and HPS_2F_2 (8.0), were combined and stirred together for 48 hr at room temperature and then heated at 50° for an additional 18 hr. The gaseous HCl and excess HPS_2F_2 were removed; then 25 ml of acetone was added to the solid phase and the solution was filtered. Hexane, 25 ml, was added to the filtrate. The resulting solution was slowly evaporated with a nitrogen stream. Again, a yellow-brown amorphous solid settled out of the solution. The recovery was 2.6 mmol, 60%.

Synthesis of $\pi\text{-}C_5H_5Mo(CO)_3SP(S)F_2$.—Both $\pi\text{-}C_5H_5Mo(CO)_3H$ (4.0) and HPS_2F_2 (8.1) were stirred together for 48 hr at ambient temperature. The volatile products (4.4) at −80° were withdrawn and analyzed as hydrogen along with trace amounts of H_2S and $HP(S)F_2$. The excess HPS_2F_2 was removed by allowing the reactor to warm while evacuating. To the remaining solid 10 ml of CH_2Cl_2 was added and the resulting red solution was chromatographed; the product eluted with CH_2Cl_2 and was obtained as a red-orange solid by evaporating the solvent to dryness. The solid was redissolved in 10 ml of benzene and 10 ml of heptane was added. Crystallization was caused by slowly removing the more volatile benzene using a stream of nitrogen. The solid was triturated twice with 5-ml portions of petroleum ether to remove trace quantities of the bidentate

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(1) F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, **9**, 629 (1970).

(2) In a preliminary report, the reaction between $CsPs_2F_2$ and $\pi\text{-}C_5H_5Fe(CO)_2Cl$ was found to give a unidentate complex $\pi\text{-}C_5H_5Fe(CO)_2SP(S)F_2$: M. Lustig and L. W. Houk, *Inorg. Nucl. Chem. Lett.*, **5**, 851 (1969).

(3) J. K. Ruff and M. Lustig, *Inorg. Chem.*, **7**, 2171 (1968).

(4) F. A. Hartman and M. Lustig, *ibid.*, **7**, 2669 (1968).

(5) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

(6) T. S. Piper and G. Wilkinson, *ibid.*, **3**, 104 (1956).

(7) R. B. King, "Organometallic Syntheses," Academic Press, New York, N. Y., 1965.

(8) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

(9) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **8**, 281 (1969).

(10) R. W. Mitchell, M. Lustig, F. A. Hartmann, J. K. Ruff, and J. A. Merritt, *J. Amer. Chem. Soc.*, **90**, 6329 (1968).

derivative which slowly forms even at room temperature. The recovery was 2.0 mmol (50%). The compound decomposes at 101–103°. *Anal.* Calcd for $C_5H_5Mo(CO)_3SP(S)F_2$: C, 25.40; H, 1.33; F, 10.05; P, 8.19; mol wt 378. Found: C, 25.40; H, 1.24; F, 11.87; P, 8.26; mol wt 417 (osmometry in benzene).

Synthesis of π-$C_5N_5Mo(CO)_2S_2PF_2$. A. From π-$C_5H_5Mo(CO)_3Cl$ and HPS_2F_2.—The reactants π-$C_5H_5Mo(CO)_3Cl$ (1.79) and HPS_2F_2 (4.47) were allowed to react at 50° for 48 hr. The volatile products were HCl and CO, excess HPS_2F_2, and small amounts of H_2S, $HP(S)F_2$, PSF_3, PF_3, and SiF_4. The solids which were soluble in 10 ml of benzene were passed through a chromatographic column and the product was eluted with 9:1 petroleum ether–benzene solution. From the purple solution purple needles were crystallized by the slow evaporation of the solvent to near dryness. The recovery was 0.84 mmol (47%), mp 39–40°. *Anal.* Calcd for $C_5H_5Mo(CO)_2S_2PF_2$: C, 24.01; H, 1.44; F, 10.85; P, 8.85; mol wt 350. Found: C, 24.46; H, 1.77; F, 11.10; P, 8.90; mol wt 350 (osmometry in benzene).

B. Decarbonylation of π-$C_5H_5Mo(CO)_3SP(S)F_2$.—The compound (0.67) was dissolved in 50 ml of benzene and refluxed for 90 min. The orange-red solution turned purple rapidly. The solution was concentrated to 5 ml and then passed through a chromatographic column. The product was eluted and crystallized in the way described above. The yield was high, but because a small sample of reactant was used and because of some loss in the work-up, the recovery was 0.21 mmol (31%), mp 39.5–40°.

Synthesis of π-$C_5H_5W(CO)_3SP(S)F_2$.—The hydride, π-$C_5H_5W(CO)_3H$ (0.28), and HPS_2F_2 (1.0) were stirred at 50° for 24 hr. After removal of the hydrogen and the excess HPS_2F_2, the solids were dissolved in 10 ml of CH_2Cl_2 and chromatographed. Benzene was used for the elution of the π-$C_5H_5W(CO)_3SP(S)F_2$. Crystallization was accomplished by the slow evaporation of the solvent. The recovery of the rust crystals, dec pt 115–117°, was 0.86 mmol (31%). *Anal.* Calcd for $C_5H_5W(CO)_3SP(S)F_2$: C, 20.62; H, 1.08; F, 8.15; P, 6.62; mol wt 466. Found: C, 20.81; H, 1.27; F, 8.14; P, 6.70; mol wt 455 (osmometry in benzene). Heating this compound in cyclohexane for 24 hr at 75° resulted in decomposition. There was no infrared spectroscopic evidence of chelation of the dithio ligand.

Synthesis of $Mn(CO)_4S_2PF_2$.—In a similar fashion, $Mn(CO)_5Br$ (3.86) and HPS_2F_2 (5.0) were heated for 36 hr at 50°. The HBr and CO (3.8 each) and the unreacted HPS_2F_2 were removed and the product was put through the chromatographic column using petroleum ether as the eluent. After the removal of the eluate by distillation at −45°, the red-orange $Mn(CO)_4S_2PF_2$ (bp 24° (8 mm), mp 13.0–13.7°) was distilled and 3.04 mmol (78.5% yield) was obtained. *Anal.* Calcd for $Mn(CO)_4S_2PF_2$: C, 16.01; F, 12.66; P, 10.32; mol wt 300. Found: C, 16.16; F, 12.58; P, 10.39; mol wt 306 (cryoscopic in benzene).

Synthesis of $Mn(CO)_3P(C_6H_5)_3S_2PF_2$.—The $Mn(CO)_4S_2PF_2$ (1.99) and a slight excess of $P(C_6H_5)_3$ (2.3) were combined in 50 ml of benzene. Reaction occurred immediately with evolution of CO. After 1.5 hr of stirring the volume of the solvent was reduced until solid began to crystallize out of solution. The solution was passed through a chromatographic column and the product eluted with benzene was then crystallized from benzene–heptane solution. The recovery of the yellow solid was 0.56 mmol (28%), mp 118–120° dec. *Anal.* Calcd for $Mn(CO)_3P(C_6H_5)_3S_2PF_2$: C, 47.20; H, 2.82; F, 7.11; P, 11.59; mol wt 534. Found: C, 47.20; H, 2.99; F, 7.28; P, 11.41; mol wt 531 (osmometry in benzene).

Synthesis of $Mn(CO)_3(diphos)SP(S)F_2$.—A 50-ml benzene solution containing $Mn(CO)_4S_2PF_2$ (2.09) was mixed with another 50-ml benzene solution containing diphos (2.09). The reaction mixture was stirred for 18 hr to ensure complete reaction with the diphos. A yellow solid began to settle out soon after the reaction commenced. After termination of the reaction, the solid was separated by filtration and 0.71 mmol of the crude diphos complex was obtained. The solution was concentrated to about 5 ml and another 0.60 mmol of the same substance was found. The fractions of the product were combined and eluted through the chromatographic column with CH_2Cl_2. The solvent was removed to near dryness and the yellow-orange solid was washed twice with 5-ml portions of petroleum ether. The recovered complex was 1.52 mmol (72.1%), dec pt 181°. *Anal.* Calcd for $Mn(CO)_3(diphos)SP(S)F_2$: C, 51.96; H, 3.61; F, 5.67; P, 13.86; mol wt 670. Found: C, 51.92; H, 3.54; F, 5.87; P, 13.96; mol wt 677 (osmometry in benzene). A sample of this compound was refluxed for 30 hr in benzene and the infrared spectrum indicated no change.

Discussion

The manner in which the $PS_2F_2^-$ ligand coordinates depends upon the relative lability of the atom(s) or groups(s) bound to the metal and the reaction conditions. The lability of any particular moiety attached to the metal atom is also dependent on the metal. To illustrate, both $CsPS_2F_2$ in the presence of a solvent and HPS_2F_2, neat, react with π-$C_5H_5Fe(CO)_2Cl$, although the latter reaction proceeds under more forceful conditions, *i.e.*, at 50° as opposed to ambient temperature for the former. In both cases a unidentate difluorodithiophosphate complex results by displacement of the chloride only. Difluorodithiophosphoric acid also reacts with π-$C_5H_5Mo(CO)_3Cl$ at 50°, but in this case both chloride and carbon monoxide are expelled and a bidentate complex is formed. Further evidence is thus provided for the enhanced lability of one of the carbonyl groups of the molybdenum tricarbonyl compared to that of the corresponding iron dicarbonyl.[2,11] On the other hand a reaction at room temperature between HPS_2F_2 and the hydride, π-$C_5H_5Mo(CO)_3H$, rather than the chloride, leads to a unidentate complex (Figure 1) with the evolution of hydrogen. Upon warming the unidentate complex at 50°, carbon monoxide is released and a bidentate complex is formed. When the corresponding tungsten hydride is substituted for the molybdenum, more forceful conditions are required to achieve reaction with HPS_2F_2, and, even so, at 50° only a unidentate complex is prepared (Figure 1). Therefore, both the hydride and the CO groups bound to molybdenum are more labile toward attack by HPS_2F_2 than those attached to tungsten. This is consistent with results from other similar systems.[12] In all cases the halide or hydride is displaced prior to removal of the carbonyl.

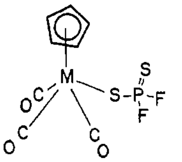

Figure 1.—π-Cyclopentadienyltricarbonylmetal(II) difluorodithiophosphate (M = Mo or W).

Difluorodithiophosphoric acid reacts readily with $Mn(CO)_5Br$ to displace the bromide and CO and form the bidentate difluorodithiophosphate, $Mn(CO)_4S_2PF_2$. A second CO is easily displaced by allowing a

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(11) F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, **3**, 1398 (1964).

(12) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

TABLE I

INFRARED SPECTRA OF METAL CARBONYL DIFLUORODITHIOPHOSPHATE COMPLEXES AND RELATED COMPOUNDS

Compound	Freq, cm^{-1}		
	C═O	P—F	P—S
π-$C_5H_5Fe(CO)_2SP(S)F_2$	2051 vs, 1998 vs[a]	850 ms, ~830 sh[a]	706 s[a]
π-$C_5H_5Mo(CO)_3SP(S)F_2$	2062 s, 1988 vs, 1973 vs[b]	858 s, 832 s[c]	741 s, 704 ms[c]
π-$C_5H_5Mo(CO)_2S_2PF_2$	1978 vs, 1899 vs[c]	882 vs, 865 s[c]	700 ms, 675 sh[c]
π-$C_5H_5W(CO)_3SP(S)F_2$	2054 s, 1960 vs, 1972 vs[b]	862 ms, 842 ms[c]	719 s, 705 m[c]
$Mn(CO)_4S_2PF_2$	2111 s, 2037 vs, 2020 vs, 1981 vs[d]	897 s, 883 m[c]	704 ms, 692 sh[c]
$Mn(CO)_3P(C_6H_5)_3S_2PF_2$	2040 vs, 1962 s, 1932 ms[d]	878 ms, 860 m[c]	708 ms, 695 ms[c]
$Mn(CO)_3(diphos)SP(S)F_2$	2022 vs, 1950 vs, 1927 vs[c]	852 m, 817 m[c]	716 vs, 711 s[c]
π-$C_5H_5Mo(CO)_2S_2CN(CH_3)_2$	1955, 1865[e]		
π-$C_5H_5Mo(CO)_2S_2CN(C_2H_5)_2$	1931, 1839[e]		
π-$C_5H_5Fe(CO)_2SC(S)N(CH_3)_2$	2030, 1990[c]		
π-$C_5H_5Fe(CO)_2Cl$	2055 vs, 2014 vs[b]		
π-$C_5H_5Mo(CO)_3Cl$	2050 vs, 1991 vs, 1969 vs[b]		

[a] Potassium bromide pellet. [b] Cyclohexane. [c] Nujol mull. [d] Hexane. [e] Methylene chloride.

tertiary phosphine, $P(C_6H_5)_3$, to react with $Mn(CO)_4S_2PF_2$. However when a ditertiary phosphine, diphos, reacts with this compound, a very interesting result is observed. The diphos ligand not only displaces one carbonyl group but also renders one of the sulfur atoms nonbonding to the metal with the formation of a unidentate dithiophosphato tricarbonyl compound (Figure 2). The substitution of sulfur by phosphorus has been observed in a similar case.[13]

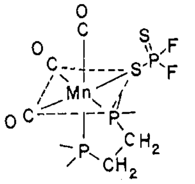
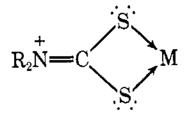


Figure 2.—Tricarbonyl-1,2-bis(diphenylphosphino)ethanemanganese(I) difluorodithiophosphate (the phenyl groups are omitted).

The infrared and nmr spectra corroborate the proposed structures, and, further, the position of the metal–carbonyl stretching bands (Table I) of the compounds prepared in this work also gives indication of the relative electron-donating effects of the difluorodithiophosphate group compared to other electron donors. For example, the compounds of the type π-$C_5H_5Mo(CO)_2S_2CNR_2$ (R = CH_3,[11] C_2H_5[2]) absorb at lower frequency than the corresponding π-$C_5H_5Mo(CO)_2S_2PF_2$. The increased donation of negative charge into the antibonding CO molecular orbitals would result in a shift to the lower frequencies observed for the dithiocarbamates. The observed lowering is probably the result of the inductive effect as well as resonance effect indicated by the canonical form



Indeed, from a comparison of the carbonyl stretching frequencies in the spectra of compounds of the form π-$C_5H_5Fe(CO)_2L$, where L is unidentate dimethyldithiocarbamate,[14] unidentate difluorodithiophosphate,[2] or chloride,[5] those of the dithiocarbamate are, again, the lowest and those of the difluorodithiophosphate are close to the frequencies of the chloride (Table I). A similar comparison may be made between π-$C_5H_5Mo(CO)_3Cl$ [ν(CO) 2050, 1991, and 1969 cm^{-1}][6] and the corresponding unidentate difluorodithiophosphate compound [ν(CO) 2062, 1988, and 1973 cm^{-1}].

The number of the ν(CO) fundamental stretching modes as well as the position of the P–F stretching frequencies are suggestive of the manner in which the PS_2F_2 group is linked to the metal. Both π-$C_5H_5Mo(CO)_3SP(S)F_2$ and π-$C_5H_5W(CO)_3SP(S)F_2$ which presumably possess C_s symmetry have the predicted three carbonyl stretching bands. The analogous π-$C_5H_5Fe(CO)_2SP(S)F_2$ has two stretching fundamentals. These compounds also show two absorptions near 850 cm^{-1} assigned to the P–F asymmetric and symmetric stretching modes, *i.e.*, in the region associated with the P–F stretching motions of other unidentate PS_2F_2 complexes.[1] On the other hand, the C_{2v} π-$C_5H_5Mo(CO)_2S_2PF_2$ also shows two ν(CO) stretching frequencies as well as a band at 888 cm^{-1}, features characteristic of a bidentate complex.[1] The spectrum of $Mn(CO)_4S_2PF_2$ exhibits four carbonyl stretching modes expected for C_{2v} symmetry and the ν(P–F) modes are located near 900 cm^{-1} implying bidentate bonding of the PF_2F_2 ligand. Upon substitution of one carbonyl group with $P(C_6H_5)_3$, one less carbonyl band is present while the P–F modes are located at only slightly lower frequencies than those observed in the preceding case, and chelation of the PS_2F_2 group is still suggested. However, when diphos is present in the molecule, three carbonyl bands are still present and an exaggerated shift of the P–F stretching absorptions to lower frequency occurs indicating that one metal–sulfur bond has been cleaved and the ditertiary phosphine is chelated. Although steric factors would favor the trans configuration, the three approximately equal-intensity, strong ν(CO) absorption peaks as well as the molecular weight data encourage the prediction of the monomeric cis.[15]

The nmr spectra are consistent with the formula-

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(13) L. W. Houk and G. R. Dobson, *Inorg. Chim. Acta*, **1**, 287 (1967).

(14) C. O'Connor, J. D. Gilbert, and G. Wilkinson, *J. Chem. Soc. A*, 84 (1969).

(15) R. J. Angelici, F. Basolo, and A. J. Poë, *J. Amer. Chem. Soc.*, **85**, 2215 (1963).

tions. The ^1H spectra of π-$C_5H_5Mo(CO)_3SP(S)F_2$ and π-$C_5H_5Mo(CO)_2S_2PF_2$ show resonances at τ 4.29 and 4.50, respectively, which are assigned to the cyclopentadienyl groups. The ^{19}F nmr spectra may be used to assign the manner of bonding of the PS_2F_2 ligand, because phosphorus–fluorine coupling constants approximating 1200 and 1300 Hz have been assigned to unidentate and bidentate structures, respectively, in another group of transition metal complexes containing the same ligand.[1] The coupling constants and chemical shifts of π-$C_5H_5Mo(CO)_3$-$SP(S)F_2$ and $Mn(CO)_3(diphos)SP(S)F_2$, believed to possess the unidentate structure, are 1204 and 1216 Hz, respectively, and 12.4 and 13.7 ppm, respectively. The same data for $Mn(CO)_4S_2PF_2$ are 1304 Hz and −2.4 ppm consistent with the bidentate structure. It is not always safe to generalize coupling constants or even the positions of stretching frequencies in terms of unidentate of bidentate structures when comparing different sets of compounds. However, other data partially justify the structural assignments, and comparisons have been made between two series of transition metal complexes.

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CONTRIBUTION FROM THE DEPARTMENT OF MEDICAL CHEMISTRY,
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A Potentiometric Study of Equilibria in Aqueous Divalent Metal Orthophosphate Solutions[1]

BY C. W. CHILDS[2]

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Aqueous solutions containing potassium nitrate (0.15 mol l.$^{-1}$) and relatively small amounts of orthophosphoric acid and divalent metal nitrate have been titrated potentiometrically with potassium hydroxide at 37°. Data for each of the metal ions magnesium(II), calcium(II), zinc(II), and copper(II) have been analyzed by a least-squares method in terms of the possible formation of 1:2 and 2:2 as well as 1:1 species. To reduce the possibility of chance improvement in fit, data from three different titrations (five for magnesium(II)) have been analyzed simultaneously for each system. In each case the data are consistent with the presence in solution of the species $MH_2PO_4^+$, $MHPO_4^0$, $MH_3(PO_4)_2^-$, and $M_2H_2(PO_4)_2^0$, and, in addition, MPO_4^- in the case of magnesium(II). Approximate values for the equilibrium constants expressed as concentration quotients for 0.15 mol l.$^{-1}$ of potassium nitrate of these species are presented. Possible structures for $MH_3(PO_4)_2^-$ and $M_2H_2(PO_4)_2^0$ in solution are similar to arrangements in solid divalent metal orthophosphates.

Introduction

Knowledge of the interactions between divalent metal ions and orthophosphate anions in aqueous solutions is pertinent to the study of many natural systems. Of the previous equilibrium studies[3,4] of these interactions, most have been concerned with the determination of the equilibrium constant of the species $MHPO_4^0$ (where M is a divalent metal ion—usually calcium(II) or magnesium(II)) and sometimes $MH_2PO_4^+$. In one study[4] of calcium orthophosphate solutions an equilibrium constant for $CaPO_4^-$ was obtained.

In all such studies the assumption has been made that only 1:1 metal ion–orthophosphate species are formed. However the evidence for the dimeric species $H_5(PO_4)_2^-$,[5–7] $H_4(PO_4)_2^{2-}$, and $H_3(PO_4)_2^{3-}$ [7] in orthophosphate solutions suggested the possibility of the existence of 1:2 and 2:2 species in divalent metal orthophosphate solutions. Gardner and Glueckauf have recently shown[8] that the formation of 1:2 or 2:1 (or both) and 2:2 species is consistent with osmotic coefficient data for the sulfates of magnesium(II), calcium(II), zinc(II), nickel(II), and copper (II) in aqueous solution.

The present paper reports pH measurements at 37° with the cell

glass electrode|H_3PO_4 (c_1), $M(NO_3)_2$ (c_2), KOH (c_3),
KNO_3 (0.15 mol l.$^{-1}$)¦KCl(satd)|calomel electrode

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(1) Presented in part at the 12th International Conference on Coordination Chemistry, Sydney, Australia, Aug 1969.

(2) Correspondence should be addressed to the author at the Canada Centre for Inland Waters, Box 5050, Burlington, Ontario, Canada.

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