[CONTRIBUTION FROM WM. A. NOYES LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

A Coördination Model as an Alternative to the Solvent System Concept in Some Oxychloride Solvents. I. Similarity in the Behavior of Phosphorus Oxychloride and Triethyl Phosphate as Non-aqueous Solvents

BY DEVON W. MEEK[1] AND RUSSELL S. DRAGO

RECEIVED MAY 29, 1961

The solution behavior of anhydrous ferric chloride in triethyl phosphate [$PO(OEt)_3$] has been shown to be very similar to the reported behavior of ferric chloride in phosphorus oxychloride. Spectral investigations demonstrate that the tetrachloroferrate(III) ion, $[FeCl_4]^-$, is the principal absorbing species present in dilute as well as concentrated solutions of $FeCl_3$ in $PO(OEt)_3$. The formation of $[FeCl_4]^-$ on dissolution of ferric chloride in triethyl phosphate is a direct proof that ionization of some $FeCl_3$ has occurred to produce a cationic iron(III) species. This is interpreted as strong support for using a similar Lewis acid-base mechanism to explain the data in both $POCl_3$ and $PO(OEt)_3$. It is not necessary to obtain a chloride ion from the solvent $POCl_3$ to form $[FeCl_4]^-$. The equilibria shown are proposed to explain the behavior of ferric chloride in triethyl phosphate and to serve as an alternative to the solvent system explanation for phosphorus oxychloride solutions.

$$FeCl_3 + Y_3PO \longrightarrow [FeCl_3OPY_3] \rightleftharpoons [FeCl_{3-x}(OPY_3)_{1+x}]^{x+} + X[FeCl_4]^- \rightleftharpoons [Fe(OPY_3)_n]^{3+} + 3[FeCl_4]^-$$

Introduction

Reactions in non-aqueous solvents have attracted much interest in recent years. The essential equilibria existing in oxyhalide and several other solvents are currently being described by the solvent system concept. Extensive compilations of literature references[2] are available concerning the application of this concept to phosphorus oxychloride, $POCl_3$. The following discussion is a brief review of the literature to afford a comparison with our alternative explanation.

The limited electrical conductivity of pure $POCl_3$ suggests a slight self-ionization

$$POCl_3 \rightleftharpoons POCl_2^+ + Cl^-_{(solvated)} \qquad (1)$$

According to the solvent system concept an "acid" is defined as a solute capable of increasing the concentration of the cation characteristic of the pure solvent, whereas a "base" increases the concentration of the corresponding anion of this self-ionization. Addition of $FeCl_3$ forms $FeCl_4^-$ and $POCl_2^+$; hence, ferric chloride is an acid in $POCl_3$.

The ultraviolet absorption spectra of dilute solutions of ferric chloride ($\sim 10^{-4}$ M) in phosphorus oxychloride demonstrate that tetrachloroferrate(III) ion, $[FeCl_4]^-$, is the principal absorbing species present.[3] No conclusive evidence is available to establish the presence of $POCl_2^+$ in this solution.

At higher concentrations of $FeCl_3$ (about 0.1 M) in the absence of sufficient chloride ion from the solvent to convert all of the $FeCl_3$ to $[FeCl_4]^-$, a red addition compound $[FeCl_3(POCl_3)_x]$ forms. The essential equilibria are represented by

$$FeCl_3 + POCl_3 \rightleftharpoons [FeCl_3ClPOCl_2] \rightleftharpoons POCl_2^+ + [FeCl_4]^- \qquad (2)$$

The color transformation from red to yellow is completely reversible upon dilution or concentration. Addition of a chloride ion donor converts the red color to the yellow color characteristic of $[FeCl_4]^-$.

Conductometric titrations of ferric chloride solutions in phosphorus oxychloride give sharp breaks at a mole ratio of one chloride to one $FeCl_3$. According to the solvent system concept, the net ionic equation for this reaction is

$$POCl_2^+ + Cl^- \longrightarrow POCl_3 \qquad (3)$$

The total reaction for the titration of ferric chloride is then represented by

$$R_4NCl + [POCl_2][FeCl_4] \longrightarrow [R_4N][FeCl_4] + POCl_3 \qquad (4)$$

Recent radiochemical investigations,[4-8] X-ray structure determinations,[9,10] Raman[11] and infrared[12] investigations indicate that the chloride ion transfer mechanism probably has been overemphasized for oxychloride solvents. The data suggest that oxygen is the most basic coördination position in the $POCl_3$ molecule.

X-Ray single crystal studies[9,10] on the addition compounds $SbCl_5 \cdot OPCl_3$ and $[TiCl_4 \cdot OPCl_3]_2$ show that both metals are octahedrally coördinated through the oxygen atom of the $POCl_3$ molecule. The Raman spectra[11] of the compounds $AlCl_3 \cdot OPCl_3$ and $GaCl_3 \cdot OPCl_3$ indicate that coördination occurs through the oxygen. The infrared spectra[12] of phosphoryl halide addition compounds with $TiCl_4$, $SnCl_4$ and $TiBr_4$, also support the assignment of oxygen as the coördinating atom.

Proponents[13,14] of the solvent system concept argue that although the oxygen coördinated species exist in the solid, or under conditions of the spectral studies, different competitive equilibria exist

(1) Department of Chemistry, The Ohio State University, Columbus, Ohio; paper abstracted in part from the Ph.D. thesis of D. W. Meek, University of Illinois, 1961; General Electric Foundation Fellow.

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in $POCl_3$ solutions and are responsible for the observed phenomena (equations 1 to 4).

Radiochlorine exchange experiments[5,6] on the phosgene solvent system indicate conclusively that the self-ionization mechanism is not operative in this solvent.

In the phosphorus oxychloride solvent, chloride exchange between BCl_3 and $POCl_3$ occurs only in excess $POCl_3$.[8] It can be concluded that the species $POCl_2^+$ BCl_4^- does not exist in excess BCl_3, but the possibility of self-ionization cannot be rejected in excess $POCl_3$. Proponents[15] of the solvent system concept argue that appreciable ionization does not occur in excess BCl_3 because of the low dielectric constant of this solvent.

The problem of the mechanism of complex formation in $POCl_3$ is still unsolved. The published information on the properties of $POCl_3$ solutions does not permit a clear decision to be made between a chloride ion transfer mechanism (*i.e.*, the solvent system concept) and a Lewis acid–base interaction between the phosphoryl oxygen atom and the acid. We report information in this article that casts considerable doubt on the validity of the application of the solvent self-ionization mechanism to solutions of acids in phosphorus oxychloride. The solution behavior of anhydrous ferric chloride in triethylphosphate has been shown to be very similar to the reported behavior in $POCl_3$.[3] Use of the solvent $PO(OEt)_3$ excludes the possibility for formation of the $[FeCl_4]^-$ ions by a chloride ion transfer from the solvent. The adduct is insoluble in BCl_3 and this may account for no exchange.

A general mechanism is proposed which accounts for the behavior of ferric chloride solutions and most probably many other Lewis acids in both $POCl_3$ and $PO(OEt)_3$. The mechanism is consistent with the reported X-ray, Raman and infrared studies. This general proposal is also very probably applicable to many other oxyhalide nonaqueous solvents for which the solvent system explanation has been invoked.

Experimental

Reagents.—Sublimed anhydrous iron(III) chloride (Matheson, Coleman and Bell) was resublimed at 200° and stored in a weighing bottle inside a desiccator. Triethylphosphate (Eastman) was dried by refluxing over solid barium oxide and fractionated under high vacuum. The phosphate was stored in a receiver which was protected from light and moisture.

Tetramethylammonium Tetrachloroferrate (III).—One-tenth mole of anhydrous ferric chloride was dissolved in a mixture of 100 ml. of benzene and 75 ml. of ethanol. The product precipitated upon treatment with 0.1 mole of tetramethylammonium chloride in ethanol and was recrystallized from absolute ethanol.

Anal. Calcd. for $C_4H_{12}NFeCl_4$: C, 17.67; H, 4.45; N, 5.15. Found: C, 17.81; H, 4.46; N, 5.33.

Tetramethylammonium chloride was recrystallized from a 50–50 acetone-ethanol mixture and dried in an anhydrous atmosphere.

Tetra *n*-butylammonium chloride was prepared from the corresponding iodide. Analytical reagent grade lithium chloride was used without further purification.

Preparation of Solutions.—Master solutions, 10^{-2} to 10^{-1} *M*, were prepared in a dry box by adding the solvent and weighed quantities of resublimed iron(III) chloride to volumetric flasks. Solutions for spectral measurements were prepared by dilution of the master solutions with pure solvent. Stock solutions of $[(CH_3)_4N][FeCl_4]$ were prepared by dissolution of weighed quantities of the salt in triethylphosphate. Diluted solutions were used to determine molar absorption coefficients of 7600, 6900 and 11,700 l. mole^{-1} cm.$^{-1}$ at 362, 314 and 240 mμ, respectively. The absorbance at these wave lengths obeys Beer's law in the concentration range 10^{-2} to 10^{-5} *M*.

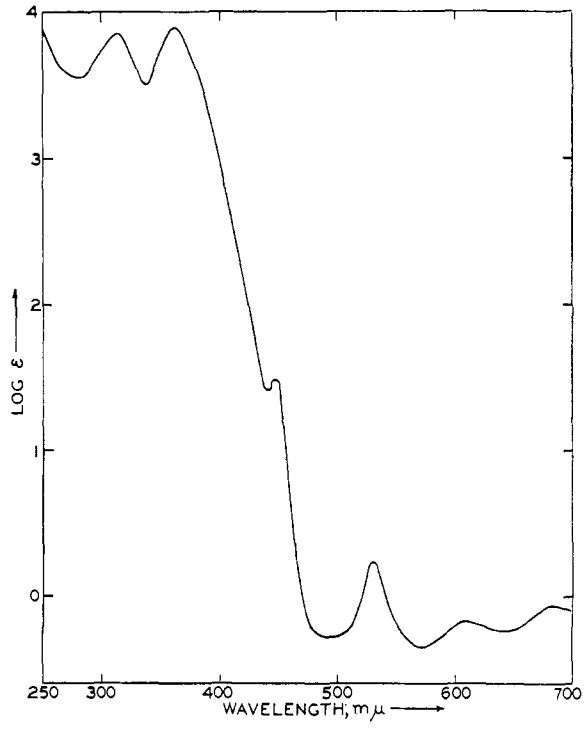

Fig. 1.—Visible and ultraviolet spectrum of $[(CH_3)_4N]$-$[FeCl_4]$ in triethyl phosphate.

Spectrophotometric Measurements.—Visible and ultraviolet absorption spectra were obtained with a recording Cary spectrophotometer, Model 14M. Quantitative data in the ultraviolet region were also obtained with a manually operated Beckman Model D.U. quartz spectrophotometer, with a hydrogen discharge lamp as the light source.

The optical densities of solutions were measured in matched quartz cells of 0.1, 1.0 and 5.0 cm., against the solvent as a reference. A quartz cell of 2.65×10^{-3} cm. path length was used to investigate the spectra of concentrated solutions.

Conductometric Titrations.—Lithium chloride solutions of known concentration were titrated under anhydrous conditions with 0.1 *M* solutions of ferric chloride and antimony trichloride. Conductances were measured at 1000 cycles per second with an Industrial Instruments Conductivity bridge, Model RC 16B2. The solutions were stirred with a magnetic stirrer after addition of each increment of titrant. The conductance curves are characterized by two linear segments intersecting at a mole ratio of one chloride to one $FeCl_3$ or $SbCl_3$.

Results and Discussion

A. Visible and Ultraviolet Spectra. 1. Tetrachloroferrate(III) in Triethyl Phosphate.—The absorption spectra of solutions of $[FeCl_4]^-$ in $PO(OEt)_3$ were examined in detail to aid in establishing the presence of this ion in ferric chloride solutions. Characteristic maxima[16–18] are obtained at 530, 447, 362, 314 and 240 mμ. The

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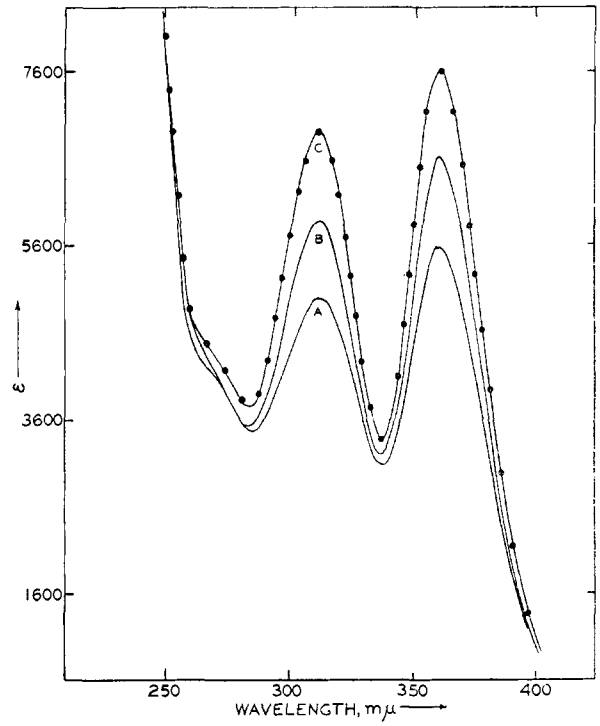

Fig. 2.—Ultraviolet spectra of iron(III) chloride in triethyl phosphate: A, $FeCl_3$, 1×10^{-4} *M*; B, $FeCl_3$ plus 0.50 LiCl; C, $FeCl_3$ plus 1.00 LiCl; . . . $[(CH_3)_4N][FeCl_4]$.

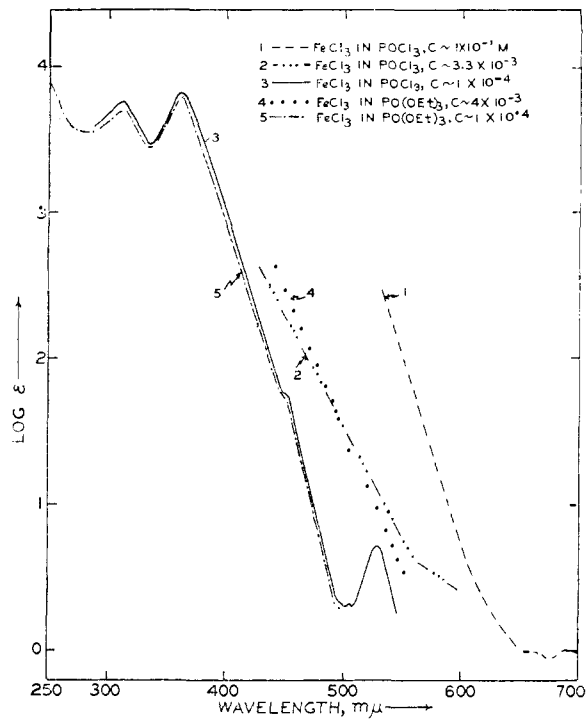

Fig. 3.—Visible and ultraviolet spectra of ferric chloride in triethyl phosphate and phosphorus oxychloride.

spectrum of 10^{-4} *M* solutions contains only the three most intense peaks and is indicated in Fig. 2 by the series of dots. Addition of two moles of lithium chloride to this solution has no effect upon the spectrum, indicating that the tetrachloroferrate (III) ion is completely associated (within experimental error) at a 4 to 1 chloride to iron(III) mole ratio. Evidence regarding the characteristic nature of the spectra and the non-dissociation of $[FeCl_4]^-$ in $PO(OEt)_3$ is further obtained from the similarity of ϵ_{max} and λ_{max} values for this ion in the solvents $PO(OEt)_3$, $POCl_3$,[3] $C_6H_5POCl_2$,[19] Et_2O[16] and concentrated hydrochloric acid solutions.[16,17] Thus, no solvent molecules can be present in the coördination sphere of the iron.

2. Solutions of Ferric Chloride in Triethyl Phosphate.—Dissolution of anhydrous ferric chloride in $PO(OEt)_3$ produces solutions that are similar to those obtained in $POCl_3$. The solutions are red at concentrations of 0.1 *M*. Dilution of a red (0.1 *M*) solution with the solvent causes a progressive change in color to yellow. As is the case in $POCl_3$ this color change is reversible with concentration changes.

The ultraviolet spectrum of a dilute solution of $FeCl_3$ in $PO(OEt)_3$ ($\sim 10^{-4}$ *M*) is indicated by curve A of Fig. 2. This curve has the same general shape and λ_{max} values as the one for the tetrachloroferrate(III) ion and establishes the presence of $[FeCl_4]^-$ in dilute ferric chloride solutions. The formation of the $[FeCl_4]^-$ ion is a direct proof that ionization of some $FeCl_3$ has occurred to produce a cationic iron(III) species. The solutions are also good electrical conductors. Use of triethyl phosphate as a solvent excludes the possibility of the tetrachloroferrate (III) ion being formed from a chloride ion which was been liberated by a self-ionization of the solvent, as has been postulated for $POCl_3$.[3] The set of equilibria (5) is suggested to explain the formation of $[FeCl_4]^-$ in both $PO(OEt)_3$ and $POCl_3$.[20]

$$FeCl_3 + Y_3PO \longrightarrow [FeCl_3OPY_3] \rightleftharpoons [FeCl_{3-x}(OPY_3)_{1+x}]^{x+} + X[FeCl_4]^- \rightleftharpoons [Fe(OPY_3)_6]^{3+} + 3[FeCl_4]^- \quad (5)$$

This representation of the equilibria is in agreement with the experimental evidence that demonstrates oxygen coördination in the $POCl_3$ addition compounds.[9-12] The infrared spectra of $FeCl_3 \cdot OP(OEt)_3$ also indicate that coördination of the solvent molecule occurs *via* the phosphoryl oxygen atom. Comparison of equations 2 and 5 demonstrates the essential difference in the species present at equilibrium according to the solvent system concept and our proposed explanation of the equilibria.

Curves B and C of Fig. 2 demonstrate the quantitative conversion of added chloride to the $[FeCl_4]^-$ ion in this solvent. At a 1:1 mole ratio of $FeCl_3$ to added Cl^- ion donor (curve C), the absorption spectrum is identical to that of $[(CH_3)_4N][FeCl_4]$. Addition of $ZnCl_2$, $HgCl_2$ and $SbCl_3$ to red $FeCl_3$ solutions does not change the color to yellow. Thus, these materials do not act as chloride ion donors toward $FeCl_3$ in triethyl phosphate. Likewise, addition of a 12 molar excess of $SbCl_3$ to a dilute $[FeCl_4]^-$ solution does not change the amount of $[FeCl_4]^-$ present.

(19) M. Baaz, V. Gutmann and L. Hübner, *Monatsh. Chem.*, **92**, 135 (1961).

(20) Some of the intermediate solvated iron(III) ions may have a coördination number of six instead of four.

The behavior of more concentrated ferric chloride solutions in $POCl_3$ and $PO(OEt)_3$ is very similar. The absorption spectra of orange-red solutions ($\sim 4 \times 10^{-3}$ *M*) in $POCl_3$ and $PO(OEt)_3$ are given by curves 2 and 4, respectively, of Fig. 3. The spectra in both solvents are very similar in position and shape. Upon addition of one mole of a chloride ion donor, both solutions become yellow and exhibit absorption curves characteristic of $[FeCl_4]^-$ (Fig. 1). Dilution of the red solution in $PO(OEt)_3$ to a concentration of 10^{-4} *M* produces a yellow solution whose absorption spectrum is identical to the one obtained by diluting red $POCl_3$ solutions (curves 3 and 5 of Fig. 3). This effect is a manifestation of a higher degree of ionization in the more dilute solution as is common for most weak electrolyte equilibria (*e.g.*, acetic acid).

The absorption spectra of concentrated solutions were investigated with a 2.65×10^{-3} cm. quartz cell in an attempt to determine whether the $[FeCl_4]^-$ ion was present in the red solution.

The only detectable peaks in the 0.1 *M* solution were those characteristic of $[FeCl_4]^-$. Although no λ_{max} could be obtained for the species producing the red color of concentrated $FeCl_3$ solutions, the spectra show a contribution to the absorbance in the 410 mμ region due to a species other than $[FeCl_4]^-$. Calculation of the ratios of the absorbance at λ_{max} (362, 314 and 240 mμ) and λ_{min} (338 and 286 mμ) for various concentrations of $FeCl_3$ and $[FeCl_4]^-$ solutions indicates that in ferric chloride solutions species other than $[FeCl_4]^-$ are absorbing. Thus, a quantitative estimate of the amount of $[FeCl_4]^-$ ion present cannot be made from these data. In the more concentrated solutions the underlying absorption becomes very intense in the visible region and results in the red color. The red complex has too high an extinction coefficient to permit observation of the maxima at concentrations consistent with this color. The source of the red color probably is a solvated ferric chloride molecule and/or a tetrahedral cationic species, *e.g.*, $[FeCl_{3-x}(OPY_3)_{1+x}]^{x+}$.

There are several features of the equilibrium represented by equation 5 that are unique to our proposed explanation of the solution behavior. The position of the equilibria will depend upon the basicity, dielectric constant and solvating ability of the solvent. In solvents which coordinate strongly, have a high dielectric constant and solvate chloride ions, the species obtained will be $[Fe(solv.)_n]^{+3} + 3Cl^-$. The red color of the concentrated $POCl_3$ solutions was attributed to a $FeCl_3 \cdot (POCl_3)_x$ addition compound.[8] Since the basicity of $POCl_3$ is less than that of $PO(OEt)_3$[21] more of the undissociated species would be expected in $POCl_3$ than in $PO(OEt)_3$. The absorption spectra of 0.1 *M* solutions of $FeCl_3$ in $POCl_3$ and $PO(OEt)_3$ have ϵ values of 10 at 580 and 525 mμ, respectively. This shift of 55 mμ into the red for the $POCl_3$ solution compared to a $PO(OEt)_3$ solution of equal concentration indicates a greater concentration in $POCl_3$ of the species producing the red color. This is equivalent to a more complete ionization to the $[FeCl_4]^-$ ion in $PO(OEt)_3$ than in $POCl_3$.

B. Conductometric Titrations.—Conductometric titrations were carried out in triethyl phosphate to demonstrate further the similarity in behavior of $PO(OEt)_3$ and $POCl_3$. Sharp breaks in the conductance curves were obtained at a 1:1 molar ratio for the titration of both $FeCl_3$ and $SbCl_3$ with chloride ion. These breaks correspond to the formation of $[FeCl_4]^-$ and $[SbCl_4]^-$ ions. Analogous behavior has been reported to occur in $POCl_3$.[3c] According to our scheme the equation for the titration involves the conversion of all iron(III) species to the $[FeCl_4]^-$ ion. This is substantiated by the spectrophotometric data. The equations for the reaction are[20]

$$[FeCl_{3-x}(OPY_3)_{1+x}]^{x+} + (x+1)Cl^- \longrightarrow (x+1)POY_3 + [FeCl_4]^- \quad (6)$$

$$Y_3POFeCl_3 + Cl^- \longrightarrow POY_3 + [FeCl_4]^- \quad (7)$$

These equations should be contrasted to those proposed according to the solvent system concept (equations 3 and 4).

All of the essential behavior of ferric chloride solutions in phosphorus oxychloride which has been used to support the solvent system concept has been reproduced in triethyl phosphate. A comparison of the conductometric and spectrophotometric studies of ferric chloride in the two solvents indicates that solvent ionization is not a requirement in order to explain the equilibria and chemical reactions that occur in phosphorus oxychloride.

Acknowedgment.—The authors wish to acknowledge the generous support of the research by the Chemistry Branch of the Atomic Energy Commission through Contract No. AT (11-1)758.

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