[Contribution from the Chemical Laboratories of the University of Notre Dame]

Crystalline Dioxanates and Aquodioxanates of Iron(III) Chloride and Tetrachloroferric(III) Acid[1,2]

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Dioxane forms an anhydrous crystalline monodioxanate and several crystalline aquodioxanates with iron(III) chloride. The presence of water in the complexes increases the number of molecules of dioxane held in the crystals. With tetrachloroferric(III) acid only the monoaquotridioxanate is readily isolated. Approximate dissociation pressures of the various complexes have been measured. All the aquo-complexes are converted at low pressure by loss of water and/or hydrogen chloride into the anhydrous monodioxanate of iron(III) chloride which has a dissociation pressure of less than 1 mm. at 20°. Conductivity data in nitrobenzene indicate that all the complexes are ionic in character. Formulas for the complexes, based on their ionic character and indicated coördination number, are proposed. Electric moment and solubility data for the iron(III) chloride complexes in dioxane indicate a non-ionic solute species in dioxane with the aquo-complex being appreciably more polar than the anhydrous complex.

Previous studies have been made in these Laboratories[3] on the interaction of iron(III) chloride with dioxane using electric moment data. During the course of this work the formation of a well-defined crystalline complex of iron(III) chloride and dioxane was observed. Other complexes containing water and hydrogen chloride also have been found to be readily obtained. A number of these crystalline complexes have been prepared and studied and the results are reported in the present paper.

Experimental

Anhydrous iron(III) chloride was prepared, dioxane was purified and electric moments were obtained as described previously.[3] The measurements of approximate dissociation pressures were also made as described previously.[4]

Iron(III) Chloride Monodioxanate.—A weighed quantity (1–4 g.) of iron(III) chloride was added slowly in a dry box to 5–15 ml. of dioxane freshly distilled from sodium. Yellowish-green solid formed immediately. The mixture was then warmed on a hot plate in the dry box until nearly complete solution occurred. Filtration and cooling gave finely divided green crystals. The crystals were freed of adhering dioxane by suction filtration, dried between filter papers or alternatively kept in a vacuum desiccator at 1 mm. for 48 hr. and analyzed for chlorine and iron. *Anal.* Calcd. for $FeCl_3 \cdot C_4H_8O_2$: Cl, 42.3; Fe, 22.2. Found: Cl, 42.2; Fe, 22.3. In the preparation of the anhydrous dioxanate, introduction of moisture from any source results in the separation of the less soluble aquo-complex, described below, which contaminates the anhydrous compound.

Iron(III) Chloride Diaquotridioxanate.—To an approximately half-saturated solution of anhydrous iron(III) chloride in dioxane, water was added drop by drop. Crystals of yellow aquodioxanate separated immediately on the addition of water, with maximum precipitation occurring when 2 moles of water had been added for each mole of iron(III) chloride present. Recrystallization from dioxane resulted in the formation of well defined yellow prisms. *Anal.* Calcd. for $FeCl_3 \cdot 2H_2O \cdot 3C_4H_8O_2$: Cl, 23.0; Fe, 12.1; H_2O, 7.7. Found: Cl, 23.1; Fe, 12.0; H_2O, 7.5.

Iron(III) Chloride Diaquodidioxanate.—When crystals of the diaquotridioxanate, obtained as described above, were left on filter paper in normal atmosphere, loss of dioxane occurred readily. Conversion to the didioxanate was complete when the odor of dioxane was no longer noticeable over the crystals. Alternatively, crystals of the tridioxanate were left in a vacuum desiccator at pressures between 15 and 3 mm. with provision for removal of dioxane vapor. Under these conditions quantitative conversion of tridioxanate to didioxanate occurred. The diaquodidioxanate was obtained as a yellow powder. *Anal.* Calcd. for $FeCl_3 \cdot 2H_2O \cdot 2C_4H_8O_2$: Cl, 28.4; Fe, 14.9; H_2O, 9.6. Found: Cl, 28.3; Fe, 14.8; H_2O, 9.5.

Iron(III) Chloride Monoaquodioxanate.—To an approximately half-saturated solution of anhydrous iron(III) chloride in dioxane, the calculated amount of water was added to give a 1:1 ratio of iron(III) chloride to water. The solution was then allowed to stand in a closed container for several hours, after which a gradual separation of a mass of deep-red needles occurred. The crystals were dried as above. *Anal.* Calcd. for $FeCl_3 \cdot H_2O \cdot 2C_4H_8O_2$: Cl, 29.8; Fe, 15.6. Found: Cl, 29.6; Fe, 15.4.

Attempted Preparation of a Dioxanate of Anhydrous Tetrachloroferric(III) Acid.—Anhydrous hydrogen chloride was passed over the surface of a nearly saturated solution of anhydrous iron(III) chloride in dioxane at ice-bath temperature in a system protected from moisture. The solution became turbid as hydrogen chloride was absorbed and continued addition of hydrogen chloride resulted in the separation of two liquid phases. The lower phase increased in bulk, as absorption of hydrogen chloride continued, until a one-phase, olive-green liquid was obtained. Under a vacuum of 10–20 mm. excess hydrogen chloride and dioxane were removed to leave a thick green liquid. Cooling to Dry Ice temperature resulted in the formation of a non-homogeneous solid. Analysis of the product for iron and chloride showed a chlorine-to-iron ratio somewhat greater than 4 to 1 and the presence of excess dioxane. Attempts to obtain a homogeneous solid by variation in the cooling and vacuum conditions were unsuccessful. Under a vacuum of 3 to 1 mm., dioxane and hydrogen chloride were lost and the monodioxanate of iron(III) chloride was left as a residue.

Monoaquodioxanates of Tetrachloroferric(III) Acid.—To 50 ml. of a nearly saturated solution of a weighed quantity of iron(III) chloride in dioxane, excess anhydrous hydrogen chloride was added until a clear olive-green solution was formed. The calculated quantity of a 1 *M* solution of water in dioxane was added to give a 1:1 molar ratio of water to iron(III) chloride. Maximum precipitation of pale green crystals occurred when exactly one mole of water had been added per mole of iron(III) chloride. Attempts to obtain crystals of reproducible composition by drying between filter papers were unsuccessful. Short exposure to normal atmosphere resulted in loss of hydrogen chloride and dioxane and absorption of water. Under controlled conditions of 25–35% relative humidity, hydrogen chloride was lost and water absorbed to give crystals of iron(III) chloride diaquodidioxanate. When the crystals, obtained as above, were held for 8 hr. at 30 mm. in a vacuum desiccator over phosphoric anhydride, yellow-green crystals of tetrachloroferric(III) acid monoaquotridioxanate were formed. *Anal.* Calcd. for $FeCl_3 \cdot HCl \cdot H_2O \cdot 3C_4H_8O_2$: Cl, 29.5; Fe, 11.6; H_2O, 3.7. Found: Cl, 29.4; Fe, 11.7; H_2O, 3.7.

Attempts to isolate a monoaquodidioxanate of tetrachloroferric(III) acid by using desiccator pressures in the range 9 to 6 mm. led to partial loss of hydrogen chloride. When, however, the crystals of tetrachloroferric(III) monoaquotridioxanate were held in a desiccator at pressures below 3 mm. for several hours, complete conversion to the stable green iron(III) chloride monodioxanate occurred.

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(1) From the dissertation submitted by Sister M. Scholastica Kennard, C.S.C., in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Notre Dame, 1957. Paper I of a series on the interaction of iron(III) compounds with ethers.

(2) Contribution from the Radiation Project operated by the University of Notre Dame and supported in part under Atomic Energy Commission Contract AT-(11-1)-38.

(3) T. J. Lane, P. A. McCusker and B. C. Curran, This Journal, **64,** 2076 (1942).

(4) C. J. Kelley and P. A. McCusker, *ibid.*, **65,** 1307 (1943).

Analyses.—Chloride was determined gravimetrically. Iron was determined by precipitation as ferric hydroxide, solution in acid and titration with dichromate solution. Karl Fischer reagent was used for the water analyses, employing the dead-stop end point method as modified by Wernimont and Hopkinson[5] and correcting for the oxidizing action of ferric ion.[6]

Solubility Determinations.—The solubilities of the anhydrous iron(III) chloride monodioxanate and the iron(III) chloride diaquotridioxante in dioxane were determined by equilibrating excess solid with dioxane at 25° and analyzing the equilibrium solution which was forced by dry nitrogen pressure through a fritted glass disk.

Conductivity Measurements.—The conductivities of nitrobenzene solutions of the complexes were measured in a pipet-form cell with bright platinum electrodes. A Serfass conductivity bridge, Model RCM 15B1, was used. Nitrobenzene from Eastman was purified by a series of fractional freezings, m.p. 5.60–5.61°

Results and Discussion

The compositions of the various crystalline dioxanates of iron(III) chloride reveal a marked effect of the presence of water on the number of molecules of dioxane that can be held in the crystal lattice of the dioxanates. With anhydrous iron(III) chloride only one molecule of dioxane is associated with a molecule of iron(III) chloride. With one molecule of water present, two molecules of dioxane are held in the crystal lattice. With two molecules of water present in the crystal three molecules of dioxane can be accommodated, although in this case one molecule of dioxane is readily lost by vaporization. The nature of the association of water with iron(III) apparently has the effect of increasing the number of dioxane molecules which can coördinate with the iron(III).

The diaquotridioxanate undergoes rapid loss of one molecule of dioxane under vacuum of 15 mm. or less. This indicates that the tridioxanate has a dissociation pressure of about 15 mm. Storage of the diaquodidioxanate of iron(III) chloride in a vacuum desiccator at 2 mm. results in no loss of dioxane or water in the absence of a desiccant. When held at 1 mm. or less in the presence of phosphoric anhydride, however, the diaquodidioxanate loses both water and dioxane to form the anhydrous monodioxanate. The monodioxanate undergoes no loss of dioxane on long standing even at pressures below 1 mm. Thus a dissociation pressure of less than 1 mm. is indicated for the anhydrous monodioxanate.

Since at sufficiently low pressures all the aquo-complexes may be converted to the anhydrous monodioxanate, it must be concluded that the bonding of dioxane to iron(III) chloride is stronger in the monodioxanate than the bonding of water to iron(III) chloride in the diaquo-complexes. The strength of the dioxane bonding in the monodioxanate is further shown by the fact that heating of the crystals in a capillary tube results in extensive decomposition and charring at temperatures above 165° but no direct loss of dioxane.

The crystalline aquodioxanates of tetrachloroferric(III) acid show a close parallel in composition to the aquodioxanates of iron(III) chloride if it is assumed that hydrogen chloride replaces one water molecule. The principal difference in the properties of the two types of dioxanates is that the acid complex loses hydrogen chloride by vaporization more readily than the aquo-complex loses water. Also in moist atmosphere, hydrogen chloride in the complex is replaced by water and the monoaquodidioxanate of tetrachloroferric(III) acid is converted to the diaquodidioxanate of iron(III) chloride.

The ease of isolation of the aquo-complex of tetrachloroferric(III) acid and the difficulty of isolation of the anhydrous dioxanate is not necessarily an indication of greater stability for the aquo-complex. It is probably an incidental result of the difference in solubility of the complexes in dioxane–hydrogen chloride. This is further suggested by the results observed by Laurene, Campbell, Wiberly and Clark[7] who found that an anhydrous diisopropyl etherate of tetrachloroferric(III) acid was readily obtained as a slightly soluble crystalline solid from isopropyl ether–hydrogen chloride. The hydrated isopropyl etherate of tetrachloroferric(III) acid was found to be quite soluble in the solvent and was not isolated by these workers.

Conductivity data for the complexes in nitrobenzene are listed in Table I.

TABLE I

MOLAL CONDUCTIVITIES OF COMPLEXES IN NITROBENZENE

$FeCl_3.C_4H_8O_2$		$FeCl_3.2H_2O.2C_4H_8O_2$		$FeCl_3.H_2O.HCl.3C_4H_8O_2$	
$m \times 10^3$		$m \times 10^3$		$m \times 10^3$	
1.41	41.3	1.96	35.4	1.79	60.0
2.99	35.9	1.98	32.8	4.40	53.9
4.09	35.1	3.38	33.8	4.81	52.6
5.99	33.3	6.93	29.7	7.54	51.7

The conductivity data demonstrate that the dioxanates are ionic in character. Anhydrous iron(III) chloride solutions showed only a small conductivity which did not increase with concentration. This small conductivity is believed to be due to small amounts of impurities.

A coördination number of four is indicated for the anhydrous monodioxanate, $FeCl_3 \cdot C_4H_8O_2$, by its green color. The ionic character and coördination number of four suggest the formation $[Fe_2Cl_4(C_4H_8O_2)_2]^{++}2Cl^-$ for this complex. The yellow color of the diaquodioxanate suggests a coördination number of six for iron in these complexes. This coördination number and the ionic character suggest the formulation, $[FeCl_2(C_4H_8O_2)_2(H_2O)_2]^+ Cl^-$ for the diaquodidioxanate of iron(III) chloride. The tridioxanate is reasonably formulated as $[FeCl_2(C_4H_8O_2)_2(H_2O)_2]^+[Cl]^- \cdot C_4H_8O_2$ with one molecule of dioxane being held in the crystal lattice as dioxane of crystallization. In the case of the red monoaquodidioxanate, the unusual red color suggests an odd coördination number. Assuming a coördination number of five, the complex may be formulated as $[FeCl_2(C_4H_8O)_2(H_2O)]^+Cl^-$.

In no case was the formation of the red monoaquo-complex observed by removal of one molecule of water from the diaquo-complex under vacuum desiccation. This suggests that the monoaquo-complex is inherently less stable than the diaquo-complex or the anhydrous complex.

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[5] G. T. Wernimont and F. J. Hopkinson, *Anal. Chem.*, **15**, 272 (1943).

[6] R. J. Myers, D. E. Metzler and E. H. Swift, THIS JOURNAL, **72**, 3768 (1950).

[7] A. H. Laurene, D. E. Campbell, S. E. Wiberly and H. M. Clark, *J. Phys. Chem.*, **60**, 901 (1956).

A reasonable structure for the monoaquotridioxanate of tetrachloroferric(III) acid is not readily arrived at unless one assumes that hydrogen chloride can replace water in the complex. On this basis the formulation $[FeCl_2(C_4H_8O_2)_2(H_2O)(HCl)]^+[Cl]^- \cdot C_4H_8O_2$ is a plausible one.

While the conductivity data in nitrobenzene indicates ionic character for the anhydrous dioxanate of iron(III) chloride and for the diaquotridioxanate, the electric moments of these two complexes in dioxane indicate a low polarity in solution in dioxane. The value previously reported[3] for the anhydrous compound is 1.27 Debye units. This suggests that the solute species present in dioxane solution and the solute species present in nitrobenzene are markedly different. Apparently ionic character does not persist in dioxane solution and a covalently bonded species is present. The electric moment found for the diaquodioxanate of iron(III) chloride in dioxane solution is 3.33 Debye units. This indicates that again a non-ionic species is present in solution in dioxane. The increase in moment from the anhydrous dioxanate to the diaquo-complex indicates that the diaquo-solute species has a much greater polarity than the anhydrous complex. This would be expected as a result of the interaction between iron and water in the complex. The greater polarity of the aquo-complex in dioxane solution is reflected in a marked difference in the solubilities of the anhydrous and aquo-complexes in dioxane. Data obtained at 25.0° show a solubility, in moles of complex per 1000 g. of dioxane, of 0.0841 for the diaquo-complex compared to 0.9521 for the anhydrous complex. Qualitative observations on the solubility of the monoaquodidioxanate of iron(III) chloride show that its solubility in dioxane is intermediate between that of the anhydrous dioxanate and the diaquodidioxanate.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

A Spectrophotometric Study of Anhydrous Iron(III) Chloride and Tetrachloroferric(III) Acid in Dioxane and Other Ethers[1,2]

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The ultraviolet absorption spectra of anhydrous iron(III) chloride in several alkyl ethers are essentially the same, but the spectra in various cyclic ethers differ from those in alkyl ethers and from one another. The assumption that a single absorbing solute species is present in ether solutions of iron(III) chloride, in the concentration range, 10^{-3} to 10^{-4} molar, is supported by the fact that such solutions obey Beer's Law at the several wave lengths of maximum absorption. Spectra in mixtures of dioxane and *n*-butyl ether show that dioxane is at least four times more basic than *n*-butyl ether toward iron(III) chloride. Spectral data on anhydrous iron(III) chloride–hydrogen chloride in dioxane and other ethers is consistent with the assumption that only two absorbing species, solvated iron(III) chloride and tetrachloroferric(III) acid, are present. Tetrachloroferric(III) acid, in contrast to iron(III) chloride, is spectrophotometrically identical in all the ethers studied. In dioxane–aqueous hydrogen chloride solutions the concentration of tetrachloroferric(III) acid is determined primarily by the hydrogen chloride–water concentration ratio. Dissociation constants of tetrachloroferric(III) acid in dioxane and several other ethers reveal that the chloro-complex is much more stable in ethers than in aqueous solution and that its stability varies from ether to ether.

The formation of a very stable crystalline complex of iron(III) chloride and dioxane, as reported in the first paper of this series,[1] demonstrates that strong interaction occurs between ethers and iron(III) chloride, at least in saturated solutions. On the other hand dipole moment data, previously reported,[3] did not provide evidence of strong polar interaction. Although only one solid compound, the 1:1 complex of dioxane and iron(III) chloride is formed, the possibility remained that other solute species, in which more than one molecule of dioxane is associated with one molecule of iron(III) chloride, might be present in dilute solution. It was, therefore, considered of interest to study the ultraviolet absorption spectrum of iron(III) chloride in dioxane for evidence of other solute species in dilute solution. The ultraviolet spectrum of iron(III) chloride in an anhydrous ether has been determined only in isopropyl ether,[4] although the visible spectrum in ethyl ether[5] has been reported. For this reason our spectral studies were extended to include a number of ethers.

Numerous studies have been carried out on the aqueous iron(III) chloride–hydrogen chloride system[6-9] and on ether extracts of this system[4,5,10,11] using spectrophotometric and other means. From these studies, the absorbing species in strong hydrochloric acid and in the ether extracts has been identified as tetrachloroferric(III) acid. There appears, however, to have been no work reported on completely anhydrous systems of iron(III) chloride–hydrogen chloride in ethers. We have investigated

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(1) Paper II of a series on the interaction of iron(III) compounds with ethers. Paper I, THIS JOURNAL, **81**, 2974 (1959). From the doctoral dissertation of Sister M. Scholastica Kennard, C.S.C., 1957.

(2) Contribution from the Radiation Project operated by the University of Notre Dame and supported in part under Atomic Energy Commission Contract AT-(11-1)-38.

(3) T. J. Lane, P. A. McCusker and B. C. Curran, THIS JOURNAL, **64**, 2076 (1942)

(4) N. H. Nachtrieb and J. E. Conway, *ibid.*, **70**, 3547 (1948).

(5) H. L. Friedman, *ibid.*, **74**, 5 (1952).

(6) V. S. Kiss, J. Abraham and I. Hegedus, *Z. anorg. allgem. Chem.*, **244**, 98 (1940).

(7) G. A. Gamelin and D. O. Jordan, *J. Chem. Soc.*, 1453 (1953).

(8) L. N. Mulay and P. W. Selwood, THIS JOURNAL, **77**, 2693 (1955).

(9) R. J. Myers and D. E. Metzler, *ibid.*, **72**, 3772, 3776 (1950).

(10) J. Axelrod and E. H. Swift, *ibid.*, **62**, 33 (1940).

(11) R. J. Myers, D. E. Metzler and E. H. Swift, *ibid.*, **72**, 3763 (1950)