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]

BY PATRICK A. MCCUSKER AND S. M. SCHOLASTICA KENNARD, C.S.C.

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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).

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[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).

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the system: anhydrous iron(III) chloride–hydrogen chloride in dioxane and in several other ethers, and in dioxane–water mixtures, by means of ultraviolet absorption spectra.

Experimental

Materials.—Anhydrous iron(III) chloride was prepared and stored and Commercial Solvents 1,4-dioxane was purified as previously described.[3] Matheson–Coleman pure grade tetrahydrofuran, Matheson, Coleman and Bell practical grade tetrahydropyran and Carbide and Carbon practical grade 1,3-dioxolane were dried by refluxing over solid sodium hydroxide and were distilled from sodium amalgam through a 2-ft. glass-helix packed column into oven-dried, metal-foil covered, glass stoppered receivers. The alkyl ethers were fractionated through a similar column and collected and stored under the same conditions. Absolute ethyl ether was distilled from sodium amalgam, Matheson, Coleman and Bell practical grade isopropyl ether was dried over phosphoric anhydride and distilled from sodium amalgam, and Eastman practical grade di-*n*-butyl ether was dried over phosphoric anhydride, refluxed over sodium and distilled. All ether fractions, taken for spectrophotometric work, distilled within a 0.1 degree range; they were stored in their receivers in a dry box and used within 24 hours of distillation.

Anhydrous hydrogen chloride was prepared by a slight modification of a standard procedure[12] and was subjected to further drying by passage through phosphoric anhydride.

Preparation of Solutions.—All solutions were prepared and stored and dilutions made in a dry box, having open containers of phosphoric anhydride, and with dry nitrogen passing through the box. Solutions were protected from light by storing in metal-foil covered flasks. Storage period for solutions never exceeded 24 hr.

Master solutions, 10^{-2} to 10^{-1} M, were prepared by weighing anhydrous iron(III) chloride into glass stoppered flasks, adding solvent ether and reweighing. The contents of the flasks were cooled during addition of solvent since solution was exothermic and uncooled solutions discolored. Dioxane, tetrahydrofuran and alkyl ether solutions, 5×10^{-2} M, were stable when prepared in this way, but more dilute master solutions were used with tetrahydropyran and dioxolane. Dioxolane solutions of iron(III) chloride polymerized to a white waxy mass on long standing. Solutions for spectral measurements were prepared by dilution of weighed quantities of master solutions with weighed quantities of solvent. The molarity of iron(III) chloride in the ether solutions was calculated directly from the weight and density data, assuming the density of the diluted solutions to be equal to the density of the pure solvents. Solutions of iron(III) chloride in dioxane-*n*-butyl ether mixtures were prepared by adding *n*-butyl ether to dioxane master solutions; dioxane was added to ethyl ether master solutions in the study of the spectra of iron(III) chloride in mixtures of dioxane and ethyl ether. Master solutions of iron(III) chloride–hydrogen chloride were prepared by passing hydrogen chloride gas over the surface of cold iron(III) chloride–ether solutions of known molarity, in a system protected from atmospheric moisture, until the golden yellow color turned to green. The hydrogen chloride content of the ether solutions was determined by dissolving or suspending the solution in water and titrating with 0.03 N base from a 10-ml. microburet, using a mixed indicator of phenolphthalein and brom thymol blue. Weighed quantities of solutions of iron(III) chloride–hydrogen chloride in ether were added to weighed portions of master solutions of iron(III) chloride in ether in a dry box. Molarities of iron(III) chloride and hydrogen chloride were calculated from the weight data, and the experimentally determined densities of hydrogen chloride–ether solutions, listed in Table I.

For the determinations of dissociation constants, the total iron molarity in the solutions containing iron(III) chloride and tetrachloroferric(III) acid was determined from optical densities at isosbestic points and molar absorption coefficients determined independently.

Spectrophotometric Measurements.—Ultraviolet absorption spectra were obtained with a manually operated Beckman model D.U. quartz spectrophotometer, using a hydrogen discharge lamp as light source. Cell chamber temperature was 30 ± 2°. Repeated observations demonstrated that the temperature variation did not introduce errors exceeding the reproducibility of the instrument. When solutions exhibited instability on standing or on exposure to radiation, wave lengths of maximum absorption were established in a preliminary survey with a second Beckman spectrophotometer having a Warren Spectrachord attachment.

TABLE I

DENSITIES OF HYDROGEN CHLORIDE–ETHER SOLUTIONS

Isopropyl ether		*n*-Butyl ether		Tetrahydrofuran		Dioxane	
HCl, M	d^{25}	HCl, M	d^{25}	HCl, M	d^{25}	HCl, M	d^{25}
0.000	0.7188	0.000	0.7637	0.000	0.8824	0.000	1.0279
.029	.7195	.034	.7644	.025	.8828	.075	1.0282
.039	.7197	.067	.7650	.051	.8832	.371	1.0292
.059	.7201	.100	.7656	.088	.8836	.490	1.0297
.112	.7210	.200	.7670	.112	.8839	.826	1.0309
.268	.7242	.466	.7713	.176	.8846	1.652	1.0339

The optical densities of solutions were measured in matched 10-mm. quartz cells; rectilinear quartz spacers, 7 × 9 mm. in thickness, were used with the cells and permitted a choice of 1, 3 and 10-mm. light paths. Matched 10-cm., glass-stoppered cylindrical cells were used with very dilute solutions. The path lengths of the cells, with and without spacers in place, were checked with alkaline chromate solution.[13] Reference solvents were taken from the same fraction of distillate used in the preparation of the iron(III) chloride solutions. For mixed ethers reference solutions with corresponding compositions were prepared from the pure components.

Results and Discussion

While iron(III) chloride has been shown to have a layer structure in the solid state[14] and to be dimeric in the vapor[15] and in such solvents as carbon disulfide, chloroform and benzene,[16] it is monomeric in ethers.[17] It is clear that the solvent ethers break up the layer structure of iron(III) chloride and that the solute species present must involve some type of association between solvent and solute. Furthermore all the iron(III) chloride must be present in solution as a solvated complex; no unsolvated iron(III) chloride will exist in solution.

Data obtained from spectral measurements of 10^{-4} to 10^{-3} molar solutions of anhydrous iron(III) chloride in various ethers are summarized in Table II. In this table are listed the ethers used as sol-

TABLE II

MOLAR ABSORPTION COEFFICIENTS FOR ANHYDROUS IRON(III) CHLORIDE IN ETHER SOLUTIONS

Ether	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ
Ethyl	220	7070	250	8410	342	8646
Isopropyl	220	7200	250	8615	342	7120
n-Butyl	225	5400	250	7025	342	7200
Dioxane	235	7585	272	6085	340	8115
Tetrahydropyran	238	7400	255–265	6400	340	7940
Tetrahydrofuran	233	8570	255–265	6330	340	8825
1,3-Dioxolane	236	5770	260–265	4809	340	5880

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(12) R. N. Maxon, "Inorganic Syntheses," Vol. 1, McGraw-Hill Book Co., 1939, New York, N. Y., p. 147.

(13) G. W. Haupt, *J. Research Natl. Bur. Standards*, **48**, 414 (1952).

(14) N. W. Gregory, THIS JOURNAL, **73**, 472 (1951).

(15) C. Friedel and J. M. Crafts, *Compt. rend.*, **107**, 301 (1888).

(16) A. F. Wells, "Structural Inorganic Chemistry," 2nd Ed., Clarendon Press, Oxford, England, 1950, p. 110.

(17) E. Beckmann, *Z. physik. Chem.*, **46**, 853 (1903).

vents, the λ_{max} for each ether–iron(III) chloride solution and the molar absorption coefficients at these maxima. Figure I shows the absorption spectra of iron(III) chloride in dioxane, tetrahydropyran and *n*-butyl ether. These three curves are representative of the types of absorption curves found for all the ether solutions.

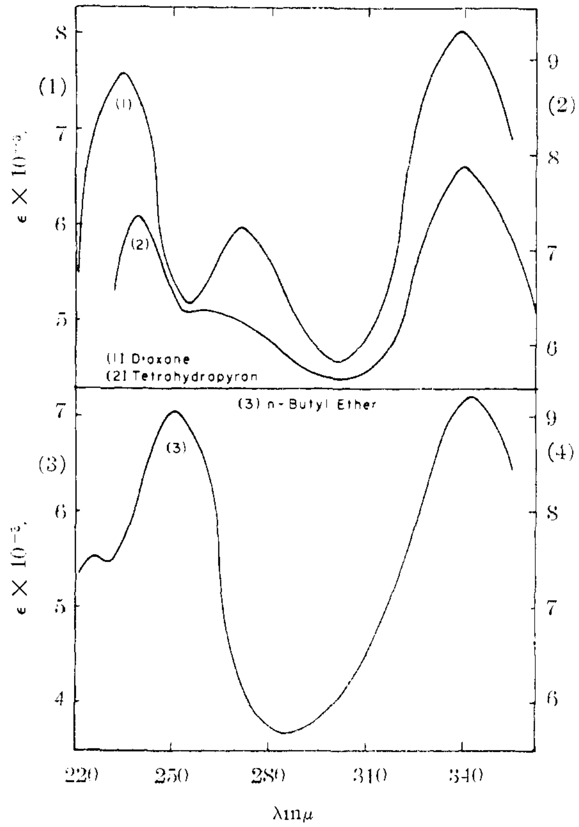

Fig. 1.—Absorption curves for $FeCl_3$ in several ethers.

The molar absorption coefficient, at 340 mμ in dioxane, is considered to be within 1% of the true value. The 235 and 272 mμ values in dioxane and the two values of molar absorptions for the *n*-butyl ether solutions are believed to be within 5% of the true values. The molar absorption coefficients for the remaining ether solutions were obtained from relatively few measurements and represent order of magnitude only.

Iron(III) chloride solutions in the three alkyl ethers have absorption maxima at exactly the same wave lengths. Differences in the molar absorption coefficients are not considered significant because of the rather large experimental errors in the determination of the concentrations in solutions of the volatile ethyl and isopropyl ethers. From the identical wave lengths of maximum absorption, it may be concluded that the effect of solvent association on the electronic energy levels in iron(III) is the same with all the alkyl ethers.

With the cyclic ethers, however, the absorption maxima at wave lengths below 300 mμ are different from those in the alkyl ether solutions and show differences from one another. Only the cyclic ether solutions show an absorption band in the 260–275 mμ region. In the case of the dioxane solutions, this appears as a sharp peak at 272 mμ. The remaining cyclic ether solutions have an absorption band in the same general region, but it is much broader and occurs at somewhat shorter wave lengths. In the 340 mμ region a very small but definite difference exists in the position of the wave length of maximum absorption for the alkyl and cyclic ether solutions. All the alkyl ether solutions of iron(III) chloride have a λ_{max} at 342 mμ while the cyclic ether solutions have λ_{max} at 340 mμ.

The intermediate absorption band in the 260–275 mμ region appears to be characteristic of the cyclic ethers. It is possible, however, that the intermediate band does not show up in the spectra of the alkyl ether solutions, for the reason that it is masked by the strong nearby band at 250 mμ.

Numerous determinations of optical densities, at the several different wave lengths of maximum absorption, on solutions of iron(III) chloride in dioxane and *n*-butyl ether, in the concentration range 10^{-3} to 10^{-4} molar, showed that, within our experimental error, Beer's Law was followed. Data for the dioxane solutions are given in Fig. 2. There is no evidence supplied by the absorption spectra of iron(III) chloride solutions in ethers that more than one solute species is present in such solutions. It may then be concluded that the absorption bands in these solutions arise from different transitions in electronically identical iron(III) atoms.

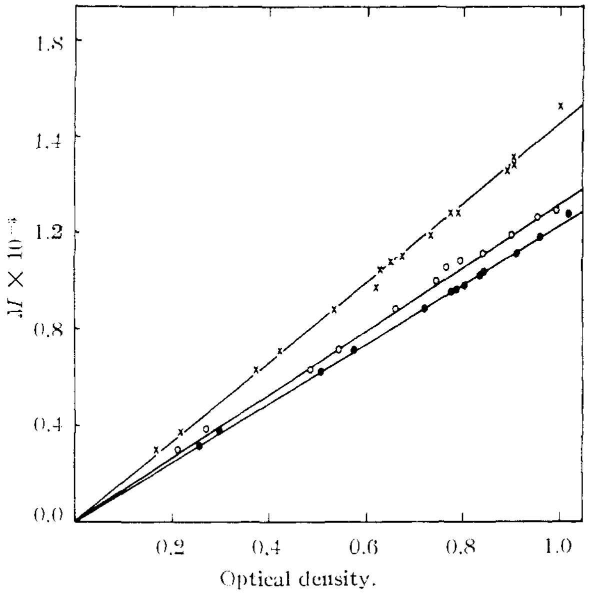

Fig. 2.—Iron molarity *vs.* optical density for $FeCl_3$–dioxane solutions: ●, λ = 340 mμ; ○, λ = 235 mμ; ×, λ = 272 mμ.

Since the absorption curves for solutions of iron(III) chloride in dioxane and in *n*-butyl ether are, except for the 340 mμ region, quite different, the spectra of iron(III) chloride in mixtures of dioxane and *n*-butyl ether can be used to determine the distribution of iron(III) as dioxanate or di-*n*-butyl etherate in mixtures of the two ethers. This distribution can give information on the relative basicities of the two ethers toward iron(III) chloride and possibly indicate a relationship between the relative basicities and the characteristic absorption spectra in the two ethers. The spectra of 1 × 10^{-4} molar iron(III) chloride in 57.3 mole % dioxane–*n*-butyl ether and in 32.9 mole % dioxane–*n*-butyl ether were measured and are shown in Fig. 3. It will be observed that, even in the 32.9 mole % dioxane solution, which has a large excess of *n*-butyl ether, the characteristic shape of the spectra of a dioxane solution still persists. The intermediate band in each of these solvent mixtures is shifted toward a shorter wave length and becomes less prominent, as the mole fraction of *n*-butyl ether increases. Theoretical curves were then constructed for the absorption spectra of iron(III) chloride in mixed dioxane–*n*-butyl ether solutions containing 70, 73.5 and 80 mole % dioxane. These curves were constructed on the assumption that the ethers were of equal basicity, that one molecule of ether was associated with one molecule of iron(III) chloride and that the distribution of iron(III) chloride as dioxanate or di-*n*-butyl etherate would, therefore, be proportional to the mole fractions of the ethers in the solvent mixture. Data for the theoretical curves were obtained using the relation

$$\epsilon_{\text{obsd}} = \epsilon_{\text{Dx}}X + \epsilon_{\text{Bu}_2\text{O}}\,(1 - X)$$

where ϵ_{Dx} is the molar absorption coefficient of iron(III) chloride in dioxane, $\epsilon_{\text{Bu}_2\text{O}}$ is the molar absorption coefficient of iron(III) chloride in *n*-butyl ether, and X is the mole fraction of iron(III) chloride present as dioxanate. In the calculation it is assumed that Beer's Law is followed in the mixed ether solvent and that the iron(III) chloride is all present either as monodioxanate or mono-*n*-butyl etherate.

An examination of Fig. 3 reveals that the intermediate band, characteristic of the iron(III) chloride dioxanate, is more prominent in the experimental 32.9 mole % dioxane curve than in the theoretical curve for 73.5 mole % dioxane. It is also clear from Fig. 3 that the intermediate band is less prominent in the experimental 32.9 mole % solution than it is in the theoretical curve for 80 mole % dioxane. This permits the conclusion that, in the 32.9 mole % dioxane solution, more than 73.5% and less than 80% of the iron(III) chloride is present in solution as dioxanate.

Using the equilibrium expression

$$\frac{[\text{FeCl}_3\cdot\text{Bu}_2\text{O}][\text{Dx}]}{[\text{FeCl}_3\cdot\text{Dx}][\text{Bu}_2\text{O}]} = K$$

for the reaction

$$\text{FeCl}_3\cdot\text{Dx} + \text{Bu}_2\text{O} \rightleftarrows \text{FeCl}_3\cdot\text{Bu}_2\text{O} + \text{Dx}$$

in which *n*-butyl ether may be considered to replace part of the dioxane in the association complex, upper and lower limits for the value K may be calculated. In this calculation the ratio of the concentrations of the two ethers is taken as equal to the original solvent composition, all the iron(III) chloride is assumed to be present as complex, either dioxanate or *n*-butyl etherate, and one molecule of ether is assumed to be complexed with iron(III) chloride. A lower limit of 0.12 and an upper limit of 0.18 were obtained for K, using 73 mole % as the lower limit of the concentration of dioxanate and 80 mole % as the upper limit. Use of these values of K in the equilibrium expression gave results showing that, in an equimolar mixture of dioxane and *n*-butyl ether, the ratio of the concentrations of iron(III) chloride dioxanate to iron(III) chloride *n*-butyl etherate lies between 5.5 and 8.1. If it is assumed that 2 molecules of *n*-butyl ether are associated with one molecule of iron(III) chloride, a similar calculation gives a dioxanate–*n*-butyl etherate ratio of 7.7 rather than 5.5. Thus, even if the assumption of the presence of mono-*n*-butyl etherate is not correct, the qualitative result is not changed. Since, however, the calculation on which the theoretical curve is based involves the use of molar absorption coefficients which may be in error by as much as 5%, the precision of the above relative basicity values is not high.

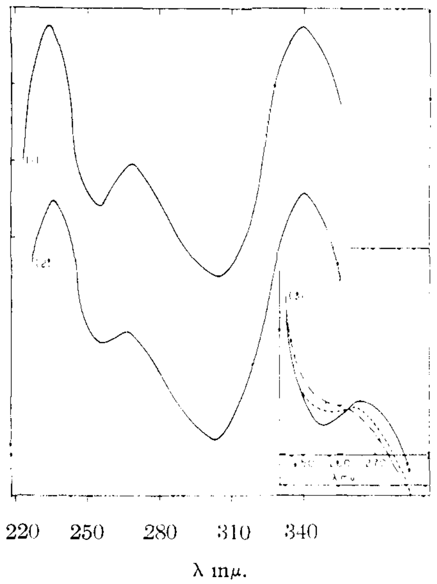

Fig. 3.—Absorption curves for FeCl_3 in *n*-butyl ether–dioxane mixtures: 1, experimental curve, 57 mole % dioxane; 2, experimental curve, 32.9 mole % dioxane; 3, theoretical curves, 80 mole % dioxane ———; 73.5 mole % dioxane - - - -, 70 mole % dioxane — — —.

To obtain some additional data on the relative basicity of dioxane and di-*n*-butyl ether toward iron(III) chloride, other values for K were calculated from optical density data at 250 mμ, at which wave length there is a maximum difference between the molar absorption coefficients of iron(III) chloride in dioxane and in *n*-butyl ether. Values for K ranging from 0.15 to 0.20 were thus obtained. These values are close to those obtained from a consideration of the shapes of the experimental and theoretical curves shown in Fig. 3. It appears then to be well established from the above considerations that dioxane is at least four times more basic than *n*-butyl ether towards iron(III) chloride.

An indication that a second alkyl ether was also much less basic than dioxane toward iron(III) chloride was given by observations of the spectrum of iron(III) chloride in a dioxane–ethyl ether mixture containing 57 mole % dioxane. In this solvent mixture the three bands characteristic of iron-

(III) chloride dioxanate were very prominent, while the 250 mμ band characteristic of alkyl ether solutions of iron(III) chloride was absent.

It thus seems reasonable to conclude that the stronger solvent–solute interaction that occurs in dioxane solutions of iron(III) chloride, in comparison to alkyl ether solutions, is responsible for the difference in the electronic energy levels of iron (III) in the different solute species.

In Fig. 4 is shown a plot of molar absorption coefficients against wave lengths for dioxane and dioxane–hydrogen chloride solutions of iron(III) chloride varying from 0.04 to 3.49 molar in hydrogen chloride. The existence of four well-defined isosbestic points at 263, 294, 322 and 356 mμ, and a less exactly determined fifth isosbestic point near 225 mμ, in the series of curves of Fig. 4, establishes that in these solutions there exist only two absorbing species. That one of these species is tetrachloroferric(III) acid is shown by the identity of the wave lengths of maximum absorption with those in aqueous hydrochloric acid solutions above 7 molar,[9] and in ether extracts of strong hydrochloric acid solutions of iron(III) chloride, in which the absorbing species has been shown[11] to be tetrachloroferric(III) acid. This is confirmed by the equilibrium data to be discussed later in this paper. The second species is solvated iron(III) chloride.

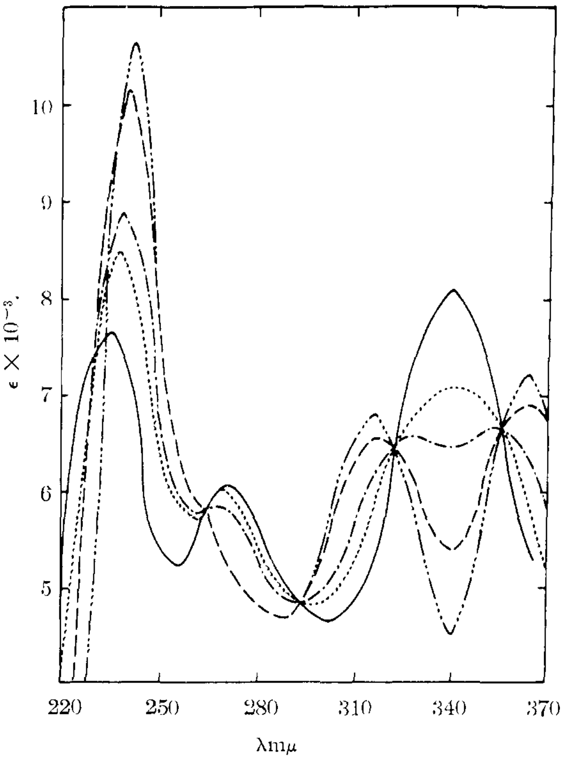

Fig. 4.—Absorption curves for the system: $FeCl_3$–anhydrous HCl–dioxane at various HCl molarities: *M* HCl ——— 0.0; - - - -, 0.04; — - —, 0.08; — —, 0.24; —- - -—, 3.49.

While the characteristic spectrum of tetrachloroferric(III) acid appears in aqueous solutions only when the hydrogen chloride concentration exceeds 7 molar,[9] it shows up in the dioxane solutions at a much lower hydrogen chloride concentration. In Fig. 5 are shown the results of measurements at the wave lengths of maximum absorption for solutions of iron(III) chloride in dioxane–hydrogen chloride at varying hydrogen chloride concentrations. These results show that, at hydrogen chloride concentrations which are above 3.6 molar, there is substantially complete conversion of iron(III) chloride to tetrachloroferric(III) acid and that the molar absorption coefficients approach determinable limiting values. From the data reported in Fig. 5 the values for the molar absorption coefficients for tetrachloroferric(III) acid are found to be: $\epsilon_{242\ m\mu}$, 11,500; $\epsilon_{316\ m\mu}$, 7100 and $\epsilon_{364\ m\mu}$, 7600. These values are slightly higher than the values indicated by the spectral curves for the isopropyl ether extracts reported by Myers and Metzler[9] and appreciably higher than those reported for aqueous solutions, 11.7 molar in hydrogen chloride. The proportion of iron(III) present as tetrachloroferric(III) acid in hydrogen chloride solutions is greatly reduced by the presence of water which promotes the formation of various hydrolytic and other cationic species. The lower absorption coefficients in ether extracts, compared to anhydrous dioxane, are probably the result of the presence of some water in these extracts.

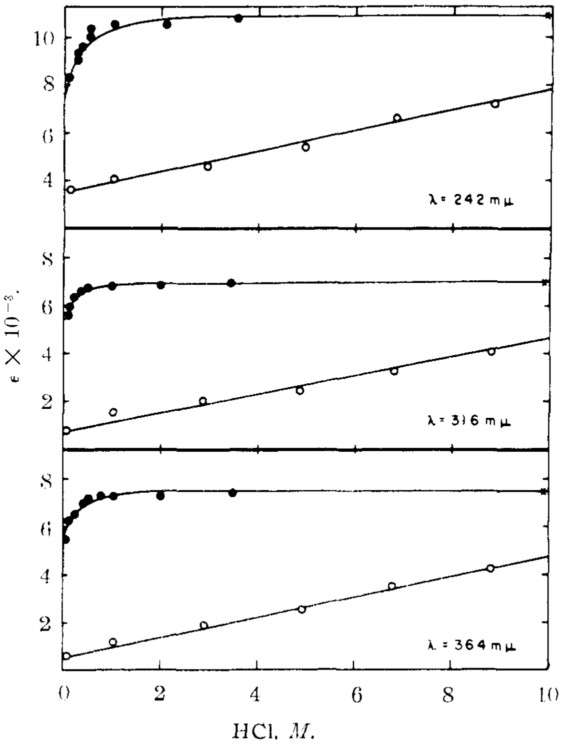

Fig. 5.—Molar absorption coefficients for $FeCl_3$ in dioxane–HCl and in aqueous HCl solutions: ●, 1,4-dioxane; ×, calculated from $K = 0.14$ for $HFeCl_4$ in dioxane; ○, aqueous HCl.

The proportion of iron(III), present as tetrachloroferric(III) acid in water–dioxane mixtures, is not proportional to the gross hydrogen chloride concentration but is more nearly proportional to the water–hydrogen chloride ratio. This was shown by comparison of the spectrum of iron(III) chloride in aqueous 12.23 molar hydrogen chloride with that in a solution, diluted with an equal volume of dioxane, to give a solution, 6.12 molar in hydrogen chloride. As will be seen from the curves in Fig. 6, reduction of the hydrogen chloride concentration by dilution with dioxane does not cause a decrease in the concentration of tetrachloroferric(III) acid but actually results in an increase in concentration. The decrease in hydrogen chloride concentration is compensated for by the corresponding decrease in the concentration of water which competes with the hydrogen chloride for reaction with iron(III) chloride. Thus it is the ratio of the water to the hydrogen chloride which is the more important factor. The increase in the concentration of tetrachloroferric(III) acid on dilution with dioxane is not so readily explained. The effect of dioxane in decreasing the action of water, more than the action of hydrogen chloride, on iron(III) chloride may be due to the decreased dielectric constant in the water–dioxane mixture. Since the solute species formed by reaction of iron(III) chloride with water are cationic, a lower dielectric constant may cause a decrease in the concentration of these ionic forms and favor the formation of unionized tetrachloroferric(III) acid.

For comparison of other ethers with dioxane, spectral data were also obtained on hydrogen chloride–iron(III) chloride solutions in isopropyl ether, *n*-butyl ether and tetrahydrofuran. It was observed, in the case of each of these ethers, that the characteristic tetrachloroferric(III) acid spectrum was developed at lower hydrogen chloride concentrations than in dioxane. Again, as for dioxane solutions, the spectra of solutions of low hydrogen chloride concentrations were composites of the spectrum of iron(III) chloride in the particular ether and the spectrum of tetrachloroferric(III) acid. In each case a number of isosbestic points, where the spectral curves of the two solute species intersected, were observed to persist over all intermediate hydrogen chloride concentrations. The identity of the wave lengths of maximum absorption with those of other solutions containing tetrachloroferric(III) acid establishes the nature of the chlorocomplex present in these ether solutions. At sufficiently high hydrogen chloride concentrations, the molar absorption coefficients, at various wave lengths, for each of the ether solutions were found to have within experimental error the same values found as limiting values for dioxane–hydrogen chloride solutions.

The spectral identity of the absorbing species, present in all the hydrogen chloride–ether solutions, is of significance in comparison to the differences noted in the spectra of iron(III) chloride in different types of ethers. While the solvation interaction of different types of ethers with iron(III) chloride, resulting from difference in the basicities of the ethers, evidently effects different changes in the electronic energy levels in iron(III), the interaction of solvent ethers with tetrachloroferric(III) acid causes no such differences. It is reasonable to assume that solvent interaction with tetrachloroferric(III) acid is almost negligible and that the complex acid may exist as an ion pair which is effectively non-solvated.

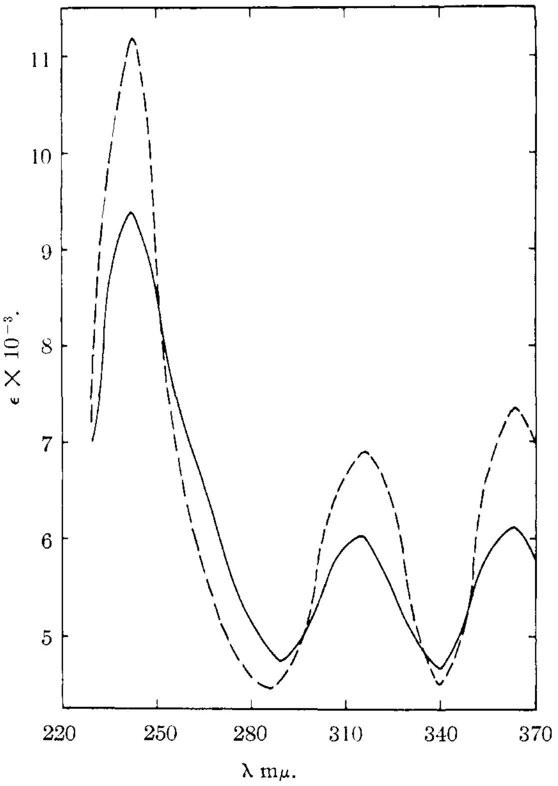

Fig. 6.—Absorption spectra for $FeCl_3$–aqueous HCl–dioxane: 12.23 *M* HCl in H_2O ———; 6.12 *M* HCl in H_2O–dioxane— — —.

With values of molar absorption coefficients for solvated iron(III) chloride and tetrachloroferric(III) acid in ethers available, a determination of the equilibrium concentrations of the two solute species was possible. From Fig. 4 it may be seen that, at 340 mμ in dioxane, there is a maximum absorption for iron(III) chloride and a minimum absorption for tetrachloroferric(III) acid. There is also a large difference in the molar absorbancies at this wave length. Equilibrium concentrations of the two iron species in dioxane solutions of varying hydrogen chloride concentration were calculated from the expression

$$C_1 = \frac{d_0 - \epsilon_2 C_0}{\epsilon_1 - \epsilon_2}$$

where C_0 is the total concentration of iron(III) in moles per liter, C_1 is the equilibrium concentration of iron(III) chloride; ϵ_1 is the molar absorption coefficient of iron(III) chloride in dioxane at 340 mμ, taken as 8115; ϵ_2 is the molar absorption coefficient of tetrachloroferric(III) acid at 340 mμ, taken as 4230; and d_0 is the observed optical density of the solution at 340 mμ with 1-cm. light path. In the calculation of equilibrium concentrations it is assumed that Beer's Law is followed.

Based on data for 45 dioxane solutions, ranging up to 4.6 molar in hydrogen chloride, values for the equilibrium constant *K* for the reaction

$$HFeCl_4 \rightleftarrows HCl + FeCl_3$$

were calculated, taking concentrations as equal to activities. A mean value, $K = 0.14$, with an average deviation of 0.016, was obtained. Values calculated on the assumption that a pentachloro- or hexachloro-complex acid was formed showed large changes with hydrogen chloride concentration. In Fig. 7 is shown the agreement between optical densities, calculated from the equilibrium expression, using K equal to 0.14, and a large number of experimental optical densities. The agreement between the observed and calculated optical densities gives an independent basis for concluding that the complex is tetrachloroferric(III) acid.

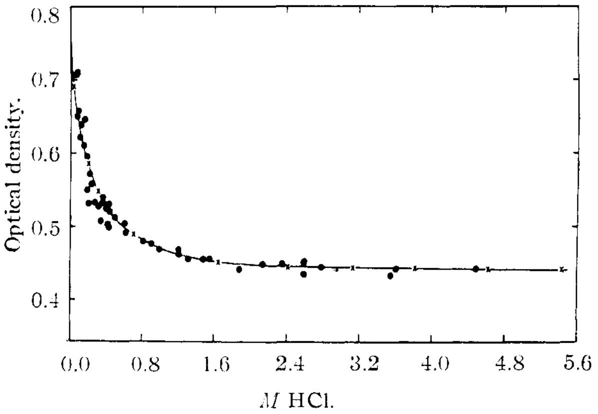

Fig. 7.—Optical density of 1×10^{-3} M $FeCl_3$ in HCl–dioxane solutions at 340 mμ; ●, experimental; ×, calculated from $K = 0.14$.

Preliminary qualitative observations had indicated that, in alkyl ethers, iron(III) chloride was completely converted to tetrachloroferric(III) acid at much lower hydrogen chloride concentrations than in dioxane. To obtain more quantitative information on this point, a limited number of spectral measurements were made on hydrogen chloride solutions of iron(III) chloride in *n*-butyl ether, tetrahydrofuran and isopropyl ether. From these data the dissociation constants of tetrachloroferric(III) acid were calculated in the same manner as for the dioxane solution. The values obtained are not considered to be precise but to represent correctly the order of magnitude. The dissociation constants in these ethers are listed in Table III. The value for dioxane, and a value calculated from the stability constant reported by Gamelin and Jordan[7] for aqueous solutions, are also listed in Table III.

TABLE III

DISSOCIATION CONSTANTS OF TETRACHLOROFERRIC(III) ACIDS IN VARIOUS SOLVENTS

Solvent	K
Water	95
Dioxane	0.14
Tetrahydrofuran	.0025
n-Butyl ether	.002
Isopropyl ether	.0001

It is evident from the values of the dissociation constants that the chloro-complex is much less stable in water than in the ethers and that the stability in the ethers is least for dioxane. The high value of the dissociation constant in water is understandable, as discussed above, because of the competing reaction of water with iron(III) chloride resulting in the formation of cationic species. Differences in the stability of tetrachloroferric(III) acid in the various ethers must similarly be due to differences in the solvation interaction of the various ethers with iron(III) chloride and with hydrogen chloride.

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The Reaction of Chloramine with Some Trisubstituted Phosphines[1]

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The reaction of chloramine with trisubstituted phosphines has been explored. The ionic quaternary aminophosphonium chlorides, $[R_3PNH_2]Cl$, formed by this reaction are analogs of the 1,1,1-trisubstituted hydrazinium chlorides prepared by the reaction of chloramine with tertiary amines. Stable, crystalline salts are formed by the interaction of the aminophosphonium chlorides with the sodium, potassium or ammonium salts of the following anions: hexafluorophosphate, perchlorate, anthraquinone-2-sulfonate, nitroprusside, periodate, hexachloroplatinate, picrate. Tertiary phosphine oxide and ammonium chloride are products of the aqueous and alkaline hydrolysis of the aminophosphonium chlorides. A mechanism for the reaction of chloramine with tertiary phosphine is suggested.

In earlier communications[2,3] we reported new methods for the synthesis of substituted hydrazines and hydrazinium salts by the chloramination of primary, secondary and tertiary amines. This paper describes analogous chloramination reactions with a series of tertiary phosphines which produced P-trisubstituted aminophosphonium chlorides in excellent yields. Further chloramination studies of phosphorus compounds as well as of arsenic, anti-

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[1] From a portion of the dissertation by Adib Sarkis in partial fulfillment for the degree of Doctor of Philosophy. This research was reported in part at a Meeting of the American Chemical Society in Chicago, Ill., in September, 1958.

[2] G. M. Omietanski and H. Sisler, THIS JOURNAL, **78**, 1211 (1956).

[3] G. M. Omietanski, A. D. Kelmers, R. W. Shellman and H. H. Sisler, *ibid.*, **78**, 3874 (1956).