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The Extraction of Ferric Iron from Hydrochloric Acid Solutions by Dichloroethyl Ether and the Formula of the Iron Compound in the Ether

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Introduction

Although the extraction of ferric iron from hydrochloric acid solutions by ethyl ether has been an analytical procedure for over fifty years, only recently has the use of other than ethyl ether been investigated; furthermore, although there have been studies of the molecular condition of anhydrous ferric chloride in ethyl ether[1,2] only very recently does there appear to have been any experimental investigations to establish the molecular nature of the iron compound in the ether phase obtained in the extraction process.[3] Dodson, Forney and Swift[4] have shown recently that isopropyl ether possesses certain advantages over ethyl ether for the extraction of ferric iron from hydrochloric acid solutions, and unpublished experiments by Dodson have shown that the ferric chloride in the isopropyl ether phase was associated with hydrogen chloride. He found that with high initial concentrations of acid and of iron in the aqueous phase, two ether phases separated and obtained ratios of hydrogen chloride to ferric chloride of 1.25 and 1.32 in the two ether phases. In addition, it seemed necessary to assume polymerization of the iron in the ether layer in order to explain the dependence of the distribution ratio upon the concentration of iron.

This paper presents the results of studies of, first, the distribution of ferric iron between hydrochloric acid solutions and dichloroethyl ether, and, second, the nature of the ferric iron compound in the ether phase. Preliminary experiments by Mr. John Gates had shown that the mutual solubilities of this ether with hydrochloric acid solutions are small so that extractions are practical with even quite concentrated acid solutions, and, in addition, so little acid passes into the ether phase that conditions are favorable for studying the association of hydrogen chloride with the iron. Dichloroethyl ether also has a practical advantage over either ethyl or isopropyl ether for the extraction of iron in that it separates as the lower phase when shaken with hydrochloric acid solutions and repeated extractions from a single separatory funnel are therefore possible.

The Distribution of Iron between Dichloroethyl Ether and Hydrochloric Acid Solutions

Experimental.—The β,β'-dichloroethyl ether was a redistilled grade. It was found to have a boiling range of less than 3° and gave a negative test for peroxide. It was used repeatedly, being washed and distilled each time. Various solutions of ferric chloride in hydrochloric acid were prepared; both reagent grade hexahydrate and anhydrous sublimed ferric chloride were used. Standard solutions of sodium thiosulfate, ammonium thiocyanate, silver nitrate, hydrochloric acid and sodium hydroxide were prepared and standardized by conventional methods.

The distribution data were obtained by shaking equal volumes of the ether with iron and hydrochloric solutions of the desired concentrations in a thermostat at 25° for from thirty to sixty minutes in order to obtain thermal equilibrium. The equilibrium of the iron between the two phases appeared to be established very rapidly. The probable accuracy of the distribution ratios is indicated by the reproducibility of duplicate experiments and the conformity of the points to the curves of Fig. 1. The separatory funnel was then allowed to stand in the thermostat until the two layers separated and the ether layer drawn off. Duplicate twenty-five ml. portions of the acid phase were pipetted into conical flasks, the acid concentration made approximately one normal and the iron determined iodometrically.[5] Where the amount of iron present was small, a 0.01 normal thiosulfate solution was used. Duplicate twenty-five ml. portions of the ether phase were shaken with twenty-five ml. portions of water, the water layer separated and the iron determined as above. Experiments showed that the hydrochloric acid and iron were quantitatively extracted from the ether layer by an equal volume of water. In Table I below is shown the initial concentration of the acid in the aqueous phase and the acid concentration after equilibrium had been established. This latter value was calculated by correcting the original acid concentration for the hydrogen chloride dissolved as such and as $HFeCl_4$ by the ether, for dilution of the aqueous phase by dissolved ether, and for concentration by the water passing into the ether phase. The solubility of ether in 7.5 formal hydrochloric acid and in a solution 7.5 formal in hydrochloric acid and 1 formal in ferric chloride was found to be substantially the same. It should be

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[1] E. Beckmann, *Z. physik. Chem.*, **46**, 860 (1903).

[2] Forster, Cooper and Yarrow, *J. Chem. Soc.*, **111**, 810 (1917).

[3] Not until after this article was prepared for publication did the work of Kato and Isii, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **36**, 82–96 (1939), on the molecular formula of the iron compound in ethyl ether come to the attention of the authors. As the result of analytical and absorption spectra studies of the ether phase these investigators assign the compound in ethyl ether the formula $2[FeCl_3\cdot HCl]\cdot 9H_2O\cdot 15(C_2H_5)_2O$.

[4] Dodson, Forney and Swift, THIS JOURNAL, **58**, 2573 (1936).

[5] Swift, THIS JOURNAL, **51**, 2682 (1929).

pointed out that the acid concentrations given are formal, not molal, concentrations as there is undoubted association of the iron and acid in the aqueous phase.[6]

The results of the distribution experiments are collected in Table I and curves showing the percentage extraction at various acid concentrations are shown in Fig. 1.

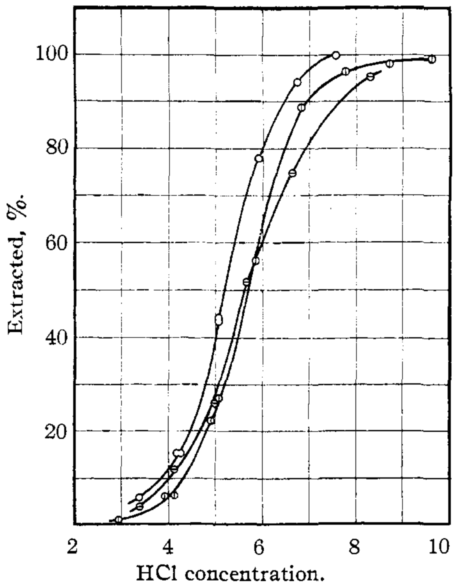

Fig. 1.—Iron extracted into dichloroethyl ether from HCl solutions: ○, initial iron concentration, 0.01 *F*; ⦶, initial iron concentration, 0.07 *F*; ⊖, initial iron concentration, 0.57 *F*.

An inspection of the data of Table I and the curves of Fig. 1 shows that, over the concentration range studied, the extraction of the iron by dichloroethyl ether becomes more effective the higher the hydrochloric acid concentration. This was confirmed by preliminary experiments which extended to 11.5 formal acid without showing any evidence of a decrease in the distribution ratio. This is contrary to the results of Dodson, Forney and Swift which show regions of maximum extraction at approximately 6 and 8 formal acid for ethyl and for isopropyl ether, respectively, and indicates that in the aqueous phase there is a continuous increase with increasing acid concentration of the concentration of the molecular compound passing into the ether phase.

The curves also show that dichloroethyl ether can be used for the practical extraction of iron from solutions in which the hydrochloric acid concentration is greater than seven formal. Mention should be made, however, that the time required for the separation of the two phases is somewhat longer than for either ethyl or isopropyl ether.

TABLE I

THE DISTRIBUTION OF FERRIC IRON BETWEEN HYDROCHLORIC ACID SOLUTIONS AND DICHLOROETHYL ETHER

HCl (moles/liter) aqueous layer Initial	HCl (moles/liter) aqueous layer Final	Iron (moles/liter) aqueous layer Initial	Distribution ratio $\frac{Fe(ether)}{Fe(H_2O)}$	Extracted, %
3.45	3.42	0.00895	0.065	6.0
4.24	4.19	.00895	.187	15.4
4.31	4.26	.00895	.186	15.4
5.17	5.10	.00895	.820	44.5
5.17	5.10	.00895	.795	43.6
6.03	5.93	.00895	3.64	78.0
6.90	6.77	.00895	17.8	94.5
7.75	7.58	.00895	...	>99.8
2.99	2.97	.0720	0.013	1.26
4.00	3.95	.0720	.066	6.1
4.20	4.14	.0720	.071	6.5
5.00	4.93	.0720	.294	22.3
5.17	5.09	.0720	.379	27.1
5.99	5.88	.0720	1.32	56.4
7.00	6.84	.0720	7.74	88.2
7.99	7.80	.0720	29.8	96.6
9.00	8.75	.0720	51	98.0
9.99	9.65	.0720	132	99.2
3.45	3.40	.574	0.043	4.05
4.24	4.15	.574	.136	11.9
5.17	5.02	.574	.350	26.0
6.03	5.66	.574	1.06	52.0
6.90	6.64	.574	2.88	75.0
8.63	8.33	.574	19.4	95.4

The unexpected behavior of the lower portion of the curve for the solutions 0.57 formal in iron may be due to the ferric iron causing an abnormal increase in the ionic strength of the solutions. When a large fraction of the iron is extracted into the ether, this effect diminishes and the upper portion of the curve conforms more nearly to the other two.

The Determination of the Formula of the Iron Compound in the Ether Phase.—In the determination of the formula of the iron in the ether phase the analytical procedure was essentially as follows, although minor refinements and modifications were made as the experiments progressed. Equal volumes of the ether and the iron–hydrochloric acid solutions were shaken together, allowed to separate and the ether layer was analyzed for chloride by shaking it with an equal volume of water, removing the water layer, adding an excess of standard silver nitrate, coagulating the precipitate, and titrating the excess silver nitrate

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(6) Complex acids such as $HFeCl_4 \cdot 2H_2O$ and $H_2FeCl_5 \cdot 4H_2O$ have been prepared, as have salts such as $KFeCl_4$. In addition, studies of the heat of solution of ferric chloride in hydrochloric acid solutions show evidence of such compound formation. Kangro and Flugge, *Z. physik. Chem.*, **A175**, 187 (1935).

with a standard thiocyanate solution. A second portion of the ether layer was analyzed for acid and ferric iron by similarly shaking it with an equal volume of water, separating the water layer, titrating it with standard hydroxide until the ferric hydroxide could be coagulated by heating, then again titrating with the hydroxide to a phenolphthalein end-point. The titrated solution was then made approximately one normal in hydrochloric acid and the iron determined iodometrically. The amount of hydrogen chloride passing into the ether layer from pure hydrochloric acid solutions of various concentrations was determined by separate experiments and this amount subtracted from the total amount found with the iron extracts. The analytical data have been collected and are shown in Table II below; also the molecular ratios of chloride and of acid to iron in the ether phase are calculated and tabulated. It was not at first thought necessary to entirely free the water extracts (containing the iron and acid) from ether before heating the solution for the acid titration; however, upon heating 100 ml. of water with a small amount of the ether for an hour it was found that an acidity had developed roughly equivalent to one per cent. of the acid found in the previous analyses. In the last two experiments the water extracts were separated from the ether and then filtered through paper filters before making the titration for acid, thus removing suspended droplets of ether.

TABLE II

ANALYSES OF THE ETHER EXTRACTS

Concentration (moles liter)			Ratios	
Fe^{III}	Cl^-	$H^+ + 3Fe^{III}$	Cl^-/Fe^{III}	H^+/Fe^{III}
Initial HCl concentration, 6.2 formal. Solubility of HCl in ether, 0.0022 formal				
0.3059	1.232	1.237	4.03	1.05
.3065	1.233	1.227	4.02	1.00
.2961	1.187	1.206	4.01	1.07
Initial HCl concentration, 7.1 formal. Solubility of HCl in ether, 0.0032 formal				
0.2114	0.848_1	0.858_0	4.01	1.06
.2117	$.857_0$	$.856_3$	4.05	1.04
.2111	$.845_5$	$.857_8$	4.01	1.06
Initial HCl concentration, 8.2 formal. Solubility of HCl in ether, 0.0077 formal				
0.1527	0.612_3	0.615_7	4.01	1.03
.1537	$.612_4$	$.620_6$	3.98	1.04
.1535	...	$.618_5$	..	1.03
.1541	$.616_9$	$.615_7$	4.00	0.997
.1544	$.616_0$	$.618_1$	3.99	1.000

From the data of Table II it is seen that, exclusive of water and ether, the formula of the iron compound can be written as $HFeCl_4$. The closeness of the agreement of the ratios with this formula makes it appear reasonable to conclude that no other complex with a higher ratio of chloride to iron exists in appreciable amounts in the ether.

As Schwarz and Meyer[7] in their study of the various chloro acids found that they could not prepare anhydrous $HFeCl_4$, and as the evaporation of ethyl ether extracts containing iron gives evidence of more water than that normally dissolving in the ether, attempts were made to analyze dichloroethyl ether extracts for their water content. The presence of hydrogen chloride and ferric chloride cause interference with most chemical methods, so, in spite of obvious decomposition in the ether solution during the process, a distillation method was used. A 100-ml. round-bottomed flask was sealed to a fractionating column connected by a ground-glass joint to a condenser which drained into a 15-ml. graduated centrifuge tube initially containing 5 ml. of petroleum ether. Decomposition in the solution in the distilling flask began after approximately 40% of the water was collected and by the time complete recovery was obtained (as shown by the analysis of artificially prepared solutions) a dark viscous mixture was left. Probably because of this decomposition the analysis of the artificial solutions of known content gave an excess of water which was independent of the amount of water originally present and varied in volume from 0.62 to 1.05 ml. with an average value of 0.89 ml.; this volume was subtracted from the total volume of water obtained in the subsequent distillation, as was also the volume of water found to be dissolved by the ether from pure hydrochloric acid solutions. Hydrogen chloride also was distilled over and collected with the water; therefore, the distillate was titrated to determine the acid concentration and the volume corrected accordingly. The data obtained from analyses of ether extracts of iron from 7.5 formal hydrochloric acid solutions are shown in Table III. In the first column are shown the millimoles of iron present in the 50.0 ml. of ether solution; in column two is shown the total volume of water obtained by the distillation procedure outlined above; in column three the corrected volume; and in the last column the calculated molal ratio of water to iron.

The data of Table III show that from four to five molecules of water are associated with each

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(7) Schwarz and Meyer, *Z. anorg. allgem. Chem.*, **166**, 190 (1927).

TABLE III

DETERMINATION OF WATER IN THE ETHER EXTRACT

Initial volume of ether, 50.0 ml.

Fe^{III} present (millimoles)	Total H_2O recov., ml.	Corrected H_2O, ml.	Ratio: H_2O/Fe
37.8	4.97	3.11	4.56
39.8	5.4	3.41	4.76
40.3	5.4	3.40	4.68
39.8	5.1	3.11	4.34
38.6	5.13	3.06	4.40
40.7	5.23	3.32	4.53
40.6	5.21	3.22	4.40
			Mean 4.52

molecule of iron. The average ratio is 4.52; this value and the formula assigned to the iron compound in the ethyl ether phase by Kato and Isii[3] suggests the possibility that at least two iron atoms are associated in the molecule existing in the ether phase; however, because of the large corrections applied in obtaining the water volumes, and because a water determination was made with only one concentration of acid and of iron, too great significance should not be placed on the ratio values.

No attempt was made to determine the extent to which the ether may be associated with the iron compound. That there may be such association is indicated by the fact that the compounds $FeCl_3 \cdot (C_2H_5)_2O$[2] and $FeCl_3 \cdot HCl \cdot 2(C_2H_5)_2O$[8] have been prepared, and by the results of Kato and Isii. Although the first of the compounds mentioned is stated to be immediately decomposed by water, this does not preclude the possibility of the existence in an ether solution of a mixed compound containing both water and ether molecules. Because of the uncertainty regarding the association of ether molecules, an exact formulation of the compound or its structure cannot be made. It seems probable that the four chlorides are bonded tetrahedrally to the iron and that the waters are held by hydrogen bonds to the chlorides. As previously stated, Schwarz and Meyer could not prepare anhydrous $HFeCl_4$, which indicates that these hydrogen bonds are needed to stabilize the tetrahedral complex.

Acknowledgment: The authors are greatly inindebted to Mr. John Gates and Mr. R. C. Jones for carrying out an extensive series of preliminary experiments. These experiments were of value in showing the dependence of the distribution ratio on the acid concentration and in establishing the ratio of acid and of chloride to iron in the ether solution.

Summary

The distribution of ferric iron between hydrochloric acid solutions and β,β'-dichloroethyl ether has been studied for various concentrations of acid and iron. Dichloroethyl ether can be used for the quantitative extraction of ferric iron from solutions greater than 7 formal in hydrochloric acid.

Chemical analyses of the ether solution have shown that one molecule of hydrochloric acid and from four to five molecules of water are present for each molecule of iron present in the ether layer. Neglecting polymerization and the possible presence of ether in the molecule, the empirical formula can be written as $HFeCl_4 \cdot 4\text{–}5H_2O$.

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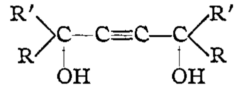
[8] Houben and Fischer, *J. prakt. Chem.*, **123**, 89 (1929).

[CONTRIBUTION FROM RÖHM AND HAAS COMPANY, INC.]

Cycli-Alkylation of Aromatic Compounds by the Friedel and Crafts Reaction

BY HERMAN ALEXANDER BRUSON AND JOHN W. KROEGER

The method recently described by Kazarian[1] for preparing acetylenic alcohols by the interaction of calcium carbide, potassium hydroxide and a ketone, has made more readily available, many acetylenic tertiary glycols heretofore obtainable only with considerable difficulty and expense. These acetylenic tertiary glycols have the general formula (I)



$$\mathrm{R'(R)C(OH){-}C{\equiv}C{-}C(OH)R'(R)} \qquad \text{I}$$

Upon catalytic hydrogenation with Raney nickel at 60–85° and 100 lb. pressure/square inch (7 atm.), the acetylenic bond of these glycols can be completely saturated with hydrogen, thus making available in quantity 1,4-ditertiary glycols (II) having unique interest for further synthetic work.

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[1] Kazarian, *J. Gen. Chem.* (*U. S. S. R.*), **4**, 1347 (1934), *C. A.* **29**, 3978 (1935); Russian Patent 41,516 (1935), *C. A.* **30**, 8241 (1936); *J. Gen. Chem.* (*U. S. S. R.*), **7**, 956 (1937), *C. A.* **31**, 5320 (1937).