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PREPARATION AND PROPERTIES OF SOME MIXED FERROCENE/FERRICINIUM SALTS

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SUMMARY

Ferrocene–ferricinium bromide–MEK complex, (I), ferrocene–tris [ferricinium tetrabromoferrate(III) hydrate], (II), were prepared as new compounds and compared with ferricinium tetrabromoferrate(III). The complexes were prepared by crystallization from ferrocene rich polar solutions. (I) decomposed at 217°, (II) melted reversibly at 187°, while ferricinium tetrabromoferrate(III) decomposed at 244°.

When placed in water $FcH^+FeBr_4^-$ dissolves completely, but both (I) and (II) yield insoluble ferrocene. The amount of ferrocene thus obtained from (II) agreed with the calculated amount of ferrocene in the complex. IR and visible spectrum comparisons were inconclusive in detection of ferrocene in the compounds. The compounds were further characterized by their X-ray powder patterns and optical microscopic observations.

INTRODUCTION

As part of a study on crystals containing the same material in two different oxidation states, we looked at possible ferrocene/ferricinium compounds. Although the chemistry of both ferrocene and ferricinium salts has been the subject of considerable study, no compound containing both ferrocene and the ferricinium cation had been reported.

This report concerns the preparation and properties of two such compounds.

RESULTS AND DISCUSSION

Reaction of ferrocene (FcH) with excess bromine in non-polar solvents produces ferricinium tetrabromoferrate(III) as an end product[1,2]. Due to the insolubility of the initial ferricinium salts in these solvents, a precipitate is obtained which decomposes rapidly under the isolation conditions. It was felt that if ferrocene were oxidized in a mutual solvent for both ferrocene and ferricinium salt, the stability of the ferricinium ion would be enhanced by solvation to where one could obtain reasonably stable compounds. In the presence of an excess of ferrocene, it might then be possible to obtain mixed ferrocene/ferricinium compounds.

Partial oxidation of ferrocene in methyl ethyl ketone (MEK) with bromine gave a small yield of a compound analysing for $(FcH)_2Br \cdot C_4H_8O$, ferrocene ferricinium bromide with one molecule of solvation of MEK, [compound (I)]. This decomposed at 217° on a DTA without melting. Conversely, in several oxidations of ferrocene in CCl_4 by 20 to 50 equivalent percent of bromine, where the initial ferricinium salt is insoluble and non-solvated, there was obtained a mixture of ferrocene and ferricinium tetrabromoferrate(III). When such a mixture was redissolved in a mutual solvent, evaporation of the solvent produced mixed crystals of $FcH(FcH^+FeBr_4^- \cdot H_2O)_3$ [compound (II)]. (The water probably was introduced from the air or from the solvents during the relatively long period of handling.) Compound (II) melted reversibly at 187°.

Though both Nesmeyanov *et al.*[3] and Spilners[4] invoke possible ferrocene or ferrocene/ferricinium transitory complexes, such complexes were not actually observed by them.

The complexes with MEK in compound (I) and with water in compound (II) are paralleled by other ferricinium complexes. Spilners[4] reported three ferricinium and biferricinium salts containing water of hydration. Smith[5] proposed the presence of $FcH^+(H_2O)_2$ and $FcH^+(SCN)^- \cdot ROH$ in the alcohol/water solutions of ferricinium thiocyanate he worked with.

When crystals of compounds (I) or (II) were placed in water, either acidified to $pH = 4.0$ or neutral, they gradually dissolved and particles of ferrocene were seen in the blue-red ferricinium solutions. Ferrocene was analysed for quantitatively in compound (II) by dissolving it in acidified water and collecting the insoluble fraction. The weight collected agreed with the theoretical. It was identified spectroscopically and by its chemical properties. Solid ferrocene was only observed upon dissolution of the two ferrocene/ferricinium complexes. Ferricinium tetrabromoferrate(III) dissolved much faster than either complex and no ferrocene could be observed in the solution.

In confirmation of the postulated solvent of crystallization, MEK, infrared spectra of compound (I) in CsI pellets showed the presence of aliphatic CH_2/CH_3 groups (absorption at 2920 and 2965 cm^{-1}) and of carbonyl group (broad absorption at about 1700 cm^{-1}).

Element analyses show one H_2O per ferricinium ion for compound (II). The formation of the compound from $FcH^+Br^-FcH \cdot MEK$ upon exposure to humidity (see Experimental) implies that compound (II) should contain water.

The visible and UV spectra of compound (II) in different media were taken and compared with that of ferricinium tetrabromoferrate(III). In acetonitrile, the spectrum of the complex was very similar to that of the tetrabromoferrate. Both showed the ferricinium[2,6] and the $FeBr_4^-$ (refs. 7–9) absorption bands. Such similarity is expected due to the similarity of the active species and to the fact that $FcH^+FeBr_4^-$ has a much larger molar extinction coefficient ($\varepsilon = 5800$ at $\lambda = 4600$ Å)[6,8] than ferrocene ($\varepsilon = 87$ at $\lambda = 4400$ Å)[6,10], thus completely masking ferrocene absorption bands. Solvent-dependent shifts in the positions of two peaks were noted. The $FeBr_4^-$ peak shifted from 498 mμ in KBr to 477 mμ in 1,2-dibromoethane to 462 mμ in acetonitrile. The ferricinium peak shifted from 635 mμ in KBr to 625 mμ in 1,2-dibromoethane to 620 mμ in acetonitrile and 615 mμ in water. These changes clearly show the effect of solvation on the electronic transitions in both active species.

d-Spacings of the X-ray reflections from the two new compounds and ferricinium tetrabromoferrate(III) are listed in Table 1. The pattern for compound (I) was quite weak and diffuse and had only nine reflections. As these match most of the strong reflections of compound (II), they are probably due to decomposition products of compound (I) rather than to the material itself, which is probably poorly crystalline.

TABLE 1

INTERPLANAR SPACINGS AND RELATIVE INTENSITIES OF X-RAY DIFFRACTIONS

$FcH^+Br^-FcH\cdot MEK$		$(FcH^+FeBr_4^-\cdot H_2O)_3FcH$		$FcH^+FeBr_4^-$	
I^a	*d* (Å)	I^b	*d* (Å)	I^b	*d* (Å)
mw	6.06	4	9.205	3	9.253
w	3.02	4	6.804	25	7.190
w	2.79	100	6.140	1	6.702
vw	2.47	7	5.675	55	6.167
w	2.02	15	5.092	35	5.676
w	1.83	4	4.619	100	5.092
w	1.75	2	3.616	8	4.779
vw	1.52	8	3.477	20	4.631
vw	1.20	5	3.264	29	4.555
		39	3.025	15	4.092
		5	2.873	22	3.820
		11	2.786	14	3.742
		3	2.513	36	3.620
		3	2.473	75	3.522
		4	2.307	25	3.269
		1	2.231	8	3.197
		9	2.017	15	3.056
		1	1.951	40	2.871
		2	1.868	35	2.787
		4	1.826	5	2.659
		2	1.786	7	2.568
		3	1.751	16	2.522
		2	1.714	15	2.479
		1	1.654	1	2.361
		8	1.515	7	2.314
		1	1.381	7	2.247
				6	2.139
				6	2.116
				7	2.051
				5	2.021
				2	1.981
				6	1.951
				5	1.905
				11	1.872
				15	1.829
				3	1.786
				12	1.754
				3	1.723
				2	1.654
				1	1.518

[a] Estimated from visual observation of exposed Debye–Scherrer photographs. [b] Measured on wide angle diffractometer tracings.

Compound (II) showed identical diffractometer tracings when crude or recrystallized, indicating the sample was quite pure. The dissimilarity between the patterns of compound (II) and ferricinium tetrabromoferrate(III) clearly indicate that the compounds are two different ones.

The transformation from compound (I) to compound (II) on standing in humid air could be easily observed from the changes in the X-ray pattern. The lines increased in their number and sharpness.

When ferrocene is oxidized with bromine in a solvating solvent, apparently the energy of solvation is sufficient to stabilize the ferricinium bromide at room temperature. [In the absence of a solvating solvent, decomposition is rapid at $-20°$ (ref. 2).] When the ferricinium bromide was precipitated from solution in the presence of a large amount of ferrocene, the metastable solvated mixed salt, $FcH^+Br^-FcH \cdot MEK$ was obtained. Its lack of solubility or decomposition in non-polar solvents indicates that the ferrocene is held fairly strongly, perhaps by electron exchange interactions.

In the presence of humidity, this mixed salt decomposes to a second, more stable mixed solvated salt, compound (II). This can be recrystallized from halogenated solvents and melted with no significant decomposition. It can also be made directly from ferricinium tetrabromoferrate(III) and ferrocene using a mutual solvent in the presence of traces of water. Here the ferrocene is held weakly, as it can be extracted slowly by benzene.

In spite of the instability of compound (I), it plainly differs from the other two. IR shows carbonyl and aliphatic hydrogen bands, and element analysis shows two Fe to one Br. It is probably amorphous as we prepared it. Compound (II) is quite stable in the absence of excess water or alcohol. It can be recrystallized, has a sharp melting point *without* decomposition, and shows high crystallinity by X-rays. Compound (II) is different again from ferricinium tetrabromoferrate(III). $FcH^+FeBr_4^-$ decomposes at 244° without melting, has a different X-ray spectrum, and of course each compound has a different element analysis and crystal form.

Two conditions were found to be needed for the formation of the ferrocene/ferricinium complexes. The first is that crystallization of the complex must proceed in a mutual solvent and preferably in the presence of excess ferrocene. The second condition (not quite as certain) is that the solid products be precipitated out by the addition of a non-solvent for ferricinium ion, or by the fast evaporation of the mutual solvent. When such a precipitation was not induced, and the MEK in which the reaction took place was allowed to evaporate slowly, a different product crystallized out of the mother liquor, namely ferricinium tribromoferrate(II)[11].

EXPERIMENTAL

Materials

Prior to use, ferrocene was recrystallized from hot absolute ethanol. Elemental bromine and all the solvents were or reagent or spectro-grades and were used without further purification, except for MEK which was distilled.

Preparation of $FcH^+Br^-FcH \cdot MEK$, ferrocene–ferricinium bromide–MEK complex (I)

To a solution of 0.05 mole (9.3 g) of ferrocene in 100 ml MEK, 0.02 mole (1.6 g) of bromine dissolved in 10 ml CCl_4 were added, yielding a deep brown solution. Upon evaporation at room temperature under reduced pressure, a gummy brown residue remained. This material was redissolved in MEK. A gummy but hard material precipitated from the saturated solution upon the dropwise addition of toluene. When the precipitate was washed sparingly with methanol, black particles were left behind. This was highly soluble in such solvents as dichloromethane and ethylene chloride. It was moderately soluble in alcohols, poorly soluble in ketones and virtually insoluble in CCl_4, hexane and aromatic solvents. When put in water the compound decomposed, yielding ferrocene and a blue solution indicating the presence of ferricinium ions.

Element analysis was performed after drying under 4 mm pressure at room temperature for a week. (Found: C, 55.13; H, 4.78; Br, 15.39; Fe, 20.18. $C_{24}H_{28}BrFe_2O$ calcd.: C, 55.00; H, 5.35; Br, 15.25; Fe, 21.35%.) Yield 0.5 g (5.5% of theory). DTA scans of the compound indicated a decomposition temperature of 217° with no melting point. The density of the sample, determined by flotation in a CBr_4/CCl_4 solution, was 2.18 g/cm^3 at room temperature.

Compound (I) seems to be stable in dry air for over half a year. When exposed to air humidity for two weeks it decomposed, yielding the crystalline ferrocene–tris-[ferricinium tetrabromoferrate(III) hydrate], compound (II) (see below), as detected by a changing X-ray pattern.

Preparation of $(FcH^+ FeBr_4^- \cdot H_2O)_3FcH$*, ferrocene–tris[ferricinium tetrabromoferrate(III) hydrate] (II)*

To 0.20 mole (37.2 g) of ferrocene in 250 ml CCl_4 was added 0.10 mole (8.0 g) of elemental bromine in 50 ml CCl_4. After 24 h the solution was evaporated under 15 mm pressure at room temperature to yield a relatively dry mixture of two components, one of which was ferrocene. To this mixture of solids, a solution of 200 ml absolute ethanol and 200 ml MEK was added to dissolve the solids completely. Upon partial evaporation, a crystalline precipitate of (II) was formed. Yield 12.1 g (75% of theory). This was recrystallized from boiling 1/1 ethylene dichloride/CCl_4. The resultant crystals are dark violet in color and have a metallic lustre. (Found C, 25.16; H, 2.08; Br, 50.46; Fe, 19.87. $C_{40}H_{46}Br_{12}Fe_7O_3$ calcd.: C, 24.95; H, 2.41; Br, 49.83; Fe, 20.30%.) DTA scans showed a narrow melting point at 187° which was reproduced on cooling and remelting, and a violent decomposition in air at 250°. (Ferrocene melts at 174°.) Pycnometric measurements in bromoform/cyclohexane yielded a density of 2.36 g/cm^3 at room temperature.

Compound (II) was tested with potassium ferrocyanide and ferricyanide and it was found that all the ionic iron was in the ferric state.

Another method to prepare compound (II) was to expose quantities of (I) in wide mouth flasks to the atmosphere for periods of about two weeks, after which the visual appearance, DTA scans and X-ray diffraction patterns of the samples became the same as those of (II) prepared in the aforementioned procedure. The amount of water needed for the hydration of the compound is relatively small and could be introduced either by absorption from air, as an azeotrope with the MEK or as an impurity in the other solvents employed. Once formed, the hydrated crystalline compound is stable in dry air for over a year.

When fine crystals of $(FcH^+FeBr_4^- \cdot H_2O)_3FcH$ were suspended in benzene under the microscope, they were observed to decompose slowly. When the benzene evaporated, two kinds of crystals were left behind: one was ferrocene and the other was possibly ferricinium tetrabromoferrate(III). The benzene seemed to extract the ferrocene from the complex and then deposit it when evaporated.

When 1.0 g of complex was dissolved in acidified water (pH = 4.0) ferrocene was precipitated out. The ferrocene was collected, dried and weighed: Yield 8.5%. The calculated amount of ferrocene in the complex is 9.6%. The precipitate was proved to be ferrocene by visible spectroscopy and by solution in acetonitrile and treatment with HNO_3 to form ferricinium ion.

Preparation of $FcH^+FeBr_4^-$, ferricinium tetrabromoferrate(III)

The preparation was according to Riemschneider and Helm[1], with quantitative yield. Recrystallization was from a hot 12/2/1 mixture of absolute ethanol/benzene/CCl_4: about 50% of the solids remained dissolved in the solvent system. The ferricinium tetrabromoferrate(III) crystallized in microcrystalline form with a drab khaki color. DTA scans showed only a decomposition temperature of 244° in the air, with no melting point. The density of the compound, determined by flotation in a CH_2I_2/CCl_4 mixture at room temperature, was 2.275 g/cm^3. (Found: C, 21.50; H, 1.75; Br, 55.53; Fe, 20.52. $C_{10}H_{10}Br_4Fe_2$ calcd: C, 21.40; H, 1.79; Br, 56.92; Fe, 19.89%.) Ferro- and ferricyanide tests showed the presence of only the ferric state in the ionic iron. Mohr method titration showed the presence of 56.7% bromide ions.

Characterization

DTA scans were run on a DuPont model 900 DTA unit, in air atmosphere. IR spectra were obtained with Beckman IR 8, IR 5A, CsBr IR 5A and Perkin–Elmer model 421 spectrometers. Samples were prepared as KBr or CsI pellets containing 1% by weight of the samples, as mulls in Nujol or as solutions in CS_2 and CCl_4. Since the solubilities in those two solvents were extremely poor, highly dilute solutions were used. Grinding compounds (I) and (II) with the alkali halides caused degradation of the samples. In all pelletized samples the ferricinium bands were broad and masked the ferrocene absorption. In solutions the large extinction of ferricinium and $FeBr_4^-$ masked the ferrocene absorption bands.

Visible and UV spectra were obtained with a Beckman DB-G double beam spectrometer using pyrex 1 cm cells with either water, acetonitrile or 1,2-dibromoethane as solvents, or using the pellets which had been made for IR determinations.

X-ray diffraction patterns were made with a General Electric X-ray diffractometer and a Picker, Debye–Scherrer type, 57.3 mm radius powder camera. The first instrument used copper target with nickel filter while the second used chromium radiation with a vanadium foil filter. Reflection intensities were determined from the diffractometer output traces using a planimeter.

A Reichert–Zetopan microscope was used for the optical microscopy and a Hitachi model 11-A microscope was used in electron microscopy.

Observation under monochromatic cross-polarized light showed that the $(FcH^+FeBr_4^- \cdot H_2O)_3FcH$ crystallized as parallelopiped shaped platelets. The acute and obtuse angles of the parallelogram are, respectively, 80° and 100°. Light was polarized by the crystals along their angle bisectors and not along the diagonals of the parallelograms. The color of the transmitted light was affected by the thickness of the crystals, changing from light green for thin crystals, through orange to deep red for thick crystals. This is probably the familiar dichroism observed in solutions of ferricinium ions.

When the ferricinium tetrabromoferrate(III) was observed under the optical microscope, it appeared as a glowing golden powder in transmitted light. No extinction was observed, as the crystals were too small to discern. In the electron microscope the material was stable. The crystals were observed to be hexagonal or truncated diamond platelets in shape. The average diameter of the crystals was about 700 to 800 Å and their average thickness about 150 to 200 Å. Virtually no crystals larger than 1000 Å were seen.

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