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ABSORPTION SPECTRUM OF FERRIC SULFATE COMPLEX

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Leonard I. Katzin and Elizabeth Gebert

In studies on the radiation oxidation of ferrous to ferric iron conducted in sulfuric acid solutions, the question has arisen as to the possible role of hydrolysis in influencing the chemical yields of irradiation.¹ Since the absorption spectrum and dissociation constant² of the FeOH^{++} complex are known, the possibility exists of spectrophotometric analysis of the proportion of the ferric iron in the complexed state.¹ Since sulfate is known to complex ferric iron also, it is necessary to show that this complex will not interfere.

Ferric iron in 2 N and 1 N perchloric acid solution shows the same absorption spectrum in the ultraviolet, characterized by an intense broad peak at about 245 millimicrons (absorption coefficient ca. 2500) falling off steadily towards lower wave lengths to an intensity of 0.1 the peak at 290 millimicrons and 0.01 at ca. 320 millimicrons. The solution in 0.1 N perchloric acid (0.9 N KClO_4 added) shows a very slight shift of the absorption. With progressive decrease of the acidity, an increase in absorption is noted at wave lengths above ca. 272 millimicrons, and a decrease at shorter wave lengths. A series of such curves is shown in Figure 1. The absorption found at acid concentrations of 0.001-.002 N shows a minimum at about 250 millimicrons (extinction ca. 840) and a broad peak at about 295 millimicrons (extinction ca. 1375). This is the spectrum taken to be that of FeOH^{++} .

With solutions 2 normal in acid and composed of various ratios of sulfuric and perchloric acids an absorption centered at about 303 millimicrons appears which increases with increasing sulfuric acid concentration (Figure 2). The absorption peak is even broader than that for the FeOH^{++} complex, but there is a smaller absorption decrease below about 268 millimicrons (the point of constant absorption) than for the FeOH^{++} - Fe^{+++} pair. This is clearly an absorption due to a sulfate complex of the iron. Whether it is to be formulated as FeSO_4^+ or FeHSO_4^{++} cannot be decided from the data at hand. The peak extinction coefficient found is about 1600. The minimum, at about 275 millimicrons, is about 1275.

The chloride complex may also be obtained by making a solution 1 N each in HCl and HClO_4 . The spectrum of this complex is grossly similar to the preceding two, but its maximum is somewhat sharper and

¹E. J. Hart, personal communication.

²A. R. Olson and T. R. Simonson, Jour. Chem. Phys. 17: 1322-5 (1949).

comes at about 335 millimicrons with a minimum at 285 millimicrons (Figure 3). The absorption at lower wave lengths resembles that of Fe^{+++} and the sulfate complex rather than that of FeOH^{++} . It did not prove practical to demonstrate the nitrate complex since the nitrate ion itself absorbs at 300 millimicrons with a spectral structure very like that of the FeOH^{++} and sulfate complexes.

If one takes a sulfuric acid solution of ferric iron and progressively dilutes the acid, the absorption changes slowly from that characteristic for the sulfate complex to that for the hydroxy complex. This is most evident in the region of 260 millimicrons, where the absorption minimum of the hydroxy complex falls. The wave length shift of the peak around 300 millimicrons is also detectable, as is the intensity change in going from the more absorbing sulfate complex to the hydroxy complex. It would seem therefore that the latter is a stronger complex in the region of pH 3. If the sulfate complex is in reality a bisulfate complex, one can see that the pH increase, by shifting the ionization equilibrium of the bisulfate, would assist in increasing the apparent relative stability of the hydroxy complex at lower acidities.

Since the above observations were made, a summary of absorption spectra of ferric salts in a number of acids has been found,³ in which the spectra for perchloric, sulfuric, and hydrochloric acid solution given agree with our data.

The conclusion to be drawn from these findings is that under the conditions of the usual irradiation experiments in sulfuric acid¹ the hydroxy complex seems to dominate the sulfate complex. However, exact distribution of the ferric iron between Fe^{+++} and the two complexes cannot be reliably derived from simple spectrophotometric measurements inasmuch as the spectra for the two complexes are not sufficiently distinct.

Addendum: Some indication was seen that in the presence of sulfate the slow reaction leading to colloidal ferric hydroxide was accelerated over the rate in perchloric acid alone. Presumably a charge effect of the anion, frequently observed with coagulation processes, is involved. *2/end.*

³ A. v. Kiss, J. Abraham, and I. Hegedus, Zeitschr. anorg. allg. Chem. 244: 98-110 (1940).