way. Such a hypothesis seems quite implausible physically, and the data thus offer a strong presumption in favor of the OH radical theory.

At the lowest concentration, more than half the benzoic acid present must have been consumed during the longest exposure. The fact that the rate of Fe^{+2} production does not decline under these conditions, but rather appears to increase, indicates that the reaction products (hydroxybenzoic acids) are also reactive toward OH radicals.

Experimental

G. Frederick Smith Chemical Co. ferric and ferrous perchlorate were used. Other reagents were reagent grade chemicals.

The light source was a G.E. AH-4 lamp (rich in 365 mμ light) run from a Sola transformer. The irradiations were made in a cylindrical optical silica cell 2 cm. thick, 2 cm. diameter, reproducibly positioned about 7 cm. from the lamp. The temperature was about 23° (room temperature).

Solutions contained 0.02 *M* $HClO_4$, 0.01 *M* ferric perchlorate, and 1, 2, 5, or 10 $\times$ 10^{-4} *M* each of ferrous perchlorate and benzoic acid. They were deaerated before irradiation by bubbling prepurified nitrogen through the cell. Irradiation times were 100, 200, 300 and 400 sec. Solutions and irradiation times were picked in random order to eliminate any possible effect of light source drift.

Analyses for Fe^{+2} were performed in duplicate on 3-ml. aliquots using *o*-phenanthroline (9 ml. of saturated aqueous solution) and NaF (0.6 ml. of 1 *M*), making up to 25 ml. with water, and measuring the light absorption at 508 mμ in 1 cm. cells with a Beckmann DU spectrophotometer.

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Iron(II)–Iron(III) Complex Exchange Reactions

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Ruben, Kamen, Allen and Nahinsky[1] have shown that the iron of the tris-(2,2′-dipyridyl)-iron(II) and the tris-(1,10-phenanthroline)-iron(II) is rapidly exchangeable with the iron(II) ion. In contrast to this observation magnetic data on these complexes indicates that they are chiefly covalently bonded.[2]

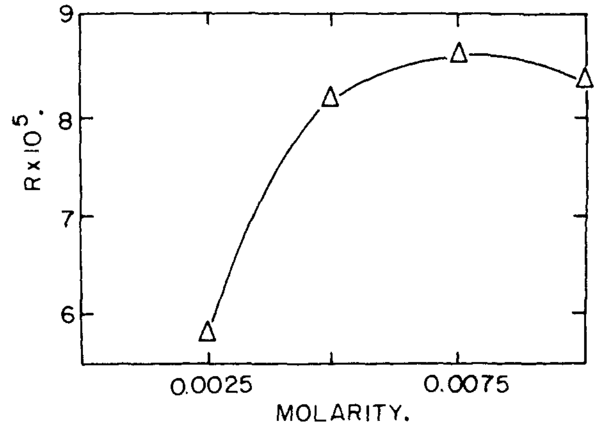

Fig. 1.—Reaction rate *versus* concentration of tris-(1,10-phenanthroline)-iron(II) chloride at 30° and 0.005 *M* (H+).

Iron-55, a radionuclide of 2.5 years half-life emitting X-rays, and obtained through the Atomic Energy Commission, was used to prepare 0.02 *M* solutions of the complexes according to the method of Blau.[3] Equal volumes of the tagged complex and 0.02 *M* iron(II) chloride solution were mixed. At suitable intervals one-ml. samples were removed and the iron(II) precipitated with ammonium hydroxide, centrifuged at 7100 g. thrust and the precipitate dissolved in nitric acid. The solution was transferred to stainless steel counting cups, dried thoroughly and the radioactivity determined with a proportional counter.

Reaction rates at different temperatures were found by using the equation

$$R = \frac{2.303ab}{(a + b)} \log \frac{(E)}{(E - X)}$$

where a and b are the concentrations of the reacting substances, E is the equilibrium activity and X is the difference between the radioactivity at zero time and at time t. The logarithm of 100 minus the percentage exchange was plotted *versus* time. These plots for different temperatures were straight lines. The plot of the log of the reaction rate *versus* the reciprocal of temperature gave straight lines from which the activation energies were determined. The activation energy for the 1,10-phenanthroline complex exchange was determined to be 19.4 ± 0.8 kcal. per mole and that for the 2,2′-dipyridyl complex was 14.9 ± 0.5 kcal. per mole.

The reaction rate increased directly with the hydrogen ion concentration. The rate of increase was greater for the 2,2′-dipyridyl complex than for the 1,10-phenanthroline complex. With constant hydrogen ion concentration (0.005 *M*) and temperature (30°) a variation in the concentration of the tris-(1,10-phenanthroline)-iron(II) ion changed the reaction rate as indicated in Fig. 1. Baxendale and George[4] have shown that in hydrochloric acid solutions the rate of dissociating the tris-(2,2′-dipyridyl)-iron(II) ion increases as the hydrogen ion concentration increases. This observation would account for the results shown in Fig. 1.

Both complexes have been successfully resolved into optical isomers, and it is believed that the rates of racemization are quite rapid.[5,6] This suggests that the racemization process may be brought about by dissociation of the complex, since the exchange rates seem to be of a magnitude comparable to the racemization rates.

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