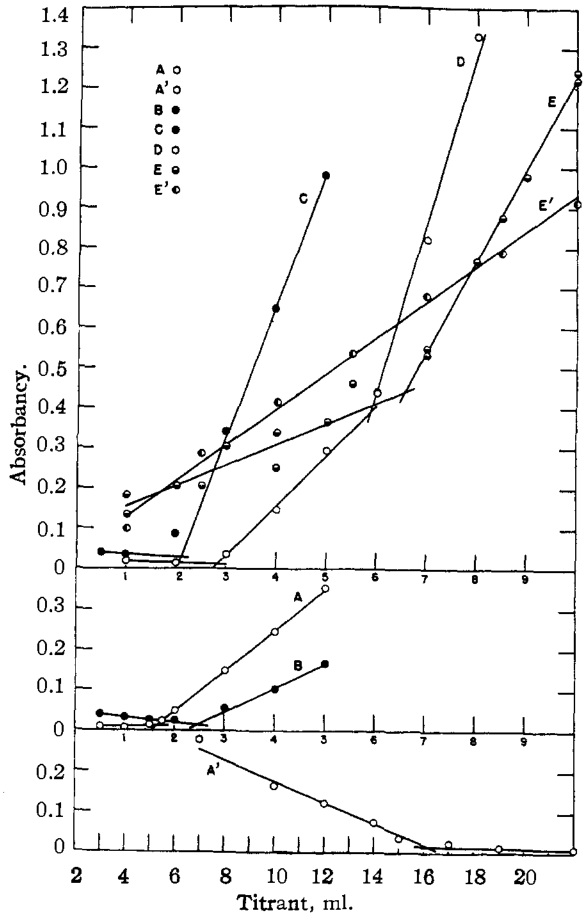

Fig. 1.—Spectrometric titration curves of thorium ion with various sulfonic acid dyes, and Amaranth dye with thorium ion. The reaction mixtures were brought up to the indicated volumes with distilled water before filtering: (A) five ml. of 0.0001 *F* thorium nitrate solution titrated with 0.0001 *F* Amaranth solution; total volume 20.0 ml.; (A′) five ml. of 0.0001 *F* Amaranth solution titrated with 0.0001 *F* thorium nitrate solution; total volume 25.0 ml.; (B) five ml. of 0.0001 *F* thorium nitrate solution titrated with 0.0001 *F* Acid Alizarin Red B solution; total volume 10.0 ml.; (C) five ml. of 0.0005 *F* thorium nitrate solution titrated with 0.0005 *F* Alizarin Cyanine Green G solution; total volume 10.0 ml.; (D) five ml. of 0.001 *F* thorium nitrate solution titrated with 0.001 *F* sodium indigo disulfonate solution; total volume 15.0 ml.; (E) five ml. of 0.001 *F* thorium nitrate solution titrated with 0.001 *F* Orange II solution; total volume 15.0 ml.; (E′) five ml. of 0.0001 *F* thorium nitrate solution titrated with 0.0001 *F* Orange II solution; total volume 15.0 ml.

the equivalence points can both be extrapolated back to the abscissa to indicate the 5:5 ratio for the thorium–Orange II compound and the second thorium–Indigo Disulfonate compound, if both compounds were highly insoluble.

The five insoluble thorium–dye compounds supported on cellulose all underwent ion exchange with 10 p.p.m. fluoride ion solution to release dye into the solution. Those formed by procedure (I) showed little or no bleeding in distilled water, while those formed by procedure (II) were spotty in appearance and tended to bleed considerably. Orange II showed the greatest tendency to bleed and bled an equal amount regardless of the method of preparation.

Discussion

The data appear to indicate that thorium ion reacts in neutral to slightly acid solution with dyes to form insoluble compounds only through sulfonate ion groups. The maximum number of thorium ions reacting with a dye molecule is equal to the number of sulfonate ion groups per dye molecule. Apparently both the 1:1 and the 2:1 compounds are formed under the conditions of the titration of thorium ion with Sodium Indigo Disulfonate, where both solutions are 0.001 *F*, with the 2:1 compound being the less soluble. Thorium ion in dilute aqueous solution under approximately neutral conditions binds strongly to cellulose, possibly through hydrogen bonding or a condensation reaction with hydroxy groups on the cellulose. It would be expected to have a reduced positive charge due to substitution of hydroxide ions for coördinated water molecules in the hydrated ion, and might well act as a monovalent cation in forming salt-like compounds of the general type

$$\text{Cellulose–O–Th(OH}_2)^{+}_{n}\,{}^{-}\text{O}_3\text{S–Ar(Dye)}$$

The proposed chelate ring structure[1] is not substantiated. The speed of fluoride ion-dye exchange, and the similarity of color of the free dye and the corresponding insoluble thorium compound indicate that the thorium–dye bond is predominantly ionic in nature.

The greater solubility of the thorium–dye compounds formed by procedure II is probably due to the solubilizing effect of sulfonate ion groups which have not reacted with thorium–cellulose. When formed by procedure I, with an excess of thorium ion present, all sulfonate ion groups presumably react with thorium–cellulose and the compound is much less soluble. Thorium–Orange II compound shows the same solubility when made by either I or II, as only one compound would be predicted with its lone sulfonate ion group.

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DEPARTMENT OF CHEMISTRY
KANSAS STATE COLLEGE
MANHATTAN, KANSAS

Photoinitiated Oxidation of Benzoic Acid by Ferric Ions in Aqueous Solution[1]

BY JEROME SALDICK AND AUGUSTINE O. ALLEN

RECEIVED AUGUST 12, 1954

Evans and co-workers[2–4] have proposed that the photochemical action of $Fe(OH)^{+2}$ ions on organic substrates proceeds *via* free OH radicals in solution.

Bates and Uri[4] studied the photosensitized oxida-

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] M. G. Evans and N. Uri, *Nature*, **164**, 404 (1949).

[3] M. G. Evans, M. Santappa and N. Uri, *J. Polymer Sci.*, **7**, 243 (1951).

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tion of benzoic acid by ferric ions. They proposed the following mechanism (A), which involves the formation of free OH radicals which then attack the organic substrate.

1. Light absorption

$$Fe^{+3}OH^- \xrightarrow[k_e]{h\nu} Fe^{+2}OH$$

2. Primary dark back reaction

$$Fe^{+2}OH \xrightarrow{k_d} Fe^{+3}OH^-$$

3. Dissociation of excited complex

$$Fe^{+2}OH \xrightarrow{k_s} Fe^{+2} + OH$$

4. Secondary dark back reaction

$$Fe^{+2} + OH \xrightarrow{k_0} Fe^{+3} + OH^-$$

5. Free radical attack on the substrate

$$RH + OH \xrightarrow{k_1} R\cdot + H_2O$$

6. Oxidation of organic free radical by ferric ion

$$R\cdot + Fe^{+3}OH^- \xrightarrow{k_t} ROH + Fe^{+2}$$

This mechanism leads to the following equation for the rate of ferrous ion formation

$$\phi_{Fe^{+2}} = \frac{dFe^{+2}}{dt}\Big/ k_e I = \frac{k_s}{k_d + k_s}\,\frac{2}{\dfrac{k_0}{k_1}\dfrac{(Fe^{+2})}{(RH)} + 1} \qquad (1)$$

They found experimentally that $1/\phi_{Fe^{+2}}$ increased linearly with ferrous ion concentration at constant (RH), in agreement with this equation.

Another mechanism (B) can be formulated, which does not involve free OH radicals in solution, but postulates direct reaction between the organic substrate and a long-lived photo-excited ferric ion.

1. Light absorption

$$Fe^{+3}OH^- \xrightarrow[k_e]{h\nu} Fe^{+2}OH$$

2. Primary dark back reaction

$$Fe^{+2}OH \xrightarrow{k_d} Fe^{+3}OH^-$$

3. Secondary dark back reaction

$$Fe^{+2}OH + Fe^{+2} \xrightarrow{k_b} Fe^{+3}OH^- + Fe^{+2}$$

4. Forward reaction

$$RH + Fe^{+2}OH \xrightarrow{k_f} R\cdot + Fe^{+2} + H_2O$$

5. Oxidation of organic free radical by ferric ion

$$R\cdot + Fe^{+3}OH^- \xrightarrow{k_t} ROH + Fe^{+2}$$

Mechanism B leads to equation (2)

$$\phi_{Fe^{+2}} = \frac{dFe^{+2}}{dt}\Big/ k_e I = \frac{2}{\dfrac{k_b}{k_f}\dfrac{(Fe^{+2})}{(RH)} + \dfrac{k_d}{k_f(RH)} + 1} \qquad (2)$$

which can also be fitted to the experimentally determined relationship. Hence further evidence was required to rule out the possibility of direct reaction between the photo-excited ferric species and the benzoic acid.

Equation 2 predicts a dependence of yield on (RH), at constant $(Fe^{+2})/(RH)$. Estimates of k_d/k_f and k_b/k_f may be made from the data of Bates and Uri on benzoic acid, assuming that equation 2 is valid. From their Fig. 1, and statement that $\phi_{Fe^{+2}} \cong 5\phi_{\text{salicylic acid}}$, $1/\phi_{(Fe^{+2})} \cong 18 + 10800\,(Fe^{+2})$. Since $(RH) = 10^{-3}$, $k_d/k_f \cong 0.035$ and $k_b/k_f \cong 21.6$. When $(Fe^{+2})/(RH) = 1$, $\phi_{Fe^{+2}} \cong 2/[22.6 + 0.035/(RH)]$. Then, at equal benzoic acid and Fe^{+2} concentrations of 10^{-4}, 2×10^{-4}, 5×10^{-4} and 10^{-3} *M*, the yields of Fe^{+2} under otherwise identical conditions should be in the respective proportions 1:1.61:3.42:6.45.

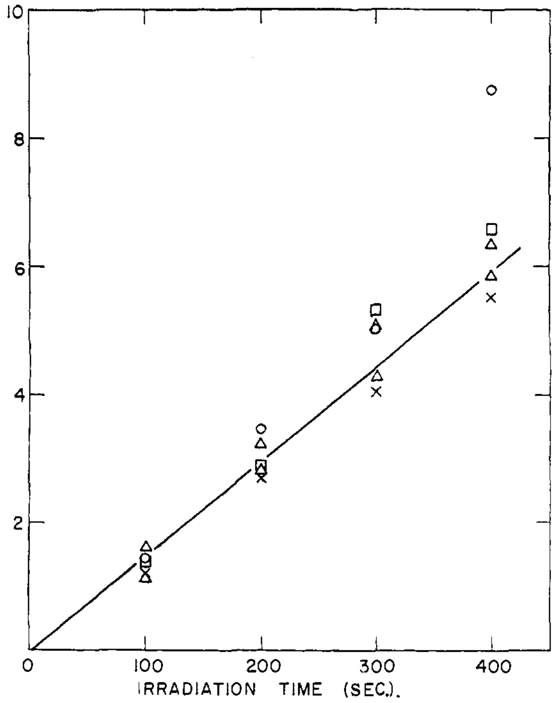

Fig. 1.—Photochemical reduction of ferric ion: initial benzoic acid (= initial Fe^{+2}) 10^{-4} *M* ○; 2×10^{-4} *M* □; 5×10^{-4} *M* △; 10^{-3} *M* ×.

Experiments were performed to test this point. The results (Fig. 1) show that the benzoic acid concentration had no effect on the reaction rate at a given ratio of $(Fe^{+2})/(RH)$. The graph shows total iron reduced as a function of time, so that the yield is proportional to the slope of the curve traced by the experimental points.

The present data are thus in agreement with the free radical mechanism A, and in disagreement with the alternative hypothesis of reaction of the photo-activated complex with the organic substrate (mechanism B). Taken together with the work of Bates and Uri,[4] the data indicate the existence of an active intermediate which can react with either Fe^{+2} or the organic compound, and serve to rule out any mechanism in which this intermediate disappears by reaction with itself or by unimolecular deactivation. The only non-radical mechanism consistent with these conditions and with the low observed quantum yields would seem to be one in which a constant small fraction of the absorbed quanta leads to an excited state of $Fe(OH)^{+2}$, having such a long lifetime that it always reacts with 10^{-4} *M* solutes before being deactivated in any other 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 10×10^{-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.

DEPARTMENT OF CHEMISTRY
BROOKHAVEN NATIONAL LABORATORY
UPTON, N. Y.

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

BY IRA B. WHITNEY, GEO. K. SCHWEITZER AND C. L. COMAR

RECEIVED MAY 7, 1954

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]

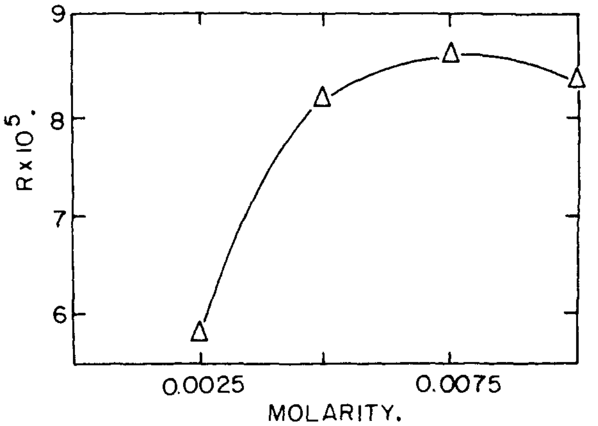

Fig. 1.—Reaction rate *versus* concentration of tris-(1,10-phenanthroline)-iron(II) chloride at 30° and 0.005 *M* (H+).

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.

UNIVERSITY OF TENNESSEE
KNOXVILLE, TENNESSEE, AND
ATOMIC ENERGY COMMISSION AGRICULTURAL
RESEARCH PROGRAM
OAK RIDGE, TENNESSEE

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