X-Ray diffraction was used to determine the unit cell dimensions of sodium tetrametaphosphate. Single crystal precession pictures taken with Cu Kα radiation yielded the following monoclinic cell dimensions: $a = 9.65 \pm 0.04$ Å., $b = 12.32 \pm 0.04$ Å., $c = 6.17 \pm 0.04$ Å., $\beta = 92°30' \pm 10'$. The systematic absences are $h0l$ with h odd and $0k0$ with k odd; they determine uniquely the space group $P_{2_1/a}$. The density is 2.18 ± 0.01 g./cm.^{3} found by the pycnometric method using toluene. Assuming the unit cell contains $2(Na_4P_4O_{12}\cdot 4H_2O)$, the calculated density is 2.173 ± 0.006 g./cm.^{3}. These data are in agreement with those of Andress, *et al.*[15]

Since the unit cell contains 8 PO_3 groups, the trimetaphosphate is ruled out. Dimetaphosphate is impossible because of the predicted low stability of such a compound. X-Ray powder pictures of $Na_2HPO_4\cdot 12H_2O$, NaH_2PO_4, Na_3PO_4 and $Na_4P_2O_7$ were compared with powder pictures of the $Na_4P_4O_{12}\cdot 4H_2O$. There was no indication of any of these compounds as impurities in the sodium tetrametaphosphate.

As a final test for the absence of pyro- and tripolyphosphate an enzymatic method was employed. Rat kidney contains an enzyme or enzymes which hydrolyze lower polyphosphates to orthophosphate at *p*H 8 and 36°. Sodium tetrametaphosphate was incubated for 2 hours with rat kidney extract prepared from freshly killed Wistar rats. The orthophosphate liberated was determined by the molybdenum blue method of Lowry and Lopez.[16] Less than 0.2% of the phosphorus was hydrolyzed to orthophosphate. That the metaphosphate was not acting as an inhibitor to the enzymatic reaction was shown by determining the extent of hydrolysis of added pyrophosphate in the presence of metaphosphate.

The titration curves and enzymatic analysis establish the absence of hydrolysis products or polyphosphates in the sample. The fact that the ion-exchange column effects a complete separation of the tri- and tetrametaphosphates proves the absence of trimetaphosphate in the final product and strongly indicates that other metaphosphates would be absent. The solubility indicates that indeed only one material is present and the X-ray work establishes the product as sodium tetrametaphosphate.

Acknowledgments.—We are indebted to Professor J. D. H. Donnay and Dr. Gabrielle Donnay for supervision of the X-ray work. Mr. Robert J. Gross performed the solubility experiments. In addition, Mr. Gross and Miss Ella Ball were of considerable assistance in all phases of the work. One of us (D. L. B.) was the recipient of a du Pont Fellowship for the academic year 1952–1953, and of a grant-in-aid from the Hynson–Westcott and Dunning Fund for the academic year 1951–1952.

(15) K. R. Andress, W. Gehring and K. Fischer, *Z. anorg. Chem.*, **260**, 331 (1949).

(16) O. H. Lowry and J. A. Lopez, *J. Biol. Chem.*, **162**, 421 (1946).

[CONTRIBUTION NO. 373 FROM THE INSTITUTE FOR ATOMIC RESEARCH, DEPARTMENT OF CHEMISTRY, AND VETERINARY MEDICAL RESEARCH INSTITUTE, IOWA STATE COLLEGE]

Kinetics of the Reduction of Ferric Ion by Hydroquinone in the Presence of 1,10-Phenanthroline[1]

BY FREDERICK R. DUKE AND FRANK R. PARCHEN

RECEIVED JANUARY 8, 1955

The reduction of ferric ion by hydroquinone in the presence of 1,10-phenanthroline is found to proceed by direct complexing of the hydroquinone by the ferric ion in competition with the 1,10-phenanthroline. This mechanism is in contrast to that generally believed to be operative when the iron–1,10-phenanthroline complex acts as indicator, there being no displacement of 1,10-phenanthroline in the latter process.

Hydroquinone is often used as the reducing agent in the colorimetric determination of iron with 1,10-phenanthroline and in some procedures is added simultaneously or immediately preceding the addition of 1,10-phenanthroline to a ferric solution. This kinetic study was undertaken for the purpose of determining the effect, if any, that the presence of 1,10-phenanthroline might have on the rate of reduction of ferric ion by hydroquinone.

When the ferrous or ferric 1,10-phenanthroline complex is used as an indicator, no loss of 1,10-phenanthroline occurs from the complex. In the oxidation or reduction of the indicator, the electrons apparently are transferred in and out of the complex molecule to the oxidant or reductant through a 1,10-phenanthroline bridge. With a substance like hydroquinone, another possible mechanism involves displacement by a hydroquinone molecule of a 1,10-phenanthroline molecule as

$$FePh_n^{+++} + Ph \rightleftharpoons FePh_{n-1}^{+++} \quad (1)$$

$$FePh_n^{+++} + QH_2 \rightleftharpoons (Fe_{n-1}QH_2)^{+++} + Ph \quad (2)$$

and the hydroquinone complex may subsequently react to give the desired products. Equation 2 is written as an equilibrium displacement reaction because this provides a very plausible reason for the inverse order in 1,10-phenanthroline, and it fits in with the theory, substantiated in other reactions[2] in which such complexes are intermediates; the concentrations are, however, too low for the complex containing hydroquinone to be kinetically detectable. The integer, n, is probably two or three.[3] The kinetics for this mechanism would be expressed by the equation

$$\frac{-d[A]}{dt} = \left[\frac{k_1K_1K_2[QH_2]}{1 + K_1[Ph]}\right][A] \quad (3)$$

(1) Work was performed in part in the Ames Laboratory of the Atomic Energy Commission.

(2) F. R. Duke and R. F. Bremer, THIS JOURNAL, **73**, 5179 (1951) and the references in footnote 2, this reference.

(3) A. Gaines, Jr., L. P. Hammett and G. H. Walden, Jr., *ibid.*, **58**, 1668 (1936).

where [A] is total ferric ion (the assumption made that the concentration of the ferric complex involving hydroquinone is relatively small), $[QH_2]$ and [Ph] are the uncomplexed concentrations of hydroquinone and 1,10-phenanthroline, respectively; k_1, the specific rate constant for the reaction of the ferric–hydroquinone complex; and K_1 and K_2, the equilibrium constants for reactions (1) and (2). Equation 3 may be subjected to experimental verification by determining the rate of disappearance of ferric ion when the hydroquinone and 1,10-phenanthroline concentrations are varied independently. By experimental design a series of first-order and second-order (in total ferric ion) pseudo rate constants may be obtained. The first-order pseudo rate constant k' is identified with the bracketed portion of equation 3 with the 1,10-phenanthroline and hydroquinone concentrations high enough to remain essentially constant. The second-order pseudo rate constant is

$$k'' = \frac{k_1K_2K_1}{1 + K_1[\mathrm{Ph}]} \qquad (4)$$

with the hydroquinone concentration held constant and stoichiometrically equal to the ferric ion concentration.

Experimental

Chemically pure reagents were used. The experiments were carried out at the temperature of 25 ± 0.1°. A spectrophotometer cuvette was used as the reaction vessel. In all experiments the ferric solution to give the desired final concentration was placed in the cuvette. The hydroquinone and 1,10-phenanthroline solutions to give the desired final concentrations were mixed and placed in a flask. All solutions were placed in the constant temperature bath. The hydroquinone and 1,10-phenanthroline solution was then added to the cuvette and the timer started during mixing. The cuvette was placed immediately in the spectrophotometer, a "cold finger" for circulating constant-temperature water was inserted, and readings were made from 15 seconds after mixing until the reaction had gone to completion.

Results and Discussion

First-order pseudo constants obtained with various concentrations of hydroquinone taken from the slope of plots of log [A] *vs.* t are recorded in Table I.

TABLE I

FIRST-ORDER PSEUDO-RATE CONSTANTS

$[Fe^{+++}] = 4.50 \times 10^{-5}\ M$, $[Ph] = 2.69 \times 10^{-4}\ M$

$[QH_2] \times 10^5$, mole/l.	$k' \times 10^2$, sec.$^{-1}$	$k'/[QH_2] \times 10^{-2}$ mole^{-1} l. sec.$^{-1}$
3.36	0.898	2.67
4.48	1.23	2.75
6.72	1.65	2.46
8.96	2.20	2.45
11.20	2.36	2.11

Second-order pseudo constants obtained with various concentrations of 1,10-phenanthroline taken from the slope of plots of $1/[A]$ *vs.* t are recorded in Table II. Also included in this table is $1/k''$ and reference to equation 4 shows that a plot of $1/k''$ *vs.* [Ph] should be a straight line. Figure 1 shows a plot of $1/k''$ *vs.* [Ph]. The value of the uncoördinated 1,10-phenanthroline concentration has been approximated by subtracting from the initial 1,10-phenanthroline concentration, in the first case, two and, in the second case, three times the total ferric ion concentration.

TABLE II

SECOND-ORDER PSEUDO RATE CONSTANTS

$[Fe^{+++}] = 4.50 \times 10^{-5}\ M$, $[QH_2] = 2.24 \times 10^{-5}\ M$.

[Ph] $\times 10^4$, mole/l.	$k'' \times 10^{-2}$ mole^{-1} l. sec.$^{-1}$	$1/k''$ $\times 10^3$ mole l.$^{-1}$ sec.	[Ph] $\times 10^4$, mole/l.	$k'' \times 10^{-2}$ mole^{-1} l. sec.$^{-1}$	$1/k''$ $\times 10^3$ mole l.$^{-1}$ sec.
1.34	8.80	1.14	3.59	2.24	4.46
1.79	7.00	1.43	4.03	1.94	5.15
2.24	4.86	2.06	4.47	1.82	5.50
2.69	3.90	2.56	4.93	1.67	5.99
3.14	2.74	3.55	5.38	1.52	6.58
3.22	2.58	3.88			

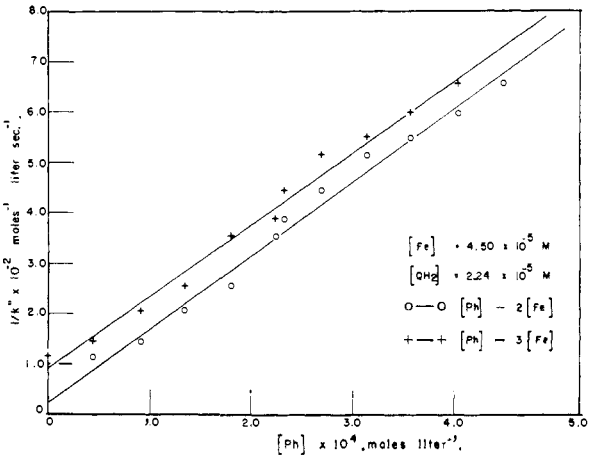

Fig. 1.—Plot of equation 3 in reciprocal linear form, where $k'' = k_1K_2K_1/(1 + K_1[\mathrm{Ph}])$.

If the reduction of the ferric–1,10-phenanthroline complex occurs by the mechanism involving the 1,10-phenanthroline bridge the rate of reduction should become constant at relatively high 1,10-phenanthroline concentration. However, the rate of reduction decreased as the 1,10-phenanthroline concentration was varied over a range of three to twelve times the ferric ion concentration. This is compatible with equation 3 and with the intermediate coördination complex mechanism.

The lack of agreement between $k'/[QH_2]$ from Table I and the corresponding k'' in Table II probably stems from two sources: (1) the experimental error, since it is apparent that the common point from Table II falls below the line as a reciprocal, and (2) any complexing of hydroquinone by ferric ion would tend to lower the first-order pseudo constants, these being taken at higher hydroquinone concentration than the second order constants.