CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
OKLAHOMA STATE UNIVERSITY, STILLWATER, OKLAHOMA

Reaction of Oxygen with Cobalt(II) and Cysteine

BY B. J. McCORMICK[1] AND GEORGE GORIN[2]

Received January 15, 1962

The course of the reaction between aqueous cobalt(II)–cysteine mixtures and oxygen depends on pH, concentration, and cysteine/cobalt ratio. The oxidation has been studied at pH 11.0, 7.8, and 5.8 with 10^{-2} *M* cobalt. With excess cysteine at pH 11.0, the main reaction with oxygen is the conversion of purple triscysteinatocobaltate(II) to green triscysteinatocobaltate(III). At pH 7.8 brown biscysteinatocobaltate(III) is formed, presumably from green biscysteinatocobaltate(II). At pH 5.8 a large amount of cystine is produced and a mechanism involving cobalt as a catalyst is suggested for this reaction.

The reaction of cobalt(II), cysteine [$HSCH_2CH(NH_2)COOH$], and oxygen, as well as the resulting complexes, have been studied by several workers.[3-10] A major point of interest is the possible similarity between this reaction and those involved in the reduction of oxygen by living organisms.

The earlier investigations do not agree in all respects and they leave many questions still unexplored. Michaelis and others[3,4] first observed that mixtures of cobalt(II) and cysteine reacted at pH 7.5–8.5 with oxygen to give a brown product, the amount of which apparently increased with cysteine/cobalt ratio up to a value of about 3. With excess cysteine (written as HScyH or H_2Scy) 1 atom of oxygen was consumed per cobalt ion, and with excess cobalt (*i.e.*, at ratios less than 3) $^1/_3$ atom of oxygen was consumed per molecule of cysteine. On this basis,[5] it was proposed that the brown product was a cobaltous cysteine–cystine complex formed according to the equation [$SCH_2CH(NH_2)COO^{-2}$ = Scy]

$$2Co^{+2} + 6HScyH + O_2 \longrightarrow 2[Co(Scy)(cyS\text{-}Scy)]^{-2} + 2H_2O + 8H^{+1} \quad (1)$$

where cyS-Scy is cystine. This formulation of the brown product is controverted by all subsequent evidence, and is untenable in the light of present knowledge.

Kendall and Holst[6] confirmed these experimental results but found that some free cystine was formed in addition to the brown complex. Furthermore, the brown product was formulated as $[Co(Scy)_2]^{-1}$ and this oxidation scheme was proposed

$$3[Co(Scy)_2]^{-2} + \text{oxidant} \longrightarrow 2[Co(Scy)_3]^{-3} + Co^{+2} \quad (2a)$$

$$[Co(Scy)_3]^{-3} \longrightarrow [Co(Scy)_2]^{-1} + (Scy)^{-2} \quad (2b)$$

$$2(Scy)^{-2} + \text{oxidant} \longrightarrow [cyS\text{-}Scy]^{-2} \quad (2c)$$

$$2(Scy)^{-2} + Co^{+2} \longrightarrow [Co(Scy)_2]^{-2} \quad (2d)$$

The relative importance of reactions 2c and 2d depended on the oxidizing agent and the conditions. For example, with indigo disulfonate, no cystine and the maximum amount of brown complex were formed, whereas with oxygen, some of both products were obtained. These equations represent the concurrent over-all reactions

$$4[Co(Scy)_2]^{-2} + O_2 + 2H_2O \longrightarrow 4[Co(Scy)_2]^{-1} + 4OH^{-1} \quad (3)$$

$$4HScyH + O_2 \longrightarrow 2HcyS\text{-}ScyH + 2H_2O \quad (4)$$

The formulation of the brown complex was confirmed by Schubert,[7,8] who isolated a brown complex of empirical formula $H[Co(Scy)_2]\cdot 4.5H_2O$ by acidifying the solution obtained from cobalt, cysteine, and oxygen at pH 8.0. This investigator also was able to obtain green $[Co(Scy)_3]^{-3}$ but found that this complex was stable only at high pH. Schubert did not believe that Kendall and Holst's mechanism was correct,[9] and suggested that brown $[Co(Scy)_2]^{-1}$ was formed from the corresponding cobaltous complex, $[Co(Scy)_2]^{-2}$. It should be noted that Schubert's experiments were conducted at a much higher concentration than the earlier investigations.

Neville[10] was able to show that, in the condi-

(1) National Science Foundation Coöperative Fellow, 1960–1962.
(2) To whom inquiries should be addressed.
(3) L. Michaelis and E. S. G. Barron, *J. Biol. Chem.*, **83**, 191 (1929).
(4) L. Michaelis and S. Yamaguchi, *ibid.*, **83**, 367 (1929).
(5) L. Michaelis, *ibid.*, **84**, 777 (1929).
(6) E. C. Kendall and J. E. Holst, *ibid.*, **91**, 435 (1931).
(7) M. P. Schubert, *J. Am. Chem. Soc.*, **53**, 3851 (1931).
(8) M. P. Schubert, *ibid.*, **55**, 3336 (1933).
(9) M. P. Schubert, *ibid.*, **54**, 4077 (1932).
(10) R. G. Neville, *ibid.*, **78**, 5511 (1956).

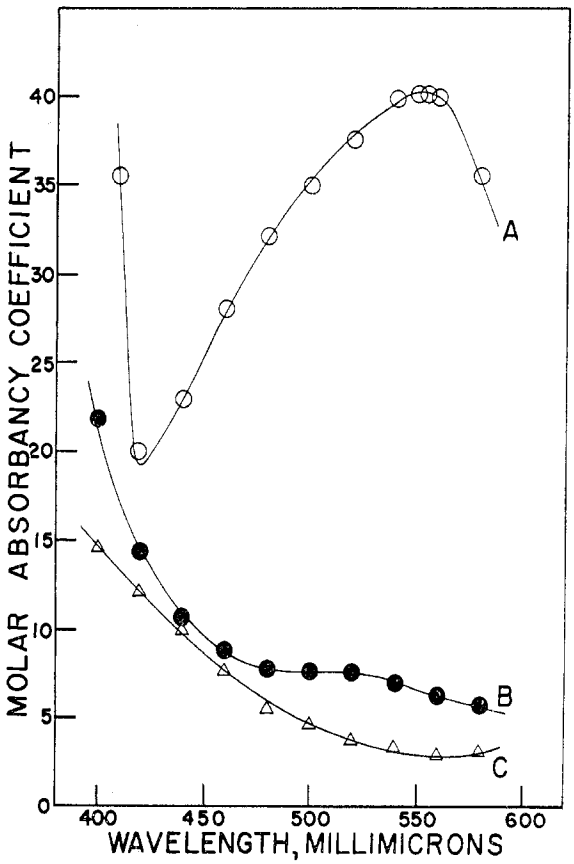

Fig. 1.—Spectra of cobaltous complexes at cysteine/cobalt ratio of 4: A, pH 11; B, pH 7.8; C, pH 5.8.

tions employed by Schubert, the amount of oxygen absorbed was 0.5 atom per cobalt ion, and that the same stoichiometry also applied at pH 7.8 and lower concentrations (*ca.* 0.015–0.01 *M* cobalt) for cysteine/cobalt ratios up to 3; at higher ratios, more oxygen was consumed.

Since, as we shall show, cobalt(II)–cysteine complexes are involved in the reaction with oxygen, brief reference should be made to what is known about them. Schubert[7,8] was able to prepare and isolate three complexes, containing one, two, and three molecules of cysteine per ion of cobalt(II). Albert[11] investigated the formation of complexes by the pH titration method of Bjerrum and calculated values of $10^{8.8}$ and $10^{16.2}$ for the stability constants of the 1:1 and 2:1 complexes, respectively. Neville[12] measured the spectrum of the 2:1 complex and deduced from the similarity between it and the corresponding complex of 2-aminoethanethiol that N,S-coördination was involved in both cases.

In this investigation the reaction was studied at pH 5.8, 8.0, and 11.0, and the results indicate that the products and mechanism of the reaction depend critically on the pH. The results can be explained by the occurrence of two concurrent reactions. The oxidation mechanism proposed by Kendall and Holst appears to be applicable in part at pH 11.0 but not over the entire pH range investigated.

Results

Cobalt(II) ion at 0.01 *M* concentration and excess cysteine mixed at pH 11 in the strict absence of oxygen formed a deep purple-violet complex, and the intensity of color was not appreciably decreased as the cysteine/cobalt ratio was reduced to 3. The complex presumably is the same as the 3:1 complex isolated in solid form by Schubert.[8] The "delicate pink" color observed by Michaelis and Barron on mixing cobalt(II) and excess cysteine likely was due to this complex in more dilute solution. The spectrum of the complex is represented by curve A in Fig. 1. Curves B and C in the same figure show that no appreciable amount of this complex was formed at pH 7.8 or 5.8 and the same cysteine/cobalt ratio, although lower complexes were formed.

Exposure of the purple triscysteinatocobaltate(II) complex to oxygen resulted in its very rapid, quantitative oxidation to a green product. The spectrum of this product was the same as that obtained in pH 11 buffer from limited oxygen, cobalt(II), and excess cysteine as well as from hexamminecobalt(III) chloride and cysteine.[13] That this product was identical to the green $K_3[Co(Scy)_3]\cdot 3H_2O$ complex prepared by Schubert[8] was demonstrated with certainty by repeating Schubert's preparation and determining its spectrum.

The success of this method of preparation, in which the amount of oxygen was not carefully regulated, indicates that the green tris complex is fairly resistant to further oxidation. However, upon prolonged exposure to oxygen, the complex reacted further to give brown products of undetermined nature; the reaction was quite slow, in contrast to the oxidation of the purple triscysteinatocobaltate(II) complex. Some confusion about this matter was caused by the observation that dilute aqueous solutions of the green tris complex, prepared for spectrophotometric de-

(11) A. Albert, *Biochem. J.*, **50**, 690 (1952).
(12) R. G. Neville and G. Gorin, *J. Am. Chem. Soc.*, **78**, 4893 (1956).
(13) G. Gorin, J. E. Spessard, G. A. Wessler, and J. P. Oliver, *ibid.*, **81**, 3193 (1959).

terminations, quickly turned brown. This, however, is due mainly to hydrolysis rather than oxidation, as the complex is rapidly decomposed when the pH is lowered. The spectrum of the brown product which formed immediately upon adding an aliquot of the green complex to pH 7.8 buffer is shown in Fig. 2, curve A. When the green tris complex was dissolved in 0.1 *M* sodium hydroxide rather than water, the green solutions became discolored only very slowly.

At pH 7.8, the oxidation of cobalt(II)–cysteine mixtures produced a brown product, in accordance with previous reports.[3–6] In a representative experiment, 0.01 *M* cobalt(II) and 0.03 *M* cysteine were mixed in buffer at pH 7.8 under air-free conditions, and an aliquot portion of the mixture was diluted with 100 volumes of air-containing buffer. The brown color developed quickly, a constant absorbance having been attained by the time the first measurement was taken, after 7 min. The spectrum in the region between 260 and 460 mμ is shown in Fig. 2, curve B. A series of experiments then was conducted

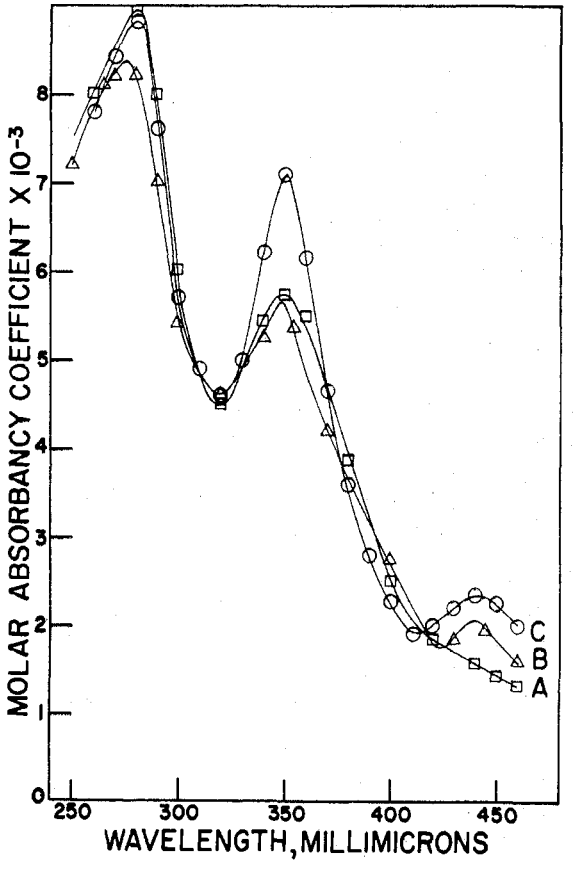

Fig. 2.—Spectra of cobaltic complexes: A, pH 7.8 hydrolysis product of $[Co(Scy)_3]^{-3}$; B, pH 7.8 oxidation product; C, pH 5.8 oxidation product.

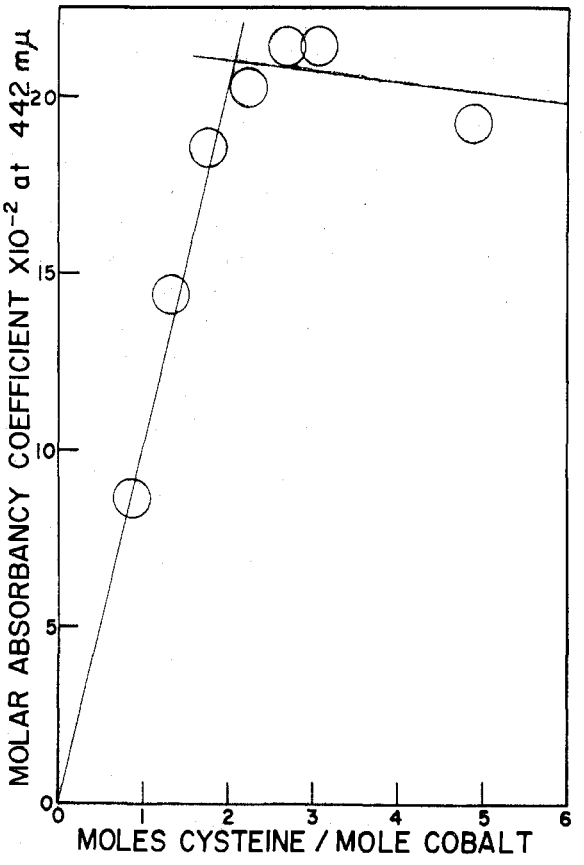

Fig. 3.—Relation of brown color development to cysteine/cobalt ratio at pH 7.8.

in a similar manner, with cysteine/cobalt ratios varying between 1 and 5; the results are plotted in Fig. 3. The results were not very precise, as indicated roughly by the size of the experimental points, but it can be seen clearly that a break occurs at a ratio of about 2.

In another series of experiments, the concentration of cobalt(II) was made 0.01, 0.001, and 0.0001 *M* and the cysteine/cobalt ratio kept constant at 2.8. The molar absorbancy (calculated on the basis of the cobalt taken) which developed upon exposure to air was 1950, 2050, and 1650, respectively. No cystine could be recovered from the most concentrated reaction mixture.

At pH 5.8, a brown complex also was formed, with a spectrum similar to but not identical with that of the other brown products so far discussed (Fig. 2, curve C). The rate of the reaction was much slower, about 5 hr. being required to attain a constant absorbance in conditions similar to those employed at pH 7.8. Most important, substantial amounts of cystine were formed. At 0.01 *M* cobalt(II) and a cysteine/cobalt ratio

of 3, the absorbancy coefficient of the product attained a value of 1940, and an amount of cystine corresponding to 20% of the cysteine originally taken could be isolated from the reaction mixture. At 0.001 and 0.0001 *M* concentration, direct isolation of the cystine was not attempted, but the molar absorbancy coefficients became constant at values of 1350 and 550, respectively.

In very concentrated solutions of cysteine, cobalt(II), and oxygen at pH 5.5, a red tris complex, $[Co(ScyH)_3]\cdot 3H_2O$ is formed slowly.[12] The concentrations used in the experiments described in this paper are much lower than those needed for formation of the red complex. A future contribution from this Laboratory will give additional information on this interesting complex, which is polymeric and involves a different type of bonding.

At pH 5.8 in the absence of cobalt, cysteine was oxidized very slowly. Over a period of 5 hr., a 0.1 *M* cysteine solution absorbed essentially no oxygen.

Discussion

The reaction of oxygen with cobalt(II) and excess cysteine at pH 11 involves a simple oxidation of the purple triscysteinatocobaltate(II) complex to the green triscysteinatocobaltate(III) complex

$$4[Co(Scy)_3]^{-4} + O_2 + 2H_2O \longrightarrow 4[Co(Scy)_3]^{-3} + 4OH^{-1}$$

Since the reaction involves the transfer of four electrons, it indubitably proceeds by way of some intermediate steps, but the nature of these steps cannot be inferred from the evidence now available.

The reaction at pH 7.8 with 0.01 *M* cobalt(II) in the conditions described produces a brown product, the spectrum of which is very similar to, but not identical with, that of the brown biscysteinatocobaltate(III) complex prepared and isolated by Schubert.[7] Since complex formation attains a maximum at a cysteine/cobalt ratio of 2, this product appears to be a bis complex. As five stereoisomeric forms are possible for biscysteinatocobaltate(III) complexes, it seems likely, indeed it should be expected, that the two products in question are mixtures containing somewhat different proportions of the possible isomers.[13]

A similar interpretation is offered for the decomposition of the green triscysteinatocobaltate(III) complex as the pH is lowered

$$[Co(Scy)_3]^{-3} + H^{+1} \longrightarrow [Co(Scy)_2]^{-1} + HScy^{-1}$$

The brown bis isomers produced in this case have, presumably, *cis*-diaquo structures. The occurrence of this reaction stands in marked contrast to the stability of the biscysteinatocobaltate(III) complex(es), which can be dissolved in concentrated sulfuric or hydrochloric acid with little change in spectrum. The binding constant for the third ligand molecule must be many orders of magnitude smaller than the constants for the first two.

At pH 5.8, the reaction is much slower, and considerable amounts of cystine are produced. The yield of this product was determined by isolation in the experiments conducted with 0.01 *M* cobalt and estimated at the lower concentrations on the assumption that the cysteine not bound in the brown complex had been converted to cystine. The cysteine converted to cystine at 0.01, 0.001, and 0.0001 *M* cobalt(II) concentration and a cysteine/cobalt ratio of 3 was, then, 20, 55, and 82%, respectively. At pH 7.8, on the other hand, no cystine was recovered from experiments done with 0.01 *M* cobalt, and the maximum amount of complex was formed even at 0.001 *M* cobalt concentration (up to 30% cysteine could, of course, be converted to cystine without reducing the final yield of complex); at 0.001 *M* cobalt concentration, however, the amount of complex was diminished, and the percentage of cysteine converted to cystine under these conditions is estimated to be 40%. These estimates must be considered approximate owing to the limited precision of the data and to the way in which they must be used; nevertheless, it can clearly be seen that cystine is produced in varying amounts, depending on the conditions. Low pH and low absolute concentration of reagents favor the reaction.

The occurrence of this reaction can explain the puzzling stoichiometric relationships observed at pH 8.0. Neville found, in experiments done with higher cysteine/cobalt ratios than those already mentioned (3 to 8.8), that the consumption of oxygen was 0.75 atom per cobalt ion; he also reported that "appreciable amounts of crystalline cystine were formed."[10] The results can be taken to indicate that, under these conditions, 0.5 mole of cystine was formed per mole of complex.

Kendall and Holst[6] deserve credit for postulating, at an early date, a mechanism for the reaction which recognized the formation of cystine as a product under some conditions and which might account for the catalytic effect of cobalt(II) in

the formation of this product. However, their suggestion must be modified in many essential details in view of what has been subsequently ascertained about cysteine complexes in particular and complex formation in general. What Kendall and Holst proposed as a general mechanism for the reaction appears to be applicable in part to the reaction at pH 11; the (purple) triscysteinatocobaltate(II) complex reacts with oxygen to give the (green) triscysteinatocobaltate(III). However, formation of the brown biscysteinatocobaltate(III) complex takes place very rapidly in conditions, such as pH 7.8 and a cysteine/cobalt ratio of 2, in which the purple triscysteinatocobaltate(II) complex cannot be present in appreciable amounts. Schubert suggested[9] that the precursor of brown biscysteinatocobaltate(III) is the corresponding cobalt(II) complex, and this suggestion is more logical and at least qualitatively consistent with what is known about this complex. The decrease in the rate of brown complex formation observed as the pH is lowered from 7.8 to 5.8 then can be ascribed to the decrease in the concentration of biscysteinatocobaltate(II) complex under these conditions.

The formation of cystine increases as the pH is lowered and the absolute concentration is decreased; these changes favor the simplest complex. Accordingly, we suggest, as a speculation, that the mechanism of cystine formation at pH 5.8 involves the oxidation of a [Co(Scy)] complex to $[Co(Scy)]^{+1}$, followed by disproportionation to cobalt(II) and cystine; thus the catalyst is regenerated. Such a mechanism is consistent with what is known in general about the properties of cobalt(III) ion.

Experimental

Materials.—All reagents were of analytical reagent grade, except as otherwise specified. L-Cysteine hydrochloride monohydrate (B grade) was obtained from the California Corporation for Biochemical Research, Los Angeles 63, California; it was analyzed for −SH content by a ferricyanide oxidation method. In 100 ml. of pH 7.0, 0.1 *M* phosphate buffer was dissolved a 30-mg. sample of cysteine. A 1.0-ml. aliquot of this solution was mixed with 1.0 ml. of 0.00386 *M* potassium ferricyanide and the mixture diluted to 10.0 ml. with buffer. The difference in absorbance at 410 mμ between this solution and a blank composed of 1.0 ml. of 0.00386 *M* potassium ferricyanide and 9.0 ml. of buffer then was measured. The –SH content was calculated from this difference using 990 for the molar absorbancy coefficient of ferricyanide. The cysteine used in this work was 90% pure.

Nitrogen of commercial grade was deoxygenated by passing it through acid vanadous solutions.[14] Air-free water was prepared by boiling de-ionized water for 30 min.; it was allowed to cool and stored under nitrogen.

Apparatus and Special Procedures.—A Beckman Model GS pH meter equipped with glass and calomel electrodes was used for pH measurements. Spectrophotometric measurements were made in 1-cm. cells with a Beckman Model DU spectrophotometer.

Preparations and measurements to be conducted in the absence of air were executed in a 180 or 300-ml. lipless beaker fitted with a rubber stopper which had holes drilled in it to accommodate glass and calomel electrodes, the tip of a 10-ml. microburet, a gas inlet tube, and an exhaust port. The beaker first was flushed with oxygen-free nitrogen, then air-free water and reagents were added as desired, with nitrogen flowing through the vessel at a brisk rate. For spectral determinations, aliquot samples were withdrawn with a hypodermic syringe and transferred to a special cell which has been described elsewhere.[15]

Preparation and Oxidation of Purple $[Co(Scy)_3]^{-4}$.—The preparation and spectral measurements were done in the absence of air. Cysteine hydrochloride monohydrate was added to 100 ml. of air-free 10^{-2} *M* cobalt(II) chloride to give a cysteine/cobalt ratio of 4. Air-free 1 *M* sodium hydroxide then was added to give a pH of 11. At this pH the solution had a purple-violet color. To oxidize $[Co(Scy)_3]^{-4}$, air was passed through the solution for 30 min. and the absorbancy determined at 585 mμ after 1:10 dilution with water. No change in absorbancy was observed on allowing the solution to stand exposed to the air for one additional hour.

Rate of Color Formation Upon Oxidation of Cobalt–Cysteine Mixtures.—One ml. of air-free 1.00 *M* cobalt(II) chloride was mixed with 100 ml. of air-free phosphate buffer, pH 7.8. Air-free 1 *M* cysteine hydrochloride then was added to give the desired cysteine/cobalt ratio and air-free 1.0 *M* sodium hydroxide was added to restore the pH to 7.8. The spectrum of an aliquot portion of this solution then was determined without dilution. All of these operations were conducted in the absence of air. One ml. of the solution then was added to 100 ml. of air-saturated phosphate buffer and the absorbance at 442 mμ determined as a function of time. The oxidation was complete before the first measurement was taken, after 7 min.

A similar experiment was done in phthalate buffer at pH 5.8; in this case, the absorbance became constant only after several hours.

Cystine Formation.—To 100 ml. of air-free pH 5.8 buffer was added 1.0 ml. of 1.00 *M* cobalt(II) chloride and enough cysteine hydrochloride monohydrate to make the cysteine/cobalt ratio 3. The solution then was oxygenated by blowing a stream of air through it; 1.0-ml. aliquots were withdrawn at various times, diluted with water, and the absorbance was measured at 442 mμ. After the absorbance reached a constant or nearly constant value, the solution was filtered under suction through a weighed, 2.5-ml., medium-porosity, fritted-glass filter crucible; the crystalline cystine obtained was washed with a small amount of water and dried. The amount of cystine then was determined by weighing the crucible; as a

(14) L. Meites, "Polarographic Techniques," Interscience, New York, N. Y., 1955, p. 34.

(15) B. J. McCormick and G. Gorin, *Anal. Chem.*, **33**, 157 (1961).

check, the cystine was dissolved with dilute HCl and the crucible again dried and weighed.

A similar experiment was conducted at pH 7.8 using the same procedure as above. At both pH 5.8 and 7.8, cystine is quite insoluble[16] and no correction for solubility was made.

Cysteine/Cobalt Ratio and Brown Complex Formation.—Six 2-oz. polyethylene bottles were fitted with stoppers having a nitrogen inlet and exhaust port. The bottles were deaerated by passing nitrogen through them for several minutes. One ml. of air-free 0.2500 *M* cobalt chloride, air-free 0.1166 *M* cysteine, and pH 7.8 1 *M* phosphate buffer were mixed in the bottles to give the desired cysteine/cobalt ratio and a total volume of 25 ml. The cysteine solution was prepared by dissolving 2.1954 g. of cysteine hydrochloride monohydrate in 50 ml. of pH 7.8 buffer, adding 10 *M* NaOH to adjust the pH back to 7.8, and diluting the resulting solution to 100 ml. with buffer. During the addition of reagent, nitrogen was passed rapidly through the containers. The solutions then were carefully shaken for several minutes. Then the stoppers were removed and 1-ml. aliquots were withdrawn and transferred to 100-ml. volumetric flasks. These aliquots were allowed to stand exposed to the air for 45 min., then diluted to 100 ml. with water, and the absorbance was measured at 442 mμ.

Oxygen Uptake of Cysteine Solutions.—The rate of oxygen uptake of cysteine and cobalt(II)–cysteine solutions at pH 5.8 was determined with a constant pressure apparatus consisting of a thermostated two-compartment flask connected to a gas buret. In the first experiment, 1.0 ml. of approximately 0.1 *M* cysteine in pH 5.8 buffer was placed in one compartment of the flask and the rate of oxygen uptake measured with the gas buret; no appreciable amount of oxygen was absorbed over a period of 5 hr. The second experiment was conducted in the same fashion except that 1.0 ml. of a 0.1 *M* solution of cobalt(II) chloride was placed in the other compartment of the flask; to initiate the experiment, the cobalt was poured into the cysteine-containing compartment. In this case, oxygen was quite rapidly absorbed by the solution. In both experiments, the solution was vigorously stirred with a magnetic stirrer and Teflon-covered stirring bar.

Acknowledgment.—This work was supported in part by grant G-5966 from the National Science Foundation.

(16) K. Sano, *Biochem. Z.*, **168**, 14 (1926).

CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND

The Rates of Oxidation of Nitrite Ion by Several Peroxides[1]

BY JOHN O. EDWARDS AND JOHN J. MUELLER

Received March 14, 1962

The reaction of nitrite ion with three peroxides has been investigated kinetically. With peroxyacetic acid, the reaction is first order each in peroxyacid and in nitrite ion concentrations. Rate constants over a range of conditions are presented. Less complete data for the reactions of nitrite ion with Caro's acid and with hydrogen peroxide are given. The mechanism of these reactions is discussed.

The rate of oxidation of bromide ion by hydrogen peroxide and various monosubstituted peroxides increases in the order $H_2O_2 < H_2PO_5^- < CH_3CO_3H < HSO_5^- < H_3PO_5$; and in oxidations by a single peroxide, the halides react in the order $Cl^- < Br^- < I^-$. The mechanism of these oxidations has been postulated to be a nucleophilic displacement on oxygen.[2]

It was the purpose of this study to investigate the kinetics of the oxidation of nitrite ion by several peroxides in order to find out if this ion also acts as a nucleophile in displacements on oxygen. Previous data from oxygen isotope experiments strongly suggested that such is the case; it has been found that one oxygen atom is transferred to nitrite ion from peroxynitrous acid,[3] Caro's acid,[3] hypochlorous acid,[4] and hypobromous acid.[4] In view of the fact that nitrite ion and bromide ion have similar nucleophilic reactivities,[5] kinetic investigations seemed feasible; the results are presented here.

Experimental

Equipment.—The course of the reaction was followed using a Beckman Model DK-1 spectrophotometer. A preliminary study showed that while the nitrite ion has an

(1) Taken from the Sc.B. thesis of J. J. M. at Brown University, 1960.

(2) The subject of nucleophilic displacements on oxygen has been reviewed recently in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, pp. 67–106.

(3) M. Anbar and H. Taube, *J. Am. Chem. Soc.*, **76**, 6245 (1954).

(4) M. Anbar and H. Taube, *ibid.*, **80**, 1073 (1958).

(5) J. O. Edwards, *ibid.*, **76**, 1540 (1954).