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 aliquots were withdrawn and transferred to 100-ml.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.

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[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

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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

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[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).

absorption peak at a wave length of 357 mμ, none of the other reactants, products, or materials used as buffers absorbs significantly in this region. Initial concentrations of about 0.04 M in nitrite ion were found to be optimum for following the kinetics of the reaction. The temperature was maintained constant to within 0.1° by the use of a thermostated cell-holder.

All pH measurements were made on a Beckman Model G meter.

Materials.—Caro's acid was prepared by adding Becco 98% hydrogen peroxide to a stoichiometric amount of freshly distilled chlorosulfonic acid. The peroxyacetic acid was Becco 40% practical grade. The buffers used were acetic acid, sodium acetate; sodium dihydrogen phosphate, sodium monohydrogen phosphate; and sodium tetraborate. All were reagent grade. Distilled water was used in preparing all solutions.

Procedure.—Approximately 7.5 ml. of peroxyacetic acid was diluted to 500 ml. in the preparation of a stock solution. It was analyzed as follows: A 25-ml. aliquot was put into a flask containing 150 ml. of 5% sulfuric acid, previously cooled to 0°. This solution was titrated with 0.1 N ceric sulfate solution, using ferroin as indicator. Then 10 ml. of 10% potassium iodide solution was added, and the liberated iodine was titrated with standard sodium thiosulfate solution. The concentrations of hydrogen peroxide and peroxyacetic acid in the original solution were calculated from the amounts of ceric sulfate and sodium thiosulfate, respectively. A similar procedure was used in preparing and standardizing the Caro's acid solutions.

The sodium nitrite stock solutions were prepared by weighing out the correct amount of the salt and dissolving it in the appropriate buffer solutions.

The reactants were brought to the required temperature in a constant temperature bath, and 5 ml. of each was quickly pipetted into a beaker. The reaction mixture was transferred rapidly to the thermostated cell and the course of the reaction was followed by the change in absorbancy. Since the success of this method depends largely upon the initial concentrations being equal, and upon a stoichiometric reaction, several samples were allowed to stand overnight. Upon measuring, it was found that the absorbancy of the solutions had dropped to 1–2% of its original value, indicating that the reaction was essentially quantitative. The linearity of the kinetic plots also is an indication of the quantitative nature of the reaction.

In view of the slowness of the reaction with hydrogen peroxide, normal sampling techniques and spectrophotometric analyses of aliquots were used.

Results

Stoichiometry.—Chemical analysis (by two methods) and the extinction coefficient showed that the sodium nitrite was 100 ± 1% pure. When this salt was treated with known amounts of peroxyacetic acid and of Caro's acid, the stoichiometry

$$\mathrm{ROOH} + \mathrm{NO_2^-} \longrightarrow \mathrm{ROH} + \mathrm{NO_3^-}$$

was followed to well within the experimental error (*ca.* ± 1%). The same stoichiometry was assumed to hold for the hydrogen peroxide; the assumption was necessary because the reaction was so slow (some peroxide was lost by decomposition.)

Peroxyacetic Acid.—This reaction is first order each in peroxide concentration and in nitrite ion concentration. These orders were confirmed by the fact that excellent linear plots (to 90% of reaction) were obtained both when the reactants were in equal concentration and when the peroxide was in excess. The results of seven runs are presented in part A of Table I; the data therein demonstrate that the second-order rate constant is not a function of the initial concentrations.

TABLE I

RESULTS OF KINETIC RUNS[a]

A. Determination of order

$[\mathrm{NO_2^-}]$, M	$[\mathrm{CH_3CO_3H}]$, M	pH	k_2[b]
0.04547	0.04547	5.7	0.0337
.04547	.04547	5.7	.0345
.04547	.04547	5.7	.0346
.04268	.04268	6.0	.0328
.02100	.02100	5.9	.0340
.04469	.08938	5.1	.0378
.04469	.08938	5.1	.0375
B. Effect of pH			
0.0455	0.0455	4.5	0.0636
.0455	.0455	5.0	.0393
.0455	.0455	5.5	.0339
.0455	.0455	6.7	.0297
.0455	.0455	7.7	.01

[a] All kinetic runs at 25° and $\mu = 0.2$. [b] Units are l. mole^{-1} sec.$^{-1}$.

The influence of pH on the second-order rate constant is shown in the data of part B of Table I, as well as the data of part A. Between pH 5.0 and 6.7, there is very little rate dependence on pH; thus, over a fiftyfold change in hydrogen ion concentration, the order in hydrogen ion concentration is zero. Near pH 4.5, where some protonation of the nitrite ion occurs, the rate constant increases; presumably a new kinetic path is entering in at this lower pH. At pH 7.7, the observed rate was found to be lower; this almost certainly results from the fact that peroxyacetic acid decomposes fairly rapidly at this pH.[6]

As expected for the reaction between an ion ($\mathrm{NO_2^-}$) and a neutral molecule (peroxyacetic acid), the rate is not influenced by ionic strength. For three otherwise identical runs ($[\mathrm{NO_2^-}] = [\mathrm{CH_3CO_3H}] = 0.0438$ M, $t = 25°$, pH = 5.6),

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[6] E. Koubek and J. O. Edwards, unpublished data.

the rate constants at μ = 0.2, 0.4, and 0.6 were 0.0339, 0.0335, and 0.0349 l. mole^{-1} sec.$^{-1}$, respectively.

The results of runs at four different temperatures are presented in Table II. The data gave a linear Arrhenius plot from which an activation energy E_a of 13.7 kcal. mole^{-1} was derived. Using standard equations, values for ΔF^*, ΔH^*, and ΔS^* of 19.5 kcal. mole^{-1}, 13.1 kcal. mole^{-1}, and -22 cal. mole^{-1} deg.$^{-1}$, respectively, were calculated.

TABLE II

INFLUENCE OF TEMPERATURE ON RATE CONSTANT[a]

Temp.	Final pH	k_2^b
5°	5.6	0.00604
20°	5.5	.0228
25°	5.5	.0339
30°	5.6	.0468

[a] μ = 0.2 and $[NO_2^-]$ = $[CH_3CO_3H]$ = 0.045 *M*. [b] Units of k_2 are l. mole^{-1} sec.$^{-1}$.

Caro's Acid.—The results obtained with peroxyacetic acid indicated that the reaction with peroxymonosulfuric acid should have a measurable rate; this stems from the fact that HSO_5^- oxidizes Br^- a little faster than does CH_3CO_3H.[2] The results of some kinetic experiments on mixtures of HSO_5^- and NO_2^- are presented in Table III. In all cases the kinetic plots assuming second order were linear to over 85% reaction. Because of the difficulty of working with such a strong and unstable acid as H_2SO_5 and because the reaction was so fast, we did not attempt to obtain more precise rate data.

TABLE III

RATES OF OXIDATION BY CARO'S ACID[a]

$[NO_2^-]$, *M*	$[HSO_5^-]$, *M*	k_2^b
0.0410	0.0410	0.306
.0399	.0399	.317
.0386	.0386	.299
.0404	.0404	.330
.0374	.0374	.290
.0450	.0450	.340

[a] At 25° and μ = 1.5. Buffer is dihydrogen phosphate and monohydrogen phosphate. [b] Units are l. mole^{-1} sec.$^{-1}$.

One kinetic run was made at 4°. The rate plot showed good linearity and the constant was calculated to be 5.74×10^{-2} l. mole^{-1} sec.$^{-1}$. Using this value and the value 0.310 for 25°, the parameters E_a, ΔH^*, and ΔS^* were calculated to be 13.2 kcal. mole^{-1}, 12.6 kcal. mole^{-1}, and -20 cal. mole^{-1} deg.$^{-1}$, respectively.

Hydrogen Peroxide.—The reaction of hydrogen peroxide with nitrite ion is known to proceed rapidly near pH 5 by a mechanism related to that of amine nitrosation.[3] Thus, it is necessary to go to higher pH in order to find any evidence for a pathway involving a nucleophilic displacement on oxygen. The situation is further complicated by the fact that such a pathway would have a low rate constant; the prediction from relative rates of oxidation was 10^{-6} l. mole^{-1} sec.$^{-1}$.

In Table IV, the results of four kinetic runs are given. Pseudo-first-order plots (log $[NO_2^-]$ against time) were linear in each case, thus the reaction is first order in nitrite ion concentration. However, the calculated second-order constants are not as consistent as for the previous two peroxides; the value of k_2 tends to increase with increase in peroxide concentration. It is not possible to say exactly why such is the case here, but it presumably is a consequence (directly or indirectly) of the fact that it was necessary to have rather large concentrations of peroxide to get measurable rates. Such peroxide concentrations as in the highest case (4 *M*) certainly have a definite influence on solvent nature. It is worth noting that the change in pH is too large to be used as the sole explanation for the change in k_2 if one invokes a kinetic order in acid concentration. We have not, however, rigorously proved the rate law in this case; therefore, it is not known why the rate constants vary.

TABLE IV

RATES OF OXIDATION BY HYDROGEN PEROXIDE[a]

$[H_2O_2]$, *M*	pH	k_2^b
3.96	6.38	5.9×10^{-7}
2.93	6.50	4.4
1.90	6.86	3.4
1.07	7.08	3.0

[a] At 25°; $[NO_2^-]$ = 0.040 *M*; phosphate buffer. [b] Units are l. mole^{-1} sec.$^{-1}$.

The values obtained for the two lowest peroxide concentrations are in agreement both with each other and with the predicted value, and we shall therefore use 3×10^{-7} as the best value.

Discussion

In Table V, rate data for the oxidation of three anions by three peroxides are given. The simi-

TABLE V

COMPARISON OF RATE DATA[a]

Peroxide	Nucleophile Cl^-	 NO_2^-	 Br^-
H_2O_2	1.1×10^{-7}	3×10^{-7}	2.3×10^{-5}
CH_3CO_3H	...	3.4×10^{-2}	0.258[b]
HSO_5^-	1.4×10^{-3}[c]	0.31	1.04[d]

[a] Data are in aqueous solution at 25° from ref. 2 and from this study. [b] ΔH^* and ΔS^* are 13.1 and −17.4. [c] ΔH^* and ΔS^* are 14.0 and −24.1. [d] ΔH^* and ΔS^* are 10.0 and −24.8.

larity in magnitude of nitrite rates to those of bromide ion was expected in view of the similarity in nucleophilic power.[5] The nitrite discrimination among the peroxides is larger than that of bromide although not greatly so.[7] The thermodynamic activation parameters are similar also. There can be little doubt that the mechanism of nitrite ion oxidation by these peroxides is a nucleophilic displacement by nitrogen (of nitrite) on oxygen (of peroxide).

It is of interest to note that the nitrite ion reaction with hypochlorous acid is similar to that of nitrite ion with peroxides. Lister and Rosenblum[8] have found a second-order rate law, a rate constant smaller than for the corresponding bromide oxidation, and similar activation parameters (low ΔH^* and low ΔS^*) to those found here. Coupled with the oxygen isotope data,[4] these results indicate that the mechanism of hypochlorous acid reactions with nucleophiles is closely related to those of the peroxides.

The results obtained here and those obtained on the halide oxidations by peroxides[2] can be used to explain the quantitative order of an effect recently reported in the literature. Anbar[9] has observed an oxyacid (*e.g.*, periodate) induced exchange between hydrogen peroxide and water. Presumably the exchange occurs through nucleophilic attack by water on the oxygen of an intermediate peroxyacid XOOH (as is proposed by Anbar). This exchange was found to be inhibited by bromide, nitrite, and chloride ions in decreasing order of inhibitory power. As the nucleophilic strengths in displacement on oxygen are $Br^- > NO_2^- > Cl^- \gg H_2O$, the three anions can inhibit the exchange by competitively reacting with the intermediate. Such reactions of XOOH with the three anion nucleophiles would lower the amount of the intermediate, and thereby lower the rate of oxygen exchange in the order observed.

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(7) At pH 6 and at 25°, the second order rate constant for oxidation of nitrite ion by peroxymonophosphate was found to be about 7×10^{-4} l. mole^{-1} sec.$^{-1}$ by C. J. Battaglia of this Laboratory. Under the same conditions, bromide ion is oxidized with a rate constant of 20×10^{-4}.

(8) M. W. Lister and P. Rosenblum, *Can. J. Chem.*, **39**, 1645 (1961).

(9) M. Anbar, *J. Am. Chem. Soc.*, **83**, 2031 (1961).