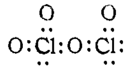
and transfer of labeled oxygen to sulfite. This is proved by the fact that there is very little effect on *n* by the large changes in SO_2/H_2O produced by reversing the order of mixing. It seems therefore that there are two modes of attack of HOX on sulfite. In one, oxygen is transferred to sulfite: $Cl\overset{*}{O}^- + SO_3^- \rightarrow Cl^- + SO_3\overset{*}{O}^-$; in the other, X^+ is transferred, forming a compound which then hydrolyzes.

$$OCl^- + SO_3^{=} + H^+ \longrightarrow ClSO_3^- + OH^-$$
$$ClSO_3^- + H_2O = SO_4^{=} + 2H^+ + Cl^-$$

The result obtained on the disproportionation of ClO_2 in alkali is explained most simply by assuming an unsymmetrical configuration for $(ClO_2)_2$ in the transition state



$$\begin{array}{ccccc} & O & & O & \\ O: & \overset{..}{\underset{..}{Cl}} & :O: & \overset{..}{\underset{..}{Cl}} & : \end{array}$$

formal charge: +2 +1

It can be supposed that in the majority of cases attack by OH^- takes place on the more acidic chlorine, *i.e.*, that which bears the formal charge +2. This mode produces ClO_2^- identical in isotopic composition with ClO_2, and puts solvent oxygen in the product ClO_3^-. If in a small fraction of the events, OH^- attacks the chlorine bearing the formal charge +1, the deviations from $n_{\text{calcd.}}$ in Table VI, are accounted for.

A few features of the exchange results merit comment. It seems likely that the difference in lability between IO_3^- on the one hand and BrO_3^- and ClO_3^- on the other can be attributed to the greater tendency of I(V) as compared to Br(V) and Cl(V) of assuming configurations with coördination numbers greater than 3. In crystalline bromates and chlorates, the coördination number of the halogen is three, but in iodates, the coördination numbers 6, 10 and 12 have been observed.[19] The slow exchange observed for ClO_2 proves that this oxide does not participate in rapid equilibria of the type

$$H_2O + ClO_2 = H_2ClO_3 = HClO_3^- + H^+$$

It confirms the conclusion reached in other studies[20] that equilibrium between ClO_2, ClO_3^- and ClO_2^- is not reached rapidly in acid solution. There is an apparent disagreement between the exchange results we have recorded for sulfite in alkaline solution, and the results reported by Hall and Alexander.[6] These authors reported a slow exchange in alkaline solution. The experiments were, however, performed differently (quenching by I_2, SO_2 aq. passed into O^*H^- in our case, K_2SO_3 dissolved in alkaline solution, sampling by distillation in the ether). Either of these differences, or the combination may be responsible for the difference in the results.

Acknowledgment.—This work was supported by the Office of Naval Research under contract N6-ori-02026. The funds for the purchase of the mass spectrometer used in this research were supplied by the Atomic Energy Commission under contract AT(11-1)-92.

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CHICAGO, ILLINOIS RECEIVED JUNE 18, 195

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Transfer of Oxygen Atoms in Oxidation–Reduction Reactions. IV. The Reaction of Hydrogen Peroxide with Sulfite and Thiosulfate, and of Oxygen, Manganese Dioxide and of Permanganate with Sulfite

BY JOSEPH HALPERIN[1] AND HENRY TAUBE

In the reaction of hydrogen peroxide with sulfite at *p*H 5 and at higher acidity, two oxygen atoms are transferred to sulfite per molecule reacting. When thiosulfate is oxidized by hydrogen peroxide in the presence of molybdate only one atom is transferred per molecule reacting. It seems likely that in the former case, permonosulfurous acid forms as intermediate, retaining the O–O bond intact, but in the latter oxygen atoms are transferred from permolybdic acid to the sulfite rupturing the O–O bond in the permolybdate. In the reaction with sulfite of O_2 (at *p*H ~5), of MnO_2 (in 0.1 *M* HCl), and of MnO_4^- (at *p*H ~6), transfer from the oxidizing agent of 2.2, 0.97 and 0.2 atoms of oxygen, respectively, per formula unit of oxidizing agent reacting was observed.

This paper presents the results obtained in a continuation of studies on the path of oxygen in oxidation–reduction reactions in aqueous solutions. The reactions studied were: oxidation of sulfite by hydrogen peroxide, oxygen, permanganate and manganese dioxide, and the oxidation of thiosulfate by hydrogen peroxide in the presence of molybdate. The product in every one of these reactions is principally sulfate, and in each case it is of interest to learn whether the oxygen added is derived from the solvent or from the oxidizing agent. Results have been published[2] on the first two reactions mentioned, based on a procedure in which the solvent was sampled for isotope analysis. This method is inherently less sensitive than the present method of sampling the product sulfate. In addition, it should be pointed out that the items of information obtained in the two methods are not completely interdependent. The results of the present work on the reaction of oxygen with sulfite and of hydrogen peroxide with sulfite are consistent with those published, and in the case of the latter reaction have led to a further conclusion.

It will be clear that these studies are for the most part rather incomplete. The data are however dependable over the range of conditions studied and the results have seemed sufficiently interesting and

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[1] A.E.C. Predoctoral Fellow, 1949-1950.

[2] E. R. S. Winter and H. V. A. Briscoe, THIS JOURNAL, **73**, 496 (1951).

suggestive of further work to be worth presenting for publication.

Experimental

The main features of the procedure are similar to those of the experiments on the reactions of sulfite with halogenates, and have already been described.[3]

Of the oxidizing agents used, only H_2O_2 was prepared[4] in enriched form. It was prepared by passing O^{18} enriched water vapor at low pressure through a glow discharge, and freezing out the effluent gas with liquid nitrogen.[5] The isotope composition of the peroxide was assumed to be the same as that of the water from which it was made.

The experiments of Winter and Briscoe[2] as well as experiments performed here have shown that the exchange of H_2O_2 and H_2O is very slow. Zimmerman[6] has shown the exchange of MnO_4^- with water to be slow under conditions similar to those used in our experiments. The rate of exchange of MnO_2 and H_2O was measured by leaving MnO_2 in contact with sevenfold enriched water for one hour, then removing the water by evaporation. The MnO_2 was dried, then heated to yield oxygen as product. After this treatment, the mole fraction of O^{18} in the oxygen was observed to be 2.199×10^{-3}; before the treatment it was 2.189×10^{-3}. The exchange is very much slower than the rate of oxidation of sulfite.

Solutions described as at pH ~ 5 contained 0.5 M NaOAc and 0.5 M HOAc. All experiments were performed at 25°.

N_s represents the mole fraction of O^{18} in the species S.

n represents the number of oxygen atoms transferred to sulfite per molecule of oxidizing agent consumed.

n_{max} is the maximum number of oxygen atoms available for transfer to the reducing agent per molecule of oxidizing agent.

Z represents the total change in oxidation number of each molecule of oxidizing agent consumed.

Results

The Reaction of Hydrogen Peroxide and Sulfite.—The reaction between hydrogen peroxide and sulfite takes place rapidly, the principal change being represented by the equation

$$H_2O_2 + \Sigma H_2SO_3 = H_2O + \Sigma H_2SO_4$$

In addition to sulfate, a small amount (less than 1%) of dithionate is formed as oxidation product of the sulfite.[7]

The results of the tracer experiments on the system are summarized in Table I.

TABLE I

OXYGEN TRANSFER IN THE REACTION OF SULFITE AND HYDROGEN PEROXIDE

Conditions	$N^a_{H_2O}$ × 10^3	$N_{H_2O_2}$ × 10^3	$N_{SO_4^=}$ × 10^3	n^b
0.1 M HCl, H_2O_2 added to SO_2^* aq.	15.720	2.120	9.253	1.90
0.1 M HCl, SO_2^*aq. added to H_2O_2	15.720	2.120	9.220	1.91
			Av.	1.90
pH ~5, SO_2^*aq. added to H_2O_2	15.660	2.120	9.230	1.90
pH ~5, SO_2aq. added to $H_2O_2^*$	2.235	15.924	8.561	1.84
			Av.	1.87
0.1 M HCl, SO_2 passed into $H_2O_2^*$ in ordinary H_2O	2.371	15.924	8.300	1.75

[a] H_2O and SO_2aq. are in isotopic equilibrium. [b] Compare to $Z/2 = 1$ and $n_{max} = 2$.

It can be concluded from the results that under the conditions of our experiments each molecule of H_2O_2 that reacts transfers 2 atoms (very nearly) of oxygen to the sulfite, independent of concentration over a wide range. When SO_2 is passed directly into the solution containing oxidizing agent, a significantly lower value of n is observed.

The Reaction of Oxygen and Sulfite.—It seemed of interest to study oxygen atom transfer in the reaction of sulfite and oxygen, the reaction being known to be a chain reaction,[8] and involving reactive radicals as intermediates. The results obtained are presented in Table II.

TABLE II

OXYGEN TRANSFER IN THE REACTION OF OXYGEN AND SULFITE

Solutions at pH ~ 5, O_2 passed into SO_2^*aq.

N_{H_2O} × 10^3	N_{O_2} × 10^3	$N_{SO_4^=}$ × 10^3	n^a
15.148	2.214	11.666	2.15
15.148	2.214	11.458	2.28
15.713	2.100	11.813	2.29
		Av.	2.24

[a] Compare with $Z/2 = n_{max} = 2$.

The Reaction of Manganese Dioxide and of Permanganate with Sulfite.—In acid solution, the reaction of sulfite and manganese dioxide produces both sulfate and dithionate as oxidation products, and manganous ion as the reduction product. The net change producing sulfate is

$$MnO_2 + H_2SO_3 = Mn^{++} + SO_4^= + H_2O$$

In an experiment measuring oxygen atom transfer from MnO_2 to sulfite in the reaction, MnO_2 (unenriched) was added to SO_2^*aq. in 0.1 M HCl. After the reaction had continued for an hour, sulfate ion was separated and analyzed isotopically in the usual manner. The value of n observed in the experiment was 0.97 (*cf.* $Z/2 = 1$; $n_{max} = 2$).

The reaction of MnO_4^- with sulfite was carried out in a buffer mixture 0.5 M NaOAc and 0.1 M HOAc. A small volume of O^{18} enriched sulfite solution containing acetic acid was added to a solution containing MnO_4^- of ordinary isotopic composition, and sodium acetate in enriched water. The manganese dioxide was separated by centrifuging, and the experiment completed in the usual way: n was observed to be 0.2 (*cf.* $Z/2 = 1.5$; $n_{max} = 4$).

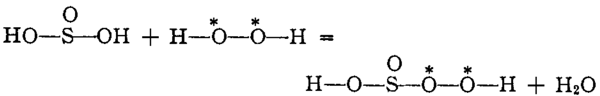
The Reaction of Thiosulfate and Hydrogen Peroxide in the Presence of Molybdate.—In the absence of particular catalysts, hydrogen peroxide and thiosulfate react to produce $S_4O_6^=$ as the major oxidation product. However, when molybdate is present as a catalyst, an additional reaction takes place forming sulfate as a product.[9] For the experiment on oxygen atom transfer which was performed, conditions were selected by reference to the work of Abel[9] to make sulfate the principal oxidation product. In the experiment 2 ml. 0.2 M $H_2O_2^*$ containing 2×10^{-6} mole MoO_3 present as ammonium molybdate was added to 1 ml. of 0.05 M $Na_2S_2O_3$ of ordinary isotopic composition in ordinary water. The solution was buffered at pH ~ 5. Isotopic analysis of the product yielded as n for the reaction

$$H_2O_2 + {}^1/_4S_2O_3^= = {}^1/_2SO_4^= + {}^3/_4H_2O + {}^1/_2H^+$$

the value 1.00. For the reaction above $Z/2 = 1.00$ and $n_{max} = 2$.

Discussion

The result that in the reaction of sulfite and hydrogen peroxide two atoms of oxygen are transferred from a molecule of hydrogen peroxide for each molecule of sulfite oxidized, although the net change requires addition of only one atom, seems quite remarkable. By analogy with the nitrous acid–hydrogen peroxide reactions in which the existence of a pernitrous acid has been proved,[10] it can be supposed that a persulfurous acid is formed in the present system



$$HO{-}\overset{O}{S}{-}OH + H{-}\overset{*}{O}{-}\overset{*}{O}{-}H = H{-}O{-}\overset{O}{S}{-}\overset{*}{O}{-}\overset{*}{O}{-}H + H_2O$$

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[3] J. Halperin and H. Taube, submitted for publication.

[4] We are indebted to Dr. J. P. Hunt for preparing the enriched hydrogen peroxide.

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In view of the rapid exchange of sulfurous acid with water, but not of peroxide and water, it is very likely that in forming the ester, the S–O rather than O–O bond is severed. The formation of the doubly labelled sulfate can take place by an intramolecular rearrangement of the persulfurous acid, or by the interaction of two molecules. Of these the second seems less likely since the extent of transfer is independent of an extreme variation in the ratio of H_2O_2/SO_2aq. The tracer result makes it unlikely that a major part of the reaction proceeds by a free radical mechanism, but does not exclude a minor contribution by this path. A slight participation by a free radical path is suggested by the observation that H_2O_2 induces the reaction of O_2 and $SO_3^=$,[11] but not at all efficiently.

The work of Winter and Briscoe[2] showed that in the reaction of hydrogen peroxide and sulfite in water, an atom of oxygen is released to the solvent for each molecule of H_2O_2 consumed. The present work shows that in acidic solutions this atom is derived from the sulfite rather than from the peroxide. In more alkaline solution the formation of the ester may be slow, and it seems possible that only one atom of oxygen is transferred from the peroxide to the sulfite on reaction.

The data on the catalyzed reaction of H_2O_2 and $S_2O_3^=$ are too incomplete to justify a definite conclusion. The experimentally measured value of $n = 1$ is in harmony with the view that a permolybdic acid (molybdate and hydrogen peroxide react very rapidly to form permolybdic acid) which is almost certainly an intermediate, will act by transferring oxygen atoms. This type of mechanism can be expected when any strongly polarizing group such as HMO_3 or HSO_3, is attached to O–$O^=$ thereby weakening the O–O linkage. The experiment is of some interest in showing the exchange of sulfur intermediates in the oxidation to sulfate is less rapid than the oxidation.

The excess of the value of n over 2 observed for the reaction of oxygen and sulfite may be due to isotope fractionation. A deviation in the observed direction can be expected if O_2^{16} reacts more rapidly than oxygen containing O^{18}. A more thorough study will be necessary to discover whether the deviation is entirely due to this cause, or whether a real exchange effect exists.

The efficient transfer observed in the reaction of sulfite with MnO_2 suggests that sulfite makes bonds with the oxygen atoms rather than with the metal ions at the surface of the solid. Permanganate ion, or the unknown oxidation state which attacks the sulfite apparently operates largely by electron transfer.

Acknowledgment.—This work was supported by the Office of Naval Research under contract N6-ori-02026. The funds for the purchase of the mass spectrometer used in this research were supplied by the Atomic Energy Commission under contract AT(11-1)-92.

CHICAGO 37, ILLINOIS RECEIVED AUGUST 16, 1951

(11) H. L. J. Bäckstrom, *Medd. Vetenskapsakad. Nobelinst.*, **6**, No. 15 (1927).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Anodic and Cathodic Voltammetry of Thallium at the Rotated Platinum Wire Electrode

BY I. M. KOLTHOFF AND JOSEPH JORDAN[1]

The anodic oxidation of thallous to thallic thallium at the rotated platinum wire electrode was studied at various pH, using an automatic recording instrument. Proportionality between diffusion current and concentration was found in sodium hydroxide solutions. This amperometric method is suitable for the determination of thallium in a concentration range between 10^{-5} and 10^{-3} M. Good results can be obtained with a manual polarograph provided that diffusion currents are measured after the same time of electrolysis. Limiting anodic potentials in various supporting electrolytes have been determined. In alkali hydroxide the oxygen overvoltage was found to be negligible. Anodic dissolution patterns of thin layers of metallic thallium and cathodic dissolution patterns of thallic oxide are presented. The standard potential of the reaction

$$2Tl^+ + 6OH^- \rightleftarrows Tl_2O_3\,(s) + 3H_2O + 4e$$

was found to be -0.23 ± 0.02 volt *vs.* S.C.E. ($+0.02$ *vs.* N.H.E.) at 25°.

Thallous–thallic potentials have been studied by various authors[2-5] in acid solutions. Jonas[6] investigated the characteristics of a thallium storage battery in alkaline medium. Recently Delahay and Stiehl[7] described the anodic oxidation of thallous thallium at a rotated platinum micro-anode using a manual technique. They obtained well defined waves in alkaline solutions; however, large deviations (from 5 to 20%) from proportionality between diffusion current and concentration were observed.

Experiments with an automatic recording polarograph, and also with a manual apparatus, reported in this paper, show that anodic diffusion currents of thallous thallium are proportional to concentration to better than 2%. Evidence is given that the anodic reaction involves two electrons. Anodic dissolution patterns of micro-quantities of metallic thallium and cathodic dissolution patterns of thallic oxide are presented and discussed.

Experimental

Materials Used.—Thallous sulfate, C. P., was obtained from Fairmount Company.

(1) On leave from the Hebrew University, Jerusalem, Israel.

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