either (a) preliminary isomerization of the double bonds to the conjugated form, or (b) 1,6-hydrogenation is required to account for appearance of the remaining double bond at other than the alpha position. Attempts to effect a catalytic isomerization of 1,5-hexadiene with active sulfide catalyst in the presence of an inert gas were fruitless; after 6 hours at 150° in the presence of nitrogen, the hydrocarbon and catalyst were recovered essentially unchanged, and no conjugated diene could be detected by ultraviolet absorption analysis. It would appear, therefore, that if isomerization does occur, hydrogen is required as in the catalytic isomerization of polyunsaturated acids.8 This has been found to be the case in the double bond shift isomerization of butenes over metal film catalysts at room temperature in these laboratories,⁹ as well as over unsupported metal sulfide catalysts¹⁰ at 250°. In the latter experiments, atmospheric pressure was used and hydrogenation of double bonds was rapid. In the present work (at 150°), pentene-2 and hexene-1 were not isomerized and only very slowly hydrogenated. Any double bond isomerization with 1,5-hexadiene is unfortunately obscured in the present case by concomitant hydrogenation. However, by combining the hydrogenation products from a number of experiments and removing the hexene by distillation, a small amount of material

(8) G. H. Twigg, Proc. Roy. Soc. (London), A178, 106 (1941).

(9) O. Beeck, et al., unpublished results.

(10) B. S. Greensfelder, R. M. Roberts and F. T. Eggertsen, Emeryville Laboratories of Shell Development Company, unpublished results. equivalent to about 10% of the original hexadiene was recovered boiling in the range expected for the hexadiene dimer (200°) and having a terpene-like odor. This indicates that at least some conjugated diene is formed, permitting dimerization *via* a Diels-Alder type reaction.

In order to establish whether or not conjugation of multiple double bonds must precede hydrogenation over the sulfide type catalysts, as in (a) above, a hydrocarbon which could not become conjugated by virtue of its structure was studied. Dihexene (I), the dimer of 2-methyl-1,3-pentadiene, having a geminally substituted carbon atom between the two double bonds, cannot be isomerized by simple double bond shift via the movement of successive adjacent hydrogen atoms to the conjugated form. When this compound was subjected to hydrogenating conditions only a small absorption of hydrogen was found.⁷ It is concluded, therefore, that selective hydrogenation with sulfide type catalysts occurs only with conjugated systems or those which first become conjugated over the catalyst through double bond isomerization in the presence of hydrogen.

Acknowledgment.—The authors are indebted to other members of the staff of Shell Development Company, in particular, to R. C. Morris for providing samples of cyclohexadiene and dihexene, to W. R. Harp, Jr., and F. S. Mortimer for spectroscopic analysis of dihexene, and to S. G. Balestrieri and Miss M. B. Hofacker for assistance in experimental work.

Emeryville 8, Calif.

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

The Transfer of Oxygen Atoms in Oxidation–Reduction Reactions. III. The Reaction of Halogenates with Sulfite in Aqueous Solution

By Joseph Halperin¹ and Henry Taube

The extent of transfer of oxygen atoms from the oxidizing agent to the reducing agent on the reaction of various halogenates with sulfite in aqueous solution has been measured with O^{18} as tracer element. The number of oxygen atoms transferred per mole of halogenate on complete reduction to halide ion was observed to be 2.29 for Clo_2^- , 1.50 for Clo_2 , 1.55 for Clo_2^- , 0.36 for Cl_2O and 2.20 for BrO_2^- , for a solution 0.1 *M* in HCl at 25°. Except for Cl_2O , which was not intensively studied, it was found that the values for transfer are independent of the order of mixing, and decrease slightly as the pHincreases. The data are interpreted on the basis that reduction takes place stepwise (*e.g.*, $ClO_2^- \rightarrow ClO_2^- \rightarrow ClO^- \rightarrow Cl^- \rightarrow)$ and that the defect from complete transfer takes place in the hypochlorite stage. With ClO_2 , the first step is a process bimolecular in ClO_2 , forming ClO_2^- of the same isotopic composition as ClO_2 . The interpretation is consistent with rate laws where they have been determined, and with the chemistry of the systems. When ClO_2 disproportionates in alkali, the ClO_2^- formed has isotopic composition almost identical with the original ClO_2 , with only a minor dilution by solvent oxygen.

In the reaction of oxy-oxidizing agents such as ClO_3^- , NO_3^- , MnO_4^- with reducing agents in an oxide labile solvent such as water, either the solvent or the oxidizing agent may be the source of oxygen which is added to the reducing agent on oxidation. Experiments using O^{18} as tracer have shown² that in the oxidation of sulfite by nitrite, the oxygen appearing on the sulfite is derived from the solvent. Preliminary tracer experiments³ in the reaction of chlorate with sulfite showed that in this reaction, a part but not all of the oxygen added to sulfite is derived from the oxidize is derived from the oxidized to sulfite to sulfite the oxidized to sulfite to sulfite the oxidized to sulfite to sulfite the oxidized to s

(1) A.E.C. Predoctoral Fellow, 1949-1950.

(2) A. C. Rutenberg, J. Halperin and H. Taube, THIS JOURNAL, 73, 4487 (1951).

(3) J. Halperin and H. Taube, ibid., 72, 3319 (1950).

The experimental technique has been considerably refined since publication of the preliminary results on the chlorate-sulfite system, and the observations on the system have been amplified. The tracer method has been applied also to the reactions with sulfite of other halogenates, namely, ClO_2 , ClO_2^- , HClO, Cl_2O and BrO_3^- . In the present paper the experimental methods are described, pertinent exchange data are presented and the results of the tracer experiments reported. Observations made on the path of oxygen in the disproportionation of ClO_2 by alkali are also included.

Experimental Method

The steps involved in carrying out a tracer experiment on the oxidation of sulfite by halogenates were: preparation of

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the O¹⁸ enriched oxidizing agent, or of the enriched sulfite in equilibrium with water, and of the reagents of normal composition; mixing the reagents to bring about reaction; sepa-rating the product sulfate as BaSO, in pure form; reducing the BaSO, with carbon; and mass spectrometric analysis of CO_2 and O_2 .

Preparation of Materials .- The tracer experiments required either the oxidizing agent or the sulfite to be enriched in O¹⁸. In most of the experiments, the sulfite was enriched since this is more conveniently done. SO_2 and H_2O reach isotopic equilibrium very rapidly (*vide infra*) and SO_2^* aq.⁴ was prepared simply by bubbling SO_2 gas into enriched water. KClO,* was prepared by the disproportionation of chlorine in enriched aqueous potassium hydroxide. On cooling the solution, the salt crystallized. It was separated and purified by crystallization. KBrO₂* was prepared in a similar manner.

Of the reagents of normal composition, only a few will be given mention. The sodium chlorite was made from a commercial preparation by recrystallizing it twice, then drying it in a vacuum. Chlorine dioxide was generated by treating sodium chlorite in excess with 1 M HNO₂. It was extracted into CCl4, this solution dried with anhydrone, then was extracted back into water. Chlorine monoxide was prepared by treating a solution of chlorine in CCl₄ with HgO.⁴ A water solution of hypochlorous acid was prepared by treating a solution of Cl₂O in CCL with water.

Procedure in Bringing about Reaction.—The oxidizing agent was used in excess (up to 50%) to avoid formation of sulfate by air oxidation of sulfite on exposure of the product solution. Air was excluded from the reaction system while reaction was in progress. In most cases, reaction was brought about by adding one solution slowly to the other, with constant stirring, and the experiment repeated reversing the order of mixing. Under most conditions, the reactions studied take place very rapidly and by reversing the order of mixing a considerable variation in the concentration of the reactants can be achieved.

The solutions of SO₂ aq. were ca. 0.1 M. Usually about equal volumes of the reactant solutions were used. The concentrations of hydrochloric acid recorded refer to acid added. The buffer solutions described as being at $pH \sim 5$ contained 0.5 M NaOAc and 0.5 M HOAc.

Isotope Analyses.—The product sulfate was separated as BaSO₄ by centrifuging the solution, it was washed three times with 0.1 M HCl, then with water and dried at ca. 110°. To bring about reduction, the salt was mixed with carbon (mole ratio ca. 1:5) in a small platinum crucible which was then placed on a platinum support in position with respect to the working coils of the induction heater. The crucible was covered, and the reaction vessel closed and evacuated. To degas the materials, they were pumped on while being heated for about 15 minutes just below the temperature re-quired to bring about rapid reaction. The reduction took place as the temperature was gradually increased over a period of 30 to 45 minutes. Under the conditions used, about 75% of the overant processor of the coabout 75% of the oxygen was converted to CO_2 , the remainder to CO. Only the CO_2 was analyzed in the mass spectrometer.

The highest precision in the reduction was obtained with graphite powder prepared by scraping a spectroscopic graphite rod. The carbon powder was heated in vacuo to degas it, nitrogen being admitted before exposing it to air. It should be pointed out that at the temperatures required for the reduction of $BaSO_4$ (*ca.* 1000°) oxides of carbon exchange fairly rapidly with quartz. By using induction heating, the glass envelope remains cool, and isotope dilution by the containing materials is avoided.

Isotopic analysis of water was made by equilibrating it with CO₂, and measuring the isotope ratio in the CO₂. SO₂ aq. was analyzed isotopically by oxidizing it with iodine, then treating the sulfate as described above. KClO3, KBrO2, KIO2, AgIO3, NaClO2 and Pb(ClO2)2 were heated to yield oxygen, and the isotope ratio was determined in the oxygen. Pb^{++} is a very suitable precipitant for ClO_2^{-} since $Pb(ClO_2)_2$ is sparingly soluble, anhydrous and is readily decomposed. On heating some of the halogenates to

(4) The symbol SO₂ aq, or the term sulfite will be used to represent the "total sulfite" in solution. The asterisk denotes any species prepared anriched in O¹⁸.

(5) "Gmeline Handbuch des auorganische Chemie," 8th edition, Vol. 6, Veriag Chemie, Leipzig, Bartin, 1925, p. 288.

generate oxygen gas a small amount of side reaction took place, presumably forming halogen oxides.

To test the precision of the results separate reductions and isotope ratio analyses were made on a single sample of basso. The average deviation from the mean was observed to be 0.3%. The mass spectrometer readings themselves can be made to a precision of 0.1%. The imprecision observed is probably produced in the reduction step. Two obvious causes are: contamination by atmospheric oxygen adsorbed on the carbon, and variations in isotope fractionation resulting from the formation of the dual products CO₂ and CO. No isotopic dilution takes place in the handling to which the BaSO4 is subjected prior to reduction and, except for variations introduced by the chemistry of the processes, a precision of $\pm 0.3\%$ on the isotopic ratios can be expected. For the substances which are decomposed completely to oxygen, the precision in the isotope ratios is limited only by the readings on the mass spectrometer.

Treatment of the Data.-Some useful symbols will be defined, and the calculation of oxygen atom transfer outlined by reference to the following reaction which is typical of those studied.

$$ClO_2 + 2^{1}/_2SO_3 + 1/_2H_2O = Cl^{-} + 2^{1}/_2SO_4 + H^{+}$$

J is the total number of oxygen atoms in the product sulfate formed by the reaction of 1 molecule of oxidizing agent. In the reaction above, J is 10.

n is the number of oxygen atoms derived from the oxidizing agent in the product sulfate per molecule of oxidizing agent reacting.

Z represents the total change in oxidation number for each molecule of oxidizing agent consumed (in this case 5).

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

 N_S is the mole fraction of O¹⁸ in the species S. The normal case can be considered to be one in which $Z/2 = n_{max}$, *i.e.*, the oxidizing agent can at maximum supply oxygen atoms equivalent to the change in oxidation number. This is the situation for ClO_1^- , ClO_2^- and ClO^- reacting with sulfite. With Cl_2O and ClO_2 , the oxygen content of the oxidizing agent is insufficient to account for the total change in oxidation number, and some oxygen must be derived from the solvent whatever be the mechanism of oxidation. In other cases, results for some of which will be described in a later publication, n_{max} exceeds Z/2. From the mass spectrometer readings, the various values of N_S are obtained and from these, together with the value of

J, n can be calculated.

$$n = \frac{N_{\rm SO_4} - N_{\rm solv.}}{N_{\rm ex} - N_{\rm solv.}} \quad (J)$$

It can be seen from the form of the equation that as $N_{\rm solv}$ is approached by $N_{\rm SO_4}$ or $N_{\rm ox}$ an error in these results is greatly magnified as an error in n. In a majority of the experiments, N_{604} or N_{cx} differed from N_{colv} by 25% or less, so that an error in the measurement of N is magnified 4 or 5 times (on a fractional basis) in the value calculated for n. The precision of the value of n in the sulfite work is about ± 0.05 , and in the work on the disproportionation of ClO₂, ± 0.015 . Effects due to isotope fractionation which arise from the circumstance that the oxidizing agent was used in slight excess are not expected to be great enough to affect noutside the precision of the measurements.

Results

Exchange Reactions .- A condition for the success of the tracer method as applied in these systems is that the oxidizing agent and the product sulfate do not exchange oxygen rapidly with the environment. Work⁶⁻⁸ on the exchange rates for some of the substances has been done, but not in every case under conditions such that the results apply directly to our tracer experiments. Studies of the exchange under the conditions of the oxidation-reduction reactions were therefore made. The results, although complete enough only for the purpose at hand, are reported since the data are considerably more accurate than in the earlier work referred to. The higher sensitivity of the present method re-

(6) N. F. Hall and O. R. Alexander, THIS JOURNAL, 62, 3455 (1940). (7) G. A. Mills, ibid., 62, 2833 (1940).

(8) B. R. S. Winter, M. Carlton and H. V. A. Briscoe, J. Chem. Soc., 181 (1940).

sults from the fact that the isotopic composition of the anions was followed directly, rather than by tracing the change in the composition of the solvent.

The experiments on the exchange of SO_2 with water were performed by passing the gas into enriched water adjusted to the desired acidity, then quenching the exchange by oxidizing with iodine. The exchange in 0.1 *M* HCl is complete in 5 min. It is so rapid in fact that when SO_2 is passed into water already containing iodine, the product sulfate has the isotopic composition of the solvent. At *p*H 5 the exchange is still rapid, but under these conditions the exchange rate and the rate of oxidation by I_2 are about the same. The data on the exchange of SO_2 and water are presented in Table I.

TABLE I

THE EXCHANGE OF SO₂ WITH WATER

Temp., 25	• •	1180.	=	2.100	х	10
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No.	Conditions	Time before I: added, min.	$N_{\rm H2O} \ imes 10^3$	$\stackrel{N_{\mathrm{SO4}}}{\times 10^{2}}$
1	0.1 M HCl	5	15.830	15.816
2	0.1 M HCl	0 ª	15.830	15.742
3	$p_{ m H}\sim 5$	5	15.713	15.885
4	$_{p\mathrm{H}}\sim 5$	5	15.713	15.838
5	$p_{\rm H} \sim 5$	0 °	15.713	14.442
6	$0.4 M OH^-$	5	15.399	15.407

M OH⁻ with ClO₂⁻ at 0.9 M, $i_{1/2}$ is greater than 190 hr. The rate remains slow in the presence of ClO₂. Since the electron exchange between ClO₂ and ClO₂ is rapid¹⁰ the experiment proves that the rate of exchange between ClO₂ and water is not rapid. The half-time for the exchange of BrO₃⁻ in 0.48 M solution can be set at > 200 hr. IO₂⁻ on the other hand exchanges very rapidly with water. A sample of enriched KIO₃ recrystallized from ordinary water was found to be normal in isotopic composition. The exchange was also studied more directly, removing IO₃⁻ from the reaction mixture as KIO₄ by chilling the solution. The exchange was found to be complete in less than 1.5 min. at room temperature.

The reaction of the oxidizing agents ClO_3^- , ClO_2^- , ClO_2^- and BrO_3^- in acid solution with SO_2 aq. is sufficiently rapid compared to the exchange to make the tracer method applicable without serious complication.

The Reaction of Chlorate and Sulfite.—The equation for the net change in the reaction of chlorate and sulfite in acid is

$$ClO_3^- + 3\Sigma H_2 SO_3 = Cl^- + 3\Sigma H_2 SO_4$$

The reaction has been studied kinetically and was found¹¹ to proceed by the rate law

$$\frac{-\mathrm{d}(\mathrm{ClO}_3^-)}{\mathrm{d}t} = k_1(\mathrm{ClO}_3^-)(\mathrm{H}_2\mathrm{SO}_3)$$

At 0° and low ionic strength k_1 is 2.4 ± 0.31 . mole⁻¹ min.⁻¹. The data on the transfer of oxygen atoms in the reaction of chlorate and sulfite are summarized in Table II.

^a SO₂ passed into I₂ aq.

Jan. 20, 1952

TABLE II

OXYGEN ATOM TRANSFER IN THE REACTION OF CHLORATE AND SULFITE (Temp. 25° except in experiments 10 and 11)

No.	Conditions	$\stackrel{N_{ m solv.}}{ imes 10^3}$	$\frac{N_{\rm Cl0s}}{\times 10^3}$	$\frac{N_{\rm BO4}}{\times 10^3}$		na
1	2 M HCl, ClO_3^{*-} aq. to SO_2 aq.	2.099	11.270	3.930		2.51*
2	2 M HCl, SO ₂ into ClO_3^{*-} aq.	2.099	11.270	3.926		2.50^{b}
					Av.	2.51
3	0.1 <i>M</i> HCl, ClO_{2}^{*-} to SO_{2} aq.	2.099	11.270	3.820		2.26
4	.1 M HCl, as above, 20 min.	2.099	11.270	3.765		2.18
5	.1 M HCl, ClO ₃ ^{*-} to SO ₂ aq.	2.099	11.270	3.872		2.32
6	.1 M HCl, SO ₂ into ClO ₃ ^{*-} aq.	2.099	11.270	3.885		2.34
7	.1 M HCl, SO ₂ to ClO ₃ in H ₂ O [*]	15.360	2.102	12.848		2.28
8	.1 M HCl, SO ₂ * aq. to ClO ₃ ⁻ aq.	15.642	2.102	13.003		2.34
9	.1 M HCl, ClO ₂ ⁻ aq. to SO ₂ [*] aq.	15.880	2.102	13.230		2.31
					Av.	2.29
10	$p m H\sim$ 5, ClO $_3^{-*}$ aq., SO $_2$ aq. at 75°	2.099	11.270	3.573		1.93
11	$p{ m H}\sim$ 5, ClO ₃ - aq., SO ₂ * aq. at 75°	15.820	2.102	13.869		1.69
					Av.	1.81

^a Compare with $n_{\text{max}} = Z/2 = 3$. ^b Corrected for ClO₂⁻ - H₂O exchange.

The result obtained for alkaline solution is of interest in connection with the conclusion of Hall and Alexander⁶ that SO_i^{-} does not exchange with water even after 5 hours in 0.2 N NaOH at 95°.

No exchange was observed in 0.9 M or 6 M H₂SO₄ during time periods of 59 and 9 hours, respectively, at room temperature. These observations place a lower limit for the half-time of oxygen exchange at ca. 1 yr. for 0.9 M H₂SO₄ and 2 months for 6 M H₃SO₄. However, the concentrated sulfuric acid in the process of dilution to the 0.9 M H₂SO₄ exchanged 1.0 \pm 0.2% of its oxygen, and during the dilution to 6 M H₃SO₄ exchanged 7.1 \pm 0.2% of its oxygen. During mixing, regions containing H₃SO₄ at high concentration in enriched water will exist, and this circumstance⁹ together with the increased temperature may account for the initial exchange.

count for the initial exchange. Chlorate ion, 0.59 M in 0.14 M HCl at 25° exchanges with the solvent at a rate corresponding to a half-time of 13 hr. In 1 M ClO₂⁻ and 1.95 M HCl the half-time is 3.4 hr. Chlorite (0.56 M) in 0.24 M HClO₄ exchanges with the solvent at a rate corresponding to a half-time greater than 18 hr. The rate remains slow when HClO₄ is replaced by HCl, and becomes even slower as the acidity is decreased. In 0.4

(9) E. R. S. Winter and H. V. A. Briscoe, J. Chem. Soc., 631 (1942).

Transfer of oxygen atoms from the oxidizing agent to the sulfite takes place under all conditions tested. In every case, however, the transfer is less than the maximum of three per ClO₃⁻. The fraction transferred is independent of the order of mixing (*i.e.*, of the ratios $(SO_2)/(H_2O)$, $(SO_2)/(ClO_3^-)$ over wide ranges). The values of *n* are independent within the limits of experimental error $(\pm 0.05 \text{ in } n)$ of whether ClO₄⁻ or SO₂ aq. is enriched. This proves that within the precision of the results there are no important effects due to contamination or isotope fractionation. There is a definite trend to lower values of *n* as the acidity decreases. At *pH* 5, the reaction becomes very slow, and it was necessary to heat the solution. The values at this *pH* diverge considerably, the lower one being less dependable.

Is a definite trend to lower values of π as the activity decreases. At pH 5, the reaction becomes very slow, and it was necessary to heat the solution. The values at this pH diverge considerably, the lower one being less dependable. The Reaction of Chlorite and Sulfite.—The reaction between chlorite and sulfite in acid is very rapid, and is essentially complete in less than 1 minute at the concentration levels used both at pH 5 and in 0.1 *M* HCl. The principal net change is

$$ClO_{9}^{-} + 2\Sigma H_{9}SO_{4} = Cl^{-} + 2\Sigma H_{9}SO_{4}$$

In addition, however, ClO₂- is formed in appreciable

(10) H. Dodgen and H. Taube, THIS JOURNAL, 71, 2501 (1949).
 (11) A. C. Nixon and K. B. Krauskopi, *ibid.*, 54, 4606 (1932).

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amounts, as well as detectable amounts of ClO₂, the latter only when the oxidizing agent is used in excess and after the sulfite has been consumed. Some experiments were conducted to learn the extent of the side reaction under the experimental conditions. In a medium 0.1 *M* HCl, ClO₂⁻ in 50% excess added to the solution containing HCl and sulfite, 0.1 mole ClO₃⁻ is formed for each mole of ClO₂⁻ consumed. With ClO₂⁻ in 15% excess, 0.085 mole ClO₃⁻ forms for each mole of ClO₂⁻ consumed. At ρ H 5, with ClO₂⁻ again in 50% excess, 0.045 mole ClO₃⁻ forms for each mole of ClO₂⁻ consumed, independent of the order of mixing.

The results of the tracer experiments are presented in Table III.

TABLE III

Oxygen Transfer in the Reaction of Chlorite and Sulfite

Temp., 25°, $N_{\rm ClO_2}^- = 2.074 \times 10^{-3}$

No.	Conditions	$rac{N_{ m solv}}{ imes 10^3}$	NS04	n^a
1	$0.1 M$ HCl, ClO_2^- aq. to SO_2^* aq.	15.430	12.739	1.61
2	.1 M HCl, SO2* aq. to ClO2 - aq.	15,430	12.846	1.55
3	.1 M HCl, SO2* aq. to ClO2 - aq.	15.880	13.330	1.48
4	.1 M HC1, C1O ₂ ⁻ aq. to SO ₂ * aq.	15.880	13.212	1.55
			Av.	1.55
5	$ ho m H \sim 5$, SO2* aq. to ClO2 $^-$ aq.	15.148	12.848	1.23
6	$p \mathrm{H} \sim 5$, SO2* aq. to ClO2 ⁻ aq.	15.713	13.621	1.26
			Av.	1,25
7	$pH \sim 5$, SO2 into ClO2 ⁻ in H2O*	15.713	13.561	1.41
۹ (Compare to $n_{\max} = Z/2 = 2$.			

TABLE IV

Oxygen Atom Transfer in the Reaction of Chlorine Dioxide and Sulfite

Temp., 25°; $N_{ClO_2} = 2.07 \times 10^{-3}$					
No.	Conditions	$\stackrel{N_{ m solv.}}{ imes 10^3}$	$\stackrel{N_{\mathrm{SO4}}}{\times} \stackrel{=}{}_{10^3}$	n^{a}	
1	0.1 M HCl, SO2* aq. to ClO2 in CCli	15.360	13.611	1.33	
2	.1 M HCl, ClO ₂ aq. to SO ₂ * aq.	15.880	13.781	1.52	
3	.1 M HCl, SO ₂ * aq. to ClO ₂ aq.	15.880	13.837	1.48	
			Av,	1.50	
4	pH 5, SO2* aq. to ClO2 aq.	15.713	14.024	1.24	
5	<i>p</i> H 5, SO ₂ * aq. to C1O ₂ aq.	15.820	14.232	1.16	
			Av,	1,20	

^a Compare to $n_{\text{max}} = 2$.

since some chlorate is formed,¹⁴ in addition to Cl^- which is the major chlorine containing product.

A summary of the results obtained in experiments on transfer of oxygen from ClO_2 to sulfite is contained in Table IV. The behavior of ClO_2 in respect to transfer of oxygen is similar to that of ClO_2^{-} .

The Reactions of Hypochlorous Acid and Chlorine Monoxide with Sulfite.—In one experiment 0.2 ml. of 1 *M* HOCl was added with vigorous stirring to 5 ml. of 0.02 *M* SO₂* aq. in 0.2 *M* HCl. This experiment yielded for *n* the value of 0.05, which lies within experimental error of what would be expected for no transfer from oxidizing agent to sulfite. The experiment must be regarded as inconclusive. A very rapid exchange of HOCl and H₂O can be expected via the chlorine equilibrium,¹⁶ if not by a more direct path. The low value of *n* may have arisen because HOCl was not distributed sufficiently rapidly for the reaction with sulfite to compete successfully with exchange.

In an experiment with Cl₂O, 0.25 ml. of 0.4 M Cl₂O in CCl₄ was mixed with 1.0 ml. 0.1 M SO₂* aq. in 0.1 M HCl. The value of n for the experiment was found to be 0.36.

The Reaction of Bromate with Sulfite.—The reaction of BrO_3^- and sulfite in acid solution takes place rapidly¹⁶ with Br^- as the only bromine containing product. The results obtained in measurements of oxygen atom transfer are presented in Table V.

The Disproportionation of Chlorine Dioxide in Alkali.---

$$2C1O_2 + 2OH^- = C1O_3^- + C1O_2^- + H_2O$$

takes place in alkali following a rate law expressed by the equation $^{\rm 17}$

$$\frac{-\mathrm{d}(\mathrm{ClO}_2)}{\mathrm{d}t} = k_3(\mathrm{ClO}_2)^2(\mathrm{OH}^-)$$

At 0° , $k_3 = 230 \ 1.^2 \ \text{mole}^{-2} \ \text{min.}^{-1}$. In the tracer experiments, ClO₂ was added to 0^{*}H^{-} aq., the products ClO₃⁻ and ClO₂⁻ were separated as KClO₃ and Pb(ClO₂)₃, respectively, and the oxygen isotope composition after analysis compared with that of the starting material. The results are summarized in Table VI. It is evident that the reaction closely approximates the

It is evident that the reaction closely approximates the condition assumed in calculating $N_{caled.}$, *i.e.*, there is very little transfer of oxygen from one molecule of ClO₂ to another in forming the products, and there is very little exchange with the solvent. There is however a small definite contribution by the solvent to the oxygen content of the chlorite, and complementarily, a defect in the amount picked up from the solvent in forming chlorate.

TABLE V

OXYGEN ATOM TRANSFER IN THE REACTION OF BROMATE AND SULFITE

(Temp., 25°)

	()	· ···· · · · · · · · · · · · · · · · ·			
No.	Conditions	$N_{\rm solv}, \times 10^3$	$N_{ m BrOs}$ - $ imes$ 10 °	$N_{\rm SO4}$ $ imes$ 10 ³	n^a
1	0.1 M HCl, SO ₂ aq. to BrO_3^{*-}	2.099	11.394	3,786	2.20
2	.1 M HCl, BrO ₃ *-	2.099	11.394	3.794	2.21
3	.1 M HCl, SO ₂ * aq. to BrO ₃ aq.	15.644	2.120	13.154	2.21
4	.1 M HCl, SO ₂ * aq. to BrO ₃ -	15.880	2.120	13.390	2.17
				Av.	2.20
5	pH 5, SO ₂ aq. to BrO ₃ * ⁻ aq.	2.104	11.394	3.763	2.14
6	pH 5, SO ₂ * aq. to BrO ₃ aq.	15.820	2.120	13.504	2.03
" Compare	to $n_{\max} = Z/2 = 3$.				

As in the chlorate case, n is lower than n_{\max} , and decreases slightly as pH increases. Experiment 7 as compared to 5 and 6 suggests that when a very low steady state concentration of SO₂ aq. is maintained, n increases slightly.

The Reaction of Chlorine Dioxide with Sulfite.—The reaction of ClO_2 and SO_2 aq. takes place very rapidly. In strongly acid solution the rate law

$$\frac{-\mathrm{d}(\mathrm{ClO}_2)}{\mathrm{d}t} = k_2(\mathrm{ClO}_2)^2(\mathrm{H}_2\mathrm{SO}_3)$$

describes the kinetics. k_2 decreases as the acidity increases, and at the lowest acidity studied by Holst,¹² 2.1 N H₂SO₄, has the value 780 at 25°. The reaction has been used for the quantitative determination of ClO₂,¹³ but is not accurate

Discussion

The results on oxygen atom transfer for chlorate and chlorite can be understood on the basis that reduction by sulfite takes place stepwise with complete transfer of oxygen from the oxidizing agents in the steps $ClO_3^- \rightarrow ClO_2^-$ and $ClO_2^- \rightarrow$ ClO^- . The defect of *n* from n_{max} can be attributed to the last stage of reduction in which hypochlorite is reduced to chloride ion. Observations on the chemistry as well as the present work on oxygen

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TABLE VI

Path of Oxygen in the Disproportionation of ClO_2 in

Alkali

Temp., 25°; $N_{\rm ClO_2} = 2.074 \times 10^{-3}$, a separate experiment was done for each of the products

Froduct analyzed	$\stackrel{N_{ m H2O}}{ imes10^3}$	$\stackrel{N_{\mathrm{prod}}}{ imes 10^8}$	$\stackrel{N^a { m calcd.}}{ imes 10^3}$	No. of O atoms from solvent
ClO_2^-	15.407	2.408	2.074	0.048 ± 0.015
C1O3-	15.184	6.340	6.444	0.972 ± 0.015
				1.1 01.0

^a Calculated on the basis that isotopic composition $ClO_2 = ClO_2^-$, and that ClO_3^- in being formed derives one atom of oxygen from the solvent.

atom transfer show that there are differences in detail between the chlorate and chlorite systems. The difference can be attributed to the differences in the concentrations of ClO₂⁻ and ClO⁻ maintained in the two systems. The first stage of reduction for ClO_3^- is slow. Since the succeeding stages are rapid, ClO^- and ClO_2^- will be present at much lower steady state concentrations than is the case with ClO_2^- as starting material. The reaction of hypochlorite (or chlorine) with chlorite is exceedingly rapid, and can be expected to play an important role in the reduction of ClO_2^- by sulfite, but only a minor role when ClO_3^{-} is the oxidizing agent. To explain the excess transfer observed for ClO_2^- as compared with ClO_3^- (the "hypochlorite'' stage has a value for $n \ ca. \ 0.2$ greater in the case of ClO_2^{-}) it must be supposed that the intermediate formed on the reaction of HOCl and ClO_2^- has a higher efficiency for transfer than has HOCl itself and that, further, under all conditions tested with chlorite as oxidizing agent, hypochlorite reacts more rapidly with chlorite than with sulfite. It should be noted that the excess transfer observed for ClO_2^- as compared to ClO_3^- is not accounted for by making correction for the net formation of ClO_3^- . The correction reduces *n* for $ClO_2^$ relative to ClO3⁻, since the "wasteful" species HOCl is in part consumed to form ClO_{3} , but the change is only of the order of 0.03.

The point of view outlined finds some support in the direct experiments made with compounds of chlorine in the +1 state. Of these experiments, only the one with Cl₂O can be regarded as significant. This substance apparently hydrolyzes slowly enough so that it remains intact at least until it is uniformly distributed in the water phase. Reasonable possibilities for the first step of the reaction of Cl_2O are: reaction with Cl^- (to form Cl₂ and HOCl), with water (to form 2 HOCl) or with sulfite (to transfer Cl⁺ and form HOCl). In any of these events, HOCl is formed hence the value of n = 0.36 probably measures the value for hypochlorite. This value is within experimental error that observed indirectly in the experiments with ClO₃-

The production of ClO_2^- when ClO_2 is reduced has been observed directly for a number of reducing agents. The production of ClO_3^- on the reduction of ClO_2 as well as of ClO_2^- suggests similar paths for reduction in the two systems. Consistent with this view, with the rate law for the reaction, and with the present results on oxygen transfer, the first step in the reduction of ClO_2 by sulfite can be formulated as $2ClO_2^* + H_2SO_3 + H_2O \longrightarrow 2ClO_2^{*-} + H_2SO_4 + 2H^+$ Although ClO₂ is a free radical, participation by two molecules in the rate determining step places the system in the class of even-electron reactions. A path for the reduction by sulfite which is first order in ClO₂ might give distinctly different results for oxygen atom transfer (ClO would be expected as intermediate in this case). A very low concentration of ClO₂ may be required, however, to bring out the first-order path.

The reduction of BrO_{3}^{-} by sulfite can be interpreted in a manner analogous to that outlined for ClO_{3}^{-} . In the system also the defect in *n* from the maximum value 3 can be attributed to the hypohalite stage. It is interesting to note that sulfite competes favorably in reacting with BrO_{2}^{-} against exchange of BrO_{2}^{-} with water, or reduction by Cl^{-} or Br^{-} .

The results on transfer rule out for the reaction of sulfite and chlorate (and of sulfite and chlorite) a mechanism involving a complex with a S-Cl bond analogous to the mechanism of the nitritesulfite reaction.² This path, in which the oxygen

$$2H^{+} + 0: \stackrel{\circ}{\underset{\circ}{\text{S}:}} + : \stackrel{\circ}{\underset{\circ}{\text{C}}{\text{I}:0}} \longrightarrow \begin{bmatrix} 0 & 0 & -\\ 0: \stackrel{\circ}{\underset{\circ}{\text{S}:}} \stackrel{\circ}{\underset{\circ}{\text{C}}{\text{I}:0}} \end{bmatrix} + H_2 0$$
$$\stackrel{\circ}{\underset{\circ}{\text{O}}{{O}}{{O}}{{O}}{\text{O}}{{O}}{\text{O}}{\text{O}}{{O}}{\text{O}}{\text{O}}{{O}}{{O}}{{O}}{{O}}{{O}{}{O}{}{O}}{{O}}{{O}}{{O}{}{O}{$$

added to the sulfite is derived from the solvent can at most make only a slight contribution. Two possibilities, both consistent with the rate law and with the experiments on oxygen transfer, remain. The first may be regarded as a replace-

ment on oxygen, SO_3^- replacing ClO_2^- . The second is analogous to the ester mechanism proposed¹⁸ for the oxidation of isopropyl alcohol by acid chromate. In forming the S-O-Cl bond, it can be expected that the S-O bond rather than O-Cl bond is ruptured, since sulfite in acid exchanges with solvent much more rapidly than does chlorate. If exchange of oxygen between water and sulfite were slow under the conditions of the oxidation, the two mechanisms could readily be distinguished. This is, however, not the case. Experiments in non-aqueous solution in which water is a reactant may lead to a decision.

If the interpretation of the data is correct, that the defect in n from n_{\max} occurs in the hypohalite state, it follows that the defect is not due to competition between exchange of HO*X with water,

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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 SO₂/H₂O 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: $ClO^- + SO_3^- \rightarrow Cl^- + SO_3^-$; in the other, X⁺ is transferred, forming a compound which then hydrolyzes.

$$OC1^{-} + SO_{2}^{-} + H^{+} \longrightarrow C1SO_{2}^{-} + OH^{-}$$

 $C1SO_{2}^{-} + H_{2}O = SO_{4}^{-} + 2H^{+} + C1^{-}$

The result obtained on the disproportionation of ClO₂ in alkali is explained most simply by assuming an unsymmetrical configuration for $(ClO_2)_2$ in the transition state

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 frac tion of the events, OH⁻ attacks the chlorine bearing the formal charge +1, the deviations from $n_{calcd.}$ in Table VI, are accounted for.

A few features of the exchange results merit comment. It seems likely that the difference in lability between IO₃⁻ on the one hand and BrO₃⁻ and CIO_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 coordination 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 ClO₂ 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 studies²⁰ 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 I2, SO2 aq. passed into O*H- in our case, K2SO3 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.

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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 Halperin¹ and Henry Taube

In the reaction of hydrogen peroxide with sulfite at pH 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 O₂ (at $pH \sim 5$), of MnO₂ (in 0.1 *M* HCl), and of MnO₄⁻ (at $pH \sim 6$), transfer from the oxidizing agent of 2.2, 0.97 and 0.2 atoms of oxygen, respectively, per formula unit of oxidizing areart reacting. 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 published2 on the first two reactions

(1) A.E.C. Predoctoral Fellow, 1949-1950.

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

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