

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(9) O. Beeck, *et al.*, unpublished results.

(10) B. S. Greensfelder, R. M. Roberts and F. T. Eggertsen, Emeryville Laboratories of Shell Development Company, unpublished results.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.

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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 O¹⁸ 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 ClO₃⁻, 1.50 for ClO₂, 1.55 for ClO₂⁻, 0.36 for Cl₂O and 2.20 for BrO₃⁻, for a solution 0.1 M in HCl at 25°. Except for Cl₂O, 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 pH increases. The data are interpreted on the basis that reduction takes place stepwise (*e.g.*, ClO₃⁻ → ClO₂⁻ → ClO⁻ → Cl⁻ →) and that the defect from complete transfer takes place in the hypochlorite stage. With ClO₂, the first step is a process bimolecular in ClO₂, forming ClO₂⁻ of the same isotopic composition as ClO₂. The interpretation is consistent with rate laws where they have been determined, and with the chemistry of the systems. When ClO₂ disproportionates in alkali, the ClO₂⁻ formed has isotopic composition almost identical with the original ClO₂, with only a minor dilution by solvent oxygen.

In the reaction of oxy-oxidizing agents such as ClO₃⁻, NO₃⁻, MnO₄⁻ 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 O¹⁸ 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 oxidizing agent.

(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.*, **73**, 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, ClO₂, ClO₂⁻, HClO, Cl₂O and BrO₃⁻. 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 ClO₂ 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

the O^{18} 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; separating the product sulfate as $BaSO_4$ in pure form; reducing the $BaSO_4$ 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 O^{18} . 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 $SO_2^* aq.$ was prepared simply by bubbling SO_2 gas into enriched water. $KClO_3^*$ 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. $KBrO_3^*$ 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* HNO_3 . It was extracted into CCl_4 , this solution dried with anhydrous, then was extracted back into water. Chlorine monoxide was prepared by treating a solution of chlorine in CCl_4 with HgO .⁵ A water solution of hypochlorous acid was prepared by treating a solution of Cl_2O in CCl_4 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 $SO_2 aq.$ 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 $BaSO_4$ 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 required 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 oxygen was converted to CO_2 , the remainder to CO . Only the CO_2 was analyzed in the mass spectrometer.

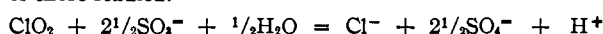
The highest precision in the reduction was obtained with graphite powder prepared by scraping a spectroscopic graphite rod. The carbon powder was heated *in vacuo* to degas it, nitrogen being admitted before exposing it to air. It should be pointed out that at the temperatures required for the reduction 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 CO_2 , and measuring the isotope ratio in the CO_2 . $SO_2 aq.$ was analyzed isotopically by oxidizing it with iodine, then treating the sulfate as described above. $KClO_3$, $KBrO_3$, KIO_3 , $AgIO_3$, $NaClO_2$ and $Pb(ClO_2)_2$ 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

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 $BaSO_4$. 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 CO_2 and CO . No isotopic dilution takes place in the handling to which the $BaSO_4$ 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.



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*_{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 O^{18} 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_2^+ , 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.

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

It can be seen from the form of the equation that as *N_{solv}* is approached by *N_{SO_4^-}* or *N_{ox}* an error in these results is greatly magnified as an error in *n*. In a majority of the experiments, *N_{SO_4^-}* or *N_{ox}* differed from *N_{solv}* 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 ClO_2 , ± 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 *n* outside 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-

(4) The symbol $SO_2 aq.$ or the term sulfite will be used to represent the "total sulfite" in solution. The asterisk denotes any species prepared enriched in O^{18} .

(5) "Gmelin Handbuch der anorganische Chemie," 8th edition, Vol. 6. Verlag Chemie, Leipzig, Berlin, 1926, p. 288.

(6) N. F. Hall and O. R. Alexander, *THIS JOURNAL*, **62**, 3455 (1940).

(7) G. A. Mills, *ibid.*, **62**, 2838 (1940).

(8) E. 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 pH 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 SO_2 WITH WATER
Temp., 25°; $N_{\text{SO}_2} = 2.100 \times 10^{-3}$

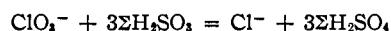
No.	Conditions	Time before I_2 added, min.	$N_{\text{H}_2\text{O}} \times 10^3$	$N_{\text{SO}_4^{2-}} \times 10^3$
1	0.1 M HCl	5	15.830	15.816
2	0.1 M HCl	0 ^a	15.830	15.742
3	$\text{pH} \sim 5$	5	15.713	15.885
4	$\text{pH} \sim 5$	5	15.713	15.838
5	$\text{pH} \sim 5$	0 ^a	15.713	14.442
6	0.4 M OH^-	5	15.399	15.407

^a SO_2 passed into I_2 aq.

M OH^- with ClO_2^- at 0.9 M , $t_{1/2}$ is greater than 190 hr. The rate remains slow in the presence of ClO_2 . Since the electron exchange between ClO_2 and ClO_2^- is rapid¹⁰ the experiment proves that the rate of exchange between ClO_2 and water is not rapid. The half-time for the exchange of BrO_3^- in 0.48 M solution can be set at > 200 hr. IO_3^- on the other hand exchanges very rapidly with water. A sample of enriched KIO_3 recrystallized from ordinary water was found to be normal in isotopic composition. The exchange was also studied more directly, removing IO_3^- from the reaction mixture as KIO_4 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



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

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

At 0° and low ionic strength k_1 is 2.4 ± 0.3 l. mole⁻¹ min.⁻¹.

The data on the transfer of oxygen atoms in the reaction of chlorate and sulfite are summarized in Table II.

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

No.	Conditions	$N_{\text{solv.}} \times 10^3$	$N_{\text{ClO}_3^-} \times 10^3$	$N_{\text{SO}_4^{2-}} \times 10^3$	n^a
1	2 M HCl , ClO_3^{*-} aq. to SO_2 aq.	2.099	11.270	3.930	2.51 ^b
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 M HCl , ClO_3^{*-} 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_2O^*	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_3^- aq. to SO_2^* aq.	15.880	2.102	13.230	2.31
				Av.	2.29
10	$\text{pH} \sim 5$, ClO_3^{*-} aq., SO_2 aq. at 75°	2.099	11.270	3.573	1.93
11	$\text{pH} \sim 5$, 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 $\text{ClO}_3^- - \text{H}_2\text{O}$ exchange.

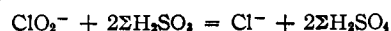
The result obtained for alkaline solution is of interest in connection with the conclusion of Hall and Alexander⁶ that SO_3^{2-} does not exchange with water even after 5 hours in 0.2 N NaOH at 95°.

No exchange was observed in 0.9 M or 6 M H_2SO_4 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 H_2SO_4 and 2 months for 6 M H_2SO_4 . However, the concentrated sulfuric acid in the process of dilution to the 0.9 M H_2SO_4 exchanged $1.0 \pm 0.2\%$ of its oxygen, and during the dilution to 6 M H_2SO_4 exchanged $7.1 \pm 0.2\%$ of its oxygen. During mixing, regions containing H_2SO_4 at high concentration in enriched water will exist, and this circumstance⁹ together with the increased temperature may account 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 ClO_3^- and 1.95 M HCl the half-time is 3.4 hr. Chlorite (0.56 M) in 0.24 M HClO_4 exchanges with the solvent at a rate corresponding to a half-time greater than 18 hr. The rate remains slow when HClO_4 is replaced by HCl , and becomes even slower as the acidity is decreased. In 0.4

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 ClO_3^- . The fraction transferred is independent of the order of mixing (*i.e.*, of the ratios $(\text{SO}_2)/(\text{H}_2\text{O})$, $(\text{SO}_2)/(\text{ClO}_3^-)$ over wide ranges). The values of n are independent within the limits of experimental error (± 0.05 in n) of whether ClO_3^- or SO_2 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.

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



In addition, however, ClO_3^- is formed in appreciable

(10) H. Dodgen and H. Taube, *This Journal*, **71**, 2501 (1949).

(11) A. C. Nixon and K. B. Krauskopf, *ibid.*, **84**, 4606 (1932).

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

amounts, as well as detectable amounts of ClO_2 , 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 , ClO_2^- in 50% excess added to the solution containing HCl and sulfite, 0.1 mole ClO_3^- is formed for each mole of ClO_2^- consumed. With ClO_2^- in 15% excess, 0.085 mole ClO_3^- forms for each mole of ClO_2^- consumed. At pH 5, with ClO_2^- again in 50% excess, 0.045 mole ClO_3^- forms for each mole of ClO_2^- 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

$$\text{Temp.}, 25^\circ, N_{\text{ClO}_2^-} = 2.074 \times 10^{-3}$$

No.	Conditions	$N_{\text{soln}} \times 10^3$	$N_{\text{SO}_4^-}$	n^a
0.1	0.1 M HCl , ClO_2^- aq. to $\text{SO}_2^* \text{ aq.}$	15.430	12.739	1.61
2	.1 M HCl , $\text{SO}_2^* \text{ aq.}$ to $\text{ClO}_2^- \text{ aq.}$	15.430	12.846	1.55
3	.1 M HCl , $\text{SO}_2^* \text{ aq.}$ to $\text{ClO}_2^- \text{ aq.}$	15.880	13.330	1.48
4	.1 M HCl , $\text{ClO}_2^- \text{ aq.}$ to $\text{SO}_2^* \text{ aq.}$	15.880	13.212	1.55
			Av.	1.55
5	$\text{pH} \sim 5$, $\text{SO}_2^* \text{ aq.}$ to $\text{ClO}_2^- \text{ aq.}$	15.148	12.848	1.23
6	$\text{pH} \sim 5$, $\text{SO}_2^* \text{ aq.}$ to $\text{ClO}_2^- \text{ aq.}$	15.713	13.621	1.26
			Av.	1.25
7	$\text{pH} \sim 5$, SO_2 into ClO_2^- in H_2O^*	15.713	13.561	1.41

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

TABLE IV

OXYGEN ATOM TRANSFER IN THE REACTION OF CHLORINE DIOXIDE AND SULFITE

$$\text{Temp.}, 25^\circ; N_{\text{ClO}_2} = 2.07 \times 10^{-3}$$

No.	Conditions	$N_{\text{soln}} \times 10^3$	$N_{\text{SO}_4^-} \times 10^3$	n^a
1	0.1 M HCl , $\text{SO}_2^* \text{ aq.}$ to ClO_2 in CCl_4	15.360	13.611	1.33
2	.1 M HCl , $\text{ClO}_2 \text{ aq.}$ to $\text{SO}_2^* \text{ aq.}$	15.880	13.781	1.52
3	.1 M HCl , $\text{SO}_2^* \text{ aq.}$ to $\text{ClO}_2 \text{ aq.}$	15.880	13.837	1.48
			Av.	1.50
4	pH 5, $\text{SO}_2^* \text{ aq.}$ to $\text{ClO}_2 \text{ aq.}$	15.713	14.024	1.24
5	pH 5, $\text{SO}_2^* \text{ aq.}$ to $\text{ClO}_2 \text{ aq.}$	15.820	14.232	1.16
			Av.	1.20

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

TABLE V

OXYGEN ATOM TRANSFER IN THE REACTION OF BROMATE AND SULFITE

(Temp., 25°)

No.	Conditions	$N_{\text{soln}} \times 10^3$	$N_{\text{BrO}_3^-} \times 10^3$	$N_{\text{SO}_4^-} \times 10^3$	n^a
1	0.1 M HCl , $\text{SO}_2 \text{ aq.}$ 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 , $\text{SO}_2^* \text{ aq.}$ to $\text{BrO}_3^- \text{ aq.}$	15.644	2.120	13.154	2.21
4	.1 M HCl , $\text{SO}_2^* \text{ aq.}$ to BrO_3^-	15.880	2.120	13.390	2.17
				Av.	2.20
5	pH 5, $\text{SO}_2 \text{ aq.}$ to $\text{BrO}_3^{*-} \text{ aq.}$	2.104	11.394	3.763	2.14
6	pH 5, $\text{SO}_2^* \text{ aq.}$ to $\text{BrO}_3^- \text{ aq.}$	15.820	2.120	13.504	2.03

^a Compare to $n_{\text{max}} = Z/2 = 3$.

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 $\text{SO}_2 \text{ aq.}$ is maintained, n increases slightly.

The Reaction of Chlorine Dioxide with Sulfite.—The reaction of ClO_2 and $\text{SO}_2 \text{ aq.}$ takes place very rapidly. In strongly acid solution the rate law

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

describes the kinetics. k_2 decreases as the acidity increases, and at the lowest acidity studied by Holst,¹² 2.1 N H_2SO_4 , has the value 780 at 25°. The reaction has been used for the quantitative determination of ClO_2 ,¹³ but is not accurate

(12) G. Holst, *Svensk Kemi. Tidssk.*, **56**, 369 (1944).

(13) M. Brandau, *Ann.*, **151**, 340 (1869).

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 $\text{SO}_2^* \text{ aq.}$ 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 H_2O can be expected via the chlorine equilibrium,¹⁵ 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 Cl_2O , 0.25 ml. of 0.4 M Cl_2O in CCl_4 was mixed with 1.0 ml. 0.1 M $\text{SO}_2^* \text{ aq.}$ 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.—The reaction



takes place in alkali following a rate law expressed by the equation¹⁷

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

At 0°, $k_3 = 230 \text{ l.}^2 \text{ mole}^{-2} \text{ min.}^{-1}$. In the tracer experiments, ClO_2 was added to $\text{O}^*\text{H}^- \text{ aq.}$, the products ClO_3^- and ClO_2^- were separated as KClO_3 and $\text{Pb}(\text{ClO}_2)_2$, 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 condition assumed in calculating $N_{\text{calcd.}}$ i.e., there is very little transfer of oxygen from one molecule of ClO_2 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.

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 $\text{ClO}_3^- \rightarrow \text{ClO}_2^-$ and $\text{ClO}_2^- \rightarrow \text{ClO}^-$. 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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(15) J. C. Morris, *This Journal*, **68**, 1692 (1946).

(16) A. Schwicker, *Chem. Z.*, **15**, 845 (1891).

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TABLE VI

PATH OF OXYGEN IN THE DISPROPORTIONATION OF ClO_2 IN ALKALI

Temp., 25°; $N_{\text{ClO}_2} = 2.074 \times 10^{-3}$, a separate experiment was done for each of the products

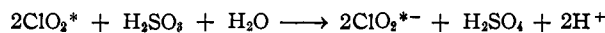
Product analyzed	$N_{\text{H}_2\text{O}} \times 10^3$	$N_{\text{prod}} \times 10^3$	$N_{\text{calcd.}} \times 10^3$	No. of O atoms from solvent
ClO_2^-	15.407	2.408	2.074	0.048 ± 0.015
ClO_3^-	15.184	6.340	6.444	0.972 ± 0.015

^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 ClO_2^- 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 ClO_3^- , 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 Cl_2O 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 Cl_2 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 ClO_3^- .

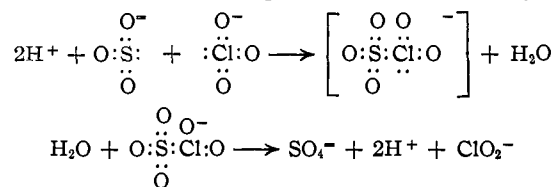
The production of ClO_2^- when ClO_2 is reduced has been observed directly for a number of reducing agents. The production of ClO_3^- on the reduction of ClO_2 as well as of ClO_2^- suggests similar paths for reduction in the two systems. Consistent with this view, with the rate law for the reaction, and with the present results on oxygen transfer, the first step in the reduction of ClO_2 by sulfite can be formulated as



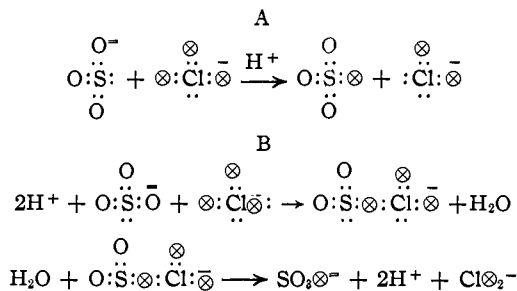
Although ClO_2 is a free radical, participation by two molecules in the rate determining step places the system in the class of even-electron reactions. A path for the reduction by sulfite which is first order in ClO_2 might give distinctly different results for oxygen atom transfer (ClO would be expected as intermediate in this case). A very low concentration of ClO_2 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 nitrite-sulfite reaction.² This path, in which the oxygen



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-

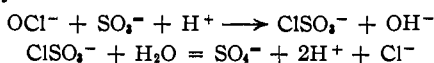


ment on oxygen, $\text{SO}_3^{\otimes-}$ replacing ClO_2^- . The second is analogous to the ester mechanism proposed¹⁸ for the oxidation of isopropyl alcohol by acid chromate. In forming the S-O-Cl bond, it can be expected that the S-O bond rather than O-Cl bond is ruptured, since sulfite in acid exchanges 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.

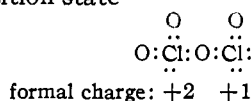
If the interpretation of the data is correct, that the defect in n from n_{max} occurs in the hypohalite state, it follows that the defect is not due to competition between exchange of HO^*X with water.

(18) F. Holloway, M. Cohen and F. H. Westheimer, *THIS JOURNAL*, **73**, 65 (1951).

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 $\text{SO}_2/\text{H}_2\text{O}$ 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: $\text{ClO}^* + \text{SO}_3^- \rightarrow \text{Cl}^- + \text{SO}_3^*\text{O}^-$; in the other, X⁺ is transferred, forming a compound which then hydrolyzes.



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



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_{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 coordination numbers greater than 3. In crystalline bromates and chlorates, the coordination number of the halogen is three, but in iodates, the coordination 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



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 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.

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CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE GOERGE 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 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 O_3 (at pH ~5), of MnO_2 (in 0.1 M HCl), and of MnO_4^- (at pH ~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 published² 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

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

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