reactions of hydroperoxo radical with iron(III) and iron(II) obtained by Barb, *et al.*,[14] and Shubin and Dolin.[17] Therefore, it seems more plausible that HO_2, and not O_2^-, is the reactive species.

It is of interest to note that the copper(II) catalyzed oxidation of arsenic(III) by persulfate at small copper concentrations is seven times as fast in the presence as in the absence of oxygen. Especially in oxidations of organic substances, oxygen usually acts as a powerful inhibitor. For example, this is the case in the copper(II) catalyzed oxidation of oxalate by persulfate.[18]

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[17] U. N. Shubin and R. I. Dolin, *Dokl. Akad. Nauk SSSR*, **140**, 1380 (1961).

[18] E. Ben-Zvi and T. L. Allen, *J. Am. Chem. Soc.*, **83**, 4352 (1961).

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Tracer Experiments with Ozone as Oxidizing Agent in Aqueous Solution

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When ozone reacts with sulfur dioxide in aqueous acid solution, as many as two ozone oxygens appear in each product sulfate ion. Corresponding to this excess transfer (only one O being required for the oxidation), the oxygen formed is found to have undergone exchange with the solvent. In alkaline solution, transfer in excess of one O for each sulfite ion is observed and some of the sulfate oxygen is derived from the solvent despite the fact that sulfite ion is not a labile species under these conditions. Ozone induces exchange between sulfate ion and water both in alkaline and acidic solution, but the reaction is so slow as not materially to affect the results which have been described. By contrast the isotopic course of the reaction of nitrite ion with ozone in alkaline solution is simple; the nitrate ion contains two oxygens derived from the nitrite and one derived from the ozone. Substantial ozone oxygen appears in the manganese dioxide and thallium(III) oxide which are formed in the reaction with ozone of Mn^{2+}(aq) and Tl^{+}(aq), respectively.

In this paper we describe the results of experiments done to trace the path of oxygen in reactions of ozone with a number of reducing agents. As will appear from the results, even in the absence of kinetic studies, which for some of the systems would be very difficult to perform, the tracer experiments illuminate the mechanisms of the reactions to a considerable extent. The reducing agents dealt with in this study are sulfite (sulfur dioxide) and nitrite ion which react with ozone in homogeneous solution, and Mn^{2+} and Tl^{+} which were studied under conditions so that the solid products, manganese dioxide and hydrous thallic oxide, are formed.

Experimental

Reagents. Ozone Preparation and Analysis.—Ozone was generated by silent electric discharge with a Welsbach Corp. Model T 23 ozonator, from tank oxygen dried with calcium sulfate. In experiments in which it was necessary to know the concentration of ozone in oxygen, several chambers with calibrated volumes (100 and 500 ml. were used), each completely immersed in a water–ice slush, were connected in series to the ozone generator, and ozone was passed through these for some time (say 30 min.). Each container was isolated, and some were taken for analysis, others for the desired reaction.

Quantitative determination of ozone concentration was carried out by gentle aspiration of a 100-ml. container of the gases into a train of two absorption flasks each containing *ca.* 25 ml. of (initially) neutral 0.1 *F* potassium iodide solution. These solutions were combined after *ca.* 10 min. of aspiration, 5 ml. of 1 *F* sulfuric acid was added (to cause any iodate formed to react with iodide to iodine), and then 10 ml. of 2 *F* sodium carbonate was added (to provide the appropriate acidity for titration). The solution was then titrated with standard 0.02 *N* arsenic(III) solution to a starch end point. Successive determinations on samples collected at the same time usually yielded values within 0.5% of the mean.

Reducing Agents in Enriched Solvents. Sulfur Dioxide Solutions.—Solutions of dissolved sulfur dioxide were prepared by syringing the required volume of anhydrous gas into 5–10 ml. of dilute perchloric acid of approximately known oxygen-18 content. The solutions were prepared and kept for a short time in capped containers, previously purged with purified nitrogen.

Sulfite Solutions.—Two types of solutions were prepared: solutions in which the sulfite ion is of normal isotopic composition in solvent enriched in oxygen-18, and solutions in which both sulfite ion and solvent are enriched in oxygen-18 to the same extent. Solutions of the former type were prepared by neutralizing sulfur dioxide gas of normal isotopic composition with excess aqueous sodium hydroxide, also normal in isotopic composition. Enriched water was then added to the solution. Solutions with sulfite ion and solvent equally enriched in O^{18} were prepared from sulfur dioxide gas (5 to 50 ml.) in enriched water (say 5–10 ml.) faintly acidified with perchloric acid. A small volume (0.1–0.5 ml., as required) of concentrated sodium hydroxide (carbonate-free) was then added. These solutions were prepared and stored briefly under purified nitrogen.

Nitrite Solutions.—As in the case of sulfite ion, two types of solutions were prepared: with normal nitrite ion in enriched solvent, and with nitrite ion and solvent equally enriched. For solutions of normal nitrite ion in enriched water, solid sodium nitrite was dissolved in the appropriate volume of enriched water containing sodium hydroxide. For preparation of solutions of nitrite ion in isotopic equilibrium with the solvent, use was made of the known exchange rates of nitrous acid in solutions of pH 4–6.[1] Sodium nitrite (1.0 *F*) was dissolved in enriched water, also *ca.* 0.2 *F* in perchloric acid. Using 4×10^{-4} as the acid dissociation quotient of nitrous acid, the calculated pH is 4. The solution was left for 20 min., which is *ca.* 60 half-lives for exchange,[1] then concentrated sodium hydroxide, carbonate-free, was added.

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[1] At pH 4, the half-time for exchange, as calculated from data of M. Anbar and H. Taube [*J. Am. Chem. Soc.*, **76**, 6243 (1954)], is 20 sec. at 25°.

Manganese(II) Ion Solutions.—These were prepared by diluting reagent grade 50% manganese(II) nitrate solution with dilute perchloric acid in enriched water.

Thallium(I) Ion Solutions.—Solid thallium(III) oxide suspended is enriched water was treated with excess gaseous sulfur dioxide until the solid disappeared. Excess sulfur dioxide was removed by heating and by passing nitrogen gas through the solution.

Procedure. Tracer Experiments.—Essentially three types of experimental procedures were used to carry out reactions of reducing agents with ozone. These are designated by the letters A, B, and C to identify the particular method used in any given experiment. (A) A pyrex container, volume *ca.* 100 ml., containing 5–20 ml. of reducing agent solution, was connected directly to the ozone generator, and oxygen gas containing *ca.* 3.5 mole % ozone was passed over the solution for the desired length of time. (B) A solution of the reducing agent was delivered into a flask containing excess ozone. (C) A solution of the reducing agent in excess was delivered into a flask containing ozone. In procedures B and C, the solution was contained in a syringe connected to the flask by Tygon tubing and was caused to enter the flask by cooling the latter with Dry Ice.

Isotopic Analyses.—Isotopic composition is expressed as the enrichment ratio, E, that is the isotopic ratio for O^{18}/O^{16} compared to that in a sample of normal isotopic composition.

Anbar–Guttman Procedure.[2]—The solid was placed in a break-off tube along with 0.1–0.2 g. of an equimolar mercury(II) chloride–mercury(II) cyanide mixture, evacuated, and sealed. This was heated in a furnace at 400° for 2 hr. The resulting gases were then condensed into another evacuated break-off tube containing 2 g. of a liquid zinc–mercury solution. The sealed break-off tube was heated to 200° for 2 hr.[3]

The ratio (mass number 46)/(mass number 44) in the purified carbon dioxide was determined on the mass spectrometer. When the sample was sufficiently free of impurities a double collector reading was made; otherwise, the ratio was measured by the single collector procedure, which is generally less precise (±1%).

Water.—In general, a sample of solvent was taken for isotopic analysis in each individual tracer experiment. The oxygen-18 content was determined on carbon dioxide which either had been equilibrated with the solvent, or which was obtained by the Anbar–Guttmann procedure on a small portion of the solvent. The two methods yielded results that are generally in excellent agreement; the equilibration technique was employed in most experiments.

Sulfate Ion.—In all except a few experiments in which barium ion was used as precipitant, lead sulfate was precipitated by addition of lead(II) nitrate solution (of normal oxygen isotopic content) to the sulfate ion solution. (When sulfate ion was in basic solution, the minimum volume of 60% perchloric acid was used to render the solution acid before precipitation of the lead sulfate.) The resulting precipitate was collected on a sintered glass filter and washed with water, then with methanol. The usual drying procedure for lead sulfate was to heat it in an oven at 120°. A portion of the dried solid (0.05 g.) was converted to carbon dioxide by the procedure of Anbar and Guttmann.

Blank experiments were done to test the method of analysis. Sulfur dioxide in an acidic solution in enriched water was oxidized by chlorine and lead sulfate was precipitated and treated as described. The enrichment ratio, E, of the lead sulfate was found to be 2.25 for the solvent compared to 2.31 for the solid, and again 5.42 for the solvent compared to 5.34 for the solid.

Nitrate Ion.—A solution, 1 F in nitrate ion and 0.4 F in hydroxide ion, was neutralized with the minimum volume of 60% perchloric acid, and lead(II) perchlorate solution and then acetone were added. The solution was cooled in methanol–Dry Ice almost to freezing. Precipitated lead(II) nitrate (*ca.* 60% yield) was washed with several small portions of cold acetone and dried overnight at 120°. Experiments depending on the precipitation of $Ba(NO_3)_2$ were usually unsuccessful for the reason that barium nitrate rarely was found to yield carbon dioxide in the Anbar–Guttmann procedure.

Manganese Dioxide and Thallium(III) Oxide.—Precipitated manganese dioxide, which generally appears quite crystalline when prepared by the reaction of manganese(II) and ozone in perchloric acid solution, was washed with water in some experiments and dried at 120° in an oven; in other experiments, acetone alone was used as wash liquid and the solid dried in a vacuum desiccator overnight. The oxygen contained in the manganese dioxide was converted to carbon dioxide by the procedure of Anbar and Guttmann.

(I) The Reaction of Ozone with S(IV)

(A) Sulfur Dioxide and Ozone in Perchloric Acid Solution.—Under the conditions of the tracer experiments, the stoichiometry of the reaction between sulfur dioxide and ozone in acidic solution conforms closely to the equation

$$SO_2 + O_3 + H_2O = HSO_4^- + H^+ + O_2 \qquad (1)$$

In three experiments the molar ratio of ozone consumed to sulfur dioxide consumed was found to be 0.92, 0.92, and 0.89. The cause of the deviation from exact stoichiometry was not found. It may simply be a result of a slight loss of sulfur dioxide during transfer, or it may be an intrinsic effect reflecting partial formation of dithionate as product, or reaction of oxygen with sulfur dioxide induced by the reaction of the reducing agent with ozone. Whatever the cause, it does not materially affect the tracer experiments which will be described.

Since exchange of oxygen between dissolved sulfur dioxide and solvent takes place rapidly, tracer experiments cannot be done which distinguish the sulfur dioxide oxygen from the solvent oxygen in the product sulfate ion. Under the conditions of our experiments, ozone[4] and sulfate[5] ion undergo inappreciable exchange with water. Results of tracer experiments using solvent and sulfur dioxide tagged with oxygen-18 are presented in Table I.

Since the predominant net change in the reaction of ozone with sulfur dioxide in acidic solution is given by eq. 1, it follows that if more than one atom of ozone oxygen appears in each product sulfate as is the case for all the experiments referred to in Table I, the oxygen which is formed must have undergone some exchange with the solvent. The oxygen in expt. 4 of Table I initially contained 3.49 mole % of ozone. After reaction with slightly less than the stoichiometric amount of sulfur dioxide had taken place, the remaining gas was collected and dried, and its isotopic composition was determined. Its enrichment ratio was found to be 1.083. The enrichment in O^{18} corresponds to 1.7 oxygen atoms per product sulfate being derived from ozone, a

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[2] M. Anbar and S. Guttman, *Intern. J. Appl. Rad. Isotopes*, **5**, 233 (1959).

[3] The treatment with zinc amalgam is intended to remove impurities from the carbon dioxide, especially cyanogen, but was often quite ineffective. In some later experiments, attempts were made to separate carbon dioxide from impurities by a gas chromatographic technique. The column had acid-washed Chromosorb P as the solid phase; *sec*-butyl phthalate as the covering phase gave good separation of C_2N_2 and CO_2. The column is described in detail by R. B. Jordan, "Oxygen Isotope Studies on Carboxylpentaamminecobalt(III) Complexes," Ph.D. Dissertation, University of Chicago, 1965.

[4] O. L. Forchheimer and H. Taube, *J. Am. Chem. Soc.*, **76**, 2099 (1954).

[5] T. C. Hoering and J. W. Kennedy, *ibid.*, **79**, 56 (1957).

TABLE I

RESULTS OF TRACER EXPERIMENTS ON REACTION OF SULFUR DIOXIDE AND OZONE IN PERCHLORIC ACID SOLUTION

Expt. no.	Initial concn., *M* (SO_2)	($HClO_4$)	Reaction conditions	E_{PbSO_4}[a,b]	E_{solv}[a,b]	No. of O on sulfate from ozone[c]
1	0.08	0.1	B	4.75	8.25	1.9
2	0.08	0.1	B	5.31	7.66	1.4
3	0.08	0.1	B	5.65	7.92	1.3
4	0.16	0.2	B	4.54	7.53	1.8
5	0.08	0.1	C	4.32	7.62	2.0
6	0.4	0.2	C	4.19	7.37	2.0

[a] All measurements are by single collector method. [b] E, the enrichment ratio, is the O^{18}/O^{16} ratio in the substance specified compared to the ratio in a standard sample of oxygen of normal isotopic composition. [c] Number of oxygens per sulfate derived from ozone calculated from the equation $4(E_{solv} - E_{solid})/(E_{solv} - 1)$.

result which compares within the limits of experimental error with 1.8, the value observed by determining the isotopic composition of the product sulfate.

It is found that ozone brings about oxygen exchange between sulfate and solvent, although the rate of exchange is not great enough to have a significant effect on the tracer experiment. Oxygen containing 1.52 moles of ozone per liter was passed over a solution of 0.1 *F* H_2SO_4 and 0.2 *F* $NaClO_4$ in solvent *ca.* 7.5-fold enriched in O^{18} at a rate of *ca.* 0.2 l./min. The sulfate after 30 min. was found to be 1.28-fold enriched in O^{18}; exchange under the same conditions but without ozone being present would have been too small to measure.[5] An effect which is more serious in its implications for the data shown in Table I is that exchange between sulfate and solvent is induced by the reaction of ozone with SO_2(aq). The conditions for the experiment which revealed this effect were: 0.17 *F* Na_2SO_4, 0.35 *F* $HClO_4$, 0.02 *F* SO_2 in water enriched 6.80-fold in O^{18}, ozone being used in excess. The sulfate resulting from the oxidation was found to be 1.88-fold enriched in O^{18}. If it is assumed that 2.0 atoms of oxygen are transferred to S for each sulfate formed (and this would seem to be an upper limit, *cf.* Table I), the total sulfate would be expected to show an enrichment ratio of only 1.34. Ozone is consumed rapidly by sulfur dioxide, and thus the total contact of ozone with sulfate is small, much too small for exchange to account for the difference between the enrichment ratios of 1.34 and 1.88. We therefore conclude that the reaction of ozone with sulfur dioxide induces sulfate-solvent exchange. The effect of this exchange is to reduce the values recorded in the last column of Table I, and it may account for the nonintegral values recorded there.

(B) The Reaction of Sulfite Ion and Ozone in Basic Solution.—An experiment on the stoichiometry of the reaction of ozone with sulfite in alkaline solution showed that the consumption ratio of the reactants is 1.00; thus the net change is described by the equation

$$O_3 + SO_3^{2-} = SO_4^{2-} + O_2 \qquad (2)$$

Despite the simplicity of the net change, complex effects are revealed in the tracer studies, as the results summarized in Table II will show.

Since the exchange of sulfite ion with water in alkaline solution is slow[6] (a result which was substantiated in the course of the present work), it is possible to distinguish the three possible sources of oxygen in the product sulfate, namely that from ozone (and the accompanying oxygen), that from sulfite, and that from the solvent.

Two different types of experiments were done: (1) with sulfite and solvent equally enriched in O^{18}, and with ozone of normal isotopic composition; (2) with the solvent only enriched in O^{18}, sulfite and ozone of normal isotopic composition. The results of the tracer experiments are shown in Table II.

The results shown in part A of Table II demonstrate that even in alkaline solution more than one atom of oxygen derived from ozone appears in each product sulfate. Those in part B show that the product sulfate derives oxygen from the solvent despite the fact that exchange between sulfite and solvent in alkaline solution is slow.

An experiment was done to discover whether reaction of sulfite ion and ozone in basic solution induces exchange of sulfate ion and solvent. A solution of 0.18 *F* Na_2SO_4, 0.02 *F* SO_3^{2-}, 0.36 *F* NaOH, with water and sulfite enriched *ca.* 7.6-fold, was brought into reaction with ozone. Duplicate experiments led to enrichment ratios for the sulfate of 1.98 ($E_{solv} = 7.684$) and 1.77 ($E_{solv} = 7.603$). The expected value of E is 1.4, assuming the sulfate initially present does not incorporate solvent oxygen and that sulfate formed by oxidation of sulfite contains 1.5 ozone (normal) oxygens (*cf.* Table II (A)). Even if each such sulfate is assumed to contain only one ozone oxygen, the expected value of E would be only 1.5. Thus, some induced exchange of sulfate takes place, but it is far from complete. The effect can cause nonintegral transfer results in the tracer experiments.

Experiments were also done to discover whether ozone catalyzes exchange of oxygen between sulfate ion and solvent. In one experiment a solution of 0.1 *F* Na_2SO_4, 0.2 *F* NaOH in enriched water was connected to the ozone generator, and for 30 min. 3.5 mole % ozone was passed over the solution at 0.2 l./min. The sulfate ion, as lead sulfate, had $E = 1.07$ ($E_{solv} = 7.6$). In an experiment using a solution of 0.2 *F* $NaSO_4$, 0.4 *F* NaOH, through which ozone was passed for 3.8 hr., the precipitated $PbSO_4$ had $E = 1.35$ ($E_{solv} = 7.21$). Exchange at the rate measured is negligible during the time required for tracer experiments on the reaction of sulfite and ozone, but is in itself a point of some interest.

(C) Related Observations.—An experiment was done to learn whether an intermediate in the decomposition of persulfate ion in alkaline solution can induce the exchange of sulfate ion with solvent. Other work[7] has shown that in the alkaline decomposition of persulfate the oxygen released originates entirely in the solvent, and that the isotopic composition of the persulfate remains unchanged, but the isotopic composi-

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[6] N. F. Hall and O. R. Alexander, *J. Am. Chem. Soc.*, **62**, 3455 (1940).

[7] I. M. Kolthoff and I. K. Miller, *ibid.*, **73**, 3055 (1951).

TABLE II

RESULTS OF TRACER EXPERIMENTS ON REACTION OF SULFITE ION WITH OZONE IN BASIC SOLUTION

(A) Enriched Sulfite Ion in Enriched Solvent

Expt. no.	Initial concn., M (SO_3^{2-})	(OH^-)	Reaction conditions	E_{solid}	E_{solv}	No. of O from SO_3^{2-} + OH^-	O_3
7	0.1	0.05	A	4.054	5.193	2.91	1.09
8	0.09	0.02	B	4.882	7.555	2.37	1.63
9	0.09	0.02	B	4.715	7.025	2.47	1.53
10	0.16	0.05	B	3.985	6.517	2.16	1.84
11	0.4	0.4	C	2.533	3.880	2.13	1.87

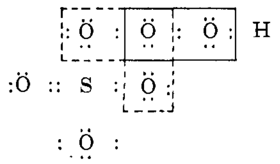
(B) Normal Sulfite Ion in Enriched Solvent

Expt. no.	Initial concn., M (SO_3^{2-})	(OH^-)	Reaction conditions	E_{solid}	E_{solv}	OH^- (aq)	No. of O from SO_3^{2-} + O_3
12	0.2	0.4	A	1.213	5.734	0.18	3.82
13	0.2	0.4	A	1.415	5.698	0.35	3.65
14	0.2	0.4	B	1.705	5.705	0.60	3.40
15	0.2	0.4	B	2.845	5.712	1.57	2.43
16	0.1	0.4	B	2.454	5.461	1.30	2.70
17	0.1	0.4	B	1.830	5.350	0.76	3.24
18[a]	0.6	0.4	C	1.744	5.566	0.65	3.35
19[a]	0.6	0.4	C	1.617	5.297	0.57	3.43

[a] In these experiments the precipitation was made in basic solution, barium ion, rather than lead, being used as precipitant. After sulfate ion is precipitated as barium sulfate, the excess sulfite is oxidized with bromine to sulfate and this is also precipitated with barium ion. The solvent oxygen content of the SO_4^{2-} formed by bromine was found to correspond to 0.92 atom out of 4 in expt. 18 and 1.04 in expt. 19, in each case close to that introduced of necessity by the oxidation step.

tion of the product sulfate was not examined. We have checked the isotopic composition of the sulfate resulting from the decomposition of persulfate in 0.12 F NaOH at 90 ± 5° and found it to be normal in isotopic composition although the reaction was carried out in a solvent 5-fold enriched in O^{18}. The experiment taken in conjunction with the evidence[8] that SO_4^- is an intermediate in the decomposition of persulfate shows that SO_4^- by itself is not responsible for the ozone-induced exchange of sulfate and solvent in alkaline solution.

(D) General Discussion.—A number of the effects exposed in the tracer study of the oxidation of S(IV) by ozone seem to us to be quite remarkable and unexpected. The reaction in both acidic and basic solution has available a path involving simple transfer of one oxygen atom from ozone for each molecule of reducing agent, a path which is observed in the oxidation by ozone of U^{4+},[9] and of Pu^{4+}.[10] Yet in the reaction with S(IV) in both acidic and alkaline solution more than one atom of oxygen is transferred, even though the excess transfer demands the added complication of exchange of ozone oxygen with the solvent. In acidic solution S(IV) exists largely as SO_2, and once transfer of two oxygen atoms from ozone for each sulfate formed is demonstrated, it is not difficult to see the possibility of completing the coordination sphere of S(VI) from oxygen derived from ozone



In the above diagram the broken line represents the configuration before the rearrangement in the activated complex and the full line, after. But in alkaline solution, in view of the inertia of the S(IV)–O^{2-} bond to substitution, it is difficult to see how in a simple bimolecular process the coordination sphere of sulfite ion is broken into, so as to place more than one ozone oxygen on each sulfur atom.

An important point which must be settled before speculation becomes profitable is whether the reaction takes place by a simple bimolecular process or whether intermediates play a fundamental role, perhaps by supporting a chain mechanism for reaction. That intermediates are present in acidic solution is apparent from the results on induced exchange. It is not known, however, whether reaction *via* them merely accompanies the main reaction and provides only a minor path, or whether the bulk of the reaction flows through them. In alkaline solution intermediates are also present and here it seems very likely that the latter situation obtains, otherwise transfer of more than one oxygen for each ozone which reacts is difficult to understand, for reasons already mentioned. In the intermediate, the coordination sphere about sulfur may be labilized so that the excess bond to ozone oxygen can be formed, and exchange with the solvent can take place. Nothing further is known at this point about the intermediate(s) except that it is not the same as that formed in the decomposition of persulfate ion.

The exchange of sulfate with solvent catalyzed by ozone (or induced by its decomposition) is noteworthy because here also an intermediate must be formed which is more labile toward exchange than is sulfate itself. A detailed study of this reaction may yield insight into the nature of the intermediate and thus may provide a basis also for understanding the oxidation of S(IV) by ozone.

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[8] W. K. Wilmarth and A. Haim, "Mechanisms of Oxidation by Peroxydisulfate Ion," in "Peroxide Reaction Mechanisms," Interscience Publishers, New York, N. Y., 1961.

[9] G. Gordon and H. Taube, *Inorg. Chem.*, **1**, 69 (1962).

[10] S. W. Rabideau and B. J. Masters, *J. Phys. Chem.*, **67**, 318 (1963).

TABLE III

TRACER EXPERIMENTS ON REACTION OF NITRITE ION WITH OZONE (NORMAL) IN BASIC SOLUTION (ENRICHED)

(A) Nitrite Ion Normal

Expt. no.	Concn. before reaction, *M* (NO_2^-)	(OH^-)	Reaction conditions	E_{solid}	E_{solv}	No. of O from Solvent	$NO_2^- + O_3^-$
20	1.0	0.4	A	1.064	7.00	0	3.00
21	1.0	0.4	A	1.045	6.78	0.02	2.98

(B) Nitrite Ion Enriched

Expt. no.	Concn. before reaction, *M* (NO_2^-)	(OH^-)	Reaction conditions	E_{solid}	E_{solv}	No. of O from Nitrite ion	Solvent $+ O_3$
22	1.0	0.4	A	5.00	6.98	2.00	1.00
23	1.0	0.4	A	4.70	6.78	1.95	1.05

(II) The Reaction of Ozone with Nitrite

Since nitrite ion in strongly basic solution exchanges only slowly with solvent, it is possible to distinguish three sources of oxygen: nitrite ion, ozone, and solvent. In enriched water, with ozone of normal isotopic composition, experiments were done with both the nitrite ion of normal isotopic composition or enriched to the same extent as the solvent. The results of these experiments are presented in Table III.

Tracer experiments were not performed on the reaction of nitrous acid and ozone in acidic solution because preliminary experiments on the stoichiometry of the reaction indicated the reaction was not stoichiometric, and less than the required amount of ozone was consumed. These experiments were done by adding to a flask, containing a known amount of ozone, first a dilute perchloric acid solution, followed then by a known volume of standard sodium nitrite solution (the concentration of which was checked by two independent methods, both before and after reaction in one case). The excess of ozone was then determined. The results obtained for the number of moles of ozone reacting per mole of nitrous acid were: 0.79, 0.84, 0.80, 0.77. Before reaction, the initial solution was 0.1 *F* $HClO_4$, 0.01 *F* HNO_2; under these conditions inappreciable decomposition of nitrous acid occurs during the time of reaction. This indicates that an intermediate, perhaps a peroxynitrous acid similar to that found in the reaction of hydrogen peroxide and nitrous acid, persists at appreciable concentration in the acidic solution. At any rate, the reaction was studied no further here. In contrast to the experiments on the oxidation of sulfite or of $SO_2(aq)$, the results for NO_2^- are simple and suggest the straightforward mechanism

$$NO_2^- + O_3 \longrightarrow NO_2O^- + O_2$$

although it must be admitted that complications may be present which are not revealed by the tracer experiments.

(III) Tracer Experiments on the Oxidation of Mn^{2+} to MnO_2

Acidic $Mn^{2+}(aq)$ reacts rapidly with ozone to produce rather large shiny crystals of manganese dioxide. The supernatant often has a faint permanganate ion color, but under the conditions employed here less than 1% of manganese(II) is oxidized to permanganate ion. In our experiments, which were done at room temperature, the solutions were 0.1 *F* in $HClO_4$ and 0.3 *F* in $Mn(NO_3)_2$ and reagents were brought into contact by passing ozone over the solution containing Mn^{2+} so that the reducing agent was in excess throughout the reaction. The results of the experiments are shown in Table IV.

TABLE IV

TRACER EXPERIMENTS ON REACTION OF MANGANESE(II) ION AND OZONE IN ACIDIC SOLUTION

Expt. no.[a]	E_{MnO_2}	E_{solv}	No. of O in MnO_2 from Ozone	Solvent
24	4.416	7.831	1.00	1.00
25	4.179	7.831	1.07	0.93
26	4.060	7.857	1.11	0.89
27	2.844	5.367	1.16	0.84
28[b]	2.727	5.367	1.21	0.79
29	2.691	5.367	1.23	0.77
30[c]	4.189	5.309	0.52	1.48
31[c]	4.298	5.395	0.50	1.50
32[c]	4.349	5.395	0.48	1.52

[a] The manganese dioxide was washed with reagent grade acetone in all experiments except 24 and 25, in which washing was done with normal water. [b] The manganese dioxide from this experiment was analyzed spectrophotometrically by oxidation to permanganate with periodate. The absorbancy index at 5250 Å. calculated on the basis that this oxide is pure MnO_2 is 2.38 compared with 2.41 and 2.38 for commercial reagent manganese dioxide. [c] In these experiments a few small seed crystals of manganese dioxide were placed in the solution prior to reaction with ozone.

The results suggest that the extent of transfer of oxygen can exceed 1 for each 2 equivalents of oxidation, but we are not inclined to assert this as being proven because contamination by oxygen of normal isotopic composition would also produce this effect. In any event, it is remarkable that the transfer is as large as it is and that in the reaction the ozone oxygen remains so well identified. Having some solid MnO_2 present initially produces a dramatic change in chemistry. This result is puzzling, particularly when account is taken of the fact that even when MnO_2 is not added initially the bulk of the reaction takes place with MnO_2 present as a solid phase.

(IV) Reaction of Thallium(I) and Ozone

Experiments were conducted in different media: strongly basic solution (0.2 *F* NaOH); a solution initially neutral, but becoming quite acidic (0.1 *M* H^+) as reaction proceeds; concentrated acetate buffer to maintain pH 5 ± 1 during reaction. The solid

TABLE V
RESULTS OF TRACER EXPERIMENTS ON REACTION OF THALLIUM(I) AND OZONE

Medium	E_{solid}	E_{solv}[b]	No. of O per Tl_2O_3 from Solvent	Ozone
Strongly alk.	6.614	7.265	2.59	0.31
Init. neut. to strongly acid	3.981	7.361	1.41	1.59
Acetate buffer[a]	3.962	7.651	1.57	1.43
Acetate buffer[a]	4.243	6.651	1.72	1.28

[a] Initially, 0.2 *F* Tl(I), 0.3 *F* HOAc, 0.3 *F* OAc^-, 0.4 *F* SO_2^{2-}; after reaction, 0.5 *F* HOAc, 0.1 *F* OAc^-, 0.4 *F* SO_4^{2-}. [b] Corrected for isotope fractionation during equilibration.

thallium(III) oxide that results from oxidation with ozone in the latter two instances appears more crystalline than the slime-like gel that results from the reaction in strongly basic solution. Table V presents results of these tracer experiments.

The experiments show that transfer takes place also when Tl^+ is oxidized by O_3. In view of the fact that the oxide appears to be hydrous, and this affords opportunity for dilution by solvent oxygen of the oxygen transferred from O_3, it is remarkable that the observed transfer is as large as it is, and it is not impossible that it corresponds to one O for each Tl^+ oxidized.

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A Crystal Field Model for the Spectral Relationships in Monoacidopentaammine and Diacidotetraammine Complexes of Cobalt(III)[1a]

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The observed spectral band splittings of some monoacidopentaammine and *trans*-diacidotetraamminecobalt(III) complexes are reviewed and interpreted in terms of crystal field theory. It is shown that the ligand field strength of an acido group in a tetragonal complex may be measured in terms a new empirical parameter *Dt'*, which is related in turn to the octahedral field strength *Dq* of the acido group. Analysis of available spectral data shows that *Dt'* and hence *Dq* values of a given acido group are constant to within 5 to 10% irrespective of the compound. A similar analysis of spectral data for some chromium(III) complexes is presented. The possibility of a spectral "*trans* effect" is discussed.

The spectra of monoacidopentaammine and *trans*-diacidotetraammine complexes of trivalent cobalt have been the subject of numerous studies from which have emerged several empirical relationships concerning band splittings as a function of the ligands.[2–12]

Various complementary theoretical interpretations have been offered. Moffitt and Ballhausen[13] have given the matrix elements for the tetragonal perturbation in terms of the crystal field model which they used qualitatively to predict the signs of the tetragonal splittings. Furthermore, they have discussed the polarized crystal spectrum of $[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ and tentatively assigned the observed transitions on the basis of a vibrational analysis.

The qualitative aspects of molecular orbital theory for such compounds were first pointed out by Griffith and Orgel.[14] They suggested for *trans*-dichlorotetraammine compounds that the one-electron octahedral level e_g ought to split with $E(x^2 - y^2) > E(3z^2 - r^2)$ in either theory. However, for the t_{2g} level the molecular orbital theory predicts $E(xz,yz) > E(xy)$ on account of the π-antibonding effect of the chloride anion. This is just the opposite order from that predicted by naïve crystal field theory since the ammonia groups have a greater crystal field than the chloride ion leading to the prediction $E(xy) > E(xz,yz)$. However, as we shall see, the formal crystal field theory can accommodate either ordering when empirical parameters are used.

Yamatera[15] in his pioneering paper has provided a thorough treatment of both the crystal field and molecular orbital models for CoA_6, CoA_5L, CoA_4L_2, and CoA_3L_3 compounds. He suggested a molecular orbital

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