and the crystal structures is not known, a strong correlation is suggested with the vapor pressure measurements previously made in this alloy system. In order to place the suggested correlation on a better theoretical basis and perhaps to determine the crystal structure of the parent hexagonal lattice the authors plan a continued X-ray diffraction examination of the microphases in this alloy system.

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Arsenic(IV) as an Intermediate in the Iron(III) and Copper(II) Catalyzed Arsenic(III)–Persulfate Reaction[1]

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It is postulated that the iron(III) and copper(II) catalyzed oxidation of arsenic(III) by persulfate proceeds by a chain mechanism initiated by the symmetrical decomposition of persulfate into two sulfate free radicals. The chain involves the intermediate formation of arsenic(IV). The kinetics of the iron(III) catalysis and the values of the rate constants are in agreement with the results of previous investigations. The rate of oxidation of HO_2 by copper is not affected by a change in pH between 2.7 and 1.3, while that of iron(III) changes nearly in proportion to concentration of $FeOH^{2+}$. An interpretation has been given of the fact that the catalytic effect of small concentrations of copper(II) in the presence of oxygen is much larger than that observed in the absence of oxygen, whereas hardly any difference is observed at high copper concentrations. The acid-catalyzed decomposition of persulfate results in a two-electron transfer oxidation of arsenic(III) to arsenic(V) without the formation of reactive intermediates.

The induced oxidation of arsenic(III) by the iron(II)–persulfate reaction and the photoreduction of iron(III)[2,3] and by the iron(II)–hydrogen peroxide reaction[4] have been interpreted on the basis of the intermediate formation of the 4+ valence state of arsenic by the reaction of sulfate and hydroxyl free radicals with arsenic(III). In the absence of oxygen the intermediate arsenic(IV) was postulated to reduce iron(III) and copper(II) and oxidize iron(II). Arsenic(IV) was found to be very sensitive to oxygen, reacting to give hydroperoxo radical.

Sulfate free radicals which are formed in the thermal decomposition of persulfate[5] can oxidize arsenic(III) to arsenic(IV). If either iron(III) or copper(II) is also present, arsenic(IV) reduces these ions, the iron(II) or copper(I) produced reacting with persulfate to give sulfate free radical.[6–9] It is anticipated from these results that in the presence of iron(III) or copper(II) a chain oxidation of arsenic(III) by persulfate will occur. The kinetics of these reactions were investigated to substantiate further the reactions postulated in the preceding publications.[2–4]

In acid solution the thermal decomposition of persulfate proceeds by two parallel paths[5]

$$S_2O_8^{2-} \longrightarrow 2SO_4^{\overset{-}{\cdot}} \qquad (1)$$

$$H^+ + S_2O_8^{2-} \longrightarrow SO_4 + HSO_4^- \qquad (2)$$

In order to interpret the kinetics of a chain reaction initiated by reaction 1, it is necessary to know the extent of possible oxidation by SO_4 formed in reaction 2 and also of direct reaction between arsenic(III) and persulfate comparable to the oxidation of arsenic(III) by hydrogen peroxide.[3,4] Therefore, the kinetics of the arsenic(III)–persulfate reaction were also investigated in the absence of added metal ions.

Experimental

All materials used were identical with those described previously.[2] For the reactions in the absence of added metal ions, solutions of perchloric acid, arsenic trioxide, and sufficient sodium perchlorate to make the ionic strength 0.1 were pipetted into the reaction flasks and placed in a water bath at 25°. If the reaction was to be studied in the absence of oxygen, the solution was deaerated with nitrogen. Deaerated or air-saturated potassium persulfate solution was added and, after desired times, aliquot samples were removed and analyzed for persulfate. For the copper(II) catalyzed reactions, cupric perchlorate was added to the original mixture and the procedure followed as before. In the presence of iron(III) the reaction flasks were covered with black adhesive tape to eliminate photoreactions.[2,3] In order to oxidize any trace of iron(II) in the iron(III), solutions of sodium perchlorate, perchloric acid, ferric perchlorate, and potassium persulfate were pipetted into the reaction flasks and allowed to stand overnight at room temperature. Where relevant the solution was then deaerated and deaerated or air-saturated arsenic trioxide solution added, the reaction mixture being sampled and analyzed as before.

Persulfate was determined polarographically, the sodium perchlorate and perchloric acid present acting as supporting electrolyte. (Polyacrylamide in a concentration of 0.01% was used as a maximum suppressor.) In the presence of iron(III), sodium fluoride in a concentration of 0.1 *M* was added to the

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[1] This investigation was carried out under a grant from the National Science Foundation.

[2] R. Woods, I. M. Kolthoff, and E. J. Meehan, *J. Am. Chem. Soc.*, **85**, 2385 (1963).

[3] R. Woods, I. M. Kolthoff, and E. J. Meehan, *ibid.*, **85**, 3334 (1963).

[4] R. Woods, I. M. Kolthoff, and E. J. Meehan, *ibid.*, **86**, 1698 (1964).

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

[6] J. H. Mertz and W. A. Waters, *Discussions Faraday Soc.*, **29**, 179 (1947).

[7] J. W. L. Fordham and H. L. Williams, *J. Am. Chem. Soc.*, **73**, 1634 (1951).

[8] J. W. L. Fordham and H. L. Williams, *ibid.*, **73**, 4855 (1951).

[9] I. M. Kolthoff, I. K. Miller, and H. P. Raaen, *ibid.*, **73**, 1733 (1951).

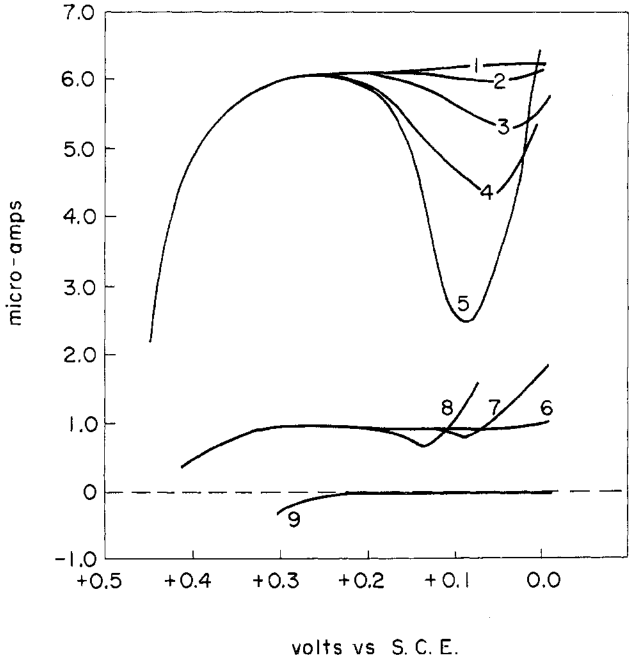

Figure 1.—Current–voltage at d.m.e.; 2 × 10^{-2} *M* As(III), 10^{-2} *M* $HClO_4$, 0.09 *M* $NaClO_4$, 0.01% polyacrylamide, 0.3% acrylonitrile: no. 1–5, 10^{-3} *M* $S_2O_8^{2-}$ with 0, 10^{-4}, 10^{-3}, 5.4 × 10^{-3}, and 2.7 × 10^{-2} *M* Cu(II), respectively; no. 6–8, 1.6 × 10^{-4} *M* $S_2O_8^{2-}$ with 0, 5.4 × 10^{-3}, and 2.7 × 10^{-2} *M* Cu(II), respectively; no. 9, residual current.

polarographic cell to eliminate its interference at the d.m.e. One drop of 0.2% *o*-phenanthroline was also added to quench the reaction. In the presence of copper(II), the chain reaction was quenched by the addition of one drop of acrylonitrile to the polarographic cell. A minimum appears on the persulfate polarographic wave in the presence of copper(II) and arsenic(III) (Figure 1) which does not occur in the presence of either constituent alone. This effect is more pronounced at the higher persulfate concentrations used and is dependent on the copper(II) concentration. Fortunately, when the persulfate diffusion current is measured at +0.25 v. *vs.* s.c.e. there is a negligible error in persulfate determination at copper(II) concentrations up to at least 2.7 × 10^{-2} *M* (Figure 1). The suppression of the current at more negative potentials is being investigated further.

Arsenic(V) was determined spectrophotometrically.[2]

The persulfate, perchloric acid, sodium perchlorate, and distilled water were analyzed for trace quantities of copper(II) with dithizone.[10]

Stock solutions 10^{-1} *M* in persulfate, 1 *M* in perchloric acid, and 10 *M* in sodium perchlorate, respectively, were prepared. These were 100 times as concentrated as those used in the rate experiments. The neutral solutions were made 0.01 *M* in perchloric acid. Ten-ml. portions of these solutions were shaken with 5 ml. of 0.001% dithizone in carbon tetrachloride for 2 min., and the absorbance of the carbon tetrachloride layer was measured in the spectrophotometer at 510 mμ. Distilled water (1 l.) was evaporated to give 10 ml., acidified to 0.01 *M* with perchloric acid, and the same procedure followed as above. A reference curve was constructed using known concentrations of cupric perchlorate in 0.01 *M* perchloric acid.

Results

All reaction rates were measured at 25°.

(i) **Absence of Added Metal Ions.**—The reaction between arsenic(III) and persulfate solutions in the absence of any other reagents was found to be first order to persulfate, but the first-order rate constant was irreproducible. In the presence of 0.01 *M* perchloric acid and 0.09 *M* sodium perchlorate, the rate of the reaction was more reproducible. The rate of persulfate decomposition was determined at the same acidity and ionic strength in the absence of arsenic(III).

Kolthoff and Miller[5] found the rate of decomposition of persulfate to be first order and unaffected by the presence of oxygen. The rate at 25° is very small, and the reaction was followed for less than one half-life period. The order of the reaction therefore cannot be determined unequivocally, but the results are consistent with first-order kinetics with a rate constant of 9 × 10^{-8} sec.$^{-1}$.

The rate of reduction of persulfate in the presence of arsenic trioxide in deaerated solution also is very small, and only the decrease from 10^{-3} to 7 × 10^{-4} *M* persulfate was followed. The arsenic(V) formed was found to be equivalent to the persulfate reduced. The order of this reaction also could not be determined unequivocally, but the results are consistent with first-order kinetics with regard to persulfate. The rate of reduction of persulfate in the presence of arsenic trioxide in air-saturated solution is much greater than in the absence of oxygen, and the rate was followed over 90% of the reaction. The reaction was found to be first order to persulfate and the arsenic(V) formed corresponded to the persulfate reduced. The first-order rate constants, $k = -d \ln [S_2O_8^{2-}]/dt$, are given in Table I.

TABLE I

RATE OF REDUCTION OF PERSULFATE

10^{-3} *M* $S_2O_8^{2-}$; 0.01 *M* $HClO_4$; $\mu = 0.1$

[As(III)], *M*	*k*, sec.$^{-1}$ × 10^7
Absence of Oxygen	
0	0.9
10^{-3}	3.0
10^{-2}	6
2 × 10^{-2}	6, 7
Air-Saturated	
0	0.9
10^{-3}	35
4 × 10^{-3}	35
10^{-2}	41, 35, 40
2 × 10^{-2}	46

The effect of allyl acetate and of acrylonitrile on the rate in air-saturated solution was determined under the same conditions of acidity and ionic strength. These reactions are very slow and only one half-life period was followed. The results are in agreement with first-order kinetics. The arsenic(V) formed was equivalent to about 90% of the persulfate reduced.

(ii) **Iron(II) Catalyzed Reaction.**—The rate of reduction of 10^{-3} *M* persulfate was measured at an ionic strength of 0.1 in the presence of varying concentrations of ferric perchlorate, perchloric acid, and arsenic trioxide. For iron(III) concentrations equal to or less than 4 × 10^{-3} *M*, the rate was found to be

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(10) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd Ed., Interscience Publishers, New York, N. Y., 1959, p. 453.

TABLE II

EFFECT OF ALLYL ACETATE AND ACRYLONITRILE IN AIR-SATURATED SOLUTION

10^{-3} *M* $S_2O_8^{2-}$; 10^{-3} *M* As(III); 0.01 *M* $HClO_4$; $\mu = 0.1$

Addition	k_1, sec.$^{-1}$ × 10^7	As(V), % persulfate reduced
1% allyl acetate	2.4	89
1% acrylonitrile	3.1	91

first order to persulfate and reproducible. At greater iron(III) concentrations, the rate was less than first order to persulfate and irreproducible, possibly due to the formation of polymeric iron(III) species which have different reaction rates. The reactions at the higher iron(III) concentrations were not studied in detail and are not reported.

The arsenic(V) formed was always equivalent to the persulfate reduced, both in oxygen-free and air-saturated solutions. The rate constants in air-saturated solution are independent of arsenic(III) concentration at arsenic concentrations of 10^{-3} *M* or greater. In oxygen-free solution the rate constants are virtually independent of arsenic(III) concentration, being increased by only 10% for a twofold increase in arsenic(III) concentration. Figure 2 shows the logarithmic plots of the first-order rate constants (sec.$^{-1}$) in nitrogen and in air against the iron(III) concentration. A straight line of slope one-half is obtained in both oxygen-free and air-saturated solutions, showing that the reaction is one-half order to iron(III).

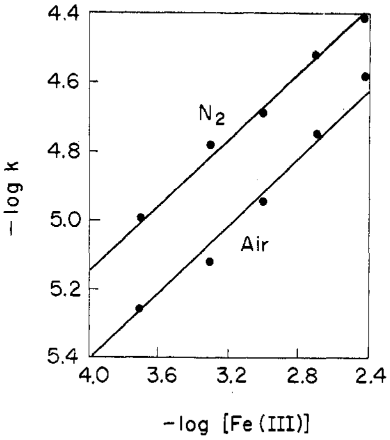

Figure 2.—First-order rate constant, iron(III) catalyzed reaction; 0.01 *M* $HClO_4$, $\mu = 0.1$; As(III) from 0.02 to 10^{-3} *M*.

The effect of varying the perchloric acid concentration at constant iron(III) concentration was also investigated. Figure 3 is a logarithmic plot of the first-order rate constant against ($[H^+] + K_a$), K_a being the first acid dissociation constant of aqueous ferric iron

$$K_a = [FeOH^{2+}][H^+]/[Fe^{3+}]$$

equal to 2.8×10^{-3} at ionic strength 0.1.[11] A straight line of slope $-1/2$ is obtained in both oxygen-free and air-saturated solutions, and therefore the reaction is minus one-half order to ($[H^+] + K_a$).

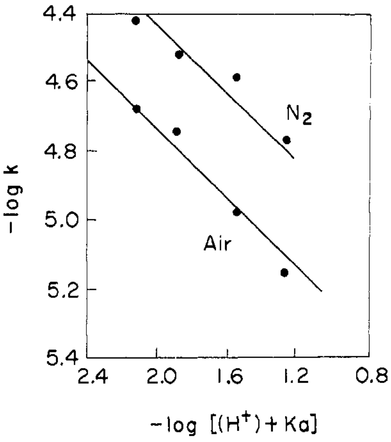

Figure 3.—First-order rate constant, iron(III) catalyzed reaction; 10^{-3} *M* $S_2O_8^{2-}$; 2×10^{-3} *M* Fe(III); $\mu = 0.1$.

From Figures 2 and 3 the relationships obtained are:
Oxygen-free solution

$$k = 7.6 \times 10^{-5} \frac{[Fe(III)]^{1/2}}{([H^+] + K_a)^{1/2}} \text{ sec.}^{-1}$$

Air-saturated solution

$$k = 4.3 \times 10^{-5} \frac{[Fe(III)]^{1/2}}{([H^+] + K_a)^{1/2}} \text{ sec.}^{-1}$$

in which [Fe(III)] is the total concentration of iron(III).

(iii) **Copper(II) Catalyzed Reactions.**—The rate of reduction of 10^{-3} *M* persulfate at an ionic strength of 0.1 was determined in the presence of varying concentrations of cupric perchlorate, arsenic trioxide, and perchloric acid. The arsenic(V) formed corresponded to the persulfate reduced both in oxygen-free and in air-saturated solutions.

The perchloric acid concentration was kept constant at 0.01 *M* and the concentration of copper(II) varied from 10^{-4} to 2.7×10^{-2} *M* for oxygen-free solutions and from 4×10^{-8} to 2.7×10^{-2} *M* for air-saturated solutions. The rate of reduction of persulfate was determined in the presence of 2×10^{-2} and 10^{-2} *M* arsenic(III). In all cases the reaction was first order to persulfate.

A plot of log *k* against log [Cu(II)] is given in Figure 4. The plot is linear with a slope of one-half for oxygen-free solution at copper(II) concentrations less than or equal to 10^{-3} *M* and for air-saturated solution at copper(II) concentrations less than or equal to 4×10^{-5} *M* or greater than 10^{-7} *M*. The rate at these copper(II) concentrations is virtually independent of arsenic(III) concentration. The first-order rate constant for the reduction of persulfate at these copper(II) concentrations is given by: oxygen-free solution, $k = 4.2 \times 10^{-3}[Cu(II)]^{1/2}$ sec.$^{-1}$; air-saturated solution, $k = 2.8 \times 10^{-2}[Cu(II)]^{1/2}$ sec.$^{-1}$.

In air-saturated solution, the slope of the log *k* against log [Cu(II)] plot decreases at copper(II) con-

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(11) R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, **77**, 1352 (1955).

Table III

Effect of Arsenic(III) Concentration

10^{-3} *M* $S_2O_8^{2-}$; 0.01 *M* $HClO_4$; $\mu = 0.1$

[Cu(II)], *M*	[As(III)], *M*	Oxygen-free solution			Air-saturated solution		
		k, sec.$^{-1}$ × 10^4	$k/[\mathrm{As(III)}]^{1/2}$ × 10^3	k, M$^{-1/2}$ sec.$^{-1}$ × 10^3	k, sec.$^{-1}$ × 10^4	$k/[\mathrm{As(III)}]^{1/2}$ × 10^3	k, *M*$^{-1/2}$ sec.$^{-1}$ × 10^3
5.4×10^{-3}	2×10^{-2}	2.6	1.8		3.7	2.6	
	10^{-2}	2.3	2.3		2.7	2.7	
	4×10^{-3}	1.8	2.8		1.8	2.8	
	10^{-3}			3.1			3.0
2.7×10^{-2}	2×10^{-2}	3.3	2.3		3.5	2.5	
	10^{-2}	2.6	2.6		2.7	2.7	
	4×10^{-3}	1.6	2.5				
	10^{-3}			2.9			

centrations greater than 4×10^{-5} *M* and becomes zero at concentrations greater than or equal to 10^{-3} *M*. In this range, the rate is significantly different at the two arsenic(III) concentrations studied. The rate in oxygen-free solution at the higher copper(II) concentrations studied tends toward the same limiting value as in the presence of oxygen.

The results (Figure 4) suggest that the rate of reduction of persulfate is independent of arsenic(III) concentration at low copper(II) concentrations but is dependent at high copper(II) concentrations. However, only a twofold change in arsenic(III) concentration was studied in these experiments, and it was necessary to extend the range of arsenic(III) concentrations to determine accurately the dependence on arsenic(III) for the two limiting kinetic relationships. The independence of the reaction on arsenic(III) concentration at low copper(II) concentrations was confirmed, the first-order rate constants with respect to persulfate being 4.3×10^{-5}, 4.7×10^{-5}, and 4.5×10^{-5} sec.$^{-1}$ in oxygen-free solution for arsenic(III) concentrations of 2×10^{-2}, 10^{-2}, and 10^{-3} *M*, respectively, at a copper(II) concentration of 10^{-4} *M*. In air-saturated solutions at a copper concentration of 10^{-6} *M* the rate constants were 2.7×10^{-5}, 2.7×10^{-5}, 2.5×10^{-5}, and 2.2×10^{-5} sec.$^{-1}$ for arsenic(III) concentrations of 2×10^{-2}, 10^{-2}, 4×10^{-3}, and 10^{-3} *M*, respectively.

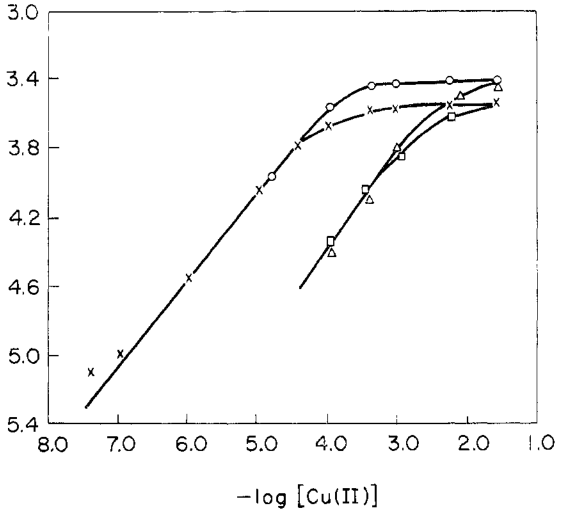

Figure 4.—First-order rate constant, Cu(II) catalyzed reaction; 10^{-3} *M* $S_2O_8^{2-}$, 0.01 *M* $HClO_4$, 0.01–0.02 *M* As(III), $\mu = 0.1$: △, 2×10^{-2} *M* As(III), oxygen-free; □, 10^{-2} *M* As(III), oxygen-free; ○, 2×10^{-2} *M* As(III), air-saturated; ×, 10^{-2} *M* As(III), air-saturated.

In order to determine the dependence of the rate of reduction of persulfate on the arsenic(III) concentration in the range where the rate is independent of copper(II) concentration, the rate was determined in the presence of 2×10^{-2}, 10^{-2}, 4×10^{-3}, and 10^{-3} *M* arsenic(III), for copper(II) concentrations of 5.4×10^{-3} *M* in air-saturated solution and 5.4×10^{-3} and 2.7×10^{-2} *M* in oxygen-free solution. The first-order plots of log $[S_2O_8^{2-}]$ against time for 4×10^{-3} *M* arsenic(III) were not strictly linear due to the decrease in the arsenic(III) concentration during the reaction. The initial slope was taken to find the rate at this arsenic(III) concentration. The reaction in the presence of 10^{-3} *M* arsenic(III) (*i.e.*, equimolar persulfate and arsenic(III)) obeys $^3/_2$-order kinetics, suggesting a $^1/_2$-order dependency on arsenic(III). This is confirmed by the rate constants at the higher arsenic(III) concentrations (Table III). The results confirm that the same limiting kinetic relationship is obtained in both oxygen-free and air-saturated solution, the relationship being

$$k = 2.9 \times 10^{-3}[\mathrm{As(III)}]^{1/2} \text{ sec.}^{-1}$$

The effect of changing the perchloric acid concentration to 0.050 and 0.002 *M* on the rate of reduction of persulfate at constant ionic strength was determined for the two limiting kinetic relationships (Table IV). A maximum variation of 1.3-fold is found for the 25-fold change in perchloric acid concentration for the reactions studied, and therefore it can be concluded that the reaction is independent of acidity at all copper(II) concentrations within the range of acidity 0.002 to 0.050 *M*.

(iv) The Rate of the Iron(II)–Persulfate Reaction.—The rate of the iron(II)–persulfate reaction at an ionic strength of 0.1 was determined by measuring the rate of oxidation of iron(II).[2] The second-order rate constant was found to be 25 *M*$^{-1}$ sec.$^{-1}$ at 25°, which compares favorably with the value of 27 *M*$^{-1}$ sec.$^{-1}$ obtained previously[2] at the same temperature and $\mu = 0.07$.

(v) Determination of Copper(II) Impurity.—The kinetics in the absence of added metal ions could be explained by the presence of a copper(II) impurity in the system. As the rate of reduction of persulfate is

TABLE IV

EFFECT OF ACIDITY

10^{-3} M $S_2O_8^{2-}$; $\mu = 0.1$

[Cu(II)], M	[As(III)], M	[$HClO_4$], M	Oxygen-free k, sec.$^{-1}$ $\times 10^5$	Air-saturated k, sec.$^{-1}$ $\times 10^5$
10^{-3}	2×10^{-2}	0.002	14	
		0.010	14	
		0.050	15	
	10^{-2}	0.002	13	
		0.010	13	
		0.050	15	
$.4 \times 10^{-3}$	10^{-2}	0.002		28
		0.010		26
		0.050		22
10^{-5}	2×10^{-2}	0.002		9.7
		0.010		8.6
		0.050		7.6
	10^{-2}	0.002		9.4
		0.010		8.3
		0.050		7.3
10^{-6}	2×10^{-2}	0.002		3.2
		0.010		2.7
		0.050		2.5
	10^{-2}	0.002		3.1
		0.010		2.7
		0.050		2.5

virtually independent of arsenic(III) concentration (Table I), the arsenic(III) cannot be the source of the impurity. No copper was detected in 0.1 M persulfate and 1 M perchloric acid solutions. At the concentrations of these agents used in the reaction mixtures the copper concentration was negligible, at least less than 0.5×10^{-9} M. The copper concentration in 0.1 M sodium perchlorate corresponded to 8×10^{-9} M, and in the water to 6×10^{-9} M. Thus, the copper concentration in 0.1 M sodium perchlorate solution was 1.4×10^{-8} M.

Discussion

The thermal decomposition of persulfate in acid solution proceeds by two parallel paths, reactions 1 and 2, the over-all rate constant, k, being given by[5]

$$k = k_1 + k_2[H^+]$$

The rate constant k_1 was determined by Kolthoff and Miller[5] to be 1.0×10^{-6} sec.$^{-1}$ at 50°, independent of acidity or ionic strength, with an activation energy of 33.5 kcal. The value of this rate constant at 25°, calculated from these results, is 1.3×10^{-8} sec.$^{-1}$. The over-all rate constant at 25° was found to be 9.0×10^{-8} sec.$^{-1}$ (Table I) at a hydrogen ion concentration of 0.01 M and an ionic strength of 0.1, giving 7.7×10^{-6} M^{-1} sec.$^{-1}$ for k_2 at this temperature and ionic strength. This value of k_2 compares favorably with 2.0×10^{-6} M^{-1} sec.$^{-1}$ at 25° and $\mu = 0.4$ calculated from the data of Kolthoff and Miller. The decomposition characterized by k_2 at an acidity of 0.01 M and an ionic strength of 0.1 accounts for 86% of the persulfate decomposed in the absence of oxidizable material other than water.

In the absence of oxygen, the presence of arsenic trioxide has only a small effect on the rate of reduction of persulfate (Table I). In air-saturated solution arsenic trioxide increases the rate of reduction of persulfate fortyfold (Table I). This increase is reduced to a factor of about three in the presence of 1% of either allyl acetate or acrylonitrile, which are efficient capture agents for sulfate free radicals and without attack on persulfate. The effect of these agents suggests that reaction 1 initiates a chain reaction in the presence of oxygen. In the presence of allyl acetate or acrylonitrile the arsenic trioxide oxidized is equivalent to 90% of the persulfate reduced, showing that a nonchain oxidation of arsenic trioxide by the k_2 persulfate decomposition path is still taking place. This oxidation of arsenic(III) by reaction 2 and its nonchain character can be explained by two-electron oxidation of arsenic(III) by the product of reaction 2

$$As(III) + SO_4 \longrightarrow As(V) + SO_4^{2-} \qquad (3)$$

Wilmarth and Haim[12] suggested that reaction 2 should be

$$H_3O^+ + S_2O_8^{2-} \longrightarrow H_2SO_5 + HSO_4^- \qquad (2a)$$

The oxidation of arsenic(III) by SO_4 or H_2SO_5 is similar to the oxidation by hydrogen peroxide, which was also shown to proceed by a nonchain mechanism.[3]

The oxidation of arsenic trioxide by the persulfate decomposition path characterized by k_2 should not affect chain oxidations initiated by the decomposition path producing sulfate free radicals and need not be considered in the iron(III) and copper(II) catalyzed reactions between persulfate and arsenic(III).

In the presence of oxygen a chain reaction occurs (Table I). The reaction is first order to persulfate, the rate constant being 4×10^{-6} sec.$^{-1}$, and practically independent of arsenic(III) concentration. The chain process could be accounted for by the series of reactions

$$S_2O_8^{2-} \longrightarrow 2SO_4^{\overline{\cdot}} \qquad (1)$$

$$SO_4^{\overline{\cdot}} + As(III) \longrightarrow SO_4^{2-} + As(IV) \qquad (4)$$

$$As(IV) + O_2 + H^+ \longrightarrow As(V) + HO_2 \qquad (5)$$

$$HO_2 + S_2O_8^{2-} \longrightarrow H^+ + O_2 + SO_4^{2-} + SO_4^{\overline{\cdot}} \qquad (6)$$

If termination occurred by either of the reactions[13]

$$SO_4^{\overline{\cdot}} + HO_2 \longrightarrow SO_4^{2-} + H^+ + O_2 \qquad (7)$$

$$2SO_4^{\overline{\cdot}} \longrightarrow S_2O_8^{2-} \qquad (8)$$

the rate of reaction would not be independent of [As(III)], contrary to fact. If termination occurred by the reaction

$$As(IV) + HO_2 \longrightarrow As(III) + H^+ + O_2$$

the reaction would be first order to persulfate and zero order to arsenic(III), as found experimentally, and half order to [O_2]. Although such a termination reaction is possible, our results are accounted for quantitatively by taking into account the trace of copper(II) in the reaction mixtures in Table I. The copper content of the reaction mixtures in Table I was 1.4×10^{-8} M Cu(II). The results of the copper(II) cata-

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(12) W. K. Wilmarth and A. Haim, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, New York, N. Y., 1960, p. 175.

(13) M. S. Tsao and W. K. Wilmarth, *Discussions Faraday Soc.*, **29**, 137 (1960).

lyzed reaction (Figure 4) revealed that at low copper(II) concentrations in air-saturated solution the rate of reduction of persulfate is given by

$$-\frac{\mathrm{d}[\mathrm{S_2O_8}^{2-}]}{\mathrm{d}t} = 2.8 \times 10^{-2}[\mathrm{Cu(II)}]^{1/2}[\mathrm{S_2O_8}^{2-}]$$

The kinetics in the absence of added copper(II) (Table I) correspond to a rate constant of 4×10^{-6} sec.$^{-1}$, which is equivalent to $[\mathrm{Cu(II)}] = 2 \times 10^{-8}$ *M*, in satisfactory agreement with the experimentally determined value of 1.4×10^{-8} *M* [Cu(II)]. Furthermore, the rate constant in the absence of oxygen when no copper(II) was added was $6\text{-}7 \times 10^{-7}$ sec.$^{-1}$ (Table I), which also is consistent with a copper(II) concentration of *ca.* 2×10^{-8} *M* (Figure 4). The copper impurity also accounts for the increased rate observed in Figure 4, when the added concentration of copper became less that 10^{-7} *M*.

The rates of the iron(III) catalyzed reactions were not corrected for the rate in the absence of iron(III) (traces of copper), although this rate is comparable to the rates in the presence of the lower iron(III) concentrations studied. Copper(II) is 25 times more reactive toward hydroperoxo radical than iron(III) in the presence of 0.01 *M* perchloric acid.[14] As the iron(III) concentration in all experiments was greater than 10^4 times the copper impurity, the reaction of this impurity with the hydroperoxo radical, and therefore its catalysis, will be eliminated. It is postulated that the iron catalyzed reaction proceeds by a chain mechanism initiated by reaction 1. The subsequent reactions constituting the chain should be the same as those in the induced oxidation of arsenic(III) by the iron(II)-persulfate reaction.[2,3]

In the absence of oxygen the chain should proceed

$$\mathrm{As(III)} + \mathrm{SO_4}^{\cdot -} \longrightarrow \mathrm{As(IV)} + \mathrm{SO_4}^{2-} \tag{4}$$

$$\mathrm{As(IV)} + \mathrm{Fe(III)} \longrightarrow \mathrm{As(V)} + \mathrm{Fe}^{2+} \tag{9}$$

$$\mathrm{Fe}^{2+} + \mathrm{S_2O_8}^{2-} \longrightarrow \mathrm{Fe(III)} + \mathrm{SO_4}^{\cdot -} + \mathrm{SO_4}^{2-} \tag{10}$$

The stoichiometry of the chain agrees with the experimental results. The previous investigations[2,4] suggest that the termination reaction will be

$$\mathrm{As(IV)} + \mathrm{Fe}^{2+} \longrightarrow \mathrm{As(III)} + \mathrm{Fe(III)} \tag{11}$$

Assuming steady-state conditions with respect to Fe^{2+}, $\mathrm{SO_4}^{\cdot -}$, and As(IV) and taking $k_{10}[\mathrm{Fe}^{2+}]/k_1 \gg 1$, we find at a given acidity

$$-\frac{\mathrm{d}[\mathrm{S_2O_8}^{2-}]}{\mathrm{d}t} = (k_1k_{10}k_9/k_{11})^{1/2}[\mathrm{Fe(III)}]^{1/2}[\mathrm{S_2O_8}^{2-}]$$

The ratio k_9/k_{11} was shown to be dependent on acidity due to different rates for the reactions of arsenic(IV) with Fe^{3+} and FeOH^{2+}.[2,4] In the acidity range studied here, only the reaction with FeOH^{2+}

$$\mathrm{As(IV)} + \mathrm{FeOH}^{2+} \longrightarrow \mathrm{As(V)} + \mathrm{Fe}^{2+} \tag{9'}$$

will be significant and therefore

$$-\frac{\mathrm{d}[\mathrm{S_2O_8}^{2-}]}{\mathrm{d}t} = \left(k_1k_{10}\frac{k_{9'}}{k_{11}}K_\mathrm{a}\right)^{1/2}\frac{[\mathrm{Fe(III)}]^{1/2}}{([\mathrm{H}^+] + K_\mathrm{a})^{1/2}}[\mathrm{S_2O_8}^{2-}]$$

In air-saturated solution, the reactions

$$\mathrm{As(IV)} + \mathrm{O_2} + \mathrm{H}^+ \longrightarrow \mathrm{As(V)} + \mathrm{HO_2} \tag{5}$$

$$\mathrm{HO_2} + \mathrm{Fe(III)} \longrightarrow \mathrm{H}^+ + \mathrm{O_2} + \mathrm{Fe}^{2+} \tag{12}$$

will replace reaction 9 in the chain, the over-all stoichiometry being unchanged in accordance with the experimental results. The chain should be terminated by the series of reactions[3,4]

$$\mathrm{Fe}^{2+} + \mathrm{HO_2} \longrightarrow \mathrm{Fe(III)} + \mathrm{H_2O_2} \tag{13}$$

$$\mathrm{Fe}^{2+} + \mathrm{H_2O_2} \longrightarrow \mathrm{Fe(III)} + \mathrm{OH}^- + \mathrm{OH}^\cdot \tag{14}$$

$$\mathrm{As(III)} + \mathrm{OH}^\cdot \longrightarrow \mathrm{As(IV)} + \mathrm{OH}^- \tag{15}$$

$$\mathrm{As(III)} + \mathrm{H_2O_2} \longrightarrow \mathrm{As(V)} + \mathrm{H_2O} \tag{16}$$

Assuming steady-state conditions with respect to Fe^{2+}, $\mathrm{SO_4}^{\cdot -}$, As(IV), $\mathrm{HO_2}$, $\mathrm{H_2O_2}$, and $\mathrm{OH}^\cdot$ yields a cubic equation for $[\mathrm{Fe}^{2+}]$ which can be put in the form

$$\frac{k_{10}}{k_1}[\mathrm{Fe}^{2+}]^2 + [\mathrm{Fe}^{2+}]\left\{1 + \frac{1}{1 + \dfrac{k_{16}[\mathrm{As(III)}]}{k_{14}[\mathrm{Fe}^{2+}]}}\right\} - \frac{k_{12}}{k_{13}}[\mathrm{Fe(III)}] = 0$$

The coefficient of $[\mathrm{Fe}^{2+}]$ obviously cannot exceed 2, while $k_{10}[\mathrm{Fe}^{2+}] \gg k_1$. Accordingly

$$[\mathrm{Fe}^{2+}] = \left(\frac{k_1k_{12}}{k_{10}k_{13}}[\mathrm{Fe(III)}]\right)^{1/2}$$

and

$$-\frac{\mathrm{d}[\mathrm{S_2O_8}^{2-}]}{\mathrm{d}t} = \left(\frac{k_1k_{10}k_{12}}{k_{13}}\right)^{1/2}[\mathrm{Fe(III)}]^{1/2}[\mathrm{S_2O_8}^{2-}]$$

It has been shown previously[3,14] that the ratio k_{12}/k_{13} is dependent upon acidity, the quantity $([\mathrm{H}^+] + K_\mathrm{a})(k_{12}/k_{13})$ being a constant $= \kappa$. Accordingly

$$-\frac{\mathrm{d}[\mathrm{S_2O_8}^{2-}]}{\mathrm{d}t} = (k_1k_{10}\kappa)^{1/2}\frac{[\mathrm{Fe(III)}]^{1/2}}{([\mathrm{H}^+] + K_\mathrm{a})^{1/2}}[\mathrm{S_2O_8}^{2-}]$$

Experimentally, in both oxygen-free and air-saturated solutions, the rate of reduction of persulfate is found to be first order to persulfate, one-half order to iron(III), minus one-half order to $\{[\mathrm{H}^+] + K_\mathrm{a}\}$, and zero order to arsenic(III), in accordance with the proposed mechanism. Furthermore, all the individual rate constants are known: $k_1 = 1.3 \times 10^{-8}$ sec.$^{-1}$ calculated from the data of Kolthoff and Miller,[5] k_{10} was determined in this research to be 25 M^{-1} sec.$^{-1}$, $k_{9'}/k_{11} = 9$,[2] $K_\mathrm{a} = 2.8 \times 10^{-3}$ at $\mu = 0.1$,[11] and $\kappa = 3.7 \times 10^{-3}$.[3] Therefore

$$\left(k_1k_{10}\frac{k_{9'}}{k_{11}}K_\mathrm{a}\right)^{1/2} = 9.0 \times 10^{-5}\ \mathrm{sec.}^{-1}$$

and

$$(k_1k_{10}\kappa)^{1/2} = 3.5 \times 10^{-5}\ \mathrm{sec.}^{-1}$$

The experimental values for these constants are 7.6 ×

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[14] W. G. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 462, 591 (1951).

10^{-5} and 4.3×10^{-5}, respectively, in excellent agreement with the calculated constants, substantiating the proposed mechanism and the values of the ratios k_9'/k_{11} and $([\mathrm{H}^+] + K_a)k_{12}/k_{13}$ determined previously.[2,3]

The rate of the copper(II) catalyzed oxidation of arsenic(III) by persulfate at low copper concentrations is first order to persulfate, one-half order to copper(II), zero order to arsenic(III), and dependent on the presence of oxygen. This is the same kinetic relationship as in iron(III) catalysis and therefore an analogous mechanism is indicated.

In the absence of oxygen, therefore, the reactions

$$\mathrm{As(IV)} + \mathrm{Cu}^{2+} \longrightarrow \mathrm{As(V)} + \mathrm{Cu(I)} \qquad (17)$$

$$\mathrm{Cu(I)} + \mathrm{S_2O_8}^{2-} \longrightarrow \mathrm{Cu}^{2+} + \mathrm{SO_4}^{\cdot-} + \mathrm{SO_4}^{2-} \qquad (18)$$

$$\mathrm{As(IV)} + \mathrm{Cu(I)} \longrightarrow \mathrm{As(III)} + \mathrm{Cu}^{2+} \qquad (19)$$

will replace reactions 9, 10, and 11, respectively. In air-saturated solution, the reactions

$$\mathrm{HO_2} + \mathrm{Cu}^{2+} \longrightarrow \mathrm{H}^+ + \mathrm{O_2} + \mathrm{Cu(I)} \qquad (20)$$

$$\mathrm{Cu(I)} + \mathrm{S_2O_8}^{2-} \longrightarrow \mathrm{Cu}^{2+} + \mathrm{SO_4}^{\cdot-} + \mathrm{SO_4}^{2-} \qquad (18)$$

$$\mathrm{Cu(I)} + \mathrm{HO_2} \longrightarrow \mathrm{Cu}^{2+} + \mathrm{H_2O_2} \qquad (21)$$

$$\mathrm{Cu(I)} + \mathrm{H_2O_2} \longrightarrow \mathrm{Cu}^{2+} + \mathrm{OH}^{\cdot} + \mathrm{OH}^- \qquad (22)$$

will replace reactions 12, 10, 13, and 14, respectively. The rate of reduction of persulfate, analogous to the iron(III) catalysis, is given by the following equations. Oxygen-free solution

$$-\frac{\mathrm{d}[\mathrm{S_2O_8}^{2-}]}{\mathrm{d}t} = (k_1k_{18}k_{17}/k_{19})^{1/2}[\mathrm{Cu(II)}]^{1/2}[\mathrm{S_2O_8}^{2-}]$$

Air-saturated solution

$$-\frac{\mathrm{d}[\mathrm{S_2O_8}^{2-}]}{\mathrm{d}t} = (k_1k_{18}k_{20}/k_{21})^{1/2}[\mathrm{Cu(II)}]^{1/2}[\mathrm{S_2O_8}^{2-}]$$

The rate of reduction of persulfate at high copper(II) concentrations becomes independent of copper(II) concentration and the presence of oxygen. This can be explained by the termination reaction

$$\mathrm{Cu(I)} + \mathrm{SO_4}^{\cdot-} \longrightarrow \mathrm{Cu}^{2+} + \mathrm{SO_4}^{2-} \qquad (23)$$

As the copper(II) concentration is increased, the copper(I) steady-state concentration is increased and the sulfate free radical reacts with the copper(I) rather than the arsenic(IV). At the higher copper(II) values the termination reaction 23 is much more pronounced than the termination reactions 19 and 21 in oxygen-free and air-saturated solutions, respectively, and therefore determines the kinetics. As the sum of reactions 5 and 20 is equal to reaction 17 and the termination does not involve competition of copper(I) with arsenic(IV) or hydroperoxo radical, it is evident that the kinetics will be independent of oxygen. Assuming steady-state conditions with respect to the intermediates and taking $k_{18}[\mathrm{Cu(I)}]/k_1 \gg 1$

$$-\frac{\mathrm{d}[\mathrm{S_2O_8}^{2-}]}{\mathrm{d}t} = (k_1k_{18}k_4/k_{23})^{1/2}[\mathrm{As(III)}]^{1/2}[\mathrm{S_2O_8}^{2-}]$$

The experimental results are in agreement with this relationship, substantiating the proposed mechanism.

Comparison of the experimental and derived rate constants, taking $k_1 = 1.3 \times 10^{-8}$ sec.$^{-1}$, gives the values: $k_{18}k_{17}/k_{19} = 1.4 \times 10^3$; $k_{18}k_{20}/k_{21} = 5.2 \times 10^4$; $k_{18}k_4/k_{23} = 6.5 \times 10^2$, all M^{-1} sec.$^{-1}$. The rate of the copper(I)–persulfate reaction, k_{18}, is not known and therefore the individual ratios cannot be determined.

Of particular interest is the effect of acidity on the copper(II) catalyzed reaction. The rate of reduction of persulfate is determined by the ratios $k_1k_{18}k_{17}/k_{19}$, $k_1k_{18}k_{20}/k_{21}$, and $k_1k_{18}k_4/k_{23}$ in oxygen-free solution at low copper(II) concentrations, in air-saturated solution at low copper(II) concentrations, and in oxygen-free and air-saturated solutions at high copper(II) concentrations, respectively. Experimentally, the rate under all these conditions was found to be independent of acidity and, as it can be anticipated that all the other rate constants are independent of acidity, it is concluded that the ratio k_{20}/k_{21}, the ratio of the rate constants for the reactions of hydroperoxo radical with copper(II) and copper(I), is independent of acidity.

Barb, *et al.*,[14] suggested that hydroperoxo radical dissociated at the acidities used here and that $\mathrm{HO_2}$ is the oxidizing and $\mathrm{O_2}^-$ the reducing species

$$\mathrm{HO_2} \rightleftharpoons \mathrm{H}^+ + \mathrm{O_2}^-$$

$$\mathrm{Cu}^{2+} + \mathrm{O_2}^- \longrightarrow \mathrm{Cu(I)} + \mathrm{O_2} \qquad (20')$$

$$\mathrm{Cu(I)} + \mathrm{HO_2} \longrightarrow \mathrm{Cu}^{2+} + \mathrm{H_2O_2} \qquad (21)$$

The ratio of the rate constants k_{20}/k_{21} should then be equal to $(k_{20}/k_{21})(K_{\mathrm{HO_2}}/[\mathrm{H}^+])$, $K_{\mathrm{HO_2}}$ being the acid dissociation constant of $\mathrm{HO_2}$. This would imply an acid dependency for k_{20}/k_{21} and therefore for the rate of reduction of persulfate in the region where reaction 21 is the chain-termination step. However, k_{20}/k_{21} should be independent of acidity if both copper species react with $\mathrm{HO_2}$ which, like As(IV), can act as an oxidizing and reducing agent. Rothschild and Allen[15] proposed this for the reaction of iron(III) with hydroperoxo radical, FeOH^{2+} being more reactive than Fe^{3+}. The experimental evidence, therefore, supports the Rothschild and Allen mechanism and is in contradiction to that of Barb, *et al.*

An alternative explanation is that arsenic(IV) forms a peroxy species, $\mathrm{As^{IV}O_2}$, as suggested by Daniels,[16] which, like the hydroperoxo radical, can react with iron(III) or copper(II) to give arsenic(V) and oxygen, and with iron(II) or copper(I) to give arsenic(V) and hydrogen peroxide. The effect of hydrogen ion concentration in the case of iron(III) catalysis can then be accounted for by a greater reactivity of FeOH^{2+} than Fe^{3+} with $\mathrm{As^{IV}O_2}$. Qualitatively, this mechanism explains the over-all reactions presented here and in previous publications.[3,4] However, it was found previously[3] that the value of the ratio of the rate constants, as well as the acid dependence, for the reactions of the peroxy intermediate ($\mathrm{As^{IV}O_2}$ or $\mathrm{HO_2}$) with iron(III) and iron(II) agreed with that for the

(15) W. G. Rothschild and A. O. Allen, *Radiation Res.*, **8**, 101 (1958).

(16) M. Daniels, *J. Phys. Chem.*, **66**, 1473 (1962).

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]

(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°.