Arsenic(IV) as an Intermediate in the Induced Oxidation of Arsenic(III) by the Iron(II)-Hydrogen Peroxide Reaction[1]

By R. Woods, I. M. Kolthoff, and E. J. Meehan
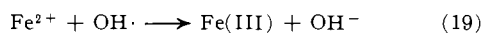
The iron(II)-hydrogen peroxide couple induces the oxidation of arsenic(III). The mechanism, involving the intermediate formation of arsenic(IV), is similar to that in the induced oxidation of arsenic(III) by the iron(II)-persulfate couple and the photoreduction of iron(III). From the results of a study of the induced oxidation of arsenic(III) at 25° the ratio of the rate constants of the reactions of the hydroxyl free radical with arsenic(III) and iron(II) was calculated to be 4, in satisfactory agreement with a value of 2 from the photoinduced oxidation of arsenic(III) by iron(III). On the other hand, this ratio for the active intermediate formed in the persulfate-iron(II) reaction is 21. It is concluded that in the iron(II)-persulfate inducing reaction, SO_4^- oxidizes arsenic(III) to arsenic(IV).

The iron(II)-hydrogen peroxide system has been the subject of extensive investigation.[2] The initial reaction 16 produces a hydroxyl free radical

$$Fe^{2+} + H_2O_2 \longrightarrow Fe(III) + OH\cdot + OH^- \quad (16)$$

The numbers of the equations are identical with those presented in previous papers.[3,4] In the absence of other oxidizable species, the hydroxyl radical can either oxidize another ferrous ion (reaction 19)

$$Fe^{2+} + OH\cdot \longrightarrow Fe(III) + OH^- \quad (19)$$

or react with hydrogen peroxide to form hydroperoxo radical, involving the chain decomposition of hydrogen peroxide.[2] This induced chain decomposition is insignificant when iron(II) is in excess of hydrogen peroxide. The hydroxyl radical produced by reaction 16 induces oxidations and polymerizations of organic substances, the so-called Fenton reaction.[2]

In a recent study,[3,4] the induced oxidation of arsenic(III) by the iron(II)-persulfate reaction and the photoreduction of iron(III) was interpreted on the basis of the intermediate formation of arsenic(IV) produced by the reactions

$$As(III) + SO_4^- \longrightarrow As(IV) + SO_4^{2-} \quad (3)$$

$$As(III) + OH\cdot \longrightarrow As(IV) + OH^- \quad (10)$$
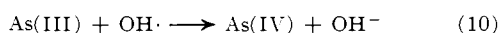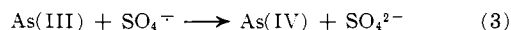
In the present paper it is shown that oxidation of arsenic(III) is induced by the iron(II)-hydrogen peroxide reaction by a mechanism similar to that which has been proposed for the persulfate-iron(II) inducing reaction.

It was assumed in the induced oxidation of arsenic(III) by the iron(II)-persulfate reaction that arsenic(III) and iron(II) react with the sulfate free radical, although the radical exchange reaction

$$SO_4^- + H_2O \rightleftarrows OH\cdot + HSO_4^-$$
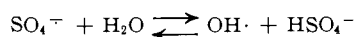
with subsequent oxidation of arsenic(III) and iron(II) by the hydroxyl radical could also explain the results. This radical exchange is known to occur in photolytic[5] and thermal[6] decompositions of persulfate.

Morgan[7] suggested that the same free radical initiates polymerization of monomers with either hydrogen per-

oxide-iron(II) or persulfate-iron(II) as activating couples. However, Kolthoff, et al.,[8] showed conclusively that in the initiation of the polymerization of styrene by the persulfate-iron(II) couple it is the sulfate free radical and not the hydroxyl radical which activates the monomer.

Quite generally, in induced oxidations by the persulfate-iron(II) couple the relative rate of the radical exchange reaction and oxidation by the sulfate radical of active species in the system should determine to what extent, if any, hydroxyl radicals are produced.

Investigations of induced oxidations of organic compounds by the two couples suggest that in the iron(II)-persulfate reaction the exchange reaction does not take place. The extent of oxidation of ethanol by the two couples is sufficiently different to allow the conclusion that the active intermediates are different.[9,10] More quantitative information is obtained from the competition ratios of the reaction rates of methyl acrylate and iron(II) with the active intermediates which are reported[11] to be 3×10^{-3} for the persulfate couple compared with 5.0 for the hydrogen peroxide couple.[12]

Comparison of the induced oxidation of arsenic(III) by the iron(II)-persulfate and iron(II)-hydrogen peroxide couples provides a means for ascertaining whether the radical exchange reaction under the experimental conditions converts sulfate radicals quantitatively to hydroxyl radicals. The conclusion arrived at in this study is substantiated by results obtained in the photoinduced oxidation of arsenic(III) by iron(III).

Experimental

The hydrogen peroxide was a 98% Becco product. All other reagents and the experimental technique are identical with those reported in a previous study.[3,4] All experiments were carried out at 25 ± 0.02°.

Results

(1) **Absence of Oxygen.**—The rate constant of the bimolecular reaction between arsenic trioxide and hydrogen peroxide was found to be 1.0×10^{-2} l. mole^{-1} sec.$^{-1}$ at 25°[4]; the rate of oxidation of arsenic(III) by peroxide is much greater than the rate of oxidation by persulfate. The hydrogen peroxide-arsenic(III) reac-

(1) This investigation was carried out under a grant from the National Science Foundation.

(2) N. Uri, *Chem. Rev.*, **50**, 375 (1952).

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

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

(5) W. K. Wilmarth and A. Haim, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 175-225.

(6) I. M. Kolthoff and I. K. Miller, *J. Am. Chem. Soc.*, **73**, 3055 (1951).

(7) L. B. Morgan, *Trans. Faraday Soc.*, **42**, 169 (1946).

(8) I. M. Kolthoff, P. R. O'Connor, and J. L. Hansen, *J. Am. Chem. Soc.*, **71**, 1419 (1949).

(9) J. H. Mertz and W. A. Waters, *Discussions Faraday Soc.*, **2**, 179 (1947).

(10) I. M. Kolthoff and A. I. Medalia, *J. Am. Chem. Soc.*, **71**, 3777 (1949); I. M. Kolthoff, A. I. Medalia, and H. P. Raen, *ibid.*, **77**, 3715 (1955).

(11) R. J. Orr and H. L. Williams, *ibid.*, **77**, 3715 (1955).

(12) J. H. Baxendale, M. G. Evans, and G. S. Park, *Trans. Faraday Soc.*, **42**, 155 (1946).

tion is slow compared with the reaction of iron(II) with hydrogen peroxide, which has a rate constant of 53 l. mole^{-1} sec.$^{-1}$.[13] The effect of acidity on the stoichiometry of the induced oxidation of arsenic(III) by the hydrogen peroxide–iron(II) couple was determined in mixtures which were 10^{-3} M in arsenic(III) and in which the ionic strength was kept at 0.5 by addition of sodium perchlorate. Using iron(II) concentrations of 6×10^{-5} to 1×10^{-5} M, direct oxidation of arsenic(III) by hydrogen peroxide becomes insignificant. Under these conditions the arsenic(III) to iron(II) concentration ratio is large enough to eliminate the reaction of hydroxyl radical with iron(II) (vide infra). The stoichiometry can be compared with that of the induced oxidation of arsenic(III) by the iron(II)–persulfate reaction, the stoichiometry of the latter system having been found to be independent of arsenic(III) concentration provided it was greater than twice the iron(II) concentration.[3] The results are presented in Table I.

TABLE I

EFFECT OF ACIDITY ON THE INDUCTION FACTOR

5.7 $\times$ 10^{-5} M Fe^{2+}, 2.5 $\times$ 10^{-5} M H$_2$O$_2$, 10^{-3} M As(III), μ = 0.5, T = 25°, I.F. = equiv. of As(III) oxidized/equiv. of Fe(II) oxidized, absence of oxygen

[HClO$_4$], M	I.F.	I.F. obtained with 2.5 $\times$ 10^{-5} M persulfate
0.50	0.16	0.17
.10	.22	.20
.010	.67	.68
.005	.92	.87
.002	1.07	1.25

The induction factor is increased in the presence of initially added ferric perchlorate. The effect on the induction factor of reducing the arsenic(III) concentration at constant iron(II) and hydrogen peroxide concentrations was investigated in the presence of sufficient iron(III) to yield an induction factor of infinity in the presence of 10^{-3} M arsenic(III). The results are presented in Table II.

TABLE II

EFFECT ON I.F. OF CONCENTRATION OF ARSENIC(III) IN PRESENCE OF Fe(III)

5.0 $\times$ 10^{-5} M Fe^{2+}, 2.5 $\times$ 10^{-5} M H$_2$O$_2$, μ = 0.5, T = 25°, absence of oxygen

[HClO$_4$], M	[Fe(III)], M	[As(III)], $M \times 10^5$	I.F.	$k_{10}/k_{19}{}^a$
0.10	2 $\times$ 10^{-2}	2.5	0.82	4.0
		5.0	1.9	4.4
		10.0	3.3	3.5
		100	∞	...
0.010	2 $\times$ 10^{-3}	2.5	0.92	4.8
		5.0	1.7	3.8
		10.0	2.8	3.2
		100	∞	...
0.002	5 $\times$ 10^{-4}	2.5	1.0	5.4
		5.0	2.1	5.0
		10.0	4.5	4.8
		100	∞	...
			Average	4

^{a} See Discussion.

In a previous study[3] the results of the photoinduced iron(III)–arsenic(III) reaction in the absence of oxygen were presented and discussed. In that study only

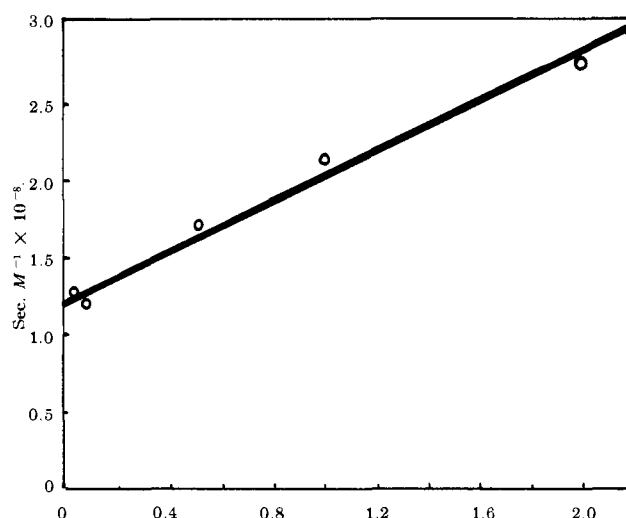(13) W. G. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, Trans. Faraday Soc., 47, 462 (1951).

Fig. 1.—Plot of the reciprocal of d[Fe^{2+}]/dt (ordinate) against [Fe^{2+}]/[As(III)] (abscissa).

results at high arsenic(III) concentration, where the rate of formation of iron(II) is independent of arsenic(III) concentration, were analyzed, although it was pointed out that the rate of formation of iron(II) is reduced at arsenic(III) concentrations less than 10^{-3} M. The rate of iron(II) formation was measured in the presence of 10^{-4} M Fe(III); 0.01 M HClO$_4$; 5×10^{-5} M Fe^{2+}; μ = 0.5; and 2×10^{-2}, 10^{-2}, 10^{-3}, 10^{-4}, 5×10^{-5}, and 2.5×10^{-5} M arsenic(III), respectively. A plot of the reciprocal of d[Fe^{2+}]/dt against [Fe^{2+}]/[As(III)] is given in Fig. 1 and shown to be linear.

(2) **Presence of Oxygen.**—The stoichiometry of the induced oxidation of arsenic(III) by the iron(II)–hydrogen peroxide reaction in the presence of oxygen was determined using solutions which were 2.5×10^{-3} M in arsenic trioxide and 2.5×10^{-5} M in hydrogen peroxide at varying perchloric acid and iron(II) concentrations. For comparison the experiments were repeated under the same conditions using 2.5×10^{-5} M persulfate instead of peroxide. The concentrations of arsenic(III) and iron(II) were such that the direct oxidation of arsenic(III) by hydrogen peroxide was insignificant. The results are given in Table III.

TABLE III

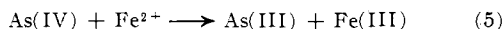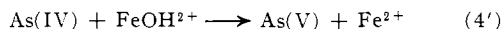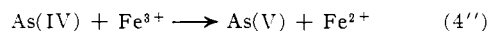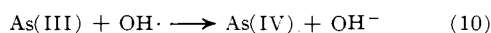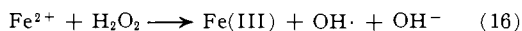EFFECT OF ACIDITY ON THE MOLAR REACTION RATIOS

R_{Fe} = moles of Fe^{2+} oxidized/moles of actor reduced; R_{As} = moles of As(III) oxidized/moles of actor reduced; 2.5×10^{-3} M As(III), 2.5×10^{-5} M actor, μ = 0.5, T = 25°, air saturated

[HClO$_4$], M	[Fe^{2+}], $M \times 10^5$	Actor = H$_2$O$_2$ R_{Fe}	Actor = H$_2$O$_2$ R_{As}	Actor = S$_2$O$_8{}^2{}^-$ R_{Fe}	Actor = S$_2$O$_8{}^2{}^-$ R_{As}
0.50	53.1	19.7	9.6	19.1	8.9
.10	53.1	17.0	8.2	15.5	7.6
.010	17.9	6.1	3.2	5.6	3.0
.005	17.9	5.10	2.75	4.81	2.60
.002	7.77	2.58	1.85	2.47	1.80

Discussion

The hydroxyl free radical produced in the reaction of iron(II) with hydrogen peroxide oxidizes arsenic(III) to arsenic(IV),[3,4] which, in the absence of oxygen, can oxidize iron(II) and reduce iron(III), FeOH^{2+} being 90 times as reactive as Fe^{3+}.[3] Under our experimental conditions, where iron(II) and arsenic(III) were always in excess of hydrogen peroxide, the reaction of a hydroxyl radical with hydrogen peroxide will be negligible. If the arsenic(III) concentration is large enough to

eliminate the reaction of iron(II) with the hydroxyl radical, the mechanism of the induced reaction in the absence of oxygen is given by the sequence

$$Fe^{2+} + H_2O_2 \longrightarrow Fe(III) + OH\cdot + OH^- \quad (16)$$

$$As(III) + OH\cdot \longrightarrow As(IV) + OH^- \quad (10)$$

$$As(IV) + Fe^{3+} \longrightarrow As(V) + Fe^{2+} \quad (4'')$$

$$As(IV) + FeOH^{2+} \longrightarrow As(V) + Fe^{2+} \quad (4')$$

$$As(IV) + Fe^{2+} \longrightarrow As(III) + Fe(III) \quad (5)$$

As in the iron(II)–persulfate induced oxidation, the stoichiometry should depend only on the relative concentrations of iron(II) and iron(III) and on the hydrogen ion concentration which determines the relative amounts of Fe^{3+} and $FeOH^{2+}$. Under identical conditions of acidity and actor and iron(II) concentrations, the induction factors for the two induction couples should be identical. Table I shows that the measured induction factors are the same within the experimental error.

In the presence of initially added iron(III), the induction factor is increased (Table II). When the induction factor reaches infinity, all the arsenic(IV) produced by reaction 10 reacts with iron(III). Iron(II) can compete with arsenic(III) for the hydroxyl radical (reaction 19). The infinite induction factor in the presence of sufficient iron(III) shows that this reaction is insignificant when the arsenic(III) to iron(II) concentration ratio is at least 20. However, as this ratio is reduced, reaction 19 becomes significant and a decrease of I.F. from its value of infinity results (Table II). This gives a method for determining the competition ratio k_{10}/k_{19} for, assuming steady state kinetics with respect to As(IV) and OH$\cdot$.[3]

$$\frac{k_{10}}{k_{19}} = 2 \frac{\ln\ ([As(III)]_0/[As(III)]_\infty)}{\ln\ ([Fe^{2+}]_0/[Fe^{2+}]_\infty)}$$

The average value of k_{10}/k_{19} calculated from the results in Table II is equal to 4 and independent of acidity.

The value of k_{10}/k_{19} can also be obtained from the results of the photoinduced oxidation of arsenic(III) by iron(III) in the absence of oxygen. In a previous paper,[3] a relationship between the rate of formation of iron(II) and the reactants present was derived.

$$\frac{d[Fe^{2+}]}{dt} =$$

$$\frac{k'[FeOH^{2+}]}{\left(1 + \frac{k_5}{k_4}\frac{[Fe^{2+}]}{[Fe(III)]}\right)\left(1 + \frac{k_7k_9}{(k_7 + k_8)k_{10}}\frac{[Fe^{2+}]}{[As(III)]}\right)}$$

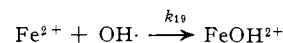At constant $[Fe^{2+}]$, $[FeOH^{2+}]$, and $[Fe(III)]$ we obtain

$$1\left/\frac{d[Fe^{2+}]}{dt}\right. = k''\left(1 + \frac{k_7k_9}{(k_7 + k_8)k_{10}}\frac{[Fe^{2+}]}{[As(III)]}\right)$$

The rate constants k_7, k_8, and k_9 refer to the reactions

$$Fe^{2+} + OH\cdot \underset{k_8}{\overset{k_9}{\rightleftharpoons}} Fe^{2+}OH\cdot$$

$$Fe^{2+}OH\cdot \overset{k_7}{\longrightarrow} FeOH^{2+}$$
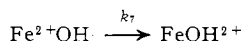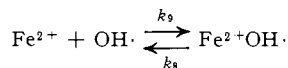
which is equivalent to the over-all reaction 19

$$Fe^{2+} + OH\cdot \overset{k_{19}}{\longrightarrow} FeOH^{2+}$$

Assuming steady-state conditions with respect to Fe^{2+}-OH$\cdot$

$$k_{19} = k_7k_9/(k_7 + k_8)$$

and therefore

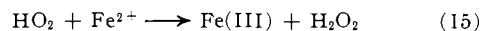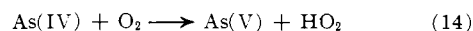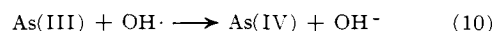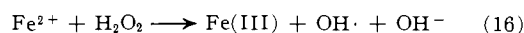$$1\left/\frac{d[Fe^{2+}]}{dt}\right. = k''\left(1 + \frac{k_{19}}{k_{10}}\frac{[Fe^{2+}]}{[As(III)]}\right)$$

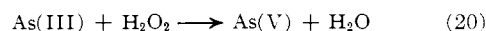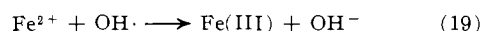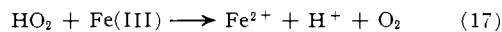Figure 1 shows a plot of $1\left/\frac{d[Fe^{2+}]}{dt}\right.$ against $[Fe^{2+}]/$ [As(III)] and from the slope and intercept, $k_{10}/k_{19} = 2$. This ratio is the same order of magnitude as the ratio of 4 obtained from the entirely different experiments involving the induced oxidation of arsenic(III) by the iron(II)–hydrogen peroxide reaction. These values of k_{10}/k_{19} are significantly different from the value[3] of 21 obtained for the ratio of the rate constants k_3/k_2 for the reactions of arsenic(III) and iron(II) with the active intermediate formed in the iron(II)–persulfate reaction. Therefore, it is reasonable to conclude that in the iron(II)–persulfate–arsenic(III) system the sulfate free radical is an active intermediate. The possibility of some exchange cannot be excluded.

The induced oxidation of arsenic(III) by the iron(II)–persulfate reaction in the presence of oxygen was shown to proceed through a chain mechanism involving hydrogen peroxide.[4] This chain should also be initiated by the iron(II)–hydrogen peroxide reaction. The mechanism will therefore be

Chain

$$Fe^{2+} + H_2O_2 \longrightarrow Fe(III) + OH\cdot + OH^- \quad (16)$$

$$As(III) + OH\cdot \longrightarrow As(IV) + OH^- \quad (10)$$

$$As(IV) + O_2 \longrightarrow As(V) + HO_2 \quad (14)$$

$$HO_2 + Fe^{2+} \longrightarrow Fe(III) + H_2O_2 \quad (15)$$

With terminations

$$HO_2 + Fe(III) \longrightarrow Fe^{2+} + H^+ + O_2 \quad (17)$$

$$Fe^{2+} + OH\cdot \longrightarrow Fe(III) + OH^- \quad (19)$$

$$As(III) + H_2O_2 \longrightarrow As(V) + H_2O \quad (20)$$

The stoichiometry of this induced oxygen oxidation should depend, as in the iron(II)–persulfate induced oxidation, only on the relative rates for the termination and propagation reactions and therefore on the concentrations of iron(II), iron(III), and arsenic(III) and on the acidity because k_{15}/k_{17} is hydrogen ion dependent.[4,13] Provided the arsenic(III) to iron(II) concentration ratio is sufficiently low to render termination reaction 20 insignificant, the stoichiometry of the chain oxidations by the two induction couples should be identical. The measured molar reaction ratios reported in Table III agree within the experimental error, substantiating the proposed mechanism.