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Arsenic(IV) as an Intermediate in the Induced Oxidation of Arsenic(III) by the Iron(II)-Persulfate Reaction and the Photoreduction of Iron(III). II. Presence of Oxygen¹

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Oxygen greatly affects the stoichiometry of the induced oxidation of arsenic(III) by the iron(II)-persulfate reaction. The intermediate arsenic(IV) reacts with oxygen to yield arsenic(V) and the perhydroxo radical, thereby initiating a chain oxidation by dissolved oxygen of iron(II) and arsenic(III) through intermediate formation of hydrogen peroxide and the hydroxyl radical. In this chain reaction one mole of oxygen gives rise to oxidation of 2 moles of iron(II) and 1 mole of arsenic(III), respectively. Iron(III) or copper(II) act as breakers of the oxygen-induced chain reaction; when present in sufficient concentration they eliminate the effect of oxygen and give rise to a stoichiometric reduction of persulfate by arsenic(III) (reaction A). The photoinduced iron(III)-arsenic(III) reaction in the presence of oxygen also is postulated to yield perhydroxo radical as an intermediate. The kinetics of this photoinduced reaction quantitatively account for the intermediate formation of the perhydroxo radical.

The results of the induced oxidation of arsenic(III) in the absence of oxygen have been presented and interpreted on the basis of intermediate formation of the 4+ valence state of arsenic with its subsequent oxidation or reduction by iron(III) or iron(II), respectively.² The presence of oxygen greatly affects the stoichiometry and kinetics of the induced oxidation. The effect of oxygen on the induced oxidation of arsenic(III) by the iron(II)-persulfate reaction and by the photoreduction of iron(III) is the subject of the present paper. For an interpretation of the results it was necessary to determine the rate and mechanism of the reaction between arsenic trioxide and hydrogen peroxide.

Experimental

Hydrogen peroxide was Becco 98% inhibitor-free.

All other materials used and procedures were identical with those described in part I² with the exception that air- or oxygen-saturated solutions were used throughout instead of solutions deaerated with nitrogen. All experiments were carried out at 25°.

Determination of Rate of Reaction between Arsenic Trioxide and Hydrogen Peroxide.—The rate of this reaction was determined by titrating, after suitable times with standard ceric solution, aliquot samples of a mixture which originally was $2.5 \times 10^{-2} M$ in both reactants. The hydrogen peroxide remaining was first titrated using ferroin as indicator. Three drops of 0.01 *M* osmium tetroxide solution were then added and the arsenic trioxide remaining titrated. Blank titrations with freshly prepared mixtures yielded the correct titers for peroxide and arsenic(III). The reaction rate was measured with solutions saturated with air or nitrogen, in the presence of 0, 0.01 *M*, 0.05 *M*, or 0.1 *M* HClO₄. The reaction was followed to about 80% completion. The effect of 1% acrylonitrile was also investigated.

Results

Induced Oxidation of Arsenic(III) by the Iron(II)-Persulfate Reaction in the Presence of Oxygen.—The stoichiometry of the induced oxidation of arsenic(III) by the iron(II)-persulfate reaction is affected by the presence of oxygen. Table I presents data of R_{Fe} , the ratio of moles iron(II) and persulfate reacted, *i.e.*, $R_{Fe} = \text{moles Fe(II) oxidized/moles } S_2O_8^{2-} \text{ reduced}$. For comparison, values of R_{Fe} are also given under the same experimental conditions in the absence of oxygen. These values have been calculated from results obtained in a previous study.² R_{Fe} increases with increasing hydrogen ion concentration, both in the absence and presence of oxygen. In the absence of oxygen R_{Fe} approaches the stoichiometric value of 2 at the highest acidity, while in the presence of oxygen it is much greater than 2, indicating induced oxygen oxidation of iron(II).

(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).

TABLE I

R_{Fe} AT DIFFERENT ACIDITIES IN THE ABSENCE AND IN THE PRESENCE OF AN EXCESS OF OXYGEN
 $1.33 \times 10^{-4} M [Fe^{2+}]$, $2.5 \times 10^{-5} M [S_2O_8^{2-}]$, $2.5 \times 10^{-2} M [As(III)]$, $\mu = 0.5 (HClO_4 + NaClO_4)$

[HClO ₄], <i>M</i>	R_{Fe}	
	N ₂	Air saturated
0.50	1.94	5.07
.10	1.89	4.52
.010	1.55	3.10
.005	1.42	2.80
.002	1.29	2.50

The addition of $5 \times 10^{-3} M$ fluoride to the air-saturated reaction mixture which complexes iron(III) produced during the reaction substantially reduces the hydrogen ion effect. With the concentrations of arsenic(III), iron(II), persulfate and the ionic strength given in Table I and perchloric acid concentrations of 0.002 *M*, 0.010 *M*, and 0.10 *M*, molar reaction ratios were obtained of 4.05, 4.30, and 4.70, respectively, as compared to 2.50, 3.10, and 4.52 in the absence of fluoride.

In the absence of oxygen, the sum of equivalents of iron(II) and arsenic(III) oxidized is equal to the equivalents of persulfate reduced

$$\frac{1}{2}R_{Fe} + R_{As} = 1$$

where $R_{As} = \text{moles of As(III) oxidized/moles of } S_2O_8^{2-} \text{ reduced}$. In the presence of oxygen, however, the sum ($\frac{1}{2}R_{Fe} + R_{As}$) exceeds unity (see Tables I, II, and III). From the values of R_{Fe} and R_{As} (Table II) it is clear that induced oxidation by dissolved oxygen of both iron(II) and arsenic(III) takes place.

The effect of arsenic(III) and iron(II) concentrations on the induced oxidation was determined in 0.5 *M* perchloric acid (Table II).

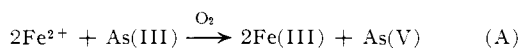
TABLE II

EFFECT OF $[Fe(II)]$ AND $[As(III)]$ ON THE INDUCED OXIDATION. AIR-SATURATED
 $[S_2O_8^{2-}] = 2.5 \times 10^{-5} M$, $[H^+] = 0.5 M$

Expt.	$[Fe(II)]$, $\times 10^4 M$	$[As(III)]$, <i>M</i>	R_{Fe}			
			R_{Fe}	R_{As}	$(\frac{1}{2}R_{Fe} + R_{As})$	$\frac{R_{Fe}}{R_{As}}$
1	1.33	2.5×10^{-2}	5.07	3.25	5.79	1.56
2	2.03	2.5×10^{-2}	4.78	3.22	5.61	1.48
3	5.31	2.5×10^{-3}	19.1	8.9	18.5	2.15
4	6.64	2.5×10^{-3}	15.2	7.0	14.6	2.17
5	2.66	2.5×10^{-4}	7.90	3.15	7.10	2.51
6	3.32	2.5×10^{-4}	6.46	2.29	5.52	2.82

The results show that under suitable conditions a considerable chain oxidation by dissolved oxygen can be induced, with the sum ($\frac{1}{2}R_{Fe} + R_{As}$) as high as 18.5. When the chain is long, and therefore initiation

and termination reactions become negligible compared to the chain propagation reactions, the stoichiometry approximates the reaction



corresponding to a ratio $R_{\text{Fe}}/R_{\text{As}}$ of 2.00. This situation is approached in experiments 3 and 4 in Table II. The decrease in chain length in the other experiments is interpreted in the Discussion section.

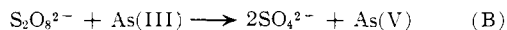
Both iron(III) and copper(II) inhibit the induced chain oxidation (Table III) and, when present in suffi-

TABLE III
EFFECT OF [Fe(III)] AND [Cu(II)] ON INDUCED OXYGEN REDUCTION

$[\text{S}_2\text{O}_8^{2-}] = 2.5 \times 10^{-3} M$, $[\text{Fe(II)}] = 6.85 \times 10^{-5} M$,
 $[\text{As(III)}] = 2.5 \times 10^{-2} M$, $[\text{H}^+] = 0.010 M$, $\mu = 0.5$

[Fe(III)], <i>M</i>	[Cu(II)], <i>M</i>	R_{Fe}	R_{As}	$1/2 R_{\text{Fe}} + R_{\text{As}}$
(a) Air-saturated				
..	..	2.09	1.92	2.97
10^{-4}	..	1.88	1.81	2.75
10^{-3}	..	0.50	1.30	1.55
10^{-2}	..	.00	1.00	1.00
..	10^{-3}	.02	1.00	1.01
(b) Oxygen-saturated				
..	..	2.15	2.00	3.08
10^{-4}	..	1.95	1.75	2.73
10^{-3}	..	0.53	1.35	1.62
10^{-2}	..	0.00	1.00	1.00

cient concentrations, $(1/2 R_{\text{Fe}} + R_{\text{As}})$ becomes 1.00. Under these conditions the effect of oxygen is eliminated and a quantitative induced oxidation of arsenic(III) by persulfate occurs



The same induced reaction has been found to occur in the absence of oxygen.²

Saturating the reaction mixtures containing iron(III) with oxygen instead of air had practically no effect on the values of R_{Fe} and R_{As} (Table III).

The rate of reduction of persulfate at an initial concentration of $10^{-3} M$ in air-saturated solution and in the presence of arsenic trioxide and ferric perchlorate was measured polarographically after addition of small amounts of ferrous perchlorate under conditions where the induced quantitative oxidation of arsenic(III) by persulfate is obtained. The reaction was found to be first order to persulfate with a rate constant proportional to the iron(II) concentration (Table IV), a result also found in the absence of oxygen.²

TABLE IV
RATE OF REDUCTION OF PERSULFATE. AIR-SATURATED
 $10^{-3} M \text{S}_2\text{O}_8^{2-}$, $10^{-2} M \text{As(III)}$, $10^{-2} M \text{Fe(III)}$, $0.01 M \text{HClO}_4$,
 $\mu = 0.07$, $R_{\text{Fe}} = 0.0$, $R_{\text{As}} = 1.00$

$[\text{Fe}^{2+}] \times 10^3 M$	k , $\text{sec.}^{-1} \times 10^4$	$k_1 = k/[\text{Fe}^{2+}]$, $1. \text{ mole}^{-1} \text{ sec.}^{-1}$
0.57	1.59	28
1.14	3.49	31
2.28	5.95	26
4.57	11.1	24

If the rate-determining step in this system is the iron(II)-persulfate reaction and the iron(II) is regenerated at the same rate at which it is oxidized, the rate of reduction of persulfate, $-d[\text{S}_2\text{O}_8^{2-}]/dt$, will be pseudo first order with a first-order rate constant given by $k = k_1[\text{Fe}^{2+}]$, k_1 being the rate constant of the iron(II)-persulfate reaction. The rate constant k_1 was calculated from the experimental data and gave an average value $27 \text{ l. mole}^{-1} \text{ sec.}^{-1}$, which is the same as that obtained²

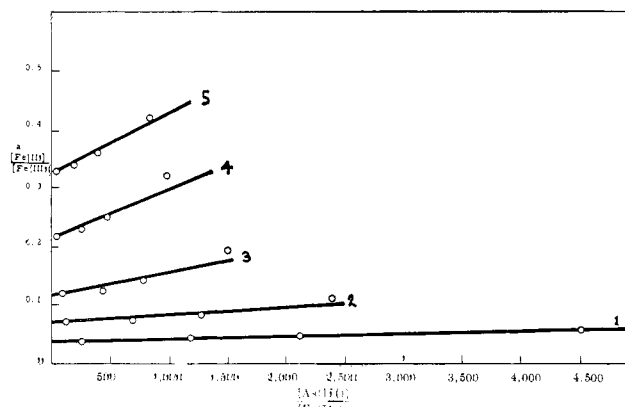


Fig. 1.—Plot of $[\text{Fe(II)}]/[\text{Fe(III)}]$ against $[\text{As(III)}]/[\text{Fe(II)}]$: 1, 0.103 $M \text{HClO}_4$; 2, 0.048; 3, 0.024; 4, 0.010; 5, 0.005.

in the same medium in the absence of arsenic(III) and oxygen.

Photoinduced Fe(III)-As(III)-O₂ Reaction.—Upon the photoreduction of $10^{-4} M$ ferric perchlorate in the presence of arsenic(III), perchloric acid, and oxygen at an ionic strength of 0.1, the concentration of iron(II) produced was found to increase to a constant value, even though arsenic trioxide was being oxidized continuously. By comparing results in air- and oxygen-saturated solutions, the reaction appeared to be zero order to oxygen. Additional iron(II) was added to the system after a constant concentration of iron(II) had been attained. The additional iron(II) was oxidized until the original constant ratio of $[\text{Fe(II)}]/[\text{Fe(III)}]$ was restored.

The constant ratio was found to be dependent on the hydrogen ion concentration and to a small extent on the arsenic(III) concentration. The dependency on arsenic(III) concentration at constant hydrogen ion concentration was determined for arsenic(III) concentrations of $10^{-3} M$, $5 \times 10^{-3} M$, $10^{-2} M$, and $2.5 \times 10^{-2} M$. Figure 1 shows that the constant ratio $[\text{Fe(II)}]/[\text{Fe(III)}]$ increases with, and is approximately linearly related to, the ratio $[\text{As(III)}]/[\text{Fe(II)}]$, as anticipated by the proposed mechanism (see Discussion).

The plots of $[\text{Fe(II)}]/[\text{Fe(III)}]$ against $[\text{As(III)}]/[\text{Fe(II)}]$ were extrapolated to zero $[\text{As(III)}]/[\text{Fe(II)}]$. A linear relationship was found to exist between the reciprocals of the extrapolated ratios $\frac{[\text{Fe(II)}]}{[\text{Fe(III)}]}$ ($[\text{As(III)}]/[\text{Fe(II)}] \rightarrow 0$) and the perchloric acid concentration (Fig. 2).

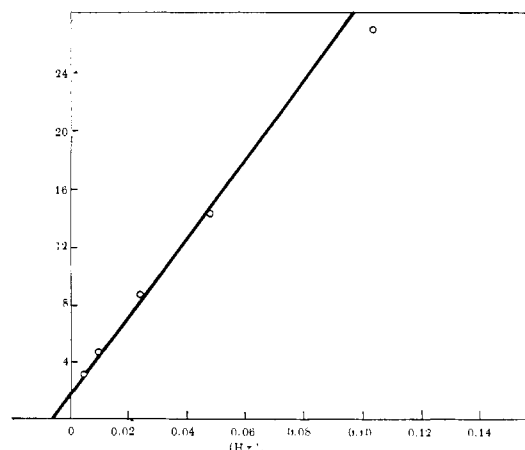


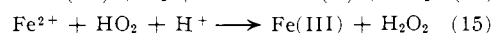
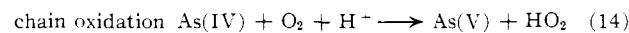
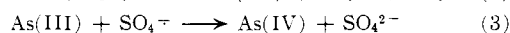
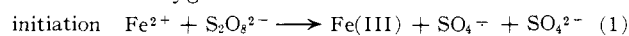
Fig. 2.—Plots of the values of $[\text{Fe(II)}]/[\text{Fe(III)}]$ extrapolated to $[\text{As(III)}]/[\text{Fe(II)}] = 0$ (ordinate) against $[\text{H}^+]$ (abscissa).

Rate of the Reaction between Arsenic Trioxide and Hydrogen Peroxide.—The reaction was found to be second order with a rate constant of $0.0101 \text{ mole}^{-1} \text{ sec.}^{-1}$ at 25° . It was found independent of acidity and unaffected by the presence of oxygen or of acrylonitrile and no polyacrylonitrile was precipitated. The stoichiometric relationship of $1 \text{ As(III)} \equiv 1 \text{ H}_2\text{O}_2$ was always obeyed.

Discussion

The presence of oxygen in the iron(II)-persulfate induced oxidation of arsenic(III) results in an induced oxidation of both iron(II) and arsenic(III). This induced oxidation proceeds by a chain mechanism, as the value $(\frac{1}{2}R_{\text{Fe}} + R_{\text{As}})$, which in the absence of oxygen is 1, can reach 18.5 in the presence of oxygen (Table II). The chain reaction is initiated by the reaction between iron(II) and persulfate. The initiating reaction is unaffected by oxygen and does not produce any oxygen-sensitive intermediates. Therefore, an arsenic entity must be formed which reacts with oxygen. The intermediate formation of arsenic(IV) by reaction of arsenic(III) with sulfate or hydroxyl free radicals was postulated to occur in the induced oxidation of arsenic(III) in the absence of oxygen.² The effect of oxygen can be explained by a reaction of the intermediate arsenic(IV) with dissolved oxygen to give a peroxy species capable of further oxidations, the experimental evidence suggesting the formation of the hydroperoxo radical according to reaction 14.

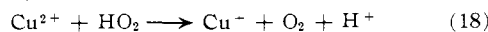
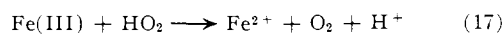
The following mechanism accounts for the characteristics of the induced chain reaction. The numbers of some of the following equations are identical with those of the same equations presented in the paper in the absence of oxygen.²



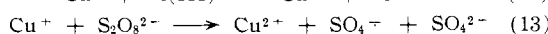
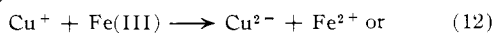
followed by (14).

In agreement with the experimental results, the sum of the reactions involved in the chain, excluding initiation and termination reactions, gives the stoichiometric relationship of eq. A.

The chain termination reactions yield additional evidence in support of this mechanism. The hydroperoxo radical HO_2 in addition to oxidizing iron(II) by (15), can also act as a reductant toward iron(III) or copper(II)



followed by either

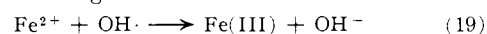


Reactions 17 and 18 result in chain termination. The possible termination reactions between arsenic(IV) and iron(III) or copper(II) found in the absence of oxygen² must be insignificant in air-saturated solutions, as a fivefold increase in oxygen concentration has no effect on the stoichiometry of the reaction (Table III), a result which indicates that only oxygen reacts with arsenic(IV) in this system.

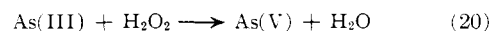
Experimentally, when the concentration of iron(III) or copper(II) is sufficiently large, the induced oxidation by oxygen was found to be eliminated completely. Under these conditions, all the hydroperoxo free radicals are oxidized according to reactions 17 or 18 and the in-

duction factor equiv. As(III) oxidized/equiv. Fe^{2+} oxidized approaches infinity as in the absence of oxygen, with the ratio R_{As} becoming equal to 1. Under these conditions, the kinetics of the reduction of persulfate (Table IV) show that reaction 1 is the rate-determining step, that only iron(II) reacts with persulfate and that iron(II) is re-formed at the same rate that it is oxidized, all in accordance with the proposed mechanism.

The mechanism is further substantiated by an increase of the induced oxidation brought about by increase of the hydrogen ion concentration (Table I). Iron(II) and iron(III) are both present in the reaction mixture and therefore compete for the hydroperoxo radical. The iron(III) reaction terminates the induced chain reaction involving oxygen while the iron(II) reaction is chain propagating. The ratio of the rate constants for these reactions is hydrogen ion dependent,³⁻⁵ the iron(III) reaction being retarded with respect to the iron(II) reaction as the acidity is increased. The effect of increasing the hydrogen ion concentration is to increase the proportion of hydroperoxo radicals reacting with iron(II) in the chain propagation reaction and, therefore, to enhance the induced chain oxidation. Furthermore, addition of fluoride, which complexes iron(III) thereby inhibiting its reaction with the hydroperoxo radical, enhances the chain oxidation at lower acidities and substantially reduces the hydrogen ion effect. When the chain is long as compared to initiation and termination reactions, the over-all reaction A is predominant and the ratio $R_{\text{Fe}}/R_{\text{As}}$ becomes equal to 2. These conditions were approached in experiments 3 and 4 in Table II. From the results in Table II it appears that the oxygen-induced oxidation passes through a maximum at a certain arsenic(III) to iron(II) concentration ratio (expt. 3 and 4 in Table II); it decreases with increasing and with decreasing ratios (Table II). The decrease in oxidation at low arsenic(III) to iron(II) concentration ratios is explained by competition between arsenic(III) and iron(II) for the $\text{OH}\cdot$ radical, reaction 19 resulting in chain termination.

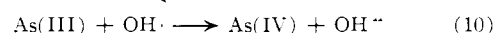
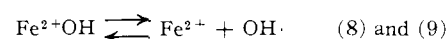
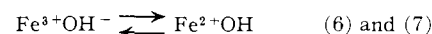


Under these conditions the ratio $R_{\text{Fe}}/R_{\text{As}}$ becomes markedly greater than 2 (expt. 5 and 6 in Table II). The decrease in oxidation at high arsenic(III) to iron(II) concentration ratios can be explained by competition between arsenic(III) and iron(II) for hydrogen peroxide, reaction 20



also resulting in chain termination. Under these conditions the ratio $R_{\text{Fe}}/R_{\text{As}}$ becomes smaller than 2 (expt. 1 and 2 in Table II). In order to terminate the chain oxidation, reaction 20 must proceed without the formation of arsenic(IV) or radical intermediates from the hydrogen peroxide which would propagate rather than terminate the chain. That this is the case is substantiated by the experimental observations that neither oxygen nor acrylonitrile, which reacts rapidly with $\text{OH}\cdot$ free radicals, affect the rate or stoichiometry of the arsenic trioxide-hydrogen peroxide reaction.

The photoinduced iron(III)-arsenic(III) reaction in the absence of oxygen² has been explained in terms of the reactions



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

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

(5) U. N. Shubin and R. I. Dolin, *Doklady Akad. Nauk SSSR*, **140**, 1380 (1961); Engl. transl. p. 808.

The subsequent reactions in the presence of oxygen should be the same as those in the induced chain oxidation initiated by the iron(II)-persulfate reaction and are accounted for by a mechanism comprising reactions 14, 15, 16, 17, and 20.

As in the oxygen-induced chain oxidation initiated by the iron(II)-persulfate reaction, the reaction between arsenic(IV) and iron(III) is found to be insignificant in air-saturated solution as a fivefold increase in oxygen concentration had no effect on the constant iron(II) to iron(III) ratio.

The photoinduced reaction is accounted for by the sequence of reactions 6-10, 14-17, and 20. Letting R_n represent the rate of reaction n , the rate of formation of Fe(II) in general is equal to $R_8 + R_{17} - (R_9 + R_{15} + R_{16})$. Steady-state conditions with respect to $\text{OH}\cdot$, $\text{HO}_2\cdot$, and As(IV) yield the relations $R_8 + R_{16} = R_9 + R_{10}$, $R_{14} = R_{15} + R_{17}$, and $R_8 + R_{16} = R_9 + R_{14}$. Using these three relations it is found that in general

$$d[\text{Fe(II)}]/dt = 2(R_{17} - R_{16})$$

hence at equilibrium $R_{17} = R_{16}$. Also at equilibrium the net rate of formation of H_2O_2 is zero, so $R_{15} = R_{16} + R_{20}$. Using the last relation, the final result at equilibrium is

$$\frac{[\text{Fe(II)}]}{[\text{Fe(III)}]} = \frac{k_{17}}{k_{15}} \left(1 + \frac{k_{20}}{k_{16}} \frac{[\text{As(III)}]}{[\text{Fe(II)}]} \right)$$

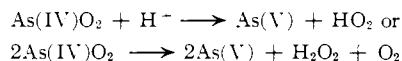
Figure 1 shows that, at constant hydrogen ion concentration, $[\text{Fe(II)}]/[\text{Fe(III)}]$ does increase with and, within the experimental error, is proportional to $[\text{As(III)}]/[\text{Fe(II)}]$, as anticipated. Extrapolating these plots to zero $[\text{As(III)}]/[\text{Fe(II)}]$ gives the values of k_{17}/k_{15} at varying hydrogen ion concentrations. The ratio k_{17}/k_{15} is known to decrease with increase in hydrogen ion concentration.³⁻⁵ Barb, *et al.*,³ concluded that k_{17}/k_{15} is inversely proportional to $([\text{H}^+] + K_a)$, where K_a is the first hydrolysis constant of iron(III) and equals $[\text{FeOH}^{2+}][\text{H}^+]/[\text{Fe}^{3+}]$; *i.e.*, $([\text{H}^+] + K_a) k_{17}/k_{15}$ is a constant. Barb, *et al.*, explained this relationship by assuming that iron(II) is oxidized by the undissociated HO_2 , while Fe^{3+} is reduced by the O_2^- ion radical, FeOH^{2+} being unreactive. Rothschild and Allen,⁴ however, proposed the HO_2 radical to be the reacting species in both reactions 15 and 17 and attribute the relationship of k_{17}/k_{15} with $([\text{H}^+] + K_a)$ to the greater reactivity of the FeOH^{2+} ion than the Fe^{3+} ion with HO_2 . Both proposed mechanisms lead to the relationship $([\text{H}^+] + K_a)k_{17}/k_{15}$ is a constant and anticipate the same effect of ionic strength.

The plot of the reciprocals of $\frac{[\text{Fe(II)}]}{[\text{Fe(III)}]} ([\text{As(III)}]/[\text{Fe(II)}] \rightarrow 0)$ *i.e.*, k_{17}/k_{15} , against the hydrogen ion concentration in Fig. 2 is linear in accordance with the above relationship of k_{17}/k_{15} with $([\text{H}^+] + K_a)$. The intersection on the $[\text{H}^+]$ axis is equal to $-K_a$ and gives a value for this constant of 6×10^{-3} at an ionic strength of 0.1. Barb, *et al.*,³ report 5×10^{-3} for K_a in perchlorate medium from their determination of k_{17}/k_{15} and its pH dependence. From spectrophotometric measurements, Milburn and Vosburgh⁶ derived a value of K_a of 2.8×10^{-3} at an ionic strength of 0.1.

The reciprocal of the slope of Fig. 2 is the constant $([\text{H}^+] + K_a)k_{17}/k_{15}$ giving a value of 3.7×10^{-3} . This compares favorably with the values of 7×10^{-3} obtained by Barb, *et al.*,³ from investigations of the ferrous perchlorate-hydrogen peroxide system, and 3.6×10^{-3} obtained by Shubin and Dolin⁵ from results of the radiation chemistry of aqueous ferrous perchlorate.

The rate of the arsenic trioxide-hydrogen peroxide reaction was found to have a rate constant $k_{20} = 0.010$ l. mole⁻¹ sec.⁻¹ at 25°. Barb, *et al.*,³ determined k_{16} to be 53.0 l. mole⁻¹ sec.⁻¹ at 24.6°. This gives the value of the ratio k_{20}/k_{16} to be 1.9×10^{-4} . An estimate of k_{20}/k_{16} can be obtained from Fig. 1, being the ratio of the slopes to the intercepts. This gives a value, independent of hydrogen ion concentration within the experimental error, of the order of 3×10^{-4} in satisfactory agreement with the value of 1.9×10^{-4} .

In a recent paper, Daniels⁷ postulated the formation of a peroxide As(IV)O_2 by the action of oxygen on arsenic(IV) and its subsequent decomposition by either



He was not able to distinguish between the two decomposition routes. However, the second reaction could not give the chain oxidation found here. The induced oxidation of arsenic(III) in the presence of oxygen is adequately explained by reactions involving HO_2 . The fact found in this paper, that the ratio of the rate constants of the reaction of HO_2 with iron(II) and iron(III) is in agreement with known values, substantiates the postulated formation and role of this radical in the proposed mechanism in the presence of oxygen. Formation of As(IV)O_2 with its subsequent formation of HO_2 leads to the same reaction mechanism as reaction 14, and in the absence of any evidence of peroxide formation need not be considered.

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

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