

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA, MINNEAPOLIS 14, MINN.]

**Arsenic(IV) as an Intermediate in the Induced Oxidation of Arsenic(III) by the Iron(II)-Persulfate Reaction and the Photoreduction of Iron(III). I. Absence of Oxygen<sup>1</sup>**

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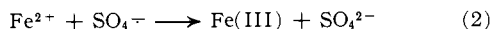
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The persulfate-iron(II) couple induces the oxidation of arsenic(III). The induction factor in the absence of oxygen at high dilutions of persulfate and iron(II) can become greater than 1. Iron(III) and copper(II) increase the induction factor, which can approach infinity. The mechanism is accounted for by the postulation of the intermediate formation of arsenic(IV) which can oxidize iron(II) and reduce iron(III),  $\text{FeOH}^{2+}$  being 90 times as reactive as  $\text{Fe}^{3+}$ . At 25° the rate constant of the reaction of the sulfate free radical with arsenic(III) is 21 times as great as that of its reaction with iron(II). The kinetics of the induced reaction are in agreement with the proposed mechanism. Additional evidence for the intermediate formation of arsenic(IV) was obtained in a study of the photosensitized oxidation of arsenic(III) in solutions containing iron(III).

The reaction of iron(II) with persulfate is known to proceed through two steps, the first being the formation of a sulfate free radical.<sup>2-4</sup>

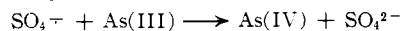


Fe(III) denotes all forms of iron in the trivalent state. In the absence of other oxidizable species, the sulfate free radical oxidizes another ferrous ion

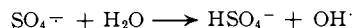


The sulfate free radical produced by reaction 1 is able to induce oxidations and polymerizations in organic substances<sup>2-4</sup> and its presence is confirmed by the incorporation of  $\text{S}^{35}$ , from  $\text{S}^{35}$ -labeled persulfate, into polymer chains.<sup>5,6</sup>

No studies are found in the literature on the induced oxidation of inorganic constituents by the couple persulfate (actor) and iron(II) (inductor) under the conditions where the acceptor does not react or reacts only very slowly with persulfate. In the present paper, in which all the experiments have been carried out in the absence of oxygen, it is shown that the above couple induces the oxidation of arsenic(III), the oxidation being initiated by the reaction



and/or by the hydroxyl free radical, formed in the reaction

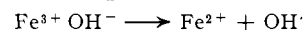


Csanyi<sup>7</sup> postulated the reaction between  $\text{SO}_4^-$  and As(III) to occur in the titration of a mixture of persulfate and hydrogen peroxide with one-electron transfer oxidants. He also proposed the formation of As(IV) in the induced reduction of chlorate by arsenic(III).<sup>8</sup>

Daniels and Weiss<sup>9</sup> proposed the production of As(IV) by the reaction of a hydroxyl radical with arsenic(III) to occur during the oxidation of arsenite by the action of X-rays. Very recently Daniels<sup>10</sup> also concluded that this reaction takes place in the photosensitized reaction between hydrogen peroxide and arsenite.

In order to substantiate the interpretation of the induced oxidation of As(III) by the persulfate-iron(II) couple, it was thought desirable to investigate the induced oxidation of arsenic(III) upon photochemical reduction of iron(III). In the present paper, results are presented on the oxidation of arsenic(III) upon ultra-

violet radiation of a mixture of iron(III) perchlorate and arsenic trioxide. Evans, Santappi, and Uri<sup>11</sup> studied the photochemical reduction of iron(III) by irradiation with the 3650 and 3130 Å. lines of a mercury arc and its initiation of vinyl polymerizations. They concluded that the photochemically active species is an ion pair complex of the formula  $\text{Fe}^{3+}\text{X}^-$  (where  $\text{X}^- = \text{OH}^-, \text{Cl}^-, \text{N}_3^-, \text{etc.}$ ), e.g.



This conclusion has been confirmed by other workers.<sup>12-14</sup> The production of the hydroxyl radical was also postulated for the photoreduction of cerium(IV).<sup>15,16</sup>

**Experimental**

**Materials. Water.**—Conductivity water was distilled from alkaline permanganate and redistilled under nitrogen.

**Arsenic Trioxide.**—Mallinckrodt  $\text{As}_2\text{O}_3$  was recrystallized from dilute hydrochloric acid (1:2), washed, dried, and sublimed. The product was free of chloride. An approximately 0.1 M stock solution was prepared by boiling the oxide with water.

**Potassium Persulfate.**—Merck  $\text{K}_2\text{S}_2\text{O}_8$  was recrystallized twice.

**Perchloric acid** was G. F. Smith reagent grade.

**Ferrous Perchlorate.**—An excess of iron wire (99.9% Fe) was added to standard perchloric acid in an atmosphere of nitrogen and, after the reaction was completed, the solution was filtered, acidified with standard perchloric acid, and diluted. The solution, which was 0.1 M in perchloric acid and  $5.21 \times 10^{-3}$  M in iron(II), was stored under nitrogen.

**Ferric Perchlorate.**—G. F. Smith reagent grade ferric perchlorate was recrystallized from perchloric acid solution.

**Cupric perchlorate** was G. F. Smith reagent grade.

**Sodium perchlorate** was G. F. Smith reagent grade recrystallized from water.

**Nitrogen.**—Linde nitrogen (99.99%  $\text{N}_2$ ) was further purified from oxygen by passage over a column of finely divided copper deposited on infusorial earth and heated to 200°. The oxygen content was thereby reduced to the order of  $4 \times 10^{-5}\%$ .

**Reaction Vessels.**—Pyrex flasks were cleaned with concentrated nitric acid which was 5% in hydrofluoric acid, rinsed thoroughly, and steamed out for 2 hr.

**Analytical Methods.**—Iron(II) was determined spectrophotometrically with *o*-phenanthroline,<sup>18</sup> the pH being adjusted where necessary to about 3.5 by addition of sodium citrate. It may be noted that spectrophotometric titration with cerium(IV) at 0° using ferroin as indicator,<sup>19</sup> which ordinarily yields good results in acid medium (pH < 2), cannot be used in the presence of much perchlorate because of precipitation of ferrous phenanthroline perchlorate at 0°.

**Arsenic(V)** was determined spectrophotometrically<sup>20</sup> by the formation of 12-molybdoarsenic acid, extracting this species into 2-butanol, and subsequent reduction with stannous chloride to molybdenum blue, the absorption being measured at 740  $\mu$ .

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

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

(3) J. W. L. Fordham and H. L. Williams, *J. Am. Chem. Soc.*, **73**, 1634, 4855 (1951).

(4) I. M. Kolthoff, A. I. Medalia, and H. P. Raaen, *ibid.*, **73**, 1733 (1951).

(5) W. V. Smith, *ibid.*, **71**, 4077 (1949).

(6) I. M. Kolthoff, P. R. O'Connor, and J. L. Hanson, *J. Polymer Sci.*, **15**, 459 (1955).

(7) L. J. Csanyi, *Discussions Faraday Soc.*, **29**, 146 (1960).

(8) L. J. Csanyi and M. Szabo, *Talanta*, **1**, 359 (1958).

(9) M. Daniels and J. Weiss, *J. Chem. Soc.*, 2467 (1958).

(10) M. Daniels, *J. Phys. Chem.*, **66**, 1473, 1475 (1962).

(11) M. G. Evans, M. Santappi, and N. Uri, *J. Polymer Sci.*, **7**, 243 (1951).

(12) J. Saldick and O. Allen, *J. Am. Chem. Soc.*, **77**, 1388 (1955).

(13) J. H. Baxendale and J. Magee, *Trans. Faraday Soc.*, **51**, 205 (1955).

(14) F. S. Dainton and M. Tondoff, *ibid.*, **53**, 666 (1957).

(15) J. Weiss and D. Porret, *Nature*, **139**, 1019 (1937).

(16) T. J. Sworski, *J. Am. Chem. Soc.*, **77**, 1074 (1955).

(17) F. R. Meyer and G. Ronge, *Z. angew. Chem.*, **52**, 637 (1939).

(18) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p. 537.

(19) I. M. Kolthoff and R. Woods, *Microchem. J.*, **5**, 569 (1961).

(20) M. Daniels, *Analyst*, **133**, 82 (1957).

The extraction technique was necessary to avoid oxidation of arsenic(III) by perchlorate which occurs when molybdoarsenic acid is reduced by hydrazine sulfate in the reaction mixture.<sup>21</sup> In the absence of perchlorate such extraction is unnecessary.

**Procedure.**—The ionic strength was kept constant at 0.50 by addition of sodium perchlorate in all experiments with the exception of those of Table II (effect of ionic strength) and of Table III (in which a low ionic strength was desirable, *vide infra*).

**Induced Oxidation by the Persulfate-Iron(II) Couple. Determination of Induction Factor.**—Solutions of ferrous perchlorate, perchloric acid, arsenic trioxide, and, where relevant, ferric or cupric perchlorate, were pipetted into flasks covered with black adhesive tape to eliminate photoinduced reactions, deaerated with nitrogen, and placed in a thermostat bath at 25°. Potassium persulfate, also deaerated with nitrogen, was added from a syringe and the solution mixed. The reaction was allowed to go to completion and the solution analyzed for iron(II) and As(V). An excess of iron(II) was always used.

**Rate of Reduction of Persulfate in the Presence of Iron(III).**—Solutions of ferrous and ferric perchlorate, perchloric acid, and arsenic trioxide were pipetted into tape-covered flasks, deaerated with nitrogen, and placed in a thermostat bath at 25°. Deaerated potassium persulfate was added as before. Aliquot samples were removed at desired times, entrance of oxygen being prevented by continuous bubbling of nitrogen, and analyzed polarographically for persulfate remaining. One drop of 0.5% *o*-phenanthroline was added to the polarographic cell to arrest the reaction. Sodium fluoride in a concentration of 0.1 *M* was used as supporting electrolyte to eliminate interference by iron(III) at the d.m.e. Polyacrylamide in a concentration of 0.01% was used as a maximum suppressor. The current was measured at 0.15 volt *vs.* s.c.e. and shown to be proportional to persulfate concentration. Oxygen did not interfere and was not removed from the polarographic cell.

**Photochemical Experiments.**—The light source consisted of two 200-w. tungsten bulbs fitted with a reflector and a diffusing screen to give an evenly distributed illumination. The light passed through the glass wall of a thermostat bath before reaching the samples. Glass bottles were used as reaction vessels. The absorbance of glass approaches infinity for wave lengths less than 300  $\mu$ . Ferrous perchlorate does not absorb radiation of wave length greater than 300  $\mu$  and therefore the photooxidation of iron(II)<sup>22-24</sup> will be negligible during this experiment. Ferric perchlorate, however, is photoreduced by radiation of wave lengths greater than 300  $\mu$ .<sup>11</sup> Solutions containing known concentrations of ferrous and ferric perchlorate, perchloric acid, and arsenic trioxide were placed in the water bath, deaerated with nitrogen, and the light source turned on. Aliquot samples were taken, and the iron(II) and arsenic(V) formed were determined as described above.

## Results

**The Induced Oxidation of Arsenic(III) by the Persulfate-Iron(III) Couple.**—The persulfate oxidation of arsenic trioxide is very slow compared with its oxidation of iron(II). However, the iron(II)-persulfate reaction induces the oxidation of arsenic trioxide. The induction factor for the induced oxidation was found to be dependent on perchloric acid concentration (Table I) but independent of arsenic trioxide concentration provided the latter was greater than twice the ferrous concentration. An increase in either  $[H^+]$  or  $[Fe^{2+}]$  produced a decrease in the induction factor.

In the presence of initially added iron(III) the induction factor is shown to increase to infinity. This "catalytic" effect of iron(III) is more pronounced with decreasing acidity.

Reduction of ionic strength to 0.01 or 0.002 caused an increase in both I.F. and  $k_4/k_5$  compared to the values at the same  $[H^+]$  and  $\mu = 0.5$  (Table II).

The rate of reduction of persulfate at an initial concentration of  $10^{-3}$  *M* in the presence of arsenic trioxide and ferric perchlorate was measured polarographically after addition of small amounts of ferrous perchlorate, under conditions where the induction factor is infinity. (In this set of experiments the ionic strength was 0.07, rather than 0.5, in order to have the maximum fraction

(21) E. B. Sandell, ref. 18, p. 282.

(22) C. Heller, Ph.D. Thesis, University Microfilms, Ann Arbor, Mich., Mic 60-499, 1957.

(23) E. Hayon and J. Weiss, *J. Chem. Soc.*, 3866 (1960).

(24) L. J. Heidt, M. G. Mullin, W. B. Martin, Jr., and A. M. J. Beatty, *J. Phys. Chem.*, **66**, 336 (1962).

TABLE I

VARIATION OF INDUCTION FACTOR (I.F.) AT CONSTANT  $[S_2O_8^{2-}]$ ,  $[As(III)]$ , AND IONIC STRENGTH,  $\mu$ , WITH VARYING IRON(II) CONCENTRATION AND ACIDITY

I.F. = $\frac{\text{equiv. As(III) oxidized}}{\text{equiv. Fe(II) oxidized}}$		$[S_2O_8^{2-}] = 2.5 \times 10^{-5} M$ ; $\mu = 0.5$ ; $T = 25^\circ$					
$[Fe^{2+}]$ , $\times 10^6$ <i>M</i>	$[Fe(III)]$ , <i>M</i>	I.F.	$k_4/k_5^a$	$[Fe^{2+}]$ , $\times 10^6$ <i>M</i>	$[Fe(III)]$ , <i>M</i>	I.F.	$k_4/k_5^a$
0.50 <i>M</i> HClO <sub>4</sub>				0.005 <i>M</i> HClO <sub>4</sub>			
5.71		0.17	0.20				
4.56		0.23	.14	6.85		0.75	2.6
4.56	$5 \times 10^{-4}$	1.5	.10	5.71		0.87	2.5
4.56	$10^{-3}$	4.6	.14	4.56		1.07	2.6
		Av.	0.14	2.74		1.80	2.9
0.1 <i>M</i> HClO <sub>4</sub>				$5 \times 10^{-5}$			
				2.74	$10^{-4}$	10.4	2.6
5.71		0.20	0.26			Av.	2.6
4.56		0.32	.27				
4.56	$5 \times 10^{-4}$	2.7	.21				
4.56	$10^{-3}$	5.2	.21			0.002 <i>M</i> HClO <sub>4</sub>	
		Av.	0.24	6.85		0.95	3.7
0.010 <i>M</i> HClO <sub>4</sub>				5.71			
				4.56		1.25	4.6
6.85		0.56	1.6	2.74		1.32	3.8
5.71		.68	1.6	2.05		2.10	4.2
4.56		.88	1.8	2.05	$10^{-5}$	2.50	3.5
2.74		1.4	1.5	2.05	$2.5 \times 10^{-5}$	4.38	4.5
2.74	$10^{-4}$	6.8	1.6	2.05	$5 \times 10^{-5}$	6.7	4.1
2.74	$10^{-3}$	$\infty$	...	2.05	$10^{-5}$	10.1	3.6
		Av.	1.6			$\infty$	...

<sup>a</sup> See Discussion.

TABLE II

EFFECT OF IONIC STRENGTH

$[S_2O_8^{2-}] = 2.5 \times 10^{-5} M$ ,  $[As(III)] = 10^{-2} M$ ,  $T = 25^\circ$

$[HClO_4]$ , <i>M</i>	$\mu$	$[Fe^{2+}]$ , $\times 10^6$ <i>M</i>	$[Fe(III)]$ , <i>M</i>	I.F.	$k_4/k_5$
0.010	0.010	6.85	...	0.83	3.1
		5.71	...	1.03	3.4
		4.56	...	1.23	3.3
		2.74	...	1.86	3.1
		2.74	$10^{-4}$	12.9	3.2
		Av.			3.2
0.002	0.002	6.85	...	1.4	5.0
		4.56	...	1.54	5.1
		2.74	...	2.22	4.7
		2.05	...	2.9	5.3
		2.05	$2.5 \times 10^{-5}$	8.4	5.4
		Av.			5.1

of iron(III) present as  $FeOH^{2+}$  rather than as  $Fe^{3+}$ .) The reaction was found to be first order to persulfate with the rate constant proportional to the iron(II) concentration (Table III). If the rate-determining step in this

TABLE III

RATE OF REDUCTION OF PERSULFATE

$10^{-3} M S_2O_8^{2-}$ , 0.01 *M* As(III), 0.01 *M* Fe(III), 0.01 *M* HClO<sub>4</sub>, I.F. =  $\infty$ ,  $\mu = 0.07$ ,  $T = 25^\circ$

$[Fe^{2+}]$ , $\times 10^6$ <i>M</i>	$k_1$ , sec. <sup>-1</sup> $\times 10^4$	$k_1 = k/[Fe^{2+}]$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>
0.57	1.84	32
1.14	3.75	33
2.28	6.38	28
4.57	12.5	27

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,  $-d[S_2O_8^{2-}]/dt$ , will be

pseudo first order with a first-order rate constant given by  $k = k_1[\text{Fe}^{2+}]$  (where  $k_1$  is the rate constant of the iron(II)-persulfate reaction). The rate constant  $k_1$  can be calculated from the experimental data (Table III) and gave the average value 30 l. mole<sup>-1</sup> sec.<sup>-1</sup>.

The rate of the iron(II)-persulfate reaction in the absence of arsenic(III) was measured in the presence of the same concentrations of ferric perchlorate and perchloric acid, the ionic strength of the solution therefore being the same as that in the experiment in the presence of arsenic(III). The iron(II) concentration was determined at given periods of time. The rate constant was found to be 27 l. mole<sup>-1</sup> sec.<sup>-1</sup>, which agrees favorably with the rate constant obtained above. These results show that the iron(II)-persulfate reaction is the rate-determining step in the induced oxidation of arsenic(III), that only iron(II) reacts with persulfate, and that, in the presence of sufficient iron(III), iron(II) is re-formed at the same rate at which it is oxidized.

Copper(II) behaves similarly to iron(III), producing an increase in the induction factor and giving a limiting value approaching infinity (Table IV). Unlike iron(III), however, its effect is virtually independent of the hydrogen ion concentration.

TABLE IV

## EFFECT OF COPPER(II) ON INDUCTION FACTOR

$[\text{Fe}^{2+}] = 5.71 \times 10^{-5} M$ ,  $[\text{S}_2\text{O}_8^{2-}] = 2.5 \times 10^{-5} M$ ,  $[\text{As(III)}] = 10^{-2} M$ ,  $\mu = 0.5$ ,  $T = 25^\circ$

HClO <sub>4</sub> , M	Molar concn. [Cu <sup>2+</sup> ]		
	0	10 <sup>-3</sup> M	10 <sup>-4</sup> M
0.50	0.17	1.6	12
.10	0.20	1.7	13
.010	0.68	1.9	10
.002	1.25	1.9	9

The effect on the induced oxidation of reducing the ratio of concentrations of arsenic(III) to iron(II) to values less than two was investigated in the presence of iron(III). The concentration of iron(III) in each case was sufficient to yield an induction factor of infinity when the ratio  $[\text{As(III)}]/[\text{Fe(II)}]$  was equal to or greater than two.

TABLE V

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

$[\text{Fe}^{2+}] = 5.0 \times 10^{-5} M$ ,  $[\text{S}_2\text{O}_8^{2-}] = 2.5 \times 10^{-5} M$ ,  $\mu = 0.5$ ,  $T = 25^\circ$

[HClO <sub>4</sub> ], M	[Fe(III)], M	[As(III)], × 10 <sup>3</sup> M	I.F.	$k_3/k_2^a$
0.10	2 × 10 <sup>-2</sup>	2.5	4.55	17
		5.0	13.7	18
		10.0	∞	..
0.010	2 × 10 <sup>-3</sup>	2.5	5.75	19
		5.0	13.3	24
		10.0	∞	..
0.002	5 × 10 <sup>-4</sup>	2.5	6.35	27
		5.0	15.7	22
		10.0	∞	..

Av. 21

<sup>a</sup> See Discussion.

Iron(III) is produced during the reaction and is therefore present in all experiments in which the induction factor was determined (Table I). In order to deduce the course of the reaction in the absence of ferric ions, the effect of the addition of fluoride, which complexes the iron(III), was determined. Fluoride was found to reduce the induction factor to values approaching zero. For example, in an oxygen-free mixture 0.002 M in perchloric acid and originally 2.5 × 10<sup>-5</sup> M in persulfate,

5.71 × 10<sup>-5</sup> M in iron(II), and 0.01 M in arsenic(III), the induction factor decreased from 1.25 in the absence of fluoride to 0.82, 0.18, and 0.10, respectively, in the presence of 5 × 10<sup>-5</sup>, 5 × 10<sup>-4</sup>, and 5 × 10<sup>-3</sup> M sodium fluoride. It was found that fluoride did not affect the rate of the iron(II)-persulfate reaction, and therefore this cannot be the cause of the reduction in the induction factor.

**The Photoinduced Reaction between Iron(III) and Arsenic(III).**—Radiation of wave lengths greater than 300 mμ was found to induce a reaction between iron(III) and arsenic(III), in the absence of oxygen, according to the stoichiometric relationship: 2Fe(III) + As(III) → 2Fe(II) + As(V).

The initial rate of formation of iron(II) was measured in the initial presence of 10<sup>-4</sup> M Fe(III), 5 × 10<sup>-5</sup> M Fe(II), 0.01 M HClO<sub>4</sub>,  $\mu = 0.5$ , and was found to be independent of the concentration of arsenic(III) when this was varied from 0.025 to 10<sup>-3</sup> M. When [As(III)] was decreased to 5 × 10<sup>-5</sup> M, the initial rate of formation was reduced to about half of the value found at the larger concentrations of arsenic(III). The initial rate of formation of iron(II) also was measured in 0.01 M As(III) and the same [H<sup>+</sup>] and  $\mu$  as above, and varied [Fe(III)]. It was found to be proportional to [Fe(III)] up to about 10<sup>-4</sup> M, and to increase less than proportionally to [Fe(III)] at higher concentrations.

The effect of initial [Fe(II)] upon  $d[\text{Fe(II)}]/dt$  was measured in solutions 10<sup>-4</sup> M in Fe(III), 0.01 M in As(III), either 0.01 or 0.005 M in HClO<sub>4</sub>, ( $\mu = 0.5$ ), and from 0 to 1.25 × 10<sup>-4</sup> M initially in Fe(II). Figure 1 shows that the reciprocal of the initial rate increases linearly with initial [Fe(II)].

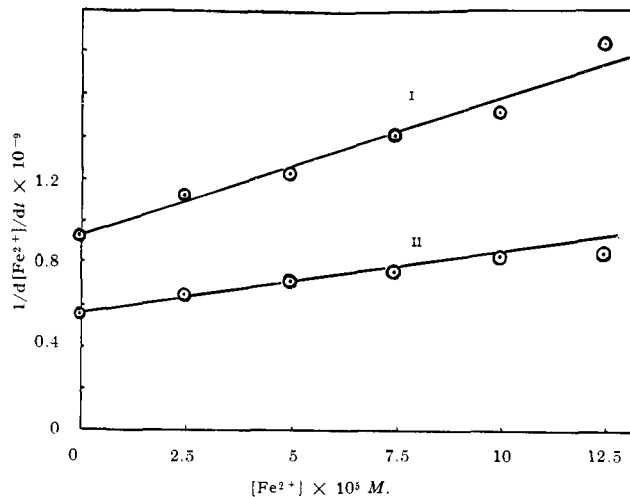
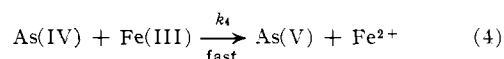
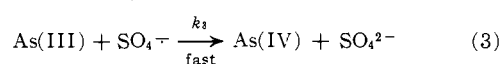
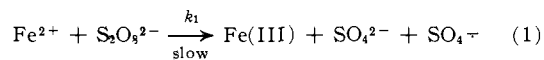


Fig. 1.—The effect of initial  $[\text{Fe}^{2+}]$  on  $d[\text{Fe}^{2+}]/dt$ ;  $[\text{Fe}^{3+}] = 10^{-4} M$ ,  $[\text{As(III)}] = 0.01 M$ ,  $[\text{HClO}_4] = 0.005 M$  or  $0.01 M$ : I, 0.01 M HClO<sub>4</sub>; II, 0.005 M HClO<sub>4</sub>.

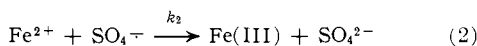
## Discussion

The induced oxidation of arsenic trioxide by the persulfate-iron(II) couple in the presence of an excess of iron(III) can be explained by the intermediate formation of the 4+ oxidation state of arsenic according to the reaction mechanism



The stoichiometry of this mechanism is in accordance with the induction factor of infinity found when sufficient iron(III) was added. The mechanism is substantiated by the kinetics of the reduction of persulfate (Table III) which 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.

Iron(II) and arsenic(III) compete in reacting with the sulfate free radical



Reaction 2 becomes insignificant compared with reaction 3 at arsenic(III) to iron(II) concentration ratios greater than two. Under these conditions the induced oxidation becomes independent of arsenic(III) concentration. However, as this ratio is reduced to less than two, reaction 2 becomes significant and a reduction of the induction factor from its value of infinity occurs (Table V).

Assuming steady state kinetics with respect to As(IV) and  $\text{SO}_4^{\cdot-}$ , the rate of oxidation of iron(II) will be given by

$$\frac{-d[\text{Fe}^{2+}]}{dt} = k_1[\text{Fe}^{2+}][\text{S}_2\text{O}_8^{2-}] \frac{2k_2[\text{Fe}^{2+}]}{k_2[\text{Fe}^{2+}] + k_3[\text{As(III)}]}$$

and the rate of oxidation of arsenic(III) by

$$\frac{-d[\text{As(III)}]}{dt} = k_1[\text{Fe}^{2+}][\text{S}_2\text{O}_8^{2-}] \frac{k_3[\text{As(III)}]}{k_2[\text{Fe}^{2+}] + k_3[\text{As(III)}]}$$

Therefore

$$\frac{d[\text{As(III)}]}{d[\text{Fe}^{2+}]} = \frac{1}{2} \frac{k_3}{k_2} \frac{[\text{As(III)}]}{[\text{Fe}^{2+}]}$$

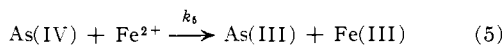
Integrating over the whole reaction gives

$$\frac{k_3}{k_2} = 2 \frac{\ln([\text{As(III)}]_0/[\text{As(III)}]_\infty)}{\ln([\text{Fe}^{2+}]_0/[\text{Fe}^{2+}]_\infty)}$$

$[\text{As(III)}]_0$ ,  $[\text{Fe}^{2+}]_0$  and  $[\text{As(III)}]_\infty$ ,  $[\text{Fe}^{2+}]_\infty$  being the initial and final concentrations, respectively. Table V shows that  $k_3/k_2 = 21$  and is independent of acidity.

In all other experiments of this paper the arsenic(III) concentration greatly exceeds the iron(II) concentration and therefore reaction 2 need not be considered in the reaction mechanism.

When iron(III) is complexed with fluoride, the induction factor is reduced to a limiting value approaching zero. In the absence of iron(III), therefore, the As(IV) produced is postulated to react with iron(II) to re-form As(III).



Reaction 5 also explains the decrease in the induction factor brought about by an increase in iron(II) concentration at constant pH (Table I).

In the induced oxidation of arsenic trioxide by the persulfate-iron(II) couple, both ferrous and iron(III) are present and As(IV) reacts with both.

Assuming steady state with respect to As(IV) and  $\text{SO}_4^{\cdot-}$ , the rate of oxidation of iron will, therefore, be given by

$$\frac{-d[\text{Fe}^{2+}]}{dt} = \frac{2k_1[\text{Fe}^{2+}][\text{S}_2\text{O}_8^{2-}]}{1 + (k_4[\text{Fe(III)}]/k_5[\text{Fe}^{2+}])}$$

and the rate of reduction of persulfate by

$$-d[\text{S}_2\text{O}_8^{2-}]/dt = k_1[\text{Fe}^{2+}][\text{S}_2\text{O}_8^{2-}]$$

Combining these equations gives the relationship

$$\left(1 + \frac{k_4[\text{Fe(III)}]}{k_5[\text{Fe}^{2+}]}\right) d[\text{Fe}^{2+}] = 2d[\text{S}_2\text{O}_8^{2-}]$$

The iron(III) concentration is given by the initial concentration plus that formed by the oxidation of iron during the reaction

$$[\text{Fe(III)}] = [\text{Fe(III)}]_0 + [\text{Fe}^{2+}]_0 - [\text{Fe}^{2+}]$$

where  $[\text{Fe(III)}]_0$  and  $[\text{Fe}^{2+}]_0$  are the initial concentrations. Substituting this relationship in the differential equation and integrating gives the relationship

$$\left(1 - \frac{k_4}{k_5}\right)([\text{Fe}^{2+}]_0 - [\text{Fe}^{2+}]_\infty) + \frac{k_4}{k_5}([\text{Fe}^{2+}]_0 + [\text{Fe(III)}]_0) \ln \frac{[\text{Fe}^{2+}]_0}{[\text{Fe}^{2+}]_\infty} = 2[\text{S}_2\text{O}_8^{2-}]_0$$

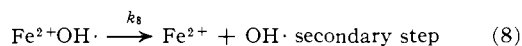
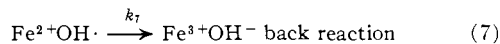
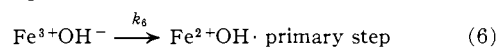
(where  $[\text{Fe}^{2+}]_\infty$  and  $[\text{S}_2\text{O}_8^{2-}]_0$  are the remaining iron(II) concentration and the initial persulfate concentration, respectively), provided excess of iron(II) is used and, therefore, all the persulfate is reduced.

The only unknown in this equation is the ratio of the rate constants for the reactions of As(IV) with iron(III) and iron(II),  $k_4/k_5$ , which can therefore be calculated.

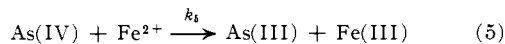
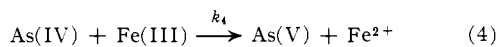
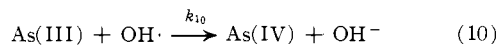
Table I shows that within the experimental error, the ratio  $k_4/k_5$  is a constant for varying  $[\text{Fe}^{2+}]$  and  $[\text{Fe(III)}]$  at a given pH, substantiating the proposed mechanism. The ratio increases with decreasing hydrogen ion concentration (*vide infra*).

The photosensitized Fe(III)-As(III) reaction is also interpreted in terms of the formation of As(IV) and its reaction with iron(II) and -(III).

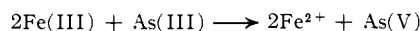
The photoactive species in the photoreduction of iron(III) is the ion pair complex  $\text{FeOH}^{2+}$ <sup>11</sup> and the reaction will proceed



The hydroxyl radical produced in reaction 8 induces the oxidation of As(III)



The over-all stoichiometry of this reaction is in accordance with the experimental result



The rate of formation of  $[\text{Fe}^{2+}]$  in the photochemical reaction 6 is given by

$$d[\text{Fe}^{2+}]/dt = kI_{\text{abs}} = kI_0\{1 - \exp(-ab[\text{FeOH}^{2+}])\}$$

where  $I_0$  and  $I_{\text{abs}}$  are incident and absorbed intensities, respectively,  $a$  is molar absorptivity of  $\text{FeOH}^{2+}$ , and  $b$  is the path length;  $k$  is a proportionality constant. At small  $[\text{FeOH}^{2+}]$  this simplifies to

$$d[\text{Fe}^{2+}]/dt = kI_0ab[\text{FeOH}^{2+}] = k'[\text{FeOH}^{2+}]$$

Hence at small  $[\text{FeOH}^{2+}]$  the net rate of formation of  $[\text{Fe}^{2+}]$  in the presence of As(III) is given by

$$d[\text{Fe}^{2+}]/dt = \frac{k'[\text{FeOH}^{2+}]}{\left(1 + \frac{k_6}{k_4} \frac{[\text{Fe}^{2+}]}{[\text{Fe(III)}]}\right) \left(1 + \frac{k_7k_9[\text{Fe}^{2+}]}{k_8k_{10}[\text{As(III)}]}\right) (k_7 + k_8)}$$

$[\text{FeOH}^{2+}]$  is related to the total ferric iron present,  $[\text{Fe(III)}]$ , by the relationship

$$[\text{FeOH}^{2+}] = [\text{Fe(III)}] \frac{K_a}{([\text{H}^+] + K_a)}$$

where

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

The term containing  $[\text{Fe}^{2+}]/[\text{As(III)}]$  must be negligible as no effect of varying As(III) concentration at con-

stant  $\text{Fe}^{2+}$  was found under conditions where the As(III) was in large excess.

Therefore

$$\frac{d[\text{Fe}^{2+}]}{dt} = \frac{2k'k_8K_a[\text{Fe(III)}]}{\left(1 + \frac{k_8}{k_4} \frac{[\text{Fe}^{2+}]}{[\text{Fe(III)}]}\right)(k_7 + k_8)([\text{H}^+] + K_a)}$$

The initial rate of production of iron(II) when  $[\text{Fe}^{2+}] \rightarrow 0$  will be independent of  $[\text{As(III)}]$  and, at small  $[\text{Fe(III)}]$ , proportional to  $[\text{Fe(III)}]$ . It was found experimentally that the former relationship is obeyed and that the production of ferrous iron increases with increase in  $[\text{Fe(III)}]$ ; the deviation from exact proportionality is due to the difference between  $\{1 - \exp(ab \cdot [\text{FeOH}^{2+}])\}$  and  $ab[\text{FeOH}^{2+}]$ .

At constant  $[\text{Fe(III)}]$  and  $[\text{H}^+]$ , the reciprocal of the rate of formation of iron(II) is predicted from the mechanism to be linearly related to the iron(II) present. Experimentally, this was found to be the case (Fig. 1). The ratio  $k_4/k_8$  can be obtained from the slopes and intercepts of the plots of Fig. 1, and has the values 1.4 and 2.3, respectively, in 0.01 M and 0.005 M perchloric acid ( $\mu = 0.5$ ). The values agree with experimental error with the entirely independent values (cf. Table I) of 1.6 and 2.6 at the same acidities obtained from the induced oxidation by the persulfate-iron(II) couple, further substantiating the proposed mechanism.

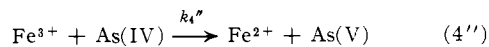
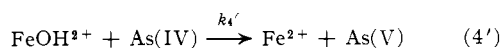
The ratio of the reaction rate constants  $k_4/k_8$  is dependent on the hydrogen ion concentration. Table VI shows that the ratio increases as the hydrogen ion concentration is decreased. At hydrogen ion concentrations less than 0.01 the ratio is approximately proportional to  $1/([\text{H}^+] + K_a)$ , taking  $K_a$  to be  $1.9 \times 10^{-3}$  at  $\mu = 0.5$  in perchlorate medium,<sup>26</sup> i.e.,  $([\text{H}^+] + K_a) \cdot k_4/k_8$  is constant at  $[\text{H}^+]$  less than 0.01.

TABLE VI

DEPENDENCE OF  $k_4/k_8$  ON  $[\text{H}^+]$ ;  $\mu = 0.5$

$\text{HClO}_4$ , M	$k_4/k_8$	$([\text{H}^+] + K_a)k_4/k_8$
0.50	0.14	0.070
.10	0.24	.024
.010	1.6	.019
.005	2.6	.018
.002	4.0	.016

In order to account for the constancy of  $([\text{H}^+] + K_a)k_4/k_8$  at low acidity and its increase at higher acidity we must consider that in the range of acidities used iron(III) is present as  $\text{FeOH}^{2+}$  and  $\text{Fe}^{3+}$ . It is reasonable to assume that both species react with arsenic(IV) but with different rates.



This leads to the expression

$$\frac{k_4}{k_8} = \frac{k_4'}{k_8} \frac{K_a}{([\text{H}^+] + K_a)} + \frac{k_4''}{k_8} \frac{[\text{H}^+]}{([\text{H}^+] + K_a)}$$

As shown in Fig. 2, a plot of  $([\text{H}^+] + K_a)k_4/k_8$  vs.  $[\text{HClO}_4]$  yields a straight line with a slope of  $k_4''/k_8 = 0.1$  and an intercept of  $K_ak_4'/k_8 = 0.017$  corresponding to a value of  $k_4'/k_8 = (1.7 \times 10^{-2})/(1.9 \times 10^{-3}) = 9$ .

The fact that  $k_4'$  is 90 times as large than  $k_4''$  explains the constancy of  $([\text{H}^+] + K_a)k_4/k_8$  at low acidity as the term in  $[\text{H}^+]$  will then become negligible.

The effect of ionic strength  $\mu$  on the ratio  $k_4/k_8$  also substantiates the assumption that  $\text{FeOH}^{2+}$  is the principal reacting species at low  $[\text{H}^+]$ . The dependence of the ratio  $[\text{FeOH}^{2+}]/[\text{Fe}^{3+}]$  upon  $\mu$  and  $[\text{H}^+]$  can be

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

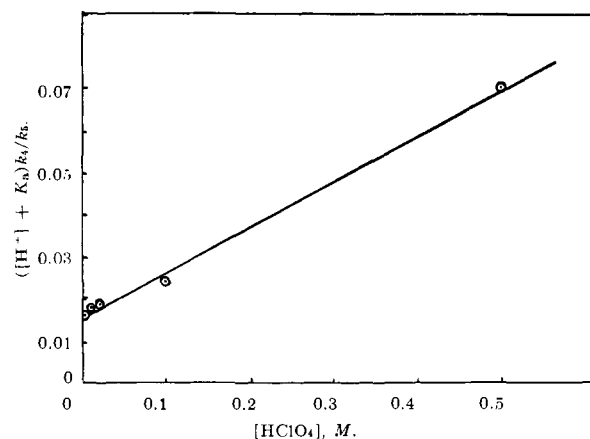
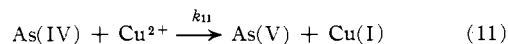


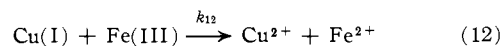
Fig. 2.—Plot of  $([\text{H}^+] + K_a)k_4/k_8$  against  $[\text{HClO}_4]$ .

calculated from the data of Milburn and Vosburgh.<sup>25</sup> When  $[\text{H}^+] = 0.01$  M, this ratio of concentrations increases 1.9-fold when  $\mu$  is changed from 0.5 to 0.01 M; and when  $[\text{H}^+] = 0.002$  M, the ratio increases 1.5-fold when  $\mu$  is changed from 0.5 to 0.002. The observed values of  $k_4/k_8$  (Tables I and II) upon decrease of  $\mu$  increase by 2.0-fold and 1.3-fold at  $[\text{H}^+] = 0.01$  M and 0.002 M, respectively, in excellent agreement with the predicted values.

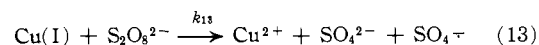
The effect of copper(II) on the iron(II)-persulfate induced oxidation of As(III) is similar to that of iron(III) and gives a limiting induction factor apparently approaching infinity which is explained by the mechanism



followed by either



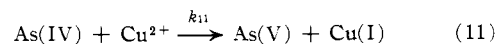
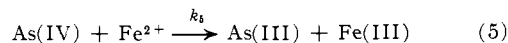
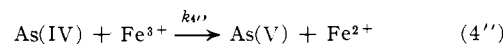
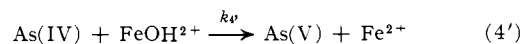
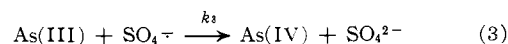
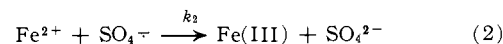
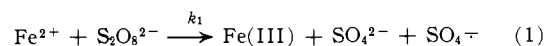
OR



The induction factor in the presence of copper(II) was found to be practically independent of pH (Table IV). This is to be expected as copper(II) does not form any species comparable to  $\text{FeOH}^{2+}$  at the acidities used. Also the independence of the induction factor of hydrogen ion concentration in the presence of copper(II) excludes the possibility that the reaction in eq. 5 is  $[\text{H}^+]$  dependent.

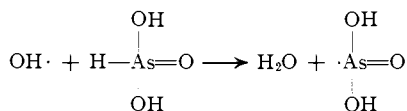
It is possible to estimate the value of  $k_{11}/k_8$ ; i.e., the ratio of the reaction rate constants for the reactions of As(IV) with  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$ , from the effect of copper(II) on the iron(II)-persulfate induced oxidation of arsenic(III). From Tables I and IV it is seen that the effect of copper(II) is approximately equivalent to that of the same concentration of  $\text{FeOH}^{2+}$  and therefore  $k_{11}/k_8$  must be approximately equal to  $k_4'/k_8$ .

The over-all mechanism is therefore



with the ratios  $k_4'/k_8 = 9$ ,  $k_4''/k_8 = 0.1$ ,  $k_{11}/k_8$  about 9, and  $k_3/k_2 = 21$ .

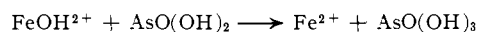
Arsenic(III) is not easily oxidized by one-electron oxidants without the addition of catalysts but is readily oxidized by two-electron transfer. Waters<sup>26</sup> suggests that a one-electron oxidation of arsenic(III) can occur only when the oxidant is capable of withdrawing a hydrogen atom from the favored tautomer; *e.g.*



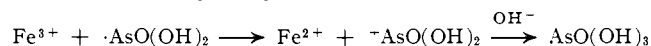
The sulfate free radical can also be considered as a hydrogen-extracting radical, producing  $\text{HSO}_4^-$  instead of

(26) W. A. Waters, *Discussions Faraday Soc.*, **29**, 170 (1960).

the formulated  $\text{SO}_4^{2-}$ . This proposed structure of As(IV) could also explain why the ion pair complex  $\text{FeOH}^{2+}$  reacts faster with As(IV) than the  $\text{Fe}^{3+}$  does. The former reaction will be the direct transfer of a hydroxyl



while the latter will involve electron transfer followed by the addition of hydroxyl ion



In conclusion, it is mentioned that oxygen has a great effect on the iron-arsenic-persulfate system, which is discussed in a subsequent paper.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIF.]

## Properties and Infrared Spectra of Ethylenediaminetetraacetic Acid Complexes. V. Bonding and Structure of Several Metal Chelates in Solution

BY DONALD T. SAWYER AND JAMES E. TACKETT

RECEIVED JANUARY 14, 1963

The ethylenediaminetetraacetic acid complexes of the alkaline earth ions, cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), manganese(II), lead(II), bismuth(III), cerium(III), aluminum(III), iron(III), chromium(III), thorium(IV), and vanadium(IV) in aqueous solution have been studied by infrared spectroscopy using deuterium oxide as the solvent. The effect of solution acidity upon the spectra has been determined and from this stability constants have been estimated for several of the chelate systems. The shift in peak position and area for the carboxylate-carboxylic acid absorption band has been used to propose structures for the complexes in solution. The data indicate that there is some tendency for metal-nitrogen coordination in the alkaline earth-EDTA chelates, but that such bonding is present to a much greater extent with the complexes of the divalent transition metal ions. The structures proposed for the iron(III), aluminum(III), and chromium(III) complexes are more complex and involve hydroxide groups as well as the EDTA ligand.

Although there have been a number of previous infrared studies of the metal-ethylenediaminetetraacetic acid (EDTA) complexes, these have been restricted to the solid phase; a previous paper in this series summarizes the literature.<sup>1</sup> The major importance of metal chelates is their behavior in solution, and in the case of EDTA, in aqueous solutions. Absorption of infrared radiation by water and the limitations imposed by cell materials have restricted studies of aqueous solutions. However, by using deuterium oxide and barium fluoride cells, certain regions of the infrared spectra for metal-EDTA chelates may be investigated, particularly the carbonyl region.

The present study is concerned with the effect of solution pH upon the peak position and area for the carboxylate-carboxylic acid absorption band for a number of metal-EDTA complexes in aqueous solution. The metal ions considered include the alkaline earths, the divalent transition metals, lead(II), iron(III), aluminum(III), chromium(III), bismuth(III), cerium(III), thorium(IV), and vanadium(IV). On the basis of the spectral changes with pH and the conclusions made earlier with respect to the structure of the free ligand,<sup>2a,b</sup> structures are proposed for the various metal-EDTA complexes in solution.

### Experimental

**Equipment.**—The infrared spectra were recorded with a Perkin-Elmer model 421 spectrophotometer equipped with a high resolution grating. Some preliminary spectra were recorded with a Perkin-Elmer model 221G. The aqueous solutions of the metal chelates were contained in barium fluoride cells with 0.025-mm. spacers. The low solubility of this material in water prevented significant attack by the solutions; barium fluoride trans-

mits radiation down to 800  $\text{cm}^{-1}$ . The pH of the solutions was measured with a line-operated Leeds and Northrup pH meter equipped with microelectrodes. With such electrodes the total solution volume could be as small as 0.5 ml. The meter was standardized with N.B.S. buffers.

**Reagents.**—Deuterium oxide ( $\text{D}_2\text{O}$ ) was used for the preparation of all solutions to avoid the interfering absorption bands of the  $\text{H}_2\text{O}$  molecule in the carbonyl region. The material was obtained from the Bio-Rad Laboratories, Richmond, Calif., and had an assay of 99.9%  $\text{D}_2\text{O}$ . The disodium salt of EDTA (as the dihydrate from the J. T. Baker Co.) was used without further purification and had an assay of 99.9%. All other materials were reagent grade. The metal ions were introduced as the metal chloride or nitrate salts, with the exception of thorium(IV) perchlorate.

The metal-EDTA solutions were prepared by combining weighed portions of the disodium salt of EDTA ( $\text{Na}_2\text{H}_2\text{Y}$ ) and the metal salt with  $\text{D}_2\text{O}$  to give an equimolar stock solution of ligand and metal ion. Concentrated NaOH or HCl was added to aliquot portions of the prepared metal-EDTA solution to give the desired pH. Because the major acidic species present in the solutions was the solvated deuterium ion, the indicated pH values on the pH meter had to be corrected to give true acidity by using the equation of Mikkelsen and Nielson<sup>3</sup>

$$\text{pD} = \text{"meter reading"} + 0.40$$

By measuring the peak areas for differing carboxylate groups, the relative number of such differing groups was determined. The peak areas were measured using the base-line technique and ascertaining the absorbance at the base and at the peak. By taking the peak width at the half-height (in terms of absorbance) and multiplying by the peak height the approximate concentration of a given absorbing species was determined.

### Results

The spectral shifts as a function of solution acidity (pD) for the alkaline earth-EDTA chelates in solution are quite similar, especially for the carbonyl region. A representative example of the effect of solution pD upon the carboxylate absorption band is given in Fig. 1 for the barium-EDTA complex. At low values of pD two peaks are observed, one at 1720  $\text{cm}^{-1}$

(1) D. T. Sawyer and J. M. McKinnie, *J. Am. Chem. Soc.*, **82**, 4191 (1960).

(2) (a) D. T. Sawyer and J. E. Tackett, *ibid.*, **85**, 314 (1963); (b) K. Nakamoto, Y. Morimoto, and A. E. Martell, *ibid.*, **85**, 309 (1963).

(3) K. Mikkelsen and S. O. Nielson, *J. Phys. Chem.*, **64**, 632 (1960).