The Silver Catalyzed Oxidation of Arsenious Acid by Persulfate

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The uncatalyzed oxidation of arsenious acid by persulfate has been studied by Gupta & Ghosh⁽¹⁾ and Gupta⁽²⁾ has found the specific influence of several ions in this oxidation. The oxidation is similar to other uncatalyzed oxidations such as those of thiosulfate⁽³⁾ and oxalate⁽⁴,⁵⁾ ions. Catalysis by silver ion has been reported by Gupta and Ghosh, but no systematic study was made by them. Silver catalyzed oxidations by persulfate are reported to be of three types. Hence a detailed study of this silver catalyzed reaction was made to evaluate a possible mechanism and to compare the results with those of other silver catalyzed oxidations.

Experimental

Persulfate oxidations are very susceptible to impurities of the solutions and the nature of the glass vessel, and hence all the vessels and apparatus used in this investigation, were of Jena glass. The medium of reaction was redistilled water.

All the chemicals used were of B.D.H.A.R. or E. Merck G.R. quality. A stock solution of 0.20 N arsenious acid was prepared. For this, a requisite amount of arsenious oxide, sufficient to give a little more than 0.20 N acid, was dissolved by boiling in redistilled water. After allowing it to cool, it was filtered and standardized against permanganate solution. Persulfate solution was always freshly prepared and its concentration checked by Eckardt's method⁽⁶⁾. All other solutions were prepared in the usual way.

The reaction was studied at 24°C in a thermostat and silver nitrate was added at the end. A preliminary study indicated that there was practically no reaction between persulfate and arsenious acid at 24°C for about 30~40 min., the time for which they were kept together in the reaction vessel. The reaction speed becomes measurable only at higher temperatures. Gupta and Ghosh studied the uncatalyzed reaction at 45°C.

Five milliliters of the reaction mixture were pipetted out at suitable intervals of time, in a beaker containing 3 ml. of pure and concentrated hydrochloric acid and 10~15 ml. of distilled water. One drop of 0.0025 M KIO_3 added and the contents were titrated against 0.01 N $KMnO_4$ from a microburette. Persulfate did not interfere with this titration. The reaction was completely checked by inhibiting chloride ions⁽²⁾.

Results and Discussion

The oxidation is of the first order in persulfate and the constants have been calculated from the relation,

$$k=(2.303/t)\times(1/C_{Ag^+})\times\log[a/(a-x)]$$

where '*a*' and '*a−x*' are the concentrations of the persulfate initially and after time '*t*', respectively, and C_{Ag^+} is the concentration of the silver ions. The reaction is in fact bimolecular, but has a first order rate constant because the concentration of the catalyst Ag^+ does not change during the course of the reaction. Hence *k*, though a first order constant, has the units of l. equi^{-1} min^{-1}.

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1) Y. K. Gupta and S. Ghosh, *J. Inorg. & Nuclear Chem.*, **11**, 62 (1959).
2) Y. K. Gupta, *J. Ind. Chem. Soc.*, **36**, No. 9 (1959).
3) C. V. King and O. F. Steinbach, *J. Am. Chem. Soc.*, **52**, 4779 (1930).
4) C. V. King, ibid., **50**, 2089 (1928).
5) T. L. Allen, ibid., **73**, 3589 (1951).
6) Le Blank Eckardt, *Chem. News*, **81**, 38 (1900).

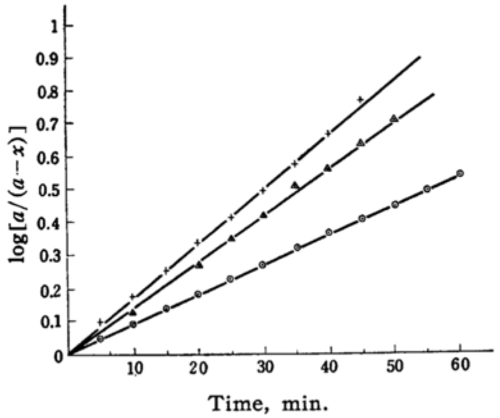

Fig. 1. Silver catalyzed oxidation of H_3AsO_3 by $K_2S_2O_8$.
⊙ Sample 1; $k=23.96$
△ Sample 2; $k=31.49$
× Sample 3; $k=36.77$

Gupta and Ghosh[1] obtained different results with different samples of arsenious acid solution. It was, therefore, imperative to study also the catalyzed reaction with different samples of acid solution. Three experiments out of 20 are shown in Fig. 1 where the average k varied within appreciable limits.

However, the results are quite reproducible with the same sample of arsenious acid solution and hence in order to compare the results amongst themselves, it was necessary to use the same stock solution of arsenious acid as was done by Gupta and Ghosh. Efforts were made to eradicate the cause of this trouble, but without any success. The present paper reports the results of experiments using sample 1 of Fig. 1. The reaction is specifically influenced by the ions and hence no electrolyte was added to keep the ionic strength constant. Nor was there any need for it, because in any particular experiment no change in k was observed as the reaction progressed.

Table I shows the results using different concentrations of the reactants.

It may be seen that the reaction is independent of the concentration of arsenious acid — a fact found in other persulfate oxidations where it is independent of the concentration of the reductant. The rate of reaction increases with the increase in the concentration of the persulfate, but the constants decrease, probably due to the inhibition by potassium ions. The inhibiting character of the potassium ions have been reported in the oxidation of formate[7], oxalic acid[8] and oxalate[9], and the decomposition of persulfate[10]. Alkali metal ions, in general, inhibit many persulfate oxidations.

Table I

$K_2S_2O_8$, N	H_3AsO_3, N	k
0.005	0.0102	25.80
0.01	0.0102	23.96
0.02	0.0102	19.80
0.04	0.0102	13.82
0.01	0.0051	24.01
0.01	0.0102	23.96
0.01	0.0204	24.59

Specific Effect of the Ions.—Table II gives the average values of k for the kinetics of this reaction in the presence of several electrolytes.

Table II

$K_2S_2O_8=0.01$ N; $H_3AsO_3=0.0102$ N; $AgNO_3=0.001$ M

Electrolyte	Concn., M	k
—	—	23.96
K_2SO_4	0.25	7.49
K_2SO_4	0.125	8.49
$(NH_4)_2SO_4$	0.25	11.22
$(NH_4)_2SO_4$	0.125	11.71
$MgSO_4$	0.25	7.93
$MgSO_4$	0.125	9.88
KNO_3	0.50	10.72
KNO_3	0.25	11.44
$NaNO_3$	0.25	16.50
$NaNO_3$	0.125	18.96
NH_4NO_3	0.50	13.80
NH_4NO_3	0.25	18.21

There is no regular variation in k with the change in the ionic strength of the reaction mixture and hence no conclusion regarding the salt effect could be obtained. A comparison of the results shows that the inhibiting action is in the order $K^+ > Na^+ > NH_4^+$—a conclusion similar to that of uncatalyzed oxidation[2]. When the results for nitrates and sulfates are compared, it may be seen that either sulfate ion inhibits or the nitrate ion accelerates. However, the possibilty of both is also considered. In any reaction a sulfate ion is gradually produced, but no increase or decrease in the constants was observed as the reaction progressed. Hence the sulfate ion seems to have no effect or little effect in this reaction and the reaction rate is higher in presence of nitrates than

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[7] S. P. Srivastava and S. Ghosh, *Z. physik. Chem.*, **202**, 198 (1953).

[8] S. P. Srivastava and S. Ghosh, ibid., **205**, 332 (1956).

[9] Y. K. Gupta and S. Ghosh, *J. Inorg. & Nuclear Chem.*, accepted (1959).

[10] A. Kailan and L. Olbrich, *Monatshe. Chem.*, **47**, 449 (1927).

of sulfates, due to the acceleration by nitrate ions.

Reaction in Presence of CH_3COONa, CH_3COONH_4 and CH_3COOH.—Five concentrations of CH_3COONa were investigated and it was found that there exists an optimum concentration of sodium acetate for which the reaction is fastest. Fig. 2 shows the average constants for different concentrations of sodium acetate.

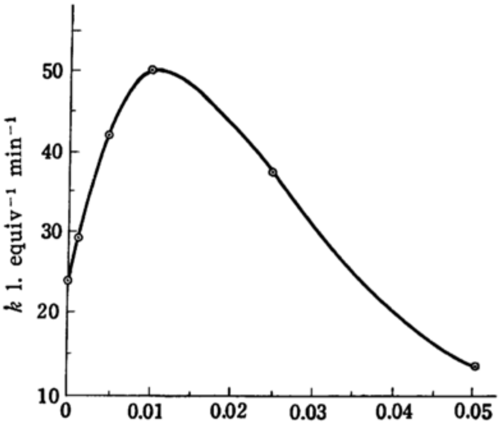

Fig. 2. Effect of CH_3COONa in the silver catalyzed oxidation of H_3AsO_3 by $K_2S_2O_8$.

The sodium ion has been found to inhibit and hence the acetate ion must catalyze the reaction. It appears that at lower concentrations of CH_3COONa, the catalyzing influence of acetate ions predominates over the inhibiting action of sodium ions; whereas the reverse is true at higher concentrations of sodium acetate. The accelerating action of acetate ions may further be seen in Table III where the results with acetic acid and ammonium acetate are shown.

TABLE III

$K_2S_2O_8=0.01$ N; $H_3AsO_3=0.0102$ N; $AgNO_3=0.001$ M

Electrolyte	Concn., M	k
CH_3COOH	0.40	40.27
CH_3COOH	0.10	39.70
CH_3COONH_4	0.50	4.94
CH_3COONH_4	0.25	6.16

Higher concentrations of sodium acetate could not be employed because a precipitate of possibly sodium arsenite formed. This, however, disappeared as the reaction progressed. Results with ammonium acetate are quite as expected.

Reaction in Presence of Sulfuric Acid.—Seven concentrations of sulfuric acid were employed and the results are graphically shown in Fig. 3.

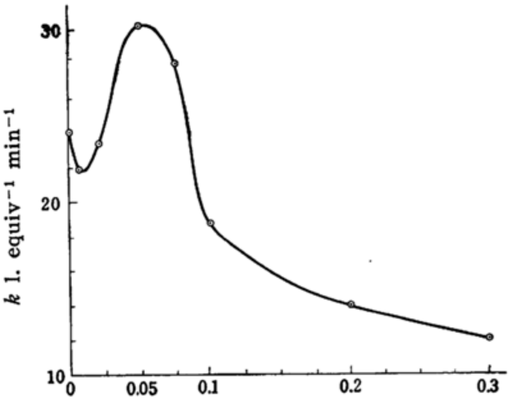

Fig. 3. Effect of H_2SO_4 in the silver catalyzed oxidation of H_3AsO_3 by $K_2S_2O_8$.

There is a concentration of sulfuric acid for which the reaction is fastest. The rate decreases below or above that concentration. The rate constant is 30.26 l. $equi^{-1}$ min^{-1} at this concentration. It may appear from Fig. 3 that hydrogen ions inhibit and sulfate ions slightly accelerate, although the latter have been found to be without any effect. The actual mechanism is not clear. In fact, it is difficult to explain the behavior of sulfuric acid in persulfate oxidations. In the silver catalyzed oxidations of oxalic acid[11] and hydrogen peroxide[12], sulfuric acid retards the rate, whereas it accelerates the rate in the uncatalyzed oxidation of oxalic acid[8] and silver catalyzed oxidation of potassium oxalate[9].

Action of Nitrate, Aluminum and Manganous Ions.—When nitric acid is used, the reaction is very slow in the initial stages, but the rate increases quickly with time. The average constants as shown in Table IV, are found to increase till the end of the reaction.

It seems that there is some impurity in nitric acid which helds up the reaction in the beginning. Further on comparing these results with those in the presence of sulfuric acid, it is evident that the rate is higher in the presence of nitric acid. Hence nitrate ions accelerate the rate.

The results with aluminum nitrate and

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[11] Y. K. Gupta and S. Ghosh, *Proc. Nat. Acad. Sci., India*, **27A Part V**, 258 (1958).

[12] S. P. Srivastava and S. Ghosh, ibid., **23A Part VI**, 44 (1954).

TABLE IV

$K_2S_2O = 0.01$ N; $H_3AsO_3 = 0.0102$ N; $AgNO_3 = 0.001$ M

Time min.	0.016 M HNO_3		0.16 M HNO_3	
	$KMnO_4$ ml.	k	$KMnO_4$ ml.	k
0	5.10	—	5.10	—
5	4.96	1.61	—	—
10	4.28	15.57	—	—
15	3.66	20.80	—	—
20	3.16	22.95	4.92	0.86
25	2.68	24.91	4.52	4.04
30	2.24	26.76	4.04	7.10
35	1.90	27.64	3.62	9.51
40	1.58	28.82	3.20	11.16
45	1.38	28.60	—	—
50	1.18	28.88	2.56	13.38
55	0.98	29.63	2.28	14.28
60	—	—	2.00	15.33

TABLE V

$K_2S_2O_8 = 0.01$ N; $H_3AsO_3 = 0.0102$ N; $AgNO_3 = 0.001$ M

Electrolyte	Concn., M	k
$Al(NO_3)_3$	0.0625	80.60
$Al(NO_3)_3$	0.01	80.01
$Al_2(SO_4)_3$	0.0625	28.66
$Al_2(SO_4)_3$	0.01	25.93
$MnSO_4$	0.002	7.32
$MnSO_4$	0.001	11.45

aluminum sulfate are shown in Table V. The reaction is very fast in the presence of aluminum nitrate. The rate only slightly increases in the presence of aluminum sulfate.

From this it appears that nitrate ions greatly catalyze the reaction and sulfate does so only slightly, whereas aluminum is without any effect. It may, however, be mentioned that the rate constants gradually decreased in the case of aluminum nitrate and increased in the case of aluminum sulfate till the end of the reaction, and that the above table gives only the average constants. The increase or decrease was 15 to 20%.

Manganous sulfate was used because it has been found to act as a catalyst or an anticatalyst in many of the persulfate oxidations. The authors believe that Mn(II) has a specific inhibiting effect.

Energy and Entropy of Activation.—The energy of activation has been calculated from the results of experiments at three different temperatures. Table VI gives the constants at these temperatures.

TABLE VI

$K_2S_2O_8 = 0.01$ N; $H_3AsO_3 = 0.0102$ N; $AgNO_3 = 0.001$ M

Temp. °C	k
24	23.96
29	30.54
39	50.00

The average energy of activation was .8941 cal. The frequency factor[13] and the entropy[14] calculated from this, are 1.55×10^6 l. equiv^{-1} sec^{-1} and -31.06 E.U., respectively. These values correspond to the overall reaction and they may be quite different for the rate determining step. Also these values may vary from sample to sample of arsenious acid, but their nature and order of magnitude do help us to arrive at a possible mechanism.

The rate is the first order in persulfate and independent of the concentration of arsenious acid. No conclusion regarding the salt effect could be obtained. The authors propose the following mechanism for the silver catalyzed oxidation of arsenious acid by persulfate.

$$S_2O_8^{2-} \rightleftarrows 2SO_4^{-} \qquad \text{rapid (1)}$$

$$2SO_4^{-} + Ag^{+} \rightarrow 2SO_4^{2-} + Ag^{3+} \qquad \text{slow (2)}$$

$$Ag^{3+} + 2H_2O \rightarrow Ag^{+} + 2H^{+} + 2OH \qquad \text{fast (3)}$$

$$H_3AsO_3 + 2OH \rightarrow H_3AsO_3 + H_2O \qquad \text{fast (4)}$$

The existence of free radicals[15] SO_4^- and OH, and higher valent silver, Ag^{3+} is now beyond doubt. Gupta and Ghosh[16] have discussed the possibilty of higher valent silver in a paper on the silver catalyzed oxidation of Mn(II) by persulfate. The rate determining step 2 is preceded by an equilibrium which has a very small equilibrium constant K, of the order of 10^{-8} or even less. Step 2 is really bimolecular or rather termolecular, but has a first order dependence on the concentration of the persulfate as shown below.

$$-dc/dt = k_2[Ag^+][SO_4^-]^2$$

but $K[S_2O_8^{2-}] = [SO_4^-]^2$ from reaction 1.

$$\text{Hence} \quad -dc/dt = k_2K[S_2O_8^{2-}][Ag^+]$$

$$= k_r[S_2O_8^{2-}] \quad \text{where } k_r = k_2K[Ag^+]$$

The silver ion concentration remains constant and hence the slow step is the first order in persulfate. Experimentally determined k is equal to $k_r/[Ag^+]$. Hence

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[13] Calculated from the relation $k = A \times e^{-E/RT}$ where A is the frequency factor.

[14] Calculated from the relation $k = (KT/h) \cdot e^{\Delta S/R} \cdot e^{-\Delta H/RT}$ where Δs the entropy change and ΔH is not much different than E.

[15] N. Uri, *Chem. Revs.*, **50**, 375 (1952).

[16] Y. K. Gupta and S. Ghosh, *J. Inorg. & Nuclear Chem.*, **9**, 178 (1959).

$k = k_2 K$ or $k_2 = k/K = 23.96/10^{-8}$ or 23.96×10^8 l. equiv^{-1} min^{-1}. Based on this value of k_2, the entropy change for the slow step is +5.47 E.U. Absolute entropy values have no meaning. Reactions are faster or slower according as their entropy changes are positive or negative as compared to standard values. A standard value for comparision for bimolecular reactions is about −12 E.U. (calculated for the frequency factor, 10^{11}). There is an entropy increase[17] if the reactants are oppositely charged ions and hence the slow step 2 is supported by a positive entropy change. The generally accepted mechanism is, $S_2O_8^{2-} + Ag^+ = 2SO_4^{2-} + Ag^{3+}$. If this were the rate determining step, entropy change for the overall reaction should directly support this. The overall entropy change is negative and hence the authors disapprove the slow step between $S_2O_8^{2-}$ and Ag^+. With a prior equilibrium, the entropy change for the slow step 2 is positive and hence step 2 must be preferably between oppositely charged ions, i. e. the reaction is between positively charged silver ion and a negative ion from persulfate, but not persulfate itself.

Gupta and Ghosh[1] have proposed two mechanisms for the uncatalyzed oxidation of arsenious acid by persulfate.

$$S_2O_8^{2-} \rightleftarrows SO_4 + SO_4^{2-} \qquad \text{slow}$$

or

$$S_2O_8^{2-} + 2H_2O \rightleftarrows 2HSO_4^- + 2OH \qquad \text{slow}$$

Since the silver catalyzed oxidation of arsenious acid is very similar to the uncatalyzed oxidation, particularly in so far as the specific effect of the ions is concerned, it is reasonable to conclude that reaction mechanisms must also be similar. Hence it is believed that OH is preferably the radical responsible for oxidation in the uncatalyzed reaction.

This silver catalyzed oxidation is comparable to the fast oxidation of oxalate[9], and is much faster than the other type of catalyzed reactions wherein the specific rate constant lies between 0.2 and 0.3 at 25°C. Such oxidations are those of Cr(III)[18], VO(II)[19], Mn(II)[20], Ce(II)[21] and many other ions.

Summary

The kinetics of silver catalyzed oxidation of arsenious acid has been followed by estimating the acid with the permanganate. The results are reproducible only with the same stock solution of arsenious acid. This oxidation is much faster than other silver catalyzed oxidations, such as those of Cr^{3+}, VO^{2+}, Mn^{2+}, Ce^{2+}, etc. The oxidation is of the first order in persulfate and independent of the concentration of the acid. The entropy of activation has been calculated and a mechanism has been suggested. No conclusion regarding the salt effect could be obtained due to the specific effect of the ions. K^+, Na^+, NH_4^+ and Mg^{2+} inhibit in the order given. Nitrate ion accelerates the rate and sulfate ion seems to have no effect.

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[17] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", John Wiley & Sons, Inc., New York (1953), p. 132.

[18] D. M. Yost, *J. Am. Chem. Soc.*, **48**, 152 (1926).

[19] D. M. Yost and W. Claussen, ibid., **53**, 3349 (1931).

[20] A. O. Dekker, H. A. Levy and D. M. Yost, ibid., **59**, 2129 (1937).

[21] W. H. Cone., ibid., **67**, 78 (1945).