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Copper Catalyzed Oxidation of As(III) by Peroxydisulphate

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A kinetic study of the oxidation of As(III) by peroxydisulphate catalyzed by Cu(II) has been made. The rate has been measured by estimating As(III) by the permanganate. The data follow the rate expression,

$$-\frac{\mathrm{d}[\mathrm{As(III)}]}{\mathrm{d}t}=\frac{k'[\mathrm{Cu(II)}]^{1/2}[\mathrm{S_2O_8{}^{2-}}][\mathrm{As(III)}]}{1+K_2[\mathrm{As(III)}]}$$

A chain mechanism has been suggested in which the decomposition of peroxydisulphate is the chain initiating step. Cu(II) and As(III) participate in the chain propagating steps. Allyl acetate and Mn(II) inhibit the reaction. The mechanism also involves a complex formation between Cu(I) and As(III) with an equilibrium constant, K_2, having a value of about 1475 M^{-1} at 35°C. Energy and entropy of activation have been found to be 24190 calories and +10.46 e. u. respectively.

Universality of Ag^+ as a catalyst in peroxydisulphate oxidations is very well known[1] and there is probably no species of lower oxidation state which the higher valent silver so formed can not oxidise. If there is no reducing substance, the medium itself, whether it is water, alcohol, dioxane or any other solvent, is oxidised.[2,3] The use of copper(II) as a catalyst, however, is limited to a particular type of reactions. The catalysed reactions reported so far are those of thiosulphate,[4-6] oxalate,[7,8] 2-propanol[9] and hydrogen peroxide.[10] Some catalytic activity of Cu(II) has also been found in the persulphate oxidations of phenylacetic and aliphatic acids.[11]

Gupta and Ghosh[12] found that Cu(II) catalyses the oxidation of As(III) by persulphate, and based on this catalytic activity, there appeared a paper[13] on the determination of As(III). Recently Woods and coworkers[14] have investigated the kinetics of this oxidation. This study is mainly based on the assumption of As(IV) as an intermediate and that Cu(II) is reduced to Cu(I) which is subsequently oxidised back to Cu(II) by peroxydisulphate. This mechanism is more or less similar to the one adopted by Morgan[5] in the oxidation of thiosulphate. Another mechanistic view involving the

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[7] R. S. Bhakuni and S. P. Srivastava, *Z. Physik. Chem.*, **213**, 129 (1960).

[8] E. Ben-Zvi and T. L. Allen, *J. Am. Chem. Soc.*, **83**, 4352 (1961).

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[10] H. S. Samant and S. P. Srivastava, *Proc. Natl. Acad. Sci. (India)*, **27A**, 282 (1958).

[11] R. G. R. Bacon and R. W. Bott, *Chem. & Ind.*, **1953**, 1285.

[12] Y. K. Gupta and S. Ghosh, *J. Inorg. Nucl. Chem.*, **11**, 62 (1959).

[13] G. Prasad and Y. K. Gupta, *Z. Anal. Chem.*, **198**, 173 (1963).

[14] R. Woods, I. M. Kolthoff and E. J. Meehan, *Inorg. Chem.*, **4**, 697 (1965).

transient formation of Cu(III) is held by Ben-Zvi and Allen8) and Srivastava7,10) in the oxidation of oxalate and hydrogen peroxide. Ball and coworkers9) on the other hand assume the formation of both Cu(III) and Cu(I) to explain their results. In view of two differing views, though not opposed, it appeared to us that the problem is still worth investigation. Some work on As(III) in this laboratory was done three years back and it was therefore, thought worthwhile to begin an investigation with As(III). In fact the investigation has been extended to the oxidation of other related compounds also and the results will appear in subsequent papers.

Experimental

Potassium sulphate, copper sulphate, arsenious oxide and all other chemicals used were of B. D. H. Analar or E. Merck G. R. quality. Stock solutions of 0.1 M arsenious acid was prepared by dissolving the requisite amount of arsenious trioxide, sufficient to give a little more than 0.1 M acid, in boiling water. After cooling it was filtered and standardised against standard permanganate solution.15) It was found and as reported12,16) earlier that the results were reproducible within 5% only when the same stock solution of arsenious acid was used and that the rate constants changed within a factor of ten if different solutions of arsenious acid were used. Hence wherever the results have been compared the same stock solution has been used. No definite reason could be assigned for this behaviour but it appeared that some impurity to which the reaction is very much susceptible, enters into the solution of As(III) or the distilled water while it is being prepared and the amount of this impurity is always changing. However, this explanation has to be accepted with slight reservation because this type of behaviour in peroxydisulphate oxidations is reported only in a few cases *e. g.* oxalate,17) thiosulphate4) and arsenious acid.12,16)

Apart from the impurities, peroxydisulphate oxidations are susceptible to a small extent to the nature of the glass vessel and hence all the vessels and apparatus used were of pyrex glass. The medium was redistilled water, the second distillation being done, in presence of permanganate. Peroxydisulphate solution was always freshly prepared and its concentration checked, by Eckardt's18) or arsenite19) method.

All the reactions have been carried out at 35°C unless otherwise mentioned, in a thermostat and peroxydisulphate was always added at the end. There was no reaction between copper sulphate and arsenious acid or precipitation in acid solutions of the concentration employed. Ten millilitres of the reaction mixture were pipetted out at suitable intervals of time, and the concentration of the unreacted arsenious acid was determined by titration against a standard permanganate solution. Peroxydisulphate or copper sulphate did not interfere with the titration. The reaction was completely checked by inhibiting chloride ions.29) All solutions were prepared in freshly boiled and cooled double distilled water from day to day except that of As(III). The reaction rates are different in presence and absence of oxygen as reported by Woods and coworkers.14) A few experiments were carried out in an atmosphere of nitrogen and the rate was found to be slightly faster than the situation when reactions are carried out in boiled and cooled distilled water as stated above, but the rates were quite different if the solutions are air or oxygen saturated. Bacon11) has reported large induction periods in peroxydisulphate polymerisation reactions in oxygen saturated solutions. Inhibiting action of air is much less than that of oxygen. The importance of absence or presence of oxygen or air becomes much less in presence of a reducing substance. In no case we could observe an induction period even though the solutions were not completely free of air.

A literature survey reveals that air does not readily oxidise As(III) in acid solution21) even in presence of Cu(I) or Cu(II) which have been regarded as catalysts.22,23) These oxidations take place only in alkaline medium. In view of the fact that the nature of the reaction in ordinary solutions is not different than in nitrogen saturated systems, we thought it convenient to work in air atmosphere. Another reason which led us to do so was the fact that the results were less reproducible in case when nitrogen gas was flushed through the reaction mixture, probably because nitrogen gas itself brings some impurities with it.

Results and Discussion

The reaction is first order with respect to peroxydisulphate and some of these first order plots are

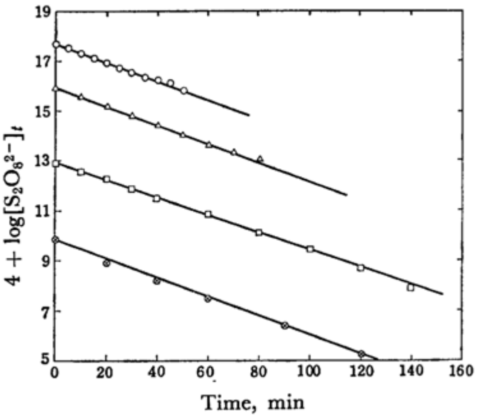

Fig. 1. Effect of change of $[S_2O_8^{2-}]$; $[NaClO_4]=0.2$ M; $[HClO_4]=0.2$ M; $[As(III)]=0.02$ N; $[CuSO_4]=1\times10^{-4}$ M.
○ 0.06 N $S_2O_8^{2-}$ △ 0.04 N $S_2O_8^{2-}$
□ 0.02 N $S_2O_8^{2-}$ ⊗ 0.01 N $S_2O_8^{2-}$

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15) D. E. Metzler, R. J. Mye and E. H. Schift, *Ind. Eng. Chem., Anal. Ed.*, **16**, 625 (1944).

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18) Le Blank Eckardt, *Chem. News*, **81**, 38 (1900).

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21) D. Ya Evdokimov, *Ukrain Khim. Zhur.*, **26**, 132 (1960); *Chem. Abstr.*, **54**, 15864 e. (1960).

22) Y. Kato and T. Murakami, *J. Soc. Chem. Ind., Japan*, **33**, 226 (1930); *Chem. Abstr.*, **24**, 44516(1930).

23) W. Reinders and S. I. Vles, *Rec. Trav. Chim.*, **44**, 29 (1925); *Chem. Abstr.*, **19**, 15232 (1925).

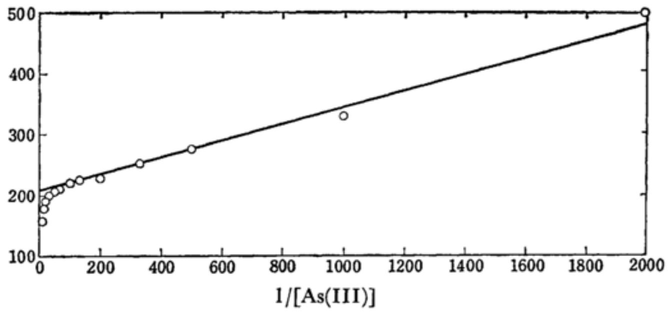

Fig. 2. $[S_2O_8^{2-}]=0.02$ N; $[CuSO_4]=1\times10^{-4}$ M; $[NaClO_4]=0.2$ M; $[HClO_4]=0.2$ M.

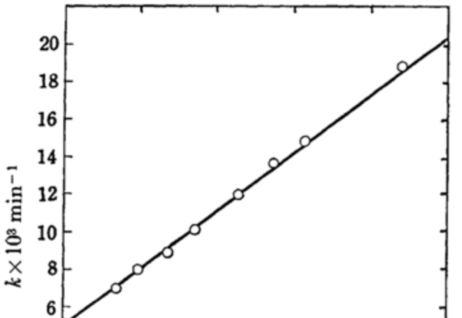

Fig. 3. $[S_2O_8^{2-}]=0.02$ N; $[As(III)=0.02$ N; $[NaClO_4]=0.2$ M; $[HClO_4]=0.2$ M.

shown in Fig. 1. The order with respect to reducing substance, aresenite is not zero, as found in the other silver catalyzed oxidations *i. e.* of Mn(II),24) hydrazine,25) Ce(III),26) Cr(III),27) Tl(I),2) *etc.* and for the concentrations employed in the investigation, is found to be 0.17 by van't Hoff's differential method. A plot of the reciprocal of the observed rate constant *vs.* reciprocal of the arsenite concentration gives a straight line not passing through the origin (Fig. 2). The rate has one half order dependence on the concentration of the catalyst, $CuSO_4$ (Fig. 3). The rate law, therefore, should be of the form,

$$-\frac{d[As(III)]}{dt}=\frac{[Cu^{2+}]^{1/2}[S_2O_8^{2-}][As(III)]}{1+K_2[As(III)]}$$

For the same concentration of Cu^{2+} and high As(III), the rate law assumes the form:

$$-\frac{d[As(III)]}{dt}=k'[S_2O_8^{2-}]$$

with k' as the observed first order rate constant. However, whether k' will have uniformly the same values or not would depend on the relative magnitudes of 1 and K_2[As(III)]. K_2 has a value of 1475 (as will be found later) and, therefore, for concentrations of As(III), 1×10^{-2} M and above, 1 may be neglected in comparison to the term K_2[As(III)] and for constant concentration of [Cu(II)], the rate will be first order with respect to $[S_2O_8^{2-}]$. For low concentrations of As(III) such as 1×10^{-4} M or less the second term of the denominator may be neglected and the order with respect to As(III) would be one. The combined total order for As(III) and $[S_2O_8^{2-}]$ would be two. If, however, $[S_2O_8^{2-}]$ is in excess over that of [As(III)], the reaction would be of pseudo first order. Such low concentrations of [As(III)] could not be employed because of the difficulty in its determination. However, for concentrations of 1×10^{-3} or 5×10^{-4} M of As(III), we do find this tendency to give pseudo first order straight lines with respect to As(III).

The first order plots with respect to peroxydisulphate for As(III) concentration 1×10^{-3} to 7.5×10^{-3} M deviate from the straight line relationship towards the end of the reaction, but the tendency becomes less and less as the concentration of As(III) is increased and we have good first order plots for 7.5×10^{-3} M concentration or above (Fig. 1). For concentrations, 2×10^{-3}, 3×10^{-3} and 5×10^{-3} M, *etc.* of As(III), good half order plots with respect to As(III) are also obtained, but for 1×10^{-3} or 5×10^{-4} M a tendency for first order reaction is indicated. These half order plots and the tendency of some of them indicating first order reaction are shown in Fig. 4. Woods and coworkers14) have also reported the order of 1/2 for 1—2×10^{-3} M As(III). They did not investigate a wider range of concentration and hence failed to notice the rate being a complex function of As(III) concentration.

Effect of Ionic Strength. The ionic strength was changed by varying the concentration of sodium perchlorate at constant $HClO_4$ concentration. A plot of log k' *vs.* $\sqrt{\mu}$ gives a straight line with a slope of -1.18. Although this would

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24) Y. K. Gupta and S. Ghosh, *J. Inorg. Nucl. Chem.*, **9**, 178 (1959).
25) A. O. Dekker and D. M. Yost, *J. Am. Chem. Soc.*, **59**, 2129 (1937).
26) W. H. Cone, *ibid.*, **67**, 78 (1945).
27) D. M. Yost, *ibid.*, **48**, 152 (1926).

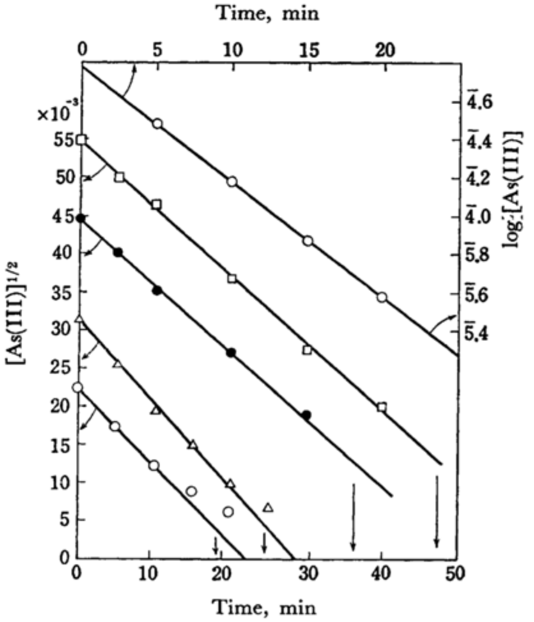

Fig. 4. $[S_2O_8^{2-}]=0.02$ N; $[NaClO_4]=0.2$ M; $[HClO_4]=0.2$ M; $[CuSO_4]=1\times10^{-4}$ M; half order plots ○, 5×10^{-4} N [As(III)]; △, 1×10^{-3} N [As(III)]; ●, 2×10^{-3} N [As(III)]; □, 3×10^{-3} N [As(III)]; first order plot ○, 5×10^{-4} N [As(III)].

indicate a slow reaction step involving ions of unit opposite charge,[28] the reaction is quite complicated (the rate determining step being preceded by a number of steps) to draw any such conclusion, particularly when the ionic strengths are not in the range in which Debye-Hückel theory is applicable.

Effect of Hydrogen Ions. The concentration of hydrogen ions was varied with the help of perchloric acid at almost constant ionic strength (0.2 M $NaClO_4$). The rate slightly decreases by increasing the concentration of perchloric acid as shown in Table 1.

TABLE 1

$[As(III)]=1\times10^{-2}$ M; $[S_2O_8^{2-}]=1\times10^{-2}$ M; $[CuSO_4]=1\times10^{-4}$ M; $[NaClO_4]=2\times10^{-1}$ M

$[HClO_4]$, M$\times10^{-2}$	0	0.5	1	2	4
$k'\times10^2$ min^{-1}	1.996	1.90	1.81	1.675	1.37

Increase in the concentration of perchloric acid involves a small increase in the ionic strength also but the change in the rate constant is not much. It, therefore, appears that the effect of hydrogen ion concentration reaches a limiting value. This would happen if arsenious acid which is almost unionised, is involved in an equilibrium like

$$H_3AsO_3 \rightleftarrows H_2AsO_3^- + H^+ .$$

All reactions were, therefore, studied in a high concentration *e.g.* 0.2 M $HClO_4$ where small changes in $[H^+]$ would be without any effect. Similarly ionic strength was kept constant by adding 0.2 M $NaClO_4$. Table 2 brings out the fact that the effect of perchloric acid in higher concentration range is equivalent to that of decrease in ionic strength. The concentrations of perchlorate and perchloric acid have been changed so that the ionic strength does not change. It was found that the rate constants also are reasonably constant.

TABLE 2

$[As(III)]=1\times10^{-2}$ M; $[S_2O_8^{2-}]=1\times10^{-2}$ M; $[CuSO_4]=1\times10^{-4}$ M

$[NaClO_4]$, M$\times10$	1	1.5	2	2.5	3	3.5
$[HClO_4]$, M$\times10$	3	2.5	2	1.5	1	0.5
$k'\times10^3$ min^{-1}	7.16	7.05	8.06	7.37	7.78	8.05

At low concentrations of perchloric acid the first order plots deviated a lot from the straight line towards the end of the reaction, but this tendency decreased as the concentration of perchloric acid was increased. No such tendency was noticed if the concentration of perchloric acid is 0.1 M and above. This behaviour is in some way connected with the different forms of As(III) in which it can exist in solution.

Effect of Reaction Products. Bisulphate and As(V) are the products of the reaction, but they do not seem to affect the rate (Table 3).

TABLE 3

$[As(III)]=1\times10^{-2}$ M; $[S_2O_8^{2-}]=1\times10^{-2}$ M; $[CuSO_4]=1\times10^{-4}$ M; $[HClO_4]=2\times10^{-1}$ M; $[NaClO_4]=2\times10^{-1}$ M

$NaHSO_4$, M$\times10^2$	0.5	1	2	5	10
$k'\times10^3$ min^{-1}	5.25	5.29	5.18	5.08	5.11

Similarly added disodium hydrogen arsenate (5×10^{-3}, 1×10^{-2} and 2×10^{-2} M) had absolutely no effect on the rate. The rate determining step is, therefore, not a mass law term.

Energy and Entropy of Activation. Table 4 gives the rate constants at different temperatures.

A plot of log k' *vs.* $1/T$ gives a straight line from the slope of which the energy of activation was calculated and found to be 24190 calories. The entropy of activation was found to be +10.46 e.u.

TABLE 4

$[As(III)]=1\times10^{-2}$ M; $[S_2O_8^{2-}]=1\times10^{-2}$ M; $[CuSO_4]=1\times10^{-4}$ M; $[HClO_4]=2\times10^{-1}$ M; $[NaClO_4]=2\times10^{-1}$ M

Temperature, °C	25	30	35	40
$k'\times10^3$ min^{-1}	2.245	4.50	8.06	14.69

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28) A. A. Frost and R. G. Pearson, *Kinetics and Mechanism,* **1961,** 151.

Table 5

[As(III)]$=2\times10^{-2}$ M; [$S_2O_8^{2-}$]$=2\times10^{-2}$ M; [$CuSO_4$]$=1\times10^{-4}$ M;
[$HClO_4$]$=2\times10^{-1}$ M; [$NaClO_4$]$=2\times10^{-1}$ M

[$MnSO_4$], M$\times10^3$	0	1	2	4	6	50	100	200
$k'\times10^4$ min^{-1}	80	16.31	4.35	1.73	1.67	0.84	0.83	0.83

Effect of Manganous Ions. Mn(II) has been found to be an anticatalyst in the silver catalysed peroxydisulphate oxidations of oxalate,(29) formate,(30) As(III),(16) citrate,(31) tartrate,(31) malonate(31) and also in the uncatalysed oxidation of As(III).(20) This behaviour of Mn(II) is also found in the present reaction. Table 5 gives the rate constants for different concentrations of manganous sulphate.

It is observed that as the concentration of Mn(II) is increased, the rate constants appreciably decrease. For 100×10^{-3} M Mn(II), the rate constant has the value which is comparable to that of the rate constant for the decomposition of peroxydisulphate which at 35°C calculated from the data of Kolthoff and Miller,(32) is 5.49×10^{-5} min^{-1}. It is thus found that Mn(II) acts in such a way that it checks all the steps of the catalysed reaction and only thermal decomposition of peroxydisulphate can take place. Incidentally here we come across the main difference between the silver catalysed reactions(31) and this copper catalysed reaction. In the former case the rate approaches a limiting value (0.3—0.5 min^{-1}) as the concentration of Mn(II) is increased. This points to a two term rate law in case of Ag(I) catalysed reactions. One of them is a non-chain process and the other is a chain mechanism which is altogether stopped in presence of sufficient concentration of Mn(II). In case of copper(II) catalysed reaction which as we shall see, is a chain reaction, the catalytic activity of Cu(II) is completely masked by the presence of sufficient Mn(II).

Allyl Acetate Inhibition. A few reactions were studied in presence of allyl acetate to see whether the reaction is a chain process or not. As the permanganate reacts with allyl acetate, the reaction could not be followed by estimating the arsenite with permanganate. In all such experiments alcoholic iodine was used to estimate the arsenite iodometrically. Preliminary work in connection with such titrations, showed that peroxydisulphate and allyl acetate do not interfere. Following the kinetics in this way the rate constant was found to be 1.56×10^{-2} min^{-1} (with 0.2 M $NaClO_4$ and no $HClO_4$) which is reasonably of the same order of magnitude as the value (1.99×10^{-2} min^{-1}) obtained by the permangnate method under almost similar conditions.

Rate inhibition by allyl acetate is very well known.(8,33) It has been shown by Kolthoff and coworkers(34) that allyl acetate is a highly efficient captor of sulphate radicals. Since peroxydisulphate has been reported to initiate polymerisation of vinyl compounds(35,36) through the sulphate ion radical,(37) it seems reasonable that the allyl acetate reacts with sulphate ion radical and its presence is confirmed by the incorporation of ^{35}S from ^{35}S labelled peroxydisulphate into polymer chains. The very marked inhibition in the present investigation by allyl acetate is indicative of a chain reaction involving sulphate free radicals. In presence of 0.5 or 0.2 M allyl acetate, there is almost no change in the concentration of As(III) even after 150 min. The rate constant in presence of 0.1 M allyl acetate is 3.58×10^{-5} min^{-1}. This rate is even lower than the thermal decomposition(23) of $S_2O_8^{2-}$ according to the following reaction:

$$S_2O_8^{2-} \xrightarrow{k} 2SO_4^{-}$$
$$(k=5.49\times10^{-5}\ \mathrm{min}^{-1}\ \text{at}\ 35°\mathrm{C})$$

because it is here $-d[\mathrm{As(III)}]/dt$ which is being measured and so sulphate ion radicals will be captured by allyl acetate leaving none or few SO_4^- for the oxidation of As(III). If it were possible to estimate peroxydisulphate in such a case, $-d[S_2O_8^{2-}]/dt$ will have a value of 5.49×10^{-5} at 35°C. At higher concentrations of allyl acetate, As(III) is not at all oxidised, but $S_2O_8^{2-}$ will decompose with a rate constant of 5.49×10^{-5} min^{-1}.

It is, therefore, obvious that neither As(III) nor Cu(II) participates in the chain initiating reaction which is the homolytic cleavage of $S_2O_8^{2-}$, but they are definitely involved in chain propagating steps. Allyl acetate cuts off all these chains by taking away the sulphate free radical.

Comparison with Reported Results. The notable point of difference observed in the present investigation and between that in the work of

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29) Y. K. Gupta and S. Ghosh, *J. Inorg. Nucl. Chem.*, **11**, 320 (1959).

30) Y. K. Gupta and R. K. Nigam, *J. Ind. Chem. Soc.*, **37**, 125 (1960).

31) H. G. S. Senger and Y. K. Gupta, Communicated, 1966.

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

33) K. B. Wiberg, *J. Am. Chem. Soc.*, **81**, 252 (1959).

34) I. M. Kolthoff, E. J. Meehan and E. M. Karr, *ibid.*, **75**, 1439 (1953).

35) J. H. Mertz and W. A. Waters, *Disscussions Faraday Soc.*, **29**, 179 (1947).

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

37) P. Bartlett, E. J. Meehan and E. M. Carr, *ibid.*, **3**, 216 (1948).

Woods and coworkers is that the rate is not independent of arsenite concentration at low Cu(II) concentration, although the effect is not much. A two hundred fold change in As(III) concentration (5×10^{-4}—1×10^{-2} M) increases the rate approximately only three times (1.94×10^{-3}—6.33×10^{-3}). The change in k' is so small that the earlier workers failed to notice this. Apart from this, the more important fact is the increase in the order of As(III) as its concentration is lowered in conformity with the linear relationship of Fig. 2. These workers also report a half order dependence on As(III) when the concentration of the latter is approximately 1×10^{-3} M. In spite of the conditions which were by no means identical, under which the two investigations have been made the values of the rate constant (2.25×10^{-3} min^{-1}) found by us compare remarkably well with that of Woods and coworkers14) (2.7×10^{-3} min^{-1}) both at 25°C.

These workers further report that the rate constant tends to a limiting value at higher concentration of Cu(II) (1×10^{-3} M and more). In our case, though the rate constant at higher [Cu(II)] was less than that expected no limiting value was reached even for 5×10^{-3} M Cu(II). It appears that the reason for the limiting value is the formation of a turbidity of copper arsenite in absence of sufficient hydrogen ions. We did not notice any such limiting tendency because we used higher (0.2 M) concentration of perchloric acid.

Mechanism. Any proposed mechanism must incorporate (a) the first order character in respect of peroxydisulphate (b) half order dependence on Cu(II) concentration (c) variation of order from 0 to 1 with respect to As(III) (d) inhibition by Mn(II) and allyl acetate.

We postulate sulphate ion free radicals and As(IV) as intermediate as was done by Woods and coworkers.14) Sulphate ion free radicals are now well known to be formed by the thermal and photochemical decomposition of peroxydisulphate.32,35,38–40) Similarly the intermediate formation of As(IV) now seems to be well founded. Woods and coworkers41,42) have found it in the induced oxidation of As(III) by $S_2O_8{}^{2-}$-Fe(II) and Fe(II)-H_2O_2 systems. Daniels and Weiss43) proposed the production of As(IV) by the reaction of hydroxyl radical with As(III) to occur during the oxidation of arsenite by the action of X-rays. In the photochemically induced oxidation of As(III) also, Daniel44) concluded the existence of As(IV). Csyani postulated its intermediate formation in the titration45) of As(III) by $S_2O_8{}^{2-}$-H_2O_2 mixture and also in the induced induction46) of chlorate by As(III).

We propose the following mechanism:

$$S_2O_8{}^{2-} \xrightarrow{k_1} 2SO_4{}^- \tag{1}$$

$$SO_4{}^- + \mathrm{As(III)} \xrightarrow{k_2} SO_4{}^{2-} + \mathrm{As(IV)} \tag{2}$$

$$\mathrm{As(IV)} + \mathrm{Cu(II)} \xrightarrow{k_3} \mathrm{As(V)} + \mathrm{Cu(I)} \tag{3}$$

$$2\mathrm{Cu(I)} \overset{K_1}{\rightleftarrows} \mathrm{Cu}^0 + \mathrm{Cu(II)} \tag{4}$$

$$\mathrm{Cu(I)} + \mathrm{As(III)} \overset{K_2}{\rightleftarrows} [\mathrm{Cu^IAs^{III}}] \tag{5}$$

$$[\mathrm{Cu^IAs^{III}}] + S_2O_8{}^{2-} \xrightarrow{k_4} \mathrm{Cu}^{3+} + \mathrm{As(III)} + 2SO_4{}^{2-} \tag{6}$$

$$\mathrm{Cu}^{3+} + \mathrm{As(III)} \xrightarrow{k_5} \mathrm{Cu}^{+} + \mathrm{As(V)} \tag{7}$$

$$\mathrm{Cu}^0 + S_2O_8{}^{2-} \xrightarrow{k_6} 2\,SO_4{}^{2-} + \mathrm{Cu(II)} \tag{8}$$

$$SO_4{}^- + \mathrm{As(IV)} \xrightarrow{k_9} SO_4{}^{2-} + \mathrm{As(V)} \tag{9}$$

If $k_3>k_2$, k_5 and $k_6>k_4$; $k_2[SO_4{}^-][\mathrm{As(III)}]>k_9[SO_4{}^-][\mathrm{As(IV)}]$ (because the steady state concentration of $SO_4{}^-$ and As(IV) both will be small) and K_1 and K_2 are rapid equilibria, the rate of decrease of As(III) is given by the equations,

$$-\frac{d[\mathrm{As(III)}]}{dt} = k_5[\mathrm{As(III)}][\mathrm{Cu}^{3+}] + k_2[SO_4{}^-][\mathrm{As(III)}] = \frac{K_2}{K_1{}^{1/2}}\frac{k_4[\mathrm{Cu(II)}]^{1/2}[\mathrm{As(III)}]}{1+K_2[\mathrm{As(III)}]} + \frac{k_1}{2}[S_2O_8{}^{2-}]$$

k_1 is of the order32) of 1×10^{-5}—10^{-6} min^{-1} and hence can be neglected in comparison to the first term:

$$-\frac{d[\mathrm{As(III)}]}{dt} = \frac{K_2}{K_1{}^{1/2}}\frac{k_4[\mathrm{Cu(II)}]^{1/2}[\mathrm{As(III)}]}{1+K_2[\mathrm{As(III)}]}[S_2O_8{}^{2-}]$$

The above expression has the same form as the experimental rate law provided the concentrations of Cu(I), Cu(II) and Cu^0 and also the complex of Cu(I) are very small and the only significant species of copper in solution is Cu(II). Cu(II) is not known to form any complex with arsenite and a spectrophotometric investigation in the range 600—750 mμ also indicated no complex formation. In the above mechanism a complex

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formation between Cu(I) and As(III) has been postualted although there is no direct evidence for it. However substituted arsine complex of Cu(I) has been reported by Cass and coworkers.[47] Cu(I) complex of peroxydisulphate itself has been postulated by Chaltkyan and Beileryan[48] in the oxidation of Cu(I) by persulphate, and a complex of Cu(I) and thiosulphate by Morgan[5] in the oxidation of the latter by peroxydisulphate. The existence of tripositive copper is now beyond doubt, though the knowledge about it is limited. Sneed, Maynard and Brasted[49] report quite a few complex compounds of Cu(III) and Latimer[50] has given its approximate oxidation potential. Of particular mention in this study is the fact that a series of complex salts containing tripositive copper has been prepared by peroxydisulphate oxidation.[51] The disproportionation reaction of cuprous ion (step 4) postulated to explain half order dependence on Cu(II) is well known in aqueous solution.[52,53] The equilibrium constant for the reaction (4) is 1.2×10^6 and thus the concentration of Cu (I) or Cu(I) complex is very small. The oxidation of zerovalent copper to cupric ion (step 8) is also known.[54]

From the intercept (=205) and the slope (=0.139) of the straight line in Fig. 2, the value of K_2, the equilibrium constant for the complex formation (step 5) of the mechanism is found to be approximately 1475. With this value of K_2, it can now be easily understood that 1 can be neglected as compared to K_2[As(III)] in the denominator of the above rate expression. This would give a zero order dependence on As(III). For sufficiently low concentrations of As(III) (10^{-4} M or less), K_2[As(III)] can be neglected as compared to one, giving first order dependence on As(III). It has already been mentioned earlier about this tendency. From the interecept which is equal to $K_1^{1/2}/K_4[\mathrm{Cu(II)}]^{1/2}$, the approximate value of k_4 can be calculated, provided we know K_1 at 35°C. Its value at 25°C (1.2×10^6) is known from the works of Fenwick[52] and Heinerith[53], but we have no straight line at 25°C corresponding to Fig. 2. However, the intercept for a corresponding straight line plot at 25°C would be within a factor of two or three and this would give a value of approximately 150 to 270 for k_4.

We have assumed the following chain terminating step in the mechanism.

$$\mathrm{SO_4^-} + \mathrm{As(IV)} \rightarrow \mathrm{SO_4^{2-}} + \mathrm{As(V)} \qquad (9)$$

The other probable chain breaking steps,

$$\mathrm{Cu(I)} + \mathrm{SO_4^-} \rightarrow \mathrm{Cu(II)} + \mathrm{SO_4^{2+}} \qquad (10)$$

$$\mathrm{Cu(I)} + \mathrm{Cu(III)} \rightarrow 2\mathrm{Cu(II)} \qquad (11)$$

have not been considered important because the increase in the concentration of Cu(II), produces an almost expected increase in the rate (Fig. 3), though at higher concentrations of Cu(II) than those employed, these chain breaking steps are likely to become important.

In presence of Mn(II), $\mathrm{SO_4^-}$ oxidises it to Mn(III) and the latter oxidises As(III) instantaneously. Thus no chains are initiated and the rate decreases considerably. Allyl acetate also takes away the sulphate ion radical but it does not oxidise As(III) at all and hence in presence of its sufficient concentration, no decrease in concentration of As(III) would be found. Peroxydisulphate, however, would decrease at the same rate as that of its thermal decomposition.

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