The Kinetics of Formation of a Silver(II) and a Silver(III) Complex by Peroxydisulphate Oxidation

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The kinetics of oxidation of the bisbipyridyl and the ethylenebisbiguanide complexes of silver(I) by the peroxydisulphate anion have been studied. The silver(II)–bipyridyl complex is formed in a reaction which is first order in both reagents, while the silver(III) complex is formed by two consecutive reactions, each being first order in both reagents. This evidence suggests that the interaction between silver and peroxydisulphate involves a one-electron process.

THERE are many known complexes of silver(II), one of which is the bisbipyridyl complex.[1,2] However, there are few reported complexes of silver(III); one of these is formed with the ligand ethylenebisbiguanide (enbig).[3] A comparison of the rates of their formation by oxidising the silver(I) complexes with the peroxydisulphate anion should help to distinguish between the possible occurrence of one- or two-electron steps in the catalysis of peroxydisulphate oxidations by silver ions.[4]

RESULTS AND DISCUSSION

Owing to the limited solubility of the silver(I)–bipyridyl complex in water, its oxidation was followed in a 50% acetone medium. The rate of reaction was observed spectrophotometrically at 4540 Å, the visible absorption maximum of the silver(II) complex. The rate of reaction is such that no appreciable oxidation of solvent occurs during the time of study, and the rate of decay of the optical density after reaction is complete is very much slower. A Unicam SP 600 spectrophotometer, modified to allow the use of a pen recorder,[5] and a rapid mixing device were used.

The order in complex was determined by showing that the data were consistent with the usual second-order rate equation[6] over the whole range of reaction studied (80—90%). The order in peroxydisulphate (1·04 ± 0·04) was determined by varying its concentration, while the ionic strength was maintained by adding potassium sulphate. All experiments were repeated several times and shown to be reproduceable. These data are summarised in Table 1.

The variation of rate with temperature was studied over the range 15·0—45·0° (Table 2). From these experiments, the activation energy is found to be (9·5 ± 1·0) kcal. mole^{-1}, while the value of $\log_{10}A$ is 7·6.

As this oxidation–reduction reaction is relatively rapid, and the Ag^{II} complex behaves as a rapid oxidant,[7,8] the stoicheiometry of the reaction can not be measured by a simple titration. However, by studying the variation

TABLE 1

Order of reaction in peroxydisulphate; 25°, $\mu =$ 6·48 × 10^{-2}, 2·58 × 10^{-4} M-Ag bipy$_2{}^+$

10^3[S$_2$O$_8{}^{2-}$] (M)	10^2k (sec.$^{-1}$)	
10·75	10·7 ±	0·2
9·68	9·4	0·2
8·60	8·00	0·13
7·53	7·0	0·4
6·45	6·0	0·4
5·38	5·4	0·4
4·30	3·69	0·08

TABLE 2

Variation of the rate constant with temperature; 4·3 × 10^{-3} M-S$_2$O$_8{}^{2-}$, 2·58 × 10^{-4} M-Ag bipy$_2{}^+$

Temp.	k (l. mole^{-1} sec.$^{-1}$)	
15·0°	2·32 ±	0·16
20·0	4·03	0·23
25·0	4·79	0·27
30·0	7·20	0·22
35·0	8·26	0·38
40·0	10·3	0·6
45·0	11·9	0·6

of the final optical density of a reaction solution with the ratio of reagents, one gram ion of S$_2$O$_8{}^{2-}$ is shown to oxidise two gram ions of the Ag^I complex; *i.e.* for a constant [Ag bipy$_2{}^+$] the final optical density is essentially constant for all initial concentrations of S$_2$O$_8{}^{2-}$ greater than a half that of the initial Ag^I concentration.

The rate of formation of Ag enbig^{3+} was markedly slower, and exhibited an induction period: the data for a typical run, one in which the induction period is easily seen, are shown in Figure 1. The results were consistent with the rate equation for two consecutive first-order

[1] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.,* 1963, 2594.
[2] R. S. Banergee and S. Basu, *J. Inorg. Nuclear Chem.,* 1964, **26,** 821.
[3] P. Ray, *Inorg. Synth.,* 1960, **6,** 74.
[4] D. A. House, *Chem. Rev.,* 1962, **62,** 185.
[5] D. N. Hague, Ph.D. Thesis, Cambridge, 1963.
[6] S. W. Benson, ' The Foundations of Chemical Kinetics,' McGraw-Hill, London, 1960, p. 33.
[7] B. M. Gordon, L. L. Williams, and N. Sutin, *J. Amer. Chem. Soc.,* 1961, **83,** 2061.
[8] A. Malaguti, *Ann. Chim. (Italy),* 1952, **42,** 138.

reactions,[6] for those runs where the peroxydisulphate is in sufficient excess to be assumed constant. As the larger of the two rate constants becomes unimportant after the initial stages of the reaction, reactions where the excess of oxidant is less than twentyfold are also quoted, as the effect of the larger rate constant is more readily observed under these conditions and the conditions for the concentration ratio will be less rigorous in these early stages of reaction. The fitting of the illustrated run is shown in Figure 2.
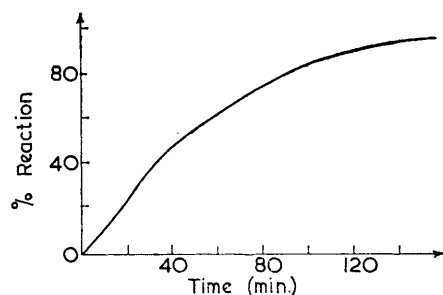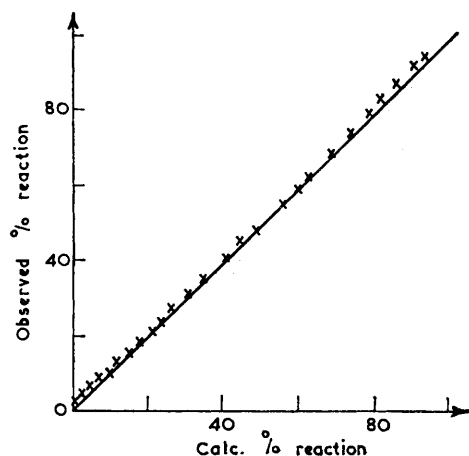

FIGURE 1 Rate of formation of Ag enbig^{3+} at 20.0°

FIGURE 2 Comparison of observed and calculated data for the reaction shown in Figure 1; $k_1 = 0.0102$ and $k_2 = 0.119$ l. mole^{-1} sec^{-1}

The use of 50% acetone as the solvent was found to be impossible as oxidation does not occur in this medium. This phenomenon is presumably caused either by interaction between solvent and ligand, or by a change in the oxidation–reduction potentials of the reagents. The reaction was therefore carried out in water, and followed at 3700 Å, at which wavelength the silver(III) complex has an extinction coefficient of 470.

The order of reaction in peroxydisulphate was again determined by varying its concentration, as shown in Table 3. The optical density of solutions of the silver(III) complex in water slowly drops, owing to the oxidation of the solvent. This drop is sufficiently slow to have no noticeable effect on the experimental results unless the temperature is raised above 40°, or the reaction requires several hours to proceed essentially to completion.

From these results, the orders of reaction in peroxydisulphate for the two rate constants are 1.06 ± 0.05 and 1.0 ± 0.2 respectively. The larger rate constant, given

TABLE 3

Order of reaction in peroxydisulphate; 25°, $\mu = 0.177$

$10^4[Ag(enbig)^+]$ (M)	$10^4[S_2O_8^{2-}]$ (M)	$10^5 k_1$ (sec.$^{-1}$)		$10^5 k_2$ (sec.$^{-1}$)	
20.3	589	58	± 1	*	
4.4	589	60	2	*	
2.2	392	42	2	*	
20.3	295	31	1	340	± 40
4.4	245	22.0	0.5	240	20
4.4	196	17	1	142	4
20.3	147	13.4	0.1	105	5
4.4	118	10.5	0.1	94	6
4.4	98.1	9.3	0.3	101	7
2.2	49.1	4.6	0.2	41	4

* Unreproduceable results obtained.

the subscript 2, may in fact be that for the first or second reaction; this can not be determined as the rate equation for two consecutive first-order reactions governed by k_1 and k_2 is symmetrical with respect to the interchange of k_1 and k_2. It should also be noted that the standard deviation in the determination of k_2 is greater than that for k_1, as the magnitude of the exponential term in $-k_2 t$ drops much more rapidly than that in $-k_1 t$. The variation of the rate constants with temperature was determined over the range 15.0—40.0° and is summarised in Table 4. From these data, the values of the activation energies are calculated to be 13.1 ± 0.7 and 14.3 ± 3.8 kcal. mole^{-1} for k_1 and k_2 respectively; the corresponding values for $\log_{10} A$ are 7.7 and 9.6.

The preparation of the Ag^{III} complex of ethylenebisbiguanide is not quantitative in silver.[3] When this experimental procedure is followed in the determination of the stoicheiometry of reaction, except that the initial ratio Ag$^+$: ligand : S$_2$O$_8^{2-}$ is 1 : 1 : 3, the oxidation of 1 ion of Ag$^+$ is accompanied by the consumption of 2.2 peroxydisulphate ions (the excess being determined by

TABLE 4

Variation of rate constants with temperature;
2×10^{-3}M-Ag enbig$^+$, 2.945×10^{-2}M-S$_2$O$_8^{2-}$

Temp.	$10^3 k_1$ (l. mole^{-1} sec.$^{-1}$)		$10^3 k_2$	
40.0°	44.5	± 4	490	± 50
35.0	32.4	0.6	294	25
30.0	20.4	0.2	284	12
25.0	15.8	0.4	139	15
20.0	10.3	0.2	117	8
15.0	7.25	0.3	70.5	1.5

back titration), 4.15 SO$_4^{2-}$ ions being formed (determined gravimetrically as the insoluble salts of Ba^{2+} and the Ag^{III} cation), and 0.56 ions of the Ag^{III} complex (as its sulphate and determined spectrophotometrically in solution). No H$_2$O$_2$ could be determined after reaction was complete, but any such formed may have been reduced catalytically in the presence of a silver complex. Thus it appears that the oxidation of each mole of the Ag^I complex to Ag^{III} requires 2 mol. of peroxydisulphate, and that the Ag^{III} product slowly decomposes. This

result may be confirmed by measuring the final optical densities of reaction solutions containing differing ratios of reagents, within the experimental concentration range; if, and only if, a slight excess of Ag^+ ions is present, the reaction is slightly more rapid, sufficiently so for reproduceable results to be obtained. Under these conditions for a given initial concentration of the Ag^I complex essentially constant values of the final optical density are obtained when the $S_2O_8^{2-}$ concentration is more than twice as large.

From these experiments, it appears that the oxidation of silver(I) complexes by peroxydisulphate occurs in one-electron steps, the silver(III) complex being formed by the process

$$Ag\ enbig^+ + S_2O_8^{2-} \longrightarrow Ag\ enbig^{2+} + X$$

$$Ag\ enbig^{2+} + S_2O_8^{2-} \longrightarrow Ag\ enbig^{3+} + X$$
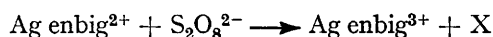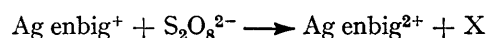
where X may be $S_2O_8^{3-}$ or both SO_4^- and SO_4^{2-}. X does not react with the silver complexes, but probably oxidises water. This is in marked contrast to the case with bipyridyl as ligand, where the overall stoicheiometry and rate data suggest that the intermediate, presumably SO_4^-, formed in the initial reaction is a rapid oxidant reacting with a further Ag^I complex ion.

The observation [8] that both the aquo- and bisbipyridyl-complexes of silver(I) catalyse the reaction between hydrogen peroxide and peroxydisulphate to the same degree suggests that the mechanism of catalysis is unchanged by complexing the silver ions; that is, a one-electron step occurs in both cases. If a termolecular rate determining step is discounted, the mechanism may be postulated to occur in two stages, firstly by the formation of an ion-pair, or a complex, $AgS_2O_8^-$, followed by

a one-electron charge transfer within this species (cf. ref. 4, p. 187).

Such a mechanism implies that the absence of available co-ordination sites in a silver(I) complex should have a marked effect on the oxidation of the metal ion. This may explain the slow formation of a black precipitate as the only reaction resulting from the addition of a solution of potassium peroxydisulphate to one of silver nitrate and the dipotassium salt of EDTA. The production of silver(III) oxide would occur if oxidation were preceded by dissociation of the silver(I) complex.

Comparison of the data described here with those tabulated by House [4] shows that the frequency factors for silver-catalysed oxidations are similar to those reported here, unless the reductant is capable of forming a complex with silver, e.g. water and formic acid. In conclusion, therefore, it is reasonable to assume that the oxidation of silver(I) species by the peroxydisulphate anion does not normally involve a two-electron process.

EXPERIMENTAL

[9] J. Pliva, V. Spirko, and S. Toman, *J. Mol. Spectroscopy*, 1966, **21**, 106.