Inorganica Chimica Acta, 45 (1980) L165–L167

Kinetics and Mechanism of Oxidation of Tris(bipyridyl)Iron(II) Sulphate by Peroxomonosulphate

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Received July 12, 1980

There have been many investigations on the oxidation of ferrous and osmium complexes using the well known peroxodisulphate ion (PDS) [1] whereas the corresponding monoperoxygen compound, namely peroxomonosulphate (PMS), has not been widely used as oxidant for such studies. Oxidation of halide [2] and nitrite [3] ions by PMS and radiolytic chain decomposition [4] are reported in literature. Recently Appelman and coworkers [5] have carried out the oxidation of azide and coordinated azide ligand in $Cr(NH_3)_5N_3^{2+}$ by PMS in aqueous solution. They have proved by ^{18}O tracer experiments that the reaction proceeds by transfer of terminal peroxide oxygen of the PMS to the reductant. They have also suggested that PMS is a more convenient reagent and in its reaction with azide complexes it might have application in synthesis where only nitrosyl complexes of the NO^- class could be formed.

Tests on some of the ferrous complexes with PMS showed a gradual disappearance of the intense colour of the complex hinting that the reaction be slow enough that it can be studied conveniently even at room temperature. The reactions of PMS with ferrous complexes should be of interest since the kinetics of oxidation of coordinated metal ion would throw more light on the behaviour of this peroxo anion towards metal complexes and possible comparison of its reactions with those of $S_2O_8^{2-}$. As a representative, preliminary report, the results on the reactions of $Fe(bipy)_3^{2+}$ with PMS is presented.

Experimental

$[Fe(bipy)_3]SO_4$ was prepared and purified as described previously [6]. Potassium peroxomonosulphate was obtained from E.I. Du Pont Company as 'OXONE', a mixture composition $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. Solutions of this salt were assayed iodometrically and by cerimetry [4]. Other chemicals such as Na_2HPO_4, NaH_2PO_4, borate were of AnalaR grade. Experiments were carried out in acidic (pH = 4.6), neutral (pH = 7.0) and alkaline (pH = 9.0) media and the range of the concentration of the reactants was [PMS] = 1–5 × 10^{-3} and $[Fe(bipy)_3^{2+}]$ = 1–1.8 × 10^{-4} *M*. The kinetics were obtained by following the disappearance of the complex at 525 nm. All the reactions were carried out in buffered media; the concentration of the buffer used was in each case 0.05 *M* to ensure no change in pH during the reaction. Acetic acid–acetate buffer was found to give irreproducible results and consequently phosphate buffer was used for pH = 4.6.

Results and Discussion

Plots of log OD *vs.* time were linear at all pH showing a first order dependence on $[Fe(bipy)_3^{2+}]$. From the slopes of the above plots, the pseudo-first order rate constants, k′ (s^{-1}) were evaluated. Variation of [PMS] did not affect the rate indicating a zero order dependence on [PMS]. Increase of pH from 4.6 to 9.0 decreased the rate to a small extent. Added bipyridyl ligand to the reaction mixture was found to decrease the rate. Acrylamide or acrylonitrile monomer, when added to the oxygen-free reaction mixture, got polymerized and the amount of polymer formed was much higher when both the PMS and complex were present than in the presence of the oxidant alone.

The observed rate law,

$$\frac{-d[Fe(bipy)_3^{2+}]}{dt} = k'[Fe(bipy)_3^{2+}] \qquad (1)$$

is a sharp contrast to that of the corresponding reaction of peroxodisulphate [1] wherein a total second order, first order each with respect to [complex] and $[S_2O_8^{2-}]$ was observed. However, a rate law similar to (1) was observed for the peroxodisulphate oxidation of tris-[α-(2-pyridyl)benzylideneaniline] iron(II) and bis(maleonitriledithiolato)cobaltate(II) complexes [1c]. The reaction proceeds *via* an entirely dissociative mechanism with no evidence for any direct oxidation. In the case of reaction of tris-[N-(2-pyridylmethylene)aniline] iron(II) complex [1c] and tris(1,10-phenanthroline)iron(II) complexes containing strongly electron-withdrawing nitro- or sulphonato derivatives [1d], a two-term rate law,

$$-\frac{d[complex]}{dt} = \{k_1 + k_2[S_2O_8^{2-}]\}[complex] \qquad (2)$$

was observed indicating parallel redox (like the bipyridyl complex with $S_2O_8^{2-}$) and dissociative (as in the present investigation) paths. Similar dissociative reac-

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TABLE I. Rate Constants.

pH	T, °C	k', sec^{-1}
4.6	15	3.60×10^{-5}
7.1	15	3.54×10^{-5}
9.0	15	2.85×10^{-5}
4.6	25	2.18×10^{-4}
7.1	25	1.73×10^{-4}
9.0	25	1.39×10^{-4}
4.6	35	8.75×10^{-4}
7.1	35	7.47×10^{-4}
9.0	35	6.94×10^{-4}

$E_a = 28.9$ kcal mol^{-1};
$\Delta S^{\ddagger} = 19.67$ cal deg^{-1} mol^{-1},
$\Delta G^{\ddagger} = 22.45$ kcal mol^{-1} [a].

[a] The parameters [8] observed for the dissociation of $\mathrm{Fe(bipy)}_3^{2+}$ are: $k' = 1.32 \times 10^{-4}$ s^{-1} (25 °C); $E_a = 28.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = 17$ cal deg^{-1} mol^{-1} and $\Delta G^{\ddagger} = 22.73$ kcal mol^{-1}.

tion mechanism was observed in the oxidation of tris(bipy)iron(II) by peroxodiphosphate [7] provided the oxidant concentration was at least two hundred times higher than that of the complex. In the present investigation, the rate constants (Table I) are found to be, within a factor of two, equal to the rate constant for ligand exchange reaction [8] of $\mathrm{Fe(bipy)}_3^{2+}$. Increase of pH from 4.6 to 9.0 decreased the rate only to a small extent similar to the complex dissociation which was affected only at pH extremes [8]. The activation energy and entropy of activation are also found to be similar in magnitude to those of the ligand exchange reactions [8] (Table I).

The equality of ligand dissociation in $\mathrm{Fe(bipy)}_3^{2+}$ and PMS reaction rates demonstrates that the reactions have a common rate determining step suggesting the mechanism,

$$\mathrm{Fe(bipy)}_3^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Fe(bipy)}_2^{2+} + \mathrm{bipy} \qquad (3)$$

$$\mathrm{Fe(bipy)}_2^{2+} + \mathrm{HSO}_5^- \xrightarrow{k_2} \text{products} \qquad (4)$$

The reaction occurs by rate-determining step of loss of one ligand molecule followed by a rapid reaction of bis complex with PMS. That the observed reaction is indeed a redox process was proved by the formation of ferric–thiocyanate system on the addition of SCN^- and when, on completion of the reaction addition of sodium dithionite, a strong reducing agent rapidly brought back the colour of the ferrous bipyridyl complex. However, the formation of the blue iron(III) complex, as in the case of $\mathrm{Fe(bipy)}_3^{2+}$–Ce(IV) system, after the reaction is over, could not be detected. But a similar complex, $\mathrm{Fe}(o\text{-phen})_3^{2+}$, distinctly produced the blue colour after the reaction with PMS [9].

The stoichiometry of the reaction, [PMS]:[$\mathrm{Fe(bipy)}_3^{2+}$] was found to be 1:2 inferring that PMS is consumed only for oxidizing the metal ion and not for the reaction with the dissociated ligand or for self-decomposition*. Since the complex is a one electron reductant and PMS is a two electron oxidant the step (2) may involve the following reaction

$$\mathrm{Fe(bipy)}_2^{2+} + \mathrm{HSO}_5^- \xrightarrow{k_2} \mathrm{Fe(bipy)}_2^{3+} + \begin{matrix} \mathrm{SO}_4^{2-} + \dot{\mathrm{O}}\mathrm{H} \\ \text{or} \\ \dot{\mathrm{S}}\mathrm{O}_4^{-} + \mathrm{OH}^- \end{matrix} \qquad (5)$$

These radicals may be responsible for the initiation of polymerization. It is difficult to predict unambiguously which radical species ($\dot{\mathrm{O}}\mathrm{H}$ or $\dot{\mathrm{S}}\mathrm{O}_4^-$) is formed. However, in the radiolytic decompositon [4] of PMS, it is proved that $\dot{\mathrm{O}}\mathrm{H}$ radicals are produced four times more frequently than $\dot{\mathrm{S}}\mathrm{O}_4^-$ radicals. These radicals may further undergo fast reactions with the metal complex to complete the reaction sequence.

$$\mathrm{Fe(bipy)}_3^{2+} + \begin{matrix} \dot{\mathrm{O}}\mathrm{H} \\ \text{or} \\ \dot{\mathrm{S}}\mathrm{O}_4^{-} \end{matrix} \longrightarrow \mathrm{Fe(bipy)}_3^{3+} + \begin{matrix} \mathrm{OH}^- \\ \text{or} \\ \mathrm{SO}_4^{2-} \end{matrix} \qquad (6)$$

Our interest in this study was the possible comparison of the reactions of HSO_5^- and $\mathrm{S_2O_8^{2-}}$ since these are mono- and di-$\mathrm{SO_3}$ group substituted hydrogen peroxide. The present experimental results confirm that HSO_5^- reaction with $\mathrm{Fe(bipy)}_3^{2+}$ is completely controlled by the first dissociation process of the complex wherein that of $\mathrm{S_2O_8^{2-}}$ is a total second order process. It warrants more investigation

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*Separate experiments carried out at acidic and alkaline pH in the temperature range 20–55 °C indicate no detectable amount of self-decomposition of PMS.

on similar ferrous complexes to make a generalised mechanistic difference between these two oxidants.

References

1 (a) D. H. Irvine, *J. Chem. Soc.*, 2977 (1959).
(b) J. Burgess and R. H. Prince, *J. Chem. Soc. A*, 1772 (1966).
(c) J. Burgess, *J. Chem. Soc. A*, 497 (1968).
(d) J. Burgess and R. H. Prince, *J. Chem. Soc. A*, 2111 (1970).
2 (a) D. H. Fortnum, C. J. Battaglia, S. R. Cohen and J. O. Edwards, *J. Am. Chem. Soc.*, *82*, 778 (1960).
(b) F. Secco and M. Venturini, *J. Chem. Soc., Dalton Trans.*, 1410 (1976).
3 J. O. Edwards and J. J. Muller, *Inorg. Chem.*, *1*, 696 (1962).
4 P. Maruthamuthu and P. Neta, *J. Phys. Chem.*, *81*, 937 (1977).
5 R. C. Thompson, P. Wieland and E. H. Appelman, *Inorg. Chem.*, *18*, 1974 (1979).
6 C. Ferrari, *Gazz. Chim. Ital.*, *67*, 604 (1937).
7 (a). E. Chaffee, I. I. Creaser and J. O. Edwards, *Inorg. Nucl. Chem. Letters*, *7*, 1 (1971).
(b) J. O. Edwards, *Coord. Chem. Rev.*, *8*, 87 (1972).
8 (a) J. Burgess and R. II. Prince, *J. Chem. Soc.*, 6061 (1965).
(b) R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 341 (1962).
9 R. Renganathan and P. Maruthamuthu, to be published.