441. *The Oxidation of the Trisdipyridylosmium*(II) *Ion by the Peroxydisulphate Ion in Aqueous Solution.*

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The oxidation of the trisdipyridylosmium(II) by the peroxydisulphate ion follows second-order kinetics up to about 45—50% of reaction. The breakdown of second-order kinetics probably arises through participation in the reaction of the sulphate radical produced in the primary step. The velocity constant of the reaction is given by the expression $k_0 = 2{\cdot}8 \times 10^8 \exp(-9400/\boldsymbol{R}T)$. An explanation is given for the lower values of the A and E factors than with the corresponding ferrous-ion oxidation. The reaction is speeded up by hydrogen ions, chloride ions, and sulphate ions. It is suggested that this is due to the participation of a conjugate acid species in the former case, and of ion-pair complexes in the latter cases.

Few oxidation–reduction reactions involving complex ions have been studied kinetically in detail. Such reactions are invariably too fast for ordinary kinetic investigations, particularly if the oxidation–reduction process involves only the transfer of a single electron.[1] Such reactions, if they could be studied, would undoubtedly yield valuable data on oxidation–reduction processes in solution, especially in respect to the factors governing their speed. Some attempt has been made to explain theoretically the observed difference in rates between electron-transfer reactions in solution involving complex ions and those involving simple aquated ions.[2] The theory, however, does not explain why single-electron-transfer reactions involving complex ions are fast irrespective of the nature and magnitude of the charges in the reacting species (see also ref. 1). Further, the rate of oxidation of the trisdipyridylruthenium(II) ion [1] by ceric ion is too fast to be measured in aqueous perchloric acid but is measurable in aqueous sulphuric acid. This observation led George and Irvine [1] to suggest that a small, favourable free-energy or heat change may greatly increase the rate of electron exchange. It seems probable that an explanation in terms of free-energy or heat-change difference might also account for the fact that thallic ion oxidises the trisdipyridylosmium(II) ion reversibly at a reasonable rate but does not oxidise the tris-*o*-phenanthrolineiron(II) ion reversibly, or, if it does so, the rate is extremely slow.[3]

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[1] George and Irvine, *J.*, 1954, 587.
[2] Zwolinski, Marcus, and Eyring, *Chem. Rev.*, 1955, **55**, 157.
[3] Irvine, *J.*, 1957, 1841.

In a more recent theory Marcus[4] concluded that it is the standard free-energy change of the redox step and not the overall free energy which is important in determining the speed of electron-transfer reactions. He also showed that other factors which affect the rate of such reactions are the Coulombic interaction of the ionic charges of the reactants and the solvation of the charged reactants. The theory will account for the different speeds of many electron-transfer reactions[4] but many more results are clearly needed for such reactions for further testing of such a theory.

While one-electron-transfer reactions involving complex ions are nearly always fast there are examples of slow reactions in which a complex ion is oxidised by a two-electron oxidant. Such reactions might help to answer some of the above problems.

In looking for reactions of this kind which could be investigated kinetically we found that both hydrogen peroxide and the peroxydisulphate ion oxidised the trisdipyridylosmium(II) ion. Preliminary experiments having indicated that the reaction with hydrogen peroxide was more complicated, we first examined the peroxydisulphate reaction. The choice of the trisdipyridylosmium(II) ion was based on its favourable redox potential[5] and its remarkable stability in solution.[6]

The oxidation of the trisdipyridylosmium(II) ion [$Os(dipy)_3^{2+}$] by the peroxydisulphate ion ($S_2O_8^{2-}$) initially follows second-order kinetics, but departs from them after about 45—50% of reaction. This is illustrated in Fig. 1, where a = initial concentration of $Os(dipy)_3^{2+}$, b = initial concentration of $S_2O_8^{2-}$, and x is the amount of $S_2O_8^{2-}$ which is reduced in time t. A check on the stoicheiometry of the reaction showed that 1 mole of $S_2O_8^{2-}$ oxidised only 1·5 moles of $Os(dipy)_3^{2+}$ instead of the 2·0 moles expected. Since there was no evidence of equilibrium or of any destruction of the $Os(dipy)_3^{2+}$ ion (the latter was completely recoverable at the end of a kinetic run by addition of a suitable reducing agent) the result implies that some $S_2O_8^{2-}$ was used in secondary reactions. Change of concentration of $S_2O_8^{2-}$ hardly affected the stage at which departure from second-order kinetics occurred. This suggests that it is not reactions involving the $S_2O_8^{2-}$ ion as such which are responsible for the breakdown of second-order kinetics; possibly the primary step in the oxidation involves the production of the sulphate radical, *viz.*:

$$Os(dipy)_3^{2+} + S_2O_8^{2-} \longrightarrow Os(dipy)_3^{3+} + SO_4^{-} + SO_4^{2-} \quad . \quad . \quad . \quad (1)$$

and there is then competition for this radical between $Os(dipy)_3^{2+}$ on the one hand and traces of reducing matter or water itself on the other. Reaction (1) is analogous to that suggested for the oxidation of ferrous ion by peroxydisulphate.[7, 8]

Dependence of the Rate of Reaction on Ionic Strength and Temperature.—The rate was measured at 25·5°, 18·0°, and 10·2° C under various conditions of ionic strength, which was changed by adding sodium perchlorate. The results are illustrated in Fig. 2, the slopes being 3·60, 3·50, and 3·10 respectively. These values are in fair agreement with the theoretical value of 4·0 expected for a reaction between oppositely-charged bivalent ions, and is good evidence that the rate-determining step involves the species $Os(dipy)_3^{2+}$ and $S_2O_8^{2-}$.

Extrapolation of the $\sqrt{I}$ plots to zero ionic strength gives values for k_0, the true velocity constant, of 52·0, 33·8, and 22·7 l. mole^{-1} sec.$^{-1}$ at 25·5°, 18·0°, and 10·2° respectively. A plot of $\log_{10} k_0$ against $1/T$ yields

$$k_0 = 2{\cdot}8 \times 10^8 \exp(-9400/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The corresponding value for the ferrous ion oxidation is

$$k_0 = 1 \times 10^{11} \exp(-12{,}100/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

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[4] Marcus, *J. Chem. Phys.*, 1957, **26**, 867.

[5] Barnes, Dwyer, and Gyarfas, *Trans. Faraday Soc.*, 1952, **48**, 269.

[6] Burstall, Dwyer, and Gyarfas, *J.*, 1950, 953.

[7] Fordham and Leverne Williams, *J. Amer. Chem. Soc.*, 1951, **73**, 4855.

[8] Kolthoff, Medalia, and Raaen, *J. Amer. Chem. Soc.*, 1951, **73**, 1733.

The smaller value of the A factor for the reaction involving the complex ion is presumably, in terms of Zwolinski, Marcus, and Eyring's [2] picture, a consequence of the smaller degree of rearrangement of the hydration sphere required by the complex ions. A value as low as 10^8 is, however, unusual for a reaction of this charge type where values between 10^{13} and 10^{19} are normally expected.[9] The low value may be characteristic of reactions involving complex ions but there are insufficient data to confirm this.

The activation energy for the reaction involving the complex ion is also smaller than that for the corresponding ferrous ion reaction. This again could be interpreted on Zwolinski, Marcus, and Eyring's picture as due to the smaller amount of reorganisation required by the complex ion in the transition state.

FIG. 1.

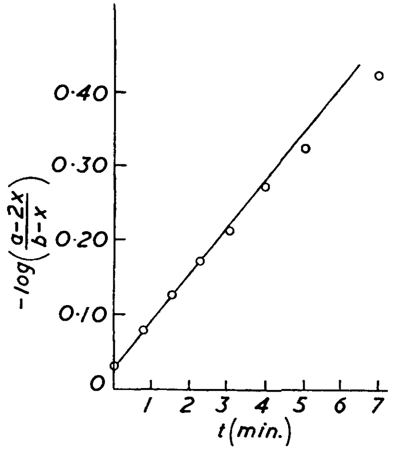
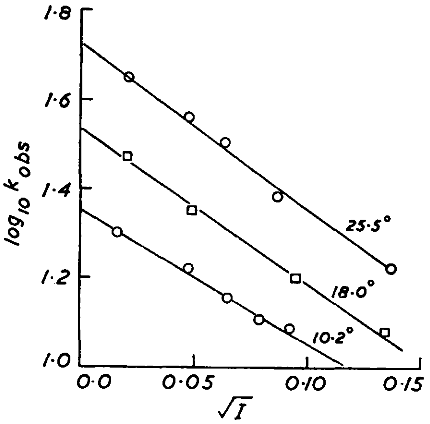


FIG. 2.



The Effect of Hydrogen-ion Concentration on the Rate of Reaction.—At very low ionic strength there was no detectable effect of hydrogen-ion concentration on the rate but at ionic strengths greater than about 0·05 the rate increased with it. The effect was more pronounced the higher the ionic strength. Table 1 shows the results of experiments

TABLE 1. *The effect of hydrogen ions on the rate of the reaction at* 25·5°.

I	—	—	1·76	—	—	0·106	—
$[H^+]$ (M)	1·76	1·06	0·35	0·00	0·106	0·070	0·00
k_{obs} (l. mole^{-1} sec.$^{-1}$) ...	3·13	2·50	1·96	1·70	7·78	7·54	7·10

carried out at $I = 0{\cdot}106$ and $I = 1{\cdot}76$. A plot of k_{obs} against $[H^+]$ in each case is linear; this can be explained by assuming either that $S_2O_8^{2-}$ reacts both with $Os(dipy)_3^{2+}$ and its conjugate acid $HOs(dipy)_3^{3+}$, or that $Os(dipy)_3^{2+}$ reacts both with $S_2O_8^{2-}$ and its conjugate acid $HS_2O_8^-$. In either case one obtains the following expression:

$$k_{obs} = (k_a[H^+] + k_bK_a)/(K_a + [H^+]) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where k_a and k_b are the velocity constants for the reactions involving the conjugate acid and base species respectively, and K_a is the dissociation constant of the acid.

If $K_a \gg [H^+]$, then expression (4) reduces to

$$k_{obs} = k_a[H^+]/K_a + k_b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and a plot of k_{obs} against $[H^+]$ is linear with slope equal to k_a/K_a and intercept k_b. Values of k_a/K_a (sec.$^{-1}$/mole^2) at 25·5° at different ionic strengths (in parentheses) were 0·80 (1·76), 2·38 (0·53), 6·40 (0·106), and 13·0 ± 3·0 (0·035). The increase as the ionic strength

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[9] Gladstone, Laidler, and Eyring, "Theory of rate processes," McGraw-Hill, New York, 1941.

decreases is consistent with either of the mechanisms above since in either case k_a/K_a, in the Debye–Hückel region at any rate, is given by the expression

$$\log (k_a/K_a) = \text{constant} - 4{\cdot}0\sqrt{I} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It is noteworthy that Kolthoff and Miller[10] postulated the existence of the acid $HS_2O_8^-$ in order to account for the dependence on the hydrogen-ion concentration of the rate of decomposition of $S_2O_8^{2-}$, and estimated the value of its dissociation constant to be 1·0 or greater at $I = 0{\cdot}01$. These experiments show that at $I = 0{\cdot}106$, K_a must be about 1·0 or greater in order to account for the linearity of k_{obs} with $[H^+]$. This order of magnitude of K_a is therefore not inconsistent with participation of the species $HS_2O_8^-$ in the reaction.

The absence of any detectable effect of $[H^+]$ at low ionic strength is presumably due to the fact that under such conditions $k_b \gg k_a[H^+]/K_a$ so that changes in k_{obs} are small, and lie within experimental error.

The Effect of Nitrate, Chloride, and Sulphate Ions.—The rate of the reaction was the same, within experimental error, whether nitrate or perchlorate ions were used to adjust ionic strength. Thus at $I = 0{\cdot}85$ and $I = 0{\cdot}53$ values of k_{obs} with nitrate ion were 2·39 l. mole^{-1} sec.$^{-1}$ and 3·11 l. mole^{-1} sec.$^{-1}$ respectively. The corresponding values with perchlorate ion were 2·24 and 3·12 l. mole^{-1} sec.$^{-1}$. On the other hand, at $I = 0{\cdot}85$ the value of k_{obs} obtained with chloride ion was 4·00 l. mole^{-1} sec.$^{-1}$ and with sulphate 5·78 l. mole^{-1} sec.$^{-1}$. At constant ionic strength k_{obs} increased as the concentration of chloride or sulphate ions increased as shown in Table 2. In each case a plot of k_{obs} against anion concentration is linear. One interpretation of this is that both chloride and sulphate anions form ion-pair complexes with $Os(dipy)_3^{2+}$ which also react with $S_2O_8^{2-}$. If, for example, in the case of chloride it is assumed that an ion-pair complex $[Os(dipy)_3Cl]^+$ as well as $Os(dipy)_3^{2+}$ reacts with $S_2O_8^{2-}$, then

TABLE 2. *The effect of chloride and sulphate ions on k_{obs} (l. mole^{-1} sec.$^{-1}$) at $I = 0{\cdot}10$ and 25·5°.*

$[Cl^-]$ (M)	0·10	0·07	0·04	0·00	$[SO_4^{2-}]$ (M)	0·033	0·022	0·011	0·00
k_{obs}	9·45	8·59	8·10	7·10	k_{obs}	10·9	9·64	8·10	7·10

$$k_{obs} = (k_1[Cl^-] + k_2K_{Cl})/(K_{Cl} + [Cl^-]) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where k_1 and k_2 are the velocity constants for the reactions involving $[Os(dipy)_3Cl]^+$ and $Os(dipy)_3^{2+}$ respectively, and K_{Cl} is the dissociation constant of $[Os(dipy)_3Cl]^+$. If $K_{Cl} \gg [Cl^-]$, eqn. (7) approximates to

$$k_{obs} = k_1[Cl^-]/K_{Cl} + k_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and a plot of k_{obs} against $[Cl^-]$ is linear. At very high ionic strength the plot of k_{obs} against $[Cl^-]$ was no longer linear; at $I = 0{\cdot}85$ k_{obs} (l. mole^{-1} sec.$^{-1}$) was 4·00, 3·25, 2·79, 2·41, and 2·24 at $[Cl]^- = 0{\cdot}85$, 0·60, 0·40, 0·20, and 0·00M respectively, showing that k_{obs} is proportional to $[Cl^-]^x$, where $1 < x < 2$. A possible explanation is that at high chloride concentration other ion-pair chloro-complexes, *e.g.*, $[Os(dipy)_3Cl_2]^0$, also take part in the reaction. At very low ionic strength there was no noticeable effect of chloride ions on the rate of the reaction, but presumably, as with hydrogen ions, changes in k_{obs} were so small as to be within experimental error.

Much the same behaviour was observed with sulphate ions. At $I = 0{\cdot}90$, k_{obs} was almost proportional to the square of the sulphate ion concentration whereas at very low ionic strength k_{obs} was very much the same as in the presence of perchlorate ions.

Although no spectrophotometric evidence was obtained for the formation of ion-pair complexes between $Os(dipy)_3^{2+}$ and chloride or sulphate ions, there is some justification for assuming their existence since other complex ions are known to form such complexes. Thus

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[10] Kolthoff and Miller, *J. Amer. Chem. Soc.*, 1951, **73**, 3055.

$Co(NH_3)_6^{3+}$ forms mono-complexes with chloride and sulphate ions having association constants of 4·1 and 3×10^3 moles^{-1} at 25° and $I = 0{\cdot}05$ and 0·0 respectively.[11, 12] Association of sulphate ions has also been shown to occur with $[Co(NH_3)_5\,H_2O]^{3+}$,[12] the association constant of the monosulphate complex being about 16·0 moles^{-1} at 31·1° and $I = 1{\cdot}0$. These results indicate that for the same charge sulphate is more firmly bound than chloride.

Although absolute values of the association constants for the chloride and sulphate complexes of $Os(dipy)_3^{2+}$ cannot be obtained from the results of these experiments, some idea of the relative strength of attachment of these ions can be deduced from the slopes of the plots of k_{obs} against anion concentration. These slopes give values of k_1/K_{anion}. At $I = 0{\cdot}10$ the values are 7·7 and 120·0 sec.$^{-1}$/mole^2 for chloride and sulphate respectively. It seems reasonable to assume that the less positively charged sulphate complex would not react faster with $S_2O_8^{2-}$ than the chloride complex, and hence that the higher value of k_1/K_{anion} for sulphate arises through a smaller value of K_{anion}. This in turn implies a higher value for the association constant of the sulphate complex, which is in accord with the observations on other systems.

EXPERIMENTAL

Materials.—Solutions. Trisdipyridylosmium(II) perchlorate was prepared and standardised as previously.[3]

" AnalaR " potassium peroxydisulphate was used after being dried at 105°. A stock solution was made by weight and stored at 0° in a dark bottle. Fresh solutions were prepared after every four or five days.

Sodium perchlorate solution was prepared by neutralising " AnalaR " perchloric acid with " AnalaR " sodium hydroxide and filtering.

B.D.H. 60% " AnalaR " perchloric acid was used for the experiments involving hydrogen ions. All other reagents were of " AnalaR " quality.

Conductivity water was used for all solutions, obtained as previously.[3]

Procedure.—The reaction was followed spectrophotometrically as previously.[3] Duplicate kinetic runs agreed to within 3%.

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[11] Garrick, *Trans. Faraday Soc.*, 1937, **33**, 486.
[12] Taube and Posey, *J. Amer. Chem. Soc.*, 1953, **75**, 1463.