Kinetics and Mechanism of the Oxidation of Thiosulfate Ion by Hexachloroiridate(IV)

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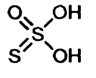
In the oxidation of thiosulfate ion by hexachloroiridate(IV) ion the value $\Delta[IrCl_6^{2-}]/\Delta[S_2O_3^{2-}]$ has been determined to be 1.08 ± 0.06 (where Δ indicates concentrations used in the reaction). The reaction is first-order with respect to $[S_2O_3^{2-}]$ whereas k_{obs}, the pseudo-first-order rate constant ($[IrCl_6^{2-}] \ll [S_2O_3^{2-}]$), increased with increasing pH. The dependence of k_{obs} on $[H^+]$ indicated that both $HS_2O_3^-$ and $S_2O_3^{2-}$ are involved in the reduction which can only be explained on the basis of an asymmetrical structure for thiosulfuric acid. The reactivity of the $S_2O_3^{2-}$ ion is almost 10^4 times greater than that of the $HS_2O_3^-$ ion. The $\Delta H^{\ddagger}$ values for the two paths is almost identical indicating that the energy barrier for the electron transfer is the same in the two cases. The electron is probably transferred from the thiolic sulfur.

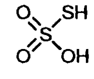
There have been very few studies on the oxidation of thiosulfate ion compared to the oxidation of sulfite ion.[1] These include oxidations by tetramminegold(III),[2] octacyanomolybdate(V),[3] hexacyanoferrate(III),[4] alkaline osmium tetroxide[5] and di-μ-cyanobis[tetracyanoferrate(III)] ion[6] which proceded *via* an inner-sphere mechanism. The oxidation by $[IrCl_6]^{2-}$, on the other hand, is outer-sphere in nature[7] and the study did not extend beyond establishing a bimolecular rate law based on the first-order dependence both on $[IrCl_6]^{2-}$ and $S_2O_3^{2-}$ ions at a fixed $[H^+]$. The dependence of the rate on $[H^+]$ or the ionic strength was not investigated. Hence, a meaningful mechanism cannot be predicted. A detailed study was, therefore, desirable to propose the most likely mechanism of oxidation of thiosulfate ion by $[IrCl_6]^{2-}$.

Thiosulfuric acid may have either a symmetrical or asymmetrical structure. That it exists in the asymmetrical form is strongly supported by the formation of organic thiosulfates from thiols and chlorosulfonic acid.[8] A recent study of the reaction of I_2 and I_3^- ion with $S_2O_3^{2-}$ suggested that the intermediates $I_2S_2O_3^{2-}$ and $IS_2O_3^-$ are formed *via* an asymmetrical structure.[9]

The first and second ionisation constants of O–H bonds of the symmetrical structure are 0.45 mol dm^{-3} ($pK_{a_1} = 0.35$) and 0.097 mol dm^{-3} ($pK_{a_2} = 1.01$) at 25 °C.[10] The ionisation constants of S–H and O–H bonds in the asymmetric structure, to our knowledge, have not been reported in the literature. However, it is expected that pK_{SH} might be similar to that of sulfanyl acids[11] for which values of pK_{SH} are around 10. The important result of this study is that the effect of the initial $[H^+]$ on the observed rate is best explained on the basis of an asymmetrical structure.



Symmetrical



Asymmetrical

Experimental

Materials.—The solutions of $Na_2[IrCl_6]$ and $Na_3[IrCl_6]$ (Johnson Matthey), freshly prepared in perchloric acid–perchlorate solution to minimise the rate of aquation,[12] were standardised spectrophotometrically at 488 ($\varepsilon_{488} = 4050$),[13] and 358 nm ($\varepsilon_{358} = 74$ dm^3 mol^{-1} cm^{-1})[14] respectively and used within a few hours. A solution of $LiClO_4 \cdot 3H_2O$ (1 mol dm^{-3}) (G. F. Smith), filtered and standardised gravimetrically, was used to adjust the ionic strength.

The solution of $Na_2S_2O_3$ (E. Merck, GR) was standardised against a standard $CuSO_4$ (BDH, AnalaR) solution iodometrically with starch as the indicator. The solution was always freshly prepared each day.

The buffer solutions of acetic acid–sodium acetate (E. Merck, GR) and phosphate buffer solutions of the desired pH were prepared as outlined in the literature.[15] The pH of the buffer solutions and the reaction mixtures was checked with a pH-meter.

Rate Measurements.—The kinetics was mainly studied in an acetate buffer (pH 4.27) under pseudo-first-order conditions ($[S_2O_3^{2-}] \gg [IrCl_6^{2-}]$) at constant ionic strength (0.56 mol dm^{-3}, $LiClO_4$). The phosphate buffer was used to study the effect of pH beyond 5.89 and several runs at the same pH were studied using the two buffer systems. Since the rate constants from the two buffer systems were similar it was concluded that the conjugate base did not affect the rate. The study was restricted to pH 7 because Ir^{IV} is spontaneously reduced in alkaline solutions.[16]

The $S_2O_3^{2-}$ and Ir^{IV} solutions in the desired buffer were brought to thermal equilibrium at the desired temperature (±0.1°), maintained by circulating water from a Haake D8G refrigerated circulatory water bath, in the stock cylinders of a Union-Giken RA-401 stopped-flow spectrophotometer. The rate was followed at 488 nm, λ_{max} of $[IrCl_6]^{2-}$,[13] at which other components of the reaction mixture were transparent. At least 10 to 12 runs were averaged before analysing for the values of the pseudo-first-order rate, k_{obs}, by an in-built program in the computer used for collecting the data. The reproducibility of the k_{obs} value was within the range 5–7%.

Test for Free Radicals.—The reactant solutions were purged with nitrogen and acrylonitrile (1 cm^3) was added to each solution. No cloudiness appeared even after some time, although a precipitate appeared on mixing the two solutions indicating the formation of a free radical or free radical ion in the course of the reaction.

Spectral Studies.—The spectral changes in the Ir^{IV} solution on mixing with $S_2O_3^{2-}$ ion could not be measured by a conventional spectrophotometer because the reaction was completed on the stopped-flow time-scale. Therefore the

Table 1 Stoichiometric results of the reaction between $[IrCl_6]^{2-}$ and $S_2O_3^{2-}$ at room temperature; total $[S_2O_3^{2-}] = 0.04$, $I = 0.56$ mol dm^{-3}

pH	$\Delta[IrCl_6^{2-}]$/ mol dm^{-3}	$\Delta[S_2O_3^{2-}]$/ mol dm^{-3}	$\Delta[IrCl_6]^{2-}$/ $\Delta[S_2O_3^{2-}]$
3.2	0.005	0.0044	1.14
3.4	0.004	0.0036	1.11
4.0	0.003	0.0028	1.07
5.0	0.002	0.0020	1.00

Table 2 Dependence of k_{obs} on the initial $[S_2O_3^{2-}]$ at pH 4.27 and 24.8 °C; $[Ir^{IV}] = 2.5 \times 10^{-5}$ and $I = 0.56$ mol dm^{-3}

$[Na_2S_2O_3]$/ mol dm^{-3}	k_{obs}/s^{-1}	$k_{obs}/[Na_2S_2O_3]$/ dm^3 mol^{-1} s^{-1}
0.002	0.42	210
0.005	1.18	236
0.01	2.30	230
0.02	4.59	230
0.05	11.6	232
0.10	22.6	226
0.20	45.7	229

Table 3 Dependence of k_{obs} on the pH of the reaction mixture at different temperatures; $[Ir^{IV}] = 2.5 \times 10^{-5}$, $[S_2O_3^{2-}] = 0.02$ and $I = 0.56$ mol dm^{-3}

pH	15 K	20.5 K	24.8 K	29 K
3.72	1.78	2.63	4.12	5.73
4.05	1.84	2.77	4.24	5.94
4.27	1.91	2.85	4.42	6.24
4.45	2.02	3.06	4.64	6.48
4.63	2.13	3.23	5.02	6.88
4.99	2.64	4.16	6.16	8.84
5.57	5.16	8.56	12.2	18.1
5.89	8.78	14.6	21.3	31.1
6.31	20.3	36.2	50.2	72.8
6.62	40.2	69.1	94.2	145
6.91	75.6	132	185	272

Table 4 Dependence of k_{obs} on the initial ionic strength at 27.8 °C; $[Ir^{IV}] = 2.5 \times 10^{-5}$, $[S_2O_3^{2-}] = 0.02$ mol dm^{-3} and pH 4.27

I/dm^3 mol^{-1}	k_{obs}/s^{-1}
0.18	2.45
0.26	2.92
0.36	3.47
0.46	4.04
0.56	4.42
0.66	5.10

Table 5 Dependence of k_{obs} on alkali-metal cations (M^+) at 24.8 °C; $[Ir^{IV}] = 2.5 \times 10^{-5}$, $[S_2O_3^{2-}] = 0.016$, $[M^+] = 0.38$, $I = 0.56$ mol dm^{-3} and pH 4.27

M^+	Li^+	Na^+	K^+	Cs^+
k_{obs}/s^{-1}	3.52	6.04	17.6	33.8

absorbance of the reaction mixture at the time of mixing was computed from the stopped-flow traces at different wavelengths covering a span of 488 ± 40 nm. No significant changes in the initial absorbance were noted. The formation of an intermediate is thus not evident. The rate was independent of wavelength in the region studied. However, this does not preclude the possibility of the formation of a transition state in which the alkali-metal ions act as a bridge between the reactants.

Results

Stoichiometry.—The stoichiometry of the reaction, with excess of $[IrCl_6^{2-}]$, was cursorily examined and the previous results[7] confirmed. The consumption ratio increased rapidly as the initial concentration ratio varied. The results imply that the primary free radical has more than one reaction path by which to react further to give the final end-product. Extrapolation of the trend at high initial concentration ratios suggested a limiting consumption ratio of 8:1 corresponding to the stoichiometry given in equation (1).

$$8[IrCl_6]^{2-} + S_2O_3^{2-} + 5H_2O \longrightarrow 8[IrCl_6]^{3-} + 2SO_4^{2-} + 10H^+ \quad (1)$$

The stoichiometry, with excess of $[S_2O_3^{2-}]$, was studied in detail in solutions of pH 3–5 but at constant ionic strength (0.56 mol dm^{-3}). The excess of unreacted $S_2O_3^{2-}$ ion was titrated with a standard solution of iodine. The correction for the blanks were made to estimate the $[S_2O_3^{2-}]$ used ($\Delta[S_2O_3^{2-}]$) by the respective $[IrCl_6^{2-}]$ ($\Delta[IrCl_6^{2-}]$) present in the reaction mixtures. The average value of $\Delta[IrCl_6^{2-}]/\Delta[S_2O_3^{2-}] = 1.08 \pm 0.06$, Table 1, which is independent of pH. The stoichiometry is thus given by equation (2).

$$2[IrCl_6]^{2-} + 2S_2O_3^{2-} \longrightarrow 2[IrCl_6]^{3-} + S_4O_6^{2-} \quad (2)$$

Dependence on $[S_2O_3^{2-}]$.—The effect of the initial $[S_2O_3^{2-}]$ on the observed rate at constant ionic strength ($I = 0.56$ mol dm^{-3}), maintained with lithium perchlorate, was studied, and the results are given in Table 2. The value of k_{obs} increased proportionately indicating a first-order dependence on $[S_2O_3^{2-}]$.

Dependence on $[H^+]$.—The dependence of k_{obs} on the initial pH of the reaction mixture, at different temperatures and constant ionic strength, Table 3, increased with increasing pH. The correlation between the observed rate and $[H^+]$ is discussed below.

Dependence on Ionic Strength.—The value of k_{obs} increased with increasing ionic strength ($LiClO_4$), Table 4, indicating that the reactants were similarly charged. The plot of log k_{obs} against $I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ was linear with a slope and intercept of 2.08 and −0.237 respectively.

Dependence on Cation Size.—The effect of alkali-metal ions ($M^+ = Li^+$, Na^+, K^+ or Cs^+) on k_{obs} was studied at a fixed [MCl] (0.38 mol dm^{-3}) and ionic strength (0.56 mol dm^{-3}). The difference between the total ionic strength and that from MCl is due to the Na^+ ion present in the buffer and $S_2O_3^{2-}$ ion. Thus k_{obs} represents the relative rate, Table 5, which increases in the order $Cs^+ > K^+ > Na^+ > Li^+$. This kind of cation effect is a feature of redox reactions between anionic species and is generally attributed to ion-pair formation.

Mechanism and Discussion

Thiosulfate ion is a powerful reducing agent, $E^0_{S_4O_6^{2-} \rightarrow 2S_2O_3^{2-}} = 0.169$ V, and a strong nucleophile ($n = 6.36$ on the Swain–Scott scale).[17,18] The strong reducing power is confirmed by the completion of the reaction on a stopped-flow time-scale. The strong nucleophilic nature could not be observed because $[IrCl_6]^{2-}$ is inert to substitution. The spectral evidence and the kinetics, strict first-order dependence on $[S_2O_3^{2-}]$, provide no evidence for the intermediate.

The pH dependence of the rate, Fig. 1, indicates that the reaction proceeds by two parallel paths, one of which is independent of $[H^+]$. Since the pH of the reaction mixture is far

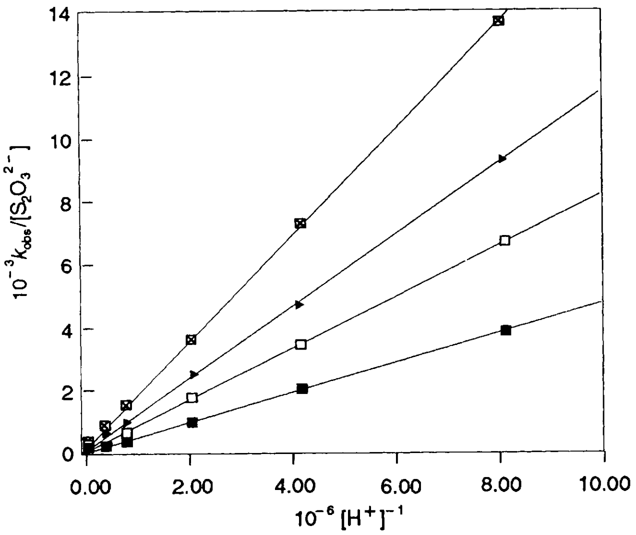


Fig. 1 Linear plots of k_{obs} *vs.* $[H^+]^{-1}$, with positive intercepts on the rate ordinate, at 15 (■), 20.5 (□), 24.8 (▲) and 29 °C (⊠); $[Ir^{IV}] = 2.5 \times 10^{-5}$, $[S_2O_3^{2-}] = 0.02$ and $I = 0.56$ mol dm^{-3}

greater than pK_{a_1} and pK_{a_2} values of the symmetrical $H_2S_2O_3$, the ionisation of $H_2S_2O_3$ into $S_2O_3^{2-}$ is complete and therefore the rate is expected to be independent of pH. A pronounced effect of pH on the rate could arise if $S_2O_3^{2-}$ and $HS_2O_3^-$ were in equilibrium at higher pH and if $S_2O_3^{2-}$ were more reactive than $HS_2O_3^-$. It is well known that a less protonated anionic species is more reactive in redox reactions. The desired equilibrium is probable in the asymmetric structure because pK_{SH} is likely to have a high value (so that pH < pK_{SH}). The exact pK_{SH} value has not been determined previously but has been estimated to be around 10.* This estimation arose from the fact that for oxidation by tetramminegold(III) in which the pH was varied from 3.9 to 10.8, a limiting rate with respect to $[S_2O_3^{2-}]$ was observed at the highest pH range (10.6–10.75). Also, the pK_{SH} value was reported to be 9.96, which is consistent with the S–H ionisation constant of thio acids[11] (thioglycolic *s*-acid, $pK_a = 9.90$; thiolactic *s*-acid, $pK_a = 9.93$; 3-sulfanylpropanoic acid, $pK_a = 10.84$; thiomalic *s*-acid $pK_a = 10.38$) being of the order of 10^{-10} at 25 °C. In the analysis of rate constants we have assumed a value of 10 for the pK_{SH}. The maximum pH value that could be used in the present study was pH 7 because of the self reduction of Ir^{IV} in alkaline solutions. The asymmetrical structure has recently been considered in the mechanism of the reaction of iodine with thiosulfate. We therefore propose the reaction mechanism given in equations (3)–(6) in which the charges on the reactant species are

$$HS_2O_3^- \overset{K_{SH}}{\rightleftharpoons} H^+ + S_2O_3^{2-} \qquad (3)$$

$$[IrCl_6]^{2-} + S_2O_3^{2-} \xrightarrow{k} [IrCl_6]^{3-} + S_2O_3^{\bullet -} \qquad (4)$$

$$[IrCl_6]^{2-} + HS_2O_3^- \xrightarrow{k_1} [IrCl_6]^{3-} + S_2O_3^{\bullet -} + H^+ \qquad (5)$$

$$S_2O_3^{\bullet -} + S_2O_3^{\bullet -} \xrightarrow{\text{fast}} S_4O_6^{2-} \qquad (6)$$

consistent with the slope (2.08) of the Davies[19] plot based on the effect of ionic strength on the rate. The transient existence of the $S_2O_3^{\bullet -}$ radical ion was detected previously by the induced polymerisation of acrylonitrile in aqueous solution.[20] Reaction (6) is analogous to the dimerisation of the $SO_3^{\bullet -}$ radical ion to the $S_2O_6^{2-}$ ion with a rate constant of 1.8×10^8 dm^3 mol^{-1} s^{-1} at zero ionic strength.[21]

Table 6 Values of k and k_1 (dm^3 mol^{-1} s^{-1}) at different temperatures and the related activation parameters

T/°C	$10^{-6}k$/dm^3 mol^{-1} s^{-1}	k_1/dm^3 mol^{-1} s^{-1}
15	4.55	88.4 ± 9
20.5	7.97	132 ± 19
24.8	11.1	199 ± 41
29	16.4	287 ± 42
	$\Delta H_k^\ddagger = 63 \pm 2$ kJ mol^{-1}	$\Delta H_{k_1}^\ddagger = 59 \pm 3$ kJ mol^{-1}
	$\Delta S_k^\ddagger = 118 \pm 7$ J K^{-1} mol^{-1}	$\Delta S_{k_1}^\ddagger = 13 \pm 10$ J K^{-1} mol^{-1}

However, with excess of $[Ir^{IV}]$ reaction (6) is superceded by reactions (7)–(9) leading to the formation of SO_4^{2-} as the final

$$[IrCl_6]^{2-} + S_2O_3^- + H_2O \longrightarrow [IrCl_6]^{3-} + S_2O_4^{2-} + 2H^+ \qquad (7)$$

$$S_2O_4^{2-} \rightleftharpoons 2SO_2^{\bullet -} \qquad (8)$$

$$3[IrCl_6]^{2-} + SO_2^{\bullet -} + 2H_2O \longrightarrow 3[IrCl_6]^{3-} + SO_4^{2-} + 4H^+ \qquad (9)$$

end-product and accounting for the value $\Delta[IrCl_6^{2-}]/\Delta[S_2O_3^{2-}]$ of 8. The dithionite ion, formed in reaction (7), is unique in its ability either to reduce as the intact $S_2O_4^{2-}$ ion and/or *via* the dissociated $SO_2^{\bullet -}$ radical anion[22] as proposed in the mechanisms of its oxidation by metal complexes.[23–26]

The rate law, based on reactions (3)–(6), is given by equation (10), where $[HS_2O_3^-]_0$ is the initial concentration and K_{SH}, the

$$\frac{-d[Ir^{IV}]}{dt} = \left(k_1 + \frac{kK_{SH}}{[H^+]}\right)\frac{[HS_2O_3^-]_0[H^+][IrCl_6^{2-}]}{[H^+] + K_{SH}} \qquad (10)$$

ionisation constant corresponding to S–H ionisation, is of the order of 10^{-10} mol dm^{-3} so that $[H^+] \gg K_{SH}$. Equation (10) is therefore reduced to equation (11) which is in agreement with

$$k_{obs} = \left(k_1 + \frac{kK_{SH}}{[H^+]}\right)[HS_2O_3^-]_0 \qquad (11)$$

the linear plots of k_{obs} *vs.* $[H^+]^{-1}$ with a positive intercept on the rate ordinate (Fig. 1).

The values of k_1 and k evaluated from the intercepts and slopes of the plots in Fig. 1, respectively, with the assumption that $K_{SH} = 1 \times 10^{-10}$ mol dm^{-3}, are given in Table 6 together with the activation parameters. The $S_2O_3^{2-}$ ion is approximately 10^4 times more reactive than $HS_2O_3^{2-}$. The ion-pair of $S_2O_3^{2-}$ with an alkali metal ion, present in the electrolyte added to maintain the ionic strength, has an effective charge of -1 (z_1) and that on Ir^{IV} is -2 (z_2); therefore, z_1z_2 corresponds to the value of the slope, 2.08, of the Davies[19] plot.

The similar values of $\Delta H_k^\ddagger$ (63 ± 2) and $\Delta H_{k_1}^\ddagger$ (59 ± 3 kJ mol^{-1}) indicate the analogous nature of the energy barrier for the electron transfer from the thiolic sulfur and not through the oxygen or hydroxyl bonds to the other sulfur atom. The positive entropy for the k path [equation (4)] (118 J K^{-1} mol^{-1}) is due to repulsion between negatively charged reactant species[27] whereas it is nearly zero (13 ± 10 J K^{-1} mol^{-1}) for equation (5) because of the lack of a charge on the $HS_2O_3^-$–M^+ ion-pair.

In conclusion, the kinetics of the reaction has provided support for the asymmetrical structure of the thiosulfate ion.

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