Kinetics of the Reaction Between $S_2O_3^{--}$ and I_3^- in Aqueous Solution

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The kinetics of the reaction between I_{3aq}^- and $S_2O_{3aq}^{--}$ has been studied under conditions of production of iodine at a known rate by the persulfate-iodide reaction and its consumption by $S_2O_3^{--}$. The effective concentration of iodine during the steady state is measured from its reduction potential at a bright platinum foil electrode. The reaction is of first order with respect to I_3^- and $S_2O_3^{--}$ individually and hence of over all second order. The specific rate is $1.51 \times 10^5\ M^{-1}\ sec^{-1}$ and the frequency factor is $1.69 \times 10^{12}\ M^{-1}\ sec^{-1}$ at 25 °C. The energy of activation for the reaction is 9.58×10^3 cal/mole and the entropy of activation is -2.55 cal/mole deg.

Introduction

It is well known that sodium thiosulfate reacts quantitatively[1, 2] with iodine according to the equation:

$$2\ S_2O_3^{--} + I_3^- \rightarrow S_4O_6^{--} + 3\ I^- .$$

The reaction occurs very fast and several reports[3, 4] in literature are not conclusive about its kinetics and mechanism.

In the present work the reaction has been studied under conditions where iodine is produced at a controlled rate and consumed by $S_2O_3^{--}$. The iodine is generated by the slow second order reaction[5, 6]:

$$S_2O_8^{--} + 2\ I^- \rightarrow 2\ SO_4^{--} + I_2$$

in aqueous neutral medium. From its specific rate and the concentrations of the reactants, rate of the production of iodine can be determined. The reaction between iodine and thiosulfate is very fast and therefore, at low concentrations of thiosulfate a steady state is attained wherein the rate of production of iodine

$$\frac{d[I_2]}{dt} = k_2 [S_2O_8^{--}]\,[I^-] \qquad (1)$$

and its rate of consumption

$$-\frac{d[I_2]}{dt} = k [I_3^-]_*^m\,[S_2O_3^{--}]^n \qquad (2)$$

are balanced:

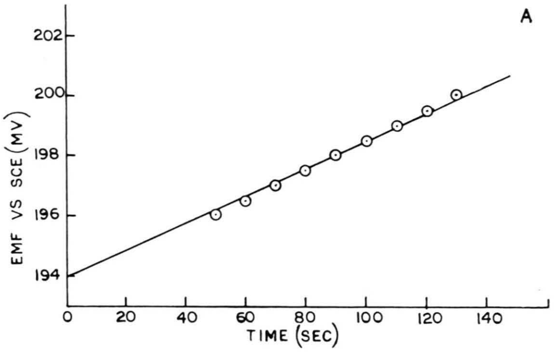
$$k_2 [S_2O_8^{--}]\,[I^-] = k [I_3^-]_*^m\,[S_2O_3^{--}]^n \qquad (3)$$

The effective concentration of iodine $[I_3^-]_*$ can be estimated by measurement of its reduction potential. Further, it is possible to establish the kinetic order of the reaction and to determine its specific reaction rate.

Experimental

A stock solution of 0.040 M $K_2S_2O_8$ is prepared (solution-A). Another stock solution is prepared which is 0.080 M with respect to KI and 2.00×10^{-3} M with respect to $Na_2S_2O_3$ (solution-B). 25 ml of these solutions are pipetted out separately in two conical flasks kept in a thermostat at 25.0 °C. The solutions are mixed and simultaneously a stop watch is started. A bright platinum foil electrode (1 cm × 0.5 cm) and a saturated calomel electrode are introduced into the solution and the emf is measured at intervals of 10 seconds for about 3 minutes. The emf increases linearly during the steady state and then sharply shoots up, indicating that the $S_2O_3^{--}$ is used up. The experiment is repeated twice to check the reproducibility of the emf measurements. These measurements are carried out with a potentiometer by the Poggendorff's[7] compensation method. The use of a platinum foil electrode eliminates concentration polarisation[8] and enables the electrode to attain quickly[9] the reversible potential due to I_3^-/I^-. These emf measurements are reproducible to ±0.5 mV. The emf values are plotted versus time and one obtains a linear curve (cf. Fig. 1 A). This is extrapolated to zero time to obtain the reduction potential due to the effective concentration of iodine at that instant. Such extrapolation to zero time has the advantage that at that instant both the rate of production of iodine and concentration of thiosulfate ions are known most accurately.

The effective concentration of iodine at zero time is evaluated from a calibration curve obtained thus: several iodine solutions in the concentration range from 10^{-3} M to 10^{-6} M are prepared in solutions containing 0.040 M KI and 0.020 M K_2SO_4. The latter is to provide the same ionic strength as due to $K_2S_2O_8$ in the actual reaction mixture. These solutions are kept in a thermostat at 25.0 °C along with the saturated calomel elec-



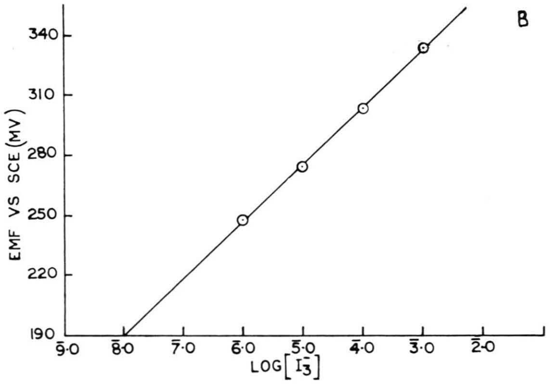


Fig. 1 A. Reduction potentials of the iodine/iodide system under steady state condition.

Fig. 1 B. Reduction potentials of iodine/iodide system at 25.0 °C.

trode and reduction potentials are measured using the same bright platinum foil electrode. The plot of $\log[I_3^-]$ versus emf is a straight line (cf. Figure 1 B). With this plot one can evaluate the effective concentration of iodine $[I_3^-]_*$ from the measured reduction potential. The reaction between potassium iodide and potassium persulfate is followed by the well known conventional method[10]. From these measurements its specific reaction rate is evaluated and hence from the known initial concentrations of I^- and $S_2O_8^{--}$ the rate of production of iodine at zero time can be calculated.

Experiments are carried out with the same initial concentrations of $S_2O_8^{--}$ and I^- but with different initial concentrations of $S_2O_3^{--}$. From these results it is possible to establish the order of the reaction with respect to each reactant and hence with respect to the reaction as a whole. It is found that the results fit quite satisfactorily into a second order rate law.

The reaction is studied at various temperatures in the range 5 °C to 25 °C and from the results, the energy of activation, frequency factor and entropy of activation for the reaction are evaluated.

A typical set of results is presented in Tables 1 to 3.

Results and Discussion

The specific reaction rate k_2 at 25 °C is found to be $3.00 \times 10^{-3}\,\text{M}^{-1}\,\text{sec}^{-1}$. Hence the rate of production of iodine at zero time is,

$$\frac{d[I_2]}{dt} = 3.00 \times 10^{-3}[0.020]\,[0.040]$$
$$= 2.40 \times 10^{-6}\,\text{M sec}^{-1}\,.$$

The effective concentration of iodine $[I_3^-]_*$ is found as stated above. Hence from Eq. (3), the specific reaction rate k can be evaluated provided m and n are known. From the stoichiometry[11] of the reaction and from general considerations it would be logical to assume $m = 1$ and $n = 2$ or $m = 1$ and $n = 1$. Studies carried out with the same initial concentrations of $S_2O_8^{--}$ and I^- but different concentrations of $S_2O_3^{--}$ show that, when m and n taken to be one, the values of k are in close agreement with one another whereas by assuming $m = 1$ and $n = 2$ one obtains very divergent values. Therefore the reaction between $S_2O_3^{--}$ and I_3^- is most probably of first order with respect to each reactant and is of overall second order.

Table 1. The specific rate constant of the reaction between $S_2O_3^{--}$ and I_3^-.

Rate of production of iodine at zero time		2.40×10^{-6} M sec^{-1}		
Temperature		25.0 °C		
Reduction potential at zero time vs SCE (mV)	Effective concentration of iodine at zero time (M)	Concentration of $Na_2S_2O_3$ (M)	Second order rate constant ($M^{-1}\,sec^{-1}$)	Third order rate constant ($M^{-2}\,sec^{-1}$)
194.0	1.590×10^{-8}	0.001	1.51×10^5	15.10×10^7
186.0	0.794	0.002	1.51	7.24
179.0	0.521	0.003	1.53	5.11

Table 2. The specific rate constant of the reaction between $S_2O_3^{--}$ and I_3^- at various instants of the steady state.

Rate of production of iodine 2.4×10^{-6} M sec^{-1}
Initial concentration of $Na_2S_2O_3$ (a) 0.002 M
Temperature 25.0 °C

Time t (sec)	EMF vs SCE (mV)	Effective concentration of iodine $[I^-_3]_*$ (M)	Total iodine produced $2.4 \times 10^{-6} \times t$ (M)	Concentration of $Na_2S_2O_3$ remaining (M)	Second order rate constant (M^{-1} sec^{-1})	Third order rate constant (M^{-2} sec^{-1})
0	186.0	7.94×10^{-9}	0.00×10^{-4}	20.0×10^{-4}	1.51×10^5	7.24×10^7
60	189.0	9.44	1.44	17.1	1.49	8.60
70	189.0	9.44	1.68	16.6	1.52	9.23
80	189.5	10.00	1.92	16.2	1.48	9.40
90	190.0	10.40	2.16	15.7	1.47	9.51
100	190.5	10.80	2.40	15.2	1.46	9.90
120	191.0	11.20	2.88	14.2	1.50	10.8
140	192.0	11.90	3.36	13.3	1.52	11.4
160	193.0	13.30	3.84	12.3	1.46	12.3

Table 3. Determination of the activation energy.

Temperature °C	°K	$1/T$	Rate constant k (M^{-1} sec^{-1})	$\log k$
25	298	3.356×10^{-3}	1.51×10^5	5.179
20	293	3.413	1.11	5.045
15	288	3.472	0.720	4.907
10	283	3.534	0.623	4.795
5	278	3.597	0.385	4.578

Activation Energy $= - 2.303 \cdot R \cdot$ slope of $\log k$ vs $1/T$ curve
$= - 2.303 \cdot 1.987 (-2.10 \times 10^3)$ cal/mole
$= 9.58 \cdot 10^3$ cal/mole.

The above conclusion is independently verified from the following study. The effective concentrations of iodine at various instants of the steady state are evaluated from the measured reduction potentials. Since the initial concentrations of $K_2S_2O_8$ (0.020 M) and KI (0.040 M) are large compared to the concentration of $Na_2S_2O_3$ (1.00×10^{-3} M), the decrease in their concentrations is neglegibly small even up to the total consumption of the sodium thiosulfate. The concentration of iodine produced up to any instant equals the rate of production of iodine multiplied by the duration up to that instant. The concentration of thiosulfate consumed is obviously twice the above concentration. The initial concentration of thiosulfate being known, the concentration of thiosulfate as a function of time can be calculated. Therefore, from Eq. (3), k can be evaluated at various instants during the steady state. It is found that the k values agree well with one another for $m = 1$ and $n = 1$ while they are much divergent for $m = 1$ and $n = 2$. It is further observed from the above study that when one plots $\log[S_2O_3^{--}]$ versus time, one obtains a straight line whereas the plot of $1/[S_2O_3^{--}]$ versus time is not at all a straight line. This confirms that the reaction is of first order with respect to $S_2O_3^{--}$.

At 25 °C the effective iodine concentration at zero time was found to be 1.59×10^{-8} M. Therefore,

$$2.4 \times 10^{-6} = k \times 1.59 \times 10^{-8} \times 1.00 \times 10^{-3}\ \mathrm{M\ sec^{-1}},$$

that is

$$k = 1.51 \times 10^5\ \mathrm{M^{-1}\ sec^{-1}}.$$

Although it is possible to evaluate the effective concentrations of iodine and thiosulfate at various instants of the steady state, they are less accurate than at zero time due to the assumption of unchanging concentrations of I^- and $S_2O_8^{--}$. Therefore the specific rates calculated at such instants are less accurate than those calculated at zero time.

From results of similar measurements at various temperatures, the energy of activation for the reaction is found to be 9.58×10^3 cal/mole. The frequency factor is 1.69×10^{12} M^{-1} sec^{-1} at 25 °C and the entropy of activation is -2.55 cal/mole deg.

It is evident in this technique that the accuracy of the determination of the rate constant k, ultimately depends upon the accurate determination of the effective concentration of iodine from its reduction potential. The other factors affecting k can be determined with much greater precision. Since the reduction potentials are reproducible to ± 0.5 mV, the error in the effective concentration of iodine is about 6%, and hence the k values have an error of this magnitude. Incidently it may be mentioned that, although $S_2O_8^{--}/SO_4^{--}$ has a reduction potential greater than that of I_3^-/I^-, yet the former does not give rise to a reversible electrode[12] and therefore it is only the reduction potential due to the effective concentration of iodine which is being measured. Further, although $S_2O_8^{--}$ can directly oxidize $S_2O_3^{--}$, this reaction[13] is so slow that the error introduced can be totally neglected.

The second order kinetics of the reaction suggests that the mechanism of the reaction is most probably:

$$S_2O_3^{--} + I_3^- \xrightarrow{\text{slow}} S_2O_3I^- + 2\,I^-,$$

$$S_2O_3I^- + S_2O_3^{--} \xrightarrow{\text{fast}} S_4O_6^{--} + I^-.$$

Almost a similar mechanism has been suggested by Dodd and Griffith[14], although they suggest the possibility of an equilibrium in the first step. Awtrey and Connick[15] have also suggested that the reaction between $S_2O_3I^-$ and $S_2O_3^{--}$ is very fast. Therefore the above mechanism is most probably correct.

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