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Investigations on the Kinetics and Mechanism of the Reduction of Mercuric Chloride by Malic Acid, Induced by Potassium Peroxodisulphate

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The $S_2O_8^{2-}$ induced reduction of mercuric chloride by malic acid has been studied by estimating the precipitated calomel. Kinetic measurements reveal the reduction rate to be independent of the acid concentration and first order in peroxodisulphate, but only to up an optimum concentration, whereafter further increase in inductor concentration decreases the reduction rate. A fractional order dependence in mercuric chloride concentration is encountered. The reaction is characterized by an initial of period induction. The initial rapid consumption of the acid results in lowering of the rate beyond a particular stage of the reaction. Increase of temperature and concentration of reactants is found to effect the period of induction. H^+ ions and oxygen inhibit the reduction rate. Products identified are mainly calomel, carbon dioxide and malonic acid. A chain mechanism in which radical ion chain carriers participate, has been suggested.

Induced reduction of mercuric chloride by certain organic acids was first observed by Dhar.[1] The role of the inductor (normally an oxidizing agent) in activating the acid was later investigated by Cartledge,[2] Weiss,[3] and others.[4] Kinetic investigations undertaken by Weiss led him to propose a chain mechanism based on free radical formation. Mathur and Bansal,[5] employing MnO_4^- as the inducing ion, have kinetically investigated the reduction of mercuric chloride by certain organic acids.[6] They have based the mechanisms, in the respective cases, on the formation of an intermediate complex which on decomposition furnishes the reducing radical. Mechanisms for aqueous decomposition of such manganic complexes have been cited as evidence for free radical generation in the reactant solutions.[7]

The reduction of mercuric chloride to the mercurous state by oxalic acid[8] and tartaric acid[9] induced by $S_2O_8^{2-}$ ion has also been studied kinetically by one of the authors. Kinetic measurements conducted to determine the exponents in the rate law

$$d(Hg_2Cl_2)/dt = k(HgCl_2)^x(C_2O_4^{2-})^y(S_2O_8^{2-})^z$$

showed that $x=0.5$ to 1, $y=0$, and $z=1$. With tartaric acid the reduction was found to obey a second order rate.

From the references cited above, it is clear that the reduction of mercuric chloride employing peroxodisulphate as the inducing ion, has been investigated only in cases of oxalic and tartaric acids. However, $S_2O_8^{2-}$ induced reduction of mercuric chloride by malic acid remains hitherto uninvestigated from the viewpiont of kinetics and mechanism.

Investigations have revealed that the mechanism, consistent with the observations on induced reduction of mercuric chloride by organic acids, were mainly dependent on the acid-inductor reaction mechanism. Therefore, observations incorporated in this paper were preceded by kinetic studies on the reaction between malic acid and potassium peroxodisulphate so as to ascertain the mechanism involved therein.[10] The paper includes our results on kinetic investigations undertaken to uncover the mechanism of peroxodisulphate induced reduction of mercuric chloride by malic acid.

Experimental

The chemicals employed were of A.R. quality and the solutions contained in pyrex conical flasks were

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[1] N. R. Dhar, *J. Chem. Soc.*, **111**, 690 (1917).

[2] G. H. Cartledge, *J. Am. Chem. Soc.*, **63**, 906 (1941).

[3] J. Weiss, *Trans. Faraday Soc.*, **188**, 2 (1947).

[4] E. Abel, *Z. Electro. Chem.*, **43**, 629 (1937).

[5] P. C. Mathur, Ph. D. dissertation, Agra Univ. (1966).

[6] P. C. Mathur and O. P. Bansal, *J. Ind. Chem. Soc.*, **42**, 863 (1965), *ibid.*, **42**, 235 (1965); *ibid.*, **43**, 215 (1966).

[7] W. A. Waters, *J. Chem. Soc.*, **1955**, 217, *ibid.*, **1964**, 1192.

[8] L. K. Saxena and C. P. Singhal, *J. Ind. Chem. Soc.*, **37**, 405 (1960); *ibid.*, **38**, 863 (1961).

[9] L.K. Saxena, Ph.D. dissertation, Agra Univ. (1961).

[10] K. Kumar and L. K. Saxena, *J. Ind. Chem. Soc.*, **44**, 612 (1967).

placed in a thermostat maintained at desired temperature. For a single kinetic run the reaction was allowed to progress for different intervals of time in different conical flasks under identical conditions of temperature and concentrations of the reactants. The kinetics was followed by estimating the amount of calomel precipitated in each flasks at desired intervals of time.

Estimation of Calomel. Calomel precipitated was filtered off through a double-walled funnel containing ice-cold water in between its walls. With this technique further reduction of mercuric chloride is prevented even during filtration. The precipitate was then washed and estimated by a standard potassium iodate solution.[11]

Estimation of Peroxodisulphate. Peroxodisulphate was also estimated during a kinetic run. Aliquot portions of the solution, usually 10 m*l* were withdrawn at intervals with a pipette plugged with wool to avoid calomel and analyzed for residual peroxodisulphate by the usual method.[12] Excess of potassium iodide removed mercuric chloride in solution, as complex. Experiments showed that the presence of this complex caused no error.

The apparent first and second order rate constants (k_1 and k_2 respectively) in mercuric chloride were calculated by the established relations. The average rate of mercuric chloride reduction between successive time intervals was calculated by the expression dx/dt, where dx is the amount of mercurous chloride (in mol l^{-1}) formed during an interval dt. Average C signifies the mean concentration of mercuric chloride, between two successive time intervals, calculated in terms of the equivalent titre volume of KIO_3 in m*l*.

Results of Rate Measurements

Preliminary experiments showed that the induced reduction of mercuric chloride by malic acid proceeds with measurable speed at 60°C and with 0.2M initial concentration of the acid. A typical set of results is shown in Table 1.

TABLE 1

Malic acid=0.2M, $HgCl_2$=0.02M, $K_2S_2O_8$=0.02M, Temp. 60°C.
Period of induction=3 min 30 sec

t min	KIO_3 m*l*	Average C m*l*	Hg_2Cl_2 mol/*l* $\times 10^{-3}$	$10^5(dx/dt)$	10^3k_1	$10k_2$
0	0.0	40.0	—	—	—	—
30	1.7	39.15	0.425	1.416	1.451	1.479
60	4.9	36.70	1.225	2.666	2.168	2.324
120	8.7	33.20	2.175	1.580	2.044	2.316
180	11.0	30.15	2.750	0.958	1.787	2.106
240	12.7	28.15	3.175	0.708	1.592	1.938
300	14.2	26.55	3.550	0.625	1.462	1.835
360	15.6	25.10	3.900	0.583	1.374	1.776
420	16.8	23.80	4.200	0.500	1.297	1.724
480	17.9	22.65	4.475	0.458	1.234	1.689
540	18.8	21.65	4.700	0.375	1.179	1.643
600	19.6	20.80	4.900	0.333	1.122	1.602

The data in Table 1 shows that reduction of mercuric chloride commences after an initial period of induc- tion (3.5 min) and proceeds to about 50% in 10 hr. Figure 1 reveals that the reaction is autocatalytic for a comparatively short period of 60 min, whereafter the rate decreases continuously with time.

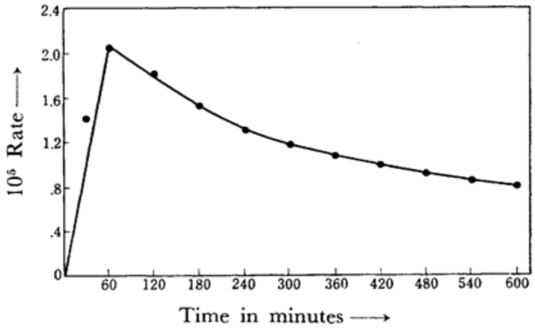

Fig. 1

Malic acid=0.2 M, $HgCl_2$=0.02 M,
$K_2S_2O_8$=0.02 M, Temp.=60°C

First and second order kinetic plots in mercuric chloride revealed marked deviations from linearity; the downward curvatures in each plot signifying the rapid fall in concentration of one of the reactants.[13] Since the reduction of mercuric chloride proceeds only to 50% and is also rapid during the initial few hours, it leads one to suspect that the acid concentration falls much below that of mercuric chloride. This could happen only if the acid is consumed rapidly during the initial stages of the run. It could also be possible that peroxodisulphate concentration may fall much below the acid concentration. But, as will be seen later, this does not happen.

In view of these observations it seems obvious that one is dealing with a complex system wherein, because of the initial rapid consumption of the acid, the reduction does not exceed 50%. This conclusion finds further confirmation from kinetic measurements with initially high acid concentration, which reveal the acid consumption to follow a similar trend. Despite the ratio (Acid)/($HgCl_2$) being kept 50 in certain experiments, we have not been able to obtain reduction of mercuric chloride beyond 50—60% in a period of 10 hr.

Dependence of the Reduction Rate on the Initial Concentration of Reactants. Table 2 records the results of a series of experiments showing the influence of the initial concentration of inductor ($K_2S_2O_8$), actor (malic acid) and acceptor ($HgCl_2$)

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11) A. Vogel, "Text book of Quantitative Inorganic Analysis," Longmans, Green & Co., Ltd. New York (1961), p. 361.

12) L. K. Saxena and C. P. Singhal, *Z. Physik. Chem.*, **161**, 211 (1959).

13) A. Weissberger, "Rates and Mechanisms of Reactions," Interscience Publishers, Inc., New York (1961), pp. 191—192.

TABLE 2

Temp. = 60°C

(a) $HgCl_2=0.01$M $K_2S_2O_8=0.02$M		(b) Acid = 0.1M $K_2S_2O_8=0.02$M			(c) $HgCl_2=0.01$M Acid = 0.1M		
$(\text{Acid})_0$ M	$IR\times10^5$	$(HgCl_2)_0$ M	$IR\times10^5$	$\frac{IR\times10^5}{(HgCl_2)_0^{0.3}}$	$(K_2S_2O_8)_0$ M	$IR\times10^5$	$\frac{IR\times10^2}{(K_2S_2O_8)_0}$
0.15	1.33	0.005	0.89	4.33	0.01	0.58	0.058
0.20	1.41	0.010	1.14	4.55	0.02	1.14	0.057
0.25	1.46	0.015	1.19	4.18	0.03	1.70	0.056
0.30	1.48	0.020	1.36	4.37	0.04	1.60	0.040
0.40	1.54	0.025	1.50	4.53	0.05	1.52	0.030
		0.030	1.62	4.65	0.06	1.50	0.025

on the rate of mercuric chloride reduction. In each experiment the concentrations of two reactants were kept constant and the third was varied as noted in the columns. Since the overall reduction rate changes with time (as shown in Fig. 1), the initial rate (IR) at each concentration was calculated for 120 min from the x–t curves.

The initial reduction rate is not appreciably affected over a range of 0.15M to 0.40M acid concentration which suggests the rate law to be zero order in (malic acid) (Table 2a), and the variation of rate with respect to mercuric chloride concentration can be expressed as $d(Hg_2Cl_2)/dt=k(HgCl_2)^{0.3}$ (Table 2b, Fig. 2).

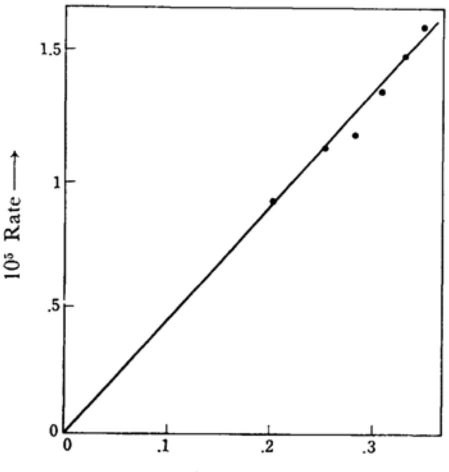
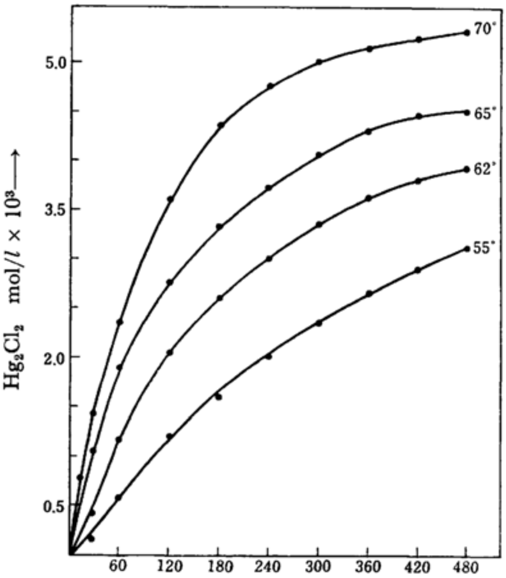


Fig. 2

Malic acid = 0.1 M, $K_2S_2O_8=0.02$ M, Temp. = 60°C

Scrutiny of results in Table 2(c) shows the reduction rate to be strictly of first order with respect to peroxodisulphate up to 0.03M concentration of the inductor. However, further increase in the initial concentration decreases the reduction rate.

Temperature Dependence. From Fig. 3 it can be seen that increase of temperature increases the overall reaction velocity. The mean energy and entropy of activation for the range 55—65°C were found to be 18 kcal/mol and −16 e.u., respectively. It may be pointed out that these values are merely qualitative in nature since they have been calculated from average values of the rate constants from regions exhibiting fair amount of constancy; nevertheless, their order and magnitude helps to evaluate the mechanism of the reaction.



Time in minutes ⟶

Fig. 3

Malic acid = 0.1 M, $HgCl_2=0.02$ M, $K_2S_2O_8=0.02$ M

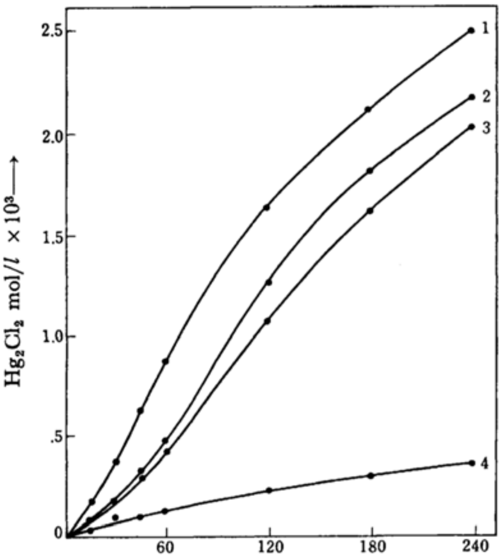
Influence of Gases. Influence of gaseous atmosphere on the reduction rate is represented graphically in Fig. 4. In nitrogen and carbon dioxide atmospheres the reduction rate is faster; the effect of nitrogen being more than carbon dioxide under comparable conditions. Oxygen is found to exert a strong inhibitive influence.

Influence of Acids and Salts. The influence of some acids and their salts was studied to ascertain the role of specific ions on the reduction rate. The percentage reduction of mercuric chloride, in each

Table 3

Malic acid=0.05M, $HgCl_2$=0.01M, $K_2S_2O_8$=0.02M, Temp. 60°C

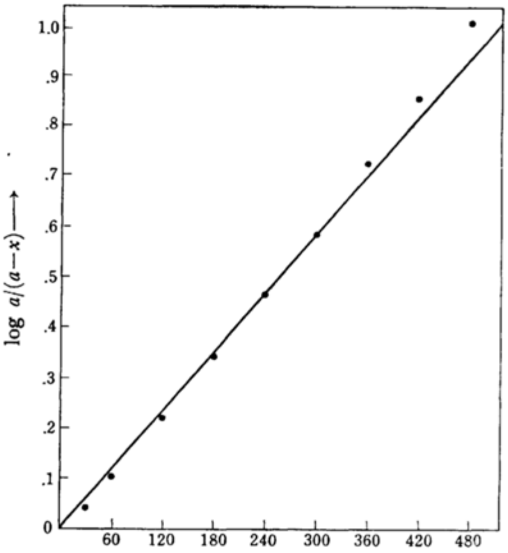
Time	Titre volume of KIO_3 in m*l*					
	Nil.	0.05M HCl	0.05M H_2SO_4	0.05M KCl	0.05M K_2SO_4	0.10M CH_3COONa
0 min	0.0	0.0	0.0	0.0	0.0	0.0
120 min	4.2	0.0	3.4	0.3	4.0	9.7
% Reduction	21.0	0.0	17.0	1.5	20.0	48.5



Time in minutes ⟶

Fig. 4

1. Nitrogen atmosphere
2. Carbon dioxide atmosphere
3. Air atmosphere
4. Oxygen atmosphere



Time in minutes ⟶

Fig. 5

Malic acid=0.1 M, $HgCl_2$=0.01 M, $K_2S_2O_8$=0.02 M. Temp.=60°C
Slope=0.0019 $k_1=4.3767\times10^{-3}$

case, was calculated as follows:

$$\% = \frac{\text{Titre vol. of } KIO_3 \text{ in m}l}{20\,\text{m}l}\times 100$$

where 20 m*l* KIO_3 volume corresponds to the amount of Hg_2Cl_2 formed on complete reduction of 0.01M $HgCl_2$ in the reaction mixture.

From the foregoing data it may be concluded that H^+ and Cl^- ions inhibit the reduction of mercuric chloride. It appears that Cl^- ion exerts a very strong inhibitive influence. The % reduction is observed to be maximum in the presence of sodium acetate.

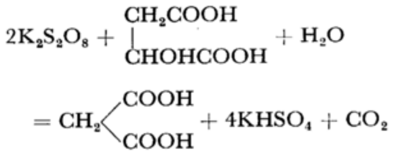
Rate of Peroxodisulphate Decomposition. As already mentioned in the experimental part, peroxodisulphate was also estimated. The first order plot at 0.02M concentration of the inductor, is a straight line with a slope giving, $k=4.37\times10^{-3}$ min^{-1}. It can be seen that almost 8 hr are required for the complete decomposition of peroxodisulphate.

The Period of Induction. When peroxodisulphate was added to a solution containing mercuric chloride and malic acid, the reduction of mercuric chloride to the mercurous state did not start immediately. The reduction was observed to begin after a certain time interval after the mixing of the reactants. This time interval has been termed as the period of induction.

Investigations on the induction period were divided into two parts: its dependence on (i) temperature, and (ii) reactant concentration. Results obtained showed that increase in concentration of any of the reactants decreased the period of induction. It was further observed that increase of temperature also decreased this period. Hence, it may be concluded that the induction period depends upon the concentrations of the reactants as well as on the temperature of the reaction. In view of these findings it appears that the induction period is related with the mechanism of the reduction of mercuric chloride.

Discussion

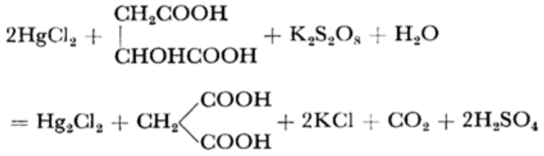
Prolonged oxidation of malic acid by peroxodisulphate involves its degradation to malonic acid and carbon dioxide, as revealed by our investigations described earlier.[10] The stoichiometric equation of the reaction verified by us approximates as follows:



$$2K_2S_2O_8 + \begin{array}{l}CH_2COOH\\ |\\ CHOHCOOH\end{array} + H_2O = CH_2\begin{array}{l}\diagup COOH\\ \diagdown COOH\end{array} + 4KHSO_4 + CO_2$$

(found: 2 equiv. $S_2O_8^{2-}$: 1 equiv. acid.)

When mercuric chloride is added, the evolution of carbon dioxide sets in immediately, indicative of the degradation of malic acid in this case as well. Products that have been identified are mainly mercurous chloride, malonic acid,[14] carbon dioxide and sulphuric acid. A steady decrease in pH is observed, as the induced reduction of mercuric chloride proceeds, signifying the increase in acidity of the system. Under such conditions the stoichiometry may be represented as follows:



$$2HgCl_2 + \begin{array}{l}CH_2COOH\\ |\\ CHOHCOOH\end{array} + K_2S_2O_8 + H_2O = Hg_2Cl_2 + CH_2\begin{array}{l}\diagup COOH\\ \diagdown COOH\end{array} + 2KCl + CO_2 + 2H_2SO_4$$

Malic acid alone, like oxalic and tartaric acids, does not reduce mercuric chloride even on boiling. However, addition of small amounts of peroxodisulphate activates the acid to reduce it. This clearly suggests that as a result of the interaction of malic acid and the inductor, some active substance is produced which reduces Hg^{2+} to Hg^+ state. The mere fact that the reduction commences after an initial period of induction, further lends support to this view. Evidently, the nature of this active species is related to the product of oxidation of malic acid by peroxodisulphate.

At this point it would be pertinent to refer to our investigations carried out earlier on the reaction between $S_2O_8^{2-}$ and malic acid (loc. cit.). The proposed mechanism consistent with the rate data, involves chain sequences with transient products SO_4^- and CO_2^- radicals. It has been our contention that these active transients act as chain carriers and control the mechanism of the process of reduction of mercuric chloride,[15] as has been suggested for oxalic and tartaric acid (loc. cit.).

We believe this reaction to be a free radical chain reaction for the following reasons:

1) It progresses through various successive zones;

2) Fractional order dependence in mercuric chloride concentration is encountered (Fig. 2, Table 2b);

3) The marked inhibition by oxygen implicates CO_2^- as a reactive intermediate, since oxygen is known to inhibit certain chain reactions involving CO_2^- radical;[16,17]

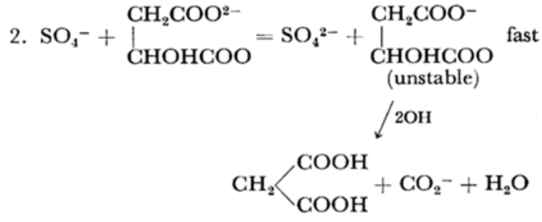
4) Peroxodisulphate-malate reaction is a chain reaction in itself.

A reasonable mechanism, similar to that proposed for oxalic and tartaric acids (loc.cit.) may have the gross features as given below:

Chain Initiating Sequence:

1. $S_2O_8^{2-} = 2SO_4^-$ slow

Chain Propagating Sequences:



$$2.\ SO_4^- + \begin{array}{l}CH_2COO^{2-}\\ |\\ CHOHCOO\end{array} = SO_4^{2-} + \begin{array}{l}CH_2COO^-\\ |\\ CHOHCOO\end{array} \quad \text{fast}$$

(unstable)

$$\xrightarrow{2OH} CH_2\begin{array}{l}\diagup COOH\\ \diagdown COOH\end{array} + CO_2^- + H_2O$$

3. $CO_2^- + S_2O_8^{2-} = SO_4^{2-} + SO_4^- + CO_2$ fast

Chain Terminating Sequences:

4. $CO_2^- + Hg^{2+} = Hg^+ + CO_2$ faster than 3

5. $SO_4^- + H_2O = HSO_4^- + OH$ slow

$2OH = H_2O + \frac{1}{2}O_2$ fast

6. $CO_2^- + O_2 = CO_2 + O_2^-$ slow

7. $O_2^- + H^+ = HO_2$ leading to H_2O_2 (3)

8. $CO_2^- + SO_4^- = CO_2 + SO_4^{2-}$ slow at low concs.

The primary step is characteristic of peroxodisulphate decomposition and sequences 2 and 3 have been postulated as the mechanism for the reaction between peroxodisulphate and malic acid (loc.cit.).

The chain initiation is caused by the thermal decomposition of peroxodisulphate ion which undergoes a fission on the weak O–O bond with formation of two sulphate radical ions.[18] In a recent review Wilmarth[19] has discussed at length the role of this active species. He maintains SO_4^- to be energetically capable of reacting with the organic substrate and with the solvent, though with unequal efficiencies. Accordingly, in the beginning step 2 would predominate, producing CO_2^- radical and malonic acid.

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[14] F. Feigl, "Spot Tests," Elsevier Publishing Co., New York (1960).

[15] K. Kumar and L. K. Saxena, *J. Ind. Chem. Soc.*, **43**, 669 (1966).

[16] E. Ben Zvi and T. L. Allen, *J. Am. Chem. Soc.*, **83**, 4352 (1961).

[17] A. J. Kalb and T. L. Allen, *ibid.*, **86**, 5107 (1964).

[18] D. A. House, *Chem. Revs.*, **62**, 185 (1962).

[19] W. K. Wilmarth and A. Haim, Peroxide reaction mechanisms, Conference, Rhode Island, 1960.

CO_2^- being a reactive species reacts with peroxodisulphate ion, thereby regenerating SO_4^-. This could lead to a two pronged attack on malate ions (as long as steps 2 and 3 are equally fast). Our results conform to this initial rapid consumption of the acid.

CO_2^- radical also reacts with Hg^{2+} ion resulting in the precipitation of calomel by step 4. Accordingly, the initial period of induction is the time required for the thermal activation of the $S_2O_8^{2-}$ ion so as to break into SO_4^- radicals which produce CO_2^- responsible for the reduction of mercuric chloride. Increase of temperature increases the velocity of the chain initiating process, resulting in the decrease of period of induction. Similarly, increase in the concentration of either malate or $S_2O_8^{2-}$ increases the rate of SO_4^- production by step 1 or by step 2, respectively, thereby decreasing the period of induction. These conclusions are supported by our observations.

The initial auto-catalytic nature of the reduction reaction probably is a result of chain sequences 2 and 3. Due to the two pronged attack on malic acid the rate of CO_2^- production increases. This results in the reaction becoming autocatalytic in the initial stages (Fig. 1). With the progress of the reaction, however, the accumulated acid would inhibit the rate of reduction since it has been observed that H^+ ions inhibit the reduction of mercuric chloride (Table 3) by catalyzing the chain terminating sequence 5 as follows:

$$\begin{array}{ll} 9. & SO_4^- + H^+ = HSO_4 \\ 10. & \underline{HSO_4 + H_2O = HSO_4^- + OH + H^+} \\ & SO_4^- + H_2O = HSO_4^- + OH \end{array} \qquad (18)$$

This increases the contribution of sequence 5 to the overall chain termination, resulting in the observed rate drop after the induction period (Table 1). Sodium acetate removes H^+ ions, thereby stabilizing SO_4^- with the result that the chains are elongated (Table 3).

The proposed mechanism also accounts for the independence of the reduction rate on malic acid concentration, since step 4 of the mechanism, which governs the reduction of mercuric chloride, involves free radical CO_2^-. Its rate of production is governed by peroxodisulphate concentration. This further explains the first order dependence in peroxodisulphate in low concentration range (Table 2c). With increase in the initial peroxodisulphate concentration, the oxygen content of the system increase, making sequence 11 quite effective:

$$11.\ O_2 + Hg^+ = Hg^{2+} + O_2^-$$

Inhibition by oxygen could also occur through reaction with CO_2^- radical (seq. 6) followed by chain termination, as observed by Allen.[17] This finds support from the enhanced rate obtained by the authors working with nitrogen and carbon dioxide atmospheres which might dispel the accumulated oxygen (Fig. 4).

Appendix

$$d(Hg_2Cl_2)/dt = k_4(CO_2^-)(Hg^{2+}) \qquad (1)$$

In the stationary state of chains:

$$\begin{aligned} d(CO_2^-)/dt = {} & k_2(SO_4^-)(Mal^{2-}) - k_3(CO_2^-)(S_2O_8^{2-}) \\ & - k_4(CO_2^-)(Hg^{2+}) - k_6(CO_2^-)(O_2) \\ & - k_8(CO_2^-)(SO_4^-) = 0 \end{aligned} \qquad (2)$$

and

$$\begin{aligned} d(SO_4^-)/dt = {} & 2k_1(S_2O_8^{2-}) + k_3(CO_2^-)(S_2O_8^{2-}) \\ & - k_2(SO_4^-)(Mal^{2-}) - k_5(SO_4^-) \\ & - k_8(CO_2^-)(SO_4^-) = 0 \end{aligned} \qquad (3)$$

from 2 and 3 we have:

$$\begin{aligned} 2k_1(S_2O_8^{2-}) = {} & k_5(SO_4^-) + 2k_8(CO_2^-)(SO_4^-) \\ & + k_4(CO_2^-)(Hg^{2+}) + k_6(CO_2^-)(O_2) \end{aligned} \qquad (4)$$

Consideration of all the termination steps 5—8 would involve a complicated rate term with various limiting-forms. It is not unlikely that one or two of these steps may be most important of all and a consideration of these would lead to a simple rate expression conforming of the experimental facts. The possibility of other steps becoming important under changed conditions is also not ruled out. However, our results can be best explained by assuming steps 6 and 8 to be insignificantly operative in the initial stages of the reaction and therefore considered negligible as compared to the propagating sequences of the proposed mechanism.
Therefore,

$$2k_1(S_2O_8^{2-}) = k_5(SO_4^-) + k_4(CO_2^-)(Hg^{2+}) \qquad (5)$$

Under these conditions, the steady-state concentration

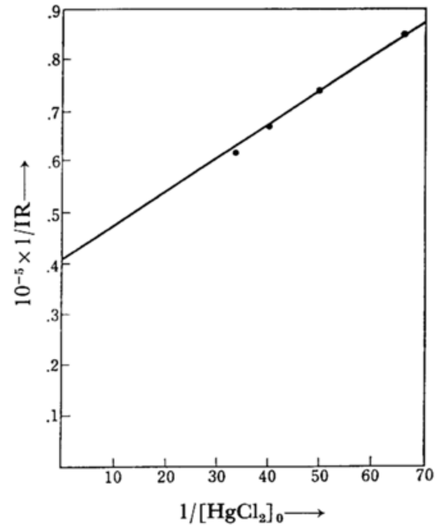

Fig. 6. Dependence of reaction rate on $HgCl_2$ concentration.
Intercept. $=0.41 \times 10^5$ Slope $=650$

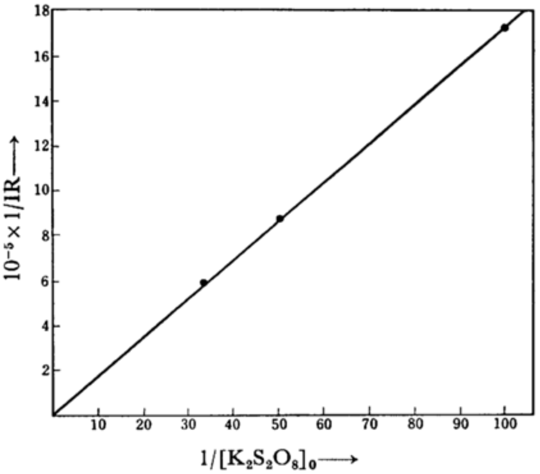

Fig. 7. Dependence of reaction rate on $K_2S_2O_8$ in low concentration range.
Slope=1745

of SO_4^- as derived from Eq. (2) is:

$$(SO_4^-) = \frac{k_3(S_2O_8^{2-})+k_4(Hg^{2+})}{k_2(Mal^{2-})}(CO_2^-)$$

Substituting this expression into Eq. (5), we get

$$(CO_2^-) = \frac{2k_1k_2(S_2O_8^{2-})(Mal^{2-})}{k_3k_5(S_2O_8^{2-})+k_4k_5(Hg^{2+})+k_2k_4(Mal^{2-})(Hg^{2+})}$$

and

$$\text{rate} = k_4(CO_2^-)(Hg^{2+}) = \frac{2k_1k_2k_4(S_2O_8^{2-})(Mal^{2-})(Hg^{2+})}{k_3k_5(S_2O_8^{2-})+k_4k_5(Hg^{2+})+k_2k_4(Mal^{2-})(Hg^{2+})} \quad \text{(A)}$$

On the other hand, at the outset of reaction when the stationary state is not yet attained, the rate is given by:

$$\text{rate} = 2k_1(S_2O_8^{2-})\frac{k_4(Hg^{2+})}{k_3(S_2O_8^{2-})+k_4(Hg^{2+})} \quad \text{(B)}$$

In either case the experimental data should fit linear plots of the type

$$1/\text{rate} = a + [b/(\text{reagent})],$$

intercept and slopes of these straight lines giving the constants *a* and *b*.

Figures 6 and 7 are such plots of the data in Table 2 and the following tables record the values of rate as obtained by the use of Eq. (B):

TABLE 4. DEPENDENCE OF THE REACTION RATE ON $HgCl_2$ CONCENTRATION
(conditions same as in Table 2)

$(HgCl_2)$ (moll^{-1})	0.01	0.015	0.02	0.025	0.03
10^5(min^{-1})(obsd)	1.14	1.19	1.36	1.50	1.62
10^5(min^{-1})(calcd)*	0.96	1.18	1.36	1.51	1.60

* IR calculated from the relation
$1/\text{rate} = 0.41\times 10^5+[650/(Hg^{2+})]$

TABLE 5. DEPENDENCE OF THE REACTION RATE ON $K_2S_2O_8$ IN LOW CONCENTRATION RANGE
(conditions same as in Table 2)

$(K_2S_2O_8)$ (moll^{-1})	0.01	0.02	0.03
10^5(min^{-1})(obsd)	0.58	1.14	1.70
10^5(min^{-1})(calcd)*	0.57	1.14	1.71

* IR calculated from the relation
$1/\text{rate} = O+1754/(S_2O_8^{2-})$

The observed rates compare reasonably well with those calculated from Eq. (B) (after appropriate choice of values for *a* and *b*), thus justifying the proposed reaction scheme and the rate equations derived therefrom.

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