THE KINETICS AND MECHANISM OF THE OXIDATION OF

FORMATE IONS BY PEROXODISULPHATE IONS

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ABSTRACT

The kinetics of the peroxodisulphate/formate reaction have been studied using four methods.

(1)   By titrating aliquots of reaction mixture.

(2)   By following pH changes.

(3)   By a manual pH-stat.

(4)   By an automatic pH-stat.

Kinetic data was obtained at pH values from pH 4.0 to pH 8.0 at an ionic strength of 0.2M and at temperatures from $30^{\circ}C$ to $50^{\circ}C$, using method (4).   Changes of rate constant with pH were considerable.   Kinetic data at pH = 8.0, temperature = $35^{\circ}C$ and ionic strength = 0.2M are, first order rate constant

$k_1 = 9.59 \times 10^{-5}$ sec $^{-1}$, $E_a = 11.9$ Kcal mole $^{-1}$ PZ = 2.49×10^4 sec $^{-1}$.

A mechanism is postulated to explain the observed kinetics for the uncatalysed reaction.

The kinetics of the cupric ion catalysed reaction were studied over a range of cupric ion concentrations from 2.5×10^{-4} to 6.25×10^{-4}M at $30^{\circ}C$ and pH 5.0 using method (4).

INTRODUCTION

The peroxodisulphate ion is one of the strongest oxidizing agents known in aqueous solution. The oxidation reduction potential for the reaction :-

$$2 \ SO_4^{2-} \ (aq) \longrightarrow S_2O_8^{2-} \ (aq) + 2 \ e^-$$
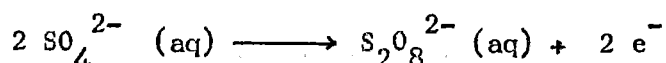
is estimated to be - 2.01 volts (1). Reactions involving this ion are however, generally slow at ordinary temperatures, and many peroxodisulphate oxidations have been studied kinetically. (2, 3).

The reaction between the peroxodisulphate ion, (4) and the formate ion has been previously investigated by Srivastava and Ghosh (5, 6) and Kappana (7). These two groups found the stoichiometry of the reaction to be:-

$$S_2O_8^{2-} + HCOO^{1-} \longrightarrow SO_4^{2-} + HSO_4^{1-} + CO_2$$
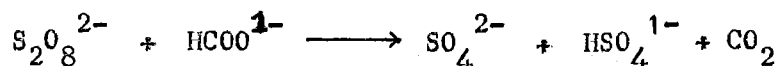
and followed the extent of reaction by titrating the free acid produced with standard alkali. Srivastava and Ghosh (5) found the reaction to be unimolecular, following the rate law:-

$$-d \left[S_2O_8^{2-} \right] \ / \ dt \ = \ k \left[S_2O_8^{2-} \right]$$

Kappanna in a later investigation, concluded that the reaction was bimolecular, following the rate law:-

$$-d \left[S_2O_8^{2-} \right] \ / \ dt \ = \ k \left[S_2O_8^{2-} \right] \left[HCOO^{1-} \right]$$

The only difference in reagents and experimental conditions was that Srivastava and Ghosh used potassium formate solution at a temperature of $30^{\circ}C$, whereas Kappana used sodium formate

solution and slightly more concentrated potassium peroxo-
disulphate at $25^{o}C$. These minor changes would not be expected
to alter the order of reaction, and to resolve this contradiction,
the kinetics of the peroxodisulphate/formate reaction have been
re-investigated.

Date obtained by both Srivastava and Ghosh and Kappana shows
a decrease in rate constant with an increase in formate ion
concentration. This is contrary to the result which could be
expected for a first order reaction, as proposed by Srivastava
and Ghosh, where the rate should be unchanged; or for a second
order reaction, as proposed by Kappana, when the rate should
increase. However, in these measurements neither group of workers
ensured that the total ionic strength of the reaction mixture was
maintained at a constant value. Thus these variations in the
rate constant could be caused by the changes in ionic strength.

Studies of the effects of inert salts were made by both
groups who agree that the rate constant decreases with an increase
in ionic strength. This result is contrary to that expected for
a reaction following the mechanism proposed by Kappana (7):-

$$S_2O_8^{2-} + HCOO^{1-} \longrightarrow Z^{3-}$$
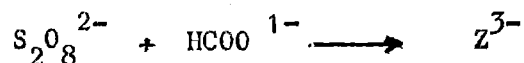
where a positive salt effect would be expected from the
activity rate theory of Bronsted and Bjerrum (8). This theory
is however, only valid for concentrations below 0.01 Molar for
1 : 1 electrolytes, and still lower concentrations for higher
charged ions, (9). As the ionic strengths used in these studies
were in the range 0.23 M to 1.03 M, any conclusions drawn from

this data could be seriously in error.

The reaction was studied over a range of temperatures by both Srivastava and Ghosh (5) and Kappana (7), who obtained values for the energy of activation of 21.93 and 24.9 kcal mole^{-1} respectively.

The kinetics of the peroxodisulphate ion/formic acid reaction were studied by Srivastava and Ghosh (10, 11), who followed the reaction by measuring the electrical conductivity of the reaction mixture at various time intervals. During reaction the conductivity increased because of the formation of H_2SO_4 according to the equation :-

$$K_2S_2O_8 \; + \; HCOOH \; \longrightarrow \; K_2SO_4 \; + \; H_2SO_4 \; + \; CO_2$$
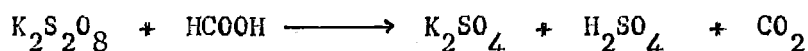
Conductivity readings were converted to concentrations of potassium peroxodisulphate using a callibration graph previously obtained. The reaction was found to be unimolecular following the rate law :-

$$-d \left[S_2O_8^{2-} \right] \; / \; dt \; = \; k \left[S_2O_8^{2-} \right]$$

as in the potassium formate oxidation it was found that an increase in formic acid concentration caused a slight decrease in rate constant. However, as the ionic strength was not maintained at a constant value, this result could be caused by a slight negative salt effect. The effect of inert salts on the reaction rate was also studied (11), and a small negative salt effect was found using K_2SO_4, but the total ionic strengths were in the range 0.030 M to 0.035 M, which is three times greater than the maximum for which any application of the theory of

kinetic salt effects is valid.

Specific inhibitory effects of Halide ions were also investigated and found to be in the order $I^- > Br^- > Cl^-$ as found in other reactions of the peroxodisulphate ion (5, 13).

The reaction was studied at temperatures of $30^\circ C$, $35^\circ C$ and $40^\circ C$, and the energy of activation calculated to be 8.18 kcals mole^{-1}. The large difference between this value and the value for the formate ion reaction of 21 - 24 kcal mole^{-1} suggests the possibility of some dependence of the reaction mechanism on the pH of the reaction mixture.

Catalytic effects of both cupric and silver ions were examined, and the effect of the silver ion found to be the greater. A more detailed study of the effects of the silver ion catalysed oxidation has been made by Gupta and Nigam (12). In their investigation these workers first examined the silver ion catalysed oxidation of sodium formate. They obtained first order rate constants from the relationship :-

$$k = \frac{2.303}{t} \quad \frac{1}{[Ag^{1+}]} \quad \log \frac{a}{a - x}$$

where a and a - x are concentrations of peroxodisulphate ions initially and after time t. Using sodium formate they found the first order rate constant to decrease with time. However when the reaction was done in 0.1 M H_2SO_4, the rate constants were lower and showed no such decrease. Hence it was concluded that the gradual drop in rate was caused either by the gradual decrease in catalyst concentration by reduction, or by the progressive formation of sulphuric acid, which slows the reaction;

or a combination of the two effects. Using formic acid no

such decrease in rate constant was observed. However the rate

was again lower in the presence of 0.1 M H_2SO_4. The reaction

was found to be bimolecular following the rate law:-

$$-d \left[S_2O_8^{2-} \right] / dt = k \left[Ag^+ \right] \left[S_2O_8^{2-} \right]$$

The effect on rate of varying the concentration of H_2SO_4 in

the reaction mixture was also investigated. It was found that

the rate constants decreased with an increase in acid concentration.

This result also points to the possibility of some dependence

of rate on the pH of reaction mixture. Thus in the present

study the rate was determined at various constant values of pH.

A study of the γ-ray induced chain decomposition of the

formic acid/peroxodisulphuric acid system has been made by Hart (14),

where the reaction was found to proceed according to the overall

equation :-

$$S_2O_8^{2-} + HCOOH \longrightarrow 2HSO_4^{1-} + CO_2$$
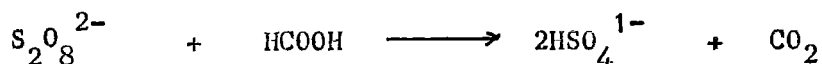
A correction was made to the γ-ray induced for the thermal reaction

taking place between peroxodisulphuric acid and formic acid. A

log - log plot of thermal rate of carbon dioxide evolution against

peroxodisulphate concentration is linear in the range 0.46×10^{-3} M

to 0.1 M, with a slope of unity, showing a first order reaction

as reported by Srivastava and Ghosh (11). The effect of changes

of pH on the yeild of CO_2 was investigated in the range pH 0.53

to pH 11.3 using 0.06 M formic acid and 0.001 M potassium

persulphate. The reaction showed a rapid rise in CO_2 yeild in the

acid range to pH 5.1, a rapid decrease in G (CO_2) in the pH

range 5.1 to 7.3 and another lesser decrease at pH 10 - 11. The

pH was maintained at fixed values by use of a series of buffer

solutions.

In view of the results obtained in these previous studies

in the present work, the kinetics of the peroxodisulphate - formate

reaction were studied at constant ionic strength over a range of

temperatures. A range of concentrations of both reagents was used

with a view to establishing the molecularity of the reaction. To

determine the pH dependence, if any, the reaction was studied over

a range of pH values using a non buffered pH-stat technique.

EXPERIMENTAL

All reagents used in this work were A. R. quality. Stock

solutions of 0.1 M potassium formate were prepared by mixing

equal volumes of 0.2 M potassium hydroxide and 0.2 M formic acid.

Solutions of potassium peroxodisulphate were prepared in 100 ml.

lots, and stored at low temperatures to minimise thermal decomposition

of this reagent. (15). For the preliminary work appropriate

amounts of potassium peroxodisulphate were weighed out directly for

each experiment. Solutions were prepared using distilled water,

(see p. 57).

In the preliminary work the reaction was studied in 10^{-3} M EDTA

solution, at a peroxodisulphate ion concentration of 0.05 M, and a

formate ion concentration of 0.025 M. The reaction was carried out

in a vessel maintained at a constant temperature in a thermastat.
At appropriate time intervals 5 ml. samples of reaction mixture
were removed, placed in small flasks in an ice bath to slow the
reaction, and titrated against 0.01 M potassium hydroxide using
phenolthalein indicator.

Preliminary investigations of the pH changes throughout the
course of the reaction were made using a Radiometer type pH M
22s pH meter coupled to a recorder. This provided continuous
plots of pH against time. Solution concentrations for this work
were 0.05 M in peroxodisulphate ion and 0.025 M in formate ion.
No EDTA was used in this case.

The reaction rate at constant pH was determined using a non-
buffer pH-stat method. Stock solution of potassium peroxodisulphate
(75 mls. 0.1M.) and potassium formate (75mls. 0.05 M) were mixed
at $35^{o}C$ and the pH was maintained at a constant value by the manual
addition of small volumes of standard alkali (KOH) from a burette.
Readings of the valume of alkali used were taken at various time
intervals. In the first of these experiments 0.1 M potassium
hydroxide was used. However, the volumes used were large, causing
considerable dilution of the reaction mixture and 1.0 M KOH was
subsequently used. The reaction rate was determined over the pH
range 4-8 and the results showed a marked dependence of the rate
on pH.

In later work, the use of an automatic titrating system
enabled more accurate results to be obtained. This apparatus
consisted of a Radiometer TTT 1c titrator coupled to a Radiometer

SBR 2c syringe burette recorder, and an SDU la micro syringe burette. A Radiometer 202c glass electrode and Radiometer K 401 calomel electrode in the reaction vessel are coupled to the titrator, providing a continuous reading of pH.

If the pH reading falls below a certain previously set value a relay in the titrator is closed. This relay, through another relay in the recorder, activates the pen motor and, via a flexible drive, the micrometer drive of the syringe. When sufficient alkali has been added by the syringe via a delivery tube to the reaction mixture, to bring the pH back to the value previously set, the relay is opened and the drive to both the pen and the syringe is ceased. Thus the movements of the pen are directly proportional to those of the syringe plunger and hence to the amount of alkali added. Throughout the entire course of the reaction another motor in the recorder drives the chart paper forward at a constant speed giving a time scale on the chart paper.

A wide range of both chart and pen and syringe motor speeds is available. Motors of 30, 4, 0.5, and 0.05 rpm are available. An external control makes a further adjustment of chart speed possible. Three settings (10, 5, and 2.5 mm/rev) are available. The speed of the pen and syringe can also be altered by means of a variable gear train, providing three settings (4, 2, and 1 %/rev.). The amount of alkali added is measured in percentages of the total output of the syringe, which in this case was 0.5 mls.

Using an appropriate combination of pen and chart speeds a

smooth curve of KOH used against time can be obtained. As the

pen and syringe are operated in short pulses the choice of chart

speed must be correct to prevent the resultant plot showing any

steps. The syringe speed is also critical, as too low a speed

will result in alkali addition lagging behind acid production in

the reaction mixture, and thus prevent any useful data being

obtained. The plot obtained would, in fact, only be a plot of

maximum rate of alkali addition against time, and would be a

straight line. Too high a speed would cause a stepwise plot and

hence inaccuracies in any data obtained from it.

With this apparatus only 10mls. of 0.1 M potassium peroxodi-

sulphate and 10 mls. of 0.1 M potassium formate were used as the

syringe burette could deliver only 0.5 mls. of alkali.

This system enabled the reaction to be followed for much

longer periods, up to 100% reaction, and the pH was maintained much

closer to the desired value than was possible with the manual method

employed previously.

Some diffusion of alkali into the reaction mixture took

place from the delivery tube. This had the effect of making the

reaction appear to reach completion before the theoretical amount

of alkali for 100% reaction had been added by the syringe. As the

reaction rate progressively slowed, diffusion of alkali eventually

became faster than the production of free acid by the reaction.

Hence no more alkali needed to be added directly by the syringe.

For this reason experimental values of vol. KOH at 100% reaction

(denoted by "a") were used in calculation of rate constants.

The volume change caused by the addition of alkali (a maximum value of 2.5% but usually less) was neglected when calculating reactant concentrations at any given time.

Work on the copper catalysed reaction was done using the automatic pH-stat apparatus. A stock solution of A.R. grade copper sulphate solution was made using the stock solution of 0.1 M potassium formate. A few drops of 0.1 M sulphuric acid were added to prevent precipitation of copper as copper hydroxide. This stock solution was diluted down with potassium formate solution to give 100 ml. lots at double the cupric ion concentration required. For each kinetic run 10 mls. of this solution was mixed with 10 mls. of the 0.1 M peroxodisulphate solution. As before the peroxodisulphate solution was made up in 100 ml. samples and stored in a refrigerator or ice bath to minimise the thermal decomposition of the peroxodisulphate ion. No cupric ion could be added to the peroxodisulphate solution before reaction as cupric ion also catalyse the thermal decomposition.

For all kinetic runs the concentrations of both peroxodisulphate and formate ions was 0.05 M. A pH of 5.0 was used for the reaction as the concentration of cupric ions used a precipitate of copper hydroxide was formed if the reaction mixture was made more alkaline. A temperature of $30^{\circ}C$ was used for all Cu^{2+} catalysed kinetic runs.
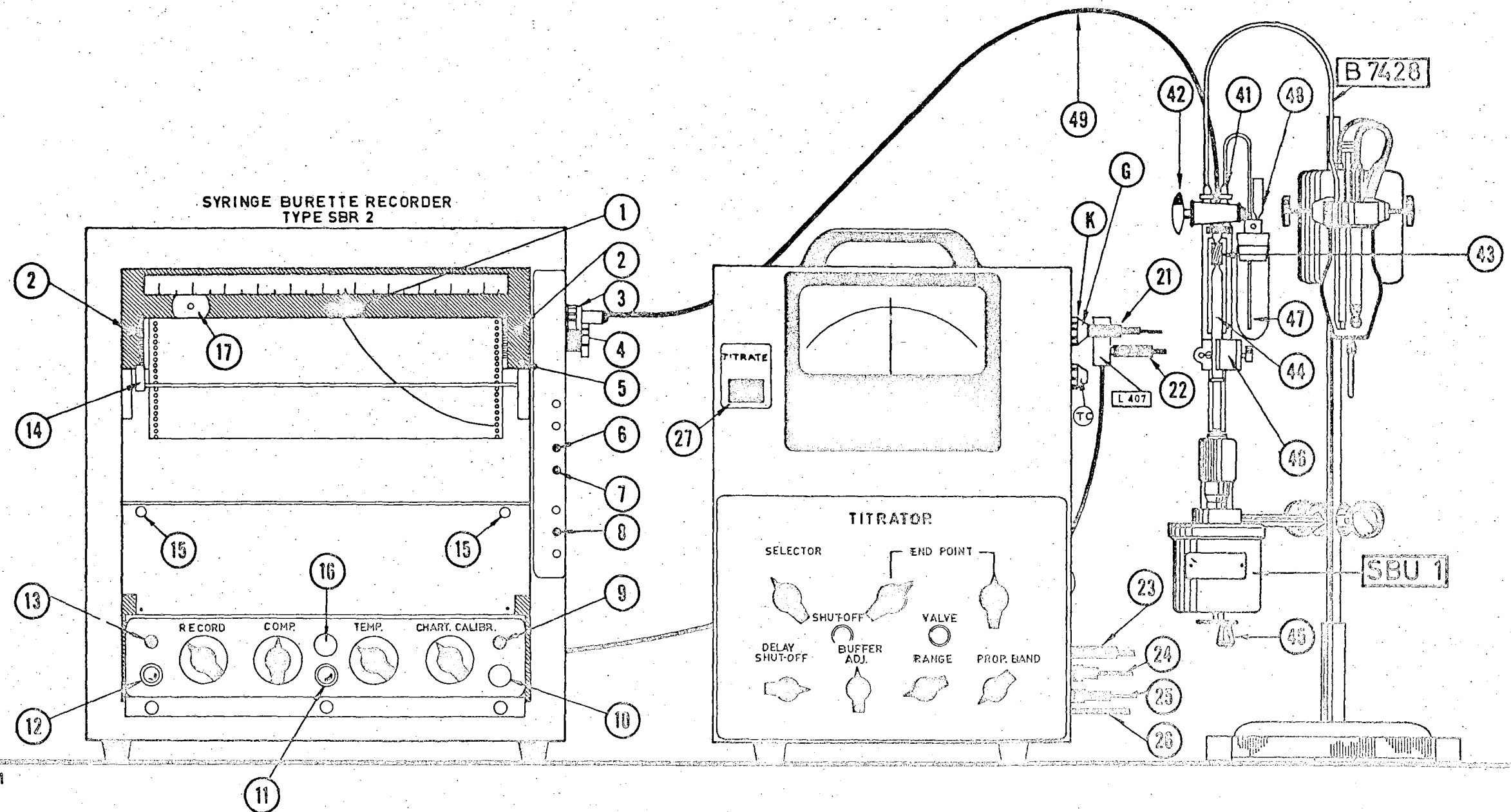
Fig 1. THE COMPLETE TITRIGRAPH EQUIPMENT

B 7428

G 202 B

K 401

D 4514

D 3301

M 11 or M 22

D 4511

B 3031

D 4326

D 4328

V 510

51

52

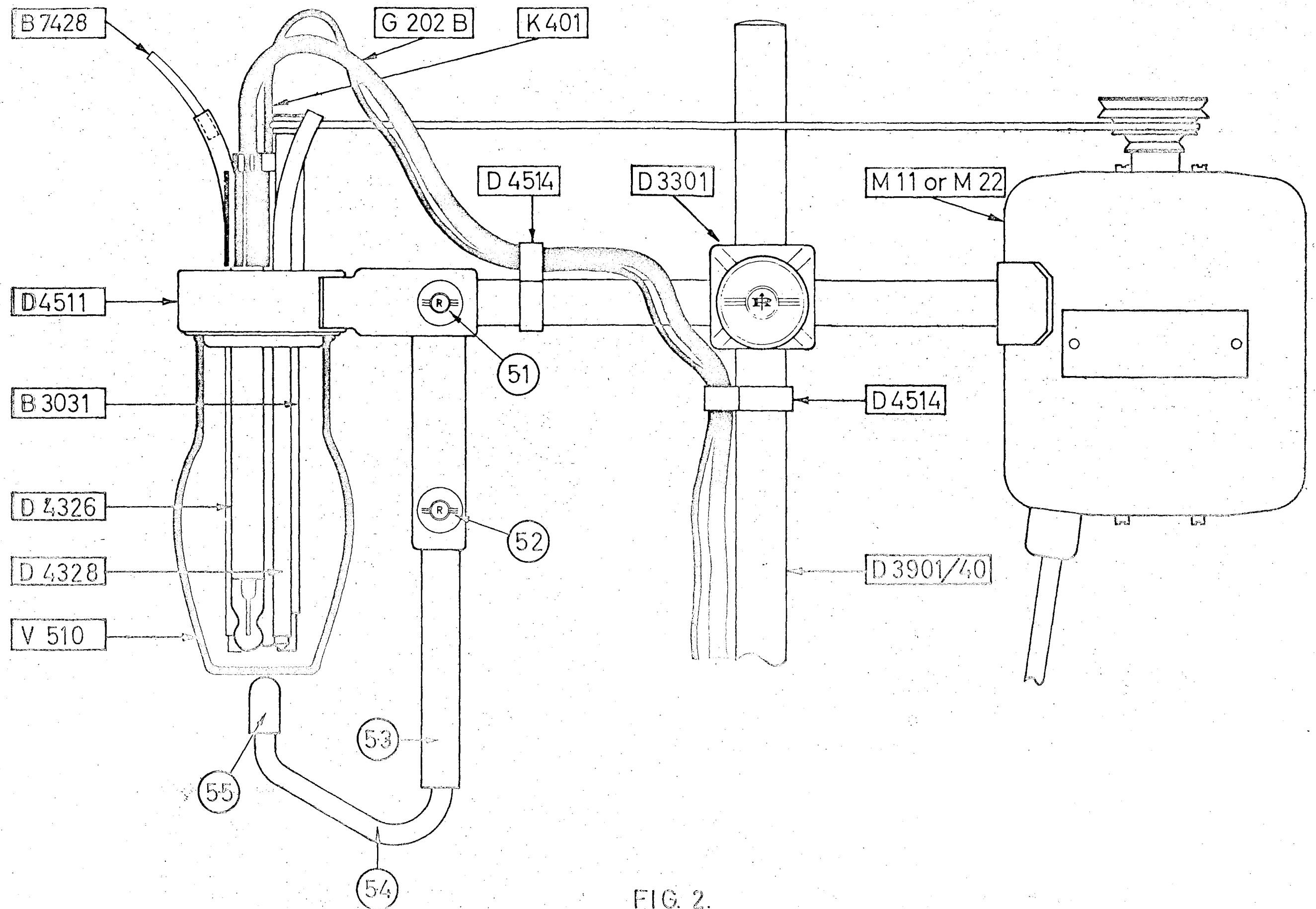53

54

55

D 4514

D 3901/40

FIG. 2.

RESULTS

1.   Preliminary Work

This work was done using the same methods as those employed

by previous workers.   However in this case EDTA solution was

used as the reaction medium to remove any effects of trace metal

catalysis (16, 17).   Data obtained showed the reaction to be

extremely slow.   Only after raising the temperature to $50^{\circ}C$ was

a measurable rate obtained.   The course of reaction was followed

by estimating the free acid produced.   At various time intervals

5mls. of reaction mixture were removed and titrated against 0.01 M

KOH solution using phenolthalein indicator.   The tables show data

from typical kinetic runs.

TABLE 1

$$[K_2S_2O_8] = 0.05 \ M \qquad \text{Temperature} = 50^{\circ}C$$

$$[HCOOH] = 0.025 \ M \qquad \text{Ionic strength} = 0.175 \ M$$

Reaction medium $10^{-3}M$ EDTA solution

Run 8		Run 9		Run 10	
Time (mins)	Vol KOH (mls)	Time (mins)	Vol KOH (mls)	Time (mins)	Vol KOH (mls)
4	0.23	15	0.26	15	0.28
59	0.41	30	0.27	31	0.33
123	9.45	45	0.39	45	0.55
180	12.70	60	0.41	60	0.73
240	13.20	70	0.54	70	1.27
300	13.40	80	2.43	80	3.33
		90	4.41	90	5.01
		95	4.80	99	7.32
		125	11.90		

Plots of volume of KOH used against time were obtained (see figure 3). The plots show the properties of an autocatalytic reaction from which no useful kinetic data could be obtained. These results could be interpreted as a reaction between potassium peroxodisulphate and the EDTA complex which would eventually release enough metal ions to act as a catalyst for the oxidation of the formate ion.

(Figure 3)

Run 8 —o———o—
Run 9 —x———x—
Run 10 —+———+—
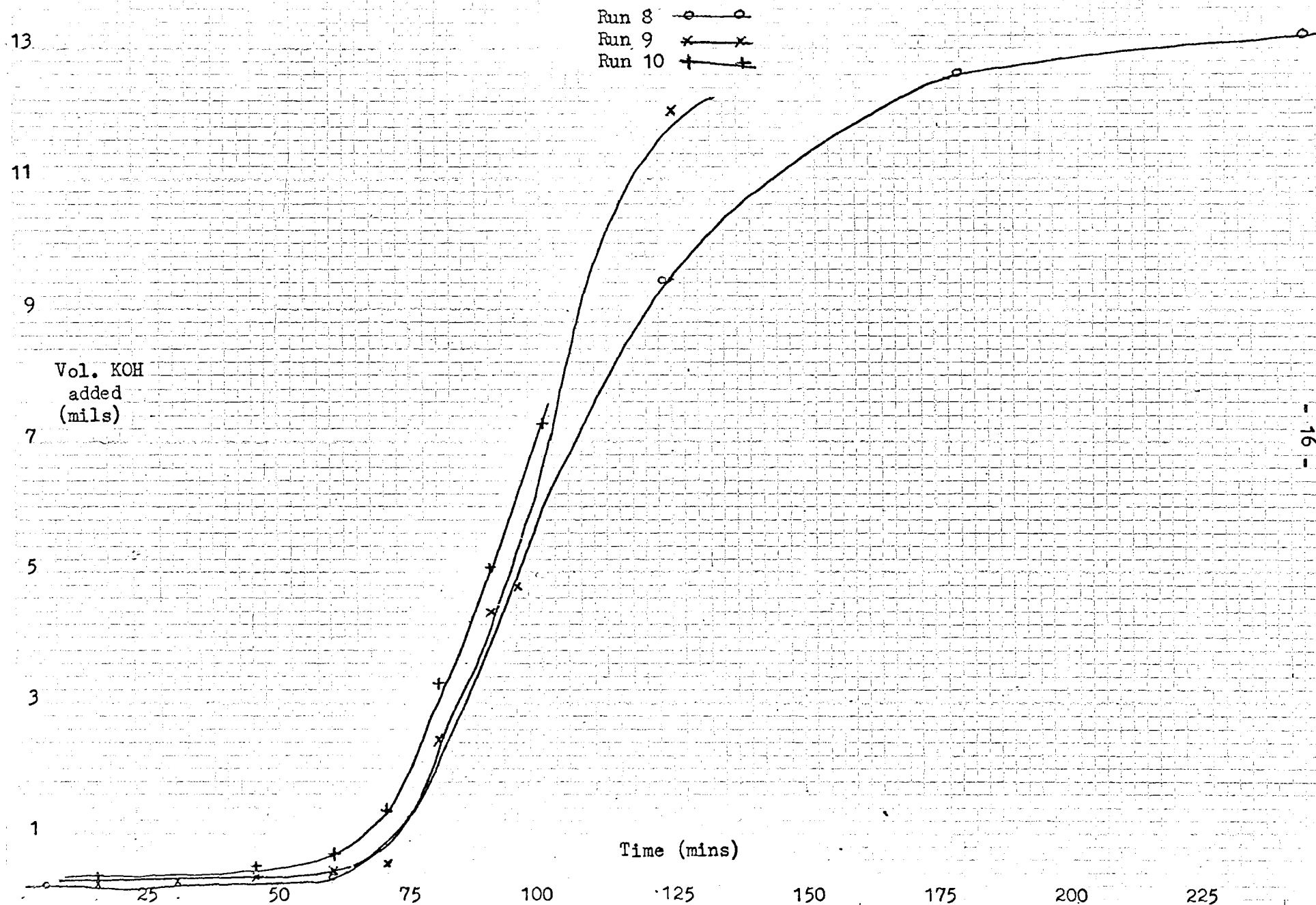
2. pH Changes during reaction

The reaction was followed by noting the change of pH with
time throughout the reaction. The use of a recorder coupled to
the pH meter enabled continuous readings of pH to be obtained
up to 100% reaction. As expected the pH changed rapidly at
first and then more slowly as the reaction mixture became more acidic.

First order rate constants were calculated for the reaction
using values of pH at various times as a measure of the extent
of reaction. The relationship :-

$$k = \frac{2.303}{t} \log \frac{PH - PH_o}{PH - PH_t}$$

$$\text{or} \quad k = \frac{2.303}{t} \log \frac{PH_o - PH}{PH_t - PH}$$

was used to obtain rate constants for the reaction. Data obtained
by this method is shown in the following table.

TABLE 2

| $[K_2S_2O_8]$ | = 0.05 M | | Temperature | = $30^\circ C$ | |
| $[HCOOK]$ | = 0.05 M | | Ionic Strength | = 0.2 M | |

Time (t) (mins)	pH	$pH_t - pH$	$\text{Log} \dfrac{H_o - H}{pH_t - pH}$	$K \times 10^{-3}$ (min^{-1})
0	7.00	4.00	-	-
15	5.91	2.91	0.138	21.60
30	5.52	2.52	0.201	15.40
45	5.28	2.28	0.246	12.60
60	5.12	2.12	0.276	10.60
90	4.85	1.85	0.335	8.57
120	4.61	1.61	0.395	7.58
150	4.40	1.40	0.456	7.01
180	4.16	1.16	0.538	6.87
210	3.96	0.96	0.620	6.79
240	3.80	0.80	0.699	6.71
	3.00	-	-	-

Other kinetic runs gave similar data.

For a first order reaction the data in the 'k' column should be constant. It can be seen from the table, however, that the value of k is decreasing with increasing time. This could be interpreted as, either the reaction is not first order, or the first order rate constant decreases with an increase in acidity. Later work shows that the reaction is first order, and thus these results indicate a dependence of the reaction rate on pH.

3. Rate at constant pH Manual pH-stat

The reaction rate at a constant pH was determined using a non-buffer pH-stat method, similar to that used by Kershaw and Prue (19) in a study of the thermal decomposition of peroxodisulphate ions. As hydrogen ions are produced in the course of the reaction the pH will gradually decrease. A continuous addition of standard KOH solution was used to maintain a constant pH in the reaction mixture. By noting the volumes of alkali added at various time intervals, the course of the reaction at a constant pH was followed. The alkali was added manually from a burette. As the total volume of reaction mixture was 150 mls. (75 mls. 0.1 M $K_2S_2O_8$ and 75 mls. 0.1 M HCOOK), and the volume of alkali used at 100% reaction was only 5 mls., the effect of volume change during reaction can be neglected. (Volume change at 100% reaction is 3.3%).

The rate was measured over a pH range from pH 4.0 to pH 8.0, at a temperature of 35°C. First order rate constants were calculated using the relationship :-

$$k = \frac{2.303}{t} \log \frac{a - x_o}{a - x}$$

where :- a = Vol of KOH used at t =

x_o = Vol of KOH used at t = 0

x = Vol of KOH used at time t

Rate constants some of which were obtained by computer calculation are shown in the following table, (see appendix 2). A plot of rate constant against pH was prepared (Fig. 4).

TABLE 3

$[S_2O_8^{2-}]$ = 0.05 M   Temperature = $35^{\circ}C$

$[HCOO^{1-}]$ = 0.05 M   Ionic strength = 0.2 M

$[KOH]$ = 1.0 M

pH	Run No.	Rate const. x 10^3 (mins^{-1})
4.0	1	4.2
4.0	2	4.9
5.0	1	7.0
5.0	2	7.2
5.0	3	7.0
5.5	1	10.5
5.5	2	10.8
6.0	1	12.4
6.0	2	11.9
6.5	1	14.4
6.5	2	13.1
6.5	3	11.0
7.0	1	8.3
7.0	2	9.6
7.0	3	8.8
8.0	1	5.9
8.0	2	5.6
8.0	3	4.8

(Figure 4)
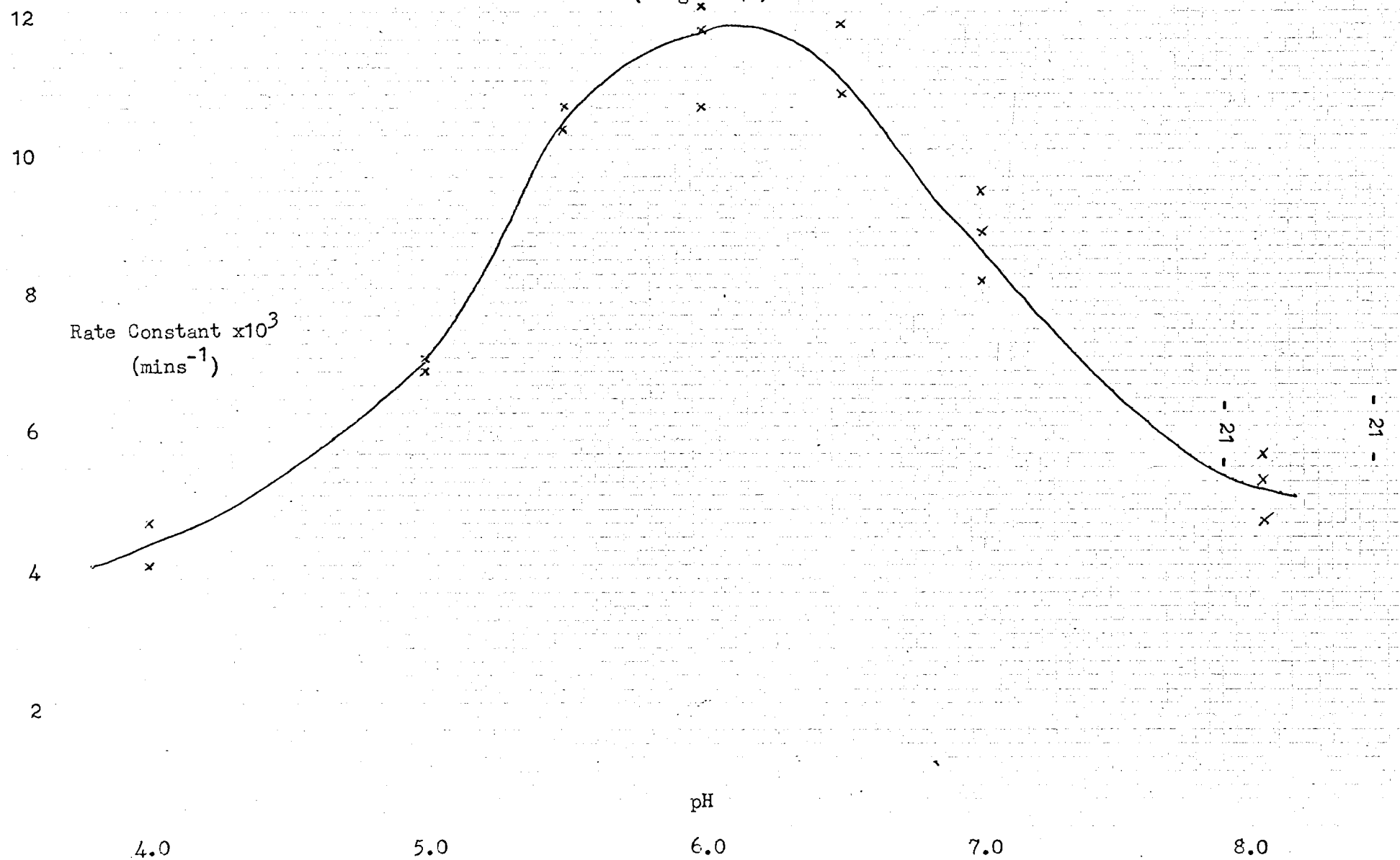
4. Rate at constant pH. Automatic pH-stat

Using the apparatus described previously (p. 8), it was
possible to obtain plots of vol. KOH added against time. From
this data plots of Log $\dfrac{a}{(a - x)}$ against time were made,

where a = Vol. KOH at 100% reaction

x = Vol. KOH at time = t

Rate constants given by the relationship :-

$$k = \dfrac{2.303}{t} \quad Log \quad \dfrac{a}{(a - x)}$$

were obtained from the slope of the plots of Log $\dfrac{a}{(a - x)}$ against
time.

A. Effect of varying the pH

The rate was evaluated at a number of pH values. The range
covered was from pH 4 to pH 8 at intervals of 0.05 pH units. Data
obtained is shown in the following tables. Unless otherwise
specified all data was obtained at $35^{\circ}C$.

A plot of rate constant against pH was prepared (Fig. 5).

TABLE 3

(i) pH = 4.00

$[S_2O_8^{2-}]$ = 0.05 M   Temperature   = 35°C

$[HCOO^{1-}]$ = 0.05 M   Ionic strength   = 0.2 M

$[KOH]$ = 1.0 M

Time(t) (mins)	Vol KOH (x) % of 0.5ml.	(a-x)	Log $\frac{a}{(a-x)}$	K x 10^{-3} (min^{-1})
16	10.00	75.0	0.055	7.91
32	17.4	67.6	0.100	7.17
48	25.0	60.0	0.152	7.28
64	32.0	53.0	0.206	7.41
80	38.0	47.0	0.258	7.66
96	43.0	42.0	0.308	7.37
112	47.4	37.6	0.355	7.30
120	51.5	33.8	0.404	7.26
144	55.2	29.8	0.456	7.28
160	58.6	26.4	0.508	7.32
176	61.8	23.2	0.565	7.39
192	64.2	20.8	0.612	7.34
208	66.4	18.6	0.660	7.31

Mean of last 10   = 7.38

Results of other kinetic run

Run No.   2

Temperature   =   35°C

Rate Const.   7.55

(min^{-1} x 10^3)

TABLE 4

(ii) pH = 5.00

$\left[S_2O_8^{2-}\right]$ = 0.05 M   Temperature   = 35°C

$\left[HCOO^{1-}\right]$ = 0.05 M   Ionic strength   = 0.2 M

$\left[KOH\right]$ = 1.0 M

Time (t) (mins)	Vol KOH (x) (% of 0.5ml)	(a-x)	Log $\frac{a}{(a-x)}$	Rate Const (k) (mins^{-1}x10^3)
16	11.2	83.8	0.054	7.76
32	21.4	73.6	0.111	7.99
48	30.6	64.4	0.169	8.11
64	38.6	55.4	0.234	8.42
80	45.8	49.2	0.286	8.24
96	52.0	43.0	0.344	8.25
112	57.2	37.8	0.400	8.22
128	62.0	33.0	0.459	8.25
144	66.4	28.6	0.521	8.32
160	70.0	25.0	0.580	8.35
176	73.0	22.0	0.635	8.30
192	75.8	19.4	0.690	8.21
208	78.2	16.8	0.753	8.34

Mean of last 9 = 8.27 x 10^{-3} (mins^{-1})

Results of other kinetic runs

Run No.	=	2	3	4
Rate Const. (min^{-1} x 10^3)	=	9.22	8.54	8.81

TABLE 5

(iii) pH = 5.5

$\left[S_2O_8^{2-} \right]$ = 0.05 M   Temperature = 35°C

$\left[HCOO^{1-} \right]$ = 0.05 M   Ionic strength = 0.2 M

$\left[KOH \right]$ = 1.0 M

Time (t) (mins)	Vol KOH (x) (% of 0.5ml)	(a-x)	Log $\frac{a}{(a-x)}$	Rate Const (k) $(min^{-1} \times 10^3)$
16	5.8	51.2	0.069	9.92
32	16.8	43.2	0.143	10.64
48	23.4	36.6	0.215	10.80
64	29.2	30.8	0.290	10.44
80	34.2	25.8	0.367	10.56
96	38.2	21.8	0.440	10.54
112	41.8	18.2	0.518	10.66
128	44.8	15.2	0.596	10.72
144	47.0	13.0	0.665	10.62
160	49.0	11.0	0.737	10.60
176	50.6	9.6	0.808	10.58
192	52.0	8.0	0.876	10.50

Mean of last 11 = 11.48 x 10^{-3} (min^{-1})

Results of other kinetic runs

Run No.	=	2	3	4
Rate Const.	=	8.53	9.10	11.95

$(min^{-1} \times 10^3)$

TABLE 6

(iv) pH = 6.0

$\left[S_2O_8^{2-}\right]$ = 0.05 M   Temperature = $35^{\circ}C$

$\left[HCOO^{1-}\right]$ = 0.05 M   Ionic strength = 0.2 M

$\left[KOH\right]$ = 1.0 M

Time (t) (mins)	Vol KOH (x) (% of 0.5ml)	(a-x)	Log $\frac{a}{(a-x)}$	Rate Const.(k) $(min^{-1}x10^{-3})$
16	17.8	72.2	0.096	13.82
32	21.2	58.8	0.185	13.42
48	41.4	48.4	0.269	12.92
64	50.4	39.0	0.356	12.80
80	57.6	32.4	0.444	12.78
96	63.4	26.4	0.533	12.78
112	68.4	21.6	0.619	12.72
128	72.8	17.4	0.714	12.86
144	75.8	14.2	0.802	12.83
160	78.4	11.6	0.890	12.80
176	80.6	9.4	0.981	12.84
192	82.4	7.6	1.073	12.88
208	84.0	6.0	1.176	13.01

Mean of last = 12.82×10^{-3} $(min.^{-1})$

Results of other kinetic runs

Run No.	=	2	3	4
Rate Const. $(min^{-1} \times 10^3)$	=	12.4	13.1	12.1

TABLE 7

(v) pH = 6.5

$[S_2O_8^{2-}]$ = 0.05 M   Temperature = $35^\circ C$

$[HCOO^{1-}]$ = 0.05 M   Ionic strength = 0.2 M

$[KOH]$ = 1.0 M

Time (t) (mins)	Vol KOH (x) (% of 0.5ml)	(a-x)	Log $\frac{a}{(a-x)}$	Rate Const.(k) $(min^{-1} x10^3)$
16	13.2	62.8	0.083	11.92
32	23.6	52.4	0.162	11.66
48	32.2	43.8	0.239	11.46
64	39.2	36.8	0.315	11.88
80	45.2	30.8	0.392	11.28
96	49.8	26.2	0.463	11.10
112	54.0	22.0	0.539	11.08
128	57.4	18.6	0.612	11.02
144	60.2	15.8	0.683	10.90
160	62.8	13.2	0.760	10.94
176	65.0	11.0	0.840	10.98
192	66.8	9.2	0.918	10.18

Mean of last 9 = 11.05×10^{-3} (min^{-1})

Results of other kinetic runs

Run No. =	1	2	3	4	5	6
Rate Const. = $(min^{-1} \times 10^3)$	10.84	11.35	10.49	11.25	12.95	12.35

TABLE 8

(vi) pH = 7.0

$\left[S_2O_8{}^{2-}\right]$ = 0.05 M   Temperature = $35^{\circ}C$

$\left[HCOO^{1-}\right]$ = 0.05 M   Ionic strength = 0.2 M

$\left[KOH\right]$ = 1.0 M

Time (t) (mins)	Vol KOH (x) (% of 0.5ml)	(a-x)	Log $\frac{a}{(a-x)}$	Rate Const.(k) $(min^{-1} \times 10^3)$
8	9.0	91.0	0.041	11.80
24	25.4	74.6	0.172	12.18
40	36.2	63.8	0.195	11.22
56	45.2	54.8	0.261	10.72
72	53.0	47.0	0.320	10.48
88	60.0	40.0	0.398	10.44
104	65.8	34.2	0.466	10.32
120	70.8	29.2	0.535	10.26
136	75.2	24.8	0.606	10.34
152	79.0	21.0	0.678	10.54
168	82.4	17.6	0.755	10.76
184	85.6	14.4	0.842	10.92
200	88.4	11.6	0.936	10.26
216	90.6	9.4	1.027	10.28

Mean of last 11 = 10.48×10^{-3} (min^{-1})

Results of other kinetic runs

Run No. =	1	2	3
Rate Const. =	10.2	10.3	10.4

$(min^{-1} \times 10^3)$

TABLE 9

(vii)   pH   = 7.5

$[S_2O_8^{2-}]$ = 0.05 M   Temperature $=35^{\circ}C$

$[HCOO^{1-}]$ = 0.05 M   Ionic strength   =0.2 M

$[KOH]$ = 1.0 M

Time (t) (mins)	Vol KOH (x) (% of 0.5ml)	(a-x)	Log $\frac{a}{(a-x)}$	Rate Const.(k) $(min^{-1}x10^3)$
16	7.6	107.4	0.031	4.46
32	17.4	97.6	0.073	5.25
48	27.6	87.4	0.119	5.71
64	37.6	77.4	0.173	6.22
80	46.6	68.4	0.226	6.51
96	54.8	60.2	0.271	6.50
112	62.2	52.8	0.338	6.94
128	68.6	46.4	0.395	7.11
144	74.4	40.6	0.453	7.25
160	79.4	35.6	0.510	7.34
176	83.6	31.4	0.564	7.38
192	87.2	27.8	0.617	7.41
208	90.0	25.0	0.663	7.34
224	93.4	21.6	0.727	7.48

Mean of last 10 = 7.12 x 10^{-3} (min^{-1})

Results of other kinetic runs

Run No.	=	1	2	3
Rate Const. $(min^{-1} x 10^3)$	=	7.12	7.96	7.49

TABLE 10

(vii) pH = 8.0

$\left[S_2O_8^{2-}\right]$ = 0.05 M   Temperature   = $35^{\circ}C$

$\left[HCOO^{1-}\right]$ = 0.05 M   Ionic strength = 0.2 M

$\left[KOH\right]$ = 1.0 M

Time (t) (mins)	Vol KOH (x) (% of 0.5ml)	(a-x)	Log $\frac{a}{(a-x)}$	Rate Const.(k) $(min^{-1} \times 10^3)$
20	8.6	91.4	0.039	4.49
40	17.9	82.2	0.085	4.89
60	26.4	73.6	0.133	5.11
80	34.2	65.8	0.182	5.24
100	41.6	58.4	0.234	5.39
120	48.4	51.6	0.286	5.48
140	54.2	45.8	0.339	5.57
160	59.4	40.6	0.391	5.62
180	63.8	37.2	0.429	5.49
200	67.8	32.2	0.492	5.66
220	71.4	28.6	0.544	5.70
240	74.4	25.6	0.592	5.68
260	77.2	22.8	0.642	5.68
280	79.4	20.6	0.686	5.64
300	80.8	19.2	0.717	5.51
320	82.4	17.6	0.775	5.44

Mean of last 12 = 5.57 x 10^{-3} (min^{-1})

Results of other kinetic runs

Run No.   = 1   2   3

Rate Const. = 5.75   5.57   5.44

$(min^{-1} \times 10^3)$

(Figure 5.)

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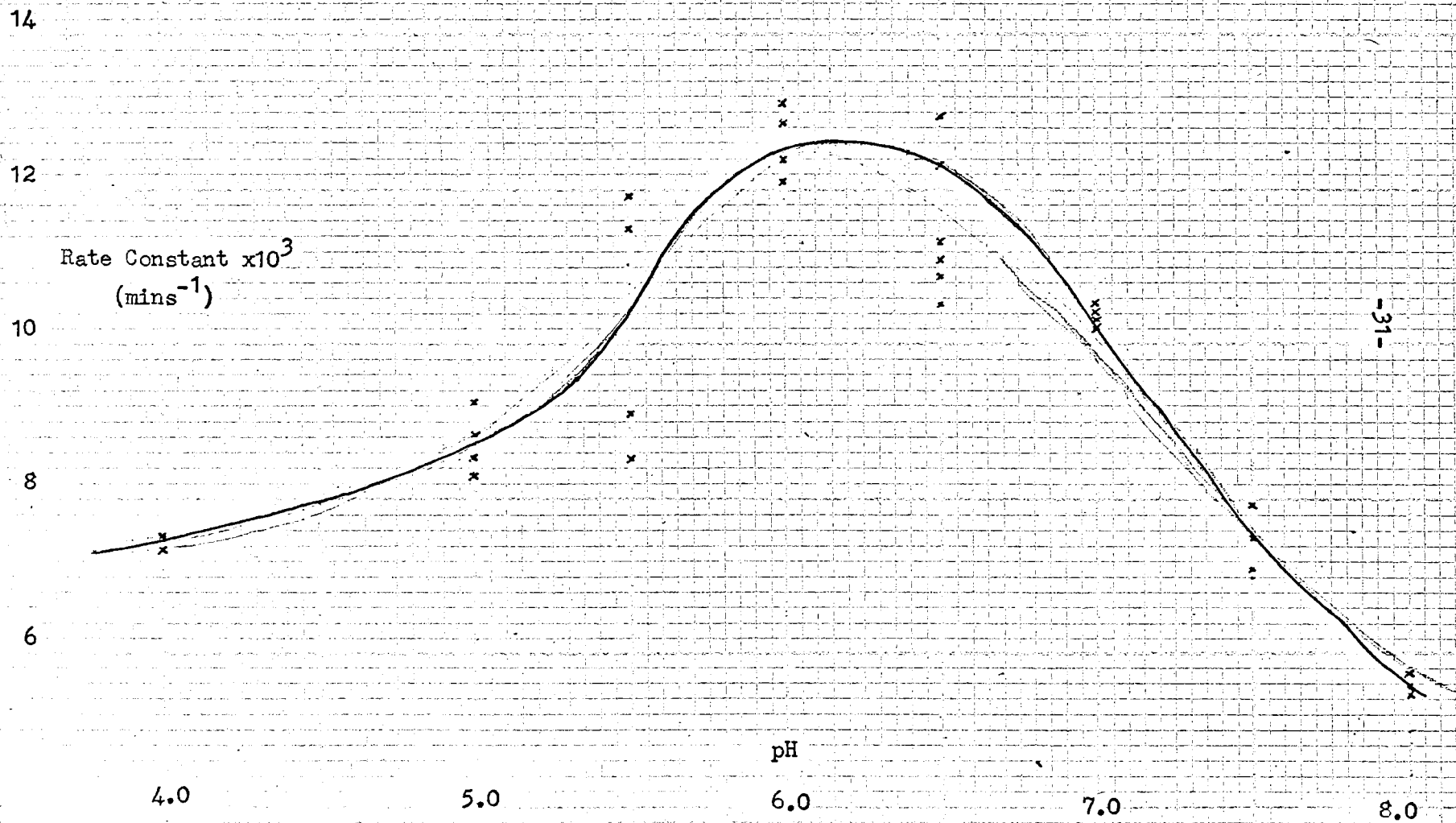
B. Effect of varying the $K_2S_2O_8$ concentration

A series of kinetic runs were performed at different
concentrations of peroxodisulphate ion. The concentrations
used were 0.05, 0.0375 and 00.025 M. The ionic strength of
the reaction mixture was maintained at a constant of 0.2 M by
the addition of calculated volumes of 0.2 M potassium sulphate
solution. Potassium sulphate is used as for this reaction it
should be an inert electrolyte. The potassium ion is already
present in the reaction mixture and its concentration is therefore
not being affected. The sulphate ion is produced by the reaction
and there is no evidence for any specific inhibitory or
catalytic effects by this ion. Hence its addition should not
effect the reaction rate. The maintenance of a constant ionic
strength is necessary to eliminate any primary salt effects.
Any changes in the reaction rate between different concentrations
of the peroxodisulphate ion would be caused by the dependence
of reaction rate on the concentration of this ion and not by
any salt effects. If the ion strength was not constant
throughout, changes in reaction rate could arise from either or
both of these causes.

In the present work the course of reaction was followed by
noting the volume of standard alkali added to maintain a constant
pH in the reaction mixture. At different concentrations of the
peroxodisulphate ion, different concentrations of potassium
hydroxide were used at a peroxodisulphate ion concentration of
0.05 M 1.0 M KOH was used; at $\left[S_2O_8^{2-} \right]$ = 0.0375 M 0.75 M KOH

was used; and at $\left[S_2O_8{}^{2-} \right]$ = 0.025 M 0.50 M KOH was used.

Thus if the reaction was first order in peroxodisulphate ion

when the reaction rate and hence the free acid production rate

was halved by halving the peroxodisulphate ion concentration,

the volumes of alkali used at any time should be the same, because

the KOH concentration had also been halved. The reaction rate

would in fact appear to be unchanged. This is what was observed.

All experiments were conducted at a temperature of 35°C

and a pH of 8.0. Half lives were obtained from the plots of

Vol KOH against time. When not quoted in a table all rate

constants were evaluated from the slope of the plot of Log $\frac{a}{(a-x)}$

against time, using the relationship :-

Rate Constant = 2.303 x Slope

RESULTS

TABLE 11

$$\left[S_2O_8^{2-} \right] = 0.05 \text{ M} \qquad \left[KOH \right] = 1.0 \text{ M}$$

$$\left[HCOO^{1-} \right] = 0.05 \text{ M} \qquad \left[K_2SO_4 \right] = 0.0 \text{ M}$$

Ionic strength = 0.2 M $\qquad$ a = 100

Time (t) (mins)	Vol KOH (x) (% of 0.5ml)	(a-x)	Log $\frac{a}{(a-x)}$	Rate Const. k x 10^3 (min^{-1})
20	8.6	91.4	0.039	4.49
40	17.8	82.2	0.085	4.89
60	26.4	73.6	0.133	5.11
80	34.2	65.8	0.182	5.24
100	41.6	58.4	0.234	5.39
120	48.4	51.6	0.286	5.48
140	54.2	45.8	0.339	5.57
160	59.4	40.6	0.391	5.62
180	63.8	37.2	0.429	5.49
200	67.8	32.2	0.492	5.66
220	71.4	28.6	0.544	5.70
240	74.4	25.6	0.592	5.68
260	77.2	22.8	0.642	5.68
280	79.4	20.6	0.686	5.64
300	80.8	19.2	0.717	5.51
320	82.4	17.6	0.755	5.44

Average of last 12 $\qquad$ 5.57

Half life $\qquad$ 125 mins.

Results of other kinetic runs at $\left[S_2O_8^{2-} \right] = 0.05$ M

Run No.	1	2	3
Rate Const. (k) x 10^3 (min^{-1})	5.57	5.75	5.44
Half Life ($t_{\frac{1}{2}}$) (mins)	127	130	145

Mean Half Life = 130 minutes

TABLE 12

$$[S_2O_8^{2-}] = 0.025 \text{ M} \qquad [KOH] = 0.50 \text{ M}$$

$$[HCOO^{1-}] = 0.05 \text{ M} \qquad [K_2SO_4] = 0.025 \text{ M}$$

Ionic strength = 0.2 M $\qquad$ a = 95

Time (t) (mins)	Vol KOH (x) (% of 0.5ml)	(a-x)	$\text{Log}\frac{a}{(a-x)}$	Rate Const. x 10^3 (min^{-1})
40	18.0	77.0	0.091	5.23
80	33.8	61.3	0.191	5.49
120	46.0	49.0	0.288	5.52
160	56.2	38.8	0.389	5.60
200	64.2	30.8	0.489	5.63
240	70.6	24.4	0.591	5.66
280	75.4	19.6	0.686	5.64
320	79.2	15.8	0.780	5.61
360	82.2	12.8	0.871	5.57
400	84.6	10.4	0.961	5.53

Mean of last 8 = 5.59 x 10^{-3} (mins^{-1})

Half Life = 120 (mins.)

Results of other kinetic runs at $[S_2O_8^{2-}]$ = 0.025 M

Run. No.	1	2	3	4
Rate Const. (k) x 10^3 (mins^{-1})	5.75	5.53	5.83	5.66
Half Life (mins)	120	135	125	130

Mean Half Life = 127.5 mins.

TABLE 13

$$\left[S_2O_8^{2-}\right] = 0.0375 \text{ M} \qquad \left[KOH\right] = 0.75 \text{ M}$$

$$\left[HCOO^{1-}\right] = 0.05 \text{ M} \qquad \left[K_2SO_4\right] = 0.125 \text{ M}$$

Ionic strength $= 0.2$ M

Run No.	1	2	3	4
Rate Const. (k) x 10^3 (mins^{-1})	5.48	5.10	5.11	6.05
Half Life ($t_{1/2}$) (mins)	120	130	130	110

Mean Half Life $=$ 122.5 mins.

A characteristic of first order reactions is the independence of the half life on the initial concentration. At the three concentrations used the half lives are the same within $\pm$ 10 minutes.

Using the formula :-

$$n = 1 + \frac{\log t' - \log T}{\log a - \log a'}$$

where   n = order of reaction with respect to the peroxodisulphate ion.

a & a' = initial concentrations of peroxodisulphate ion.

t & t' = corresponding half lives.

Applying this formula to data from tables 1 and 2 :-

$$n = 1 + \frac{\log 127 \pm 10 - \log 130 \pm 10}{\log 0.05 - \log 0.025}$$

$$= 1 + 0/\log \frac{0.05}{0.025}$$

$$= 1$$

Data from tables 1 & 3 and tables 2 & 3 give similar results.

Comparison of tables 1 & 2 shows that the volume of alkali used at any particular time is the same in each case, within the experimental error. As the alkali concentration was halved when the peroxodisulphate ion concentration was halved, the rate of acid production in the reaction must also have been halved. Hence the reaction is first order in the peroxodisulphate ion.

C. Effect of varying the HCOOK concentration

A series of experiments were performed at a constant peroxodisulphate ion concentration of 0.05 M while the formate ion concentration was changed. The formate ion concentrations used were 0.05, 0.0375 and 0.025 M. Again the total ionic strength of the reaction mixture was maintained at a constant value of 0.2 M by the addition of calculated volumes of 0.1 M potassium sulphate solution.

All kinetic runs were made at pH 8.0 and 35°C. Data obtained is shown in the following tables.

Table 14 $[\text{HCOOK}]$ = 0.05 M

Run	Half Life
1	140
2	130
3	145
Mean	= 143 minutes

Table 15 $[\text{HCOOK}]$ = 0.0375 M

Run	Half Life
1	120
2	125
3	110
Mean	= 118 minutes

Table 16 $[\text{HCOOK}]$ = 0.025 M

Run	Half Life
1	80
2	70
3	75
Mean =	75 minutes

The order of reaction with respect to the formate ion was determined from the previous relationship :-

$$n = 1 + \frac{\log t'/t}{\log a/a'}$$

The data from (1) & (2), (1) & (3), (2) & (3), gave :-
n = 0.175, 0.079, -0.12 respectively. Thus indicating the reaction is of zero order with respect to the formate ion.

D. Effect of varying the temperature

The reaction was studied over a range of temperatures from $30^\circ C$ to $50^\circ C$ at intervals of $5^\circ C$. A plot of $-\log k$ against $1000/T^\circ A$ was obtained. From the slope of this plot a value for the energy of activation was obtained. The Arrhenius equation for the effect of temperature on rate constant can be expressed in the form :-

$$k = PZ\exp(-E_a/RT)$$

where
$$k = \text{Rate Constant}$$
$$PZ = \text{Frequency Factor}$$
$$E_a = \text{Energy of Activation}$$
$$R = \text{Universal Gas Constant}$$
$$T = \text{Absolute Temperature}$$

Therefore

$$\text{Log } k = \text{Log } PZ - E_a/2.303RT$$
$$= \text{Log } PZ - E_a/4.576 \times 1000/T$$

Hence if a plot of $-\text{Log } k$ against $1000/T$ is obtained the energy of activation can be evaluated from the relationship :-

$$E_a = 4.576 \times \text{Slope}$$

Results of experiments to evaluate the energy of activation are shown in the following table.

(i)   Temperature = 30°C = 303°A : $1000/T^\circ$A = 3.295

Run No.	1	2	3	4
Rate Const. (k) x 10^3	4.01	3.74	3.55	4.17
- Log k	2.40	2.43	2.45	2.38

(ii)   Temperature = 35°C = 308°A : $1000/T^\circ$A = 3.245

Run No.	1	2	3
Rate Const. (k) x 10^3	5.45	5.55	5.75
- Log k	2.267	2.255	2.240

(iii)   Temperature = 40°C = 313°A : $1000/T^\circ$A = 3.195

Run No.	1	2	3	4
Rate Const. (k) x 10^3	7.05	8.96	6.05	6.11
- Log k	2.15	2.05	2.22	2.21

(iv)   Temperature = 45°C = 318°A : $1000/T^\circ$A = 3.145

Run No.	1	2	3	4
Rate Const. (k) x 10^3	9.72	9.79	10.36	9.33
- Log k	2.01	2.01	1.98	2.03

(v)   Temperature = 50°C = 323°A : $1000/T^\circ$A = 3.095

Run No.	1	2	3	4
Rate Const. (k) x 10^3	13.92	13.12	14.00	14.22
- Log k	1.86	1.88	1.85	1.85

From this data a plot of - log k against 1000/T was obtained and the energy of activation evaluated.   It was found to be 11.9 kcals. $\pm$ 0.2K cals.   (See figure 6)

The value of PZ, the frequency factor was calculated from a point lying on the plot of log k against $1000/T^{\circ}A$, using the relationship :-

$$Log\ k = Log\ PZ - E_a/4.576 \times 1000/T^{\circ}A$$

$$Log\ PZ = Log\ k + E_a/4.576 \times 1000/T^{\circ}A$$

$$= 2.396 + 8.570$$

$$Log\ PZ = 6.176$$

$$PZ = 1.495 \times 10^6\ min^{-1}.$$

Entropy of activation

From $303^{\circ}A$ to $323^{\circ}A$ the experimental rate constant is given by:

$$k = 1.495 \times 10\ exp\ (-11.9/RT)\ min^{-1}$$

$$= 2.49 \times 10^4\ exp\ (-11.9/RT)\ sec^{-1}$$

$$= PZ\ exp\ (-E_a/RT)$$

The rate constant can also be expressed as:-

$$k = KT/h\ exp\ (\Delta S^{\ddagger}/R)\ exp\ (-H^{\ddagger}/RT)$$

Also $E_a = H^{\ddagger} + RT$

where $H^{\ddagger}$ is the entropy of activation.

Thus:-

$$k = e\ KT/h\ exp\ (\Delta S^{\ddagger}/RT)\ exp\ (-E_a/RT)$$

From these two expressions for rate constant the relationship

$$PZ\ exp\ (-E_a/RT) = e\ KT/h\ exp\ (\Delta S^{\ddagger}/R)\ exp\ (-E_a/RT)$$

can be obtained.

Thus: $$PZ = e\ KT/h\ exp\ (\Delta S^{\ddagger}/R)$$

$$2.49 \times 10^4 = (2.713) \times 6.31 \times 10^{12}\ exp\ (\Delta S^{\ddagger}/R)$$

$$exp(\Delta S^{\ddagger}/R) = 1.45 \times 10^{-9}$$

$\Delta S^{\ddagger}/ R = 2.303 \log (1.45 \times 10^{-9})$

$= -2.303 \times 8.839$

$\Delta S^{\ddagger} = -2.303 \times 8.839 \times 1.98$

$\Delta S^{\ddagger} = -40.3 \text{ cals gn. mole}^{-1} {}^{\circ}C^{-1}$

(Figure 6)
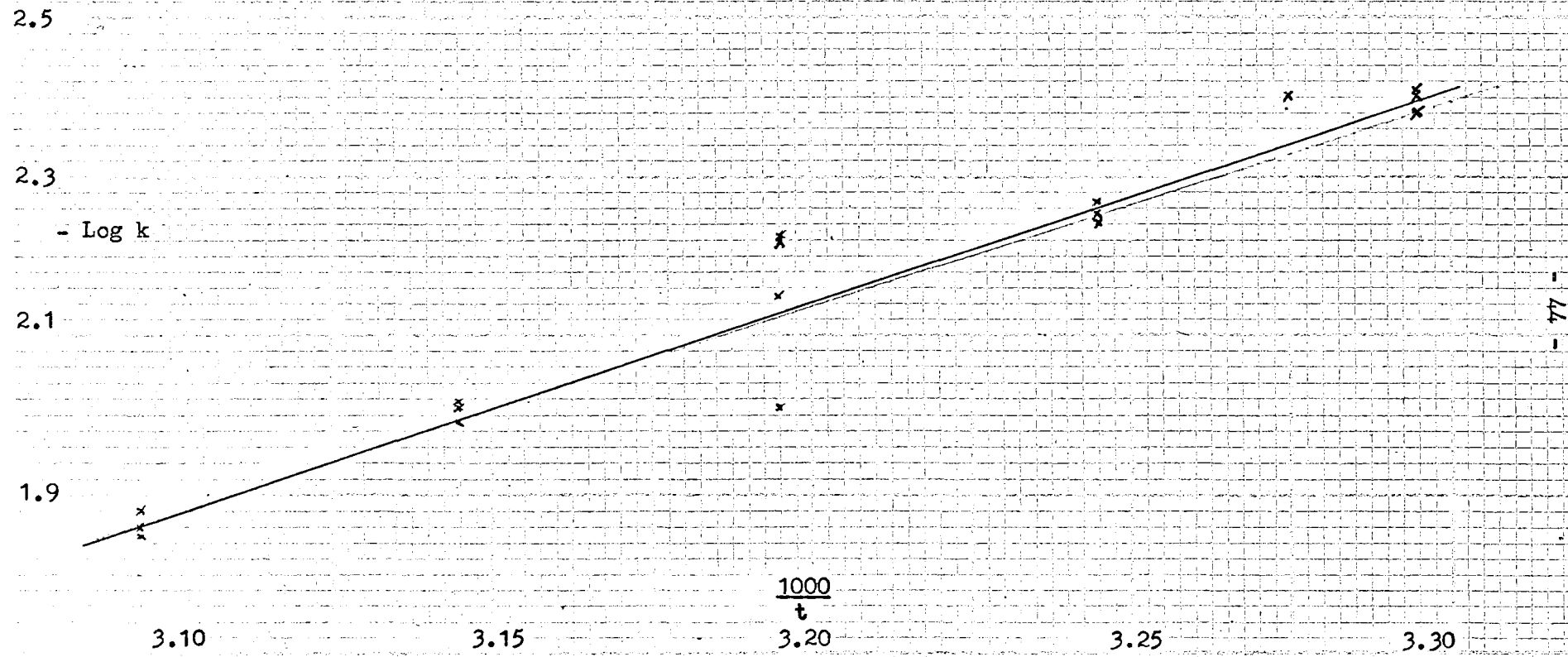
5. Cupric ion catalysed reaction

The catalytic effects of added cupric ions on the peroxodisulphate/formate reaction was studied at PH 5.0 and $30^\circ C$. Solutions of A.R. copper sulphate were prepared in potassium formate solution and used for reaction with potassium peroxodisulphate soln. The observed pseudo first order rate constants were determined at cupric ion concentrations of 2.5×10^{-4}, 3.75×10^{-4}, 5.0×10^{-4}, and $6.25 \times 10^{-4} M$. Rate constants at each of these concentrations were evaluated by the usual method. Results obtained are shown in the following table. A plot of observed rate constant (k_{obs}) against Cu^{2+} was prepared. (Fig. 4)

TABLE 18

$$\left[S_2O_8^{2-} \right] = 0.05 \text{ M} \qquad \text{Temperature} \qquad = 30^{\circ}C$$

$$\left[HCOO^{1-} \right] = 0.05 \text{ M} \qquad \text{Ionic strength} \qquad = 0.2 \text{ M}$$

$$\left[KOH \right] \quad = 1.0 \text{ M}$$

(i) $\left[Cu^{2+} \right] = 2.5 \times 10^{-4}$

Run No.	1	2	3
Rate Const. x 10^3 (mins^{-1})	17.3	17.2	17.75

(ii) $\left[Cu^{2+} \right] = 3.75 \times 10^{-4}$

Run No.	1	2	3
Rate Const. x 10^3 (mins^{-1})	20.5	20.8	20.0

(iii) $\left[Cu^{2+} \right] = 5.0 \times 10^{-4}$

Run No.	1	2	3
Rate Const. x 10^3 (mins^{-1})	23.0	24.2	23.8

(iv) $\left[Cu^{2+} \right] = 6.25 \times 10^{-4}$

Run No.	1	2	3
Rate Const. x 10^3 (mins^{-1})	26.8	26.9	27.4

From the table it can be seen that the value of k_{obs} increases with increasing cupric ion concentration. The dependence of k_{obs} on Cu^{2+} can be seen from Fig. 4, where a linear plot of k_{obs} against Cu^{2+} is obtained.

(Figure 7)

Rate Constant x 10^3 (mins^{-1})

Cupric ion concentration x 10^4

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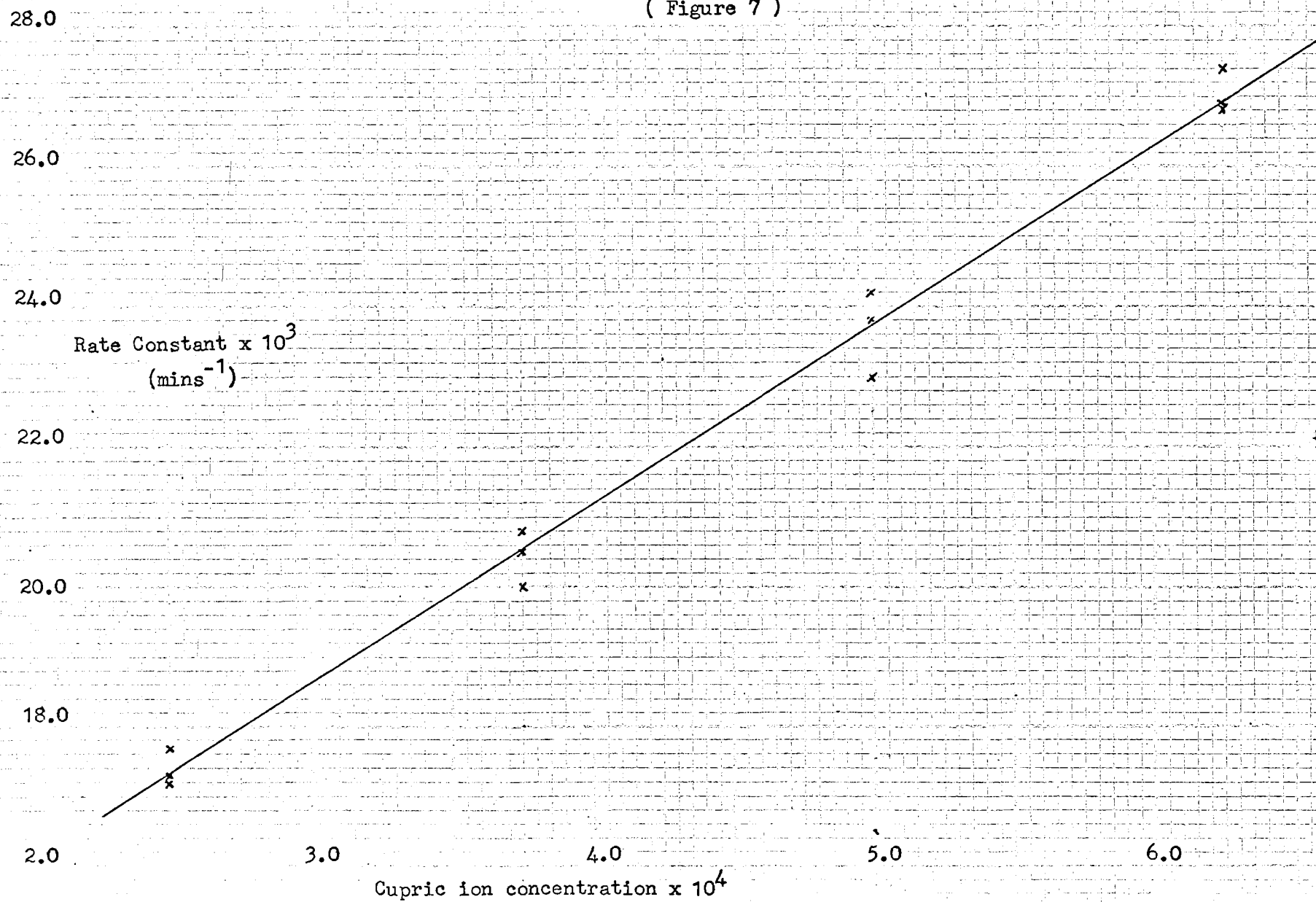
DISCUSSION OF RESULTS

Reaction in EDTA solution

The reaction of the peroxodisulphate ion with a number of reducing agents has been studied in EDTA solution. (16, 17, 18, 20.) The presence of EDTA in the reaction mixture has been used to prevent any variation in reaction rate due to catalysis by traces of metal ions, mainly cupric and argentious ions.

A study of the peroxodisulphate-oxalate reaction by Po and Allen (16), showed the reaction rate to decrease by one third as the EDTA concentration was increased from 0.15×10^{-5} to 2.0×10^{-5} molar. Above 2.0×10^{-5} M no further change was observed. Similar results have been reported for other peroxodisulphate oxidations.

In the present work an EDTA concentration of 1.0×10^{-4} M was used. This is well above the concentration needed to prevent catalysis by metal ions in the work of Po and Allen. However at $35^{\circ}C$ the reaction did not proceed and a temperature of $50^{\circ}C$ was required to obtain a measurable rate. Under these conditions a slow reaction was observed for approximately seventy minutes. Between seventy minutes and three hours the reaction was very rapid, and after this time the reaction was again slow. This behaviour is characteristic of an autocatalytic reaction. There is, however, no evidence for any catalytic effects by any of the products.

It is therefore more likely that this behaviour is caused by a slow reaction between the peroxodisulphate ion and the EDTA complex, which eventually releases a sufficient concentration of metal ions to catalyse the peroxodisulphate-formate reaction. When the reaction was done in distilled water with no EDTA present it proceeded at a measurable rate at 35°C. Also when the reaction was followed to completion there was no evidence of an autocatalytic reaction in the absence of EDTA. It showed characteristics of a normal first order reaction.

Oxidizations by the peroxodisulphate ion are extremely susceptible to catalysis. Ben-Zui and Allen (21) have shown that the method of preparing the reaction vessel has a considerable effect on the rate of the copper II catalysed reaction between peroxodisulphate ions and oxalate ions. They used four different methods of preparation and also employed an inert coating. These gave variations of rate constant from 1.80 x 10^{-4} sec^{-1} to 3.75 x 10^{-4} sec^{-1} and illustrates the extreme sensitivity of this reaction to catalysis.

In work without EDTA no effort was made to prevent background trace ion catalysis. However, the effect of added Cu^{2+} ion on the reaction rate has been studied (see Table 18). The same reaction vessel was used for all kinetic runs. It was prepared for each run by rinsing four times in distilled water. The distilled water used throughout was prepared by distillation in glass apparatus and piped in polythene pipes.

Variation of pH with Time

The reaction between the peroxodisulphate ion and the formate ion has been shown to proceed according to the equation:-
(7)

$$S_2O_8^{2-} + HCOO^{1-} \longrightarrow SO_4^{2-} + HSO_4^{1-} + CO_2$$

As HSO_4^{1-} ions are produced in the reaction to the pH of the reaction mixture must change. Thus the course of reaction can be followed by noting the pH at various times. This was done using a pH-meter and recorder, to provide continuous plots of pH against time. First order rate constants were obtained using the relationship:-

$$k = \frac{2.303}{t} \log \frac{pH_o - pH}{pH_t - pH}$$

Rate constants obtained by this method showed a steady decrease (see Table 2). This result could be interpreted as, either the reaction is not first order, or as a depence of reaction rate on pH. Work at different concentrations of both reacting species has shown the reaction to be first order in the peroxodisulphate ion and zero order in formate ion. Similar decreases in rate constant with time, and hence with pH, were observed by Gupta and Nigam (12) in their work on the silver ion catalysed oxidations of sodium formate and formic acid by peroxodisulphate ions. In the sodium formate reaction, plots of log a/(a-x) against t showed a gradual downward curve, indicating a drop in first order rate constant with time. However when the reaction was studied in 0.1 M H_2SO_4 the plot obtained was linear, but with a much smaller gradient. This indicates constant and lower

values for first order rate constants throughout the reaction.

A study varying the H_2SO_4 concentration showed that, as the

H_2SO_4 concentration increased, the rate constants decreased.

This work, together with the results obtained in the present work,

indicate a marked dependence of both the Ag^{1+} catalysed (12)

and the uncatalysed, reaction rate on pH.

Mechanism

On the basis of data obtained at constant pH, the following

sequence is proposed for the oxidation of formate ions by

peroxodisulphate ions in aqueous solution, over the pH range

from pH 4.0 to pH 8.0.

Initiation:-

$$S_2O_8^{2-} \xrightarrow{k_1} 2\ SO_4^{-} \tag{1}$$

Propogation:-

$$SO_4^{-} + H_2O \xrightarrow{k_2} OH + SO_4^{2-} + H^+ \tag{2}$$

$$OH + HCOO^{1-} \xrightarrow{k_3} HCOO^{\bullet} + OH^{1-} \tag{3}$$

$$HCOO^{\bullet} + S_2O_8^{2-} \xrightarrow{k_4} CO_2 + HSO_4^{1-} + SO_4^{-} \tag{4}$$

Termination:-

$$HCOO^{\bullet} + SO_4^{-} \xrightarrow{k_5} CO_2 + HSO_4^{1-} \tag{5}$$
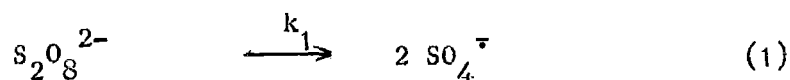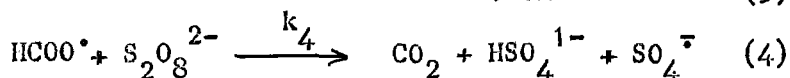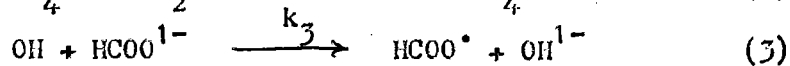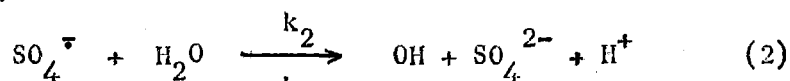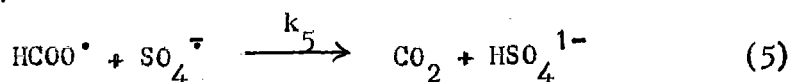
At high acidity (pH = 5-4) there is a considerable concentration

of HCOOH molecules (appendix 3), and an alternation to equation (3)

could be:-

$$OH^{\bullet} + HCOOH \xrightarrow{k_{3a}} H^{\bullet}COO + H_2O \tag{3a}$$
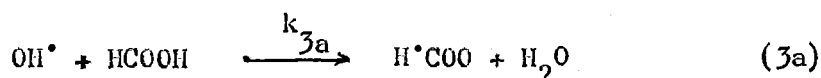
In postulating a mechanism for a first order uncatalysed

oxidating by peroxodisulphate, a major problem is to account for

the increased rate of peroxodisulphate decomposition on the

addition of a reducing agent, when the rate law is independent of the concentration of this substance.

If the primary step is decomposition of peroxodisulphate ions into sulphate free radicals:-

$$S_2O_8^{2-} \longrightarrow 2\ SO_4^{\cdot -} \qquad \text{(Rate determining)}$$
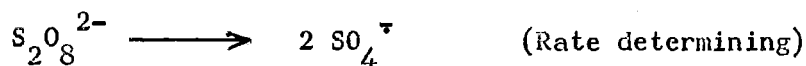
followed by a rapid attack of these on the reducing agent then, for all reducing agents, the rate of oxidation should be the same. This is, however, not observed. (2) In polymerization studies using peroxodisulphate labelled with sulphur - 35 as an initiator, polymer fragments containing radio active sulphate groups have been isolated. (21) This indicates that sulphate free radicles are produced in the decomposition of peroxodisulphate ions. Studies of the effect on reaction rate of varying both the peroxodisulphate ion and the formate ion concentrations, have shown the reaction to be first order in peroxodisulphate ion and zero order in formate ion. Thus the reaction follows the rate law:-

$$-d\left[S_2O_8^{2-}\right]/dt = -d\left[HCOO^{1-}\right]/dt = k_{obs}\left[S_2O_8^{2-}\right]$$

The rate constant observed for this reaction is greater than the rate constant observed for the thermal decomposition of the peroxodisulphate ion. (2) The mechanism proposed is compatible with the observed kinetics. A steady state analysis for this mechanism leads to the rate law:- (see appendix 1)

$$-d\left[S_2O_8^{2-}\right]/dt = (k_1\ k_2\ k_4/k_5)^{\frac{1}{2}}\left[S_2O_8^{2-}\right]$$

which is the observed rate law, where $k_{obs} = (k_1\ k_2\ k_4/k_5)^{\frac{1}{2}}$. Similar mechanisms have been postulated to explain other first order peroxodisulphate oxidations (16, 22), where the reaction rate is independent of the reductant, but varies with the reductant. In all cases this variation must arise from a variation in type and/

or concentration of the reactive radical attacking the peroxodisulphate ion in step 4.

pH dependence

A considerable variation of rate constant with pH was observed for this reaction (see fig 5). Similar variations with pH have been observed for other peroxodisulphate oxidations (16, 22,23). The rate constant rises from pH 4.0 to a maximum at approximately pH 6.5 and then falls off to pH 8.0. Linear plots of log a/(a-x) against t are obtained throughout, indicating a first order reaction over the entire pH range from 4.0 to 8.0. For a change in observed rate constant without a change in order there must be a change in the type of free radical attacking the peroxodisulphate ion in step (4) of the mechanism outlined. In acid solution (pH 4-5) there is a considerable concentration of HCOOH (Appendix 3) and the alternative to step 3 :-

$$OH^{\bullet} + HCOOH \xrightarrow{k_{3a}} H^{\bullet}COO^{-} + H_2O$$
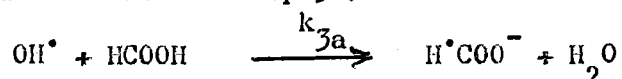
could be operating. However this would not affect the $H^{\bullet}COO^{-}$ radical concentration and thus the pH effects are probably not caused by this. Also step (3) is not a component of the expression for k_{obs}. Thus it is more likely that the pH effects arise from acid-base equilibria involving the generated free radicals. It is proposed that the variation in rate constant is due to the deprotonation of the free radical. A reaction of the type:-

$$X + OH^{-} \rightleftharpoons Y + H_2O$$
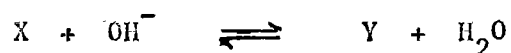
Where X and Y are free radicals.

This type of equilibria has been postulated to explain the dependence of rate constant on pH for the peroxodisulphate

oxidations of oxalate ions (16) and of hypophosphorus acid (22).

The observed increase in rate constant with increasing pH in the region pH 4.0 - pH 6.0 is probably associated with the deprotonation of the protonated $H^{\bullet}COO$ radical:-

$$H^{\bullet}COOH^{+} + OH^{-} \rightleftharpoons H^{\bullet}COO + H_{2}O$$
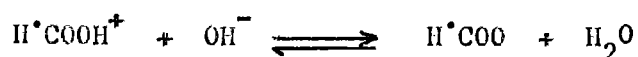
The decrease in observed rate constant from pH 6.5 to pH 8.0 can be ascribed to further deprotonation, producing the $^{\bullet}COO^{-}$ radical.

$$H^{\bullet}COO + OH^{-} \rightleftharpoons {}^{\bullet}COO^{-} + H_{2}O$$
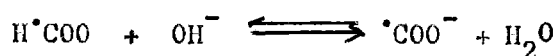
If such is the case, the order of reactivity of the radicals with $S_2O_8^{2-}$ ions must be:-

$$H^{\bullet}COOH^{+} < H^{\bullet}COO > {}^{\bullet}COO^{-}$$
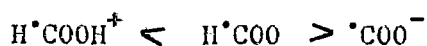
as the $H^{\bullet}COO$ radical increases and then decreases in concentration as the pH is increased.

It is surprising that the positivily charged radical is not the most reactive species. However electrostatic attractive forces may be of only secondary importance in radical-ion interactions.

Ben-Zui (22), noted the similarity of the rate constant against pH curve for the oxidation of hypophosphorus acid, to a titration curve for the neutralization of a weak acid. In this case the postulated weak acid was the $H_2PO_2^{\bullet}$ radical. From this result, he evaluated the pKa for the radical acting as the weak acid. For the $H_2PO_2^{\bullet}$ radical the pKa evaluated was 9.1. This comparison cannot be made in the present work because of the presence of two such acid-base equilibria superimposed, and a maximum rate for the $H^{\bullet}COO$ radical cannot be evaluated. However, if this rate dependence on pH is caused by a neutralization or deprotonation reaction, a plot of rate constant against hydrogen ion concentration should be linear. When the rate constant was plotted against pH

on a log scale reasonable linear plots were obtained, again

suggesting that equilibria of this type are causing the variation

of rate constant with pH. (See fig.8)

Energy of activation:

Kinetic runs were made at pH 8.0 over a temperature range from

30°C to 50°C at intervals of 5°C. Rate constants were obtained

at each temperature and a plot of $-\log$ k against $1000/T^{\circ}A$ was made

(Fg. 6). From this plot the energy of activation for the reaction

was evaluated. The energy of activation was found to be 11.9 ± 0.2

K Cals. The entropy of activation was also determined. A value

of $\overset{-40}{\cancel{24.4}}$ Cals gm mole^{-1} $^{\circ}$C^{-1} was obtained. These values do not

compare well with the values of 21.93 kcals mole^{-1} for potassium

formate and 8.19 k cals mole^{-1} for formic acid, obtained by

Srivastava and Ghosh. (5, 10). However the values obtained by

Srivastava and Ghosh were not obtained at a constant pH. The value

of 11.9 k cals mole^{-1} obtained at pH 8.0 will be the energy of

activation for the reaction between peroxodisulphate ions and

$^{\bullet}CO_2^{-}$ radical ions, while those obtained by Srivastava and Ghosh

would be for the reaction with $H^{\bullet}COOH^{+}$ or $H^{\bullet}COO$ radicals which

take place in solutions more acidic than pH 8.0.

Copper catalysed reaction

In the presence of cupric ions the rate of reaction was

appreciably faster. Data obtained showed the reaction to follow

pseudo first order kinetics. A plot of $\log \frac{a}{a-x}$ against t was

linear throughout which is characteristic of first order reactions.

The rate law determined for the reaction was :-

$$-d \left[S_2O_8^{2-} \right] \ / \ dt \ + \ k_{obs} \left[S_2O_8^{2-} \right]$$
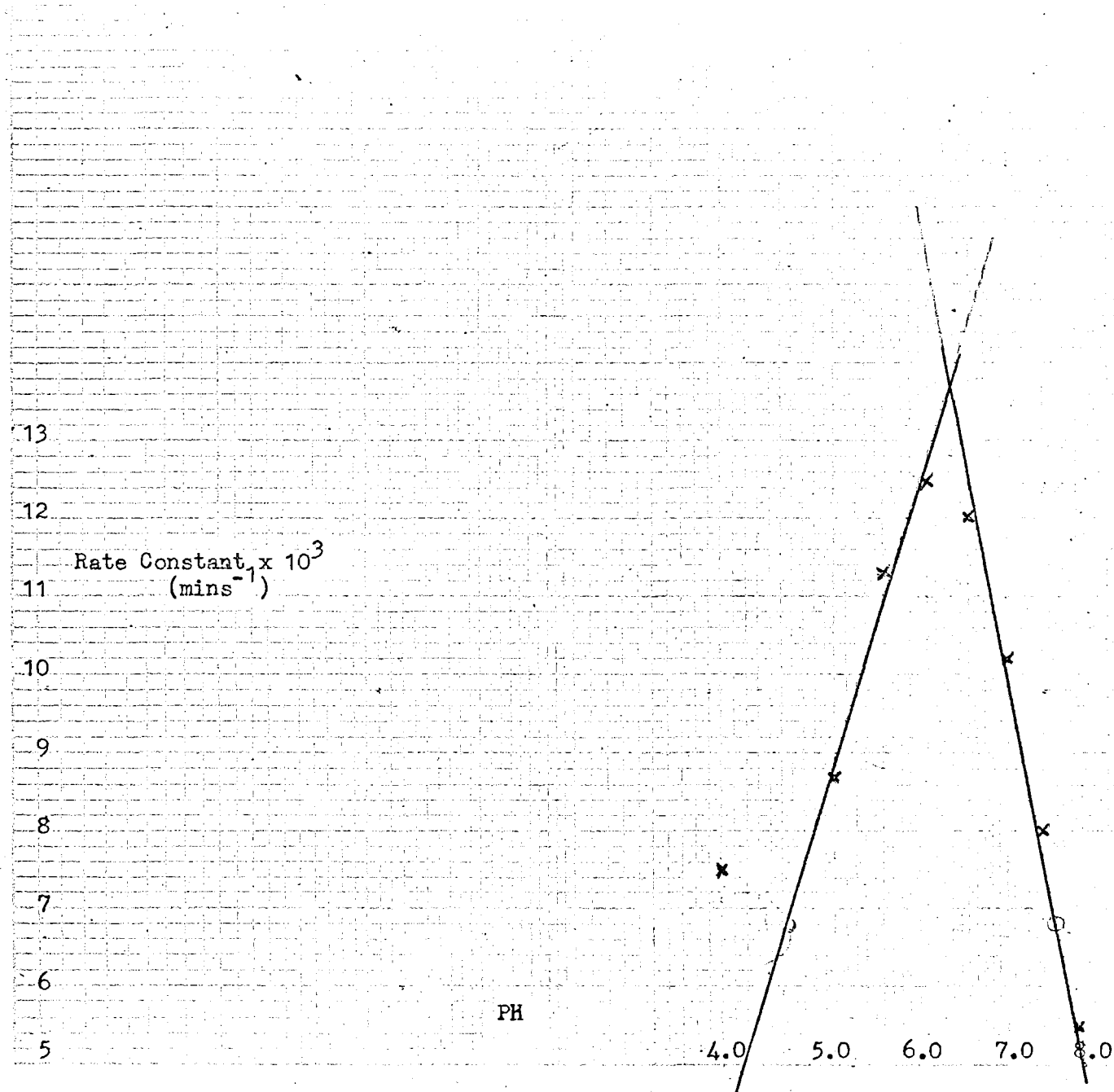
Figure 8

where k_{obs} is the first order rate constant obtained from the slope of the plot of $\log \frac{a}{a-x}$ against t.

To determine the order of reaction with respect to the catalyst, the concentration of copper ions was varied. The plot of observed rate constant against copper sulphate concentration was found to be linear (Fig. 7). Thus it can be concluded that the reaction is first order in copper ions. From the plot of k_{obs} against cupric ion concentration, the relationship:-

$$k_{obs} = k^1 \left[Cu^{2+}\right]$$

is obtained, where $\left[Cu^{2+}\right]$ is the total cupric ion concentration in the reaction mixture, and k^1 is the second order rate constant for the reaction.

From the above relationship the new expression:-

$$k^1 = \frac{k_{obs}}{\left[Cu^{2+}\right]}$$

is obtained, where k^1 = slope of the plot of k_{obs} against $\left[Cu^{2+}\right]$. Thus a value for k^1 can be obtained. The value obtained from the graph is $k^1 = 26$ min^{-1} $mole^{-1}$ litres, at $30^{\circ}C$ and pH 5.0. In the present work all kinetic runs done in distilled water show a reaction appreciably faster than that in the presence of EDTA, which can be expected to remove all traces of copper or silver ions. This there must be present in the reaction mixture, in small quantities, impurities of copper and/or silver ions catalysing the reaction. These impurities could arise from the distilled water, or from the reagent used, or both. The concentration of copper impurities present under these conditions has been estimated to be $2 \times 10^{-8}M$ (25). The concentration of copper present in Analar grade reagents has been found to be

2×10^{-9}M. (24) In a study of salt effects, Veprek-Siska and Hasnedl (24) have shown that positive salt effects can be caused by traces of impurities in the added electrolyte, which are capable of catalysing the reaction. This could cause a large number of the salt effects reported for many peroxodisulphate ion oxidations.

APPENDIX 1

Steady state analysis of the mechanism for the first order uncatalysed peroxodisulphate oxidation of formate.

The steps postulated for this reaction are :-

$$S_2O_8^{2-} \xrightarrow{k_1} 2\,SO_4^{\bullet} \tag{1}$$

$$SO_4^{\bullet} + H_2O \xrightarrow{k_2} OH^{\bullet} + HSO_4^{1-} \tag{2}$$

$$OH^{\bullet} + HCOO^{1-} \xrightarrow{k_3} OH^{1-} + H^{\bullet}COO \tag{3}$$

$$H^{\bullet}COO + S_2O_8^{2-} \xrightarrow{k_4} CO_2 + HSO_4^{1-} + SO_4^{\bullet} \tag{4}$$

$$H^{\bullet}COO + SO_4^{\bullet} \xrightarrow{k_5} HSO_4^{1-} + CO_2 \tag{5}$$
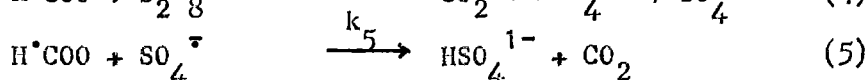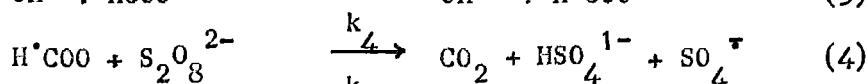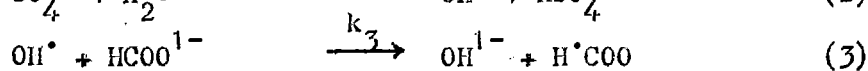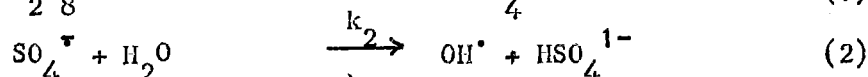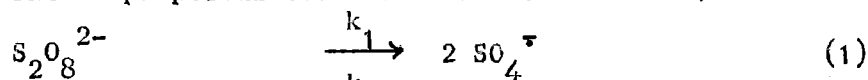
Differential equations can be set up from these steps.

$$-d\left[S_2O_8^{2-}\right]/dt = k_1\left[S_2O_8^{2-}\right] + k_4\left[S_2O_8^{2-}\right]H^{\bullet}COO \tag{6}$$

$$-d\left[HCOO^{1-}\right]/dt = k_3\left[OH^{\bullet}\right]\left[HCOO^{1-}\right] \tag{7}$$

$$d\left[SO_4^{\bullet}\right]/dt = 2k_1\left[S_2O_8^{2-}\right] - k_2\left[SO_4^{\bullet}\right]$$
$$+ k_4\left[S_2O_8^{2-}\right]\left[H^{\bullet}COO\right] - k_5\left[SO_4^{\bullet}\right]\left[H^{\bullet}COO\right] \tag{8}$$

$$d\left[H^{\bullet}COO\right]/dt = k_3\left[OH^{\bullet}\right]\left[HCOO^{1-}\right] - k_4\left[H^{\bullet}COO\right]\left[S_2O_8^{2-}\right]$$
$$- k_5\left[H^{\bullet}COO\right]\left[SO_4^{\bullet}\right] \tag{9}$$

$$d\left[OH^{\bullet}\right]/dt = k_2\left[SO_4^{\bullet}\right] - k_3\left[OH^{\bullet}\right]\left[HCOO^{1-}\right] \tag{10}$$

By steady state hypothesis, $\left[SO_4^{\bullet}\right]$, $\left[H^{\bullet}COO\right]$ and $\left[OH^{\bullet}\right]$ are constant, therefore :-

$$d\left[SO_4^{\bullet}\right]/dt = d\left[H^{\bullet}COO\right]/dt = d\left[OH^{\bullet}\right]/dt = 0 \tag{11}$$

Thus, from (10) and (11)

$$k_2\left[SO_4^{\bullet}\right] = k_3\left[OH^{\bullet}\right]\left[HCOO^{1-}\right] \tag{12}$$

Substitution of eqn. (12) in eqn. (7) gives :-

$$-d\left[HCOO^{1-}\right]/dt = k_2\left[SO_4^{\bullet}\right] \tag{13}$$

Substitution of (12) in (9) gives :-

$$d\left[H^{\bullet}COO\right]/dt = k_2\left[SO_4^{\bullet}\right] - k_4\left[H^{\bullet}COO\right]\left[S_2O_8^{2-}\right]$$
$$- k_5\left[H^{\bullet}COO\right]\left[SO_4^{\bullet}\right] = 0 \tag{14}$$

Adding equations (8) and (14) gives :-

$$k_1 \left[S_2O_8{}^{2-}\right] = k_5\left[H{}^{\bullet}COO\right]\left[SO_4{}^{\bullet}\right] \tag{15}$$

And subtracting equation (8) and (14) gives :-

$$k_2\left[SO_4{}^{\bullet}\right] = k_1 \left[S_2O_8{}^{2-}\right] + k_4 \left[H{}^{\bullet}COO\right]\left[S_2O_8{}^{2-}\right] \tag{16}$$

$$\text{or} \quad k_1\left[S_2O_8{}^{2-}\right] = k_2\left[SO_4{}^{\bullet}\right] - k_4 \left[H{}^{\bullet}COO\right]\left[S_2O_8{}^{2-}\right] \tag{16a}$$

Hence from equations (6), (13) and (16a) -

$$-d\left[S_2O_8{}^{2-}\right] /dt = {}^{-}d\left[HCOO^{1-}\right] /dt \tag{17}$$

From equation (15)

$$\left[SO_4{}^{\bullet}\right] = \frac{k_1}{} \left[S_2O_8{}^{2-}\right] / k_5 \left[H{}^{\bullet}COO\right] \tag{18}$$

Substitution of (18) in (16) gives :-

$$k_1 + k_4 \left[H{}^{\bullet}COO\right] = k_1 \, k_2/k_5 \left[H{}^{\bullet}COO\right] \tag{19}$$

$$k_4 \left[H{}^{\bullet}COO\right]^2 + k_1 \left[H{}^{\bullet}COO\right] - k_1 \, k_2/k_5 = 0 \tag{20}$$

Solving this gives :-

$$\left[H{}^{\bullet}COO\right] = -k_1 \pm (k_1{}^2 - 4 \, k_1 \, k_2 \, k_4/k_5)^{\frac{1}{2}} / 2k_4 \tag{21?}$$

Substituting for H$^{\bullet}$COO in equation (6) gives :-

$$\text{Rate} = \tfrac{1}{2} k_1 \pm (k_1{}^2 + 4k_1 \, k_2 \, k_4/k_5)^{\frac{1}{2}} \left[S_2O_8{}^{2-}\right]$$

which simplifies to :-

$$\text{Rate} = (k_1 \, k_2 \, k_4/k_5)^{\frac{1}{2}} \left[S_2O_8{}^{2-}\right]$$

if k$_1$ is small.

Appendix 2

Computer program used to calculate first order rate constants.

```
0001                DIMENSION T(30),X(30)
0002              4 READ(5,101)PH,A,NO,L1,NTOTAL,NCARD
0003            101 FORMAT(2F10.4,4I4)
0004                WRITE(6,102)PH,NO
0005            102 FORMAT('1',45X,'KINECTICS OF PERSULPHATE/FORMATE OXIDATIONS',/43X,
                   141('-'),///30X,'PH=',F6.2,15X,'RUN NO.=',I3,//30X,'S208 CONC.=0.05
                   2 M',10X,'HCOO CONC.=0.025 M',/30X,'TEMPERATURE =35 C',10X,'IONIC S
                   3TRENGTH=0.175 M')
0006                WRITE(6,103)
0007            103 FORMAT('0',/////21X,'TIME(T)',19X,'VOLUME(X)',16X,'LOG(A-XO)/(A-X)'
                   2,19X,'K')
0008                I=1
0009                DO 2 K=1,NCARD
0010                READ(5,104)T(I),X(I),T(I+1),X(I+1),T(I+2),X(I+2),T(I+3),X(I+3)
0011            104 FORMAT(8F10.4)
0012              2 I=I+4
0013                DO 3 I=2,NTOTAL
0014                OG=ALOG((A-X(1))/(A-X(I)))
0015                RATE=OG/T(I)
0016              3 WRITE(6,105)T(I),X(I),OG,RATE
0017            105 FORMAT(3(18X,F10.4),18X,E10.3)
0018                IF(L1)4,5,4
0019              5 STOP
0020                END
```

Sample of output data from IBM. 360 computer

KINECTICS OF PERSULPHATE/FORMATE OXIDATIONS

PH= 5.00   RUN NO.= 1

S208 CONC.=0.05 M   HCOO CONC.=0.025 M
TEMPERATURE =35 C   IONIC STRENGTH=0.175 M

TIME(T)	VOLUME(X)	LOG(A-XO)/(A-X)	K
3.0000	0.1900	0.0387	0.129E-01
7.0000	0.2200	0.0450	0.643E-02
10.0000	0.3000	0.0619	0.619E-02
15.0000	0.4500	0.0943	0.629E-02
18.2500	0.5500	0.1165	0.639E-02
20.5000	0.6200	0.1324	0.646E-02
27.5000	0.8400	0.1839	0.669E-02
31.5000	1.0100	0.2256	0.716E-02
34.5000	1.1100	0.2510	0.728E-02
37.2500	1.2200	0.2797	0.751E-02
42.0000	1.3700	0.3202	0.762E-02
45.0000	1.5000	0.3567	0.793E-02
156.0000	3.6700	1.3243	0.849E-02

APPENDIX 3

Concentrations of HCOOH molecules and $HCOO^{1-}$ ions
at various values of pH.

pH	(HCOOH)	$(HCOO^{1-})$
3.0	0.0464	0.0036
4.0	0.0188	0.0312
4.5	0.0076	0.0424
5.0	0.0026	0.0474
5.5	0.0008	0.0492
6.0	2.8×10^{-4}	0.04972
6.5	9×10^{-5}	0.04991
7.0	3×10^{-5}	0.04997
7.5	9×10^{-6}	0.04997
8.0	Nil	0.05

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PEROXODISULPHATE OXIDATIONS
I. THE KINETICS AND MECHANISM OF THE PEROXODISULPHATE-FORMATE REACTION

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Summary

The kinetics of the reaction

$$S_2O_8^{2-} + HCO_2^- = 2SO_4^{2-} + H^+ + CO_2$$
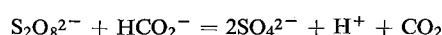
have been investigated in aqueous solution using a pH-stat to determine the extent of
the reaction. Over the pH range $4 \cdot 00$–$8 \cdot 00$, with $[S_2O_8^{2-}] = [HCO_2^-] = 0 \cdot 05$ M at
35°C, the oxidation follows the rate law $-d[S_2O_8^{2-}]/dt = k_{obs}[S_2O_8^{2-}]$, where the
magnititude of k_{obs} depends on the value of the pH. At 35°C, pH $= 8 \cdot 00$ and μ (ionic
strength) $= 0 \cdot 2$ M; $k_{obs} = 5 \cdot 75 \times 10^{-3}$ min^{-1} and $E_a = 11 \cdot 9$ kcal mole^{-1}. The
influence of Cu^{2+} ion catalysis on the oxidation rate has also been investigated and a
value of $k_2 = 25 \cdot 8$ l.mole^{-1}min^{-1} was found for the rate law $-d[S_2O_8^{2-}]/dt =
k_2[S_2O_8^{2-}][Cu^{2+}]$ at 30°C, pH $= 5 \cdot 00$ and $\mu = 0 \cdot 2$ M.

INTRODUCTION

Oxidations involving the peroxodisulphate (Chemical Society, 1960)
ion, $S_2O_8^{2-}$, (often called the persulphate ion) in aqueous solution are
usually slow and often subject to trace metal ion catalysis. The kinetics
and mechanisms of such oxidations have been reviewed by House (1962)
and Wilmarth and Haim (1962).

The oxidation of the formate ion by peroxodisulphate in aqueous solu-
tion has been previously studied (Srivastava and Ghosh, 1953; 1957;
Kappanna, 1956) and shown to proceed according to the stoichiometric
equation

$$S_2O_8^{2-} + HCO_2^- = 2SO_4^{2-} + H^+ + CO_2 \tag{1}$$
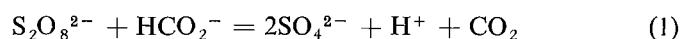
Both these groups followed the extent of the reaction by titrating
suitable aliquots of the reaction solution with standard alkali under very
similar conditions. However, the data obtained by Kappanna (1956)
were interpreted as a second order reaction, whereas those obtained by
Srivastava and Ghosh (1953) suggested the rate of reaction was inde-
pendent of the formate ion concentration and first order in peroxodi-
sulphate.

From a consideration of the data presented in these papers, and other
published data on the $S_2O_8^{2-}$ — HCO_2^- (or HCO_2H) reaction (Striva-
stava and Ghosh, 1959a; 1959b; Gupta and Nigam, 1960; Beileryan

et al., 1964; Chaltykayn *et al.*, 1964) we concluded that the rate of the reaction represented by equation (1) must be dependent upon the pH of the solution, which is also changing with time when the hydrogen ion concentration is allowed to accumulate. This hypothesis was further supported by the data of Hart (1961) who investigated the yield of CO_2 from the gamma ray induced $S_2O_8^{2-} - HCO_2^-$ reaction, and found a marked dependence of yield of CO_2 on the pH of the reactant solution.

Thus we have reinvestigated the peroxodisulphate-formate oxidation at constant ionic strength with a view to establishing (a) the molecularity and (b) any pH dependence upon the rate, using a pH-stat to maintain a constant pH during the reaction.

EXPERIMENTAL

Stock solutions of potassium formate were prepared by neutralising standard A.R. HCO_2H solution with A.R. KOH solution. Fresh solutions of A.R. $K_2S_2O_8$ were prepared every three days, using freshly distilled water, and stored at 5°c to retard the spontaneous thermal decomposition of the $S_2O_8^{2-}$ ion. Potassium sulphate was used as background electrolyte.

The reaction rate was investigated using a pH-stat. For most kinetic runs, a 10 ml sample of 0·1 M HCO_2K solution was allowed to reach thermal equilibrium in the thermostatted reaction chamber of a Radiometer TTT1c Titrator containing glass and calomel electrodes, a stirrer and the input tube from a SDU1a micro-syringe burette filled with 0·5 ml of 1 M KOH solution. The drive mechanism of the burette was coupled to a Radiometer SBR2c syringe burette recorder. A 10 ml sample of 0·1 M $K_2S_2O_8$ solution (previously at thermal equilibrium with the desired temperature) was then added to the reaction chamber and the pH brought to approximately the desired level by the dropwise addition of alkali or acid. Activation of the automatic titrator, pre-set at the desired pH, initiated the recorder and the micro-syringe burette, which responded to the change of pH as the reaction proceeded by the addition of alkali to maintain the pH at the pre-set value. Thus a plot of volume of alkali *vs.* time was obtained on the syringe burette recorder chart. Four to ten kinetic runs were performed after the variation of any particular parameter, e.g. pH, temperature, reactant concentration, etc., to establish consistent results and obtain mean rate constants.

Rate constants were evaluated from the slope of the straight line plots of log $[a/(a - x)]$ *vs.* time, where $a =$ the measured volume of KOH added at 100% reaction and $x =$ the measured volume of KOH added at time $= t$, or were calculated from the expression

$$k_{obs} = 2 \cdot 303/t[\log a/(a - x)].$$

For the Cu(II) ion catalysed reactions, standard Cu^{2+} solutions were prepared in 0.1 M HCO_2K solution, from weighed amounts of A.R. $CuSO_4.5H_2O$.

RESULTS

Rate Law

The order of the reaction was established by the half-life method (Frost and Pearson, 1961) at 35°C and pH $= 8.00$ and ionic strength $(\mu) = 0.2$ M (K_2SO_4). With a formate ion concentration of 0.05 M and peroxodisulphate ion concentrations of 0.05, 0.0375 and 0.025 M, mean half-lives were 130, 128 and 128 $\pm$ 5 min respectively, indicating a first order dependence of the rate on the peroxodisulphate ion concentration. With a constant peroxodisulphate ion concentration of 0.05 M and formate ion concentrations of 0.05, 0.0375 and 0.025 M, mean half-lives were 135, 110 and 70 $\pm$ 5 min respectively. Use of the formula, $n = 1 + \log(t_1/t_2)/\log(a_2/a_1)$, where n is the order of the reaction and t_1 and t_2 are the half-lives at concentrations of a_1 and a_2, gave values of 0.17, 0.08 and -0.12 for n, indicating a zero order dependence in formate ion concentration.
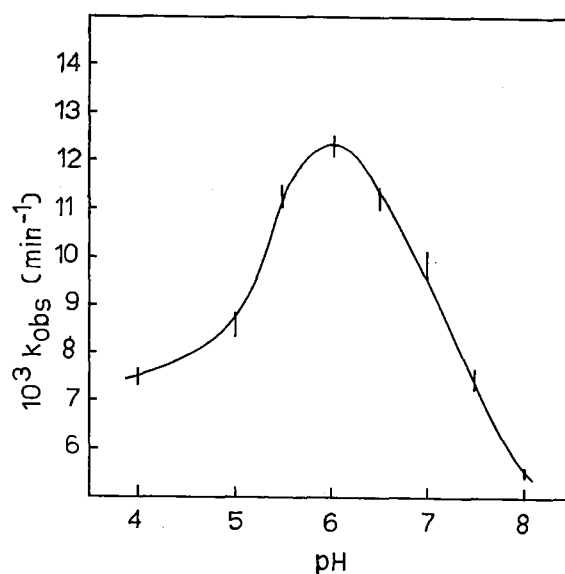
FIG. 1—Rate constant as a function of pH.

$[S_2O_8^{2-}] = [HCO_2^-] = 0.05$ M, $\mu = 0.2$ M, T $= 35$°C.

Thus the law for the reaction

$$S_2O_8^{2-} + HCO_2^- = 2SO_4^{2-} + H^+ + CO_2 \tag{1}$$
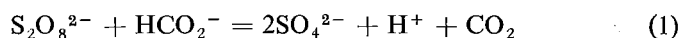
is $-d[S_2O_8^{2-}]/dt = k_{obs}[S_2O_8^{2-}]$,

similar to many other peroxodisulphate oxidations (House, 1962).

At other pH values, good first order plots were obtained and there was no evidence for a change in order in the pH range 4–8.

pH Dependence

The reaction rate constant showed a marked dependence on pH and Fig. 1 shows a plot of k_{obs} vs. pH for $[S_2O_8^{2-}] = [HCO_2^-] = 0.05$ M at 35°C and $\mu = 0.2$ M (Table 1).

Temperature Dependence

The energy of activation (E_a) for the oxidation was estimated from the first order rate constants obtained at temperatures of 30, 35, 40, 45 and 50°C with $[S_2O_8^{2-}] = [HCO_2^-] = 0.05$ M at pH $= 8.00$ (Table 1). A linear plot of $-\log k_{obs}$ vs. $1000/T°K$ was obtained (Fig. 2) and from the slope, a value of 11.9 ± 0.5 kcal mole^{-1} was calculated for the energy of activation. The experimental rate constant in the 30–50°C range is thus given by the expression

$$k_{obs} = 2.63 \times 10^4 \exp(-11.9/RT) \text{ sec}^{-1}$$

and the entropy of activation (ΔS) is estimated to be -39.4 ± 0.5 cal g mole^{-1}°C^{-1}.

Copper (II) Ion Catalysis

The oxidation is strongly catalysed by the Cu^{2+} ion and a straight line was obtained when k_{obs} (pseudo first order rate constant) was plotted

TABLE 1—Mean Rate Constant as a Function of pH and Temperature

$[S_2O_8^{2-}] = [HCO_2^-] = 0.05$ M, $\mu = 0.2$ M		
pH	$10^3 k_{obs}$ (min^{-1})	T(°C)
4.00	7.4 ± 0.1	35
5.00	8.5 ± 0.3	35
5.50	11.3 ± 0.3	35
6.00	12.4 ± 0.3	35
6.50	11.2 ± 0.2	35
7.00	10.0 ± 0.3	35
7.50	7.5 ± 0.3	35
8.00	5.6 ± 0.1	35
8.00	4.0 ± 0.2	30
8.00	5.6 ± 0.1	35
8.00	7.1 ± 0.3	40
8.00	9.5 ± 0.2	45
8.00	14.0 ± 0.1	50
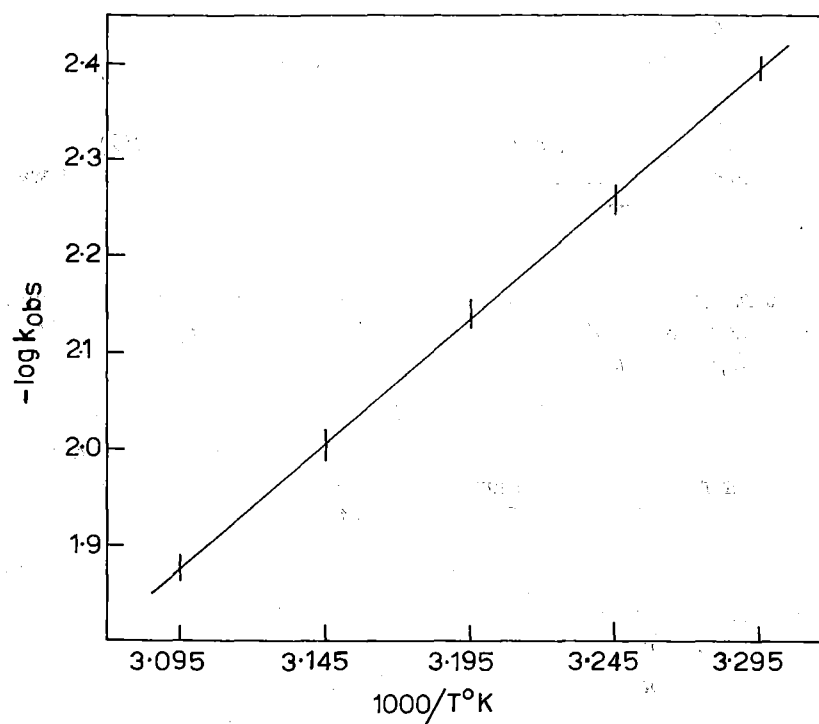
FIG. 2—$1000/T^\circ$K vs. $-\log k_{\mathrm{obs}}$. $[S_2O_8^{2-}] = [HCO_2^-] = 0 \cdot 05\ M$, $\mu = 0 \cdot 2\ M$, pH $= 8 \cdot 00$.

against $[Cu^{2+}]$ for $[S_2O_8^{2-}] = [HCO_2^-] = 0 \cdot 05\ M$ at 30°c and pH $= 5 \cdot 00$ (Table 2, Fig. 3). For this reaction

$$-d[S_2O_8^{2-}]/dt = k_2[S_2O_8^{2-}]\,[Cu^{2+}]\ \text{where}\ k_2[Cu^{2+}] = k_{\mathrm{obs}},$$

the $[Cu^{2+}]$ being constant for any particular experiment. Thus the slope

TABLE 2—Mean Rate Constant as a Function of Cu(II) Ion Concentration

$[S_2O_8^{2-}] = [HCO_2^-] = 0 \cdot 05\ M$, pH $= 5 \cdot 00$, $\mu = 0 \cdot 2\ M$, T $= 30^\circ$c

$10^4\ [Cu^{2+}]$	$10^3\ k_{\mathrm{obs}}\ (\mathrm{min}^{-1})$
2·50	17·4 ± 0·3
3·75	20·4 ± 0·4
5·00	23·6 ± 0·4
6·25	27·1 ± 0·3
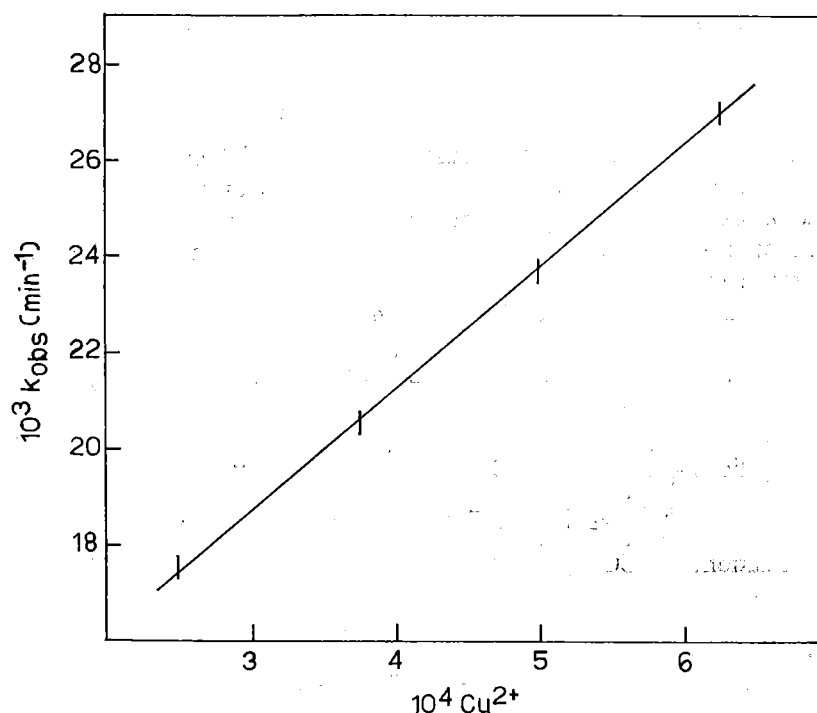
FIG. 3—Rate constant as a function of $[Cu^{2+}]$. $[S_2O_8^{2-}] = [HCO_2^-] = 0\cdot05\ M$, $\mu = 0\cdot2\ M$, T $= 30°c$, pH $= 5\cdot00$.

of the line in Fig. 3 equals $k_{obs}/[Cu^{2+}] = k_2 = 25\cdot8$ l.mole^{-1}min^{-1} at 30°c and pH $= 5\cdot00$. Temperature dependence and pH varation in the copper(II) ion catalysed oxidation were not investigated, but at pH greater than 6, $Cu(OH)_2$ starts to precipitate.

DISCUSSION

The uncatalysed oxidation of formate ion by peroxodisulphate ion is believed to be a free-radical chain mechanism for several reasons.

(1) The rate constant for the oxidation is greater than that for the thermal decomposition (House, 1962; Hakoila, 1963) of the $S_2O_8^{2-}$, even though both reactions obey the same rate law

$$-d[S_2O_8^{2-}]/dt = k[S_2O_8^{2-}].$$

This suggests that radicals from the formate ion are attacking the $S_2O_8^{2-}$ ion at a rate faster than radicals generated in the absence of formate.
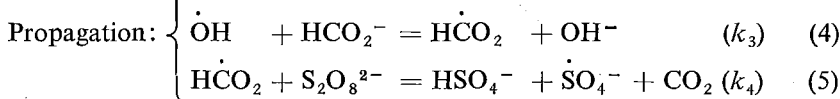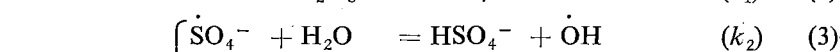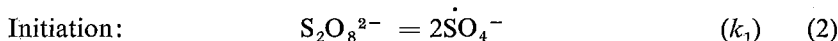
(2) The variation in rate constant with pH has a maxima at about

pH = 6, a value much higher than would be expected from the pK for the equilibrium

$$HCO_2H + OH^- = HCO_2^- + H_2O \; (pK = 3\cdot75) \qquad (1a)$$
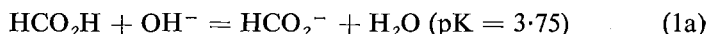
if this latter reaction were the cause of the pH variation. This suggests, as in the peroxodisulphate-oxalate oxidation (Po and Allen, 1968), that radical protonation is the cause of the pH dependence.

A reasonable radical chain mechanism is postulated conforming to the observed kinetics and compatable with other peroxodisulphate reaction mechanisms (House, 1962; Wilmarth and Haim, 1962).

Initiation: $S_2O_8^{2-} = 2\overset{\cdot}{S}O_4^-$ (k_1) (2)

Propagation: $\begin{cases} \overset{\cdot}{S}O_4^- + H_2O = HSO_4^- + \overset{\cdot}{O}H & (k_2) & (3) \\ \overset{\cdot}{O}H + HCO_2^- = H\overset{\cdot}{C}O_2 + OH^- & (k_3) & (4) \\ H\overset{\cdot}{C}O_2 + S_2O_8^{2-} = HSO_4^- + \overset{\cdot}{S}O_4^- + CO_2 \; (k_4) & (5) \end{cases}$

Termination: $H\overset{\cdot}{C}O_2 + \overset{\cdot}{S}O_4^- = HSO_4^- + CO_2$ (k_5) (6)
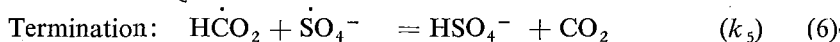
Using the steady state approximation for the free-radical species $\overset{\cdot}{S}O_4^-$, $H\overset{\cdot}{C}O_2$, and $\overset{\cdot}{O}H$, it may be shown (House, 1962) that

$$-d[S_2O_8^{2-}]/dt = (k_1k_2k_4/k_5)^{1/2}[S_2O_8^{2-}]$$

which is the observed rate law, when

$$k_{obs} = (k_1k_2k_4/k_5)^{1/2}$$

The principal characteristics of the pH dependence shown in Fig. 1 are an increase in k_{obs} from 4 to a maximum at about 6 and then a decrease as the pH is increased to 8. The dependence of rate on pH is similar to that observed by Po and Allen (1968) for the $C_2O_4^{2-} - S_2O_8^{2-}$ oxidation. Ben-Zvi (1963, 1967) and Hart (1961) have also observed a variation of rate on the pH in peroxodisulphate oxidations.

For a change in the observed rate constant without a change in order, there must be a change in the concentration or nature of the free radical attacking the $S_2O_8^{2-}$ ion in equation (5). In acid solution (pH = 4–5) there is a considerable concentration of HCO_2H molecules, and the alternative step to (4)

$$\overset{\cdot}{O}H + HCO_2H = H\overset{\cdot}{C}O_2 + H_2O \qquad (k_{3a}) \qquad (4a)$$
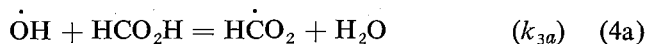
could be operating. However, this would not change the $H\overset{\cdot}{C}O_2$ radical concentration and thus the pH effects are probably not caused by reaction

(4a). In addition, steps (4) or (4a) are not a component in the expression for k_{obs} and the rate is zero order in formate or formic acid.

It thus appears that the $\dot{H}CO_2$ protonation reactions may be important. The observed increase in rate constant with increasing pH in the region pH $=$ 4–6 is probably associated with the deprotonation of the protonated $\dot{H}CO_2$ radical

$$\dot{H}CO_2H^+ + OH^- = \dot{H}CO_2 + H_2O \tag{7}$$
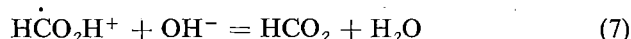
The decrease in rate constant from pH $=$ 6–8 is ascribed to further deprotonation, producing the $\dot{C}O_2^-$ radical

$$\dot{H}CO_2 + OH^- = \dot{C}O_2^- + H_2O \tag{8}$$
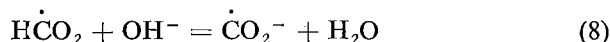
If such is the case, the order of reactivity of the radicals in the $S_2O_8^{2-}$ – HCO_2^- reaction is $\dot{H}CO_2H^+ < \dot{H}CO_2 > \dot{C}O_2^-$ as the $\dot{H}CO_2$ radical concentration increases and then decreases as the pH is increased. It is perhaps surprising that the positively charged radical is not the most reactive species for attacking the $S_2O_8^{2-}$ ion in step (5). However, electrostatic attractive forces may only be of secondary importance in these solvated radical-ion interactions. That the $\dot{H}CO_2$ is more reactive than the $\dot{C}O_2^-$, is reflected in the slower reaction rate and higher activation energy (32·7 kcal.mole^{-1}) in the $S_2O_8^{2-}$ – $C_2O_4^{2-}$ oxidation (where only $\dot{C}O_2^-$ radicals are formed) (Po and Allen, 1968), when compared with similar data in the $S_2O_8^{2-}$ – HCO_2^- oxidation.

From the midpoints of the left and right halves of the curve in Fig. 1, pK values of 5·5 and 7·0 are estimated for reactions (7) and (8) respectively. The higher value for reaction (8) is probably associated with the rupture of the H–C bond in the $\dot{H}CO_2$ radical. Similar analysis of rate constant *vs.* pH curves (Husian and Hart, 1965; Po and Allen, 1968) give a pK value of 2·8 for the OH bond rupture of the protonated $\dot{C}O_2^-$ radical ion

$$\dot{C}O_2H + OH^- = \dot{C}O_2^- + H_2O \tag{9}$$
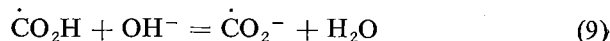
and for the H–P bond rupture in the reaction

$$H_2\dot{P}O_2 + OH^- = H\dot{P}O_2^- + H_2O \tag{10}$$
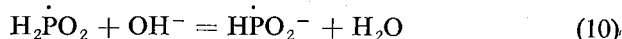
Ben-Zvi (1967) has estimated a pK of 9·1. The rate constant *vs.* pH curves, such as Fig. 1, have been termed "kinetic titration curves" by Ben-Zvi (1967).

The Arrhenius activation energy for reaction (1) has been determined over a 20°c temperature range and found to be $11 \cdot 9 \pm 0 \cdot 5$ kcal.mole^{-1} at pH $= 8 \cdot 00$. The published values of $21 \cdot 9$ and $8 \cdot 2$ kcal.mole^{-1} for the oxidation of HCO_2^- and HCO_2H respectively (Srivastava and Ghosh, 1953; 1957), suggests that this parameter may vary with pH.

The arguments presented above clearly indicate the importance of pH control in studying chain reactions of the peroxodisulphate ion. Previous investigations that have been concerned with pH control have usually involved the use of buffers, which themselves (especially acetate) may be subject to radical attack. The only previous study in peroxodisulphate oxidations using a pH-stat, has been a study of the thermal decomposition of the $S_2O_8^{2-}$ ion (Breuer and Jenkins, 1963). We hope to extend the use of this technique to investigate other peroxodisulphate oxidations.

Many oxidations by peroxodisulphate are susceptible to Cu^{2+} ion catalysis and the $S_2O_8^{2-} - HCO_2^-$ reaction is no exception. Indeed, it may well be the case that in the reaction studied here, "background" Cu^{2+} ions in the distilled water or reagents are causing some catalytic effect. It has even been suggested that the specific salt effects exhibited by many reactions could be due to trace metal ion (e.g. Cu^{2+}) catalysis (Veprek-Siska and Hasnedl, 1968).

The presence of EDTA solution has been used by several investigators to prevent metal ion catalysis by complexation (Ball *et al.*, 1960; Indelli and Bonora, 1966; Indelli *et al.*, 1966; Kershaw and Prue, 1967; Po and Allen, 1968). However, preliminary investigations showed that the $S_2O_8^{2-} - HCO_2^-$ oxidation in the presence of 10^{-3} M EDTA solution did not proceed at a measurable rate at 35°c, and at 50°c a complex autocatalytic reaction took place.

Addition of known concentrations of Cu^{2+} ion to the reaction mixture caused a marked increase in the rate, but the effect has not been studied in sufficient detail to postulate a reaction mechanism.

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