AN ABSTRACT OF THE THESIS OF

BRUCE BURNS for the MASTER OF SCIENCE in INORGANIC CHEMISTRY

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Title ___THE KINETICS OF THE REACTION BETWEEN PEROXYDISULFATE AND IODIDE IONS IN DIMETHYL SULFOXIDE___

Abstract approved _____
(Major Professor)

Persulfate oxidizes iodide ion according to the equation

$$S_2O_8^{2-} + 3I^- \longrightarrow 2SO_4^{2-} + I_3^-$$

The distinctive feature of the persulfate-iodide reaction in dimethyl sulfoxide (DMSO) is that it has a two term rate law, viz:

$$\text{Rate} = dI_3^-/dt = k_a\left[S_2O_8^{2-}\right] + k_b\left[I^-\right]\left[S_2O_8^{2-}\right].$$

A mechanism has been presented in which the iodide independent oxidation is brought about by a radical intermediate which is formed when sulfate radical ions react with DMSO. The exact nature of this radical intermediate is not certain. Evidence for the non-existence of a direct interaction between SO_4^- and I^- is given by the fact that the first-order reaction is not observed in water and that it disappears in a solvent mixture of 70% DMSO/30% H_2O.

The values of k_b exhibit a positive salt effect which seems to

be dependent on total cation concentration rather than ionic strength.
The data were found to fit the equation

$$k_b = (k_b)_o + 2.16 \times 10^{-3} [K^+] \quad \text{where} \quad (k_b)_o = 3.00 \times 10^{-5} M^{-1} \sec^{-1}.$$

The k_a exhibits a negative salt effect.

Tetraethylammonium perchlorate was found to have no effect on the reaction while barium nitrate exhibited a much greater accelerating effect on k_b than did potassium ion.

THE KINETICS OF THE REACTION BETWEEN
PEROXYDISULFATE AND IODIDE IONS
IN DIMETHYL SULFOXIDE

by

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I. INTRODUCTION

The peroxydisulfate ion is an extremely powerful oxidizing

agent (E_o = 2.01 volts) yet many of its reactions are so slow that they

are not observable at room temperature in the absence of a catalyst.

One reaction which can be followed kinetically at 25°C uncatalyzed

is the oxidation of iodide ion which follows the stoiciometry

$$S_2O_8^{2-} + 3I^- \longrightarrow 2SO_4^{2-} + I_3^-. \tag{1}$$
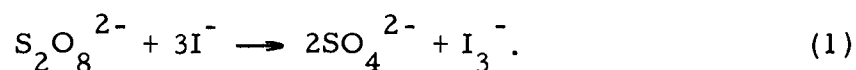
The kinetics of this reaction were first studied by Price (28) in 1898

who observed a reduction in rate constant with time due to the form-

ation of the triiodide ion as the reaction progressed. In recent years

the reaction has been studied extensively in order to verify the

Brønsted theory of ionic reactions and the Debye-Hückel limiting

law. In addition, recent investigations have disclosed the existence

of specific cation effects upon the rate which cannot be explained as

primary salt effects.

The purpose of this research is to carry out an investigation

of the reaction using dimethyl sulfoxide (DMSO) as a solvent and

attempt to determine the solvent influence on the reaction. It was

hoped that the lower dielectric constant of DMSO might cause

increased ion pairing between the reactant anions and added cations

over what might be expected in water. In addition, studying the

reaction in mixtures of water and DMSO would provide a means of

isolating specific solvent influences which are bound to be present in

an aprotic solvent. From preliminary investigations it was apparent

that the reaction was zero or near zero order in iodide ion although

iodine was produced as a product of the reaction. This suggested a

very important solvent effect. Later experiments, however, done

in the absence of oxygen showed that the iodide concentration did

affect the rate of the reaction but with an order less than one. This

indicated that the persulfate-iodide reaction in DMSO had a two term

rate law just as the persulfate-bromide reaction has in aqueous so-

lution (9, p. 182). In a later section it will be shown that a mecha-

nism can be written which leads to a rate law consistent with the

data and which involves a thermal decomposition step for persulfate.

Effect of Solvent DMSO on the Reaction

The data obtained in this study for the persulfate-iodide reac-

tion have brought several facts to light which are focused in three

areas: 1) The rate law in DMSO involves two terms including an

iodide independent term which is absent in aqueous solution; 2)

The rate of the second-order reaction is slower in DMSO than in

water; 3) Cation effects manifest themselves in a somewhat

different manner than in water. These are the three factors which differentiate these results from those obtained in aqueous solution. Thus, any conclusions to be drawn about solvent effects of this reaction must account for these differences.

The next two sections will briefly summarize the findings of other workers on the first-order decomposition of aqueous persulfate and the persulfate-iodide reaction.

First-Order Decomposition

Aqueous persulfate solutions are known to decompose slowly at somewhat elevated temperatures. The decomposition proceeds via two paths, one of which is acid catalyzed, the rate law being

$$\text{Rate} = -dS_2O_8^{2-}/dt = \left(k_1 + k_2\left[H^+\right]\right)\left[S_2O_8^{2-}\right] \quad (23).$$ Several steps have

been proposed as the initial and rate determining step for the uncatalyzed decomposition, (12), viz:

$$S_2O_8^{2-} \longrightarrow 2SO_4^- \cdot \quad (2)$$

$$S_2O_8^{2-} \rightleftharpoons 2SO_4^- \cdot \quad (2a)$$

$$S_2O_8^{2-} \rightleftharpoons SO_4 + SO_4^{2-} . \quad (2b)$$

Reactions (2a) and (2b) provide paths for the exchange of sulfur between $S_2O_8^{2-}$ and S^{35} labeled SO_4^{2-}. The mechanism for (2a) involves the entirely reasonable equilibrium

$$SO_4^- \cdot + S^*O_4^{2-} \rightleftharpoons SO_4^{2-} + S^*O_4^- \cdot .$$
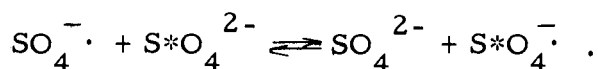
No such exchange has been observed (7, 29), and, thus, these steps are considered unlikely.

This initiating step (reaction 2) may also be brought about by light, gamma rays, or impurities or dust in the solution (12). In reactions with organic substrates and water reaction (2) is rate determining so that the observed rate is always first-order with respect to $S_2O_8^{2-}$ and zero-order with respect to the oxidizable substrate except at very low concentrations. In water the initiation step (2) is presumably followed by reaction with the solvent to produce OH· radicals

$$SO_4^-· + H_2O \longrightarrow OH· + HSO_4^- . \qquad (3)$$
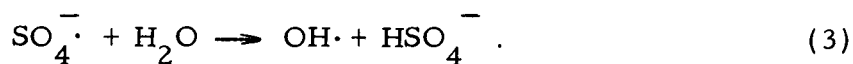
If an oxidizable substrate is present in the solution it can be attacked by the $SO_4^-·$ radicals or by the OH·, but the slow step remains the same. Yet it has been observed that the nature of the oxidizable substrate influences the observed rate constant for the reaction. Thus, the radicals produced when SO_4^- radicals attack the substrate probably influence the decomposition of the $S_2O_8^{2-}$ ion. Presumably, the SO_4^- radical itself exhibits this same effect, yet this premise has not been verified (12).

House (12) has written a general mechanism for persulfate decomposition in the presence of an oxidizable substrate which fits the organic substrates which have been reacted with persulfate;

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^{-} \cdot \quad \text{slow} \qquad (2)$$

$$SO_4^{-} \cdot + H_2O \xrightarrow{k_{2a}} OH \cdot + HSO_4^{-} \quad \begin{array}{l}\text{slow but faster} \\ \text{than (2)}\end{array} \qquad (4a)$$

$$OH \cdot + x^{2-} \xrightarrow{k_{2b}} OH^- + x \cdot \qquad (4b)$$

$$x \cdot + S_2O_8^{2-} \xrightarrow{k_3} SO_4^{2-} + SO_4^{-} \cdot + x \qquad (5)$$

$$x \cdot + SO_4 \cdot \xrightarrow{k_4} SO_4^{2-} + x \qquad (6)$$
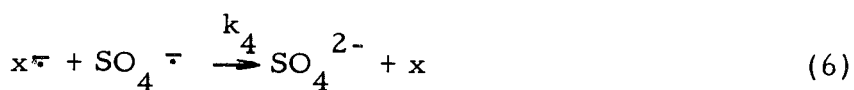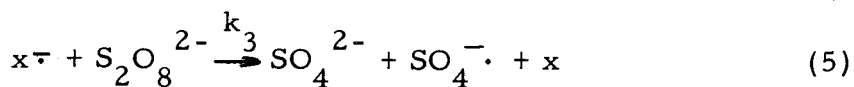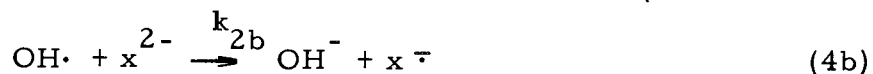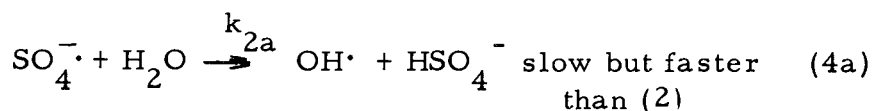
$$\frac{-d[x^{2-}]}{dt} = (k_1 + k_3[x \cdot]_{ss})[S_2O_8^{2-}]$$

where x^{2-} is the substrate, x is its reduced form and $[x \cdot]_{ss}$ is

the steady state concentration of the intermediate substrate radical.

A study has been made of the oxidation of diethyl sulfoxide by

$K_2S_2O_8$ in aqueous solution by Howard and Levitt (13). The reaction

is too slow to measure at $25°C$ but has a rate constant of 2.4×10^{-5}

$\sec^{-1}$ at $60°C$ after correction for $S_2O_8^{2-}$ reduction by the solvent.

The products were identified as sulfate and diethyl sulfone. As in

all $S_2O_8^{2-}$ reactions which are zero-order in the reducting agent

oxygen was observed to have no effect on the reaction which lends

some support to the premise that the reaction does not have a

radical chain mechanism.

The authors did not propose a mechanism for the reaction

(in acid solution) but one which might be proposed is:

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^{\bar{\cdot}} \qquad (2)$$

$$SO_4^{\bar{\cdot}} + H_2O \xrightarrow{k_{2a}} OH\cdot + HSO_4^{-} \qquad (4a)$$

$$OH\cdot + (C_2H_5)_2S\text{-}O \xrightarrow{k_{2b}} H^+ + (C_2H_5)_2\overset{\cdot}{S}(O)O^- \qquad (R) \quad (7)$$

$$(C_2H_5)_2\overset{\cdot}{S}(O)O^- + S_2O_8^{2-} \xrightarrow{k_3} SO_4^{\bar{\cdot}} + SO_4^{2-} + (C_2H_5)_2S(O)O \qquad (8)$$

$$(C_2H_5)_2\overset{\cdot}{S}(O)O^- + SO_4^{\bar{\cdot}} \xrightarrow{k_4} SO_4^{2-} + (C_2H_5)_2S(O)O \qquad (9)$$
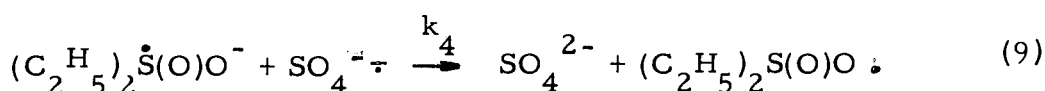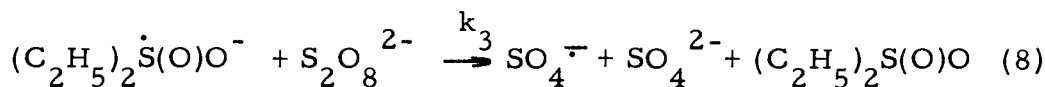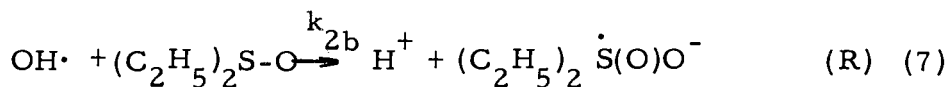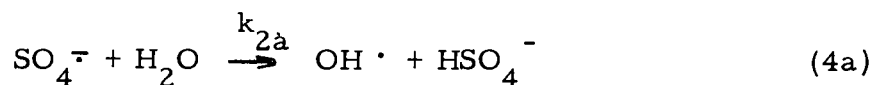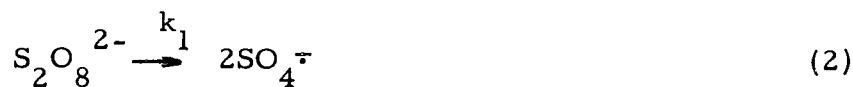
The rate law is $\dfrac{-dDMSO}{dt} = (k_1 + k_3[R])[S_2O_8^{2-}]$ consistent

with the general mechanism above, but it involves a radical chain.

Elimination of reaction (8) would break the chain and the rate law

would reduce to $k_1[S_2O_8^{2-}]$. But the authors determined the rate

constant of the Et_2SO reduction to be more than five times as great

as that of the reduction of water (0.090/0.0176) which lends support

to the inclusion of reaction (8).

Kolthoff and Miller (23) studied thermal decomposition of

persulfate in water. They gave the rate determining step for the

acid catalyzed reaction as

$$HS_2O_8^{-} \longrightarrow SO_4 + HSO_4^{-} \qquad (10)$$
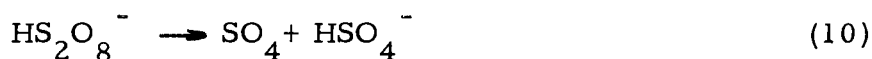
while the k_1 (uncatalyzed) rate constant was found to be independent

of ionic strength, the k_2(catalyzed) rate constant was found to

decrease with increasing ionic strength. The reactive intermediate

SO_4 has not been observed.

Reaction of Persulfate and Iodide

Mechanism

This reaction falls into a different class from the first-order

decomposition type because it is also first-order in the reducing

agent. In aqueous solution it is observed uncomplicated by any

first-order decomposition because the decomposition is so slow.

Three mechanisms have been proposed to account for its first-order

dependence on iodide and persulfate:

Reference

$$S_2O_8^{2-} + I^- \longrightarrow IS_2O_8^{3-} \quad \text{slow} \quad (28) \qquad (11)$$

$$IS_2O_8^{3-} + I^- \longrightarrow I_2 + 2SO_4^{2-} \quad \text{fast} \qquad (12)$$

$$IS_2O_8^{3-} \longrightarrow I^{\cdot} + S_2O_8^{3-} \quad \text{slow} \quad (31) \qquad (12a)$$

$$S_2O_8^{3-} + I^- \longrightarrow 2SO_4^{2-} + I^{\cdot} \quad \text{fast} \qquad (12b)$$

$$I^{\cdot} + I^{\cdot} \longrightarrow I_2 \quad \text{fast} \qquad (13)$$

$$S_2O_8^{2-} + I^- \rightleftarrows IS_2O_8^{3-} \qquad (12) \qquad (11a)$$

$$IS_2O_8^{3-} \longrightarrow I^+ + 2SO_4^{2-} \qquad (11b)$$

$$I^+ + I^- \longrightarrow I_2 . \qquad (13a)$$
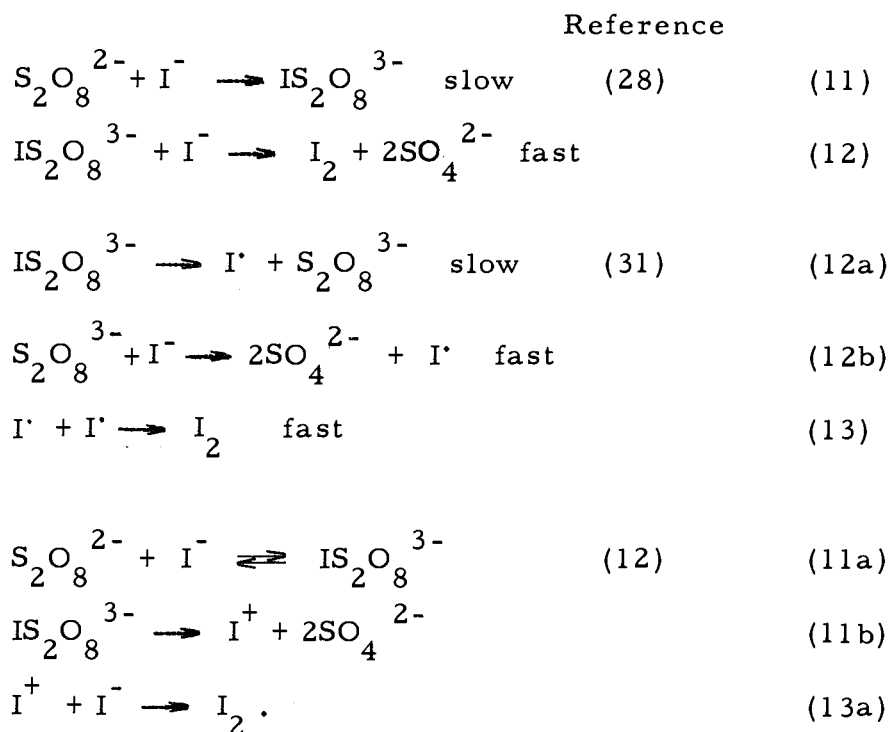
Modern authors seem to favor reactions (11a), (11b), and (13a) as

the correct mechanism principally because of the existence of the

compound bis-(pyridyl)-iodine (1) persulfate. This compound is formed when persulfate oxidizes potassium iodide in pyridine.

There is certainly a question as the exact nature of the complex $IS_2O_8^{3-}$. The above mechanisms all indicate that it is a reactive intermediate. However, since it has not been isolated, it could as well be the activated complex. The two possibilities are not kinetically distinguishable, and the point is unlikely to be resolved unless the $IS_2O_8^{3-}$ species is actually isolated in a compound. Nothing further need be said about this mechanism since its importance in this laboratory centers around the fact that it has as a rate determining step a reaction of two anions $S_2O_8^{2-}$ and I^-.

Salt Effects

The Brønsted theory of reaction rates which utilizes the Debye-Hückel limiting law gives the relationship between rate constant and ionic strength for an ionic reaction as

$$\log k = \log k_o + \frac{2Z_A Z_B \alpha\sqrt{\mu}}{1+\beta a\sqrt{\mu}} \simeq \log k_o + 2Z_A Z_B \alpha\sqrt{\mu}, \qquad 14)$$

where k_o is the rate constant at $\mu = 0$, Z_A and Z_B are the charges of the reacting ions, a is the average distance of closest approach of two ions in solution, and β and α are constants characteristic of a given solvent and temperature. The persulfate-iodide rate constant has been found to conform with equation (14) at low ionic

strengths. King and Jacobs (20) found that the rate constants agree

with those predicted by the approximate form of equation (14) up to

$\sqrt{\mu}$ = 0.16 providing the ratio of divalent to univalent ions in solu-

tion was kept low. Log k_o then was found to be -1.075. However,

in two sets of experiments where large concentrations of divalent

ions were present log k_o was -1.06. While these values are in

near agreement there may be some significance in their differences.

Negative deviations from the limiting expression were observed

with $MgSO_4$ present at $\sqrt{\mu}$= 0.06. Since it inherently contains all

the assumptions of the Debye-Huckel limiting law equation (14), and

especially its approximate form, is valid only at very low ionic

strengths and in the presence of only uni-univalent electrolytes.

Therefore, it is scarcely surprising that equation (14) has been

found invalid for a wide variety of ions at moderate ionic strengths.

Using data of their own plus those of other workers Olson

and S imonson (25) derived an equation which fits data for several

reactions between ions of like charge. The equation is

$$k = k_a \left[\frac{1}{1+K(x)} + k' \frac{K(x)}{1+K(x)} \right] \qquad (15)$$

where K and k' are empirical constants, (x) is the total concen-

tration of some ion, and k_a is the specific rate constant of the reac-

tion at some low ionic strength. If $k_a = k_o$ (ie: $k_a = k_o$ at x = o) the

term in the brackets, may be considered a substitute for Brønsted's

kinetic activity factor

$$F = \gamma_A \gamma_B / \gamma^* \tag{16}$$

$$k = F k_o \tag{17}$$

where γ_A, γ_B, and γ^* are the activity coefficients of each reactant and the activated complex.

Olson and Simonson interpret the two terms in the brackets to represent the fraction of reactant particles unaffected by other ions and the fraction affected strongly by other ions respectively.

Perlmutter-Hayman and Stein (27) have fit their data on the rate constant of the persulfate-iodide reaction to an empirical equation,

$$\log k = \log k_o + \left[Ac/(B+c) \right] + Dc \tag{18}$$

where A, B, and D are constants characteristic of the specific cation present. This equation fit their curves from very low values of c up to c = 2.0M. Furthermore, as both equations (15) and (18) imply, the effect is specific for a given cation, an obvious break-down of the limiting law which assumes all cations of like charge to exert the same influence on the reaction.

Both equations (15) and (18) reduce to a linear form at low cation concentrations viz:

$$\log k + \log k_o + \left[\frac{A}{B} + D \right] c \qquad \text{from(18)} \tag{19}$$

$$k = k_a + k_a k' K(x) \qquad \text{from(15)} \tag{20}$$

Equations (15) and (18) are not presented to replace the equation (14) but only to extend it. It should be noted that equation (14) is a limiting equation which is strictly correct only at infinite dilution.

II. EXPERIMENTAL

General

Since most of the experiments in this study were performed using pure DMSO as solvent it was considered imperative that water be excluded as thoroughly as possible. Since most reagents used were nonhygroscopic it was generally considered sufficient to dry them overnight in an oven at $110^{\circ}C$ and store them in weighing bottles over $CaSO_4$ or $CaCl_2$ as drying agents. This was the standard procedure with all solids unless otherwise noted.

Solid materials were weighed out on a Mettler balance of 200 gram capacity. In experiments where samples were analyzed by titration the burets used were Pyrex 10 ml class A burets. All pipets used to mix solutions or remove samples were calibrated by filling with freshly distilled thermostated DMSO, emptying into tared glass containers, and weighing. Densities of pure solvent and solvent mixtures were taken from Cowie and Toporowski (5).

All pipets and other glassware involved directly in making up stock solutions or solutions for kinetic runs were cleaned with dichromic acid cleaning solution and rinsed many times with distilled water. Most glassware was oven dried at $110^{\circ}C$.

Apparatus

Two constant temperature baths were used during the course of experiments. One consisted of a ceramic crock of approximately three gallon capacity fitted with a "lightnin" model L mixer, a 250 watt blade type heater, and a mercury thermoregulator switch of standard design set at $19.67 \pm 0.02^{\circ}C$. The temperature was checked with a 500 mm 50° thermometer.

The second bath consisted of a styrofoam ice chest approximately 10" x 12" x 18" fitted with a pump which circulated water through the jacket around the sample holder in the spectrophotometer, a 250 watt blade heater and thermoregulator set at $19.80 \pm 0.03^{\circ}C$. Both baths were cooled by three turn coils of copper tubing at the bottom through which flowed ordinary tap water. The coolant water for the second bath was pre-run through about 10 feet of copper tubing coiled inside a small crock filled with ice water. This procedure was necessary in the summer since the tap water was $22^{\circ}C$, but was not used in the winter.

Most of the experiments were carried out in the Beckman model DU Quartz spectrophotometer. The DU was thermostated as mentioned above. The cells used were standard Beckman Quartz cells. The DU was powered by a storage battery which was charged continuously during the time the instrument was on at ca 2.5 amp but only

a trickle (a few tenths of an amp) when the instrument was off. The instrument was operated at 6.4 volts.

Reagents

Dimethyl sulfoxide was obtained from Crown Zellerbach in polyethylene lined five gallon drums. Straight from the drum it was clear and had only a faint odor. It was guaranteed to contain less than one percent water, but for analysis of iodine solutions small concentrations of dimethyl sulfide or higher sulfides present the greatest difficulty. The solvent was distilled from an all pyrex glass system which included a 15 inch column packed with glass helices at a pressure of 10-20mm. The distillate had a boiling point which was quite constant during a distillation but varied according to the pressure obtained from the water aspirator (70-85°C). Starting with about one liter of unpurified DMSO a middle fraction of 500 ml was collected after two distillations. Although the sulfide content was not checked there seemed to be no anomalous results such as rapid reduction of persulfate to cause concern. The water content in one sample was determined by Karl Fischer titration to be 0.03%.

Potassium dichromate was obtained reagent grade and recrystallized from water before being dried and stored. It was used as a primary standard.

Ferrous ammonium sulfate was obtained reagent grade and dissolved in 0.1N H_2SO_4. It was standardized daily against standard $K_2Cr_2O_7$ solution. The $Fe(NH_4)_2(SO_4)_2$ solution was kept in a three necked standard taper joint flask. A ground glass stopper was fitted in the center neck. In one side neck was fitted a gas inlet tube which reached to the bottom of the flask and was connected to a length of Tygon tubing with a pinch clamp. The other side neck was fitted with a gas inlet tube broken near the top so that it did not reach the solution. This was connected to a short length of Tygon tubing and a short length of pressure tubing to which was attached a balloon filled with nitrogen. In this way the solution was protected from contact with the air and the titer changed very little from day to day.

Reagent grade potassium persulfate was used unpurified, but the solid was standarized against $K_2Cr_2O_7$. It was found to have an equivalent weight of 136.7 grams/equivalent. (cf. Theoretical = 135.6)

Reagent grade potassium iodide was recrystallized from water and dried.

Potassium nitrate and barium nitrate were reagent grade and were used without further purification.

Allyl acetate was made by adding acetyl chloride in excess to allyl alcohol and allowing the mixture to reflux for a few minutes. Then water was added to destroy the excess acetyl chloride. The organic layer was separated and extracted with two portions of 10%

sodium carbonate solution then shaken with anhydrous calcium chloride and allowed to stand overnight. The liquid was poured off and distilled at atmospheric pressure from an all glass system with a Vigreaux column. A middle cut of the fraction boiling at $103\text{-}4^{\circ}C$ was collected and stored in a 50 ml round bottom flask with a 24/40 standard taper stopper. About 30 ml of allyl acetate was obtained from 100 ml of allyl alcohol as starting material.

Cerous nitrate was prepared from ceric ammonium nitrate by reduction to the (III) state by sodium nitrite in dilute nitric acid medium. When the solution was completely colorless the Ce(III) was precipitated from a hot solution with sodium carbonate. After being filtered and washed with distilled water on a Buchner funnel the precipitate was redissolved in the smallest possible volume of 1:5 nitric acid. At this point there were about 15 grams of cerous nitrate dissolved in about 10 ml of water containing nitric acid. Repeated attempts to remove the nitric acid by boiling proved quite futile so an unboiled sample was simply mixed with an equal volume of double distilled DMSO, placed in a vacuum dessicator over P_2O_5 which was pumped down with an aspirator, closed off, and left for three days. After this time the sample had crystallized into colorless crystals. The crystals were broken up and spread on a petrie dish after which the desiccator was again pumped down and left for several more days. At this point the crystals seemed "dry". The

solid was always handled in a dry bag filled with dry nitrogen until

a sample was weighed into a small, dry stoppered volumetric flask

and dissolved in DMSO. Two solid samples were analyzed by oxidiz-

ing the Ce(III) and DMSO by boiling with $K_2S_2O_8$ in excess and back

titrating with standard ferrous solution using ferrous 1, 10 phenanth-

roline as indicator. Samples were reoxidized and retitrated until

two successive determinations gave molecular weight values within

0. 5%. The average value of the molecular weight was 546 $\pm$2 grams/

mole corresponding to a formula of $Ce(NO_3)_3 \cdot$ 2. 82 DMSO.

Tetraethylammonium perchlorate was prepared by precipitation

from aqueous solution according to the method of Kolthoff (22).

Eastman tetraethylammonium chloride was dried in vacuo over P_2O_5

and used without further purification.

<center>Experimental Procedure</center>

Runs in which Persulfate was Analyzed

Runs five and ten were done in solutions containing no iodide,

and, hence, were not done in the DU. The object of these runs was

to determine the rate of reduction of persulfate by the solvent.

The procedure in both experiments was to dissolve a known

amount of $K_2S_2O_8$ in DMSO, place it in the thermostated bath, and

remove samples from time to time for analysis. Unfortunately, the

persulfate is slow to dissolve in DMSO and the use of the magnetic stirrer to get it into solution in a reasonable amount of time was necessary. This caused a great deal of initial decomposition because the stirrer had quite a tendency to heat up the solution. In ten, for example, the $K_2S_2O_8$ concentration dropped by about 10% from the time the solution was mixed to the time the first sample was withdrawn. Therefore, zero time was taken as the time of withdrawl of the first sample. Time was kept with an electric timer and read to nearest second. The time of **withdrawal** of a sample was taken as the time when half the pipet had emptied into the quench solution. The quench was composed of 10.00 ml of standard ferrous solution, 50 ml lN H_2SO_4 solution and 5 ml concentrated (85%) phosphoric acid. The samples were back titrated with standard dichromate and the persulfate concentration calculated by difference.

No attempt was made to exclude oxygen from the solution since oxygen has no affect on the first-order decomposition.

Runs in which Absorbing Species (I_3^- or Ce^{+4}) were Analyzed

The solutions in the remainder of the experiments contained either iodide or cerous ion both of which yield products which can be analyzed by their absorption of light in the near U.V.-far visible region. In these experiments the products were analyzed and it was most convenient to allow the reaction to procede right in the quartz

cell in the DU. The appearance of iodine (as triiodide) was followed by observing the change in optical density of the solutions at 370 mμ; the cerium (IV) at 340 mμ .

The solutions were made up by weighing the desired amount of solid into a 25 or 50 ml ground glass stoppered flask, weighing, adding approximately the desired volume of solvent, and reweighing. In some earlier runs the $K_2S_2O_8$ solution was weighed into the reaction vessels, but in later runs the KI solution was weighed. All the other solutions were pipetted from Pyrex 5 ml graduated pipets or a Pyrex 1 ml graduated pipet. When these pipets were allowed to drain in a dropwise manner the volume delivered corresponded to the volume read to within one or two parts per thousand so the difference was ignored.

It is clear that the molar concentrations of each of the solutions which was pipetted was in error by some small amount because they were made up by weight and delivered by volume. Inherent in the method is the assumption that the molarity and molality of these solutions are equal. Since most stock solutions of $K_2S_2O_8$ and KI were .02 to .03 M the error in this assumption is probably fairly small (ca. 0. 5%). But the more concentrated solutions of KNO_3 (0. 1 to 0. 2 M) were considerably more in error (up to 4%). Generally, this would affect the ionic strength so that the μ values were least accurate of all the concentrations. Unfortunately, these errors

were unavoidable due to the slowness with which $K_2S_2O_8$ and KNO_3

dissolve in DMSO. Making the solutions up in volumetric flasks

resulted in some $K_2S_2O_8$ decomposition, and probably caused a

great deal of oxygen to redissolve in the solutions when the flasks

were shaken.

The reaction vessels were Pyrex class A 10 ml volumetric

flasks. After the initial reactant solution was weighed into the flasks

the required amount of KNO_3 solution was pipetted from the $19.67^{\circ}C$

thermostated bath. The flasks were then placed in the bath for 30

minutes and the second reactant solution added. Zero time for each

reaction was taken at the time when half of the second reactant so-

lution was added to the reaction flask. The flasks were then filled to

the mark with thermostated solvent (which always took less than 60

seconds) and carried to the DU where they were placed in the quartz

cells. The empty cells were always placed in the DU at least 30

minutes before the start of the reaction. Each solution was actually

out of the bath for two to two and a half minutes. Runs were made

up in sets of three, each set constituting an experiment. Readings

of the absorption were taken on each solution at an interval consis-

tent with the rate of formation of I_2. The reference cell was always

filled with pure DMSO. Between each set of three readings the DU

was restandardized with respect to "dark current" and reference.

Because this was an initial rate study, the amount of triiodide present in the solution never exceeded 1.0% of the total iodide and hence no difficulty was encountered due to its presence as in the case of other workers (19, 21, 28). Before making up the solutions the solvent was swept out with dry nitrogen for 20 minutes to remove any trace of oxygen. Oxygen interferes with the second-order re-action, presumably by attacking the $S_2O_8I^{-3}$ complex, and seriously reduces the apparent second-order rate constant. It was assumed that the solutions did not pick up a significant amount of oxygen from standing in stoppered flasks under air for an hour or two, but it was observed that solutions which stood for more than five hours tended to give low results.

Several experiments were done with constant persulfate and varying iodide concentrations at ionic strengths between 0.02 and 0.06 M. These runs were done to obtain the basic rate law and the relationship between ionic strength and reaction rate. When results of these experiments showed that the rate did not depend on ionic strength so much as total potassium ion concentration the remainder of the experiments were set up so that the total $[K^+]$ was constant.

Since preliminary experiments had shown that the rate law would be of the form $R_o = \dfrac{dI_2}{dt} = k_a[S_2O_8^{2-}] + k_b[I^-][S_2O_8^{2-}]$ the values of $R_o/[S_2O_8^{2-}]$ were plotted versus $[I^-]$. The slope of

this line, then, is equal to k_b and the intercept at $\left[I^- \right] = O$ is equal

to k_a. The fact that such plots did give a straight line with non-

zero intercept verifies the above rate law since the reaction has

been shown to be first-order in persulfate.

Two experiments were performed in the presence of barium

ion from $Ba(NO_3)_2$ to demonstrate the expected greater rate accel-

eration of Ba^{++} over K^+ and one experiment was done in the pre-

sence of tetraethylammonium perchlorate which was selected as an

example of a cation which would exhibit little or no ion pairing with

$S_2O_8^{2-}$, and, therefore, have less influence on the rate.

Three experiments were done with allyl acetate added to the

reaction mixtures. Allyl acetate was expected to act as a radical

trap for the SO_4^- radical ions and thus "isolate" the second-order

reaction by preventing iodine from being formed from SO_4^- ions.

Allyl acetate concentrations ran from 0.01 to 0.12 M.

Two experiments were done using Ce(III) as the reducing agent

in an attempt to "isolate" the first-order decomposition. The Ce(III)

was added as the DMSO-solvated nitrate in concentrations of 4.5 x

10^{-3} M and 1.0×10^{-3} M at varied persulfate concentrations.

Several experiments were done in various solvent mixtures of

DMSO and water from 85.00% to 50.00% DMSO by weight in order to

establish the effect of the DMSO on the reaction rate as a specific or

general one. These were done using exactly the same procedure as

the ones in pure DMSO but at only one total potassium ion concentration (0.0450 M).

A final experiment was done with tetraethylammonium chloride in the reaction mixture to discover a possible catalytic effect on the decomposition by choride ion.

In addition the results of one experiment (no. 13) are included which were not used in any calculations. This experiment is presented to verify the fact that the reaction is first-order in persulfate. The rate constants thus obtained were not used in any calculations because the experiment was done in the presence of atmospheric oxygen.

Because this reaction is so slow it must be studied by an initial rate method. Since this is true, each kinetic run yields only one value of R_o and $R_o/\left[S_2O_8^{2-}\right]$ at one initial $\left[S_2O_8^{2-}\right]$ and $\left[I^-\right]$. Thus the plots in Figures 1a through 1e represent many runs. This is somewhat of a disadvantage because less information is obtained from each experiment than may be obtained from a faster reaction. In addition, small differences in the experimental technique may influence the self-consistency of the data. Throughout this research every effort was made to adhere strictly to a standard procedure in setting up and making the runs.

Calibration of DU

The extinction coefficient of I_3^- in DMSO was determined at

370 mμ. Standard I_3^- solutions were made up by weighing re-

agent grade resublimed iodine into a weighed portion of DMSO. Fur-

ther dilutions were done by weight until final concentrations of I_3^-

were (0.8 to 3.0) x10^{-5}M. The final dilutions were made in 10 ml

volumetric flasks and diluted with spectroscopic grade DMSO which

was also 0.05 M in KI. Thus, the high ratio of I^- to I_2 assured

complete conversion to I_3^-. The extinction coefficient of I_3^- in

DMSO was determined to be (2.16 $\pm$ 0.01)x10^4. Beer's law is obeyed.

Treatment of Data

It is quite common in studying reactions involving free radi-

cals to obtain scattered values for the rate constants. This is

because free radical reactions are often catalyzed by minor impuri-

ties in the solution, dust, imperfections in the glassware, and other

gross mechanical factors which are hard to control. Clearly this

is true of the first-order persulfate decomposition. Referring to

Table (I) and Figures (1a) through (1e) it is apparant that the data

are scattered. In most cases this scatter is probably attributable

to either the factors listed above affecting the rate of the first-order

reaction or by the presence of oxygen in the solution which reduces

Table I. Data on rate variation with I⁻ at various ionic strengths.

Run	$[K_2S_2O_8] \times 10^3 M$	$[KI] \times 10^3 M$	$[K^+]_{total} \times 10^3 M$	$\mu \times 10^3 M$	$R_o/[S_2O_8] \times 10^6 \text{ sec}^{-1}$
44 I	4.97	1.008	54.9	59.9	0.605
J	4.97	1.823	54.7	59.7	0.696
K	4.97	2.789	54.6	59.6	0.724
*46 O	4.97	3.265	55.2	60.2	1.05
P	4.97	6.150	55.1	60.1	1.46
Q	4.97	8.286	55.2	60.2	1.69
48 C	5.01	4.258	54.7	59.7	0.984
D	5.01	5.477	54.9	59.9	1.25
E E	5.01	7.271	54.7	59.7	1.43
49 F	4.99	1.600	54.8	59.8	0.566
G	4.99	3.267	54.9	59.9	0.821
H	4.99	10.569	54.7	59.7	1.63
33 A	4.956	3.04	45.0	49.9	0.882
B	4.916	6.09	44.9	49.8	1.26
C	4.854	9.13	44.9	49.7	1.65
35 A	5.002	3.00	45.0	50.0	0.873
*B	5.435	5.99	44.9	50.3	1.55
*C	4.989	8.98	44.9	49.9	2.80
37 A	5.259	6.02	44.5	49.8	1.27
*B	5.258	9.04	44.5	49.8	1.77
*C	4.971	12.05	45.0	50.0	1.66
39 O	4.411	9.02	45.8	50.2	1.62
40 R	4.96	0.9935	34.9	39.9	0.835
S	4.96	2.042	35.1	40.1	0.946
T	4.96	3.029	35.2	40.2	1.07

Table 1. (continued)

Run	$[K_2S_2O_8] \times 10^3 M$	$[KI] \times 10^3 M$	$[K^+]_{total} \times 10^3 M$	$\mu \times 10^3 M$	$R_o / [S_2O_8^{2-}] \times 10^6 \, \text{sec}^{-1}$
*41 U	4.97	4.209	34.9	39.9	0.821
*A	4.97	5.146	35.0	40.0	1.14
B	4.97	6.451	35.0	40.0	1.45
42 C	4.98	4.303	35.0	40.0	1.20
*D	4.98	5.537	35.0	40.0	1.43
*E	4.98	10.236	34.9	39.9	2.19
*47 R	4.97	4.265	34.9	39.9	1.03
*S	4.97	6.332	34.9	39.9	1.51
T	4.97	8.577	35.0	40.0	1.62
50 I	5.00	1.056	24.9	29.9	0.622
J	5.00	4.014	25.1	30.1	1.02
K	5.00	7.029	25.1	30.1	1.37
51 L	4.95	1.973	24.9	29.9	0.719
M	4.95	5.060	25.0	30.0	1.20
*N	4.95	8.235	24.9	29.9	1.21
*52 O	4.98	3.053	25.1	30.1	0.751
*P	4.98	5.922	24.9	29.9	1.03
*Q	4.98	8.888	24.9	29.9	1.16
*53 R	3.72	3.143	16.2	19.9	0.710
S	3.72	6.056	16.3	20.0	1.15
T	3.72	9.360	16.8	20.5	1.39
*54 U	3.72	0.978	16.2	19.9	0.464
*A	3.72	4.191	16.3	20.0	0.923
*B	3.72	7.418	16.3	20.0	1.04
55 C	3.72	0.914	16.3	20.0	0.863
	3.72	3.097	16.3	20.0	0.965

* Omitted from least squares calculation.

Figure 1a. Plot of $R_o / \left[S_2O_8^{2-} \right]$ vs. $\left[I^- \right]$ for calculations of k_a and k_b at constant $\mu = 0.0600$ M.

Figure 1b. Plot of $R_o/\left[S_2O_8^{2-}\right]$ vs. $\left[I^-\right]$ for calculation of k_a and k_b at constant $\mu = 0.0500M$.

Figure 1c. Plot of $R_o / \left[S_2 O_8^{2-} \right]$ vs. $\left[I^- \right]$ for calculation of k_a and k_b at constant $\mu = 0.0400$ M.
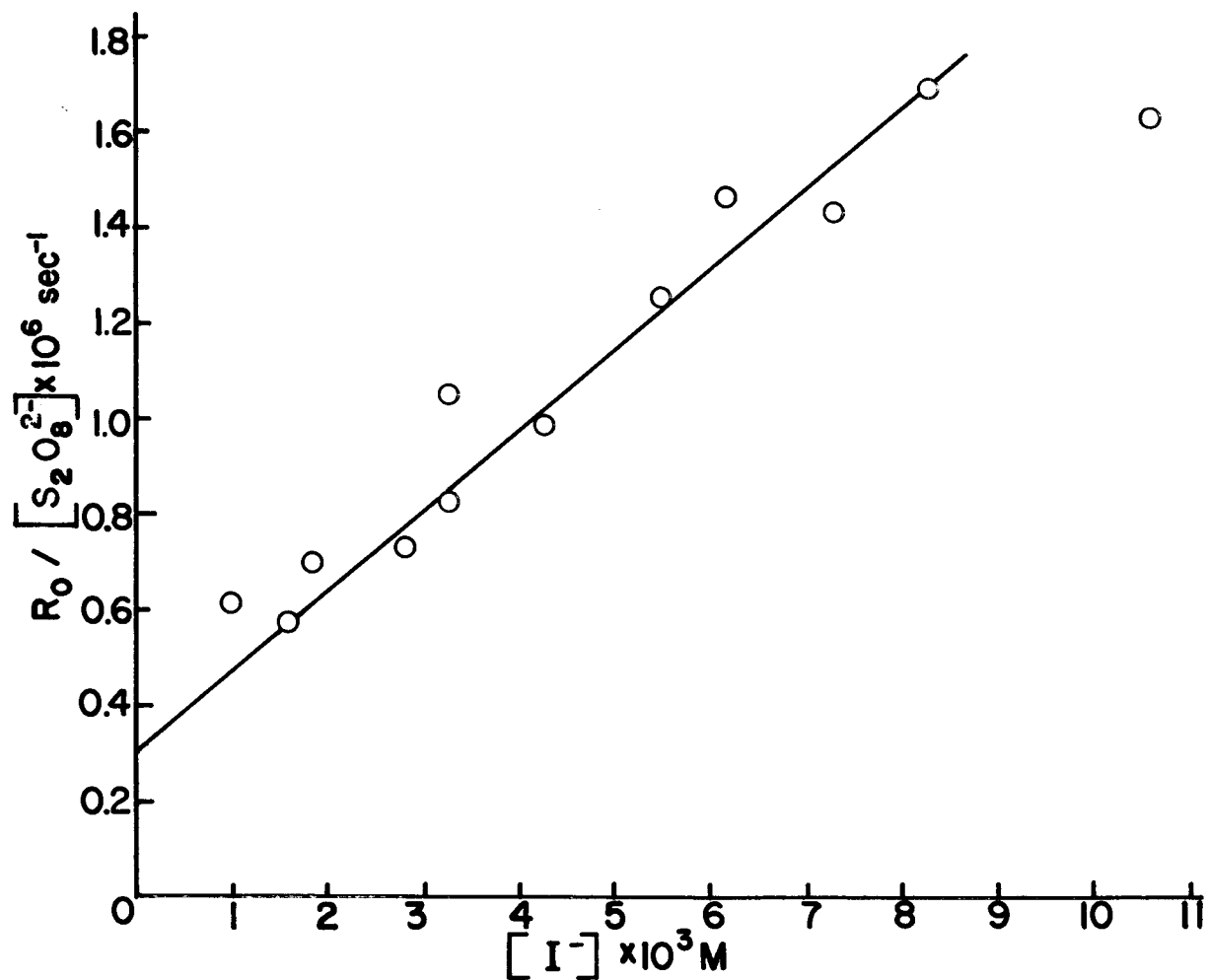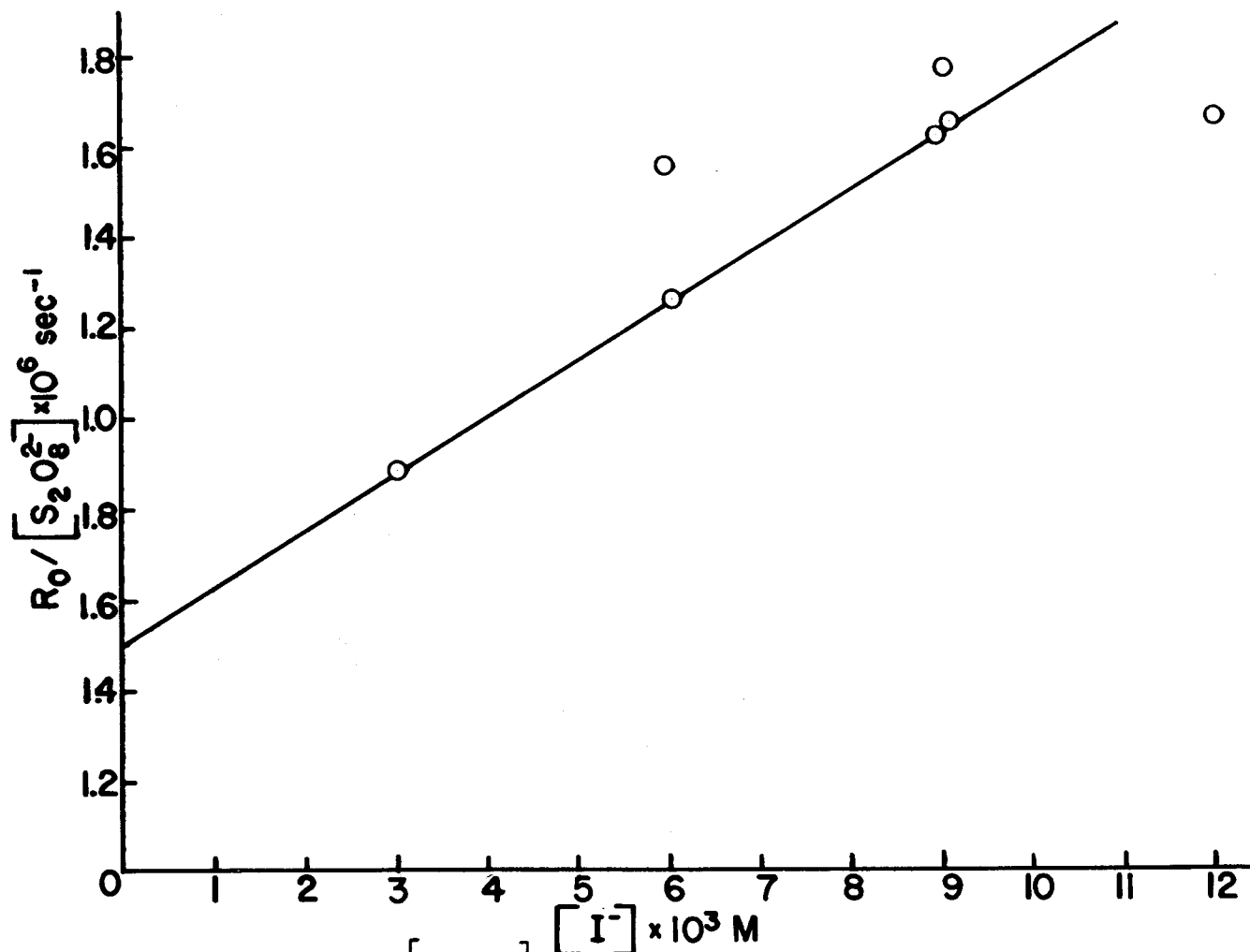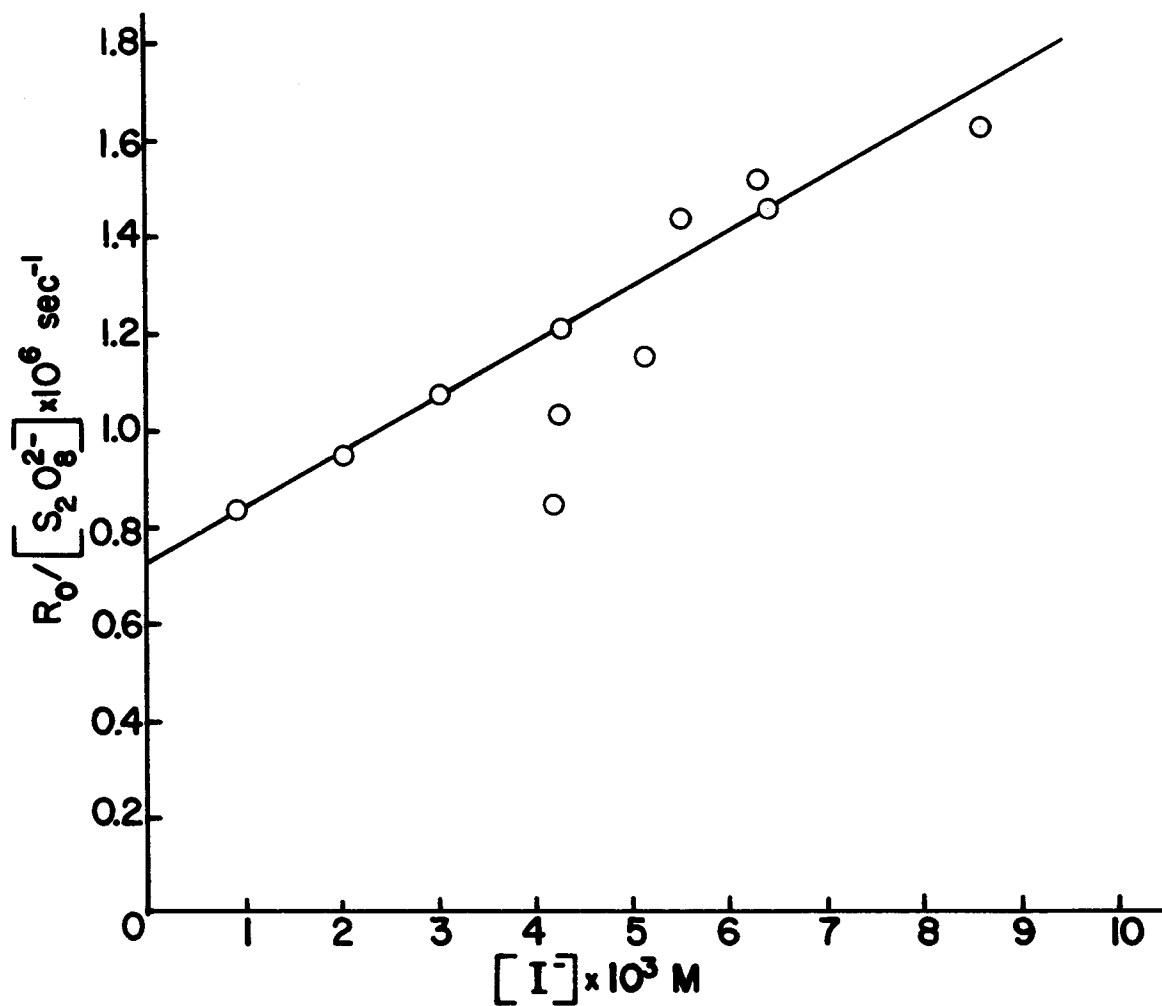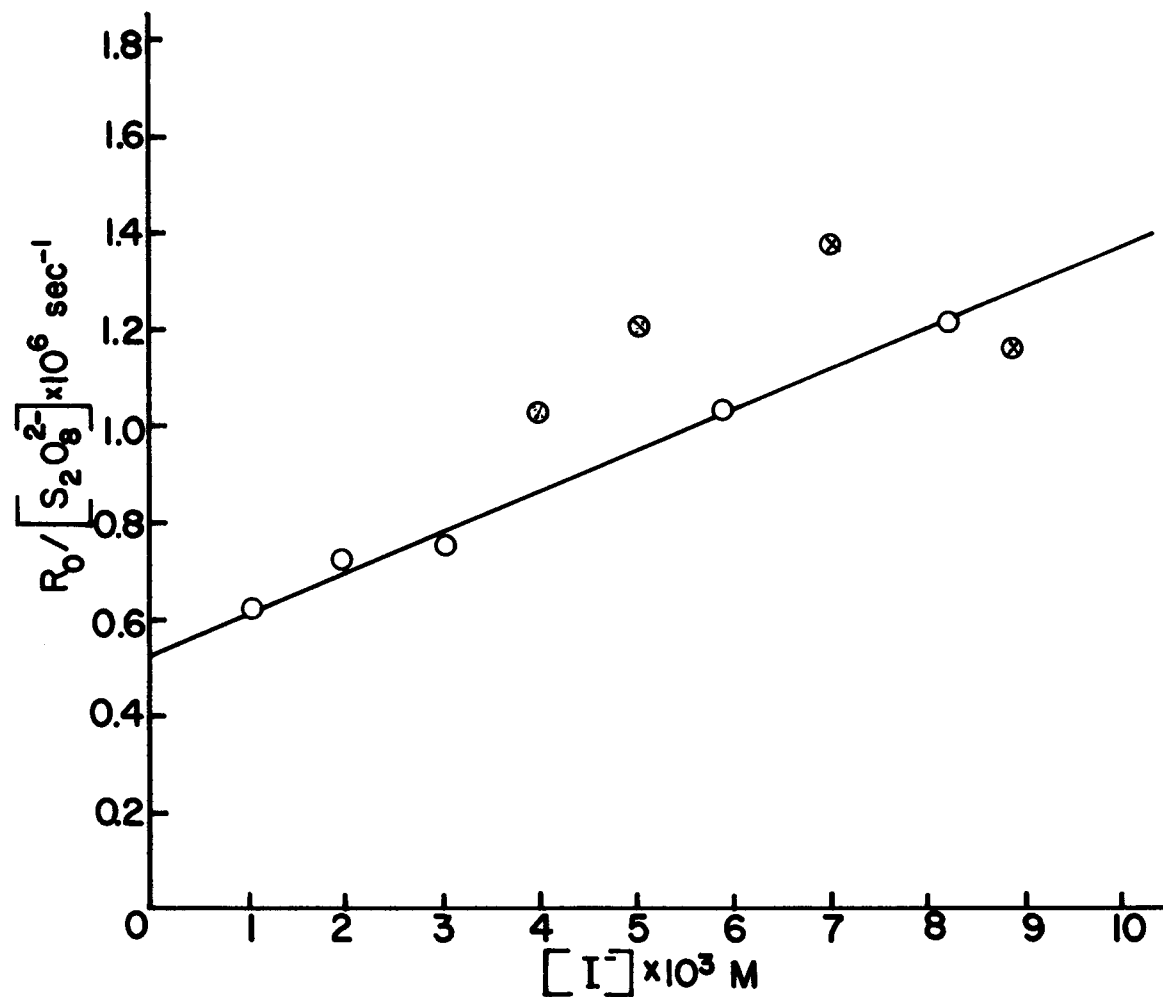
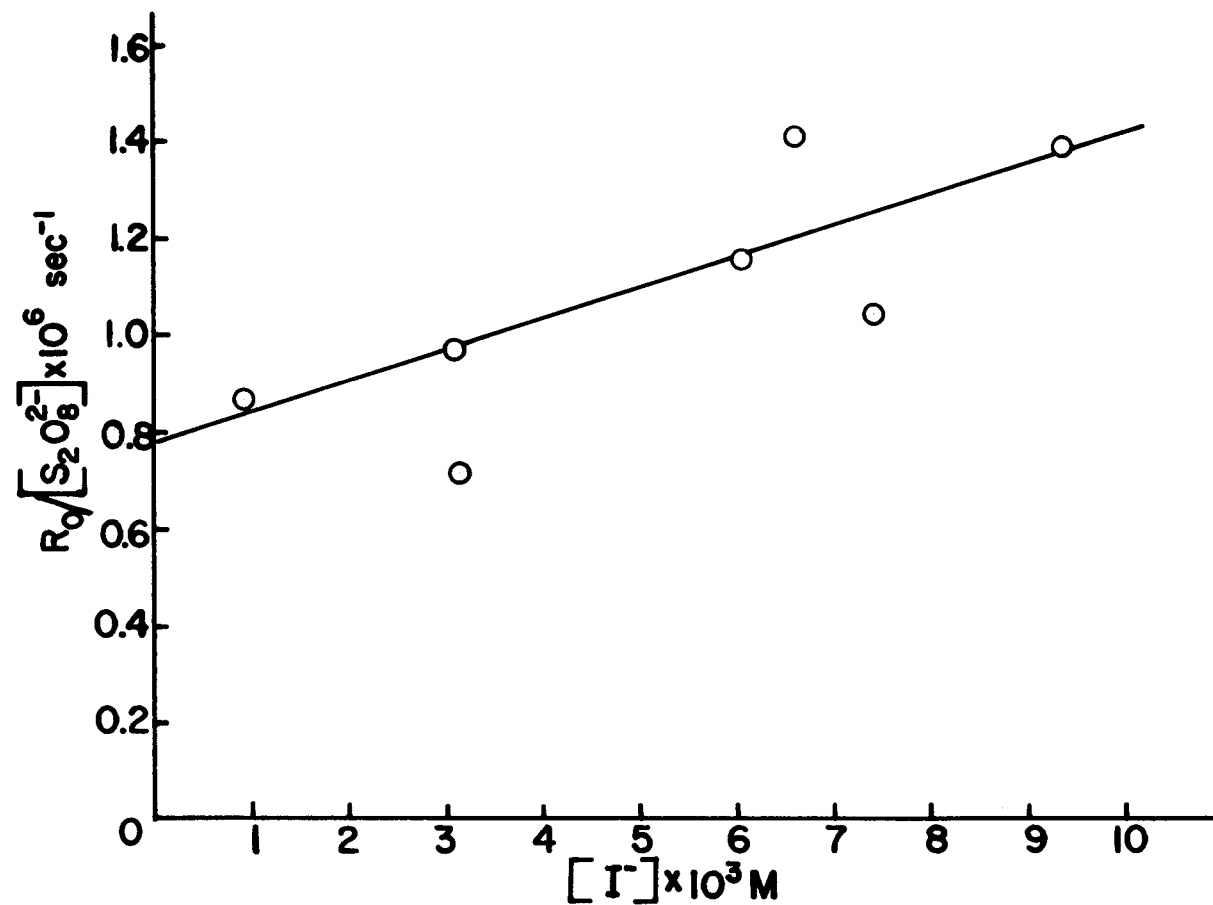Figure 1d. Plot of $R_o / [S_2O_8^{2-}]$ vs. $[I^-]$ for calculation of k_a and k_b at constant $\mu = 0.0300$ M.

Figure 1e. Plot of $R_o/\left[S_2O_8^{2-}\right]$ vs. $\left[I^-\right]$ for calculation of k_a and k_b at constant $\mu = 0.0200$ M.

the rate of the second-order reaction. Thus, it is not surprising that about half the points in each plot fall off the best straight line. The lines were drawn by the method of least squares, those points being eliminated from the calculations which were more than (1%) away from the line drawn by eye through the points. In figure 1d there are actually two straight lines of different slope and intercept which could be drawn. The indicated line was selected as the "best" because more points fell on it than the line of greater slope. The points denoted by ⊗ were not used in the least squares calculation. The same procedure was used for the studies at other solvent compositions but the requirements were relaxed somewhat for the data in 85% DMSO because there were too many "borderline cases". In the 70% and 50% solvent mixtures so few points were available that they all had to be used. The same is true of the runs done with $Ba(NO_3)_2$ added.

III. RESULTS AND DISCUSSION

Mechanism

There appear to be three reactions occurring simultaneously

in DMSO solutions of KI and $K_2S_2O_8$. The first is the oxidation of

DMSO by persulfate. The second and third produce triiodide and re-
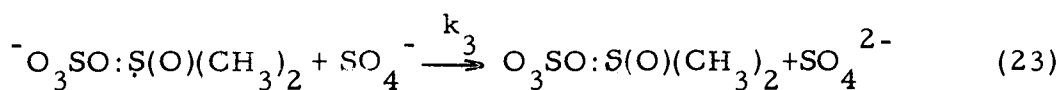
sult in the two term rate law

$$R_o = \frac{dI_2}{dt} = k_a \left[S_2O_8^{2-} \right] + k_b \left[I^- \right] \left[S_2O_8^{2-} \right] . \qquad (21)$$

The first reaction, oxidation of solvent by $S_2O_8^{2-}$, does not yield a

detectable product when solutions are analyzed for I_3^- at 370 mμ ,

but it must occur. Since the pure DMSO used in the various experi-

ments contained 0.03% water, only one water molecule was present

for every 1000 DMSO molecules. Since water is tightly bound to

DMSO in solution, as evidenced by their obviously high heat of mix-

ing as well as the non-ideal behavior of DMSO-H_2O mixtures (5),

it is unlikely that any water molecules are available to react with the

shortlived SO_4^- radical. Therefore, reaction (4a) is not possible.

So a mechanism must be written which is different from the sulfoxide-

persulfate mechanism in water. A comparison of experiments five

and ten in Table II gives evidence that the persulfate decomposition

in the solvent is at least roughly first-order in persulfate. The dif-

ference in $R_o / \left[S_2O_8^{2-} \right]$ values (which are really first-order rate

Table II. Reduction of persulfate by DMSO and KI

Run	$\left[K_2S_2O_8\right] \times 10^3 M$	$\left[KI\right] \times 10^3 M$	$\left[K^+\right]_{total} \times 10^3 M$	$\mu \times 10^3 M$	$R_o \times 10^7 sec^{-1}$	$R_o / \left[S_2O_8^{2-}\right] \times 10^6 sec^{-1}$
5	12.28	--	24.56	36.84	0.680	5.53
10	93.2	--	186.4	279.6	5.50	5.96
11	77.4	36.8	181.6	269.0	2.80	3.63

constants) is about 8% in two solutions in which the initial persulfate

value differs by about a factor of eight. One mechanism consistent

with this first-order dependence is:

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^{-} \qquad (2)$$

$$SO_4^{-} + (CH_3)_2\ddot{S}O \xrightarrow{k_2} {}^-O_3SO:\dot{S}(O)(CH_3)_2 \qquad (22)$$

$${}^-O_3SO:\dot{S}(O)(CH_3)_2 + SO_4^{-} \xrightarrow{k_3} O_3SO:S(O)(CH_3)_2 + SO_4^{2-} \qquad (23)$$
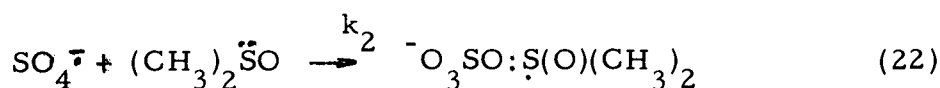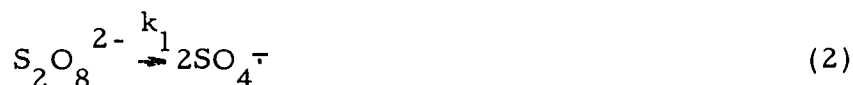
This is the simplest possible mechanism, and it leads to the

rate law

$$\frac{-d\left[S_2O_8^{2-}\right]}{dt} = k_1\left[S_2O_8^{2-}\right] \qquad (24)$$

A radical chain might be propagated by introducing the step

$${}^-O_3SO:S(O)(CH_3)_2 + S_2O_8^{2-} \xrightarrow{k_2} SO_4^{2-} + SO_4^{-} + O_3SO-S(O)(CH_3)_2 \qquad (25)$$
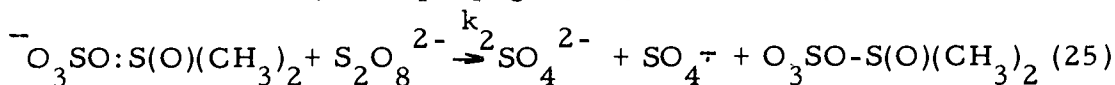
It is impossible to distinguish between these two mechanisms with

the data available at present. It will be noted from Table II that the

first-order rate constant $(k_1$ or $k_1 + k_2^{'}\left[O_3SO\dot{S}(O)(CH_3)_2\right])$ is about

$(5.7 \pm 0.2) \times 10^{-6} \, \text{sec}^{-1}$.

The above reaction product has the well known oxosulfonium ion

structure and may be called oxosulfonium sulfate.

$$
\begin{array}{ccc}
\overset{+}{O} & O & \overset{+}{O} \\
| & | & | \\
H_3C - S - CH_3 & H_3C - \overset{\cdot}{S} - CH_3 & H_3C - S - CH_3 \\
| & | & | \\
CH_3 & OSO_3^- & OSO_3^- \\
\text{trimethyl oxosulfonium} & \text{oxosulfonium-} & \text{oxosulfonium} \\
\text{ion} & \text{sulfate radical} & \text{sulfate} \\
 & \text{ion} &
\end{array}
$$
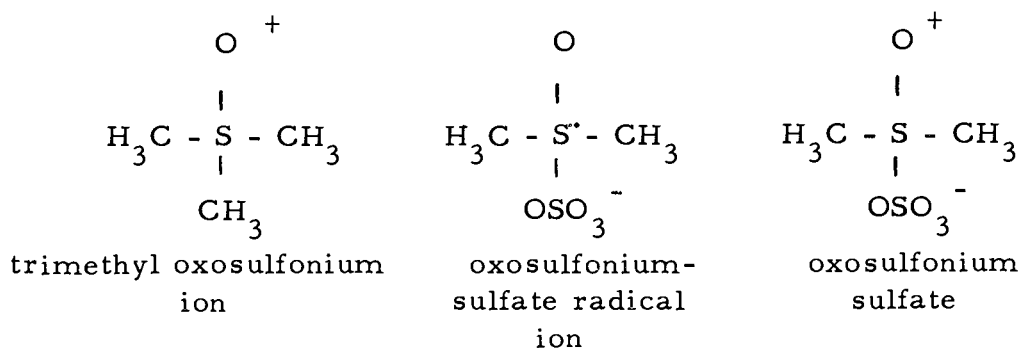
Although oxosulfonium sulfate has not been observed, trimethyl oxosulfonium iodide has been observed (32) and the above formulation is probably reasonable.

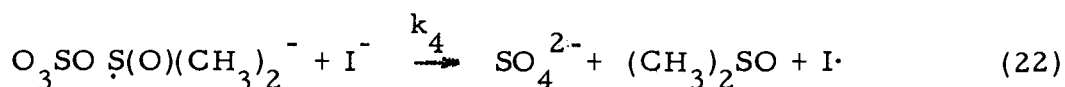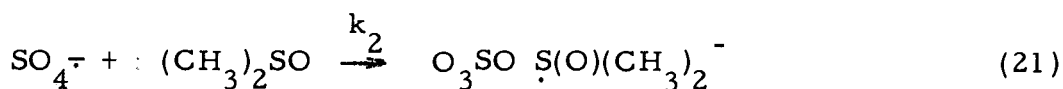Of course, the above reaction itself cannot be observed by following the production of triiodide as was done in experiment 11. Experiments 10 and 11 were done in order to compare the rate of triiodide production with the rate of persulfate decomposition. Experiment 11 was done in the DU at several wavelengths because the reaction was much faster than later experiments at lower persulfate and iodide concentrations. The ϵ_0 values used in calculating its $R / \left[S_2O_8^{2-} \right]$ value were those of triiodide in water. Clearly the I_2 production is much slower than the $S_2O_8^{2-}$ decomposition $(R / \left[S_2O_8^{2-} \right] = 3.6 \times 10^{-6}$ compared with $5.7 \times 10^{-6})$. This is in spite of the fact that the usual second-order $I^- - S_2O_8^{2-}$ reaction is also occurring to some extent (the extent is small because the reaction was done in the presence of atmospheric oxygen; an inhibitor of the second-order reaction). This difference in rate can be due

to one of two things: (1) the iodide ions and DMSO molecules are competing for the sulfate radical ions or (2) the iodide ions are not reacting directly with sulfate radical ions at all but are competing with the sulfate radical ions for the DMSO derived radical intermediate designated above as $O_3SO- \overset{\cdot}{S} -O(CH_3)_2$. Of course, there is always the possibility that both of these competitions are going on. Unfortunately, this confusing set of possibilities cannot be resolved by the data presented here. There is one fact which suggests that the second alternative is the correct one, namely, the first-order persulfate/zero-order iodide reaction is not observed in aqueous soltuion. This suggests that DMSO is indeed catalyzing the reaction by, for example, the following mechanism:

$$SO_4^{\cdot-} + (CH_3)_2SO \xrightarrow{k_2} O_3SO\; \overset{\cdot}{S}(O)(CH_3)_2^{-} \tag{21}$$

$$O_3SO\; \overset{\cdot}{S}(O)(CH_3)_2^{-} + I^{-} \xrightarrow{k_4} SO_4^{2\cdot-} + (CH_3)_2SO + I\cdot \tag{22}$$

$$I\cdot + I\cdot \longrightarrow I_2 \tag{23}$$

Any solvent molecules which react with sulfate radical ions but do not react with iodide are not significant since they produce no detectable products.

The third reaction is one in which I^- and $S_2O_8^{2-}$ react directly. The mechanism for this reaction in aqueous solution has already been discussed. There is no reason to believe that the mechanism

will be any different in DMSO.

The data in Table III show that the overall reaction is first-order in persulfate, since the basic rate law is

$$R_o = \frac{dI_2}{dt} = k_a \left[S_2O_8^{2-} \right] + k_b \left[I^- \right] \left[S_2O_8^{2-} \right], \qquad (21)$$

$$R_o / \left[S_2O_8^{2-} \right] = k_a + k_b \left[I^- \right] \qquad (26)$$

which is a constant when iodide is constant as it is in experiment

13. The numbers themselves are, however, qualitative because

the experiment was done in the presence of oxygen.

The Effect of Oxygen

Table IV contains the results of two experiments done in the

presence of atmospheric oxygen. Figure 2 shows $R_o / \left[S_2O_8^{2-} \right]$

values from Table IV plotted versus $\left[I^- \right]$. The values for the rate

constants are $k_a = 0.48 \times 10^{-6}$ and $k_b = 0.70 \times 10^{-4}$. These values

may be compared with the data from experiments 33, 35, 37 and 38

which are also plotted in Figure 2 and which yield values of

$k_a = 0.510 \times 10^{-6}$ and $k_b = 1.30 \times 10^{-4}$. The effect on k_b is mark-

ed while the effect on k_a is less important. In addition it should be

noted that values of $R_o / \left[S_2O_8^{2-} \right]$ tended to vary a great deal at

constant $\left[I^- \right]$ when oxygen was present, possibly due to slightly

varying amounts of O_2 actually in an individual solution. The

Table III. Verification of first-order in persulfate.

Run	$[K_2S_2O_8] \times 10^3 M$	$[KI] \times 10^3 M$	$[K^+]_{total} \times 10^3 M$	$\mu \times 10^3 M$	$R_o/[S_2O_8^{2-}] \times 10^6 \ sec^{-1}$
13 A	1.58	20.2	42.3	43.9	2.50
B	3.16	20.2	40.7	43.9	2.66
C					
C	4.75	20.2	39.1	43.9	2.59
D	6.33	20.2	37.6	43.9	2.29
E	7.91	20.2	36.0	43.9	2.41

Table IV. Some runs done in the presence of oxygen.

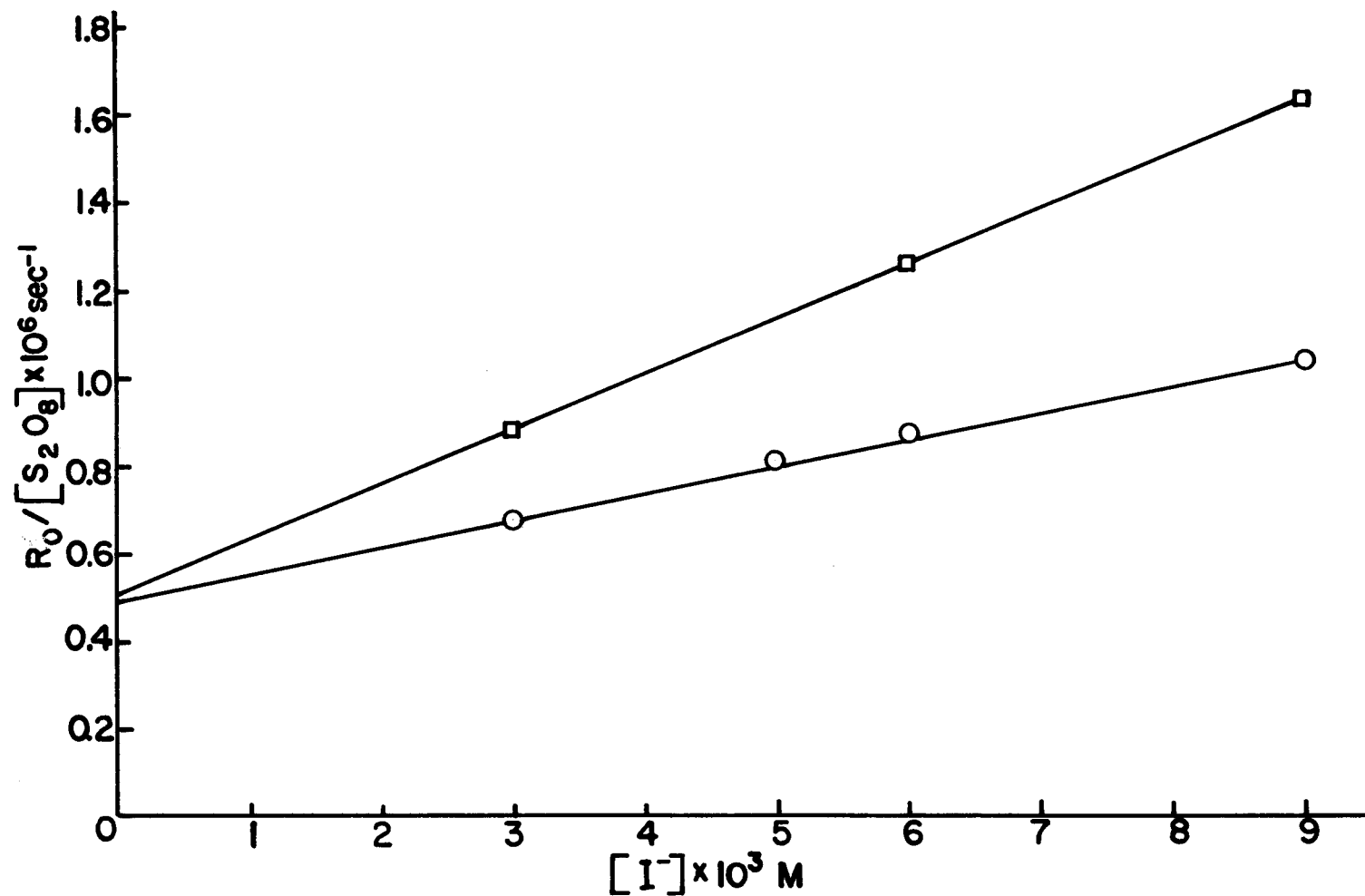| Run	$[K_2S_2O_8] \times 10^3 M$	$[KI] \times 10^3 M$	$[K^+]_{total} \times 10^3 M$	$\mu \times 10^3 M$	$R_o / [S_2O_8^{2-}] \times 10^6 sec^{-1}$
31 A	4.615	3.01	45.8	50.4	0.653
B	4.654	6.02	45.7	50.3	0.866
C	4.721	9.03	45.6	50.3	1.03
32 A	4.985	4.50	45.5	50.5	0.806

Figure 2. Comparison of runs done with (□) and without (O) nitrogen sweep at $\mu = 0.0500$ M.

results reported in Table IV are the most self consistent obtained

without sweeping the solvent with nitrogen.

The small difference in the above noted k_a values is probably

not significant. It should be remembered that all of the errors in

the runs are thrown onto these values, and they are probably only

good to within $\pm$ 10% in general. In particular, Figure 2 shows that

the scatter of points about the line is such that the k_a intercept could

be higher than the intercept of the N_2 sweep line.

The k_b values are, on the other hand, strikingly different.

Examination of the mechanisms listed above (equations 11-13) sug-

gests no clear cut mechanism by which oxygen could interfere with

the production of iodine. It is well known that oxygen has the ability

to act as a radical scavanger because it has two unpaired electrons.

For the same reason it may enter into a reaction as the propagator

of a radical chain. Thus the rates of some catalyzed persulfate

oxidations are increased by oxygen (33). The fact that oxygen does

have such an important effect on this reaction is strong evidence

that it is a radical chain mechanism.

Radical chain mechanisms may be written for the second-order

reaction, but all of them envolve either a sulfate radical ion or

something very much like it. If oxygen was a scavenger for SO_4^-

a significant effect on the first-order reaction would be observed.

Since this is not the case, the explanation for this oxygen inhibition

must remain unaccounted for.

Effect of Added Cations

In Table I are listed the results of experiments done at various ionic strength values with the iodide varied. Figure 1 shows the $R_o / \left[S_2 O_8^{2-} \right]$ values from this table plotted versus $\left[I^- \right]$ for calculation of k_b and k_a values. These values are listed in Table V.

Figure 3 shows a plot of log k_b versus $\left[K^+ \right]_{total}$ which is compared with a plot of Perlmutter-Hayman and Stein's log k_b values calculated from the A, B, and D values they obtained for K^+ (see equation 18). Clearly if the data from DMSO is to agree with equation (18) the values of the constants must be somewhat altered from their values in aqueous solution. This, in itself, is no draw back to the use of equation (18), but reference to Figure 4 shows that a plot of k_b versus $\left[K^+ \right]_{total}$ is linear as predicted by equation (15). Thus, equation (15) seems to be a better equation to describe the relationship between k_b and cation concentration for the range investigated than equation (18). The product of constants $k_a k' K$ from equation (18) is calculated to be 2.16×10^{-3} from the slope of the line in Figure 4.

Figure 5 shows a plot of log k_b versus $\sqrt{\mu}$ which is also a straight line as predicted by the Brønsted-Debye equation. The slope of this line is 3.36 which determines the value of α in

Table V. Values of k_a and k_b at various ionic strengths.

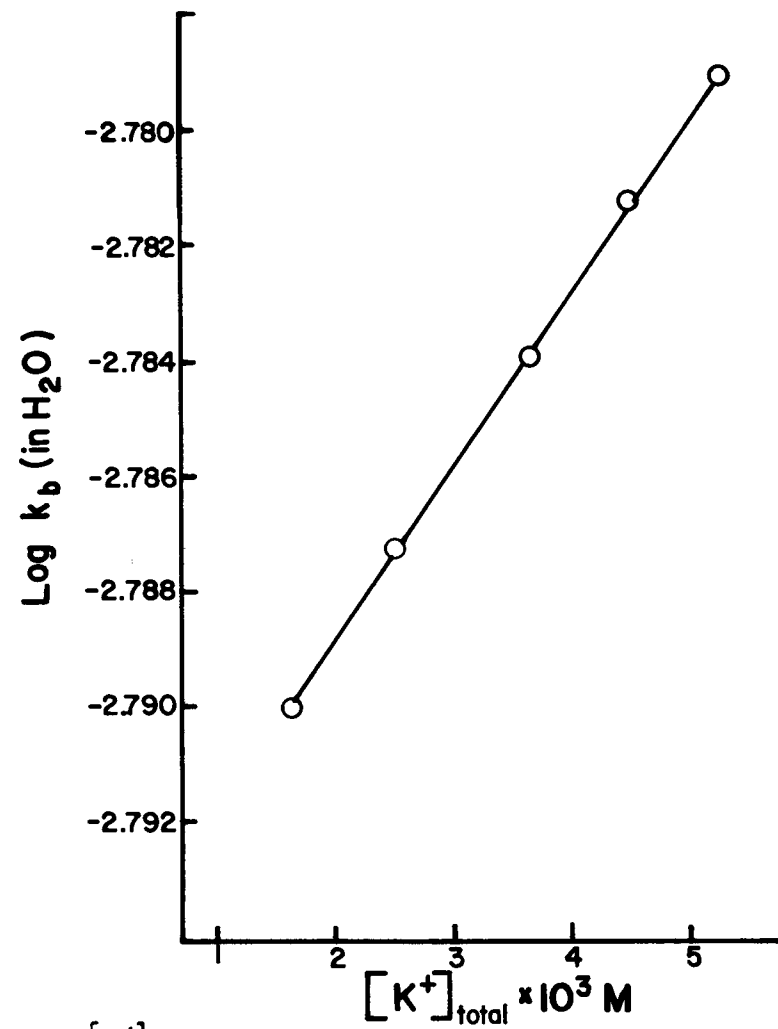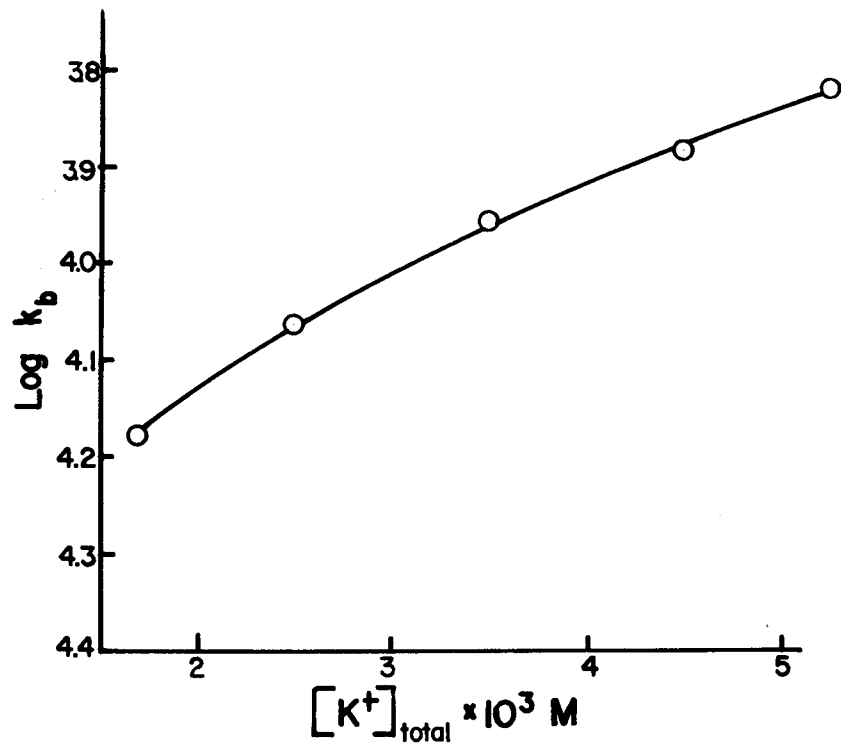| $\mu \times 10^3 M$	$[K^+]_{total} \times 10^4 M$	$k_b \times 10^4 M^{-1} sec^{-1}$	$k_a \times 10^7 sec^{-1}$
60.0	55.0	1.55	4.47
50.0	45.0	1.30	5.10
40.0	35.0	1.10	7.52
30.0	25.0	0.862	5.43
20.0	16.3	0.662	8.00

Figure 3. Log k_b vs. $[K^+]_{total}$.

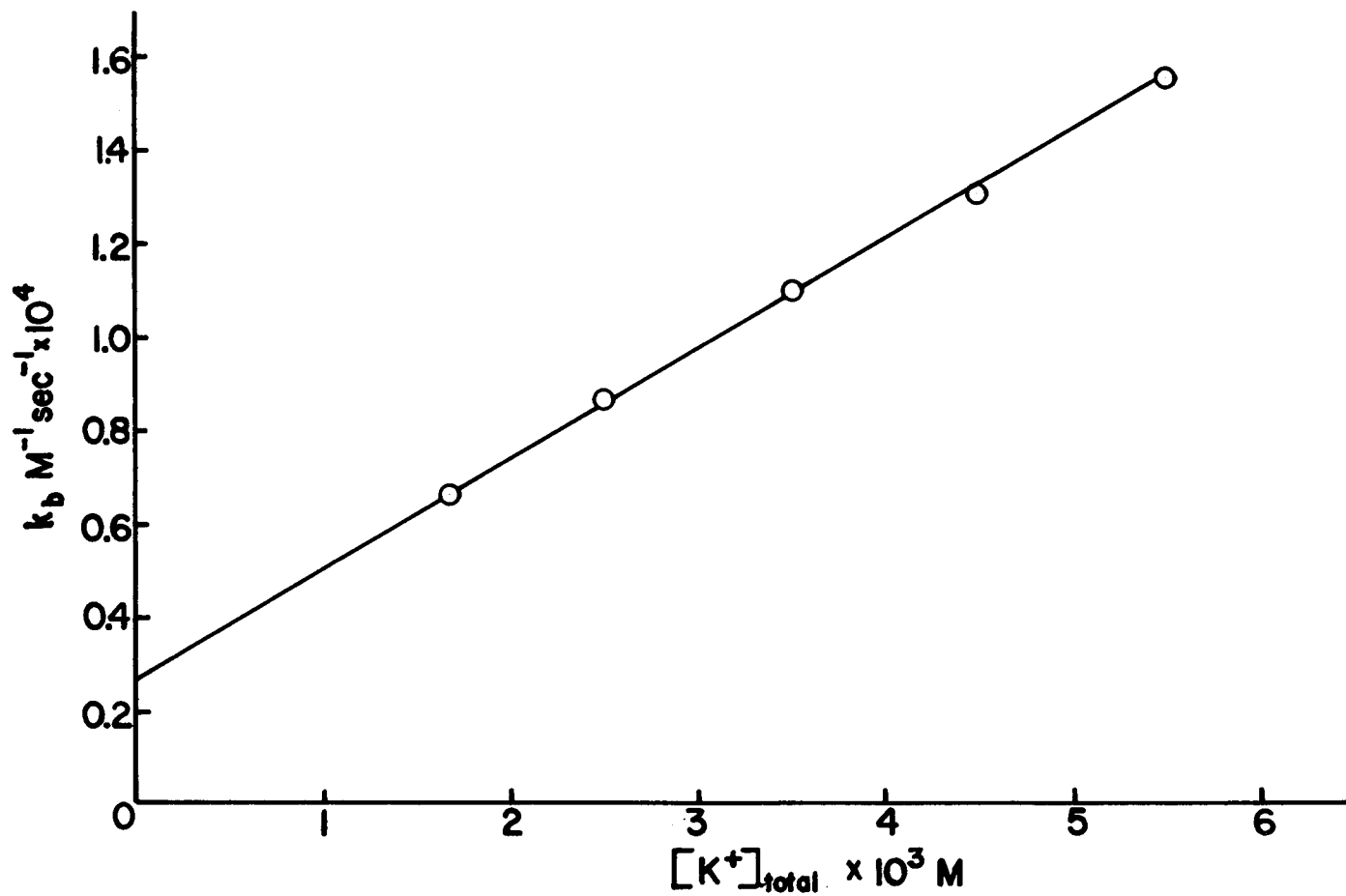actual values in DMSO

from equation (15) in H_2O

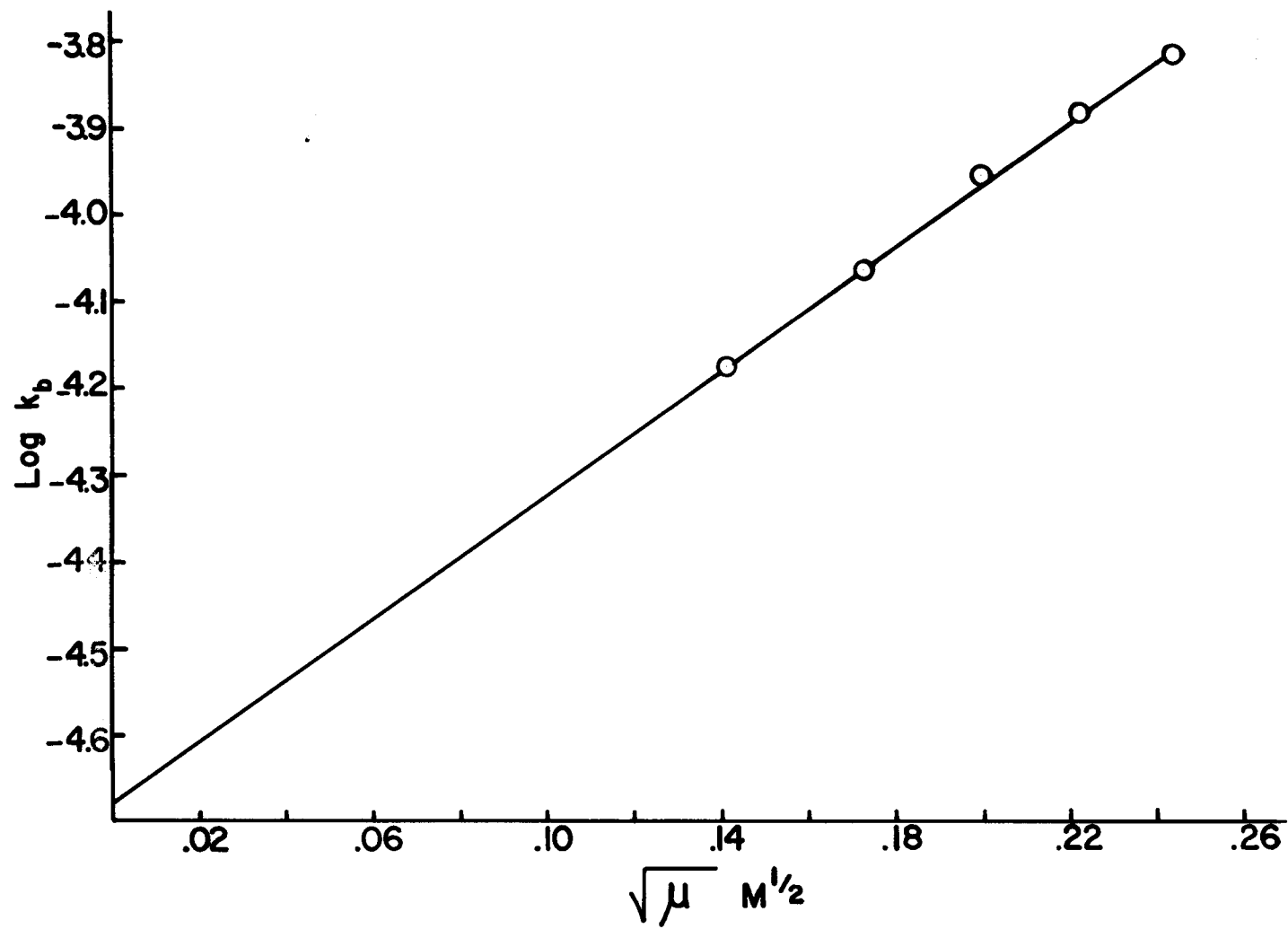Figure 4. k_b in DMSO vs. total potassium ion.

Figure 5. Log k_b in DMSO vs. square root of ionic strength.

equation (14) to be 0.840 in contrast to a value of 0.509 in water.

The values of $\sqrt{\mu}$ employed in these experiments are somewhat high-er than those usually expected to obey equation (14). Amis and Potts (1) did obtain agreement with the approximate form of equation (25) at $\sqrt{\mu}$ values of .212 and above.

The value of α is related to dielectric constant and tempera-ture by the following equation:

$$\alpha = K \, (DT)^{-3/2} \, . \tag{27}$$

Since the value of α in water at $25^{\circ}C$ is equal to 0.509 the value of α in DMSO at $20^{\circ}C$ can be readily calculated,

$$\frac{\alpha}{.509} = (\frac{80.4 \times 298}{48.9 \times 293})^{3/2} = 2.02$$
$$\alpha = 1.03 \, .$$

The values of D in water and DMSO being 80.4 (1) and 48.9 (30) respectively. The true value of α is higher than that calculated by equation (14). This apparent disagreement can readily be explained as will be shown below.

The effect of added barium ion on the reaction rate is even more striking than that of potassium ion as would be expected. Only one experiment was done with barium ion added (Table VI). The value of k_b at a total $\left[K^+\right]$ = 0.0199 M and $\left[Ba^{++}\right]$ = 4.16 x 10^{-3} M was 2.00 x 10^{-4} in contrast to a value of 0.738 x 10^{-4} from Figure 4 at the same $\left[K^+\right]_{total}$ with no added Ba^{++} . Using

Table VI a. Added $Ba(NO_3)_2$.

Run		$[K_2S_2O_8] \times 10^3 M$	$[KI] \times 10^3 M$	$[K^+]_{total} \times 10^3 M$	$[Ba^{++}] \times 10^3 M$	$R_o/[S_2O_8^{2-}] \times 10^6 \, sec^{-1}$
57	I	4.96	0.913	19.9	4.16	0.667
	J	4.96	3.170	19.9	4.16	1.08
	K	4.96	5.271	19.8	4.16	1.56

Table VI b. Added Et_4NClO_4 (65) and Et_4NCl (66).

| Run		$[K_2S_2O_8] \times 10^3 M$	$[KI] \times 10^3 M$	$[K^+]_{total} \times 10^3 M$	$[Et_4N^+] \times 10^3 M$	$R_o/[S_2O_8^{2-}] \times 10^6 \, sec^{-1}$
65	O	5.00	6.16	34.8	5.79	1.30
	P	5.00	6.16	34.8	11.58	1.30
	Q	5.00	6.16	34.8	17.37	1.30
66	R	5.03	6.13	35.0	6.88	0.524
	S	5.03	6.13	35.0	13.07	0.491
	T	5.03	6.13	35.0	19.27	0.431

equation (15) as a guide, the relationship between k_b and concentrations of various cations may be indicated by the equation

$$k_b = k_o + a\,(C_1) + b\,(C_2) + c(C_3) + \ldots \tag{28}$$

where a, b and c are empirical constants and C_1, C_2, C_3 are concentrations of each cation present. Using the one value for k_b with added barium ion the equation becomes

$$k_b = 2.90 \times 10^{-5} + 2.16 \times 10^{-3}\left[K^+\right] + 3.07 \times 10^{-2}\left[Ba^{++}\right].$$

There are two ways in which added cations may act to accelerate reactions between two anions. One, the so-called primary salt effect, is due to the ionic atmospheres associated with the anions before they react and after they have formed the activated complex. This is the effect predicted in the Brønsted-Debye equation. A second effect is ion pairing which produces deviations from equation (14). Howells (14) has found that the effect of added cations on the persulfate iodide rate constant in water increases in the order

$$H^+ < Li^+ < Na^+ < NH_4^+ < K^+ < Rb^+ < Cs^+.$$
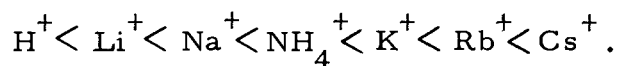
This is the reverse order to be expected if ion pairing were causing the acceleration. Howells has suggested that the electric field of the cation acts to retard the movement of the reactant anions through the solution and prevent them from coming together to form the activated complex. This effect in addition to the primary salt effect

renders the larger cations more effective (and more ideal) than the smaller ones.

In DMSO, however, ion pairing is considerably more likely. The large discrepency in the calculated and theoretical values of α calculated above indicate that K^+ ions are combined with $S_2O_8^{2-}$ ions to some extent. The value calculated from the data was less than theoretical value. Even accounting for the breakdown of the limiting law at moderate ionic strengths the equilibrium

$$K^+ + S_2O_8^{2-} \rightleftharpoons KS_2O_8^{-} \tag{29}$$
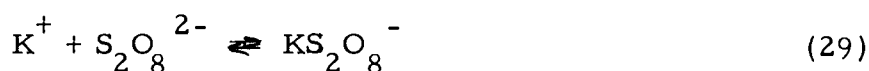
does exist, and there must be a fairly large concentration of $KS_2O_8^{-}$ ions present.

The relatively greater effect of Ba^{++} can be understood in the light of ion pairing also. For example, the pK values of the dissociation constants for $KClO_3$ and $Ba(ClO_3)_2$ are -0.1 and 0.7 respectively (6, pp. 169-170). These values give some indication of the ion pairing tendencies of the two ions.

Table VI also includes $R_o / \left[S_2O_8^{2-} \right]$ values for three runs containing added Et_4NClO_4. The results show that the added Et_4N^+ ion had no effect on the reaction rate. This result certainly contradicts the previous rough agreement with equation (14). In this experiment the ionic strength was varied from 0.046 to 0.057 which, though not a large variation, should have produced a noticeable rate increase. This suggests that there is no general cation effect on the

reaction at all but only the specific effect of something like ion pairing. In other words, the linearity of log k_b versus $\sqrt{\mu}$ noted above is coincidental.

The above results do not weaken the argument about ion pairing. The Et_4N^+ ion has a very small ionic potential. It was chosen for study because it is an ion which would be expected to ion pair very little with $S_2O_8^{2-}$. According to Table VI it exhibits no ion pairing at all.

The k_a values listed in Table V also show some dependence on ionic strength. In this case, however, the k_a value decreases with increasing ionic strength. It happens that three of the values (at μ = 0.06, 0.05, and 0.02) fall on a straight line when log k_a is plotted versus $\sqrt{\mu}$ with a slope of -2.38. The interpretation of why this effect is observed is a great deal more difficult than in the second-order reaction because the rate determining step in this reaction involves only one ion, $S_2O_8^{2-}$. If, for example, the effect is due to ion pairing it might be true that the $KS_2O_8^-$ ion, whose charge is somewhat localized on the oxygens farthest from the potassium, would be less likely to break apart than the $S_2O_8^{2-}$ ion whose charges are more or less localized at opposite ends of the ion.

Thus, the reactions are

$$
\text{unpaired} \quad
\begin{array}{c}
\overset{-}{O} \\[-2pt]
| \\[-2pt]
O - S - O - O - S - O \\[-2pt]
| \\[-2pt]
O
\end{array}
\begin{array}{c}
\overset{-}{O} \\[-2pt]
| \\[-2pt]
\\[-2pt]
| \\[-2pt]
O
\end{array}
\longrightarrow
\begin{array}{c}
\overset{-}{O} \\[-2pt]
| \\[-2pt]
O - S - O\cdot \; + \\[-2pt]
| \\[-2pt]
O
\end{array}
\begin{array}{c}
\overset{-}{O} \\[-2pt]
| \\[-2pt]
O - S - O\cdot \\[-2pt]
| \\[-2pt]
O
\end{array}
$$

$$
\text{paired} \quad
\begin{array}{c}
O \\[-2pt]
| \\[-2pt]
KO - S - O - O - S - O\cdot \\[-2pt]
| \\[-2pt]
O
\end{array}
\longrightarrow
\begin{array}{c}
O \\[-2pt]
| \\[-2pt]
KO - S - O \; + \\[-2pt]
| \\[-2pt]
O
\end{array}
\begin{array}{c}
\overset{-}{O} \\[-2pt]
| \\[-2pt]
O - S - O\cdot \; . \\[-2pt]
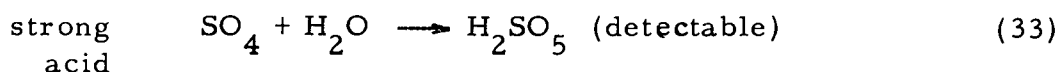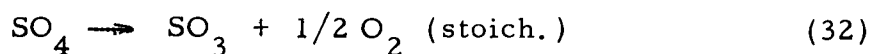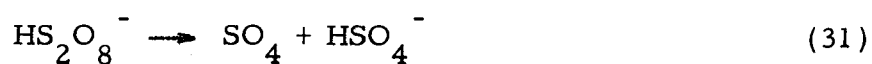| \\[-2pt]
O
\end{array}
$$
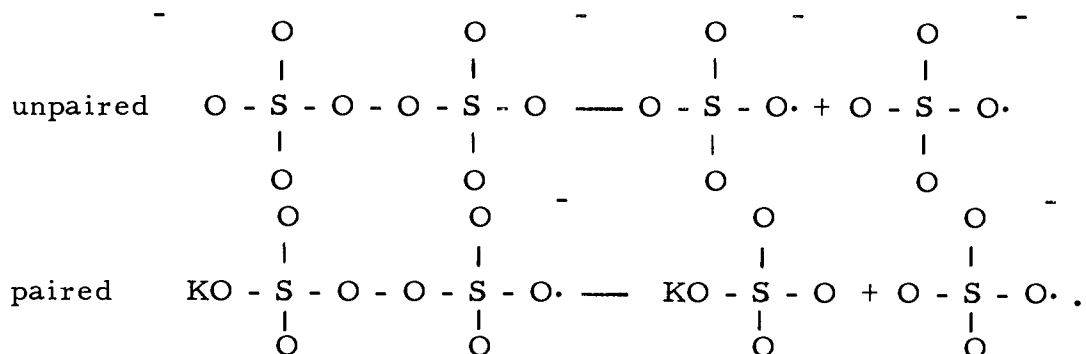
The electrostatic repulsion between the ends of the unpaired ion

would serve to enhance the transition state and products. But with

one end of the ion paired this repulsion does not exist. But it is

difficult to estimate the magnitude that this effect may be expected

to have. In addition, there may be other effects which require a

more intimate knowledge of the transition state and the $S_2O_8^{2-}$ ion

than is available at present. Nevertheless, the effect does exist

to a significant extent despite the large errors which may exist in

the listed k_a values, and it seems possible that further study of the

salt effect on k_a might lead to important discoveries about the first-

order reaction.

When Kolthoff and Miller (23) studied the thermal decomposi-

tion of aqueous persulfate solutions, they found that, while the un-

catalyzed rate constant was unaffected by added salts, the acid cata-

lyzed rate constant exhibited a negative salt effect. This fact casts

some doubt on the ion pairing argument advanced above as a

possible explanation for the salt effect on k_a in DMSO. Since, if

both the k_a reaction in water and DMSO have the same rate deter-

mining step, ion pairing should influence both reactions about equal-

ly.

Kolthoff and Miller advanced no explanation as to why their

reaction had a salt effect. The acid catalyzed decomposition

mechanism advanced as:

$$H^+ + S_2O_8^{2-} \rightleftharpoons HS_2O_8^- \tag{30}$$

$$HS_2O_8^- \longrightarrow SO_4 + HSO_4^- \tag{31}$$

$$SO_4 \longrightarrow SO_3 + 1/2\,O_2 \text{ (stoich.)} \tag{32}$$

$$\text{strong} \quad SO_4 + H_2O \longrightarrow H_2SO_5 \text{ (detectable)} \tag{33}$$
$$\text{acid}$$

seems to bear little relationship to the decomposition mechanism

proposed above for DMSO solution.

Solvent Effects

Effect on k_b

Strictly speaking, two of the previous sections (Mechanism

and Effect of Added Cations) have dealt with solvent effects. Already

then, it is apparent that there are differences between the persul-

fate-iodide reaction in water and DMSO. Another obvious difference

is the lower k_b values obtained in DMSO as opposed to water.

Most values for k_o (obtained from plots of log k versus $\sqrt{\mu}$)

obtained by various workers fall in the range

$(1.26$ to $1.30) \times 10^{-3}$ M^{-1} sec^{-1} (1, 18, 20, 21). One pair of

workers obtained a somewhat higher 1.60×10^{-3} M^{-1} sec^{-1} (27).

The value of $\left(k_b\right)_o = 2.90 \times 10^{-5}$ M^{-1} sec^{-1} was obtained by

extrapolation of the plot of k_b versus $\left[K^+\right]_{total}$ (Figure 4).

Amis and Potts (1) studied the reaction in various isodielectric

ethanol-water mixtures. They obtained the following relationship

between dielectric constant and log k valid from dielectric constants

of 80.37 to 69.00:

$$\log k = 1.92 - 229 \ (1/D). \tag{34}$$

This equation was obtained in solutions which had a high ionic

strength, but it is not exactly clear what the actual value was. If

the dielectric constant value for DMSO of 48.9 is substituted into

equation (34) a k value of 5.75×10^{-2} results which is higher than k_o

in water. This value can be corrected by realizing that the value

of k in water from equation (34) is 0.117 as opposed to

$k_o = 1.28 \times 10^{-3}$. Thus, equation (34) leads to a value which is

100 times too high, and the $\left(k_b\right)_o$ in DMSO becomes 6×10^{-4}. This

value is about 20 times as great as the actual value obtained.

It is usually found that anions have less stability in aprotic

solvents than in water. This is because many anions in water rely

on hydrogen bonding for stability. Since this hydrogen bonding is absent in aprotic solvents, the anions are more open to attack by another reactive species. This argument holds true for reactions between ions of unlike charge and reactions between ions and neutral molecules where the transition state does not rely much on solvation for stabilization. However, in reactions between ions of like charge the transition state must be more highly solvated than the reactants. Hence, the $IS_2O_8^{3-}$ species suffers more from lack of hydrogen bonding than the I^- and $S_2O_8^{2-}$ ions. It is not surprising, then, that the reaction is 20 times slower in DMSO than in a water-like solvent of dielectric constant equal to 48.9.

Solvent Mixtures

Some experiments were done in DMSO/water mixtures. The data for the k_b values thus obtained is rather surprising. Figure 6 shows $R_o / \left[S_2O_8^{2-} \right]$ values plotted versus $\left[I^- \right]$. The k values are all multiplied by the extinction coefficient because the extinction coefficient for I_3^- is not known in the various solvent mixtures. The data are of a qualitative nature, but it is still apparent that the k_b values obtained in (85.00 and 75.00)% by weight DMSO mixtures are about half that obtained in 100% DMSO at the same ionic strength. This is the reverse of the expected effect since k_b ought to increase
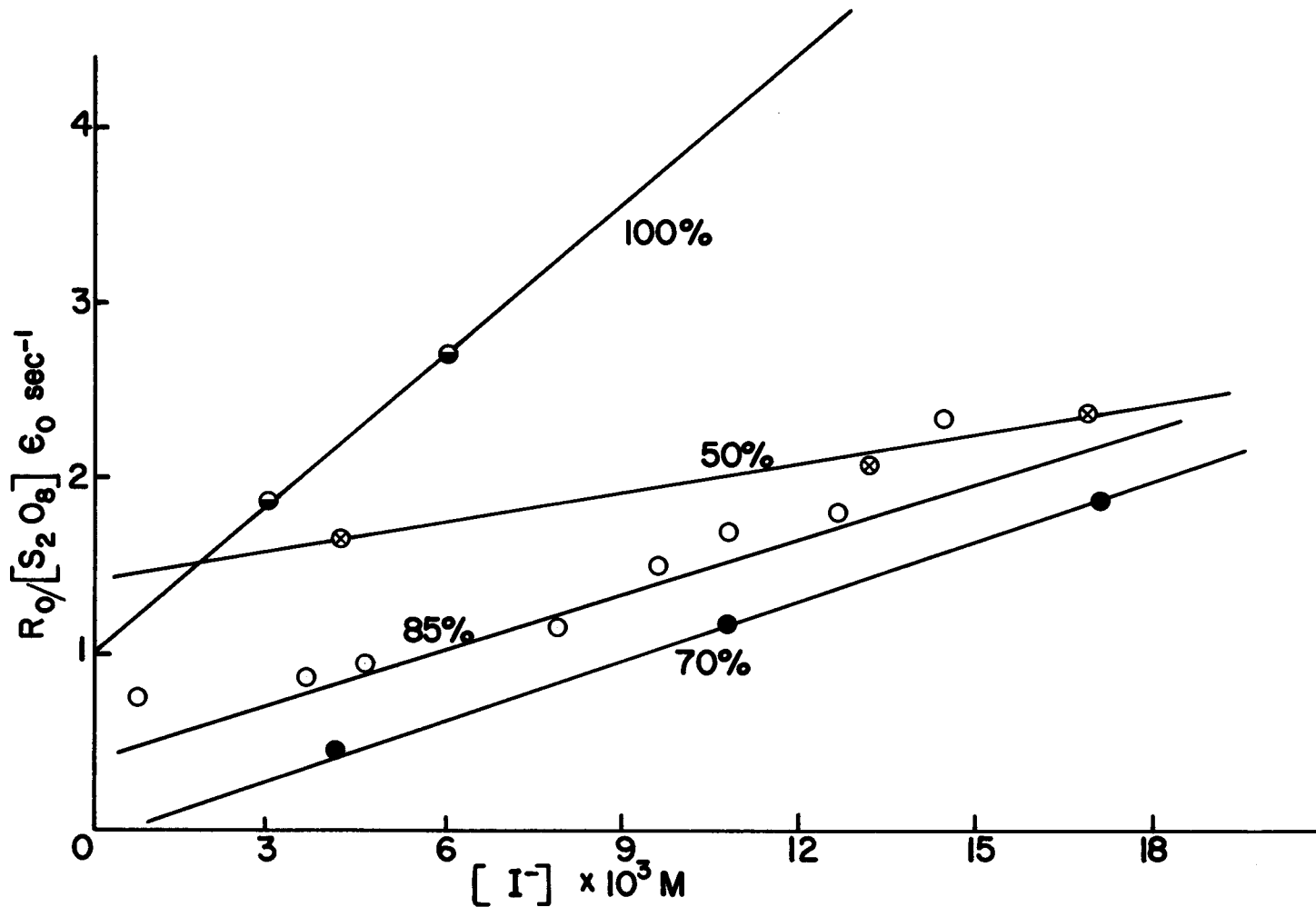
Figure 6. Plots of $R_o / [S_2O_8{}^{2-}]$ vs. $[I^-]$ for various H_2O -DMSO mixtures (100% -◒, 85.00% -○, 70.00% -●, 50.00% -⊗DMSO by weight).

as more water is added to the solvent. No ready explanation

presents itself to explain this phenomenon. The surprising k_a

and k_b values in the 50.00% DMSO by weight mixture suggest that

something was radically wrong with the experiment.

The solvent effect on k_a, however, is more reasonable. Re-

ference to Figure 6 will show that k_a seems to decrease rapidly

from 100% DMSO to 70.00% DMSO where it practically disappears.

This indicates that the k_a reaction does not occur unless the con-

centration of water is very low. This supports the contention

made above that the species which reacts will iodide ion in this

mechanism comes from DMSO and that I^- does not react with

SO_4^- directly.

Catalytic Effect of Chloride

It was thought that chloride ion might exhibit a catalytic

effect on the second-order reaction which does not exist in aqueous

solution. To discover this effect, one experiment was done with

varied amounts of tetraethylammonium chloride in the solution.

The results may be found in Table VII. All these values for

$R_0 / \left[S_2O_8^{2-} \right]$ are lower than those taken from Figure 1c which has

the same $\left[K^+ \right]_{total}$ value. This is due to two factors: (1) the data

in Table VII were obtained at 380 mμ instead of 370 mμ which was

the usual wavelength; (2) the chloride ions compete with iodide ions

Table II. Reduction of persulfate by DMSO and KI

Run		wt. % DMSO	$\left[K_2S_2O_8^{2-}\right] \times 10^3 M$	$\left[KI\right] \times 10^3 M$	$\left[K^+\right]_{total} \times 10^3 M$	$R_o / \left[S_2O_8^{2-}\right] \times 10^6 M^{-1} sec^{-1}$
59	O	85.00	4.97	1.028	44.8	0.320
	P	85.00	4.97	4.487	44.8	0.413
	Q	85.00	4.97	8.210	45.0	0.951
61	U	85.00	4.98	3.473	45.0	0.362
	A	85.00	4.98	10.453	45.0	0.682
	B	85.00	4.98	14.275	45.1	1.02
62	C	85.00	4.95	8.006	45.1	0.543
	D	85.00	4.95	9.196	45.1	0.645
	E	85.00	4.95	12.63	44.7	0.835
68	I	70.00	5.04	3.920	45.0	0.204
	J	70.00	5.04	11.027	45.2	0.672
	K	70.00	5.04	15.367	44.8	0.974
64	L	50.00	4.99	4.379	44.8	0.816
	M	50.00	4.99	12.871	45.1	0.946
	N	50.00	4.99	20.846	45.0	1.10

for iodine molecules and the I_2Cl^- ion has a lower ϵ_o value than I_3^-.

The second reason above also accounts for the slight drop in

$R_o / \left[S_2O_8^{2-} \right]$ with increasing chloride concentration. It is clear,

however, that there is no catalysis.

Effect of Allyl Acetate

Three experiments were done in which allyl acetate was added

to the reaction mixture to act as a radical trap for SO_4^- radicals and

eliminate the first-order component of the rate law from observation.

All three of these experiments were done in the presence of oxygen

since they were of a preliminary nature so their values are not included

here. However, the results did show that even when allyl acetate was

present in concentrations as high as 0.12 M with $\left[S_2O_8^{2-} \right] = 5 \times 10^{-3} M$

it had no effect on the rate of the reaction.

This is a surprising result because it tends to indicate that there

are no SO_4^- ions to trap. However, if the mechanism indicated above

is correct, the SO_4^- ions probably react with DMSO molecules very

quickly and do not exist long enough to be trapped by allyl acetate. The

allyl acetate must then compete with I^- ions for the oxosulfonium sul-

fate radical ions. Apparently, it competes poorly.

The Reaction of Persulfate and Cerous Ions

Fronaeus and Ostman (10, 11) have studied the oxidation of

cerous to ceric ion by persulfate. It follows the usual pattern of being zero-order in Ce (III) concentration except at very low values. Results of two experiments in which Ce (III) was oxidized by persulfate in DMSO are listed in Table VIII. It is hoped that by doing this reaction at various Ce(III) concentrations and extrapolating k values to zero Ce (III) some indication of the rate of the reaction.

$$S_2O_8^{2-} \longrightarrow 2SO_4^{-} \tag{2}$$

might be gained independently of the experiments done in the presence of iodide.

However, the reaction appears to be second-order in persulfate. In addition, a four fold increase in the Ce(III) concentration increased the value of $R_o/\left[S_2O_8^{2-}\right]^2$ by a factor of nearly 40. This rendered the reaction much too complex to be used in this study for any purpose.

Table VIII. The reduction of Ce(III) by persulfate.

Run	$\left[K_2S_2O_8^{2-}\right] \times 10^3 M$	$\left[Ce(III)\right] \times 10^3 M$	$\mu \times 10^3 M$	$R_o / \left[S_2O_8^{2-}\right]^2 M^{-1} sec^{-1} \times \epsilon_o^*$
34 A	1.287	4.50	49.9	0.94
B	3.753	4.50	50.3	0.980
C	6.172	4.50	50.0	0.979
56 F	3.520	1.09	60.1	0.026
G	9.049	1.09	60.2	0.0222
H	11.19	1.09	59.8	0.0278

*Data uncorrected for extinction coefficient of Ce(IV) in DMSO at 340 mμ

IV. CONCLUSION

The most remarkable facet of this reaction is the two term nature of the rate law in sharp contrast to its strictly second-order nature in water. This feature has already been discussed in some detail and it is to be regretted that so little data is available with which to determine more accurately the nature of the k_a reaction. It seems that valuable answers could be obtained by isolating the products of the persulfate decomposition in pure DMSO. Also more data is needed on the relationship between solvent composition, ionic strength and k_a. Further study of the first-order reaction could yield valuable information on the nature of all first-order persulfate oxidations.

The tentative conclusion that the second-order reaction is influenced by specific cations only and not by all cations generally, even at these moderate ionic strengths, is one which is in need of further verification. It is not surprising to find deviations from a frankly limiting equation like the Brønsted-Debye equation, but the fact that tetraethylammonium ion had no effect at all on the rate is startling indeed. It is unfortunate that more experiments were not done at various concentrations of multivalent ions like Ba^{++} or La^{+++} to firmly nail down the salt effect as being one of ionic strength or cation concentration only.

Another feature is the slowness of the second-order reaction

in DMSO as compared with water. It would be interesting to see if other reactions between ions of like charges behave in a similar fashion in DMSO. This would serve to test the conclusion that highly charged transition states are destabilized by lack of hydrogen bonding.

The question as to the extent to which ion pairing influences this reaction is one which cannot, as yet, be answered. It clearly must play some role in DMSO even with its moderate dielectric constant, especially in the case of di-and trivalent cations.

In general, DMSO is a satisfactory solvent in which to study ionic reactions. DMSO has the advantage of having the highest dielectric constant of any aprotic solvent. Most commonly employed water soluble salts are soluble in DMSO to some extent. Exceptions to this rule are chlorides, sulfates, and other salts containing anions of high ionic potential. Thus, kinetic studies of ionic reactions can be made which yield interesting solvent effects associated with lack of hydrogen bonding, etc.

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