

difference in what constitutes $[M]$ in each case) has been confirmed¹⁸ over a wide temperature range. The prediction of the pressure at which the first rate constant "falls off" has been confirmed.^{6,18} The values of the elementary rate constants in Table III are reasonable. The calculated steady-state pressures of NO_3 agree qualitatively with observations which are themselves qualitative. Thus these mechanisms are probably as well-established

as any complex mechanism in chemical kinetics.

Further work is needed on these systems. It is particularly desirable to have independently measured values of K , the extinction coefficient of NO_3 , and the ratio f/d . These three quantities appear to be more nearly available experimentally than the absolute values of the bimolecular rates involving NO_3 .

STANFORD, CALIFORNIA

RECEIVED FEBRUARY 10, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

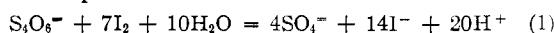
Rate Law and Mechanism of the Reaction of Iodine with Tetrathionate Ion

BY ALICE D. AWTRY AND ROBERT E. CONNICK

The kinetics of the oxidation of tetrathionate ion to sulfate by iodine was investigated under two widely different sets of conditions. The rate law was found to be $-d(\Sigma I_2)/dt = k_4(\text{S}_4\text{O}_6^{2-})(I_2)/(I^-)$ in both cases, although the value of k_4 differed by approximately a factor of two. The following mechanism is proposed: $\text{S}_4\text{O}_6^{2-} + I_2 \rightleftharpoons \text{S}_4\text{O}_6I^- + I^-$, then $\text{S}_4\text{O}_6I^- \rightarrow$ where the first reaction is a rapid equilibrium shifted far to the left and the second is the rate-determining step. It is proposed that the factor of two variation in k_4 arises from a change in the reactions following the rate-determining step. The heat and entropy of activation are 26 kcal. and 9 e.u., respectively.

Introduction

The rate of reaction of tetrathionate ion with iodine was studied in connection with the investigation of the thiosulfate-iodine reaction.¹ The oxidation of tetrathionate by iodine in acid solution seems to have been mentioned only once in the older literature. C. A. R. Wright² reported that, if an excess of iodine solution was left standing with thiosulfate overnight, a considerable amount of iodine disappeared, though volatilization of the iodine was prevented, and he showed that sulfate ion was produced.



While the present work was in progress, Dodd and Griffith³ published preliminary results of a study of this system.

Experimental

$\text{Na}_2\text{S}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$.—The salt was prepared from iodine and sodium thiosulfate, as described in the literature.⁴ Analysis gave 12.72% H_2O , and 41.54% S. Calculated values for $\text{Na}_2\text{S}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ are 11.76% H_2O , 41.87% S, molecular weight 306.3. If the solid has 12.72% H_2O , then the calculated per cent. S is 41.41, which is the observed within experimental error, and the molecular weight is 309.6. This value for the molecular weight was used. Qualitative tests⁵ showed a trace of sulfate, no iodide, no trithionate nor pentathionate.

Solutions.—Approximately $10^{-3} M$ tetrathionate solutions were made up by weight, and diluted for use in the experiments. In general, the stock solutions were not used more than a week after being prepared. The dry salt is stable, but solutions have a measurable rate of decomposition.⁵

All chemicals other than the tetrathionate were reagent-grade. Sodium perchlorate solutions were prepared by neutralization of perchloric acid with sodium carbonate. Distilled water, redistilled from alkaline permanganate solution, was used in making up all solutions.

(1) A. D. Awtry and R. E. Connick, *THIS JOURNAL*, **73**, 1241 (1951).

(2) C. A. R. Wright, *Chem. News*, **21**, 103 (1870).

(3) G. Dodd and R. O. Griffith, *Trans. Faraday Soc.*, **45**, 546 (1949).

(4) Abegg and Auerbach, "Handbuch der anorg. Chem.," Vol. 4, 1927, p. 554.

(5) Yost and Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, pp. 395, 397.

The concentrations of iodine and triiodide solutions were determined either by titration of the stock solutions with standardized thiosulfate, or spectrophotometrically.

Either hydrochloric or perchloric acid was used, and potassium chloride was added to give the desired ionic strength. Allowance was made in all calculations for the formation of I_2Cl^- .¹ All concentrations are expressed in moles per liter of solution indicated by M .

Procedure.—There were two kinds of experiments. The first had iodide and tetrathionate in large excess, so that their concentrations were constant, and the decrease in triiodide concentration was followed as a function of time. The second had no iodide added, and a slight excess of iodine over tetrathionate, so that the concentrations of all the reactants changed greatly during an experiment.

For the first kind the reaction was slow; the tetrathionate was pipetted into a solution of the other reactants, the mixture shaken and an absorption cell filled. The reaction was followed by measuring the triiodide concentration with a Beckman spectrophotometer, using a thermostated cell-holder.

For the second type, a solution of tetrathionate and potassium chloride (or sodium perchlorate) was mixed with one containing iodine and acid, by means of the small mixing device previously described.¹ The reaction was followed spectrophotometrically by measuring the optical density at both the iodine and triiodide maxima. Using the molar extinction coefficients given in Table I, the I_2 and I_3^- concentrations were calculated; from these and the triiodide equilibrium constant^{1,6} the iodide ion concentration was de-

TABLE I

MOLAR EXTINCTION COEFFICIENTS FOR I_2 , I_3^- AND I_2Cl^-

Wave length, Å.	ϵ_{I_2}	$\epsilon_{I_3^-}$	$\epsilon_{I_2Cl^-}$
4600	746	975	880
3530	19	26400	235

termined. The total iodide, *i.e.*,⁸ $(\Sigma I^-) = (I^-) + (I_3^-)$, is a measure of the amount of tetrathionate that has reacted, since no iodide was added

$$(\text{S}_4\text{O}_6^{2-}) = (\text{S}_4\text{O}_6^{2-})_0 - (\Sigma I^-)/14 \quad (2)$$

A check was made on the accuracy of the calculation of the iodine, triiodide and iodide concentration by calculating the total iodine in the solution

$$(\Sigma I) = (I^-) + 3(I_3^-) + 2(I_2) + 2(I_2Cl^-) \quad (3)$$

(6) G. Jones and B. B. Kaplan, *THIS JOURNAL*, **50**, 1845 (1928).

(7) A. D. Awtry and M. S. Tsao, to be published.

(8) Parentheses are used to designate concentrations in moles per liter.

TABLE II
 EXPERIMENTS WITH "HIGH" IODIDE AND TETRATHIONATE ION CONCENTRATIONS

Expt.	Temp., °C.	$k_4 \times 10^2$, min. ⁻¹	$k_{25} \times 10^2$, min. ⁻¹	Ionic strength	(ΣI_2) $\times 10^3 M$	Initial concentrations (I ⁻) $\times 10^3 M$	$(S_4O_6^{2-})$ $\times 10^4 M$	(H^+) $\times 10^3 M$
1	24.75 ± 0.05	1.30	1.34	0.050	1.44	1.42	5.23	1.0
2	24.0 ± .2	1.28	1.44	.050	1.45	1.42	4.89	1.0
3	25.0 ± .1	1.39	1.39	.050	1.45	1.44	5.26	1.0
4	25.00 ± .05	1.42	1.42	.050	2.9	1.41	5.24	1.0
5	25.00 ± .02	1.34	1.34	.055	5.8	2.75	10.5	1.0
6	25.00 ± .02	1.51	1.51	.055	0.5	2.85	10.45	1.1
7	25.00 ± .03	1.39	1.39	.050	2.9	1.40	5.31	0.1
8	25.05 ± .05	1.24	1.24 ^a	.050 ^b	2.0	1.37	103.2	1.0
9	29.48 ± .02	2.76	..	.050	2.9	1.41	5.24	1.0
10	25.0 ± .1	2.39	2.39	.050	1.45	1.44	0.528	1.0

^a Maximum value of k_4 ; see text. ^b Sodium perchlorate used in place of potassium chloride.

The rate of the reaction was calculated from dD/dt , where D is the optical density of the solution at 4600 Å., using an average extinction coefficient, ϵ , calculated from the data of Table I, the known iodide and chloride ion concentrations, and the I_3^- and I_2Cl^- equilibrium constants. The value for $d(\Sigma I_2)/dt$ obtained in this manner may be in error by as much as two per cent., but this is within the accuracy of the graphical measurement of dD/dt .

Results

Rate Law at "High" Iodide and Tetrathionate Ion Concentrations.—A plot of D , the optical density of the solution at the triiodide maximum, against time on semi-logarithmic paper gave a straight line, showing first order dependence on (I_2) or (I_3^-) . The constant k' for the rate law

$$-\frac{dD}{dt} = k'D \quad (4)$$

was determined from the slope of the line. From k' the constant k_4 for the rate law

$$-\frac{d(\Sigma I_2)}{dt} = k_4 \frac{(S_4O_6^{2-})(I_2)}{(I^-)} \quad (5)$$

was calculated. Here $(\Sigma I_2) = (I_2) + (I_3^-) + (I_2Cl^-)$.

The experimental data are given in Table II. Where the temperature differed from 25°, the value of k_4 was corrected to 25° by the temperature coefficient determined from experiments 4 and 9. The heat of activation is 26 kcal.

Excluding experiments 8, 9 and 10 the value of k_4 is nearly constant. The iodine and hydrogen ion concentrations vary tenfold; the iodide and tetrathionate, twofold. In addition the first order dependence of iodine was verified in each experiment.

From experiments 3, 8 and 10 the tetrathionate dependence of the rate appears to be slightly less than first order. Experiment 8 differed from the others in that k_4 was not constant but passed through a maximum during the course of the reaction, starting at approximately 0.5×10^{-2} , rising to 1.24×10^{-2} and falling to 0.35×10^{-2} . It is believed that the trend in k_4 shown by these three experiments is caused by changes in the steps following the initial reaction of iodine with tetrathionate, as will be discussed later.

Rate Law at "Low" Iodide and Tetrathionate Ion Concentration.—The following experiments differ from the previous set in having no added iodide; the average tetrathionate and iodide concentrations are roughly fifty-fold less, and the

iodine tenfold greater, than in those of Table II. The iodide concentration builds up from zero as the reaction proceeds, and the tetrathionate concentration goes to zero, there being an excess of iodine present.

The final iodine concentration, calculated from the initial iodine and tetrathionate concentrations, assuming sulfate ion to be the oxidation product, agreed with the observed within the experimental error; this is good evidence that the only important over-all reaction under these conditions is given by Eq. (1).

Data for a typical experiment are given in Table III. For considerable variation in concentrations of the reactants (see Eq. 5), k_4 remains nearly constant. The relatively low values of k_4 at the start of the experiment appear real, and were found in the other experiments of this set (see below).

TABLE III

DATA OF EXPERIMENT 13

Initial conditions: $(S_4O_6^{2-})_0 = 9.52 \times 10^{-6} M$; $(H^+)_0 = 10^{-4} M$; $(I_2)_0 = 9.5 \times 10^{-6} M$; $\frac{(I_2)}{(I_2) + (I_2Cl^-)} = 1.11$

Time, min.	$(I_2) +$ (I_2Cl^-) $\times 10^6$ M	(I_3^-) $\times 10^6$ M	(I^-) $\times 10^5$ M	$(S_4O_6^{2-})$ $\times 10^6$ M	$\frac{d(\Sigma I_2)}{dt}$ $\times 10^7$ M min. ⁻¹	k_4 $\times 10^2$ min. ⁻¹	(ΣI) $\times 10^5$ M
9.5	8.54	0.951	1.73	8.21	6.8	1.9	19.10
16.8	8.15	1.270	2.42	7.70	5.08	2.17	19.10
27.9	7.66	1.580	3.20	7.12	3.54	2.31	18.99
36	7.36	1.75	3.68	6.76	2.73	2.24	18.93
53	6.92	1.99	4.45	6.20	2.16	2.49	18.89
74	6.61	2.175	5.10	5.72	1.57	2.35	18.97
85.5	6.32	2.24	5.49	5.44	1.40	2.49	18.70
100	6.15	2.31	5.82	5.20	1.114	2.26	18.81
134	5.77	2.42	6.50	4.71	0.901	2.29	18.77
171	5.49	2.49	7.04	4.32	.714	2.35	18.77
183	5.39	2.51	7.22	4.18	.654	2.33	18.75
377	4.52	2.58	8.83	3.03	.317	2.27	18.64

The decrease in ΣI shown in the last column may be due to a systematic error in the calculation of the concentration of one of the species or possibly caused by iodine volatilization. In the latter case the correction to k_4 is within the accuracy of the experiments. The decrease in ΣI was smaller in the other experiments of this group.

The results of all the experiments of this set are given in Table IV. It is apparent that the k_4 rate law is obeyed closely, but the constant is

nearly twofold greater than for the experiments in Table II.

TABLE IV
TETRATHIONATE RATE CONSTANT AT VERY LOW IODIDE
Ionic strength = 0.050; (H⁺) = 1 × 10⁻⁴ M

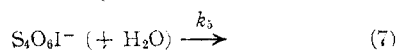
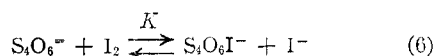
Expt.	Initial concentrations		Temp., °C.	<i>k</i> ₄ (av.) × 10 ² min. ⁻¹
	(S ₂ I ₂) × 10 ³ M	(S ₄ O ₆ ²⁻) × 10 ³ M		
11	10.9	6.55	25.00	2.27
12	19.9	12.4	25.0	2.3
13	9.5	9.52	25.00	2.3
14	19.0	19.1	25.00	2.31
15	9.3	9.52	35.55	10.0

Identical experiments at 10⁻³ and 10⁻⁴ M acid, showed the rate to be independent of the hydrogen ion concentration. In two experiments differing only in ionic strength, the one with the lower ionic strength was the slower, a shift which is in the direction predicted on the basis of the rate law found. A comparison of the rate constant at 25.00° and at 35.55° gives a value for the heat of activation in this region equal to 26 kcal.

Discussion

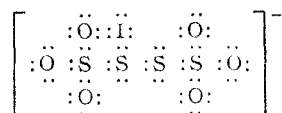
The data of Tables II and IV indicate that the *k*₄ rate law is obeyed well in the two separate sets of experiments. Dodd and Griffith⁸ found the same rate law to hold approximately for experiments at iodide concentrations intermediate between those of Tables II and IV, but at higher tetrathionate and iodine concentrations. Their *k*₄ decreased noticeably with increasing tetrathionate concentration.

The *k*₄ rate law can be explained by the mechanism



where the first equation represents an equilibrium shifted far to the left, and the second, the rate-determining step.

The species S₄O₆I⁻ is believed to have the structure



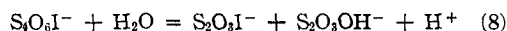
which is analogous to that postulated for S₂O₃I⁻, the intermediate in the iodine-thiosulfate reaction.¹

In spite of the good fit of the rate law, the numerical value of *k*₄ differs nearly a factor of two between the experiments of Tables II and IV. This curious fact can be explained by postulating that the primary products formed in Eq. (7) react differently for the two cases. If, each time a tetrathionate ion passes through the *k*₃ step, all of the sulfur is rapidly oxidized to sulfate ion, *k*₄ will have its maximum value. If part of the sulfur is not converted to sulfate, the value of *k*₄ will be decreased. The fact that the heat of activation is the same for both sets of experiments supports the idea that the rate-determining step is the same.

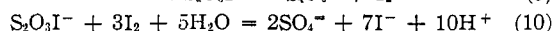
If it is assumed that the maximum observed value of *k*₄ corresponds to the rapid oxidation of all

the products of Eq. (7) to sulfate, the value of *Kk*₃ (see Eq. (6) and (7)) is *k*₄(max.)/7 or 3.3 × 10⁻³ min.⁻¹. The entropy of activation is then + 9 e.u., a value which is reasonable for the conversion of a large, doubly charged negative ion to two singly charged negative ions with no change in the number of particles involved in the reaction.

The rate law provides no information about the products of reaction (7), but one reasonable assumption is



Evidence which supports this hypothesis has been obtained by Dodd and Griffith.⁸ They showed that the reaction of iodine and tetrathionate produced a catalyst for the azide-iodine reaction; it is known^{3,9} that S₂O₃I⁻ is such a catalyst.¹⁰ The chemical behavior of S₂O₃I⁻ has already been studied,¹ and it is known that it can react according to either of the two equations



If the S₂O₃I⁻ reacts rapidly by (9), iodine is produced; if by (10), iodine is consumed. Thus the value of *k*₄, which is defined in terms of the rate of disappearance of iodine, will differ for the two cases.

An attempt was made to explain the relative values of *k*₄ in Tables II and IV by assuming that reactions (8), (9) and (10) occurred and, in addition, that the S₂O₃OH⁻, formed in Eq. (8), reacted rapidly with iodine to give sulfate. The only arbitrary parameter in the calculation was the value of *Kk*₃, since the rate constants for equations (9) and (10) are known.¹ For the experiments of Table II, the S₂O₃I⁻ reacts mainly by Eq. (9) while for those of Table IV it disappears primarily by reaction (10). The calculation is complicated by the fact that the S₂O₃I⁻ concentration builds up to an appreciable fraction of either the iodine or the tetrathionate concentration. The results of this theoretical treatment were in good qualitative agreement with the experimental data, but did not agree quantitatively within the experimental accuracy. It is therefore concluded that the system is more complicated than was assumed.

If one hypothesizes that the initial step in the reaction is always controlled by the mechanism of equations (6) and (8), then the value of *k*₄ can vary fourteen-fold: it will have a maximum value when the S₂O₃I⁻ and S₂O₃OH⁻ are both rapidly oxidized by iodine to sulfate, and a minimum value when the S₂O₃I⁻ rapidly reverts to tetrathionate by equation (9) and the S₂O₃OH⁻ remains unreacted. If the S₂O₃OH⁻ does not build up, *i.e.*, is oxidized rapidly to sulfate, *k*₄ can change only a factor of two. For the experimental conditions investigated it was found that *k*₄ varied from 2.3 × 10⁻² (Experiments 10 to 14) to 0.35 × 10⁻² (minimum value, Experiment 8). To be consistent with the initial hypothesis, one must conclude that the S₂O₃OH⁻ concentration builds up during the latter experiment.

In other experiments similar to those of Table

(9) Raschig, *Ber.*, **48**, 2088 (1915).

(10) This evidence would equally well support the formation of S₂O₃I⁺ and S₂O₃I⁺ (or a hydrate of this) in Eq. (7).

IV, but having *ca.* two-hundred-fold higher tetrathionate concentrations, k_4 increased initially and passed through a maximum as the reaction proceeded, similar to the behavior observed in Experiment 8. The values of k_4 lay within the limits cited above. It is reasonable that in all these experiments with high tetrathionate concentration, where the rate of formation of $S_2O_3OH^-$ is greatly increased, its concentration should tend to build up. Near the start of the experiment, very little of the $S_2O_3OH^-$ reacts with iodine, but as its concentration rises iodine is consumed more rapidly, and the value of k_4 is increased. A suitable choice of the rate law for the disappearance of $S_2O_3OH^-$ would account for the decrease in k_4 toward the end of the reaction.

It was noted in the experiments of Table IV that k_4 increased slightly near the beginning of the experiment. Presumably this is the same effect noted above, but occurring to a much smaller extent because of the lower tetrathionate concentration.

It is evident from the above discussion that the tetrathionate-iodine reaction is indeed complex. If the suggested explanation is correct, two intermediates are building up to appreciable concentrations under certain experimental conditions. Clearly this is not a unique explanation, and considerably more research is needed to test its validity. These results are being reported now because further work could not be carried out at this time.

WASHINGTON, D. C.

RECEIVED FEBRUARY 15, 1951

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Low Temperature Heat Capacities of Inorganic Solids.¹ VIII. Heat Capacity of Zirconium from 14 to 300°K.

BY GORDON B. SKINNER² AND HERRICK L. JOHNSTON

The heat capacities of hafnium-free zirconium have been measured in the temperature range 14 to 300°K., and the derived thermal functions have been calculated and tabulated at integral values of the temperature over this range. The entropy at 298.16°K. is 9.29 ± 0.04 e.u.

Introduction

Low temperature heat capacity measurements on zirconium have been made recently by Todd,^{3a} but the purity of his zirconium appears to be questionable. Coughlin and King,^{3b} who used the same specimen as Todd for high temperature heat content measurements, stated that, in addition to 2.15% hafnium, it appeared to contain appreciable amounts of oxygen or nitrogen, or both. The specimen used for the present measurements, having considerably higher purity, should yield more reliable values of the thermal functions of pure zirconium.

Apparatus and Materials

The zirconium used was a special hafnium-free product obtained from the Oak Ridge National Laboratory. It was in the form of small pellets sheared from larger pieces. A careful analysis carried out through the courtesy of the Battelle Memorial Institute, Columbus, Ohio, showed the presence of 0.025 mole % hafnium, 0.67 mole % iron, 0.15 mole % carbon, 0.026 mole % nitrogen, and a total of 0.082 mole % of nineteen other impurities tested for.

In our data a correction was made for the iron present. Vogel and Tonn⁴ found that several per cent. of iron will dissolve in solid zirconium. In making the correction we assumed that the solution is ideal, at least to the extent that the heat capacities are additive. The heat capacities of iron used were those given by Duyckaerts⁵ up to 20°K. and by Kelley in his review bulletin⁶ for higher temperatures. The maximum correction was about 0.3%. No analysis for oxygen could be made on the sample. However, since

the nitrogen content was found to be only 0.026 mole %, it could be expected that the oxygen content would be low also.

The pellets of zirconium were annealed by heating in high vacuum to about 800° for 15 minutes.

"Solid Calorimeter No. 1," of the group of seven vacuum calorimeters described in the first paper⁷ of this series, was used for the heat capacity measurements, and 93.461 g. of pellets (corresponding to 1.0204 moles of zirconium and 0.0069 mole of iron) was placed in it. This amount of zirconium was not sufficient to fill the calorimeter, so that the precision of these measurements is slightly lower than for some others made with the same apparatus.

Experimental Results and Calculations

Experimental heat capacities are summarized in Table I. A comparison with Todd's³ data shows that his values are lower at low temperatures and higher at high temperatures than ours, the curves crossing at about 130°K. This is what would be expected if Todd's zirconium contained oxygen or nitrogen, since the heat capacities of both ZrO_2^8 and ZrN^3 are lower at low temperatures and higher at high temperatures than the heat capacity of zirconium.

Table II gives the heat capacity and derived thermal functions for zirconium at selected integral values of the temperature. The entropy at 298.16°K. is 9.29 e.u., of which, 0.03 e.u. is contributed by the Debye T^3 extrapolation below 14°K. with θ equal to 242. Only two of our experimental heat capacity points above 60°K. deviate from a smooth curve by more than 0.3%. The maximum uncertainty in the entropy (three times the probable error) is 0.04 e.u.

Although our value of the entropy at 298.16°K. agrees well with Todd's,³ which is 9.28 ± 0.08 e.u., our values of the heat content and free energy

(7) H. L. Johnston and E. C. Kerr, *THIS JOURNAL*, **72**, 4733 (1950).

(8) K. K. Kelley, *Ind. Eng. Chem.*, **36**, 377 (1944).

(1) This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

(2) Monsanto Chemical Co. Fellow, 1950-1951.

(3) (a) S. S. Todd, *THIS JOURNAL*, **72**, 2914 (1950); (b) J. P. Coughlin and E. G. King, *ibid.*, **72**, 2262 (1950).

(4) R. Vogel and W. Tonn, *Arch. Eisenhüttenw.*, **5**, 387 (1931).

(5) G. Duyckaerts, *Compt. rend.*, **208**, 979 (1939).

(6) K. K. Kelley, U. S. Bureau of Mines, Bulletin No. 477, Contributions to the data of theoretical metallurgy. XI. Entropies of inorganic substances. Revision (1948) of data and methods of calculation.