

denum octacyanide ion and Hoard⁵ reports the anti-prism structure for the tantalum octafluoride ion.

Kimball¹⁰ has examined three of the four configurations considered here in terms of the bonding orbitals necessary to obtain each structure. On this basis he eliminates the cubic structure since it would involve *f* orbitals, no example of which has been authenticated. The antiprism and the dodecahedron could both involve the same orbitals, d^4sp^3 .

At present it seems that the antiprism and the dodecahedron structures satisfactorily account for the structure of coordination number eight but that in all likelihood the nature of the ligands will be important in determining which of the two structures applies to a specific compound.¹¹

(10) Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

(11) The trigonal prism discussed by Hoard and Nordsieck⁴ and by Kimball¹⁰ which was derived from the trigonal prism by placing the extra two groups along the normal to two of the rectangular faces was not considered in detail by the authors but a cursory examination indicates that it would show optical isomers for compounds of the class 4AA. For this reason it is also a possible form for the uranium complex.

Summary

1. Optical activity in compounds of elements exhibiting coordination number eight is established for the first time by the resolution of $K_4[U(C_2O_4)_4] \cdot 5H_2O$ into four isomers: one *d* and one *l* easily racemized modification and one *d* and one *l* stable modification by fractional precipitation of the strychnine salt.

2. A partial proof of the structure for compounds of elements exhibiting coordination number eight containing symmetrical bidentate groups is made, inasmuch as any structure not requiring optical isomers for the type of compound studied must be ruled out. The cube and the trigonal prism with two extra bonds along the unique axis are ruled out. The data are not sufficient to distinguish between the square Archimedean antiprism and the dodecahedron with triangular faces and symmetry V_d .

COLUMBUS, OHIO

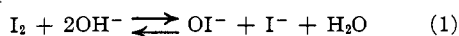
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[CONTRIBUTION FROM THE INSTITUTE OF EXPERIMENTAL BIOLOGY, UNIVERSITY OF CALIFORNIA]

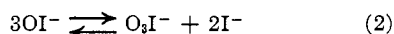
Kinetics of Hypoiodite Decomposition¹

BY CHOH HAO LI AND CAROLYN F. WHITE

When iodine dissolves in a highly alkaline solution, hypoiodite ion is formed



and it decomposes with measurable rate into iodate and iodide



The kinetics of this reaction has been studied extensively by Forster^{2a} and by Skrabal.^{2b} These investigators added arsenite in excess to stop the reaction by reacting with hypoiodite and any iodite present and determined the excess at *pH* near to 7 by the titration with triiodide. The second order specific rate was, in general, relatively low in the early stage of an experiment and approached a constant value.

In a recent study of the kinetics of di-iodotyrosine formation,³ it was proposed to use the phenol

(1) Aided by grants from the Board of Research of the University of California and the Rockefeller Foundation, New York City.

(2a) E. C. L. Forster, *J. Phys. Chem.*, **7**, 640 (1903).

(2b) Skrabal, *Monatsh.*, **32**, 167, 185 (1911); **33**, 99 (1912). References to other investigations in this field will be found in the papers cited in "I.C.T.," VII, 149 (1930). See also Bray, *THIS JOURNAL*, **52**, 3580 (1930); Chapin, *ibid.*, **56**, 2211 (1934).

(3) Li, *ibid.*, **64**, 1147 (1942).

reaction to follow the decomposition of hypoiodite ion. This method is based on the fact that phenols react with hypoiodite ion rapidly but not with the iodate which is later determined by titrating the triiodide in acid solution; it has an advantage over the arsenite method in that it enables an accurate determination of the initial rate to be made, since the small amount of the product then present may be determined directly and not as the difference of two large titration values. Using this method, we have confirmed the conclusions of Forster and Skrabal that the rate of reaction (2) at sufficiently high concentrations of hydroxide and iodide ions is proportional to the concentration of hypoiodite ion, hypoiodous acid and iodide ion. In addition, we have found that the reaction can also proceed through another path which requires only two hypoiodite ions.

The Rate Law.—The rate of reaction (2) in each experiment obeys equation (3)

$$-d(OI^-)/dt = k(OI^-)^2 \quad (3)$$

and *k* is a function of the concentrations of hydroxide and iodide ions. The increase in the con-

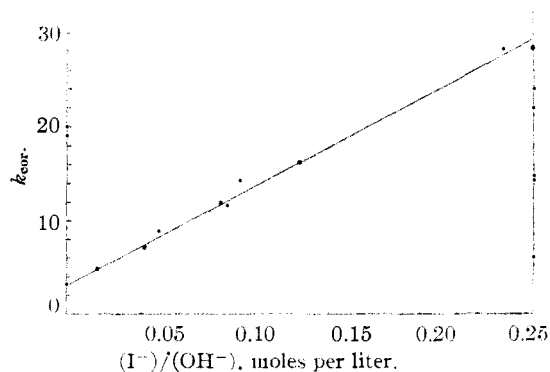


Fig. 1.—Specific rate, $k_{\text{cor.}}$, as the function of $(\text{I}^-)/(\text{OH}^-)$ at 25° .

centration of iodide ion during a run causes a small increase in k . The method of calculating $k_{\text{cor.}}$ (k after applying the correction factor) will be explained later. The results of a typical experiment are presented in Table I and summarized in the first line of Table III. The specific rate, k , was calculated for successive time intervals by means of the integrated form of equation (3). The concentrations are in moles per liter and time in minutes.

TABLE I

A TYPICAL EXPERIMENT OF HYPOIODITE DECOMPOSITION AT 25°

$(\text{I}^-) = 0.015$; $(\text{OH}^-) = 0.923$; $\mu = 0.947$			
Time, min.	$(\text{OI}^-) \cdot 10^2$	k	$k_{\text{cor.}}$
0	4.85		
5	4.37	(4.52)	(4.51)
15	3.59	4.98	4.92
30	2.84	4.87	4.74
50	2.20	5.13	4.92
80	1.61	5.56	(5.25)
			4.8

As has already been mentioned, the specific rates, k , obtained by the arsenite method were not constant throughout the experiment. They showed in most cases an abrupt rise in the early stage of the reaction. A typical run is summarized in Table II. In the later stages of the experi-

TABLE II

THE ARSENITE METHOD IN DETERMINING THE RATE OF HYPOIODITE DECOMPOSITION AT 25°

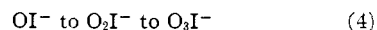
$(\text{OH}^-) = 0.904 M$; $(\text{I}^-) = 0.0565$; $\mu = 0.970$

t , min.	$(\text{OI}^-) \cdot 10^2$	$k_{\text{cor.}}^a$
0	6.50	
1	6.396	(2.50)
6	5.395	5.80
12	4.355	7.35
24	2.964	9.00
46.2	1.846	9.21
79.5	1.157	9.67

^a $k_{\text{cor.}}$ calculated from equation 5 is 9.4.

ment the specific rate approaches the value calculated by means of equation (5).

If we assume that an intermediate compound, such as iodite ion, is formed before hypoiodite ion changes into iodate



and if iodite ion does not react with tyrosine but reacts rapidly with arsenite, it may be easily understood that the low initial specific rate in the arsenite method is due to the presence of an appreciable amount of the iodite ion in the early stage of an experiment. If this theory is correct, the rate determined by the arsenite method is $d(\text{O}_3\text{I}^-)/dt$, and that determined by the tyrosine method is $-d(\text{OI}^-)/dt$ (or is closer to $-d(\text{OI}^-)/dt$ than to $d(\text{O}_3\text{I}^-)/dt$).

The Rate as a Function of $(\text{I}^-)/(\text{OH}^-)$.—Our results at 25° are summarized in Table III and in Fig. 1 by plotting $k_{\text{cor.}}$ against the ratio $(\text{I}^-)/(\text{OH}^-)$. It is evident that at 25°

$$k_{\text{cor.}} = 2.9 + 104(\text{I}^-)/(\text{OH}^-) \quad (5)$$

the intercept in Fig. 1 is $k' = 2.9$ and the slope is $k'' = 104$. The rate law (3) thus becomes

$$-d(\text{OI}^-)/dt = k'(\text{OI}^-)^2 + k''(\text{OI}^-)^2(\text{I}^-)/(\text{OH}^-) \quad (6)$$

Some points in Fig. 1 do not seem to lie perfectly on the straight line; this may be attributed to the variations in the ionic strength, μ (*cf.* the first column of Table III and the later discussion).

TABLE III

THE SPECIFIC RATE OF HYPOIODITE DECOMPOSITION AT DIFFERENT IODIDE AND HYDROXIDE ION CONCENTRATIONS AT 25°

μ	(I^-)	(OH^-)	$(\text{I}^-)/(\text{OH}^-)$	$k_{\text{cor.}}$	$k_{\text{cor.}}$ calcd. by eq. (5)
0.947	0.015	0.923	0.0162	4.8	4.6
.383	.015	.363	.0413	7.1	7.2
.197	.015	.177	.0847	11.5	11.7
.204	.015	.184	.0815	11.8	11.4
.973	.045	.923	.0487	8.8	8.0
.413	.045	.363	.1240	16.1	15.8
.227	.045	.177	.2540	28.7	29.3
1.013	.085	.923	.0920	14.2	12.5
0.453	.085	.363	.2340	28.2	27.3

The second term of equation (6) confirms the results of Forster and Skrabal in strongly alkaline solutions and the value, $k'' = 104$, is in fair agreement with Skrabal's value, 87, and that of Forster, 72. If we choose the specific rate in the last stage of Skrabal's or Forster's experiments as the corrected value, the k'' obtained is about 100 and is in much better agreement with the present k'' .

The first term of equation (6) is similar to that

found for the decomposition of hypochlorite⁴ and hypobromite^{5,6} in highly alkaline solutions. Although Skrabal⁷ in his discussions considered this term to be possible, no experimental evidence was presented. His failure to detect this term in his earlier experiments was probably due to the fact that most of his experiments were carried out in a solution containing almost the same concentrations of hydroxide and iodide ions. It is clear that in such conditions the disappearance of hypoiodite ion depends mainly on the second term of equation (6).

The Rate at Low Iodide Concentrations.—By means of experiments in the presence of silver oxide and silver iodide, Skrabal and Hohlbaum⁸ obtained evidence for the first term of the following rate law at 25°

$$-d(\text{OI}^-)/dt = 2(\text{OI}^-)^2/(\text{OH}^-) + 87(\text{OI}^-)^2(\text{I}^-)/(\text{OH}^-) \quad (7)$$

Our experiments do not confirm this result. If we assume the occurrence of the term $(\text{OI}^-)^2/(\text{OH}^-)$, the specific rate cannot exceed 0.2, which is only one-tenth of Skrabal's value. Even if the term exists, its value is so small that it need not be included in equation (6).

The corrected k , k_{cor} .—During the reaction the concentration of iodide ion increases from $(\text{I}^-)_0$ to $[\text{I}^-]_0 + 2(\text{IO}_3^-)$. Hence the specific rate, k , calculated from equation (3) gradually increases; since one path of the reaction is independent of I^- concentration as shown in equation (6), k_{cor} may be computed from equation (8)

$$k_{\text{cor}} = (k - 2.9)(\text{I}^-)_0/(\text{I}^-)_{\text{av}} \quad (8)$$

where $(\text{I}^-)_{\text{av}}$ is the averaged I^- concentration during the time interval for which the specific rate, k , was calculated.

Heat of Activation.—A few experiments were carried out at 2° with different hydroxide and iodide concentrations. The experimental error appeared to be higher than that at 25°. The values of k_{cor} vary irregularly within a run. The results, as shown in Fig. 2, may be represented fairly well by equation (9), and the path which depends only on OI^- is evidently not negligible at 2°.

$$k_{\text{cor}} = 0.9 + 18.2 (\text{I}^-)/(\text{OH}^-) \quad (9)$$

However the specific rate $k' = 0.9$ has not been accurately determined, and we have therefore not

attempted to calculate the heat of activation for this path.

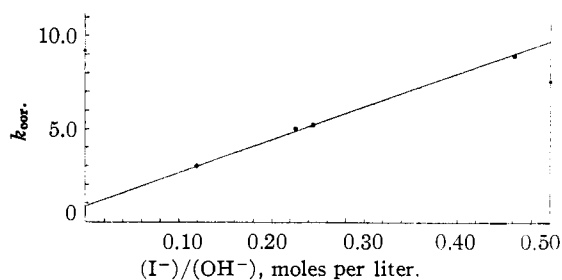


Fig. 2.—Specific rate, k_{cor} , as the function of $(\text{I}^-)/(\text{OH}^-)$ at 2°.

Combining with the k'' at 25° we have computed the heat of activation for the second path to be 12,400 calories. The values calculated from Skrabal's and Forster's data are 13,100 and 12,700 calories, respectively. Table IV summarizes the k'' values and heats of activation obtained by these authors.

Authors	Specific rate, k'' , at 25°	Heat of activation, calories
Forster	72	12,600
Skrabal	87	13,100
Present authors	104	12,400

Effect of Salt on the Rate.—When sodium nitrate was added, the rate of hypoiodite decomposition in a solution containing a constant $(\text{I}^-)/(\text{OH}^-)$ value was accelerated according to approximately the following expression

$$k_{\text{cor}} = k_{\text{cor}}^0 + B\mu \quad (10)$$

where μ is the ionic strength, which is largely due to the concentration of sodium nitrate, B a constant and k_{cor}^0 the specific rate at zero ionic strength. Results, summarized in Table V, suggest that the specific rate k' is not affected by the change of μ while k'' increases as the increment of salt concentration. The effect of salt on the rate may be described, at least approximately, by equation (11)

$$k_{\text{cor}} = 2.9 + (100 + 30.8\mu)(\text{I}^-)/(\text{OH}^-) \quad (11)$$

In Table V, the last column includes the k_{cor} computed by this equation.

Additional experimental evidences will be needed before we can accept the conclusion that the salt effect is negligible for a reaction involving two ions of the same charge, $2\text{OI}^- \rightarrow$; but it may be noted that Liebhafsky and Mohammad⁹

(4) F. Foerster and Dolch, *Z. Elektrochem.*, **23**, 137 (1917).

(5) Kretzschmar, *ibid.*, **10**, 789 (1904).

(6) Liebhafsky and Makower, *J. Phys. Chem.*, **37**, 1044 (1933).

(7) Skrabal, *Z. Elektrochem.*, **40**, 243 (1934).

(8) Skrabal and Hohlbaum, *Monatsh.*, **37**, 191 (1916).

(9) Liebhafsky and Mohammad, *J. Chem. Phys.*, **7**, 857 (1934).

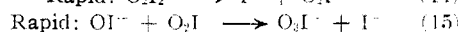
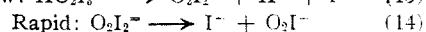
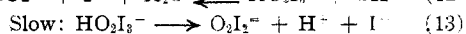
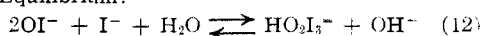
TABLE V
THE EFFECT OF IONIC STRENGTH ON THE RATE AT 25°

μ	NaNO ₃	(I ⁻)/(OH ⁻)	$k_{cor.}$	$k_{cor.}$ calcd. by Eq. 11
0.21	0.0	0.0815	11.8	11.6
.21	.0	.0848	11.5	11.9
.21	.0	.1360	17.4	17.4
.21	.0	.2540	28.7	30.0
1.04	.04	.0162	4.9	5.0
1.04	.60	.0326	7.4	7.2
1.04	.0	.0488	8.8	9.4
1.04	.0	.0921	14.2	15.2
1.04	.0	.2410	36.0	34.7
1.74	1.2	.0326	8.8	7.9
1.74	1.6	.0815	17.1	15.4
2.78	2.40	.0326	9.8	9.0
2.78	2.48	.0815	21.0	18.0

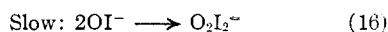
found no salt effect for the reaction $H_2O_2 + I^- + H^+ \rightarrow$ (this occurred simultaneously with $H_2O_2 + I^- \rightarrow$).

Mechanism.—It is evident from the above results that the hypoiodite decomposes in a highly alkaline solution through two different paths as described in the rate law (6). The first path depends on two hypoiodite ions while the second requires $(OI^-)^2(I^-)/(OH^-)$. The following reactions are essentially the same as those suggested by Skrabal⁷ in a supplement to his comprehensive discussion of the mechanism of the reactions that occur in less alkaline solutions.

Rapid Equilibrium:



Similarly, the rate-determining step for the first path of the rate law is probably the formation of $O_2I_3^-$ ion



This decomposes rapidly into iodate according to equations (14) and (15). The decomposition of other hypohalous ions in highly alkaline solution may also follow the same pattern.

In less alkaline solutions, when the concentration of OI^- becomes smaller than that of HOI (or I_3^-), the rates of the two reactions we have discussed are negligible in comparison with the rate by another path (compare ref. 2).

Experimental

The 0.1 *N* iodine solution (in 0.1 *M* or 0.4 *M* potassium iodide) and the sodium hydroxide solution were first brought to the temperature of the thermostat ($25 \pm 0.1^\circ$ or

$2 \pm 0.1^\circ$); 5 cc. of the iodine solution was then pipetted into 45 cc. of the sodium hydroxide solution. The time of mixing (*i. e.*, $t = 0$) was taken when half of the iodine solution had run into the alkaline solution. At time intervals of increasing length as the reaction progressed 5-cc. samples were withdrawn and added to approximately 100% excess of a solution of tyrosine (2.3 mg. per cc.) in 1 *M* sodium hydroxide in a 50-cc. flask. The flask was then stoppered and allowed to stand at room temperature for at least thirty minutes for experiments studied at 25° while one hour of standing was required for the 2° experiments. The contents were then poured into a small dropping funnel with the stem drawn out to a capillary and added drop by drop to enough 4 *N* sulfuric acid to make the final mixture about 0.1 *N* acid. The flask and dropping funnel were rinsed twice with distilled water. The acid solution was immediately titrated with 0.01 *N* thiosulfate using starch as indicator. Other phenols may be used; tyrosine is chosen simply because of availability and its comparatively non-hygroscopic nature.

A blank to obtain total iodine in the reaction mixture was made by taking 5 cc. of the reaction mixture sometime during the middle of the total time interval and carrying out the procedure above but without tyrosine. The initial concentration of hypoiodite was calculated from this result. The amount of tyrosine used to stop the hypoiodite decomposition and the rate of addition of the tyrosine mixture to the sulfuric acid solution are extremely important in determining the correct kinetic data of the decomposition. It was noted that, if 100% excess of the equivalent amount of tyrosine is used, about 5% of the hypoiodite ion will decompose before it can react. On the other hand, if iodate is present some of the iodine formed will react locally with the tyrosine before the acid concentration is high enough to prevent this. This error is increased if the excess of tyrosine used is too great, or if the tyrosine mixture is added too rapidly to the acid. A low thiosulfate titer will result, giving a low rate constant. It was found that these two errors partly compensated for each other, giving a resultant error of about $\pm 5\%$ if the above directions were followed.

We are greatly indebted to Prof. W. C. Bray for many valuable suggestions and criticisms during the preparation of this paper.

Summary

1. A method which is based on the rapid reaction between the phenol, tyrosine and hypoiodite is used to measure the rate of hypoiodite decomposition in highly alkaline solution. The method is found to be more satisfactory than the arsenite method which had been used in earlier kinetic investigations.

2. At 25° in highly alkaline solution the rate law is

$$-d(OI^-)/dt = 2.9(OI^-)^2 + 104(OI^-)^2(I^-)/(OH^-)$$

The second term is the same as that found by Forster and Skrabal whereas the first term is new.

The term $(\text{OI}^-)^2/(\text{OH}^-)$, suggested by Skrabal, is shown to be negligible as compared with these two terms.

3. The heat of activation is computed from

the kinetic data at 25 and 2° to be 12,400 which is good agreement with the value obtained by Forster and Skrabal.

BERKELEY, CALIFORNIA

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[CONTRIBUTION FROM THE WESTERN REGION BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Specific Heats at Low Temperatures of Magnesium Orthosilicate and Magnesium Metasilicate¹

BY K. K. KELLEY²

Investigation of low-temperature specific heats of metallurgically important substances has been one of the programs of study of the Pacific Experiment Station of the Bureau of Mines for several years. About three years ago, the paucity of low-temperature specific-heat and entropy data for silicates led to a modest undertaking in this field, and eleven of the simpler silicates were studied. Results for three sodium silicates,³ for beryllium orthosilicate,⁴ and for iron, manganese and zirconium silicates⁵ already have been presented. The present paper reports specific-heat data in the temperature range 51° to 298°K. and the entropies of magnesium orthosilicate and magnesium metasilicate.

Materials⁶

Procedures for the preparation of these silicates are based upon the research of Jander and Wuhler.⁷ The initial materials were (1) a good grade of finely powdered silica, which was digested overnight with 6 *N* hydrochloric acid, washed free of chlorides, dried, and heated to 800° and (2) C. P. magnesium oxide having no appreciable impurities other than water.

In the preparation of magnesium orthosilicate, a mixture of oxides containing an 0.82% excess of magnesium oxide over the theoretical 2:1 molal ratio was rotated in the chamber of a porcelain ball mill for nine hours to assure intimate mixing. (The excess magnesium oxide may have been unnecessary, but it was added to inhibit formation of magnesium metasilicate, which was present in small amounts in the best products reported by Jander and Wuhler.) The mixture was moistened, tamped into a nickel cartridge, dried at 100°, and finally heated in a tube

furnace at 1150 ± 20° for four days under a vacuum of 10⁻⁴ mm. After this treatment the product contained 3.6% uncombined magnesium oxide. It was reground and similarly heated for five additional days at 1180 ± 10°. Analysis now gave 98.6% magnesium orthosilicate, 0.8% uncombined magnesium oxide, no free silica, and no magnesium metasilicate. A 140.83-g. sample of this product was used in the measurements.

The preparation of magnesium metasilicate was much more difficult and time-consuming. A 1:1 mixture of the oxides was made up as before in the chamber of a porcelain ball mill, tamped into a nickel cartridge, and heated in a tube furnace at 1300 ± 20° for thirteen and one-half days. At this stage no uncombined magnesium oxide remained, but 27.1% magnesium orthosilicate was present. The product was reground, reheated (this time in an Arsem furnace) for forty-five hours at 1300°, and reanalyzed. This latter procedure was repeated several times, until a virtually constant analysis was obtained. The final product analyzed 92.0% magnesium metasilicate, 5.6% magnesium orthosilicate, and 2.4% uncombined silica. Although it would have been possible, in a much longer time, to obtain a better product, the operation was so time-consuming, and so little improvement was noted in the last three stages of the regrinding-reheating process, that it appeared inadvisable to continue. It is believed that adequate results were obtained with this material, as correction was made for the uncombined silica and for magnesium orthosilicate. A 97.04-g. sample was employed in the measurements. The difficulty encountered in this preparation bears out the observations of Jander and Wuhler, who report the persistence of magnesium orthosilicate after ten days of heating at 1170°.

Throughout the present work the analytical methods of Jander and Wuhler were followed in minute detail. Their description is so adequate that repetition is unnecessary. The methods are not highly accurate but are good enough for most purposes. It may be of interest to record the range of variation in the above-reported analyses. In the case of the magnesium orthosilicate sample, four analyses for uncombined magnesium oxide varied from 0.75 to 0.86%, and three analyses for magnesium orthosilicate varied from 98.4 to 98.7%. For the magnesium metasilicate sample, three analyses for magnesium orthosilicate varied from 5.48 to 5.83%, three for uncombined silica varied from 2.34 to 2.49%, and three for magnesium metasilicate varied from 91.7 to 92.2%.

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(2) Senior chemist, Pacific Experiment Station, Western Region, Bureau of Mines.

(3) Kelley, *THIS JOURNAL*, **61**, 471 (1939).

(4) Kelley, *ibid.*, **61**, 1217 (1939).

(5) Kelley, *ibid.*, **63**, 2750 (1941).

(6) These materials were prepared and analyzed by Dr. G. W. Marks, Western Region, Bureau of Mines. The author gratefully acknowledges this assistance.

(7) Jander and Wuhler, *Z. anorg. allgem. Chem.*, **226**, 225 (1936).