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THE OXIDATION OF IODIDE ION BY PERSULFATE ION. II. THE EFFECT OF REMOVING THE PRODUCTS OF THE REACTION ON THE REACTION VELOCITY[1]

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A. Introduction

The investigations reported in the first article of this series[2] showed that due to the formation and slower reaction of tri-iodide ion the reaction observed when solutions of potassium persulfate and potassium iodide are mixed is the sum of two concurrent slow reactions. It was also found that by means of an empirical procedure a velocity curve could be obtained in which the effects of the iodine and tri-iodide ion were eliminated. Further evidence of the correctness of these results was sought from experiments in which the iodine was more or less completely removed from the reaction by means of organic solvents and of a very rapid reaction. The earlier conclusions were also checked by repeating the experiments reported in the first article in solutions of considerably higher ionic strength. Experiments were likewise performed to show whether the removal of the other product of the reaction, the sulfate ion, had any effect on the reaction velocity. These experiments involved the determination of the salt effect due to the presence of several neutral salts.

B. Materials and Methods

The preparation of salts and solutions has already been described in the previous article. In some cases to be mentioned, however, it was necessary to use analyzed stock solutions for preparing solutions of the desired final concentration.

The organic solvents chloroform, carbon tetrachloride and carbon disulfide were redistilled, rejecting the first and last portions. The original materials were of "c. p." grade. The paraffin hydrocarbon was carefully treated to remove unsaturated compounds by shaking with concentrated sulfuric acid, boiling several times with alkaline permanganate solution and finally distilling; the portion boiling between 96 and 102° was collected for use.

The sealed bulb method already described was used in all experiments excepting those where sodium hydroxide was present. Bulbs of 200-cc. capacity were used in the experiments with the solvent; each bulb containing 50 cc. of the reacting mixture (measured from a standard pipet) and 50 cc. of the solvent. Before sealing off, the bulbs were filled with nitrogen. The bulbs were placed in a device which turned them end over end in the thermostat at the rate of 10–15 turns per minute. Equilibrium between the iodine in the aqueous and solvent layers was thus established very quickly.

For the experiments involving sodium hydroxide, the reaction mixture was placed in a glass-stoppered bottle and a 50-cc. sample withdrawn from time to time. Five cc.

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[1] Presented at the Swampscott Meeting of the American Chemical Society, September 12, 1928.

[2] Jette and King, This Journal, 51, 1034 (1929).

of 1 molar sulfuric acid and 2 cc. of 1 molar potassium iodide was added and the iodine liberated by the iodate present titrated immediately with 0.01 molar sodium thiosulfate, using freshly prepared starch solution as indicator. Blanks were run on the reagents used. The temperature of the thermostat in which the reaction vessels were placed was 25.00 ± 0.01°.

C. Experiments with Organic Solvents Present

The results of attempts to find the influence of removing practically all of the iodine as fast as it was formed by means of organic solvents are summarized in Table I. The symbols and concentration units are identical with those in the previous article. The value of k' is calculated from the integrated bimolecular equation

$$k' = \frac{1}{2at}\frac{x}{(a - x)} \qquad (1)$$

The initial concentration of potassium persulfate is a moles per liter, of potassium iodide $2a$ moles per liter and x is the moles of persulfate ion consumed or iodine produced during the reaction. Several observations may be noted. (1) In all four cases the velocity curves (not plotted in Fig. 1) are above that in which no solvent was present. (2) For the first three solvents in the table the values of k' within each column are practically constant.[3] The average values of k' for the chloroform case is slightly above and for the paraffin hydrocarbon case slightly below the value 0.125 which was chosen in the previous article as the velocity constant for the iodide-ion reaction.

Table I

Reaction Velocities in Presence of Organic Solvents

$C_{K_2S_2O_8} = a = 0.005$ mole per liter; $C_{KI} = 2a = 0.01$ mole per liter

$CHCl_3$		CS_2		Paraffin hydrocarbon		CCl_4	
Time, min.	k', Eq. 1	Time, min.	k', Eq. 1	Time, min.	k', Eq. 1	Time, min.	k', Eq. 1
155	0.127	180	0.154	130	0.129	120	0.161
295	.127	320	.139	290	.122	250	.159
410	.130	530	.144	500	.120	550	.149
520	.131	710	.143	750	.119	815	.135
940	.128	860	.147	1440	.118	1325	.144
1560	.124	1550	.146	..	..	..	..
Av.	.128		.146		.122		.150

No satisfactory explanation has been obtained for the higher values of k' in the carbon disulfide and carbon tetrachloride experiments nor for the continuously decreasing values of Col. 8. The high values may be due to the specific effects of these substances in spite of their minute concentration in the aqueous layer. It is to be emphasized, however, that no far-reaching conclusions are to be drawn from the individual

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[3] In their study of the HIO_3–HI reaction, Abel and Stadler, *Z. physik Chem.*, **122**, 49 (1926), found good pentamolecular velocity constants when the iodine was removed continuously by shaking with benzene.

numerical values in Table I due to an experimental difficulty involved to a greater or less, but unfortunately unknown, degree in each of the individual measurements. While the reaction bulbs were filled with nitrogen before sealing, so that no actual combustion of the vapors was observed, the local high temperatures to which the vapors of these organic substances were momentarily exposed always caused some decomposition and possibly some interaction with water vapor. Although the amount of these decomposition and interaction products was probably quite small, their nature is unknown. In some cases they may remove iodine from the solution, while in others they may liberate it from the iodide ions present or accelerate the reaction by the production of acids. In view of these conditions, the authors have limited the conclusions to be drawn from these experiments to the following statement. When the iodine formed by the reaction between persulfate and iodide ions is removed practically completely from the aqueous layer by means of an organic solvent for iodine, the values of k' obtained are generally more constant than when iodine is allowed to accumulate in the aqueous solution and in some cases the value of k' approaches closely the value of the true constant for the iodide–persulfate ion reaction.

D. The Reaction Velocity in the Presence of Sodium Hydroxide

In another series of experiments the iodine was removed from the system by means of sodium hydroxide. This method depends upon the fact that in the presence of a sufficiently high concentration of hydroxyl ions, iodine undergoes an internal oxidation-reduction according to the following equation

$$3I_2 + 6OH^- \rightleftharpoons 5I^- + IO_3^- + 3H_2O \qquad (a)$$

In combination with the iodide–persulfate ion reaction

$$S_2O_8^{--} + 2I^- \longrightarrow 2SO_4^{--} + I_2 \qquad (b)$$

the final result is the oxidation of iodide ion to iodate ion, the gross equation for which is

$$3S_2O_8^{--} + I^- + 6OH^- \longrightarrow 6SO_4^{--} + IO_3^- + 3H_2O \qquad (c)$$

In using these reactions the main assumption introduced was that the velocity determining reaction which, according to Brönsted, is

$$S_2O_8^{--} + I^- \longrightarrow (S_2O_8I)^{---} \qquad (d)$$

remains the same as in the absence of sodium hydroxide. As a corollary, it follows that regardless of its own mechanism, Reaction (a) must be assumed to proceed at a much faster rate than (d). It is also necessary definitely to assume that the final oxidation product of the iodide ion is the iodate ion. This last assumption has a very important effect on the equations for the reaction velocity, and the constancy of the velocity constant is a check on its validity. An unequivocal proof that (d) represents the velocity determining reaction is not possible, at any rate not from the present experiments. However, a close agreement in the values of the velocity constants obtained from two comparable experiments, in one of which sodium hydroxide was present while in the other it was not, would argue in favor of this view.

Two different velocity equations were used depending on the ratio of persulfate to iodide ions. If we let the initial molar concentration of potassium persulfate be a and that of potassium iodide be $2b$ then according to Reaction (c) above, when x moles per liter of persulfate ion has been reduced, $x/3$ moles per liter of iodide ion also has disappeared. We then get for the momentary concentrations of persulfate and iodide ions

$$C_{S_2O_8^{--}} = a - x \text{ and } C_{I^-} = 2b - \frac{x}{3}$$

From these and the velocity equation there is obtained

$$-\frac{dC_{S_2O_8^{--}}}{dt} = kC_{S_2O_8^{--}}\ C_{I^-} = \frac{1}{3}k(a - x)\ (6b - x)$$

which upon integration and transformation to ordinary logarithms gives

$$k = \frac{6.909}{(6b - a)t}\log_{10}\frac{a(6b - x)}{6b(a - x)} \qquad (2)$$

Results of two experiments using this equation[4] are given in Tables II and III. The results in the latter are comparable with those in Table VII, since the ionic strength is the same in both The difference in the specific effects of nitrate and hydroxyl ions and to a lesser extent of potassium and sodium ions is evident from these two tables as well as the corresponding curves.

TABLE II TABLE III

REACTION VELOCITY IN THE PRESENCE OF NAOH

TABLE II

$C_{S_2O_8^{--}} = a = 0.00493\ M$
$C_{I^-} = 2b = 0.01\ M$
$C_{NaOH} = 0.05\ M$

Time, min.	k Eq. 2
122	0.175
190	.174
280	.175
390	.173
580	.173
670	.174
1270	.172
1590	.170
Av.	.173

TABLE III

$C_{S_2O_8^{--}} = a = 0.0493\ M$
$C_{I^-} = 2b = a = 0.01\ M$
$C_{NaOH} = 0.10\ M$

Time, min.	x Moles per liter $\times 10^3$	k Eq. 2
62	0.600	0.211
130	1.174	.214
210	1.759	.217
340	2.476	.215
465	2.987	.213
1035	4.231	.208
1315	4.520	.211
	Av.	.213

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[4] In these experiments the ratio of persulfate-ion concentration to iodide-ion concentration was not as simple as in the other experiments due to a slight error in making up one of the solutions. The simplification of Equation 2 for the case where the iodide concentration is $2a$ will be obvious.

TABLE IV TABLE V

REACTION VELOCITY IN THE PRESENCE OF NaOH

TABLE IV

$C_{S_2O_8^{--}} = a = 0.005\ M$
$C_{I^-} = a/3 = 0.00167\ M$
$C_{NaOH} = 0.05\ M$

Time, min.	k Eq. 3
240	0.166
510	.166
1160	.166
1685	.167
3013	.160
3375	.168
4580	.168
7350	.166
Av.	.166

TABLE V

$C_{S_2O_8^{--}} = a = 0.005\ M$
$C_{I^-} = a/3 = 0.00167\ M$
$C_{NaOH} = 0.00833\ M$

Time, min.	x Moles per liter $\times 10^3$	k Eq. 3
585	0.503	0.115
1215	.960	.117
1740	1.269	.117
3064	1.872	.117
3430	2.007	.117
4635	2.373	.117
7400	2.928	.115
11440	3.421	.114
	Av.	.116

Tables IV and V contain the results of experiments in which the initial molar concentration of potassium iodide was one-third of that of the potassium persulfate. The velocity equation for this case is somewhat simpler, namely

$$k = \frac{3}{at} \times \frac{x}{(a - x)} \qquad (3)$$

The ionic strength of the solution used for the experiments in Table V is the same as for the experiments reported in Table I of the present article and Tables I and II of the previous article. The difference between the average value of k in Table V and the limiting value for the iodide–persulfate ion reaction obtained in the first article may be ascribed to specific effects of the sodium and hydroxyl ions, chiefly the latter, on the reaction velocity. The constancy of k in all four experiments given in Tables II, III, IV and V, and the agreement between the values of the constants in Table V with that of the limiting value (0.125) recorded in the previous article, are sufficient to justify the assumptions made regarding the velocity-determining reaction and the final oxidation product of the iodide ion.

E. The Effect of Removing the Sulfate Ion

Reaction (b) is, for all practical purposes, an irreversible reaction and therefore the presence of the final products of the reaction in actually attainable concentrations should have no measurable effect on completeness of the reaction. It was considered as a possibility, however, that the removal of the reaction products might increase the velocity. The removal of the iodine already discussed would obviously not serve as a test of this possibility.

The removal of sulfate ion is most easily accomplished by precipitation as barium sulfate. The addition of soluble barium salts increases the initial ionic strength, while the precipitation of the insoluble barium sulfate involves the continuous decrease of this factor. In order to reduce the complications involved in a large percentage change in ionic strength, the new series of experiments was performed keeping the iodide and persulfate concentrations the same as before but making the solutions also 0.10 molar with respect to potassium nitrate. The results of experiments containing potassium iodide, potassium persulfate and potassium nitrate are given in Table VII and will be discussed later. An additional complicating factor is present in that barium ions may have a specific effect on the reaction velocity quite apart from the influence due to the precipitation of barium sulfate. Therefore, the reaction velocities were also measured in the presence of magnesium and calcium salts. Since calcium sulfate is relatively insoluble, two series of experiments were made with solutions initially saturated with this salt, in one of them calcium nitrate also being present.

TABLE VI

EFFECT OF NEUTRAL SALTS ON THE REACTION VELOCITY

$K_2S_2O_8$ = 0.005, KI = 0.01 and KNO_3 = 0.10 molar in all experiments

Time, minutes	k' Eq. 1	Time, minutes	k' Eq. 1	Time, minutes	k' Eq. 1
$Mg(NO_3)_2$ = 0.01 *M*		$Ca(NO_3)_2$ = 0.01 *M*		$Na(NO_3)_2$ = 0.01 *M*	
0	(0.279)	0	(0.277)	0	(0.302)
100	.269	140	.266	140	.283
245	.258	280	.257	280	.268
455	.245	455	.248	440	.257
710	.233	765	.235	Curve 4	
Curve 3		Curve 3			
$Mg(NO_3)_2$ = 0.05 *M*		$Ca(NO_3)_2$ = 0.05 *M*		$Ba(NO_3)_2$ = 0.05 *M*	
0	(0.332)	0	(0.347)	0	(0.423)
100	.318	140	.324	140	.392
240	.301	280	.314	280	.369
450	.283	450	.301	440	.351
700	.271	765	.294	765	.327
Curve 5		Curve 6		Curve 7	
K_2SO_4 = 0.01 *M*		$CaSO_4$ (satd.)		$CaSO_4$ (satd.) + 0.01 *M* $Ca(NO_3)_2$	
0	(0.272)	0	(0.295)	0	(0.319)
110	.263	140	.280	100	.302
260	.264(?)	280	.269	240	.285
470	.241	380	.261	450	.269
710	.233	470	.259	650	.261
Curve 3		765	.246	800	.253

Results of all of these experiments are summarized in Table VI. It will be seen that barium nitrate has a definitely greater effect on the reaction velocity than the corresponding magnesium and calcium salts at the same concentration.[5] Whether the higher velocities thus ob-

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[5] The titration values at various times for the 0.01 molar solutions of calcium nitrate and magnesium nitrate fell within experimental error on the same curve and

served are to be interpreted as due to the removal of the sulfate ion or to the specific effect of barium ions cannot be decided by means of such experiments but the velocities observed seem to be somewhat too great for the latter explanation alone to suffice. It may be observed that when the values of k' are plotted against t the resulting curves for the solutions containing barium ions drop more rapidly than those of the solutions containing magnesium and calcium. The curve for the solution saturated with calcium sulfate and containing 0.01 molar calcium nitrate shows the same behavior, being very nearly parallel to the 0.01 molar barium nitrate curve, although the curve for the saturated calcium sulfate alone decreases less rapidly and cuts across the latter. A very probable explanation of these differences may be found in the fact that in these solutions the ionic strength is decreasing appreciably while in the solutions in which no precipitation takes place there is a slight increase.

F. The Influence of Tri-iodide Ion Formation in Solutions of Higher Ionic Strength

Finally, the conclusions drawn in the first article of the series were checked by experiments in which the reaction velocities were made considerably higher than previously by using solutions containing 0.10 molar potassium nitrate. The experimental methods were the same as those of the earlier article. The results are given in Tables VII and VIII and Curves 1 and 6 on Fig. 1.

TABLE VII

REACTION VELOCITY IN 0.1 M KNO_3 SOLUTIONS

$K_2S_2O_8$ = 0.005 Molar
KI = 0.010 Molar
KNO_3 = 0.10 Molar
I_2 = 0 initially

Time, minutes	x moles per liter	k' Eq. 1
60	0.000670	0.258
140	.001290	.248
220	.001747	.244
355	.002278	.235
560	.002795	.226
1075	.003455	.208
1510	.003767	.202

TABLE VIII

REACTION VELOCITY IN 0.1M KNO_3 SOLUTION SATURATED WITH I_2

$K_2S_2O_8$ = 0.005 Molar
KI = 0.010 Molar
KNO_3 = 0.10 Molar
I_2 = satd. initially

Time, minutes	x moles per liter	k' Eq. 1
120	0.000981	0.203
204	.001449	.200
360	.002071	.196
530	.002565	.199
1480	.003727	.198
	Av.	.199

In order to apply the equations already derived to the experiments, it was necessary to know the equilibrium constant for the reaction $I_2 + I^- \rightleftarrows I_3^-$ in solutions containing 0.10 molar potassium nitrate. The constant was obtained from measurements of the solubilities of iodine in

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those for 0.01 molar potassium sulfate very slightly below this curve. Plots of k' against x gave the same results but the potassium sulfate results were somewhat more definitely lower than the others.

solutions containing 0.10 molar potassium nitrate besides potassium iodide at several different concentrations. The concentrations of the individual substances were calculated by the aid of the assumption that the solubility of free iodine in solutions containing potassium iodide is the same as in the pure "solvent," which in this case is 0.10 molar potassium nitrate. The solutions were saturated in sealed pyrex bulbs, the mixtures being rotated in the thermostat at 25.00 ± 0.01° for three days. The materials and technique were in other respects the same as in determining the initial concentrations of iodine in the velocity experiments already described. The results are given in Table IX, which is self-explanatory. It is noteworthy that potassium nitrate at this concentration has but little effect on the solubility of iodine and the equilibrium constant.

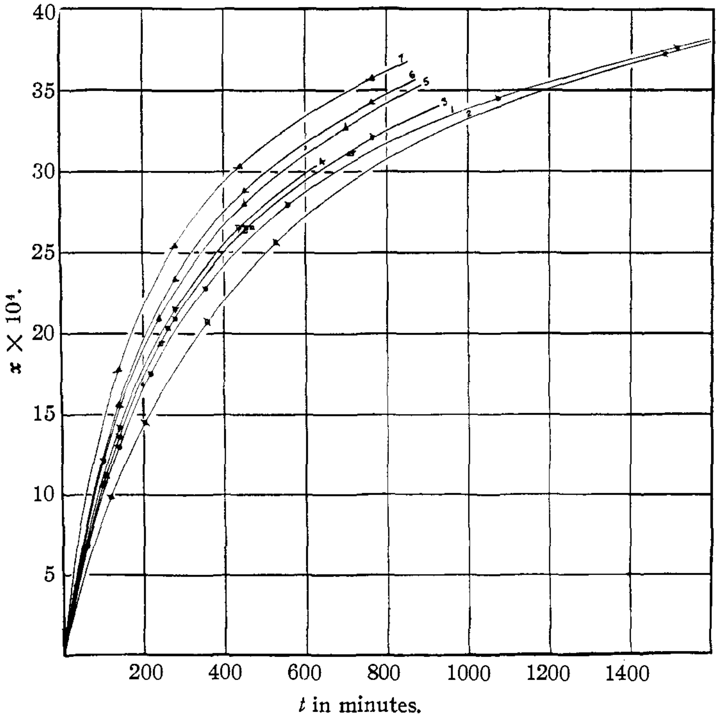

Fig. 1.—$K_2S_2O_8$, 0.005; KI, 0.01; KNO_3, 0.10. Curves: 1, salts alone; 2, with saturated iodine; 3, with 0.01 *M* magnesium nitrate, with 0.01 *M* calcium nitrate and with 0.01 *M* potassium sulfate; 4, with 0.01 *M* barium nitrate; 5, with 0.05 *M* magnesium nitrate; 6, with 0.05 *M* calcium nitrate; 7, with 0.05 *M* barium nitrate.

The value of k_{I^-} at $t = 0$ was determined by extrapolating the curves obtained by plotting k against t. The values of k were obtained from

TABLE IX

EQUILIBRIUM CONSTANT FOR $I_2 + I^- \rightleftarrows I_3^-$

Moles KI per liter	Total $I_2 = I_2 + I_3^-$	C_{I_2}	$C_{I_3^-}$	C_{I^-}	$K' = \frac{C_{I^-}}{C_{I_3^-}}$	$K = K'C_{I_2}$
0	0.001275	0.001275	.....	.....	...	.....
0.005	.003714	.001275	0.002439	0.002561	1.049	0.001339
.010	.006117	.001275	.004842	.005158	1.066	.001358
.020	.010983	.001275	.009708	.01029	1.061	.001352
				Av.	1.059	.001350

Table VII and also from the values observed (see Table X) from the smoothed curve. The extrapolation in the first case gave $k_{I^-} = 0.262$; in the second case, 0.269. The value $k_{I^-} = 0.265$ was chosen for subsequent use. The accuracy of the extrapolated values is somewhat less than in the case when no potassium nitrate was present due to the more rapid change in k with time. Accurate extrapolation of $dC_{S_2O_8^{--}}/dt$ was impossible. The value for $k_{I_3^-}$ is 0.169. The calculated results given in Table X were made with the same equations and with the same assumptions as those in Table VI of the first paper. The calculated slopes are all slightly higher than the observed values but the difference is easily within the error of determining k_{I^-}. The conclusion that the iodide and tri-iodide ions each react with the persulfate ions at characteristic rates is therefore confirmed.

TABLE X

EFFECT OF TRI-IODIDE EQUILIBRIUM ON REACTION VELOCITY

$K_2S_2O_8$ = 0.005 Molar; KNO_3 = 0.10 Molar; KI = 0.01 Molar; I_2 = 0 initially

Time, min.	x mole/liter (interp.)	$C_{I_3^-}$, moles per liter	$2k_{I^-}(a - x)^2 \times 10^6$	2nd term in Eq. 16 $\times 10^6$	$-\frac{dC_{S_2O_8^{--}}}{dt} \times 10^6$ Calcd.	Obs.
60	0.000660	0.000566	9.98	−0.33	9.65	9.59
100	.001002	.000843	8.47	− .46	8.01	7.90
160	.001418	.001173	6.80	− .57	6.23	6.16
200	.001645	.001315	5.97	− .60	5.37	5.33
300	.002083	.001581	4.51	− .63	3.88	3.78
400	.002417	.001734	3.54	− .61	2.93	2.86
600	.002870	.001842	2.41	− .54	1.87	1.82

$k_{I^-} = 0.265$; $k_{3^-} = 0.129$; $k = 0.00135$

Summary

Further investigations were made on the reaction between iodide and persulfate ions. In the first article of the series it was found possible, by means of an empirical procedure, to obtain the velocity curve for the reaction if iodine or tri-iodide ion did not interfere with the reaction. These results have been confirmed by experiments in which the iodine was removed continuously from the reaction mixture by shaking with organic solvents and by reaction with sodium hydroxide. The effect of certain neutral salts on the reaction velocity was also determined.

It was found that removal of the sulfate ion as barium sulfate or calcium sulfate probably does not increase the velocity, although the effect of adding barium ion to the reacting mixture seems to be somewhat greater than it should if it is to be explained merely as a specific salt effect. Finally, the main conclusion of the first article, that is, that the observed reaction velocity is the sum of the velocities of the iodide and of the triiodide ions reacting with persulfate ion, was confirmed by measurements at considerably greater velocities.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

STUDIES ON SILICODUODECITUNGSTIC ACID.
I. THE PREPARATION OF SILICOTUNGSTIC ACID[1]

BY ARTHUR G. SCROGGIE[2]

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Silicotungstic acid originally prepared and described by Marignac[3] in 1863, has lately become an important analytical reagent on account of its ability to precipitate alkaloids. The present official method for the determination of nicotine is based on this property.

Drechsel[4] improved the original method of separating the acid by isolating it in the form of a complex which it formed with ether in the presence of a mineral acid. This procedure was only slightly modified by North and Beal,[5] who in 1925 extended the usefulness of this reagent by producing it in the form of a dry powder, stable in air and readily handled without decomposition. They also introduced a volumetric method, in which silicotungstic acid was used for the quantitative determination of alkaloids without previous isolation and purification. More recently Salzberg[6] has questioned the purity of the acid when prepared according to North's directions, and also North's assumptions with regard to the end-products obtained following decomposition of the acid by means of excess of alkali.

Because of the lack of agreement in the literature and the unsatisfactory status of the knowledge concerning silicotungstic acid, the researches of the present writer were undertaken with the following objectives: (a)

[1] Throughout this paper the term silicotungstic acid will be understood to refer to silicoduodecitungstic acid.

[2] This communication is an abstract of a portion of a thesis submitted by Arthur G. Scroggie in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Marignac, *Ann. chim. phys.*, [3] **69**, 5 (1863).

[4] Drechsel, *Ber.*, **20**, 1452 (1887).

[5] North and Beal, *J. Am. Pharm. Assoc.*, **13**, 889, 1001 (1924).

[6] Salzberg, Master's "Thesis," University of Illinois, **1925**; unpublished report, University of Illinois, **1925**.