

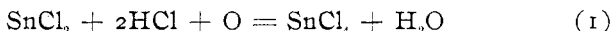
STUDIES ON SOLUTIONS OF STANNOUS SALTS, III.

By S. W. YOUNG.

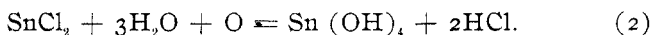
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PART I. THE COURSE OF THE REACTION BETWEEN STANNOUS CHLORIDE AND OXYGEN.

IN a previous paper¹ it was pointed out that there were two probable courses which the reaction between stannous chloride and free oxygen, in presence of hydrochloric acid, might take; *viz.*,



and



It was also suggested that it might be possible to determine which of the two reactions was the one actually occurring, since if stannic chloride were first formed it would afterward slowly hydrolyze and thereby, on account of the formation of free hydrochloric acid in the solution, one would observe a gradual increase in the conductivity of the solution for some time after the oxidation was complete. Among others Kohlrausch² has recently investigated the change of conductivity with the time, in freshly prepared solutions of stannic chloride, and found that for dilute solutions, the increase was quite noticeable, but lasted for only a comparatively short time, when the conductivity became practically constant. In stronger solutions (about half-normal) the increase in the conductivity was still perceptible after several days.

The following investigations were carried out in the hope of applying this phenomenon to the determination of the presence or absence of stannic chloride in freshly oxidized solutions of stannous chloride. In order that the results might be as conclusive as possible several oxidizing agents besides oxygen were investigated. Among these a somewhat special interest is attached to sodium hypochlorite, since Thomsen³ found that with this oxidizing agent he obtained a very constant value for the heat of oxidation of stannous chloride, whereas with chlorine the values obtained were very irregular. One might surmise from this that the course of the oxidation was somewhat different in the two cases.

¹ This Journal, 23.

² Ztschr. phys. Chem., 33, 257.

³ "Thermochemische Untersuchungen," II, 445.

The results of the research are classified as to the oxidizing agent used. The general method was to oxidize the solution as rapidly as possible, transfer it to a conductivity flask and begin measurements as soon as the solution had acquired the temperature of the thermostat. The solution for oxidation was freshly prepared for each experiment. The hydrochloric acid concentration was varied in different experiments for reasons which will appear. The concentration of the stannous chloride was the same in all experiments, *viz.*, 2 grams of the crystallized salt in 100 cc., *i. e.*, about 0.16 normal. (Titrations gave results as follows: 0.1625, 0.1623, 0.1630.)

All measurements were made in a thermostat at 25° C. The results cannot be used as a measure of isothermal reaction velocity, because, on account of lack of proper facilities, it was necessary to allow the thermostat to cool down each night.

I. OXIDATION BY MEANS OF FREE OXYGEN.

Solutions 0.1, 0.2, 0.3, 0.4, and 0.5 normal in hydrochloric acid were investigated. Since the oxidation ordinarily goes very slowly, all oxidations with free oxygen were accelerated by means of small quantities of hydrogen sulphide.¹ The time required for oxidation was from five to fifteen minutes, according to the acid contents of the solution.

Following are the tabulated results of the measurements with free oxygen. T is time in hours and K is specified conductivity in reciprocal ohms.

A. MEASUREMENTS WITH 0.1 NORMAL HCl.

1. ² T =	0	$\frac{1}{6}$	2	4	19	21	
K =	0.05999	0.06071	0.06159	0.06210	0.06247	0.06285	
2. T =	0	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{2}$	1	3	$5\frac{1}{2}$ 24 $\frac{1}{2}$
K =	0.0797	0.0813	0.0818	0.0824	0.0837	0.0845	0.0853 0.0869
T =	62	105	125				
K =	0.0880	0.0880	0.0880				

B. MEASUREMENTS WITH 0.2 NORMAL HCl.

1. T =	0	$1\frac{1}{6}$	$4\frac{1}{2}$	6	$23\frac{1}{2}$	$25\frac{1}{2}$
K =	0.1140	0.1165	0.1180	0.1192	0.1192	0.1195
2. T =	0	$14\frac{1}{2}$	$19\frac{1}{2}$	24	$68\frac{1}{2}$	92
K =	0.1123	0.1168	0.1212	0.1220	0.1223	0.1223

¹ This Journal, 23, 144.

² In this experiment only 1 gram of stannous chloride per 100 cc. was used. In all others 2 grams were used.

C. MEASUREMENTS WITH 0.3 NORMAL HCl.

1. T =	0	$\frac{1}{6}$	$22\frac{1}{2}$	28	$47\frac{1}{2}$	$97\frac{1}{2}$	120	142
K =	0.1010	0.1297	0.1523	0.1530	0.1540	0.1544	0.1544	0.1544

D. MEASUREMENTS WITH 0.4 NORMAL HCl.

1. T =	0	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$	3
K =	0.1313	0.1390	0.1405	0.1423	0.1433	0.1464	0.1625
T =	4	$4\frac{1}{2}$	$18\frac{1}{2}$	21	72	120	
K =	0.1661	0.1670	0.1783	0.1802	0.1818	0.1838	

E. MEASUREMENTS WITH 0.5 NORMAL HCl.

1. T =	0	$\frac{1}{6}$	$\frac{1}{2}$	23	$28\frac{1}{2}$	48
K =	0.1454	0.1460	0.1850	0.1910	0.1967	0.2064
T =	$72\frac{1}{2}$	$97\frac{1}{2}$	120	143		
K =	0.2110	0.2132	0.2160	0.2175		

From a consideration of the above results, it is apparent that in all cases there is an increase in the conductivity of these solutions with the time. Further, this increase is greater for solutions more concentrated in hydrochloric than for those less concentrated. This increase is very rapid at first, but its rate rapidly lessens. Thus it will be seen that a difference of a few minutes in the manipulation at the start makes a very considerable difference with the value of the total increase observed, but will have but little influence upon the total time required for the conductivity to become constant. Thus the greater length of time required for attaining equilibrium is more characteristic for concentrated solutions than is the absolute value of the increase in conductivity. In most cases the latter value is also greater for concentrated than for dilute solutions. The phenomena on the whole correspond almost exactly to those observed by Kohlrausch¹ upon dilution of stannic chloride with water, and there can be little doubt but that the oxidation of stannous chloride by free oxygen leads primarily to the formation of stannic chloride which then hydrolyzes, more rapidly in dilute than in concentrated solution. Thus the surmise made in a previous paper² that the oxidation leads directly to the formation of stannic or metastannic acid is not confirmed.³

2. OXIDATION BY MEANS OF POTASSIUM BICHROMATE.

The method of operation in this case (as in all following ones) was to weigh out the stannous chloride, add a requisite amount of

¹ *Loc. cit.*

² *Loc. cit.*, p. 133.

³ c. f. Thomsen: *loc. cit.*

hydrochloric acid, oxidize with the dissolved oxidizing agent (in this case potassium bichromate), and finally to bring the solution to required volume with water. It was then placed in the conductivity flasks, and measurements made as before. The specific conductivities in this case are naturally considerably less than when the solutions were oxidized with oxygen, on account of the conversion of hydrochloric acid to potassium and chromium chlorides.

F. MEASUREMENTS WITH 0.2 NORMAL HCl.

I.	T =	0	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{3}$	$\frac{1}{2}$	1	$1\frac{1}{2}$	$16\frac{1}{2}$	$20\frac{1}{2}$	24
	K =	0.0645	0.0650	0.0665	0.0665	0.0668	0.0674	0.0676	0.0698	0.0700	0.0702

G. MEASUREMENTS WITH 0.3 NORMAL HCl.

I.	T =	0	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{2}$	1	2	21	55
	K =	0.0898	0.0923	0.0928	0.0943	0.0958	0.0960	0.1000	0.1011
	T =	98	122						
	K =	0.1011	0.1011						

H. MEASUREMENTS WITH 0.5 NORMAL HCl.

I.	T =	0	$\frac{1}{12}$	$\frac{1}{4}$	$\frac{1}{2}$	$1\frac{1}{2}$	$20\frac{1}{2}$	$24\frac{1}{2}$
	K =	0.1192	0.1222	0.1263	0.1303	0.1357	0.1547	0.1552
	T =	54	97	122				
	K =	0.1585	0.1585	0.1585				

3. OXIDATION BY MEANS OF FERRIC CHLORIDE.

Only one set of measurements was made with ferric chloride as oxidizing agent, and that with 0.1 normal hydrochloric acid as follows:

I. MEASUREMENTS WITH 0.1 NORMAL HCl.

I.	T =	0	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{4}$	$2\frac{1}{2}$	$4\frac{3}{4}$
	K =	0.1053	0.1123	0.1153	0.1178	0.1327	0.1377
	T =	24	28	61	104		
	K =	0.01515	0.1522	0.1570	0.1581		

It will be noticed that the increase here is very much more marked than in other experiments with 0.1 normal hydrochloric acid. The explanation lies very near, since the reaction between stannous chloride and ferric chloride is in itself a slow one.¹ The method of procedure was somewhat varied in this case in that the amount of a given ferric chloride solution necessary to oxidize the stannous solution was determined from preliminary experiments and this amount added to the solution under investiga-

¹ Noyes: *Ztschr. phys. Chem.*, 16, 546.

tion. The measurements show, however, an increase in the conductivity long after the reduction must have become complete, and the results for ferric chloride lead to the same conclusions as for other substances.

4. OXIDATION BY MEANS OF HYDROGEN PEROXIDE.

Three series of measurements were made with hydrogen peroxide, upon solutions respectively 0.1, 0.3, and 0.5 normal in hydrochloric acid. A somewhat special interest attaches to these experiments, since if the course of the oxidation with hydrogen peroxide showed itself to be different from that with free oxygen, we should have direct evidence that the oxidation by means of free oxygen was not brought about by the intermediate formation of hydrogen peroxide. As the results show, however, the course of the oxidation is the same with hydrogen peroxide as with free oxygen. Naturally this fact can in no way be taken as evidence that in the oxidation by free oxygen, hydrogen peroxide is an intermediate product. Following are the results of these measurements :

J. MEASUREMENTS WITH 0.1 NORMAL HCl.

T = 0	$\frac{1}{12}$	$\frac{1}{4}$	1	23	$29\frac{1}{2}$
K = 0.0827	0.0837	0.0852	0.0881	0.0930	0.0932
T = 44	48	$72\frac{1}{2}$	144	168	192
K = 0.0940	0.0943	0.0950	0.0958	0.0963	0.0963

K. MEASUREMENTS WITH 0.3 NORMAL HCl.

T = 0	$\frac{1}{12}$	$\frac{1}{4}$	$\frac{7}{12}$	1	3	$6\frac{1}{2}$	$20\frac{1}{2}$
K = 0.1223	0.1270	0.1311	0.1368	0.1395	0.1435	0.1527	0.1550
T = 25	$49\frac{1}{2}$	122	146	170	194	218	
K = 0.1574	0.1583	0.1613	0.1616	0.1618	0.1622	0.1622	

L. MEASUREMENTS WITH 0.5 NORMAL HCl.

T = 0	$\frac{1}{4}$	$\frac{3}{4}$	$2\frac{1}{2}$	$5\frac{3}{4}$	20	24
K = 0.1477	0.1503	0.1523	0.1595	0.1705	0.1883	0.1927
T = 49	122	146	170	194	218	290
K = 0.2045	0.2157	0.2190	0.2213	0.2224	0.2238	0.2253

5. OXIDATION BY MEANS OF SODIUM HYPOCHLORITE.

Two series of measurements were made with sodium hypochlorite, in solutions containing respectively 0.1 and 0.3 normal hydrochloric acid. The sodium hypochlorite was prepared by passing chlorine through cold dilute sodium hydroxide. As was mentioned at the beginning of this paper, some special interest

attaches to these measurements, since the heat of oxidation of stannous chloride by means of hypochlorite was found by Thomsen to give very definite results, while those with chlorine were quite variable. The results given below show, however, that hypochlorite forms no exception to the other reagents studied, in regard to the course of the reaction. Into a probable explanation of Thomsen's results upon the basis of these results, we will not at present enter.

M. MEASUREMENTS WITH 0.1 NORMAL HCl.

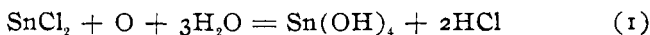
T = 0	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{5}{12}$	1	$1\frac{1}{2}$	29	53	149
K = 0.1152	0.1180	0.1192	0.1216	0.1233	0.1243	0.1320	0.1326	0.1329

N. MEASUREMENTS WITH 0.3 NORMAL HCl.

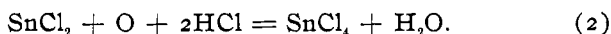
T = 0	$\frac{1}{12}$	$\frac{1}{4}$	$\frac{1}{2}$	1	29
K = 0.1319	0.1338	0.1357	0.1386	0.1410	0.1710
T = 53	149	173	197	121	
K = 0.1766	0.1830	0.1838	0.1850		

SUMMARY OF RESULTS.

In all cases examined the freshly oxidized solutions of stannous chloride show electrical conductivities which increase with the time. This increase is in general greater for solutions more concentrated in hydrochloric acid than for those less concentrated. These phenomena are, to all appearances, identical with those noted by Kohlrausch,¹ and are, it seems to me, to be considered as giving indisputable evidence as to the course of the reaction between stannous chloride and the various oxidizing agents used. The conclusion to be drawn from these phenomena is that the first stage in the oxidation of stannous chloride is the formation of stannic chloride, and that for this purpose hydrochloric acid is necessary. In a previous paper² this question was taken up speculatively and certain evidence given which led to the surmise that the reaction took place in a somewhat different manner. As a result of the experimental evidence here given this surmise is shown to be wholly unfounded. The two equations given in the ordinary chemical nomenclature, expressing the two reactions in question, are as follows :



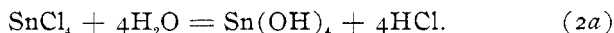
and



¹ *Loc. cit.*

² *Loc. cit.*

Reaction (2) is followed by :



The evidence shows distinctly that the reaction takes place according to (2) and (2a), which latter reaction is the cause of the increasing conductivity of the oxidized solutions with time.

The settling of this question adds one more case to those of reactions which follow the Ostwald rule¹ that "wherever an intermediate product can be formed during a reaction such product is formed," or in other words, the general tendency is for reactions to take place stepwise where possible.

The conclusion reached as a result of the preceding determinations is thus of fundamental importance in the correct formulation of the reaction-velocity in the case of the oxidation of stannous chloride with free oxygen. Part II of this paper will be devoted to a brief preliminary discussion of this point.

PART II. THE KINETICS OF THE REACTION BETWEEN STANNOUS CHLORIDE AND OXYGEN.

1. In a previous paper² the velocity coefficients for the reaction between stannous chloride and free oxygen in the presence of varying quantities of hydrochloric acid, were calculated upon the assumption that the hydrochloric acid did not enter directly into the reaction; *i. e.*, that its action was either catalytic, or else due to its influence upon the degree of hydrolysis of the stannous chloride. The values of the coefficients so calculated increased with the time in all cases. Since from the nature of the reaction the concentration of the hydrochloric acid must be greater at the end than at the beginning of the reaction, hydrolytic and catalytic influences could well explain the phenomenon. The catalytic explanation has the advantage over the hydrolytic one in that the phenomenon occurs in concentrations of hydrochloric acid so great that the hydrolysis of the stannous salt cannot well be considered to be very large. However, the results given in the first part of this paper show clearly that neither explanation is sufficient since the hydrochloric acid enters into the reaction as a definite reagent according to the laws of mass action, although it is, of course, by no means excluded that both catalytic and hydrolytic influences may also be at work.

2. Leaving hydrolytic and catalytic influences out of consider-

¹ *Ztschr. phys. Chem.*, **22**, 307.

² This Journal, **23**, 119.

ation for the present, and considering that the oxygen concentration is constant, we obtain as an expression for the reaction velocity the equation

$$\frac{dx}{dT} = K(A - x)^m(B - x + \Phi[x])^n, \quad (1)$$

where A is the initial concentration of stannous chloride, and B that of hydrochloric acid, and Φ is a function to be discussed later. For the exponents m and n we should set as most probable values, $m = 1$, $n = 2$, although it is not unlikely that $n = 1$.

3. The form of the function Φ is not determinable from any data at hand. Its value depends upon the rate of hydrolysis of stannic chloride in varying concentrations of hydrochloric acid. Kohlrausch¹ found that, in all probability, this reaction takes place according to a somewhat complicated law. For a somewhat simplified case, however, an expression for Φ is deducible. This case occurs when the primary reaction (the oxidation) is relatively slow, and the secondary one (the hydrolysis) very rapid. A low concentration of hydrochloric acid favors both conditions. In such an ideal limiting case $\Phi = 2$, since for each equivalent of hydrochloric acid used up, two are formed. Our equation then becomes

$$\frac{dx}{dT} = K(A - x)^m(B + x)^n. \quad (2)$$

By means of the integrated form of this equation I have calculated the velocity coefficients for the reaction in question, upon the assumption that $m = 1$ and $n =$ either 1 or 2. In no case was a satisfactory set of values obtained, all series showing distinctly increasing or decreasing values of K with the time. The natural explanation is that the condition that $\Phi = 2$ is not sufficiently approximated.

4. Although the above equation (2) does not, for the reason just given, correctly formulate the reaction velocity in the case under consideration, there is, nevertheless, no reason theoretically, why reactions should not occur which would be correctly formulated by it, the sole condition being that the secondary reaction should occur at a rate relatively very large in comparison with the primary one. As a matter of fact the equation has been repeatedly used for the formulation of catalytic reactions in cases where one of the products is a catalysor; *e. g.*, the hydrolysis of

¹ *Loc. cit.*, p. 275.

methyl acetate.¹ In other words, from the standpoint of formulation, a catalytic reaction of the sort mentioned (hydrolysis of esters) and a reaction such as that under consideration are identical. Thus the reaction between stannous chloride, oxygen, and hydrochloric acid lends some experimental basis to the oft-made assumption that in catalytic reactions, the catalytic influence is, in many cases, due to the action of the catalytic agent in accordance with the laws of mass action, but in such a way that it is regenerated so rapidly that we fail to find evidence that it has gone into the reaction at all. Certain it is, at least, that if in the oxidation of stannous chloride, the subsequent hydrolysis of the stannic chloride were excessively rapid, we should naturally explain the whole influence of hydrochloric acid as catalytic.

5. From the foregoing it is seen that the equation (2) may be brought to apply to reactions in which it is not at all necessary to assume the presence of catalytic influences. Equation (2) may in all cases, with proper choice of A and B , show a maximum for $\frac{dx}{dT}$. Thus the statement made by Ostwald² to the effect that such maxima can only occur when catalytic influences are at work, is too broad. Such maxima are, from the foregoing, seen to be possible from a theoretical standpoint where catalytic action is excluded, and the results of the measurements given in a previous paper³ give ample experimental evidence of their existence in case of a reaction where, at present, it does not seem necessary to assume catalytic action.

6. The perfectly general form of equation (1) for several substances, $A_1, A_2, A_3, \dots B_1, B_2, B_3$, would be

$$\frac{dx}{dT} = K(A_1 - x)^{m_1}(A_2 - x)^{m_2}(A_3 - x)^{m_3} \dots$$

$$(B_1 + \Phi_1[x])^{n_1}(B_2 + \Phi_2[x])^{n_2}(B_3 + \Phi_3[x])^{n_3} \dots,$$

where A_1, A_2, A_3 , are substances disappearing and not reappearing and B_1, B_2, B_3 , are substances disappearing but reappearing as the result of secondary action in quantities greater than the quantities disappearing. Such an equation may have a considerable number of maxima and minima, as is determinable by simple algebraic considerations. Theoretically then a series of maxima are possible in a reaction running in two or more stages, when a sufficient num-

¹ See Ostwald: "Lehrbuch", II², p. 245.

² "Lehrbuch," II², p. 270.

³ *Loc. cit.*

ber of substances are taking part in such a way that the concentrations of some of them increase, and this without necessarily assuming catalytic influences. This would, of course, be equivalent to a "periodic" reaction in a homogeneous system. I know of no cases where such periodicity has been observed. It is quite possible that the well-known tendency toward simplicity of reaction may not allow such to occur. The theoretical point is mentioned here merely as a suggestion.

NOTE.

In the first paper of this series, measurements of the electrical conductivity of stannous chloride solutions are given and likewise of the influence of certain substances on the same. In the matter of the influences of potassium chloride upon the conductivity,¹ it was shown that the calculation was one of great uncertainty, so that a measure of the ability of potassium chloride to form complex salts in solution with stannous chloride was difficult to obtain. There is one phenomenon mentioned in that paper, however, which is capable of an interpretation, that, unfortunately, did not occur to me at the time of writing, and that is the marked and ever-recurring decrease in the values of $\frac{\Delta K \times 10^4}{C}$ with increase in C . This is just what would be expected if the association of potassium chloride with stannous chloride was very marked. For such cases we have the equation

$$\frac{(C_{\text{KCl}})^m \times (C_{\text{SnCl}_2})^n}{C_{(\text{KCl})_m \cdot (\text{SnCl}_2)_n}} = K.$$

If K is very small the first portions of stannous chloride will combine almost wholly with the potassium chloride in the solution, and a large reduction of the electrical conductivity will occur. This will be the result until a large portion of the potassium chloride has entered into combination, after which subsequent additions of stannous chloride will produce smaller and smaller decreases and ultimately an increase. This is noticed in the previous paper² very distinctly in the results for 0.25 normal potassium chloride and 0.5 normal hydrochloric acid, while the same general tendency is noted in all cases. It is, perhaps, unfortunate

¹ This Journal, 23, 32.

² *Loc. cit.*

that measurements with more dilute hydrochloric acid were not made, as in all probability the phenomenon would have been even more marked in such cases.

This is related here as a bit of evidence tending strongly to confirm the conclusion reached in the previous paper that potassium chloride exhibits a more marked tendency to the formation of complex compounds with stannous chloride in solution than does hydrochloric acid.

STANFORD UNIV., March 20, 1901.

THE REACTION BETWEEN CHLORINE AND AMMONIA.¹

BY WILLIAM A. NOYES AND ALBERT C. LYON.

Received May 17, 1901.

IN Hoffmann's well-known lecture experiment for the demonstration of the composition of ammonia, the introduction of the ammonia into the tube filled with chlorine, is followed by the addition of dilute sulphuric acid. Some years ago, when performing this experiment, it occurred to one of us that the use of the sulphuric acid was unnecessary, as any excess of ammonia would be absorbed by the large amount of water which is allowed to enter the tube later. The sulphuric acid was accordingly omitted, but with the surprising result that the tube was left only one-sixth full of nitrogen instead of one-third full, as it should have been. Recently an opportunity has been found to give the subject a more careful study.

A glass tube, having a capacity of about 95 cc. and closed at each end with a stop-cock, was prepared. This tube, after cleaning and drying, was filled with chlorine which was generated from manganese dioxide and hydrochloric acid and washed with water. The gas was passed through the tube from below till the portion escaping was completely absorbed by a solution of sodium hydroxide. After removing the chlorine from the tubes outside of the stop-cocks, aqua ammonia was allowed to enter the tube from above, and, after shaking gently, was followed by water till the residual gas was at atmospheric pressure. The amount of the nitrogen was then determined by filling the tube with water from a burette which was connected with its lower end.

It was soon found that when strong ammonia is used in excess

¹ The work described in this paper forms the subject of a thesis by Mr. Lyon for the degree of Bachelor of Science at the Rose Polytechnic Institute.