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XV.—*The Interaction of Stannous and Arsenious Chlorides.*

By REGINALD GRAHAM DURRANT.

THE action of stannous chloride on arsenious oxide dissolved in hydrochloric acid was first noticed by A. Bettendorf (*Sitzungsber. Niederrhein. Ges. Bonn*, 1869, 128 *) two years after his discovery of yellow arsenic [*ibid.*, 1867, 67, and (full paper) *Annalen*, 1867, **144**, 110].

He records the formation of a voluminous, brown precipitate which proved to be arsenic (96—99 per cent.) with traces of non-removable tin. He showed that the rate of precipitation increases with ascending specific gravity of the arsenious solution. By dissolving magnesium ammonium arsenate in acid he made a standard solution and treated this with stannous chloride in varying dilutions of hydrochloric acid. (His figures will be quoted later on.) From these results he showed that the reaction is extremely delicate. It may be utilised for determining arsenic in sulphuric or crude hydrochloric acid. During a distillation with the latter he observed a faint yellow coloration, which disappeared after a few hours. Arsenic was found to be present in this sample of hydrochloric acid, but he was unable to prove that the fading coloration was due to arsenic.

The observation of this yellow coloration has decided me to record a very remarkable yellow precipitate which, in 1914, I exhibited as "yellow arsenic" to the Science Masters' Association in London. The precipitate was quite bright yellow at first, and was always kept in the dark except when shown for short periods. After a year

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* I am indebted to Dr. Hatchett Jackson who recently procured me a rescript of this paper from the Bodleian Library.

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it had become a dull mustard colour, being still in the original, well-corked flask and surrounded by the original solution (a mixture of arsenious and stannous chlorides in nearly normal hydrochloric acid). Every effort was made to repeat this, but in vain. When filtered off, the precipitate appeared very dull and shrunken on the paper. After washing, it was specially tested for sulphur (since arsenious sulphide is yellow), but no trace of sulphur was found. The presence of arsenic was proved.

On many points I find that my observations have been anticipated by Bettendorf, in particular the possibility of making the reaction a means of differentiating arsenic from antimony.

EXPERIMENTAL.

The Nature of the Arsenic Precipitated.

Arsenic is probably in a colloidal state before it is precipitated, for (i) the precipitate invariably contains a trace of tin salts (chloride as well as tin), and this cannot be removed completely by prolonged washing; (ii) two similar solutions (reactants, 0·44*N*- and 3*N*-hydrochloric acid) were left corked for two days and remained quite clear. One was then diluted with an equal volume of water. After four days both had deposited arsenic. A third solution at the start was made up to the lower of the above concentrations and remained perfectly clear for twenty-five days.

The appearance of solid arsenic is always preceded by a pale buff tint; from this a buff-brown precipitate falls, and is best observed from such admixtures as yield a very slow deposit. If this deposit, after washing, is immediately shaken with carbon disulphide, arsenic is found to be dissolved. The yield is rather greater if carbon disulphide is shaken violently with the two chloride solutions while they are interacting. On five occasions small, pale particles were observed to rise from the clear disulphide solution during spontaneous evaporation. They moved about rapidly, congregating in the centre of the surface, then darkened, and finally settled on the bottom of the dish in the form of grey arsenic.

Erdmann (*Zeitsch. anorg. Chem.*, 1902, **32**, 453) obtained arsenic soluble in carbon disulphide by reducing arsenious oxide with zinc dust in the presence of the solvent. Very small quantities were obtained by the author in this way.

These results, and those referred to in the Introduction, indicate that the very earliest deposit of arsenic is of the yellow type, but that unless certain unascertained conditions obtain, the yellow variety spontaneously becomes brown or grey.

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Nature and Conditions of the Reaction.

The obvious equation is $2AsCl_3 + 3SnCl_2 = 3SnCl_4 + 2As$, and when weights of the reactants, corresponding with this equation, are placed in hydrochloric acid of sufficiently high concentration the action reaches completion in a few hours. With other weights excess of either reactant corresponds with calculation. The action has been proved to be irreversible, for, if finely divided arsenic is boiled with solutions of stannic chloride in the presence of hydrochloric acid of varying concentration, in no case does the resulting solution give any precipitate with mercuric chloride.

A very careful experiment was made in order to ascertain if the anhydrous chlorides react.

Fresh arsenious chloride was so arranged that on movement of the handle of an air-pump some would drop on to dry, powdered stannous chloride—also under the receiver. After four days' final drying with phosphoric oxide, the experiment was made. Beyond the faintest darkening no discoloration occurred. On exposure to air a distinct brown colour overspread the powder, and when a drop of water was added a heavy crusting of arsenic appeared immediately.

General Method of Estimating the Rate of Progress of Action.

Separate solutions containing known weights of the two chlorides were made up in known concentrations of hydrochloric acid. Portions of these solutions were evaluated separately by means of standard permanganate. The results were found to agree with the known concentrations. All stock flasks were re-tested from time to time.

Small dry flasks were placed in a large thermostat, and into these definite volumes of both chloride solutions were introduced by separate pipettes.

After definite intervals water was added. The dilution effectively stops the action. The contents of each flask were then filtered and uniformly washed. Standard permanganate was used to determine the amounts of stannous and arsenious chlorides remaining in the filtrates and wash-water.

The action of the permanganate may be expressed:

$$\left\{\begin{array}{l} 2AsCl_3 + 2O = 2AsOCl_3 \\ 3SnCl_2 + 3O = 3SnOCl_2 \end{array}\right\}.$$

As the filtrates required less permanganate than did the sum of

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the separate solutions, the deficit became a measure of the change which had occurred. Two-fifths of this deficit were due to the precipitation of arsenic and the rest to the formation of stannic chloride in the reaction:

$$3SnCl_2 + 2AsCl_3 \longrightarrow 3SnCl_4 + 2As.$$

Errors.—The sources of error in this process are: (1) imperfect washing, (2) loss by adsorption, (3) oxidation of stannous chloride due to access of air.

The two first, considered together, were found to give rise to an error probably less than 2 per cent.

The third source of error was almost eliminated by keeping the stock solutions of stannous chloride in a well-corked flask and by introducing carbon dioxide immediately after use on every occasion. In the same way the reaction took place in small, corked flasks in which the air was displaced by carbon dioxide. Air had access only during the process of filtration.

Calculations.—The recognised integration equations for first and second order reactions were applied to a large number of determinations. In no case did the velocity constants conform to the second order. The results quoted are from the first-order equation, $\frac{1}{t} \log \frac{a}{a-x}$, where $a=100$, x=percentage of change, and t=time in minutes. Hence the mean value of k for each set of experiments represents a special figure by which the relative speeds may be compared.

TABLE I.

$t=12{\cdot}5°$. Normalities: $SnCl_2=0{\cdot}507$, $AsCl_3=0{\cdot}584$, $HCl=6{\cdot}06$. $N/4$-Permanganate used. Complete oxidation should correspond with a deficit of 45·6 c.c.

Interval, minutes.	Deficit, c.c.	Percentage change.	$k \times 10^2$.
2	3·65	8·0	1·81
5	9·3	20·8	2·03
8	16·65	36·5	2·46
10	17·05	[37·4]	[2·03]
12	26·25	57·5	3·09
15	29·4	64·5	3·00
20	33·85	74·2	2·94
30	38·45	84·3	2·68
40	40·1	87·9	2·29
50	40·8	89·5	2·96
65	41·9	91·9	[1·68]
100	42·85	93·9	2·21
120	43·6	95·6	2·97
180	43·9	96·3	2·40
		Mean	2·57

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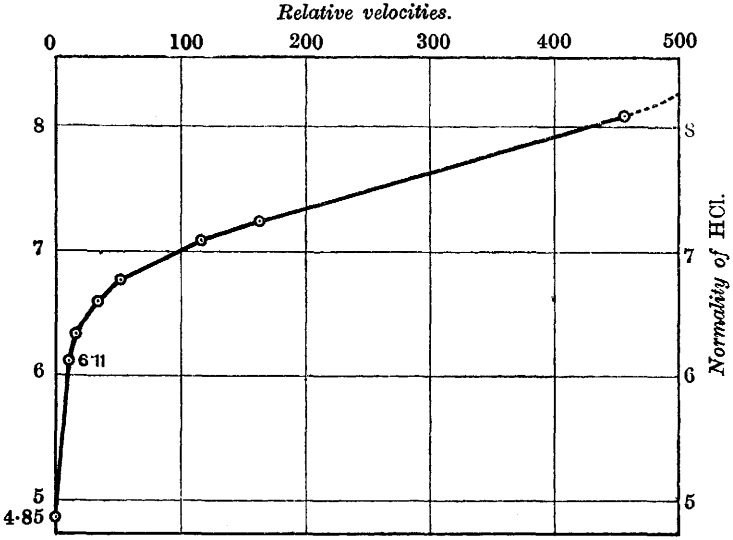
Various further unimolecular values of k were obtained. These were found to depend more on the concentration of hydrochloric acid than on anything else. The results made it possible to choose suitable concentrations for systematic study.

Influence of Hydrochloric Acid.

In the following experiments 0·2500 gram of stannous chloride acted on the equivalent weight of arsenious chloride in each case. The concentration of hydrochloric acid alone was varied.



Relative velocities of the reaction: $3SnCl_2 + 2AsCl_3 = 3SnCl_4 + 2As$, *due to alterations of hydrochloric concentration. See Table II.* *Temperature* = 12°.

TABLE II.

$t = 12°$. Reactant Normality = 0·298.

Normality of HCl.	Range of change, per cent.	Mean value, $k \times 10^2$.
10·09	40—61	21·2
8·10	36—64	13·5
7·25	32—63	4·76
7·09	34—78	3·43
6·77	13—63	1·46
6·60	21—69	0·944
6·34	26—64	0·436
6·11	41—53	0·293
4·85	19—53	0·0293

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The curve, obtained by plotting these relative velocities against concentration of hydrochloric acid between $4 \cdot 85N$ and $8 \cdot 10N$, is exceedingly regular. Its sharpest curvature is in the neighbourhood of $6 \cdot 5N$. If the regularity persisted up to the limit of possible hydrochloric acid concentration (about $10 \cdot 3N$) then the velocity at $10 \cdot 09N$ would be well over a thousand times what it is at $4 \cdot 85N$—as measured it is only 723 times as great.

Influence of Simultaneous Change in Concentration of Reactants.

In all these experiments, the concentration of hydrochloric acid remained constant at $6N$. $t = 18 \cdot 4$.

Four 250 c.c. flasks—A, B, A_1, B_1—contained, respectively, $SnCl_2 = 1 \cdot 74N$, $AsCl_3 = 1 \cdot 76N$, $SnCl_2 = 0 \cdot 87N$, $AsCl_3 = 0 \cdot 88N$.

The concentration of hydrochloric acid became $6N$ as soon as the mark in each flask was reached.

Equal volumes from A and B were mixed in six small flasks, and after 4, 6, 8, 10, 12, and 14 minutes, respectively, their filtrates were titrated with $N/4$-permanganate.

In the same way, equal volumes from A_1 and B_1 were treated from seven flasks after 24, 32, 48, 64, 80, 96, and 112 minutes, respectively, the filtrates being titrated with $N/8$-permanganate.

In each set, the range of progress was from 30 to 70 per cent.

For AB set, mean value $k \times 10^2 = 4 \cdot 33$.

For A_1B_1 set, mean value $k_1 \times 10^2 = 0 \cdot 557$.

Hence $k/k_1 = 7 \cdot 77$ for the range between 30 and 70 per cent. The range between 30 and 40 per cent., however, gave $k/k_1 = 5 \cdot 5$.

Effect of altering the Concentration of Each Reactant Separately.

Preliminary work had appeared to show that arsenious chloride reacts as a second, and stannous chloride as a first power.

The following solutions were prepared, tested, and preserved with all possible care. Five c.c. of stannous chloride solution reacted with 5 c.c. of arsenious chloride solution in each case. The washing was strictly uniform, so that errors hence arising were similar.

The mean results, (2) and (4) in the following table, are fairly concordant. Those of (3) and (5) are more so.

The results from comparison of (1), (4), and (5) confirm the preliminary work with respect to arsenious chloride, which is seen to react as a second power.

The period preceding the first appearance of arsenic, from a solution of its chloride at one-fifth the original concentration, was noticed to be just about twenty-five times as great as it had been.

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Table III.

HCl $= 6N$. $t = 16{\cdot}7°$.

		required c.c. $N/4$-KMnO$_4$ Mean of 2 readings	Required by theory after 33·3 per cent. change.
(1) N-AsCl$_3$	acting on N-SnCl$_2$ in 12 minutes	27·85	26·66
(2) N-AsCl$_3$	„ on $N/2$-SnCl$_2$ in 12 minutes	22·3	23·3
(3) N-AsCl$_3$	„ on $N/3$-SnCl$_2$ in 12 minutes	20·8	22·2
(4) N-SnCl$_2$	„ on $N/2$-AsCl$_3$ in 48 minutes	22·55	23·3
(5) N-SnCl$_2$	„ on $N/3$-AsCl$_3$ in 108 minutes	20·9	22·2

This suggested a method of working to a standard tint, as in Nesslerisation; moreover, the method compares the earlier stages of action on which calculations are more appropriately based.

The tint used in table IV was obtained by the action of hydrogen sulphide on a very dilute solution of lead acetate.

Table IV.

HCl $= 6N$. $t = 10°$.

Times to reach Standard Tint are given in Seconds.

Stannous chloride.	Arsenious chloride }	→ N.	→ $N/2$.	→ $N/3$.	Total.	Ratio.	$\sqrt{c}$.
N		30	110	260	400	1·0	1·0
$N/2$		40	160	360	560	1·40	1·41
$N/3$		50	220	460	730	1·82	1·73
Total		120	490	1080			
Ratio		1	4·08	9			
$1/c^2$		1	4	9			

A similar set of nine readings referred to another artificial standard tint gave ratios: powers of AsCl$_3$, 1 : 4·3 : 10·0; powers of SnCl$_2$, 1 : 1·37 : 1·80.

The $N/3$-stannous chloride solution, on testing, was found to have deteriorated slightly; the others had not.

A solution of $N/4$-stannous chloride was made. Using $N/2$-arsenious chloride against $N/2$- and $N/4$-stannous chloride, the times were 230 and 320 seconds respectively, giving a ratio $1/1{\cdot}39$, again closely approaching $1/\sqrt{2}$.

The results here given lead to the conclusion that in this reaction *arsenious chloride reacts as a second power and stannous chloride reacts to the power of the square root of its concentration.*

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The figure 5·5, noted in the last paragraph for the change between 30 and 40 per cent., is quite consistent with the results here given, since $2^2 \times \sqrt{2} = 5 \cdot 64$.

The action of stannous chloride to the square root of its concentration is also in agreement with Bettendorf's figures (*loc. cit.*, 1869). He took 0·001 gram of arsenic dissolved in 1 c.c. in each of five experiments, adding this to a definite amount of stannous chloride solution in the presence of hydrochloric acid. In the four last experiments he also added 50, 100, 200, and 400 c.c. of hydrochloric acid (presumably of similar concentration).

An immediate precipitate occurred in the first experiment, and the arsenic appeared in 5, 8, 12, and 20 minutes, respectively, in the others.

Neglecting 1 c.c. of arsenious chloride + an unknown volume of stannous chloride solution originally taken, his concentrations were 1 : 2 : 4 : 8, his times were 1 : 1·6 : 2·4 : 4, figures which approach 1 : 1·41 : 2 : 2·83, but exceed them in each case, because of the influence of the second power action of arsenious chloride, present in very small relative amount. (His experiments were made to show the delicacy as regards arsenic.)

Effect of Dilution with Water.

The stock solutions, when mixed, were at concentrations $HCl = 6N$ and reactants each at $0 \cdot 88N$. When undiluted, this mixture produced 70 per cent. change in twelve minutes. The dilutions (in ten steps) finally brought all the concentrations to one-third of the above.

The hydrochloric acid normalities, and the state of change after five days are noted in each case. $t = 16°$. $6N$, $5 \cdot 45N$, and $5N$ had reached complete change. $4 \cdot 61N$ 89 per cent., $4 \cdot 29N$ 59 per cent., $4N$ 24·4 per cent., $3 \cdot 75N$ 14·2 per cent., $3 \cdot 53N$ 5·6 per cent., $3 \cdot 3N$ 3 per cent., $3N$ 1 per cent., and $2N$ no change and no subsequent sign of action after 29 days. This retarding action was made use of in all previous experiments when titrations with permanganate were made, the dilution with water being sufficient to reduce the concentration to one-third or less.

Summary.

(1) There is evidence that arsenic in process of precipitation is partly soluble in carbon disulphide. In certain circumstances, arsenic may appear as a yellow deposit.

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(2) The anhydrous chlorides (arsenious and stannous) do not interact.

(3) Acceleration of the action is caused chiefly by increase in the concentration of hydrochloric acid, next by that of arsenious chloride, and least of all by that of stannous chloride. Arsenious chloride acts as a second power and stannous chloride to the power of the square root of its concentration.

Conclusions.

The various phenomena and the figures given can be accounted for on the hypothesis that this action is between chloride ions, arsenious ions, and the stannous complex H_2SnCl_4.

Stoppage by dilution must be due to the destruction of arsenious ions by hydrolytic action.

(1) Chloride ions proceed partly from arsenious chloride and partly from hydrochloric acid, and they act as a first power.

The velocity constants found in table II are thus explained.

HCl normality.	$k \times 10^2$.	k/k.	Cl′/Cl′.
10·09	21·2	1·57	7·09
8·10	13·5	2·83	3·55
7·25	4·76	1·37	1·54
7·09	3·43	2·35	2·08
6·77	1·46	1·54	1·58
6·60	0·944	2·16	1·88
6·34	0·436	3·22	2·66
6·11	0·293	10·00	5·28
4·85	0·0293		
	Aggregate	25·04	25·66

In the last column, the numerator gives the sum of chloride ions due to arsenious chloride and those due to increased hydrochloric acid concentration; the denominator is constant, and represents the chloride ions due to the 0·298*N*-arsenious chloride, which is constant throughout the table. In the lower portion of the table, the arsenious chloride is not wholly ionised; in the upper portion, hydrochloric acid becomes less ionised at its higher concentrations. As is seen, *the aggregate acceleration is directly proportional to the increase of chloride concentration.*

(2) Positively charged arsenious ions also act as a first power. Arsenious chloride as a whole appears, therefore, to act as a second power.

(3) That a compound of hydrochloric acid and stannous chloride exists in solution was indicated by Young (*J. Amer. Chem. Soc.*, 1901, **23**, 21, 450), and several stannochlorides, corresponding with

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the formula M_2SnCl_4, have recently been described (compare Druce, *Chem. News*, 1918, **117**, 193). In the reaction, this complex must be decomposed in order to produce stannic chloride, and this decomposition may account for the complex acting to the power of the square root of its concentration.

According to accepted theory, the order of a reaction is governed by the slowest reactant. The order here is unimolecular, and the slowest reactant is this complex. Essentially the action consists in the disintegration of the complex by circumambient ions.

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