27. *The Interaction of Chloramine-T and Hydrogen Sulphide, Phosphine, and Arsine.*

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Hydrogen sulphide and sodium sulphide react with aqueous chloramine-T to give sulphuric acid and sulphur respectively. Sulphites are quantitatively oxidised to sulphates and can be thus estimated volumetrically, whereas thiosulphates are converted into tetrathionates.

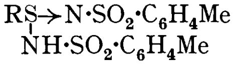
Chloramine-T, reacting with an excess of phosphine, oxidises it to hypophosphorous and phosphorous acids. When the chloramine-T is in excess, complete but slow oxidation to phosphoric acid occurs, the slow intermediate stage being the oxidation of the hypophosphorous to phosphorous acid.

Chloramine-T oxidises arsine rapidly to arsenic acid, irrespective of the proportions of the reactants; the initial oxidation to arsenious acid is, however, slower than the oxidation of the latter to arsenic acid.

A study of the interaction of chloramine-T (p-$C_6H_4Me{\cdot}SO_2{\cdot}NNaCl,3H_2O$) with hydrogen sulphide, phosphine, and arsine has revealed several points of interest that warrant detailed quantitative investigation, but present circumstances have allowed only the recognition of the main reactions involved.

The interaction of chloramine-T and the chief organic derivatives of 2-covalent sulphur is now well established: organic sulphides of type R_2S give " sulphilimines " * (I), a reaction also shown by some cyclic sulphides (Mann and Pope, J., 1922, **121**, 1052); thiols give compounds of type (II) (Clarke, Kenyon, and Phillips, J., 1930, 1225); disulphides, R_2S_2, with an excess of the reagent undergo fission at the S–S linkage, each fragment then furnishing a molecule of type (II) (Alexander and McCombie, J., 1932, 2087).

(I.) $R_2S{\rightarrow}N{\cdot}SO_2{\cdot}C_6H_4Me$



$$\begin{array}{l}RS{\rightarrow}N{\cdot}SO_2{\cdot}C_6H_4Me\\ \,|\\ NH{\cdot}SO_2{\cdot}C_6H_4Me\end{array}$$

(II.)

The interaction of chloramine-T with hydrogen sulphide has therefore been investigated, since this reaction might produce the parent unsubstituted sulphilimine, $H_2S{\rightarrow}N{\cdot}SO_2{\cdot}C_6H_4Me$, which furthermore by hydrolysis might furnish the unknown dihydrogen sulphoxide, $H_2S{\rightarrow}O$, probably tautomeric with the compound $H{\cdot}S{\cdot}OH$.

When, however, an excess of hydrogen sulphide was passed into an aqueous solution of chloramine-T at room temperature, p-toluenesulphonamide was precipitated and sulphuric acid formed; no sulphurous acid, and only a trace of sulphur, could be detected, and the reaction evidently follows equation (A).

$$H_2S + 4C_6H_4Me{\cdot}SO_2{\cdot}NNaCl + 4H_2O = H_2SO_4 + 4C_6H_4Me{\cdot}SO_2{\cdot}NH_2 + 4NaCl \quad . \quad . \quad . \quad . \quad (A)$$

This is confirmed by the almost theoretical yields of the amide and of sulphuric acid, calculated on the chloramine-T used. No indication of sulphilimine formation could be obtained. It follows from these

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* Mann and Pope gave the name " sulphilimine " to this class of compound on the advice of the late Mr. A. J. Greenaway, who named a specific member, *e.g.*, $Et_2S{\rightarrow}N{\cdot}SO_2{\cdot}C_6H_4Me$, " diethylsulphine-$p$-toluenesulphonylimine." It is clear that on the latter basis the term for this class of compound should be " sulphinimine," a name which moreover would accord with the similar " phosphinimine " and " arsinimine." The phosphinimines are represented by two types (*a*) $R_3P{\rightarrow}NR$ (Staudinger and Hauser, *Helv. Chim. Acta*, 1921, **4**, 861) and (*b*) $R_3P{\rightarrow}N{\cdot}SO_2{\cdot}C_6H_4Me$ (Mann and Chaplin, J., 1937, 527), and the arsinimines by $R_3As{\rightarrow}N{\cdot}SO_2{\cdot}C_6H_4Me$ (Mann, J., 1932, 958; Mann and Chaplin, *loc. cit.*).

results that the further oxidation of any intermediate oxy-acids of sulphur (*e.g.*, H_2SO) formed in the course of this reaction must be very rapid compared with initial oxidation of the hydrogen sulphide, and the possibility of their isolation must be remote.

When a standard sodium sulphide solution was titrated with chloramine-T, with potassium iodide–starch as an external indicator, sulphur was deposited and the solution became markedly alkaline, no trace of sulphite or sulphate being detected; although the end-point was far from sharp, the results indicated clearly that the main reaction followed equation (B). [Alternatively, since sodium sulphide

$$\overset{--}{S} + C_6H_4Me{\cdot}SO_2{\cdot}NNaCl + 2H_2O = S + C_6H_4Me{\cdot}SO_2{\cdot}NH_2 + NaCl + 2\overset{-}{O}H \quad . \quad . \quad . \quad . \quad . \quad . \quad (B)$$

is largely hydrolysed at the dilution employed, this reaction may have followed equation (B1), the two

$$\overset{-}{S}H + \overset{-}{O}H + C_6H_4Me{\cdot}SO_2{\cdot}NNaCl + H_2O = S + C_6H_4Me{\cdot}SO_2{\cdot}NH_2 + NaCl + 2\overset{-}{O}H \quad . \quad . \quad . \quad (B1)$$

routes being, of course, quantitatively identical.] No further oxidation was caused by the addition of excess of chloramine-T, and therefore even freshly deposited sulphur is not oxidised by this reagent in cold aqueous solution. Sulphur was again deposited when conversely the sodium sulphide solution was added to the chloramine-T. It follows that the oxidation of hydrogen sulphide molecules and of sulphide or hydrosulphide ions is entirely distinct, and that elementary sulphur cannot be an intermediate stage in the oxidation of hydrogen sulphide to sulphuric acid. It is suggested that in the reaction with hydrogen sulphide the trace of sulphur arises from the ionised, and the sulphuric acid from the un-ionised, hydrogen sulphide.

There is a further point of interest concerning the interaction of hydrogen sulphide and chloramine-T. When a standard dilute solution of the latter was titrated with a standard solution of the former, with potassium iodide–starch as *external* indicator, the results showed, as expected, that the reaction again followed equation (A), although the process, owing to experimental error, was useless for accurate analysis. When the order of titration was reversed, the same results were obtained, although the experimental error in the titration—due chiefly to volatilisation of hydrogen sulphide—was now greater. In each case, however, the sulphide was oxidised to sulphuric acid and not to sulphur. If, however, in the second titration the same indicator was used *internally*, the reaction followed an entirely different course, sulphur alone being formed by the oxidation, and considerably less chloramine-T solution being therefore required. This difference in reaction is ascribed to the probability that in the latter reaction oxidation of the potassium iodide by the chloramine-T precedes that of the hydrogen sulphide, the iodine thus formed then oxidising the hydrogen sulphide to sulphur: the ionic oxidation of the iodide would naturally be more rapid than the molecular oxidation of the hydrogen sulphide.

We have also investigated the interaction of chloramine-T with sodium sulphite and sodium thiosulphate. The sulphite in cold aqueous solution is rapidly and quantitatively oxidised to sulphate (equation C), and may be accurately estimated by this method. Sodium thiosulphate is oxidised to

$$Na_2SO_3 + C_6H_4Me{\cdot}SO_2{\cdot}NNaCl + H_2O = Na_2SO_4 + C_6H_4Me{\cdot}SO_2{\cdot}NH_2 + NaCl \quad . \quad . \quad . \quad . \quad . \quad (C)$$

tetrathionate, but the reaction is of little analytical value, as the end-point is not sharp. The main reaction (D) is of interest, however, because again (as in B) the interaction of two neutral substances produces an alkaline solution.

$$2Na_2S_2O_3 + C_6H_4Me{\cdot}SO_2{\cdot}NNaCl + 2H_2O = Na_2S_4O_6 + C_6H_4Me{\cdot}SO_2{\cdot}NH_2 + 2NaOH + NaCl \quad . \quad (D)$$

The complete interaction of phosphine with excess of chloramine-T in aqueous solution at room temperature is much slower than that of hydrogen sulphide. Preliminary experiments showed, however, that when *excess* of phosphine was passed into chloramine-T solution until saturation was obtained and all reaction was complete, the solution contained hypophosphorous and phosphorous acids but no phosphoric acid. Now, the initial reaction of the phosphine was obviously rapid, since if the passage of the gas was stopped before saturation was attained, the odour of the phosphine almost immediately disappeared; the same volume of pure water, similarly treated with phosphine, smelt of the gas for many hours. It follows that the oxidation of hypophosphorous or of phosphorous acid to phosphoric acid (see below) must be a markedly slower process than the rapid initial oxidation of the phosphine to the intermediate acids; had the reverse been the case, only phosphoric acid would have been obtained. (No evidence for the formation of a true phosphinimine, $H_3P{\rightarrow}N{\cdot}SO_2{\cdot}C_6H_4Me$, could be obtained in these experiments.)

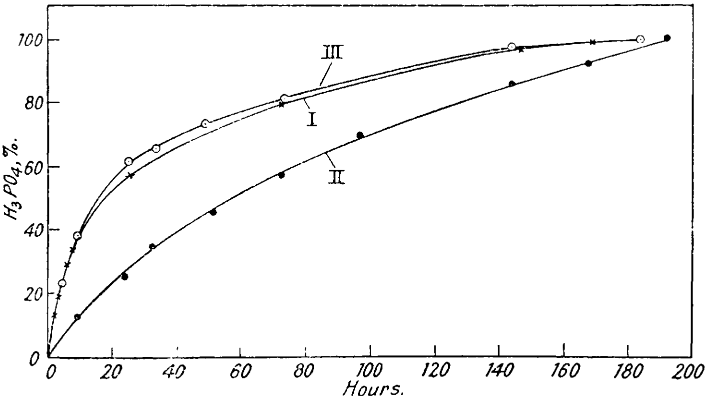
The oxidation of phosphine by *excess* of chloramine-T was therefore quantitatively investigated. A limited quantity of phosphine was passed into a considerable excess of aqueous chloramine-T solution kept at 28·5°. In these circumstances, complete but slow oxidation to phosphoric acid occurred. Aliquot portions of the solution were withdrawn at intervals, and the phosphate content estimated; the total phosphorus content was also determined, so that the percentage of phosphorus present as phosphate at known intervals could be calculated. The results are plotted in curve I, which shows that the production of phosphoric acid is comparatively rapid at first and gradually slackens, and is not complete until the oxidation has proceeded for *ca.* 190 hours.

Now the oxidation of phosphine to phosphoric acid must proceed through the stages A, B, and C, although stage A may actually be a double stage, involving the unknown and presumably very reactive

$$PH_3 \xrightarrow{A} H_3PO_2 \xrightarrow{B} H_3PO_3 \xrightarrow{C} H_3PO_4$$

intermediate $H_3P \rightarrow O$ or $H_2P(OH)$. We consider these stages in reverse order:

Stage C. (*a*) When neutral sodium phosphite (Na_2HPO_3) was treated in aqueous solution with excess of chloramine-T at 28·5°, no appreciable oxidation occurred during 24 hours. (*b*) When, however, the sodium phosphite was treated with 2 equivs. of acetic acid in order to produce an equilibrium with sodium acetate and phosphorous acid, oxidation by chloramine-T was complete in 1 hour, and was too rapid to be followed accurately by timed volumetric analysis. Stage C cannot therefore be responsible for the slow over-all oxidation of the phosphine.



I. *Oxidation of Phosphine.*
II. *Oxidation of* NaH_2PO_2.
III. *Oxidation of* $NaH_2PO_2 + CH_3{\cdot}CO_2H$.

Stage B. (*a*) When neutral sodium hypophosphite (NaH_2PO_2) was similarly treated with excess of chloramine-T, a slower but more regular oxidation was obtained (curve II) than with phosphine. Now this oxidation must proceed through the stages B′ and C′, *i.e.*, the first product of oxidation will be

$$NaH_2PO_2 \xrightarrow{B'} NaH_2PO_3 \xrightarrow{C'} NaH_2PO_4$$

weakly *acid* sodium dihydrogen phosphite, which, from the previous results, is almost certainly rapidly oxidised to the phosphate. If therefore stage C′ is very rapid, curve II shows essentially the rate of stage B′. (*b*) When, however, the neutral sodium hypophosphite was first diluted in solution with 1 equiv. of acetic acid, curve III was obtained. This curve, representing stage B, approximated closely throughout its entire length to curve I. It should be emphasised, however, that a strict quantitative comparison between these three curves is not possible, as the amount of phosphine used in (I) could not be accurately predetermined, although it was very small compared with the large excess of chloramine-T used. Repetitions of the phosphine experiment, however, always gave a curve almost identical with I, and lying between curves II and III, and usually—as in the example shown—closely approaching curve III throughout. The general and closely similar character of the three curves is thus not in doubt. In view, therefore, of the rapidity of stages A and C, and the extreme slowness of stage B, it is clear that it is the latter stage, *i.e.*, oxidation of hypophosphorous to phosphorous acid, which is the governing time factor in the over-all oxidation of phosphine to phosphoric acid.

To check these results, the experiments were repeated at 38·5°, a different method being used for phosphate estimation. The curves I, II, and III now obtained were closely similar to the previous ones, except that the initial oxidation in II and III was rather more rapid than at 28·5°, although the time required for almost complete oxidation was virtually unchanged. Disodium hydrogen phosphite at the higher temperature again underwent no appreciable oxidation in pure aqueous solution, and rapid oxidation in the acetic acid solution.

Comparison of these results with those obtained for the oxidation of the phosphorous acids by halogens is of interest. Manchot and Steinhäuser (*Z. anorg. Chem.*, 1924, **138**, 304) have shown that hypophosphorous acid is oxidised by bromine only slowly in acid solution, but more rapidly in alkaline (*i.e.*, sodium acetate) solution. Various workers (Ruff and Finck, *Arch. Pharm.*, 1902, **240**, 663; Steele, J., 1907, **91**, 1642; Wolf and Jung, *Z. anorg. Chem.*, 1931, **201**, 337) have shown, however, that hypophosphorous acid is oxidised by iodine rapidly in acid solution but negligibly so in alkaline (sodium bicarbonate) solution. Chloramine-T is intermediate between these halogens, since it gives slow oxidation in a solution of sodium hypophosphite originally neutral, but more rapid oxidation in the presence of acetic acid. (The effect of the presence of acids stronger than acetic acid would probably repay investigation.) Comparison of the oxidation of phosphorus acid is difficult, because, although Manchot and Steinhäuser (*loc. cit.*) and Ruff and Finck (*loc. cit.*) state that oxidation of this acid by bromine and iodine is retarded in acid solution but accelerated in alkaline (sodium bicarbonate) solution, Steele (*loc. cit.*) and Mitchell (J., 1923, **123**, 2241) agree that the oxidation by iodine involves two reactions, one retarded and the other accelerated by acids. This acceleration by acids is, of course, the marked feature of the oxidation of sodium phosphite by chloramine-T.

When a current of arsine was passed into a standard solution of chloramine-T until reaction was complete, the solution was found to contain arsenic acid equivalent to the chloramine-T used, and only a trace of arsenious acid was present. (No indication of the formation of an arsinimine was obtained.) It follows that if the oxidation proceeds through the stages

$$AsH_3 \xrightarrow{D} H_3AsO_3 \xrightarrow{E} H_3AsO_4$$

stage E is probably more rapid than stage D. The rapidity of stage E was confirmed by the following experiments. A current of arsine was passed into a solution of chloramine-T at room temperature and stopped whilst there was still a considerable excess of the latter. Analysis of aliquot portions of the solution, maintained at 28·5°, showed that after 1 hour 96·5% of the arsenic was present as arsenic acid, and after 1·5 hours this oxidation was complete. Furthermore, when standard aqueous solutions of arsenious acid and of excess of chloramine-T were mixed at 28·5°, complete oxidation of the arsenic to arsenic acid had occurred within 5 minutes. This reaction is indeed sufficiently rapid to enable arsenious acid to be estimated accurately by titration with a standard chloramine-T solution, provided the arsenious acid solution be warmed before titration (cf. Noll, *Chem.-Ztg.*, 1924, **48**, 845; McMillan and Easton, *J. Soc. Chem. Ind.*, 1927, **46**, 472T).

These results harmonise with those obtained in the phosphine series, since it is the *corresponding* stages C and E in the phosphine and the arsine series respectively which are so rapid; in the arsine series, however, there is no stable intermediate compound corresponding to hypophosphorous acid, the oxidation of which delays so markedly the complete reaction in the phosphine series. Hence, although stage D in the arsine series is slower than stage E, it is far more rapid than the sum of stages A and B in the phosphine series, and the complete oxidation of the arsine is therefore a very much more rapid process than that of the phosphine.

It should be borne in mind that the stages A and D in the phosphine and the arsine series are merely the first stages experimentally detectable: we have no knowledge of the unstable and highly reactive intermediate compounds that must be formed during these particular oxidation stages; *e.g.*, the true *initial* reactions may be oxidation to the compounds $H_3P\rightarrow O$ and $H_3As\rightarrow O$ respectively. On the other hand, it is noteworthy that when arsine was passed into the large excess of aqueous chloramine-T, the *p*-toluenesulphonamide precipitated as oxidation proceeded was at first coloured faintly brown in the neighbourhood of the incoming gas by the deposition of a trace of elementary arsenic, which, however, rapidly dissolved when the solution was more vigorously agitated. This indicates that elementary arsenic may be a direct, or alternatively a subsidiary, intermediate in stage D, and that it is then immediately oxidised to arsenious and arsenic acid. This oxidation of elementary arsenic is certainly possible, for a colloidal solution of arsenic, prepared by oxidation of arsine in aqueous solution by dissolved and atmospheric oxygen, was immediately decolorised by addition of aqueous chloramine-T.

EXPERIMENTAL.

The chloramine-T was commercial material which had been recrystallised from water and air-dried; analysis showed it to be the pure trihydrate and all weights recorded for this substance refer to this hydrate. When consistent titrations have been obtained in an analysis, only one value is given; in other cases, multiple values are given to indicate the order of agreement obtainable.

***Oxidation** of Hydrogen Sulphide.*—(1) *With excess of hydrogen sulphide.* A current of the gas, washed with water, was passed through a solution of chloramine-T (10·00 g.) in water (150 c.c.) at 15° until no further reaction was apparent. The precipitated *p*-toluenesulphonamide (5·60 g.), recrystallised from water to remove a trace of sulphur, had m. p. 137°; the original filtrate, treated with barium chloride and hydrochloric acid, gave barium sulphate (1·82 g.). The yields of sulphonamide and barium sulphate are 92·1 and 87·9% of those required by equation (A), calculated on the weight of chloramine-T used.

(2) *With excess of chloramine-*T. (*a*) Potassium iodide–starch as an external indicator. 50 C.c. of a chloramine-T solution containing 11·905 g./l. were titrated with a standard hydrogen sulphide solution containing 1·12 g./l., the indicator being used externally. Only a faint opalescence of sulphur was formed, and at the end-point the only acid component detected in the solution was sulphuric acid. Volume of hydrogen sulphide required = 18·1 c.c. Hence 1 g.-mol. of hydrogen sulphide has been oxidised by 56·8 g. of oxygen. The low result (calc.: 64 g.) is probably due primarily to loss of hydrogen sulphide during manipulation, and to a much smaller extent to the slight formation of elementary sulphur. When, on the other hand, the hydrogen sulphide solution was titrated with the chloramine-T, the loss of hydrogen sulphide was considerable, and erratic end-points made the analysis worthless.

(*b*) Potassium iodide–starch as an internal indicator. 25 C.c. of the hydrogen sulphide solution were placed in a stoppered bottle, a 10% solution of potassium iodide (3 drops) and starch solution (2 c.c.) added, and the mixture titrated with the chloramine-T solution until a faint permanent blue colour was obtained, the bottle being kept stoppered between additions of the chloramine-T. Much sulphur was deposited and only a trace of sulphuric acid was formed. Volume of chloramine-T required = 18·1 c.c. Hence 1 g.-mol. of hydrogen sulphide has been oxidised by 14·8 g. of oxygen (calc. for oxidation to sulphur: 16 g.). Consistent values were obtained only after experience with this titration: earlier experiments gave a series of titration values showing considerable mutual inconsistency.

To determine whether the iodide ion was responsible for this result, the experiment was repeated, but now 3 drops of 10% potassium bromide solution were used instead of the iodide and starch, and the titration was conducted with the iodide–starch indicator used externally. At the end-point, which was very indefinite, the solution contained only traces of sulphur and sulphuric acid, but smelt of bromine. Volume of chloramine-T required = 44·3, 48·1, 44·7, 47·0 c.c.; mean, 46·0 c.c., corresponding to oxidation of 1 g.-mol. of sulphide by 37·6 g. of oxygen. In view of this anomalous result, the products of this reaction would clearly repay further investigation.

Oxidation of Sodium Sulphide.—10 C.c. of a solution of pure sodium sulphide (8·56 g. of Na_2S/l.) were titrated with the chloramine-T solution, potassium iodide–starch being used as an external indicator; the variation in the end-point, although reduced by adding a dilute solution of tartaric acid to the indicator, was considerable. Much sulphur was deposited. Volume of chloramine-T required = 23·0, 24·7, 23·0, 24·2, 24·2 c.c.; mean, 23·8 c.c.; 1 g.-mol. of sodium sulphide therefore requires 14·7 g. of oxygen (calc. for equation B: 16 g.). When the above conditions were reversed, sodium sulphide being added to the chloramine-T, sulphur was again deposited, the excess of chloramine-T apparently not affecting the oxidation.

Oxidation of Sodium Sulphite.—(*a*) 20 C.c. of a sodium sulphite solution (containing 6·02 g. of Na_2SO_3/l.), diluted with a 10% solution of potassium iodide (3 drops) and starch solution (1 c.c.), were titrated with a chloramine-T solution containing 12·71 g./l. Volume of latter required = 20·1 c.c. Therefore, on the basis of equation (C), the sodium sulphite contains 5·73 g./l. (*b*) The titration was now reversed, 20 c.c. of the chloramine-T being titrated with sulphite. Volume of latter required = 18·95 c.c., whence sodium sulphite = 6·01 g./l.

Oxidation of Sodium Thiosulphate.—Initial experiments showed that when the thiosulphate was titrated with chloramine-T, potassium iodide–starch being used as an internal indicator, the end-point was very difficult to detect. When a small excess of acetic acid was added to neutralise the alkali formed, better results were obtained, but the end-point was still reached slowly and was indistinct. The best results were finally obtained thus: 20 c.c. of a solution of sodium thiosulphate, containing 8·21 g. of sodium thiosulphate/l. (by analysis), were titrated with the chloramine-T solution (12·71 g./l.) almost to the end-point; the potassium iodide and starch were then added as in the sulphite estimation, and also tartaric acid (1 g.), and the titration continued, a fairly sharp end-point being now obtained. Volume of chloramine-T solution required = 12·5, 12·55, 12·4 c.c.; mean, 12·5 c.c. Hence 1 mol. of sodium thiosulphate requires 0·54 mol. of chloramine-T, and the reaction is in accordance with equation (D).

Phosphine.—This gas was prepared by the action of dilute sulphuric acid on aluminium phosphide, and was washed by bubbling through cold, freshly boiled, distilled water. It was not spontaneously inflammable and was free from other phosphorus hydrides.

Estimation of Phosphoric Acid.—In the following experiments, it was necessary to estimate phosphoric acid in a solution containing hypophosphorous and phosphorous acids and chloramine-T, and for which, since the solution could be neither boiled nor treated with nitric acid, the usual phosphomolybdate method could not be employed. In the experiments at 28·5° the uranyl acetate method was therefore adopted, sodium salicylate being used as an indicator (Duparc and Rogovine, *Helv. Chim. Acta*, 1928, **11**, 598): a satisfactory end-point could be obtained by titration in the cold, instead of using hot solutions as these authors recommended. The uranyl acetate solution was therefore standardised by titration with a known solution of A.R. disodium hydrogen phosphate, and then used for the phosphate estimation under strictly parallel conditions. The accuracy of the method was proved by the fact that when oxidation was complete in the following experiments, and the total phosphate was then estimated both volumetrically by the uranyl acetate method and gravimetrically by the phosphomolybdate method, almost identical results were obtained. For the experiments at 38·5°, Fiske and Subbarow's colorimetric method of phosphate estimation (*J. Biol. Chem.*, 1925, **66**, 375) was used, its reliability under these conditions having previously been carefully checked.

Oxidation of Phosphine.—(a) *Excess of phosphine.* A stream of phosphine was passed into a solution of chloramine-T (5 g.) in water (100 c.c.) until the solution smelt markedly of phosphine and gave no reaction for unchanged chloramine-T (tested externally with potassium iodide and acetic acid). The white precipitate was collected, washed, and dried, and found to be *p*-toluenesulphonamide. The filtrate contained hypophosphorous and phosphorous acids but only a faint trace of phosphoric acid. The experiment was repeated with an alcoholic solution of chloramine-T; identical results were obtained except that the sulphonamide now remained in solution.

(b) *Excess of chloramine-*T. The phosphine was passed into a solution of chloramine-T (30·0 g.) in freshly boiled, cold, distilled water (500 c.c.) for 15 minutes. The mixture was then filtered, the residual *p*-toluenesulphonamide washed with water, and the united filtrate and washings diluted to 2000 c.c. with water at *ca.* 30° and placed in a thermostat at 28·5°. Samples (100 c.c.) were withdrawn periodically, and the phosphoric acid content determined volumetrically by the uranyl acetate method. Meanwhile, the total phosphorus in one sample was oxidised to phosphoric acid by boiling with nitric acid, and the phosphoric acid then determined gravimetrically as phosphomolybdate. The percentage of total phosphorus converted into phosphoric acid at known intervals was thus calculated (curve I). This phosphate content was 95·8% after 146·5 hours, and 98·5% after 169·0 hours; when oxidation was complete, the total phosphoric acid concentration was 0·975 g./l.

Oxidation of Sodium Hypophosphite.—(a) *Neutral solution.* Solutions of sodium hypophosphite, NaH_2PO_2,H_2O (3·68 g.), and chloramine-T (30·0 g.), each in water (750 c.c.), were mixed and diluted to 2000 c.c., water at the thermostat temperature (28·5°) being used throughout. The solution was at once placed in the thermostat, and the experiment then performed exactly as in (b) above, except that the quantity of sulphonamide separating at this dilution was so small that filtration was unnecessary. Curve II was thus obtained. In this case, the phosphate content was 92·0% after 168·0 hours and 99·8% after 192·0 hours, demonstrating the accuracy of the analytical methods employed. The total phosphoric acid concentration was finally 1·695 g./l.

(b) *Acid solution.* The following solutions were prepared in water at 28·5°: sodium hypophosphite (4·20 g. in 500 c.c.), acetic acid (2·3 c.c., 1 mol., in 20 c.c.), and chloramine-T (30·0 g. in 500 c.c.). The first and second were mixed and then added to the third, and the total volume made up to 2000 c.c. The experiment was precisely similar to the previous one, except that the presence of the acid caused a slight deposition of the sulphonic chloro-amide; this rapidly settled, but the aliquot portions were withdrawn through a filter-plug to avoid unnecessary contamination. Curve III was thus obtained. The phosphate content was now 97·0% after 144 hours and 99·5% after 184 hours, the total phosphoric acid concentration being finally 1·900 g./l.

Oxidation of Sodium Phosphite.—(a) *Neutral solution.* Solutions of disodium phosphite, $Na_2HPO_3,5H_2O$ (3·60 g.), and of chloramine-T (30·00 g.), each in water (500 c.c.) at 28·0°, were mixed, and the solution diluted to 2000 c.c. with water also at 28·0°. The solution was maintained at this temperature, but even after 24 hours only a trace of phosphate had been formed.

(b) *Acid solution.* This experiment was repeated, but the solution of disodium hydrogen phosphite (4·040 g.) in water (500 c.c.) was diluted with acetic acid (2·1 c.c., 2 mols.) before addition of the chloramine-T solution. A small precipitate of the chloro-amide now appeared and was removed by a filter-plug before analysis as in the oxidation of sodium hypophosphite (b). After 0·5 hour, the concentration of phosphate (calculated as phosphoric acid) was 0·799 g./l., representing an 84·4% conversion of total phosphorus into phosphate, and after 1·0 hour the concentration was 0·943 g./l., representing a 99·6% conversion. No further increase occurred. The total phosphate concentration (after oxidation with nitric acid) was 0·947 g./l.

Arsine.—The gas was prepared by the action of dilute sulphuric acid on aluminium arsenide, and washed with cold, freshly boiled, distilled water.

Estimation of Arsenate with Uranyl Acetate Solution.—It was found that arsenates in solution could be determined by precisely the same method as that adopted for phosphates. To test the accuracy of this method, 50 c.c. of a standard solution of arsenic acid were diluted with water (50 c.c.) and with a 10% sodium salicylate solution (10 c.c.), and then titrated in the cold with a solution of uranyl acetate (*ca.* 12·2 g./l.) until a permanent faint pink colour remained after 30 seconds' vigorous shaking. It was thus found that 100 c.c. of the acetate solution $\equiv$ 0·440 g. of H_3AsO_4. An arsenic acid solution of unknown strength was then titrated with the uranyl acetate solution under precisely similar conditions. Volume of uranyl acetate solution required for 50 c.c. of the arsenic acid solution = 25·1 c.c. Therefore concentration of this arsenic acid solution = 2·20 g./l. This solution was then standardised by diluting aliquot portions with a large excess of concentrated hydrochloric acid, followed by an excess of 10% potassium iodide solution, the liberated iodine being titrated with standard sodium thiosulphate solution. The arsenic acid solution was thus found to contain 2·25 g./l.

*Estimation of Total Arsenic in a Solution containing Arsenious and Arsenic Acids, Chloramine-*T, *and Sodium Chloride.*—Some of the solutions in the following experiments contained comparatively large quantities of chloramine-T, the greater part of which it was considered desirable to remove before estimating the arsenic. Concentrated nitric acid was therefore added to the chilled solution to precipitate *p*-toluenesulphonchloroamide, $C_6H_4Me\cdot SO_2\cdot NHCl$, and the solution was then filtered and the residual chloro-amide washed repeatedly with cold water. The united filtrate and washings were further acidified and then treated with an excess of 2% aqueous silver nitrate solution. The solution was again filtered and the silver chloride washed as before on the filter. The filtrate was then treated with a slight excess of sodium acetate in order to precipitate silver arsenite and arsenate. The latter were collected, washed repeatedly with water, dissolved in the minimum quantity of 50% nitric acid, and the silver then estimated by Volhard's method. In the above circumstances, it is probable that the nitric acid would oxidise much of the arsenious to arsenic acid : in any case, however, both acids would be precipitated as their trisilver ortho-salts, and total arsenic can be calculated as arsenate on the basis that $3Ag \equiv H_3AsO_4$.

Oxidation of Arsine.—(a) *Excess of arsine.* Arsine was passed into a cold solution of chloramine-T (4·00 g.) in water (200 c.c.) until all reaction was complete (*ca.* 50 mins.) and the solution had a marked odour of arsine; the surface of the solution finally developed a trace of elementary arsine owing presumably to atmospheric oxidation. After standing in a closed vessel for 20 mins., the solution was filtered to remove sulphonamide, the latter washed, and the filtrate diluted to 500 c.c. Analysis of aliquot portions by the above methods showed that the filtrate contained 0·497 g. of free arsenic acid, and total arsenic present was equivalent to 0·504 g. of arsenic acid. Theoretical yield of arsenic acid from the chloramine-T ≡ 0·500 g.

(b) *Excess of chloramine-*T. Arsine was passed into a solution of chloramine-T (30·0 g.) in water (400 c.c.) at 20° for 25 mins. Precipitated sulphonamide was removed, and the filtrate diluted to 1 l. with water at 28·5° and placed in a thermostat at this temperature. After 1 hour the free arsenic acid present was 0·502 g. and after 1·5 hours 0·520 g.; the total arsenic present was found to equal 0·520 g. of arsenic acid. The value after 1 hour corresponds to a 96·5% conversion of total arsenic into arsenic acid.

Oxidation of Arsenious Acid.—(a) Solutions of A.R. arsenious oxide (2·450 g.) and of chloramine-T (7·5 g.) in water (500 and 200 c.c.), each at 28·5°, were mixed, and the total volume made up to 1 l. with water at 28·5°. Within 5 mins. of mixing, the solution contained 3·52 g. of free arsenic acid, determined by the uranyl acetate method. Since the arsenious oxide should have given 3·516 g. of arsenic acid, complete oxidation had occurred in this period. It is possible that the oxidation is even more rapid, but the method did not allow of more rapid determinations.

(b) To use this oxidation analytically, 50 c.c. of a solution containing 1·520 g./l. of A.R. arsenious oxide were heated on a water-bath for 5 mins. and then titrated with a solution containing 11·900 g./l. of chloramine-T, the end-point being determined externally with potassium iodide–starch paper. Volume of chloramine-T solution required = 18·0 c.c. Hence the original solution contained 1·51 g./l. of arsenious oxide.

Oxidation of Colloidal Arsenic.—The arsine, prepared and washed as above, was passed into cold distilled water containing dissolved air until a marked formation of brown " colloidal " arsenic had occurred. The addition of a 10% solution of chloramine-T, followed by shaking, gave immediately a colourless, transparent solution.

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