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ference of other elements was made as follows: A mixture was made containing 100 mg. each of the elements, except cadmium, ordinarily tested for in elementary qualitative analysis. The solution was made ammoniacal, just acidified with sulfuric acid, treated with 15 grams of powdered nickel, boiled for 5 minutes, and filtered. The filtrate was made 2N in acetic acid and tested with hydrogen sulfide. A negative test was obtained. With the same amounts of each element mentioned above, and 2 mg. of cadmium, similar treatment gave a distinctly yellow precipitate of cadmium sulfide.

Discussion of Method

By the procedure outlined above, an appreciable amount of cadmium is retained mechanically in the residue of nickel and elements precipitated by nickel. However, as shown by the tests, even though a small amount of cadmium is present initially, enough will be left in the filtrate to give a distinct yellow precipitate with hydrogen sulfide. In this laboratory, the above test for cadmium has been found much more satisfactory in student hands than either of the two standard methods mentioned.

The amount of nickel needed and the time of heating required are determined by the amounts of materials to be removed and the size of the nickel particles. In the experiments described, the nickel powder was 100 mesh or finer.

Lead is the only element listed which is not readily removed with nickel powder and which precipitates along with cadmium in hydrogen sulfide solution 2 N in acetic acid. To insure ready removal of lead from solution, excess sulfate is used. This works satisfactorily, if no acetate is present.

Quantitative Determination of Phosgene¹

J. C. Olsen, George E. Ferguson, Victor J. Sabetta, and Leopold Scheflan

I N CONNECTION with an investigation of the thermal decomposition products of chlorinated hydrocarbons such as carbon tetrachloride, chloroform, etc., it became necessary to determine phosgene in the presence of chlorine, hydrochloric acid, and the chlorinated hydrocarbons originally present, as well as those formed by their thermal decomposition. Several similar investigations had THE POLYTECHNIC INSTITUTE, BROOKLYN, N. Y.

It has been definitely shown that the alcoholic caustic soda method cannot be used to determine phosgene in the thermal decomposition products of carbon tetrachloride mixtures or in samples of phosgene containing other chlorine compounds.

The modified aniline and the sodium iodide-acetone methods have been found to give concordant determinations of phosgene, and are therefore believed to be accurate and trustworthy. Amounts as small as 0.1 mg. may be determined by the acetone method in concentrations of one part per million of air.

The silver nitrate method is not so suitable as either of the preceding methods on account of reduction of the silver nitrate by some of the decomposition products.

been carried out and the results published (1, 2, 3, 4). Various methods of analyzing the gases produced had been employed, in some cases after careful study of the methods available. It soon developed in the present investigation that the methods used in other investigations for the determination of phosgene did not give concordant results. Attempts were made to improve the existing methods with some success.

Previous Methods

The methods which had been used were as follows:

(1) Absorption of the phosgene in alcoholic caustic soda and titration of the excess alkali or determination of the chlorine by some appropriate method. The following reaction takes place:

$2NaOH + COCl_2 = 2NaCl + CO_2 + H_2O$

It is obvious that chlorine and hydrochloric acid must be absent. (2) Absorption of the phosgene in silver nitrate solution to which ammonia has been added in excess of that required to dissolve the precipitate first formed. With this reagent the phosgene decomposes, forming a soluble silver ammonium chloride. On acidifying with nitric acid, the silver chloride is precipitated and may be filtered off and weighed, or the excess silver may be determined by titration. Both chlorine and hydrochloric acid must be absent.

(3) Absorption of the phosgene in a saturated water solution of aniline. Such a solution contains about 26 grams of aniline

¹Received December 12, 1930. Presented before the Division of Physical and Inorganic Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930. per liter of water. In this reaction, diphenylurea is formed, when excess of aniline is present, according to the following equation:

 $4C_6H_5NH_2 + COCl_2 = CO-(NHC_6H_5)_2 + 2C_6H_6NH_2HC1$ The diphenylurea is only slightly soluble in water as well as in water saturated with aniline and may be filtered off, washed with cold water, dried at 70° to 80° C., and weighed. This reaction is obviously characteristic of phosgene and would not be brought about by other substances. Hydrochloric acid would interfere

only by converting the free aniline into hydrochloride or other compounds. Chlorine would interfere by its oxidizing action upon aniline, producing insoluble compounds.

(4) A method studied and recently published by the German Chemisch-technischen Reichsanstalt consisted in passing the phosgene through a 2 per cent solution of sodium iodide in acetone, and titrating the liberated iodine with standard sodium thiosulfate solution. The following reaction takes place:

$2NaI + COCl_2 = 2NaCl + I_2 + CO$

This reaction is quantitative in the absence of water, according to the German Reichsanstalt. Chlorine or any substance capable of liberating iodine from sodium iodide would interfere with the accuracy of this method.

Chlorine may be removed by means of antimony trisulfide or mercuric sulfide, free sulfur and the metallic chlorides being formed. If hydrochloric acid were present, it would react with the antimony sulfide, forming hydrogen sulfide which would react with the iodine liberated in the sodium iodide-acetone solution by the phosgene. Hydrochloric acid has no action upon mercuric sulfide. Hydrochloric acid may be removed by means of zinc dust.

When using the sodium iodide-acetone method for phosgene, all absorbents for chlorine and hydrochloric acid must be free from moisture, which would decompose phosgene. This is accomplished by drying at 110° C. The sodium iodide-acetone solution must also be protected against daylight, which liberates chlorine.

When carbon tetrachloride is decomposed by heat, chlo-

rine, hydrochloric acid, phosgene, and various chlorinated hydrocarbons are formed in varying proportions depending upon the conditions present. The following typical reactions are listed in the report of the German Reichsanstalt:

$2\mathrm{CCl}_4 = \mathrm{C}_2\mathrm{Cl}_6 + \mathrm{Cl}_2$	(1)
$2CCl_4 = C_2Cl_4 + 2Cl_2$	(2)
$CCl_4 + H_2O = COCl_2 + 2HCl$	(3)
$\mathrm{CCl}_4 + 2\mathrm{H}_2\mathrm{O} = \mathrm{CO}_2 + 4\mathrm{HCl}$	(4)
$2CCl_4 + O_2 = 2COCl_2 + 2Cl_2$	(5)
$\mathrm{CCl}_4 + \mathrm{O}_2 = \mathrm{CO}_2 + 2\mathrm{Cl}_2$	(6)
$\mathrm{CCl}_4 + \mathrm{CO}_2 = 2\mathrm{COCl}_2$	(7)
$3\mathrm{CCl}_4 + \mathrm{Fe}_2\mathrm{O}_3 = 3\mathrm{COCl}_2 + 2\mathrm{Fe}\mathrm{Cl}_3$	(8)

The decomposition products are, therefore, chlorine, hydrochloric acid, phosgene, carbon dioxide, and chlorinated hydrocarbons. Any attempt to determine the gases chlorine, hydrochloric acid, and phosgene, must also take into account the chlorinated hydrocarbons which are formed during the decomposition of the carbon tetrachloride, or are present in the original fire-extinguishing liquid. Some of these compounds are present in fire-extinguishing liquids such as Pyrene.

Gravimetric and Alcoholic Caustic Soda Methods Discarded

The results of a very extensive investigation of the products obtained by the thermal decomposition of carbon tetrachloride and fire-extinguishing liquids consisting largely of carbon tetrachloride were published in an article by A. C. Fieldner, S. H. Katz, S. P. Kinney, and E. S. Longfellow in October, 1920 (2).

These investigators determined the phosgene by passing the gas through a train of reagents containing: (a) silver nitrate on granular pumice for removing hydrogen chloride; (b) powdered antimony trisulfide for removing chlorine; and (c) sodium hydroxide solution in 85 per cent alcohol for the absorption of phosgene, which hydrolyzed to produce sodium chloride.

In the present investigation this method of determining phosgene was compared with the determination by means of aniline and the sodium iodide-acetone method. The phosgene was prepared by the decomposition of carbon tetrachloride, carbon tetrachloride + 10 per cent chloroform, as well as fire-extinguishing liquids consisting mainly of carbon tetrachloride.

The results obtained by absorption in the alcoholic caustic soda solution were found to be much higher than by the aniline and the acetone-iodide method. The determination was carried out both by titrating the chlorine by means of silver nitrate, using potassium chromate as the indicator, and by precipitating and weighing the silver chloride. The results by the titration method were frequently higher than those obtained by weighing the silver chloride. In carrying out the titration, the caustic soda was first acidified by means of nitric acid and then neutralized by the addition of sodium bicarbonate, but the alcohol was not expelled. Difficulty was experienced in titration on account of reduction of the silver nitrate.

Believing that the reduction was caused by the alcohol present, the solution was evaporated nearly to dryness after neutralization with nitric acid and sodium bicarbonate, both for the titration and weighing the silver chloride. The titration results continued to be high, and, in fact, were high even when the silver chloride was filtered off and weighed from the same solution which had been titrated.

In a further study of this method, it was found that the alcoholic caustic soda solution through which the carbon tetrachloride had been passed turned dark brown on standing overnight, clearly indicating decomposition of the carbon tetrachloride. A silver mirror was also formed on heating the solution. When the solution which had been acidified with nitric acid and evaporated to expel the alcohol was neutralized and treated with silver nitrate, a yellow precipitate was formed which dissolved in nitric acid leaving white silver chloride. The silver chloride is undoubtedly formed from the hydrolysis of carbon tetrachloride, which is soluble in the alcoholic caustic soda solution. The dark color which develops on standing would indicate that other decomposition products are also formed.

Several experiments were then carried out in which the carbon tetrachloride was volatilized and passed through the alcoholic caustic soda solution without heating. Under these conditions no phosgene could be present. In these experiments considerable quantities of chlorides were found by titration and weighing silver chloride.

These reactions are believed to account for the high values obtained by titration as compared with the gravimetric determination of silver chloride.

The gravimetric method, when used to determine phosgene produced by the thermal decomposition of carbon tetrachloride and similar compounds, would give high results on account of the hydrolysis of carbon tetrachloride and other chlorinated hydrocarbons.

As this method was used by Fieldner and his associates, this source of error must have given high results in their experiments.

The alcoholic caustic soda method has been very largely used to determine phosgene when diluted with air alone. Our experiments indicate that phosgene is frequently accompanied by chlorine compounds other than phosgene which tend to give high results for phosgene when this method is used.

Experiments Using Acetone and Aniline Methods

A great many determinations of phosgene by means of the acetone and aniline methods gave quite uniformly higher results by the acetone than by the aniline method. The aniline method, being a gravimetric method, would be influenced by the solubility of the precipitated diphenylurea. This compound was known to be slightly soluble in water. A determination of its solubility in the saturated aniline water used gave 5.5 mg. diphenylurea in 100 cc. of saturated aniline solution.

In order to overcome this error, the aniline water used was saturated with diphenylurea by passing phosgene into the solution until a small amount of precipitate was formed which was filtered off, the clear filtrate being used for the phosgene determinations. Using 75 cc. of the aniline solution, the solution saturated with diphenylurea gave, in four determinations, 4.6, 7.5, 3.4, and 3.5 mg. of phosgene more than was obtained from the aniline solution unsaturated with the precipitate. When saturating the aniline solution by passing phosgene, evidence of the solubility of the precipitate could readily be observed by noting the amount of gas passed in before a permanent precipitate was obtained. A similar observation was often made in making comparative tests for phosgene with the acetone-iodide method.

The use of the aniline solution saturated with diphenylurea undoubtedly gives more accurate quantitative results and makes this method more delicate, so that lower concentrations of phosgene may be detected and determined.

Tests were also carried out to ascertain the optimum time necessary for complete precipitation of the diphenylurea. The aniline solution containing the precipitate was allowed to stand 2 hours before filtering, duplicate determinations being allowed to stand overnight. The solution which stood for 2 hours gave higher results than the one standing overnight, the differences being 1.5 and 2.2 mg. The diphenylurea evidently is slowly decomposed.

The precipitate is filtered on a Gooch crucible, washed with a small amount of the filtrate, and dried at 70° to 80° C. Precipitates dried to constant weight at this temperature lost weight when heated to 100° C. Instead of washing with cold water, it was found equally satisfactory to volatilize the excess aniline by means of sucking air through the Gooch.

The acetone method in a great many determinations gave results considerably higher than the aniline method. By drying the gases with calcium chloride, results of much better agreement were obtained. In a series of about twenty determinations in which the acetone method was compared with the aniline method using the saturated aniline solution, differences of only a few milligrams of phosgene were obtained between the two methods, the acetone method generally giving the higher result. The acetone method gives indication of very small amounts of phosgene by the reddish yellow color of the liberated iodine. Fiftieth or one hundredth normal sodium thiosulfate solution was used to titrate these small amounts of iodine. The usual starch indicator cannot be used in the acetone solution, but the color of the iodine affords a fairly sharp end point. The yellow color returns slowly on standing.

When the aniline solution saturated with diphenylurea was used, traces of phosgene could be detected by the appearance of a slight turbidity. The filtration and weighing of such slight precipitates could not be carried out as accurately as the titration of the iodine in the acetone solution.

Silver Nitrate Method Discarded

A number of determinations of phosgene were made which indicated that the silver nitrate method gave results very close to the true value. In using this method, the silver chloride was precipitated and weighed. Titration of the excess of silver was not found to be feasible because a considerable amount of silver was reduced, presumably by unsaturated hydrocarbons present in the gas mixture.

Accuracy of Methods Tested and Modification Adopted

The attempt was made to check the accuracy of these methods by using known amounts of pure phosgene. A sample of the purest liquid phosgene available at Edgewood Arsenal was obtained for this purpose. A steel cylinder was used as the container. By connecting the cylinder to a gas buret filled with dry clean mercury, it was found possible to transfer to the buret any desired amount of phosgene. As the boiling point of pure phosgene at atmospheric pressure is 8.3° C., the liquid readily volatilized at room tempera-ture and passed into the buret. The gas is sufficiently stable to give constant volumetric readings over mercury. After reading the volume and noting the temperature and pressure, the gas was usually diluted to 100 cc. with dry air. Care was taken in making the readings of the phosgene to wait until the reading was constant. No difficulty was experienced in this respect, and no change was noted in the volume of the gas before dilution with air.

The volume of gas obtained in this manner was passed through the absorbing solution, any remaining phosgene in the buret and tubes being swept out by means of air.

The results obtained in this manner were low when calculated on the assumption that the gas obtained was pure. As the experiments progressed, the differences became greater. This seemed to indicate that some decomposition was taking place in the phosgene. Experiments in which the phosgene was absorbed showed that there was some gas which was not taken up by water saturated with aniline. The cylinder containing the phosgene was then connected with a manometer and the temperature of the phosgene cylinder reduced to the boiling point of phosgene—namely, 8.3° C. At this temperature, the pressure in the cylinder was some 14 inches (35.56 cm.) higher than atmospheric pressure. The cylinder was then placed in a refrigerator, cooled very much below the boiling point, and again placed in a bath of cold water until the temperature seemed to be constant at 8.3° C. The pressure reading was even then very high.

Under these conditions it did not seem possible that the gas obtained from this cylinder was pure phosgene gas.

In a further attempt to check the method of analysis for the pure phosgene, a sample of phosgene dissolved in toluene was obtained. Samples of gas were drawn from this flask in a manner similar to that used with the cylinder of liquid phosgene, except that the flask was placed in water warmed to 35° to 40° C. The following results were obtained from this gas:

ACETONE METHOD	ANILINE METHOD
35.25 35.10	35.99 35.78
Av. 35.18	Av. 35.88

These results show very excellent checks with the two methods, with a slightly higher result with the aniline method.

A second sample of phosgene dissolved in toluene was obtained and tested. A considerable number of determinations of the gas obtained from this sample were made by the acetone, aniline, and alcoholic caustic method, the average of all the results obtained being as follows: acetone, 36.72 per cent; aniline, 36.68 per cent; caustic soda, 58.92 per cent. Two absorption bottles were used with each reagent, only traces being found in every case in the second absorption liquid. This indicates that all three reagents are very efficient absorbents of phosgene.

In the endeavor to ascertain why such high results were obtained with the caustic soda reagent, absorption trains were arranged with aniline water followed by the soda reagent, and another train with the acetone reagent followed by the soda reagent. In both cases considerable amounts of chlorine were found in the soda reagent. This shows that there are chlorine compounds in the phosgene being tested which are not phosgene. This accounts for the high results obtained with the soda reagent.

This conclusion was further confirmed by a determination of the chlorine present in the filtrate from the diphenylurea. This was found to be higher than the amount of chlorine corresponding to the phosgene present as shown by the weight of diphenylurea. In two determinations the amount was 8.48 and 7.96 per cent after deducting the result of the blank determination.

The gas obtained from phosgene dissolved in toluene is therefore not pure phosgene but contains other chlorine compounds. The close agreement of the results obtained by two such dissimilar methods as aniline and acetone solution of sodium iodide would indicate that these reagents give the true percentage of phosgene.

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