Summary

1. Sulfite cannot be determined with bromate, dichromate or permanganate alone, since they do not oxidize it completely to sulfate.

2. Sulfite may be determined accurately by titration with iodate alone or with bromate, permanganate or dichromate, by the addition to those oxidants of half their equivalent (or, in the case of bromate, even one-sixth of an equivalent) of iodide. It may also be determined with free bromine.

3. All titrations in the experiments recorded here were carried out in a vacuum flask of Pyrex glass to avoid action of air or escape of sulfur dioxide or halogens. Such a flask is to be recommended in work involving possible disturbance of a reaction by air or loss of gases.

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

AN ATTEMPT TO PREPARE NITRO-NITROGEN TRICHLORIDE

III. FAILURE TO OBTAIN A COMPOUND CONTAINING ONLY NITROGEN AND CHLORINE FROM OXIDES OF NITROGEN

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In 1913[1] an account was given of experiments which seemed to indicate the possibility of a chloride of nitrogen in which the chlorine is in the negative form, or tends to separate from the nitrogen in the negative form, in contrast with ordinary nitrogen trichloride, from which, in its normal reactions, the chlorine separates in the positive form. In 1921[2] it was reported that no conditions had been found under which a compound of nitrogen and chlorine could be obtained by passing the gases through an electric arc.

Since 1913 a considerable number and variety of experiments have been tried in the endeavor to replace the oxygen of oxides of nitrogen by chlorine. Ninety-two such experiments and 176 analyses of mixed gases have failed to show, conclusively, the formation of any chloride of nitrogen which does not contain oxygen. Nitrosyl chloride, from which the chlorine separates easily in the negative form, was obtained in many of the experiments and, at times, there seemed to be some evidence of the formation of a nitrogen dichloride, NCl_2. It seems difficult to understand why such a compound, corresponding to nitric oxide, NO, should not be formed, but the conclusion was finally forced upon me that when nitrogen and oxygen atoms separate the nitrogen atom has a greater affinity for another nitrogen atom than it has for chlorine. Apparently only nitrogen in the form of

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[1] Noyes, THIS JOURNAL, **35**, 767 (1913).

[2] Noyes, *ibid.*, **43**, 1774 (1921).

ammonia or of one of its derivatives can be induced to add chlorine and split off hydrochloric acid, leaving the chlorine combined with the nitrogen.[3]

The experiments which were most conclusive in support of this belief were suggested by the work of Geuther and Michaelis,[4] who report that phosphorus oxychloride, $POCl_3$, pyrophosphoryl chloride, $P_2O_3Cl_4$, nitrosyl chloride, NOCl, nitric oxide, NO, and nitrogen are formed when nitrous anhydride or nitrogen dioxide acts on phosphorus trichloride at a low temperature. The pyrophosphoryl chloride contains two atoms of chlorine less than the two molecules of phosphorus trichloride from which it is formed and it would seem natural that this chlorine should combine with the nitrogen atoms from which the oxygen has been removed. Instead of doing this, the chlorine combines with nitric oxide to form nitrosyl chloride and the nitrogen combines with another molecule of nitric oxide to form nitrous oxide, $N{\equiv}N{=}O$, a product which was overlooked by Geuther and Michaelis.

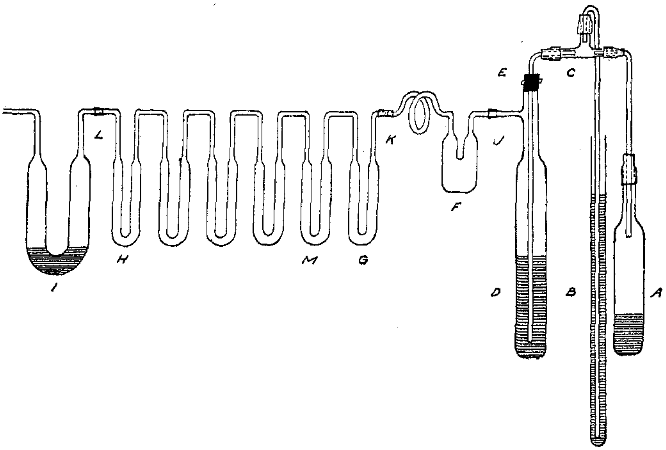

Fig. 1.—Apparatus.

The action of phosphorus trichloride on nitrous anhydride was carried out with the apparatus shown in Fig. 1. About 20 to 30 g. of the liquid anhydride, prepared by warming a mixture of arsenic trioxide with nitric acid, dried by passing the gas through a bulb surrounded with ice, through a calcium chloride tube, and finally passing nitric oxide through the liquefied gases, was allowed to evaporate slowly in the bulb A and conducted into the phosphorus trichloride contained in the tube D. Before introducing the gas, the air in the system was expelled by passing a mixture of nitric oxide and nitrogen through the U-tube I containing concd. sulfuric acid. This mixture was prepared by introducing nitric oxide in excess into a glass gasometer containing air and allowing the nitrogen dioxide to be absorbed by

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[3] Noyes, This Journal, 42, 2173 (1920).

[4] Geuther and Michaelis, *Ber.*, **4**, 766 (1871).

the water in the gasometer. The presence of the nitric oxide made it easy to see when the air was expelled from the system. The phosphorus trichloride was cooled to —18° by a freezing mixture in some experiments and to —70–80° by a mixture of carbon dioxide snow and alcohol in others. The tube B, containing water, furnished an indication of any stoppage caused by the freezing of gases condensed in F or G. The U-tube I was left connected with the gasometer containing nitric oxide and nitrogen. The connections with A and with the T-tube C were made by glass tubes fitting rather closely inside of the larger tubes and passing for a number of centimeters into the latter. In this way the rubber tubes used to secure the joints came very little into contact with the oxides of nitrogen or nitrosyl chloride, which attack rubber very vigorously. There were ground-glass joints at J, K and L. The spiral between K and F was to give some flexibility to the complex apparatus. The cork stopper at E was protected by a thin film of vaseline. After expelling the air and making all the connections, F and then G were immersed in liquid air. By immersing only the lower part of F nearly all of the condensable gases evolved were condensed there without stopping up the tubes through freezing of condensed gases in the narrower tubes at the top. As the interaction of the nitrous anhydride and phosphorus trichloride continued, a mixture of nitric oxide, nitrous oxide, nitrosyl chloride and hydrochloric acid condensed in F. The hydrochloric acid was due to the fact that moisture was not quite rigidly excluded. In some cases hydrochloric acid was passed into the phosphorus trichloride before beginning the experiment, as it was thought that this might favor the formation of the compound sought. Some vapors of phosphorus trichloride were also carried over into F and both there and in D a part of the nitrosyl chloride reacted with the phosphorus trichloride giving nitric oxide and phosphorus pentachloride—a reaction which has not, so far as I know, been reported by other observers. The amount of nitrogen formed seemed to be very small, as was indicated by the very slow passage of uncondensed gas through the U-tube I.

When the nitrous anhydride had disappeared from A, the freezing mixture was removed from D, and phosphorus trichloride and the reaction products were allowed to come to the temperature of the room and were finally heated until the nitrosyl chloride had been expelled. The apparatus was then disconnected at J and a cap placed on the end of F. The liquid air surrounding G was replaced by a Dewar cylinder containing alcohol cooled to about —100°, the liquid air was also lowered, or removed from F and a cylinder of liquid air placed under M. Three cylindrical bulbs, each with a capacity of about 70 cc. and previously weighed with a sealed counterpoise of the same volume, were introduced between H and I with rubber connections. The air in these bulbs was displaced with the dried mixture of nitric oxide and nitrogen before the connection was made with H. By holding the cylinder containing liquid air under M in such a manner that a small amount of the purple compound of nitric oxide and hydrochloric acid[5] remained, the temperature of M was kept at approximately —140°. In some experiments it was demonstrated that the nitric oxide passing on under these conditions retains only a trace of any compound of chlorine which can be hydrolyzed by water.

The cylindrical bulbs referred to were removed, successively, and after they had been filled with the gases condensed at different temperatures their tips were sealed. A variety of methods were used for the analysis of the gases. The following process, employed for the later analyses, is considered most satisfactory.

The empty bulb was weighed, before filling, with a sealed counterpoise of approximately the same volume. The temperature and pressure were noted at the time of filling, the reading of the barometer being corrected for the temperature. After weighing, the bulb was immersed in ice water and the tip broken off within a rubber tube containing distilled water and with its end dipping into a beaker containing ice water. The bulb was then connected with a gas buret containing oxygen. The oxygen entering converted the nitric oxide in the bulb to oxides of nitrogen, which were absorbed as a mixture of nitric and nitrous acids. After weighing the bulb, the solution was rinsed into a 100cc. flask and the total acid, the nitrogen in the form of nitric and nitrous acids and the chlorine were determined in aliquot portions. The nitrogen was determined by warming the solution with sodium hydroxide and Devarda's alloy, the chlorine was weighed as silver chloride and the acid titrated. After rinsing out the solution, the bulb was filled with water and weighed to find its volume and by subtracting the weight of the solution, as found above, the volume of the unabsorbed gas was also known and the number of milligram moles of the original gas and of the gas not absorbed by the water were easily calculated. The analyses gave the milligram atoms of nitrogen and of chlorine and the sum of these was nearly the same as the milligram moles of acid found by titration, giving a check on the results. The weight of the mixture of gases, calculated by adding the weight of air in the empty bulb to the difference between the weights of the bulb filled with air and filled with the gases, gave a further check or, in some cases, helped to determine the composition of complex mixtures. In a few cases mixtures of nitric oxide and nitrogen were analyzed by absorbing the nitric oxide in a solution of potassium permanganate.

In a last experiment nitrous anhydride was allowed to evaporate slowly, at intervals during 60 hours, into phosphorus trichloride kept at —78.5° by a mixture of carbon-dioxide snow and alcohol. The anhydride as it condensed gave a blue or green color to the trichloride and reacted with the

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[5] Rodebush and Yntema, THIS JOURNAL, **45**, 332 (1923).

latter very slowly. When the anhydride was allowed to accumulate, however, enough heat was soon generated so that the reaction became uncontrollable, or even explosive. The gas which passed on from the solution was a mixture of nitric oxide and nitrous oxide containing about 1% of nitrosyl chloride (Analysis III). Comparatively little nitrosyl chloride was formed in this experiment and an examination of the residue through which the gases had been passed showed that it consisted almost entirely of unchanged phosphorus trichloride and phosphorus oxychloride. Very little pyrophosphoryl chloride was found. When the reaction occurs at —18° to 0° about 10% of the trichloride is converted to the pyrophosphoryl chloride, as was reported by Geuther and Michaelis. The impression was gained that gases containing a relatively high percentage of nitrogen dioxide gave more of the pyrophosphoryl chloride than those having more nearly the composition of nitrous anhydride, but this was not demonstrated.

The following selected analyses illustrate the composition of mixtures obtained in various ways. By no means were all analyses as satisfactory as these but, taken in connection with the temperatures at which different mixtures were condensed, they have shown that no appreciable quantity of any compound could be collected other than nitric oxide, —142°, nitrous oxide, —90°, hydrochloric acid, —83°, chlorine, —33.6° and nitrosyl chloride, —5.6°.

Table I

Analyses of Mixtures of Gases

	I	II	III	IV	V	VI	VII
N_2	1.11	..	0.69	..	..	..	..
NO	1.75	..	1.77	1.84	0.22	..	..
N_2O	..	1.84	0.40	0.89	1.00	..	..
HCl	..	0.65	..	..	1.55	1.80	..
NOCl	..	.28	.04	.14	0.10	0.81	2.92
Total mg. moles	2.86	2.77	2.90	2.87	2.87	2.61	2.92
Wt. found	0.0846	0.1228	0.0927	0.1020	0.1121	0.1195	0.1917
Wt. calcd.	.0836	.1230	.0926	.1036	.1137	.1188	.1913

Following is a brief summary of the various experiments tried during the past twelve years.

Nitric oxide and phosphorus trichloride at ordinary temperatures.

Nitric oxide and hydrochloric acid under a pressure of 30 to 50 atmospheres, with or without various catalysts and with calcium chloride or phosphorus pentachloride, for periods from a few days to 20 months; nitric oxide and hydrochloric acid passed slowly through a bulb containing phosphorus pentachloride heated to 140° or 160°.

Nitric oxide with sulfur and chlorine; with aluminum chloride; with ferric chloride and phosphorus pentachloride; with phosphorus trichloride and iron, magnetic oxide of iron or aluminum oxide.

Nitrous anhydride, or nitrogen dioxide, or mixtures of the two, with phosphorus trichloride at —78°, —18° and at ordinary temperatures.

Nitrosyl chloride with phosphorus trichloride, arsenic trichloride, aluminum chloride, sulfur and phosphorus pentachloride, arsenious oxide and oxalyl chloride.

Sodium nitrite with arsenic chloride, sulfur tetrachloride, phosphorus trichloride, aluminum chloride and with phosphorus trichloride and aluminum chloride.

Nitrosyl chloride was formed in nearly all experiments but it seems to be impossible to replace the oxygen of the nitrosyl chloride with chlorine. This is in marked contrast with the ease with which the hydrogen of ammonia may be replaced by chlorine.

We may find a qualitative suggestion of the reason for this result in Table II of the heats of formation in calories of some compounds of chlorine and of oxygen.

TABLE II

HEATS OF FORMATION

	NCl_3	NO	NOCl	2 PCl_5	P_2O_5	2 NaCl	Na_2O
Cal.	−55,000	−20,850	−16,010	210,000	370,000	195,000	100,000

Nitrogen trichloride, in which the chlorine is potentially positive, is formed with the absorption of a large quantity of heat. The heat absorbed in the formation of nitric oxide is much less, and nitric oxide and chlorine combine with an evolution of heat to form nitrosyl chloride, in which the chlorine is potentially negative. The heat of formation of sodium chloride, in which the chlorine is strongly negative, is nearly twice that of the formation of sodium oxide. For phosphorus pentachloride and phosphorus pentoxide the relations are reversed and are somewhat parallel to those for nitrogen trichloride and nitric oxide. It seems clear that more heat is evolved in the formation of compounds in which the chlorine is potentially negative than in the formation of those in which it is potentially positive or more neutral. It is useless to speculate, at present, about the reasons for such facts as these and we cannot hope for much advance toward an answer to the questions raised until some satisfactory knowledge is acquired about the mechanism by which electrons unite atoms into compounds and by which the energy evolved in the combination of atoms is produced. We should not close our eyes to the fact that our ignorance on these two subjects is profound.

Summary

No method has been found by which it is possible to prepare a compound containing only nitrogen and chlorine from nitric oxide, nitrous anhydride, nitrogen dioxide, nitrosyl chloride or sodium nitrite.

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