

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

REDISCOVERY OF NITRYL CHLORIDE

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In the study of the reaction between nitrogen trichloride and nitrogen tetroxide described in the preceding paper, nitryl chloride, NO_2Cl was discovered as one of the products of the reaction. An examination of the literature showed that Richard Müller described a preparation of the compound by the action of hydrochloric acid on nitrogen tetroxide.¹ Hassenberg prepared it by passing nitrogen dioxide mixed with an excess of chlorine through a hot tube.² Odet and Vignon prepared it by passing the vapor of phosphorus oxychloride over lead or silver nitrate.³ Exner⁴ prepared the compound by the method of Hassenberg and also by that of Odet and Vignon and tried experiments which indicated that he actually had the compound in his hands.

W. Collingwood Williams,⁵ and Gutbier and Lohman,⁶ repeated the experiment of Hassenberg, but failed to get any satisfactory evidence of the formation of nitryl chloride. Geuther⁷ also tried, unsuccessfully, to obtain the compound by dropping cooled nitrogen tetroxide on cool phosphorus pentachloride. After these futile attempts, chemists generally believed that the earlier workers had been in error and the compound was omitted from textbooks and handbooks.

After discovering that the compound is formed by the interaction of nitrogen trichloride and nitrogen tetroxide, an examination of the articles cited led to the conclusion that some of the earlier workers were more careful than their critics. Especially, no one seems to have repeated the experiments of Müller, and Williams used temperatures too low and too high for a successful result.

Müller gives the equation



The first experiments by his method seemed to give only very small quantities of nitryl chloride but finally a gas was obtained which gave the following results: gas, 2.61 mg. mol.; N, 2.87 mg. at.; Cl, 1.89 mg. at.; O, 4.54 mg. at. These results give four simultaneous equations from

¹ Richard Müller, *Ann.*, **122**, 1 (1862).

² Hassenberg, *J. prakt. Chem.*, [2] **4**, 11 (1871).

³ Odet and Vignon, *Compt. rend.*, **70**, 96 (1870).

⁴ Exner, *Wien. akad. Ber.*, **65**, 11, 120 (1872).

⁵ Williams, *J. Chem. Soc.*, **49**, 222 (1886).

⁶ Gutbier and Lohmann, *J. prakt. Chem.*, [2] **71**, 182 (1905).

⁷ Geuther, *Ann.*, **245**, 98 (1888).

which the following composition can be calculated:⁸ mg. mol, NOCl, 1.20; NO₂Cl, 0.69; NO₂, 0.46, N₂O₄, 0.26.

Müller did not determine nitrogen in his compound, his determination of the molecular weight does not indicate a pure compound and since he gives a boiling point of +5°, while Schumacher¹⁰ has found a boiling point of about -13°, it seems probable that he had a mixture containing nitrosyl chloride and nitrogen tetroxide as well as nitryl chloride.

After removing the nitrosyl chloride and nitryl chloride in a current of air, nitric acid remained, as Müller states. This was entirely free from chlorine and had a composition closely approaching that of a monohydrate, or orthonitric acid, H₃NO₄. Pickering demonstrated⁹ the existence of this hydrate. Its formation is probably the reason why the nitryl chloride is not hydrolyzed by the water formed in the reaction.

Nitryl chloride has been obtained by passing the vapor of phosphorus pentachloride over carefully dried lead nitrate. As the method of Schumacher, to be referred to below, is much superior to this, details and analyses need not be given.

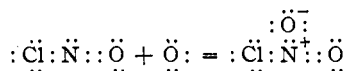
To test the method of Hassenberg some nitrogen tetroxide and an excess of chlorine were sealed in a tube in such amounts that they gave a pressure of about six atmospheres at 270°. The tube was heated for two hours in boiling toluene without apparent result, for eighteen hours in boiling naphthalene (218°), with the appearance of a reddish color after cooling to a temperature at which nitrogen tetroxide is colorless, and for five hours in an air-bath, 230-250° in the upper part and at about 300° below. After cooling, the gas remaining in the tube was transferred to a tube in which it could be weighed and analyzed. The results of the analysis were: mg. mol. Cl₂, 1.66; NOCl, 0.05; NO₂Cl, 0.63; NO₂, 0.19.

After the work described in this paper was nearly complete, Mr. Colin W. Whittaker, of the Division of Fixed Nitrogen Investigations in the Bureau of Chemistry and Soils, in Washington, called my attention to the papers of Schumacher and Sprenger,¹⁰ which I had overlooked. They have prepared nitryl chloride by the action of ozone on nitrosyl chloride. Evidently the ozone adds an electrically neutral oxygen atom to the unshared electrons of the nitrogen atom

⁸ The Editor has very kindly called my attention to the fact that nitrogen tetroxide is dissociated to the dioxide only to the extent of about 25% at 30°, the temperature of the experiment and that the ratio of the two reported is improbable. The dilution of the gases would increase the dissociation but it is evident that the results are not very accurate or reliable and the evidence for nitryl chloride is not very satisfactory in this case. I am of the opinion that the compound was present. Considerable time has been spent on the subject and it is not of sufficient importance to justify further work.

⁹ Pickering, *J. Chem. Soc.*, **63**, 436 (1893).

¹⁰ Schumacher and Sprenger, *Z. anorg. allgem. Chem.*, **182**, 139 (1929); *Z. Elektrochem.*, **35**, 653 (1929); *Z. physik. Chem.*, **B12**, 115 (1931).



Their determinations of vapor pressure indicate a boiling point of -13° , which throws discredit on the boiling point given by Müller. They state that the compound is completely decomposed at 170° and assume that it decomposes to nitrogen dioxide and chlorine and that these do not combine at any temperature. The experiments recorded above do not altogether agree with this. They also indicate that nitryl chloride decomposes to nitrosyl chloride and oxygen as well as to nitrogen dioxide and chlorine.

Summary

Nitryl chloride has been prepared by the action of hydrochloric acid on nitrogen tetroxide, by the action of phosphorus pentachloride on lead nitrate, and by the union of nitrogen dioxide and chlorine.

The method of Schumacher and Sprenger by the action of ozone on nitrosyl chloride is undoubtedly better. That method, combined with the method of Whittaker, Lundstrom and Merz¹¹ for preparing nitrosyl chloride will make nitryl chloride and nitrosyl chloride easily accessible for both laboratory and commercial use.

¹¹ Whittaker, Lundstrom and Merz, *Ind. Eng. Chem.*, **23**, 1410 (1931).

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

THE EFFECT OF SUPERSONIC RADIATION ON BROM THYMOL BLUE

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In 1929, Schmitt, Johnson and Olson¹ reported that various substances can be oxidized by subjecting solutions of such substances to ultrasonic vibrations under such conditions that air or oxygen can be cavitated from the solutions. In particular, experiments were conducted upon dilute aqueous solutions of brom thymol blue, without specifying how dilute those solutions were. Quoting from their article, "Subsequent tests showed that when a dilute aqueous solution of brom thymol blue (to which sufficient sodium hydroxide was added to produce a blue green color) was radiated, the solution changed to yellow in a very short time. It was easy to demonstrate that comparatively few of the dye molecules were destroyed in the process of radiation, for addition of alkali caused a prompt return of the blue color. Other indicators, such as brom phenol blue and litmus were affected in a similar manner. Whatever the process may be, there is no

¹ Schmitt, Johnson and Olson, *THIS JOURNAL*, **51**, 370 (1929).