

solved in a mixture of the fused amides at temperatures as low as 100° exhibit the characteristic blue color of the solutions of these metals in liquid ammonia, which resembles in every way the blue color which appears when metallic sodium is treated with ammonia gas slightly above the melting point of the amide.

Summary.

Sodium amide was prepared from pure sodium metal and water-free liquid ammonia, using a platinized platinum gauze as a catalyst.

The amide was found to be a white crystalline solid melting at 208° and having a specific conductivity of 1.665 ± 0.005 mho at 210° , when platinum electrodes were used. The specific conductivity found by Wöhler and Stanglund, using nickel electrodes, is 0.593 mho at 210° . The conductivity was found to increase with increasing temperature, but qualitative results only could be obtained, due to the decomposition of the substance.

Platinum metal was found to catalyze the decomposition of sodium amide into either sodium imide or nitride, with the evolution of ammonia gas, the platinum at the same time being dissolved.

No blue solutions of sodium metal in fused sodium amide, as reported by Titherly, could be obtained.

This investigation was begun under the direction of the late Dr. William L. Argo, who died during the war while in military service in France. The author wishes to acknowledge his indebtedness to Professor William C. Bray for his encouragement and many helpful suggestions.

TUCSON, ARIZONA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

PERCHLORO-METHYL-MERCAPTAN.¹

By O. B. HELFRICH AND E. EMMET REID.

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Introduction.

Perchloro-methyl-mercaptan, or perchloro-mercaptan, has the composition CSCl_4 and is commonly assumed to have the structure $\text{Cl}_3\text{C.S.Cl}$ analogous to methyl mercaptan. Although one of the simplest organic compounds, it has been studied only superficially, partly because of the lack of a good method of preparation and partly because of its unattractive properties. It is the purpose of this paper to present a rapid and efficient method of preparation, together with a few notes on some of its reactions. This work was undertaken originally with the Bureau of Mines on account of the possible use of perchloro-methyl-mercaptan as a "war gas," and also because it is a source of thiophosgene.

¹ This work was done in the Johns Hopkins Branch Laboratory of the Chemical Warfare Service and is published with the consent of the Chief of the Chemical Warfare Service, U. S. Army.

As our work, which was completed nearly 3 years ago, was being written up for publication, an article by Frankland, Challenger and Webster¹ appeared. Their conclusions agree well with ours, but their methods and results are somewhat different from ours.

Historical.

Rathke² first prepared perchloro-methyl-mercaptan by the chlorination of carbon disulfide which contained 0.2% iodine. He mentions a yield of 320 g. from 1 kg. of carbon disulfide, or 15% of the calculated amount. Klason³ repeated and improved Rathke's method. He chlorinated carbon disulfide in the cold with sufficient chlorine to form sulfur dichloride as a by-product, $\text{CS}_2 + 3\text{Cl}_2 \longrightarrow \text{CSCl}_4 + \text{SCl}_2$. According to Rathke's method, the monochloride resulted, $2\text{CS}_2 + 5\text{Cl}_2 \longrightarrow 2\text{CSCl}_4 + \text{S}_2\text{Cl}_2$. The advantage of this modification is apparent from a consideration of the boiling points of the products; perchloro-mercaptan, 149°; sulfur dichloride (SCl_2) 58°; and sulfur monochloride (S_2Cl_2), 138°. The more completely the sulfur chloride is converted into the dichloride, the more readily can it be separated from the perchloro-mercaptan by fractionation. Klason did not state his yields. We may assume they were of the same order as those of Rathke.

James⁴ prepared the compound in an entirely different manner, *viz.*, by the chlorination of methyl thiocyanate. His method, however, gives such a mixture of products, *e. g.*, cyanuric chloride, thiophosgene, perchloro-methyl-mercaptan, and carbon tetrachloride,—that it is hardly suitable as a method of preparation.

Johnson and Hemingway⁵ used the method of Kern and Sandoz⁶ with slight modifications and obtained a yield of 37%.

Frankland, Challenger and Webster go back to the proportions used by Rathke, but improve the methods of manipulation so that they secure a yield of 60%.

Experimental.

The method of preparation which we have found most satisfactory is a modification of that used by Rathke and by Klason. Thus, we have obtained a yield of 65% of the calculated amount.

A measured quantity of carbon disulfide containing 0.3 to 0.4% iodine is chlorinated in diffused light, at a temperature between 20 and 30°, until the volume is just double the original amount. A slower rate of chlorination gives somewhat better yields, and the yield seems to be improved by allowing the product to stand for 1 or 2 days before working it up. In one experiment 450 g. of carbon disulfide, chlorinated in 5 hours, gave a yield of 60%, while in a similar run, in which the time was 12 hours, the yield was 65%.

After the product has stood for about 48 hours, it is distilled until the temperature reaches 100°, which eliminates most of the sulfur dichloride. The residue is steam distilled, this decomposes the remaining chlorides of

¹ Frankland, Challenger and Webster, *J. Soc. Chem. Ind.*, **39**, 256T (1920).

² Rathke, *Ber.*, **3**, 859 (1870); *Ann.*, **167**, 195 (1873).

³ Klason, *ibid.*, **20**, 2376 (1887).

⁴ James, *J. Chem. Soc.*, **51**, 268 (1887).

⁵ Johnson and Hemingway, *THIS JOURNAL*, **38**, 1554 (1916).

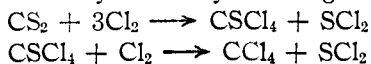
⁶ Kern and Sandoz, *Jahresber.*, **1887**, p. 2545; *Mon. sci.* [4] **1**, 1328 (1887).

sulfur and drives over the perchloro-mercaptan, which is separated from the distillate, dried and fractionated *in vacuo*. The purified product is a yellow oil, boiling at 73° at 50 mm. or, with some decomposition, at 149° under ordinary pressure. It can be distilled with steam with only slight decomposition. Its vapors are lachrymatory and toxic. For dogs it is approximately $\frac{1}{3}$ as toxic as phosgene, but for mice only about $\frac{1}{8}$.¹ The fact that its odor is stifling and unpleasant serves as a warning and decreases the danger of working with it.

Three conditions favor the formation of carbon tetrachloride in the chlorination of carbon disulfide in the presence of iodine: (1) sunlight; (2) temperature above 30°; (3) over-chlorination. Carbon disulfide containing 0.2% iodine gives only carbon tetrachloride when chlorinated in direct sunlight. Perchloro-methyl-mercaptan itself containing iodine gives carbon tetrachloride on chlorination in sunlight. The same relations hold in diffused light, if the temperature is kept above 50°. These facts must be taken into consideration if a good yield is to be obtained. The increase in volume affords a very convenient measure of the extent of chlorination and, at double volume, there is very slight danger of over-chlorination at the temperatures used. Chlorination to triple volume gives carbon tetrachloride. The absorption of the chlorine by the carbon disulfide is so rapid and complete that there is not much loss by volatilization. The reaction itself seems to become fairly slow towards the end, although the absorption of chlorine continues. It is for this reason that the chlorinated mixture is allowed to stand for 48 hours before it is worked up. Of 2 runs, made under identical conditions, one worked up immediately after the 12 hours' chlorination gave a yield of 58%, while the other, after 48 hours' standing, gave a yield of 65%.

All attempts to prepare perchloro-methyl-mercaptan by chlorination of carbon disulfide in presence of "carriers" other than iodine failed. Iron, sulfur, charcoal, phosphorus, mercury, zinc and aluminum were tried. In the case of the iron the absorption of chlorine was rapid and the product obtained was carbon tetrachloride, as expected. In the other cases there was little or no chlorination.

In the presence of iron the chlorination of carbon disulfide proceeds so rapidly to carbon tetrachloride that there is no indication of the formation of any intermediate product. In the presence of iodine, however, the chlorination proceeds very definitely in 2 stages:



In diffused light, at low temperatures, the rate of the secondary reaction is very low with iodine, which makes it possible to prepare the intermediate product. It is probably fair to assume that in the case of iron

¹ From reports of Dr. E. K. Marshall.

the same two stages really exist, but that iron catalyzes the secondary reaction so that it is practically instantaneous.

Reactions.

It has long been known that perchloro-mercaptan can be reduced by silver dust,¹ iron and acetic acid,² or stannous chloride, or tin and hydrochloric acid³ to thiophosgene, according to the reaction $CSCl_4 + SnCl_2 \longrightarrow CSCl_2 + SnCl_4$. When this reduction was tried with zinc and hydrochloric acid the perchloro-methyl-mercaptan disappeared completely; apparently it was reduced to methane, which escaped as gas. With iron and hydrochloric acid, a mixture of thiophosgene and carbon tetrachloride is obtained. When perchloro-methyl-mercaptan was refluxed with iron filings it gave nothing but carbon tetrachloride. An attempt to replace one of the chlorine atoms by fluorine failed. When perchloro-methyl-mercaptan was refluxed with zinc fluoride the inner tube of the condenser was rapidly and deeply etched, and the product was nearly pure carbon tetrachloride.

Summary.

A convenient method of preparing perchloro-methyl-mercaptan with yields as high as 65% has been worked out, and some of the reactions of this compound have been studied.

BALTIMORE, MD.

[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, LABORATORY OF ORGANIC CHEMISTRY.]

THE RÔLE OF MERCURIC NITRATE IN THE "CATALYZED" NITRATION OF AROMATIC SUBSTANCES.⁴

[FIRST PAPER.]

BY TENNEY L. DAVIS, D. E. WORRALL, N. L. DRAKE, R. W. HELMKAMP, AND A. M. YOUNG.

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When nitric acid containing mercury in solution acts upon benzene, or upon certain of its derivatives, nitro groups are introduced, but some other reaction or series of reactions also occurs; one of the hydrogen atoms of the aromatic nucleus is replaced by an hydroxyl group, and the product is a nitrated phenol. Benzene, for example, warmed with ordinary commercial nitric acid in which mercuric nitrate has been dissolved, produces nitrobenzene and picric acid, the latter in such yields that this

¹ Rathke, *Ann.*, **167**, 204 (1873); Klason, *Ber.*, **20**, 2377 (1887).

² Klason, *ibid.*, **20**, 2380 (1887).

³ Klason, *ibid.*, **20**, 2380 (1887); Kern and Sandoz, *Jahresber.*, **1887**, p. 2545; *Mont. sci.* [4] **1**, 1328 (1887).

⁴ The funds for this investigation were provided by a contract between the Ordnance Department and the Massachusetts Institute of Technology, and the present paper is published by permission of the Chief of Ordnance.