

**Behavior of Chlorine Azide toward Metals.**—Chlorine azide gas reacts violently with sodium. Of the five experiments conducted at an initial temperature of  $-78^\circ$ , four resulted in violent explosions; the fifth yielded a mixture of sodium azide and sodium chloride.

In such non-aqueous solvents as ether and carbon tetrachloride chlorine azide reacts with sodium, magnesium, and zinc at room temperature with liberation of some nitrogen gas and formation of the respective azides and chlorides. These solids were at first deposited upon the metallic surface as a protective coat, which greatly retarded the progress of the reaction.

Chlorine azide in pentane solutions reacts slowly with sodium, forming a solid product found by analysis to consist of about 90% sodium azide and 10% sodium chloride. The predominance of sodium azide may be construed to indicate that *azine* is more strongly electro-negative than chlorine.<sup>8</sup> Other lines of evidence that point toward this conclusion will be presented in a later communication. In this particular case, however, it must be borne in mind that halogenation of the solvent was proceeding concurrently with the slow reaction between chlorine azide and sodium, and that the hydrogen azide formed reacts readily with sodium. A slow evolution of gas, proved to be hydrogen, confirms this interpretation of the reaction.

**Behavior of Chlorine Azide toward Phosphorus.**—When a few drops of pure liquid chlorine azide were condensed upon yellow phosphorus at  $-78^\circ$ , a spontaneous detonation occurred in every case after the lapse of a few minutes. This was of a violence scarcely to be explained by explosion of the chlorine azide itself, which, moreover, can be stored at low temperatures, or in a sealed tube at ordinary temperatures without serious danger of decomposition. It may perhaps be ascribable either (1) to the liberation of azine,

(8) Compare Browne and Holmes, *THIS JOURNAL*, **35**, 672-681 (1913).

which would probably detonate with extreme violence, or (2) to the formation of an unstable phosphorus azide or complex chloro azide.

If small pieces of yellow phosphorus be added, with stirring, to a solution of chloride azide in carbon tetrachloride at  $0^\circ$ , the solution gradually becomes turbid, and a succession of slight explosions takes place beneath the liquid. If stirring be omitted until the maximum turbidity is attained, the slightest agitation results in a detonation that demolishes the apparatus. If stirring be omitted entirely, and if the phosphorus be not present in excess, the turbidity gradually disappears, and a clear, colorless solution is obtained.

When phosphorus was added in considerable excess to a solution of chlorine azide in carbon tetrachloride that may have contained traces of moisture a flocculent yellow solid was obtained. After most of the solvent had been distilled off, the residue was found to contain phosphorus and chlorine, but no azine; the colorless distillate, on the other hand, contained azine (in the form of hydrogen azide), but no phosphorus or chlorine. These results offer some support to the theory that chlorine tends to combine more firmly with phosphorus than does azine under the prevailing conditions.

### Summary

Chlorine azide has been prepared by two different methods, and has been liquefied (b. p. approx.  $-15^\circ$ ) and solidified (m. p. approx.  $-100^\circ$ ). It is slightly soluble in water, and readily soluble in the ten organic solvents tried.

The chemical behavior of chlorine azide toward (a) ammonia, (b) metals, (c) pentane, and (d) phosphorus has been investigated.

ITHACA, N. Y.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

## Chlorine Azide. II. Interaction of Chlorine Azide and Silver Azide. Azino Silver Chloride, $N_3AgCl$ <sup>1</sup>

BY W. JOE FRIERSON AND A. W. BROWNE

Among the purposes that have motivated the extended investigation of which the initial results are recorded in the current series of articles<sup>2</sup> is the desire for further information concerning (1) the hitherto neglected halogen-halogenoid,  $ClN_3$ , discovered by Raschig<sup>3</sup> in 1908; (2) the possible use of such compounds as the (a) inter-halogens,

(1) This article is based upon a part of the thesis presented to the Faculty of the Graduate School of Cornell University by W. Joe Frierson in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

(2) For the first article of the current series see Frierson, Kronrad, and Browne, *THIS JOURNAL*, **65**, 1696 (1943).

(3) Raschig, *Ber.*, **41**, 4194 (1908).

(b) halogen-halogenoids, and (c) inter-halogenoids in effecting the *halidation* (chloridation,<sup>4</sup> etc.) or the *haloidation* (*azidation*, etc.) of various organic and inorganic compounds; (3) the arrangement of the negative radicals, particularly the halogenoid radicals, in an activity series<sup>5</sup>; and (4) the hitherto unattained conditions under which it may be possible to isolate the long-sought halogenoid azine,  $(N_3)_2$ .

The present article contains the record of cer-

(4) See Wheat and Browne, *THIS JOURNAL*, **58**, 2410 (1936), footnote 3.

(5) See Birckenbach and Kellermann, *Ber.*, **58**, 786, 2377 (1925)

tain experiments in which chlorine azide was brought into contact with silver azide under various conditions. The chlorine azide was prepared by the modified Raschig method described in the preceding article<sup>2</sup>; the silver azide, by slow addition of a dilute solution of silver nitrate to a dilute solution of recrystallized sodium azide.

**Interaction of Chlorine Azide and Silver Azide in the Dry State.**—Chlorine azide was brought into contact with 0.1-g. samples of pure, dry silver azide, in test-tubes of medium size held at  $-78^{\circ}$ , either (1) by allowing the liquefied chlorine azide to drop upon the solid, or (2) by passing a current of the gas, diluted with nitrogen, through the tube.

(1) As soon as the first drop came into contact with the silver azide a deep blue (B)<sup>6</sup> coloration of the solid was observed. In each of the three experiments performed, the second drop brought about an explosion that demolished the test-tube.

(2) Of eight experiments, in each of which the appearance of the deep blue coloration was observed, five resulted in similar explosions. Three of these occurred spontaneously at low temperatures while the current of chlorine azide gas was still passing through the tube, while the other two took place as the tubes containing the blue samples were being allowed to warm up to room temperature.

Only one sample survived the treatment incidental to a preliminary analysis of the blue product. While still at  $-78^{\circ}$ , and before the conversion of the silver azide into the blue product was complete, the test-tube was transferred from the chlorine azide generator to a modified Schiff nitrometer containing concentrated potassium hydroxide solution as the confining liquid, and was swept free of air by a current of pure carbon dioxide. The test-tube was then allowed to warm slowly to room temperature. While the sample was still at a temperature well below  $0^{\circ}$  its color suddenly was discharged, with simultaneous evolution of nitrogen gas. The amount of silver chloride in the residual white solid, which also contained the excess of silver azide, was ascertained by dissolving the residue in ammonium hydroxide solution, and reprecipitating with nitric acid the silver chloride, which was filtered, washed, and weighed in the usual manner.

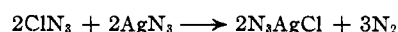
*Anal.* Nitrogen, 0.00425 g.; silver chloride, 0.0179 g. Ratio N:AgCl, calcd. for  $N_3AgCl$ , 3.00; found, 2.45.

**Interaction of Chlorine Azide in Non-Aqueous Solutions and Silver Azide.**—As was expected, the use of non-aqueous solvents greatly reduced the likelihood of explosion (1) by preventing local overheating of the reactants and (2) by stabilizing the explosive product. The appearance of the deep blue coloration was observed in every case when a solution of chlorine azide in pentane, diethyl ether, chloroform, butane, acetone, or carbon disulfide was brought into contact at  $-78^{\circ}$  with silver azide. With carbon tetrachloride the blue coloration was less conspicuous because of the rapid decomposition of the blue substance at temperatures above the freezing point of this solvent.

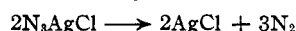
(6) Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1st Ed., Vol. I, 1905, p. 232.

With ethanol no blue coloration was observed, although a conspicuous reaction took place, with formation of a bulky brown solid and a dark brown colloidal solution which readily showed the Tyndall effect. That this brown product is in some way related to the blue substance is apparent from the fact that the two decompose at the same temperature, leaving pure white silver chloride. The brown product may well be a solvated (alcoholated) form of the blue.

During the formation of the blue substance under non-aqueous liquids a very slow but long-continued evolution of nitrogen gas was found to take place. The volume of this gas added to that of the nitrogen evolved during decomposition of the blue substance was found by nitrometric analysis to correspond to 6 atoms of nitrogen (or 2 azine radicals) per molecule of silver chloride. The formation of the blue compound may therefore be expressed by the equation

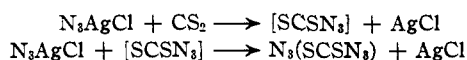


while its decomposition may be expressed



When the temperature of a suspension of the blue substance in any of the non-aqueous liquids studied is allowed to rise slowly from  $-78^{\circ}$ , the color begins to fade at about  $-30^{\circ}$ , and is completely discharged at  $-25^{\circ}$ . A suspension of pure, white silver chloride remains. It is probable that the decomposition involves initial liberation of nascent azine,  $N_3$ , which under certain conditions tends to attack the solvent, or under others to change into ordinary diatomic nitrogen.

Under carbon disulfide, for example, the blue compound decomposes without evolution of nitrogen, but with formation of a yellowish oily residue which under the microscope shows properties apparently identical with those of the similar product formed by interaction of the blue compound and azido-carbondisulfide.<sup>7</sup> It is therefore probable that the initially liberated nascent azine attacks the carbon disulfide to form the univalent azido-carbondisulfide (or azido-dithiocarbonate) radical, which then combines with another azine radical to form the interhalogenoid azine azido-dithiocarbonate,  $N_3(SCSN_3)$ , which is believed to constitute the oily residue.



The solvent for chlorine azide found to be best adapted for use in the attempt to analyze the blue product is diethyl ether. Three determinations of the ratio N:AgCl for the blue substance were made by a method identical with that described above except that the sample was in these experiments prepared and decomposed under ether.

*Anal.* Nitrogen, 0.0310, 0.0231, 0.0188 g.; silver chloride, 0.1161, 0.0833, 0.0693 g. Ratio N:AgCl, calcd. for  $N_3AgCl$ , 3.00; found, 2.75, 2.84, 2.77.

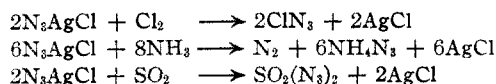
The fact that the results of these three determinations as well as that of the one determination made upon the dry product, are all lower than the theoretical value shows that the compound decomposes slowly even at low temperatures. The results seem, however, to justify the conclusion that one molecule of silver chloride is combined with

(7) See THIS JOURNAL, 45, 2541 (1923).

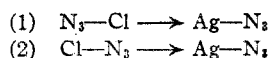
three nitrogen atoms, or one azine radical, to form a compound,  $N_3AgCl$ , for which the name *azino-silver chloride* is suggested.

**Properties of Azino-silver Chloride.**—Azino-silver chloride is a blue solid which in the pure state is so deeply colored as to be nearly black. When mixed with varying amounts of silver azide, as happens during its preparation from this substance, it ranges in color through all tints and shades of pure blue. It is stable only at temperatures below  $-30^\circ$ , but explodes violently only in the dry state. When moistened with non-aqueous liquids it decomposes rapidly but without explosion when the temperature is raised. It is not particularly sensitive to mechanical shock, but is extremely sensitive to rise of temperature.

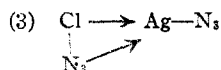
When chlorine, ammonia, and sulfur dioxide, respectively, are bubbled through ethereal suspensions of azino-silver chloride at  $-78^\circ$ , the compound is at once decomposed, as evidenced by the discharge of the blue color. Qualitative observations indicate that the reactions proceed in accordance with the equations



**Mechanism and Structure.**—It is believed that the first step toward the formation of azino-silver chloride involves the coordination of one molecule of chlorine azide with one of silver azide to form an intermediate product such as



or



The second step may involve a rearrangement that results in the formation of (1) a coordination compound

of molecular azine,  $(N_3)_2$ , with silver chloride,  $Cl-Ag \leftarrow N_3 \rightarrow N_3$ , or (2) diazo-silver chloride,  $N_3-Ag-N_3$ , in

which each of the azine radicals, as well as the chlorine atom, is attached to the silver atom by a normal covalent link, with the result that the silver atom at least temporarily assumes a valence of three.

The third and last step undoubtedly involves the loss of one of the two azine radicals by the intermediate compound, with demonstrable formation of azino-silver chloride,  $N_3AgCl$ , in which the silver in all probability is bivalent.

The assumption that silver may assume a valence of two or even three under suitable conditions seems justified (1) by the intermediate position of silver between copper and gold in the periodic system, and (2) by the work of other investigators.<sup>8</sup>

### Summary

The interaction of chlorine azide, either in the dry state or in non-aqueous solution, and silver azide has been found to result in the formation of *azino-silver chloride*,  $N_3AgCl$ , a deep blue solid compound that is fairly stable at temperatures below  $-30^\circ$ , but decomposes into silver chloride and nitrogen at higher temperatures.

Certain of the properties and reactions of this compound have been investigated.

(8) See, for example, (a) Barbieri, *Ber.*, **60**, 2424 (1927); (b) Ruff, *Z. angew. Chem.*, **47**, 480 (1934); (c) Jolibois, *Compt. rend.*, **200**, 1469 (1935), *C. A.*, **29**, 4269 (1935); (d) Braekken, *Kgl. Norske Videnskab. Selskab Forh.*, **7**, 143 (1935), *C. A.*, **29**, 4647 (1935); (e) Noyes and Hoard, *THIS JOURNAL*, **67**, 1221 (1935).

ITHACA, N. Y.

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## Heat Contents at High Temperatures of the Anhydrous Chlorides of Calcium, Iron, Magnesium and Manganese<sup>1</sup>

BY G. E. MOORE<sup>2</sup>

Existing heat capacity and fusion data of inorganic salts at high temperatures are meager and, in most instances, rather unreliable. In particular, extensive data for the liquid state are available in only a few cases. For thermodynamic calculations pertaining to certain metallurgical processes, it would be desirable to have more and better data of this kind. The Pacific Experiment Station of the Bureau of Mines is engaged, in part, in determining high-temperature heat-content data for substances of metallurgical importance;

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(2) Chemist, Western Region, Bureau of Mines.

this paper presents such data for four anhydrous chlorides of divalent metals. The solid chlorides were investigated from  $25^\circ$  to their melting points, and the liquid chlorides were studied over temperature intervals of  $125^\circ$  to  $660^\circ$ . The entropies of these compounds have been determined from low-temperature specific-heat measurements.<sup>3</sup>

### Materials and Apparatus

The preparation and analysis of the materials have been described.<sup>3</sup> The only impurities to be considered are 0.2% MgO in the  $MgCl_2$ , for which no correction was made in the present results, and 0.6%  $MgCl_2$  in the sample of

(3) Kelley and Moore, *THIS JOURNAL*, **65**, 1264 (1943).