tion of potassium hydroxide. The sample bottle was immersed in a water-bath from two to seven days and samples removed as convenient for analysis. The alkalinity was determined by titration with sulfuric acid solution using methyl orange indicator. The iodide content was determined gravimetrically as silver iodide. The density was determined by weighing a 25-ml. sample of the saturated solution. Weights were corrected for the buoyant effect of air. All chemicals used were of Reagent grade.

Equilibrium seemed to be quickly attained from the supersaturated condition. In certain experiments, equilibrium was approached from the undersaturated side and no significant variation in solubility was found.

From a number of titrations for alkalinity in the equilibrium mixtures, it was determined that about 1% of the total alkalinity was in the form of carbonate. To estimate the magnitude of the effect of this impurity on the solubility determinations, one solution was prepared with added carbonate to give a carbonate alkalinity of 0.40 *N* in a total alkalinity of 6.453 *N*., *i.e.*, 6.2%. The solubility point determined for this solution lies on the smooth curve drawn through the other experimental points, indicating that small proportions of carbonate are without appreciable effect on the solubility determinations.

Summary

The solubility of potassium iodide at 20° was determined in potassium hydroxide solutions from 0 to 14.35 *N* in alkali. The density and solubility curves show no discontinuities. The accuracy of the results is estimated to be 0.5%.

PASADENA, CALIFORNIA RECEIVED FEBRUARY 23, 1943

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

Chlorine Azide, ClN_3. I[1]

BY W. JOE FRIERSON, J. KRONRAD AND A. W. BROWNE

Although chlorine azide was recognized as a chemical individual so long ago as 1908,[2] only the most meager information concerning its properties and reactions is available at the present time. This is no doubt attributable to the extremely explosive character of the compound, which in undiluted condition usually detonates violently whatever the temperature, without apparent provocation.

A preliminary study of the behavior of chlorine azide toward numerous inorganic and organic compounds has led to the conclusion that this "halogen-halogenoid" compound[3] is chemically very reactive and that further investigation of its properties and reactions is abundantly justified, in spite of the somewhat hazardous nature of the work. Protection against personal injury has been afforded by masks and breast-plates of sheet iron worn by observers during times of danger. Each mask is provided with a rectangular pane (7 × 3 inches) of shatter-proof glass. Although scores of violent detonations have occurred, with resultant demolition of much apparatus, no personal injury has been suffered.

Preparation.—Chlorine azide has been obtained in this Laboratory either (1) by passing chlorine gas into an ethereal suspension of silver azide at ordinary temperature

$$AgN_3 + Cl_2 \longrightarrow AgCl + ClN_3$$

or (2) by the method of Raschig,[2] which involves the gradual addition of acetic acid to equimolecular amounts of sodium azide and sodium hypochlorite in aqueous solution. This reaction may be expressed by the equilibrium

$$HN_3 + HOCl \rightleftarrows ClN_3 + H_2O$$

For the purposes of the present investigation the second method was found to be preferable. In the earlier experiments, in which the chlorine azide, undiluted with air or nitrogen, was distilled from the generator under reduced pressure as recommended by Raschig, frequent explosions occurred unless the operation was conducted very slowly. Later it was found possible greatly to expedite distillation and to minimize danger of explosion by using a current of air or nitrogen at atmospheric pressure. The mixture of gases was dried thoroughly with phosphorus pentoxide, and was then passed either into suitable non-aqueous solvents or into the apparatus in which its properties or reactions were to be investigated.

Analysis.—Since a direct weighing of samples of the pure product seemed out of the question, the analytical

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[1] This article is based upon parts of the theses presented to the Faculty of the Graduate School of Cornell University by W. Joe Frierson in partial fulfillment of the requirements for the degree of Doctor of Philosophy, and J. Kronrad for the degree of Master of Science.

[2] Raschig, *Ber.*, **41**, 4194 (1908).

[3] Gardner and Browne, THIS JOURNAL, **49**, 2759 (1927).

procedure was confined to methods of ascertaining the ratio between chlorine and nitrogen in the compound. Two methods were employed.

(1) Measured volumes of a pentane solution of chlorine azide were treated with aqueous sodium hydroxide. Aqueous hydrogen peroxide, which has no effect upon sodium azide, was added to reduce the hypochlorite to chloride. The solution was then slightly acidified with acetic acid and was treated with silver nitrate, which precipitated the azide and chloride ions. From the total weight of silver azide and silver chloride was subtracted the weight of silver chloride obtained from another sample, of identical volume, and similarly treated, except that the solution was strongly acidified with nitric acid before addition of the silver nitrate, in order to prevent precipitation of the azide. The results obtained in four experiments are briefly as follows: ratio Cl:N, calcd., 0.33; found, 0.32, 0.30, 0.34, 0.31.

(2) The solution obtained by passing chlorine azide gas diluted with nitrogen into a considerable excess of liquid ammonia was evaporated to dryness (*vide infra*). Weighed samples of the residual white solid were treated in aqueous solution with silver nitrate. The amounts of silver chloride and silver azide were determined by the method described in the preceding paragraph. Ratio Cl:N, calcd., 0.33; found, 0.33, 0.34.

From these results it is evident that the samples of chlorine azide prepared contained three nitrogen atoms, or one azine radical, for each chlorine atom.

Properties.—Chlorine azide may be condensed to a yellow-orange or orange (YO-O on the Milton Bradley Standard[4]) liquid, which freezes at about −100° to a very explosive yellow (Y) solid. Owing to the extreme instability of the compound accurate determinations of the boiling and melting points have not been made as yet. Numerous explosions, often without assignable cause, have occurred during the experiments. The values thus far obtained are in the neighborhood of −15 and −100°, respectively. Supercooling of the liquid to −135° has been observed.

In the liquid state chlorine azide does not conduct the electric current appreciably. When a drop of the liquid was held between two silver electrodes about one mm. apart, no deflection of the milliammeter needle was noted when a potential difference of 110 volts was maintained across the electrodes.[5] A drop of liquid chlorine behaved similarly, while a drop of iodine monochloride readily conducted the current. Under similar conditions chlorine azide in contact with sodium azide failed to conduct, while sodium azide in anhydrous liquid hydrogen azide conducted the current readily.[6]

From these results it would appear that chlorine azide behaves neither as a polar compound nor as an ionizing solvent under the conditions prevailing in these experiments.

Although chlorine azide, as reported by Raschig, is but slightly soluble in water, it has been found to dissolve readily in butane, pentane, benzene, methanol, ethanol, diethyl ether, acetone, chloroform, carbon tetrachloride, and carbon disulfide. When cooled with solid carbon dioxide the solutions show little or no evidence of chemical action. At room temperature, however, indications of chlorination or *azination* of the solvent are obtained in some cases. When the solvent is completely evaporated from solutions of chlorine azide in benzene, methanol, and diethyl ether, for example, an oily residue showing properties similar to those of substitution products is obtained in each case.

Behavior of Chlorine Azide toward Liquid Ammonia.—When a current of chlorine azide gas diluted with nitrogen is passed at atmospheric pressure into liquid ammonia under varying conditions in different types of apparatus it was found possible to obtain either (1) a yellow liquid at the surface of contact of the reagents, or (2) a white solid, soluble in the liquid ammonia. The formation of an explosive yellow liquid under somewhat different experimental conditions was noted by Raschig,[7] who expressed the reaction believed to take place by the equation

$$ClN_3 + 2NH_3 \longrightarrow NH_2N_3 + NH_4Cl$$

but who submitted no evidence that the alternative reaction

$$ClN_3 + 2NH_3 \longrightarrow NH_2Cl + NH_4N_3$$

may not have occurred.

With chlorine azide locally in excess it is conceivable that one or more of the three possible *azinamines*, NH_2N_3, $NH(N_3)_2$, and $N(N_3)_3$, may be formed. In view of the circumstance that hydrolysis of chlorine azide in aqueous solution yields azide ion and hypochlorite ion, however, it seems more probable that in liquid ammonia ammonolysis should yield azide ion and ammono-hypochlorite ion. The explosive products obtained under the prevailing conditions are therefore more likely to be chloroamines than azinamines.

When the chlorine azide is considerably diluted with nitrogen gas the ammonia is greatly in excess, and the reaction proceeds in accordance with the equation

$$3ClN_3 + 8NH_3 \longrightarrow N_2 + 3NH_4Cl + 3NH_4N_3$$

This reaction proceeds quantitatively, and has served as the basis for one of the methods used in the current investigation for the analysis of chlorine azide (*vide supra*).

Behavior of Chlorine Azide toward Pentane.—When solutions of chlorine azide in anhydrous pentane (which probably contained the usual isomers) were allowed to stand at room temperature in stoppered vessels for about two hours, the yellow color was completely discharged without perceptible evolution of gas. Conclusive qualitative evidence of the formation of hydrogen azide and chloropentane leads to the equation

$$ClN_3 + C_5H_{12} \longrightarrow HN_3 + C_5H_{11}Cl$$

The hydrogen azide was separated readily by distillation, and yielded with aqueous silver nitrate a copious white precipitate of silver azide, completely soluble in dilute nitric acid. The residue, on the other hand, yielded no precipitate with aqueous silver nitrate, but a copious precipitate of silver chloride with alcoholic silver nitrate.

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[4] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1st ed., Vol. I, 1905, p. 232.

[5] Liquid bromine azide has been found to explode spontaneously when brought into contact with the silver electrodes, in conformity with the observations of Spencer [*J. Chem. Soc.*, **127**, 216 (1925)].

[6] Compare Browne and Lundell, THIS JOURNAL, **31**, 435 (1909).

[7] F. Raschig, "Schwefel-Stickstoff-Studien," Verlag Chemie G. m. b. H., Leipzig, 1924, p. 204.

Behavior of Chlorine Azide toward Metals.—Chlorine azide gas reacts violently with sodium. Of the five experiments conducted at an initial temperature of −78°, 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 electronegative than chlorine.[8] 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°, 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, 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°, 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°) and solidified (m. p. approx. −100°). 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.

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

[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[1]

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[2] is the desire for further information concerning (1) the hitherto neglected halogen-halogenoid, ClN_3, discovered by Raschig[3] in 1908; (2) the possible use of such compounds as the (a) inter-halogens, (b) halogen-halogenoids, and (c) inter-halogenoids in effecting the *halidation* (chloridation,[4] 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[5]; 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-

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[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).

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

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