

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

NITRIDATION STUDIES.

III. PHENYL IODIDE DICHLORIDE AND THE N-CHLORO ACID AMIDES AS NITRIDIZING AGENTS¹

BY A. LAURENCE CURL AND W. CONARD FERNELIUS

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In the development of Franklin's ammonia system of compounds, attention has been directed largely to reactions of double decomposition and to the existence of nitrogen analogs of the familiar oxygen acids, bases, and salts, in the field of inorganic chemistry, and to nitrogen alcohols, aldehydes, etc., among the carbon compounds. Recently, attention has been directed to the oxidation-reduction type of reaction. There is available for liquid ammonia work perhaps the best reducing agent known—a solution of an alkali metal in that solvent—and much work has been and is being carried out using this reagent.² The reverse process for nitrogen compounds, nitridation,³ as it has been called, has not been so thoroughly studied, and only a few nitridizing agents are known.⁴ The present investigation had for its purpose the examination of several substances for nitridizing power.

The main requirements of a good nitridizing agent aside from its ease of preparation and purification are: first, that it be of such a nature as to permit its ready and quantitative introduction into a liquid ammonia solution and, second, that its reactivity be such that it does not react with ammonia more readily than with substances in solution in that solvent. Of all substances so far examined, iodine is the most satisfactory although, even with this reagent, special precautions must be taken when introducing it into liquid ammonia.⁵ The reactivity of the elements chlorine and bromine toward both gaseous and liquid ammonia is so great as to render

¹ The material presented in this paper is an abstract of a portion of a thesis submitted by A. Laurence Curl in partial fulfillment of the requirements for the degree of Master of Science at The Ohio State University. The major portion of this material was presented at the 79th meeting of the American Chemical Society, Atlanta, Georgia, April, 1930.

² For bibliography see Johnson and Fernelius, *J. Chem. Education*, **6**, 20–35 (1929).

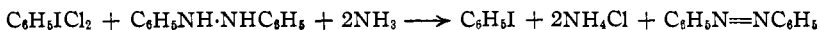
³ The term nitridizing agent was first employed by Turrentine [*THIS JOURNAL*, **34**, 386 (1912)] to describe substances which although they contain no oxygen are nevertheless capable of reacting in a fashion essentially similar to an oxidizing agent. Browne [*ibid.*, **33**, 1728 (1911)] and Franklin [*J. Phys. Chem.*, **27**, 169 (1923)] applied the term "nitridation" to all those reactions which for the ammonia system of compounds are essentially similar to oxidation reactions for the familiar water compounds. Although nitridation reactions are today classed under the broader conception of oxidation reactions, the newer term does have its use in a specific sense.

⁴ For bibliography of nitridation reactions see Schurman and Fernelius, *THIS JOURNAL*, **52**, 2425 (1930).

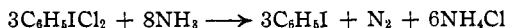
⁵ Ref. 4, p. 2428.

these elements almost useless in the present connection. A halogen may, however, as the present investigation shows, be introduced into liquid ammonia solutions in the form of an addition compound, such as phenyl iodide dichloride, $C_6H_5ICl_2$, which is less reactive toward ammonia than the elementary halogen.

When phenyl iodide dichloride is added to a solution of hydrazobenzene in liquid ammonia at its boiling point, red azobenzene precipitates. The reaction probably takes place as represented by the equation

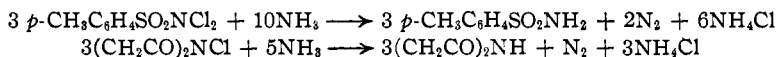


although a portion of the dichloride reacts directly with the liquid ammonia. Phenyl iodide dichloride reacts vigorously with both gaseous and liquid ammonia, in accordance with the equation



Iodine chloride, ICl , also precipitates azobenzene when added to an open Dewar test-tube containing a liquid ammonia solution of hydrazobenzene.

The oxidizing power of substances containing chlorine in a positive valence state and attached to nitrogen is well known.⁶ It was felt that such compounds might be used in a similar capacity in liquid ammonia. However, dichloramine-T, N-chloroacetanilide and N-chlorosuccinimide react so readily with liquid ammonia that they nitridize it preferentially to any hydrazobenzene which may be in solution. Hence these compounds are useless as nitridizing agents. The reaction of the N-chloro acid amides with ammonia, both liquid and gaseous, may be summarized in the equations⁷



Such reactions are frequently so vigorous and evolve so much heat that a part of the reacting halogen compound is destroyed.

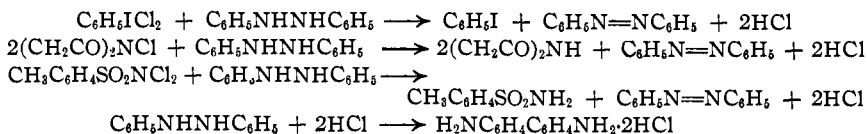
Chloramine-T is much less reactive than the other compounds. The hydrated compound reacts slowly with gaseous ammonia at room temperature while the anhydrous compound reacts very slowly or not at all. On gentle warming (50°) the hydrated compound reacts more rapidly while the anhydrous form gives a very mild explosion with the formation of a white cloud and a carbonized residue. Both the hydrated and anhydrous forms of chloramine-T go quietly into solution in liquid ammonia and *p*-toluenesulfonamide remains after evaporation of the ammonia. Chlor-

⁶ Hofmann, *Ber.*, 15, 410 (1882); Seliwanow, *ibid.*, 25, 3618 (1892); Lengfeld and Stieglitz, *Am. Chem. J.*, 15, 216 (1893); Chattaway, *J. Chem. Soc.*, 87, 145 (1905).

⁷ Hoogewerff and Van Dorp [*Rec. trav. chim.*, 6, 381 (1887)] state that potassium benzene sulfonebromoamide reacts with ammonium hydroxide to form the parent amide and a colorless gas. Similarly ammonium hydroxide reacts with N-bromosuccinimide [Lengfeld and Stieglitz, *Ref. 6*] and chloramine-T [Engfeldt, *Z. physiol. Chem.*, 126, 24 (1923)] to liberate nitrogen. Gebauer-Fülnegg and Jusa [*Monatsh.*, 50, 65 (1928)] obtained benzene sulfonanilide by adding benzene sulfonechloroanilide to liquid ammonia.

amine-T does not nitridize a liquid ammonia solution of hydrazobenzene at room temperature even in acid solution.⁸

In order to test further the oxidizing (dehydrogenating) properties of both phenyl iodide dichloride and the N-chloro acid amides, the reaction of each of the above substances with hydrazobenzene in chloroform solution was studied. In each case azobenzene and benzidine resulted. The reactions may be summarized



It is evident that the hydrogen chloride liberated in the oxidation reaction causes a part of the hydrazobenzene to undergo the benzidine rearrangement.

Experimental

Preparation of Materials.—The hydrazobenzene (m. p. 129°) was prepared as described elsewhere,⁹ and used within a few days of preparation.

Phenyl iodide dichloride was prepared by conducting a stream of dry chlorine into an ice-cold solution of phenyl iodide in chloroform.¹⁰

To obtain iodine chloride, a stream of chlorine was passed over a few grams of iodine until the liquid first formed began to solidify. The reaction mixture was then warmed gently to decompose whatever iodine trichloride had formed.¹¹

The chloramine-T, dichloramine-T and succinimide (m. p. 123°) used in these experiments were Eastman Kodak Co. products.

N-chloroacetanilide was prepared by the method of Slosson¹² by adding a solution of potassium hypochlorite to an ice-cold solution of acetanilide: m. p. 88–90°; Slosson gives 91°.

N-chlorosuccinimide was prepared by the method of Tscherniac,¹³ which consists of adding a cold solution of succinimide in dilute acetic acid to an ice-cold solution of potassium hypochlorite: m. p. 149°; Tscherniac gives 150°.

Action upon Hydrazobenzene in Liquid Ammonia. Phenyl Iodide Dichloride.—Using a technique previously described,⁹ a solution of 1 g. of hydrazobenzene in liquid ammonia at –33° was treated with 1.53 g. (1.03 equivalents) of phenyl iodide dichloride. A vigorous reaction ensued, resulting in the evolution of a gas and the formation of a red precipitate. Upon evaporation of the ammonia, the reaction products were treated with ligroin. After evaporating the ligroin, a red liquid remained which crystallized on cooling; m. p. 65–67°.

The ligroin insoluble residue was washed with water and the filtrate shown to con-

⁸ Chloramine-T has been found to be more reactive when in an acid solution [Schiemann and Novák, *Z. angew. Chem.*, **40**, 1032 (1927)].

⁹ Ref. 4, p. 2428.

¹⁰ Gattermann, "Practical Methods of Organic Chemistry," 3d American ed. from 11th German ed., translated by Schober and Babasinian, The Macmillan Co., New York, 1928, p. 245; cf. Willgerodt, *J. prakt. Chem.*, [2] **33**, 154 (1886).

¹¹ Gay-Lussac, *Ann. chim.*, **91**, 48 (1814); Bornemann, *Ann.*, **189**, 183 (1877).

¹² Slosson, *Am. Chem. J.*, **29**, 299 (1903).

¹³ Tscherniac, *Ber.*, **34**, 4213 (1901).

tain ammonium chloride. A light brown substance remained behind (m. p. 115–123°; mixed m. p. with hydrazobenzene 117–120°) in an amount roughly half that of the azobenzene formed.

Iodine Chloride.—Upon adding iodine chloride to a solution of hydrazobenzene in liquid ammonia contained in an open Dewar, a red precipitate formed immediately. After the ammonia had evaporated the residue was washed with ligroin. Upon evaporating the red ligroin solution a red liquid remained which crystallized on cooling; m. p. 58°, mixed melting point with azobenzene 61–63°.

Chloramine-T, N-chloroacetanilide, N-chlorosuccinimide and dichloramine-T failed to give a precipitate of azobenzene when added to liquid ammonia solutions of hydrazobenzene at –33°.

Chloramine-T in the presence of ammonium chloride likewise produced no azobenzene at room temperature over a period of nine days.¹⁴

Action upon Liquid Ammonia. Phenyl Iodide Dichloride.—Upon adding phenyl iodide dichloride in small portions to liquid ammonia, a gentle evolution of gas took place on each addition. A white solid and brown liquid remained after the evaporation of the ammonia. The white solid dissolved in water leaving the brown liquid, which had the odor of phenyl iodide, as a lower layer. The aqueous solution gave tests for ammonium and chloride ions—no iodide. The brown liquid was dissolved in chloroform and treated with chlorine. On standing yellow needles similar to phenyl iodide dichloride deposited.

Two samples of phenyl iodide dichloride, 0.650 g. and 0.769 g., were added to liquid ammonia as above. After evaporation of the ammonia, the residue was washed with ligroin, removed almost quantitatively, filtered and dried in a current of air. Ammonium chloride obtained: 0.240 g. and 0.288 g.; yields based on the equation, $3C_6H_5ICl_2 + 8NH_3 \rightarrow 3C_6H_5I + N_2 + 6NH_4Cl$: 94.9 and 96.2%.

Chloramine-T.—Both the hydrated and anhydrous forms of chloramine-T dissolved quietly in liquid ammonia. The residues remaining after evaporation of the ammonia were thoroughly washed with water and dried: m. p. 135–136 and 136.0–136.5°, respectively (*p*-toluenesulfonamide, 137°).

Dichloramine-T, N-chloroacetanilide and N-chlorosuccinimide reacted vigorously with liquid ammonia. The residues remaining after evaporation of the ammonia were shown to consist of ammonium chloride and the respective amide: m. p. 134–136, 113–114 and 120–124°, respectively; mixed melting point of the two latter substances with acetanilide and succinimide, respectively, 113–114 and 121–123°. The *p*-toluenesulfonamide from dichloramine-T was further identified by its solubility in a potassium hydroxide solution.

Action upon Gaseous Ammonia.—The reaction of all of these substances except chloramine-T with gaseous ammonia was vigorous, producing white fumes and a brown and white residue. The reaction of dichloramine-T was so vigorous as to evolve both heat and light. The reaction of hydrated chloramine-T was very slow and attended only by a frothing of the solid. Anhydrous chloramine-T appeared to react not at all with gaseous ammonia at room temperature. Upon warming to 50° in a current of ammonia, there resulted a very mild detonation with considerable increase in pressure and the formation of a white cloud. A tarry charred mass remained behind. Determinations of the nitrogen evolved in these reactions were discouraging. Only in the case of phenyl iodide dichloride is the yield of nitrogen approximately quantitative and seldom did two runs on the same substance check.

¹⁴ Hydrazobenzene in liquid ammonia solution in the presence of ammonium chloride (an acid in liquid ammonia) is not converted to benzidine over a space of twenty-four days at room temperature.

Action upon Hydrazobenzene in Chloroform Solution.—For these experiments a solution of 2–5 g. of hydrazobenzene in 50 ml. of chloroform was immersed in an ice-bath and a solution of an equivalent amount of the halogen compound in cold chloroform added slowly with stirring. In each case the color of the solution changed from yellow to red and a precipitate collected at the surface of the chloroform. These precipitates were filtered off, washed with chloroform, dried and dissolved in water. The resulting solutions were neutralized with potassium hydroxide and the brown precipitate resulting recrystallized from hot water. The filtrates were evaporated to dryness and the residues washed with ligroin to remove azobenzene.

Substance	Benzidine		Azobenzene		N-Compd.	
	M. p., °C.	Mixed m. p., °C.	M. p., °C.	Mixed m. p., °C.	M. p., °C.	Mixed m. p., °C.
Phenyl iodide dichloride	Insufficient		68	68
Dichloramine-T	115	121–124	62–66	63–67	120–123	131–133
N-Chloroacetanilide	101	115–120	64–67	66–68	113	113–114
N-Chlorosuccinimide	Insufficient		58–65	64–67	114–119	121–124

Summary

1. Phenyl iodide dichloride and iodine chloride may be used as nitridizing agents in liquid ammonia but the N-chloro acid amides so far investigated are valueless in this connection.
2. Phenyl iodide dichloride reacts with ammonia, either liquid or gaseous, to give nitrogen, phenyl iodide and ammonium chloride.
3. The N-chloro acid amides react with ammonia to give the parent amides, ammonium chloride, nitrogen and under certain conditions, tarry decomposition products.
4. In chloroform solution, phenyl iodide dichloride, dichloramine-T, N-chloroacetanilide, and N-chlorosuccinimide convert hydrazobenzene into a mixture of azobenzene and benzidine hydrochloride.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

ESTERIFICATION WITH THIOLACETIC ACID

BY FRANCIS B. STEWART AND PAUL V. MCKINNEY

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The relative reactivity of primary, secondary and tertiary alcohols with acid chlorides, hydrochloric acid, and in acetal formation has received considerable attention in the past few years. As early as 1879 N. Menschutkin¹ observed a similar marked influence of the structure of alcohols upon their rates of esterification. He measured the rates with which fourteen widely different alcohols react with acetic acid at 154° in the absence of catalyst, and observed that with the exception of methyl alcohol, primary and secondary alcohols show only slight variation among themselves, while the tertiary alcohols show greater differences but invariably esterify one-tenth to one-twentieth as rapidly as do the

¹ Menschutkin, *Ann.*, 195, 334 (1879); 197, 193 (1879).