probably impure benzyl bromide and the lower boiling fraction a mixture of benzyl bromide and benzyl chloride.[20] A differential halogen analysis indicated that the mole ratio of bromine to chlorine in the lower boiling fraction was 1.89/1.

The Reaction of Isopropyl Iodide with Iodine Monochloride.—A solution of 47.8 g. (0.294 mole) of iodine monochloride in 120 ml. of carbon tetrachloride was added dropwise with stirring over a one-half hour period to 25 g. (0.147 mole) of isopropyl iodide contained in a flask which was wrapped to exclude light. The reaction mixture warmed, iodine precipitated and hydrogen chloride gas was evolved during the addition. The following day the mixture was shaken with sodium thiosulfate solution to remove iodine. The carbon tetrachloride phase was dried and distilled rapidly from a modified Claisen flask. Only about 0.5 ml. of product boiling above the boiling point of carbon tetrachloride was isolated. This material vigorously evolved iodine when subjected to distillation from a small flask. Therefore there was no significant quantity of propylene chloroiodide in the reaction product. The distillate was subjected to fractionation from a modified Claisen flask. Four grams of isopropyl chloride, b.p. 38–41°, was isolated in this fashion (35% yield).

The Reaction of Triphenylbromomethane with Iodine Monochloride.—To 1.0 g. of trityl bromide[21] in 30 ml. of carbon tetrachloride was added 0.60 g. of iodine monochloride in 20 ml. of carbon tetrachloride. During the addition an amorphous suspension formed and subsequently redissolved. After the mixture was allowed to stand at room temperature for two hours and was then cooled in an ice-bath, an abundance of brick-red crystals precipitated. These were filtered and quickly air-dried. This material, m.p. 77–78.5°, weighed 0.45 g. The melting point remained unchanged after the material was recrystallized from heptane. The equivalent weight (based on adding a weighed sample to sodium iodide solution followed by titration with standard sodium thiosulfate solution) was 170; calcd. equiv. wt. for $C_{19}H_{15}Br \cdot 2ICl$, 162.

The Equilibrium Constant for the Isopropyl Iodide–Iodine Monochloride Complex.—Carbon tetrachloride solutions of isopropyl iodide and iodine monochloride, in which the organic halide concentration varied from 0.50–0.06 M and the halogen concentration varied from 1.9×10^{-3}–1.0×10^{-3} M, were prepared at 25°. Optical density measurements of these solutions at 328, 335 and 340 mμ were made immediately after mixing of the reagents, using carbon tetrachloride solutions of isopropyl iodide in the blank cells. The experimental data taken at the several wave lengths were found, by graphical interpretation, to fit the equation

$$\frac{(\mathrm{ICl})_i}{d_o} = \frac{1}{K\epsilon_0} \times \frac{1}{(\mathrm{RI})} + \frac{1}{\epsilon_0} \qquad (16)$$

TABLE III

THE EQUILIBRIUM CONSTANT (25°) FOR THE ISOPROPYL IODIDE–IODINE MONOCHLORIDE COMPLEX

λ, mμ	328	335	340
K	8.0	6.8	7.4
ϵ_0	590	370	270

where $(\mathrm{ICl})_i$ and (RI) represent the total iodine monochloride and isopropyl iodide concentrations of the solutions and d_o is the measured optical density corrected for the small absorption of free iodine monochloride. The details of the method of calculation have been described in earlier publications.[3,18] The calculated equilibrium constants, K, and extinction coefficients for the complex, ϵ_0, at the various wave lengths are given in Table III.

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[20] For physical properties see E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[21] Prepared from triphenylcarbinol by the method of H. Wieland, *Ber.*, **42**, 3024 (1909).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CATHOLIC UNIVERSITY OF AMERICA]

The Formation of the Imine Radical in the Electrical Discharge

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When an electrical discharge is passed through hydrazoic acid at low pressures, the NH radical is formed and may be condensed on a liquid nitrogen cooled surface as a blue solid. This is the most convenient way of preparing the material. Cyanic acid under similar conditions yields a purple deposit which appears to be a mixture of NH and undecomposed cyanic acid. We were unable to detect NH in the gases leaving a discharge tube when ammonia, hydrazine or nitrogen–hydrogen mixture passed through it under a variety of conditions. The greenish-blue glow at a liquid-air cooled surface formed by the gases leaving an ammonia discharge tube appears not to be due to NH.

(1) **Introduction.**—This is a continuation of work described in a previous paper[1] in which we prepared the NH radical by the thermal decomposition of hydrazoic acid. When this acid is passed through a hot tube at low pressure, the NH radical in the gases leaving the furnace can be frozen out on a liquid-nitrogen cooled finger and appears as a beautiful blue solid.

Experiments using cyanic acid were not successful, since the acid did not decompose appreciably in passing through our furnace at the highest temperature (1250°) attainable with our quartz apparatus. Subsequently we did decompose cyanic acid in a special apparatus in which a platinum furnace was heated to 1400° but no blue material formed on the cold finger. We have continued this work by studying the conditions necessary to produce NH in a discharge tube.

(2) **Electrical Discharge in Ammonia, Hydrazine and Nitrogen–Hydrogen Mixture.**—A number of investigators have studied reactions in the electrical discharge with the expectation of obtaining the nitrogen hydrides, NH or NH_2. Lavin and Bates[2] showed that when ammonia was passed through a discharge tube at low pressures, an active gas was obtained which had in part the properties of atomic hydrogen. However, in addition, a greenish-blue glow emanated from the solid ammonia condensed in a liquid air trap 1.5 meters from the discharge tube. Lavin and Bates were unable to obtain any spectroscopic evidence of the presence of NH in the gases leaving the discharge tube, but concluded from chemical evidence that the active gas leaving the discharge tube "seems to consist of atomic hydrogen and NH or NH_2"

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[1] F. O. Rice and M. Freamo, THIS JOURNAL, **73**, 5529 (1951).

[2] G. I. Lavin and J. R. Bates, *Proc. Natl. Acad. Sci.*, **16**, 804 (1930); also see E. J. B. Willey, *Proc. Faraday Soc.*, **30**, 230 (1934).

Lunt and Mills[3] confirmed the experimental findings of Lavin and Bates but concluded that the low temperature surface produced a local high concentration of excited NH molecules which reacted with hydrogen to give the glow.

In order to test if the conditions under which the greenish-blue glow forms destroy the blue deposit of $(NH)_x$, we deposited a layer of the blue compound prepared as described in section 3 and showed that it was unaffected when the greenish-blue glow appeared on the blue deposit.

We have been unable to find any chemical evidence for the presence of NH in the gases leaving a discharge tube containing ammonia or hydrazine or various mixtures of nitrogen and hydrogen. When ammonia was passed through a discharge tube at low pressures, there was no formation of the characteristic blue deposit formed by NH. The undecomposed ammonia condensed on the cold finger, contained small quantities of hydrazine. A great many experiments were performed in an attempt to obtain the blue compound from ammonia in a discharge tube but all experiments gave negative results. We even built a special discharge tube having a liquid nitrogen-cooled finger in the tube itself, but we only obtained ammonia and traces of hydrazine on the finger.

Since it was possible that NH was formed in discharge tubes containing NH_3 and then reacted with NH_3 to give two NH_2 radicals, we passed mixtures of nitrogen in the ratios of 3:1, 75:1 and 1000:1 through a discharge tube but only small quantities of NH_3 condensed out. In no case did we obtain any trace of blue material. Here again we made experiments under many different conditions. In one experiment the entire discharge tube was immersed in liquid nitrogen. In another experiment, the discharge tube was kept at −80°. We varied the current density and size and shape of the discharge tube without effect. Similar results were obtained with hydrazine which was passed through a seven-foot discharge tube with an applied potential of 15000, 4000 and 2000 volts; only small quantities of NH_3 were obtained on the finger.

In a final attempt to detect the presence of NH in the gases leaving a discharge tube, we passed pure nitrogen through the tube and then introduced a small quantity of pure hydrogen into the stream of active nitrogen leaving the tube. Minute quantities of ammonia condensed on the cold finger but no trace of the blue compound was obtained. We also introduced a stream of hydrogen atoms from a second discharge tube into the stream of active nitrogen from the first discharge tube, but again obtained no trace of the blue deposit.

It occurred to us that the blue deposit might be destroyed by hydrogen atoms or other active fragments from the discharge tube, but a test experiment showed that hydrogen atoms had no effect whatsoever on the blue compound formed by condensing NH on a liquid nitrogen cooled surface although a piece of platinum foil was quickly brought to redness by the H atoms. The same is true for active nitrogen which also had no effect whatsoever on the blue compound but would quickly bring a piece of tungsten to a red heat.

(3) **Electrical Discharge in Hydrazoic Acid.**—Hydrazoic acid was prepared as previously described[1] and passed through a discharge tube at a pressure in the range 0.1 to 0.01 mm. The discharge tube was about 1″ i.d. and the distance between the two aluminum electrodes was 14 in. with an applied potential of 15,000 volts. Using this apparatus we readily obtained a deposit of the blue material on a liquid nitrogen cooled finger located 3 in. from the discharge tube. We find that this is the most convenient way of preparing the blue compound, especially because the size and shape of the discharge tube and the applied potential are not critical.

The blue compound obtained in this way seems to be identical in all respects with that obtained by the thermal decomposition of hydrazoic acid. We confirmed that the transition temperature was −125° and that the product formed when the blue compound changed to white was ammonium azide.

In one experiment we formed the blue compound on a copper tube cooled to liquid nitrogen temperatures. On permitting the copper tube to warm up we observed that the blue compound did not suddenly change to NH_4N_3 at −125°, as it does on a glass surface but took several seconds. Probably this is due to the rapid conduction away by the copper of the heat produced by the exothermic change of the blue compound to ammonium azide.

(4) **Electrical Discharge in Cyanic Acid.**—Cyanic acid vapor was passed through the discharge tube used in the previous experiments. Under approximately the same conditions, we obtained a purple deposit on the cold finger. On warming the cold finger to −80° the purple material suddenly changed to a white solid. We determined that the transition temperature of this material was −125°, the same as the blue material $(NH)_n$. An examination of the white material obtained from the purple deposit, showed that it was a mixture, part of which volatilized from the cold finger when it was warmed to −40°. Mass spectrometer analysis showed that the non-volatile residue was ammonium azide and the volatile material was undecomposed cyanic acid.

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[3] R. W. Lunt and J. E. Mills, *Trans. Faraday Soc.*, **31**, 786 (1935).