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

The Imine Radical

BY FRANCIS OWEN RICE AND MELVIN FREAMO

When hydrazoic acid at low pressures is passed through a heated quartz tube, decomposition occurs presumably according to the equation $HN_3 \rightarrow NH + N_2$. The imine radical leaving the furnace can be frozen on a liquid nitrogen cooled surface, to give a blue solid which is paramagnetic. On allowing this to warm to −125°, it changes suddenly to ammonium azide NH_4N_3. The half-life of the NH radical is approximately 9×10^{-4} sec.

The imine radical, NH, has been studied spectroscopically in some detail[1] and has also been postulated as an intermediary in the photochemical[2] and photosensitized[3] decomposition of hydrazoic acid, HN_3, and in the synthesis of ammonia from active nitrogen and hydrogen.[4] The imine radical was actually found to be present in the thermal decomposition of ammonia[5] at about 2000° and when hydrazoic acid was decomposed by active nitrogen.[6]

We have found that when hydrazoic acid at pressures in the range of 0.05–0.2 mm. is passed through a quartz tube heated to about 1000°, it decomposes presumably according to the equation

$$HN_3 \longrightarrow NH + N_2$$

The imine radical can be frozen out by bringing the gases leaving the exit end of the furnace in contact with a cold finger containing liquid nitrogen. After the hydrazoic acid vapor passes through the furnace for a few minutes, the liquid nitrogen cooled surface becomes covered with a beautiful, blue deposit having the composition $(NH)_n$. When this is allowed to warm up, a rather sharp transition occurs at −125° to a white compound, which analyzed as follows:

Hydrogen, %	6.98	6.79
Nitrogen, %	92.84	93.12

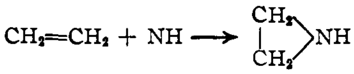
The calculated analysis for ammonium azide, NH_4N_3, is 6.71% H and 93.29% N. We proved the identity of this white powder by comparing its pattern in the mass spectrometer with the pattern of a specimen of ammonium azide prepared by neutralizing hydrazoic acid with ammonia and crystallizing the salt. Since ammonium azide is a stable white crystalline compound the color change is, of course, irreversible. The effect cannot be due to the presence of undecomposed hydrazoic acid because when this substance is passed through a cold furnace and frozen on a liquid nitrogen cooled surface, a white deposit is formed.

We next examined some of the properties of the blue material. It has a negligibly small vapor pressure at all temperatures below its transition point, and does not distil from a surface at −130° to another surface at −200° in a high vacuum. It is insoluble in the following liquefied gases: nitrogen, air, ethylene, propane and butane. The transition temperature is the same whether the substance is allowed to warm up above −125° in a vacuum, in air, or immersed in liquid ethylene or liquid butane. No visible light is emitted at the transition temperature nor does the blue material fluoresce in ultraviolet light. Heat is evolved when transition occurs because when we condensed various volatile compounds on the blue material, they suddenly vaporized at the transition temperature.

The blue material is a non-conductor of electricity. It is paramagnetic and a crude test with a powerful magnet indicated that its magnetic susceptibility lies between nickel oxide (50×10^{-6} cgs.) and ferrous ammonium sulfate (500×10^{-6} cgs.).

With regard to its chemical reactivity we have deposited different substances on the blue material at −200° and allowed the mixture to warm up but usually no reaction occurred except in the blue material itself which simply changed into ammonium azide at the transition temperature. For example, when benzene is deposited on the blue material and the whole allowed to warm up to room temperature, there is no formation of aniline.[7] Bromine seems to constitute an exception in that there seems to be some chemical interaction at the transition temperature.

In marked contrast to the behavior of the blue material, the imine radical in the vapor state, produced by the thermal decomposition of hydrazoic acid, is exceedingly reactive. It can be readily identified by passing carbon monoxide at atmospheric pressure containing about 1% of hydrazoic acid, through a furnace at 450° and testing for cyanic acid, HNCO. We hoped to supplement this identification by passing a mixture of ethylene and hydrazoic acid through the furnace under similar conditions, with the expectation that ethylene imine would form according to the equation



$$CH_2{=}CH_2 + NH \longrightarrow \begin{array}{l} CH_2 \\ | \\ CH_2 \end{array}\!\!>\!NH$$

However, we found that NH reacts vigorously with ethylene to remove hydrogen with production of a carbonaceous deposit. Similar results were obtained using benzene instead of ethylene; a deposit of carbon was obtained but no aniline could be detected. When hydrogen at atmospheric pressure and containing about 1% of hydrazoic acid is passed through the furnace at 450° and a contact time of 0.65 min. we obtained mainly ammonia accompanied by small amounts of hydrazine.

The imine radical does not show any Paneth effect.[8] We tried mirrors of lead, antimony, tellurium and even carbon without effect. The experiments with carbon mirrors were rather extensive since we hoped they would be removed by formation of the volatile hydrocyanic acid by combination of an NH radical with a carbon atom but all results were negative.

The NH radical has a half-life of approximately 9×10^{-4} sec. We determined this by fitting our apparatus with a sliding furnace and measuring the time of appearance of the blue compound for different distances of the furnace from the liquid nitrogen cooled surface. Assuming that this time is inversely proportional to the concentration of the NH radical and using the data listed in Table I, we could readily obtain the half-life of the radical by plotting log $1/t_m$ against d. This gave a value for

TABLE I

Rate of disappearance of NH radicals formed by passing HN_3 through a quartz tube 1.7 cm. diam. heated to 1060°. The pressure of the HN_3 at the inlet end of the furnace was 0.07 mm. The speed of flow through the tube was 1.3×10^3 cm./sec.; d is the distance from the end of the furnace to the liquid nitrogen cooled surface; t_m is the time required to produce a visible blue deposit.

d, cm.	3	4	5	6	7
t_m, sec. (±10%)	15	20	36	86	1.4×10^2

---

[1] See H. Sponer, "Molekülspektren," Springer, Berlin, 1935; G. Herzberg, "Molecular Spectra and Molecular Structure," Van Nostrand Co., Inc., New York, N. Y., 1950.

[2] A. O. Beckman and R. G. Dickinson, THIS JOURNAL, **50**, 1870 (1928); **52**, 124 (1930).

[3] A. E. Myers and A. O. Beckman, *ibid.*, **57**, 89 (1935).

[4] B. Lewis, *ibid.*, **50**, 27, 2427 (1928); W. Steiner, *Z. Elektrochem.*, **36**, 807 (1930).

[5] H. H. Franck and H. Reichardt, *Naturwissenschaften*, **24**, 171 (1936).

[6] K. Stewart, *Trans. Faraday Soc.*, **41**, 663 (1945).

[7] In this respect our results differ from those of Stewart, see reference 6, p. 667.

[8] F. Paneth and W. Hofeditz, *Ber.*, **62**, 1335 (1929); F. O. Rice, W. R. Johnston and B. L. Evering, THIS JOURNAL, **54**, 3529 (1932).

the half-life of 9×10^{-4} sec. as compared with 1-2 $\times$ 10^{-3} sec. obtained for the hydrocarbon radicals[9] CH_3 and CH_2.

We made a few attempts to produce the NH radical from other sources. Cyanic acid appears to exist in the form[10] HNCO and might be expected therefore to produce the blue material when decomposed. However, cyanic acid was not decomposed in our apparatus even when the furnace temperature was raised to 1250°.

We also attempted to burn off two of the hydrogen atoms of ammonia with oxygen. Two experiments were performed, the first with ammonia containing 5 molar per cent. of oxygen and the second with oxygen containing 5 molar per cent. of ammonia but neither yielded any blue material.

At the present time we do not have much evidence as to the constitution of the blue substance. The first possibility is that it is the imine radical in the solid state in which each individual NH radical is loosely coupled with its neighbors. In favor of this is the observation that NH has a forbidden transition at 8502 cm.$^{-1}$. If we make the reasonable assumptions that restrictions are relaxed for the solid state and that there is widening of the band we would have absorption in the red and a blue solid.

A second possibility is that the blue solid is the much sought for diimide, HN=NH, the parent of all the organic azo compounds. Although Thiele[11] concluded that diimide does not exist, it has been frequently postulated[12] as an intermediate in various reactions such as for example the oxidation of hydrazine which under some conditions gives good yields of ammonium azide. The rather reasonable mechanism postulated is

$$H_2N—NH_2 \xrightarrow{\hat{O}} HN=NH \longrightarrow {}^1/_2NH_4(N)_3$$

The fact that the blue compound is paramagnetic is consistent with the possibility of its being diimide which may be expected to have an electronic structure similar to oxygen.[13]

There is a further possibility that the blue compound consists of a mixture of the monomer and dimer or that it consists of still higher polymers[14] of NH but it seems that the best way at present to obtain unequivocal evidence of its constitution is to take X-ray photographs below −125°.

---

(9) F. O. Rice and A. L. Glazebrook, THIS JOURNAL, **56**, 2381 (1934); F. O. Rice, W. R. Johnston and B. L. Evering, *ibid.*, **54**, 3535 (1932).

(10) J. Goubeau, *Ber.*, **68**, 912 (1935); S. Woo and T. Liu, *J. Chem. Phys.*, **3**, 544 (1935).

(11) J. Thiele, *Ann.*, **271**, 133 (1892).

(12) See R. E. Kirk and A. W. Browne, THIS JOURNAL, **50**, 341 (1928).

(13) See L. Pauling, *ibid.*, **53**, 3233 (1931).

(14) O. Dimroth and K. Pfister, *Ber.*, **43**, 2757 (1910), tried unsuccessfuly to prepare N_3H_3.

WASHINGTON, D. C. RECEIVED MAY 5, 1951

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Ionization Equilibria of Derivatives of Triphenylchloromethane in Liquid Sulfur Dioxide

BY NORMAN N. LICHTIN AND PAUL D. BARTLETT

The equivalent conductances of triphenylchloromethane, its mono-*m*-methyl, mono-*p*-methyl, mono-*m*-*t*-butyl, mono-*p*-*t* butyl, di-*p*-*t*-butyl and tri-*p*-*t*-butyl derivatives and of 9-phenyl-9-chloro-10,10-dimethyl-9,10-dihydroanthracene have been measured in liquid sulfur dioxide at 0° over a wide range of concentrations. Similar data have been collected at −17° for triphenylchloromethane and its tri-*p*-*t*-butyl derivative. Values of $K_{\text{dissn.}}$ and Λ_0 have been calculated for all these compounds using Shedlovsky's method. $\Delta F^\circ_{0^\circ}$ of dissociation has been calculated for all compounds of the series and $\Delta H^\circ_{0^\circ}$ and $\Delta S^\circ_{0^\circ}$ for those for which data at two temperatures are available. It has been demonstrated that for the five weakest electrolytes in the series, ion pair equilibria can be treated so as to make possible the interpretation of the measured dissociation constants in terms of electronic effects within the molecules and ions.

Introduction

It has been known for some time that triarylcarbonium ions (*e.g.*, triphenylcarbonium ion) are relatively stable and can be produced reversibly.[1] Investigations of the conductance of solutions in liquid sulfur dioxide of triarylmethyl halides, perchlorates, etc., have provided major evidence establishing this fact.[2-6] Ziegler and Wollschitt[4] measured the conductance of solutions in liquid sulfur dioxide of many such compounds over a wide concentration range (10^{-2} to 10^{-5} molar). They found that the introduction of one, two, or three *p*-methyl or *p*-methoxyl substituents into triphenylmethyl perchlorate caused only slight changes in the equivalent conductance curves and they deduced that these compounds are all strong electrolytes which differ in conductance only because of the different mobilities of the organic cations. This is supported by the work of Dilthey and Alfusz[7] who found that the mono-, di- and tri-*p*-methoxy derivatives of triphenylmethyl perchlorate form orange crystals and are therefore presumably ionic in the solid state. Ziegler and Wollschitt found that the electrolyte behavior of triarylmethyl chlorides is, in contrast, sharply dependent on the structures of the molecules. They concluded that their chlorides are not strong electrolytes but that an equilibrium exists in solution between molecules in which chlorine is covalently bound, ion pairs, and ions

$$Ar_3CCl_{(SO_2)} \rightleftarrows Ar_3C^+Cl^-{}_{(SO_2)} \rightleftarrows Ar_3C^+{}_{(SO_2)} + Cl^-{}_{(SO_2)}$$

Although they were unable to express their results

---

(1) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 53-55.

(2) P. Walden, *Ber.*, **35**, 2018 (1902).

(3) M. Gomberg, *ibid.*, **35**, 2403 (1902).

(4) K. Ziegler and H. Wollschitt, *Ann.*, **479**, 90 (1930).

(5) K. Ziegler and W. Mathes, *ibid.*, **479**, 111 (1930).

(6) S. T. Bowden and T. L. Thomas, *J. Chem. Soc.*, 1242 (1940).

(7) W. Dilthey and W. Alfusz, *Ber.*, **62**, 2078 (1929).