where A is a constant at a given applied current, while B is also a constant when the concentration of mercury is kept constant. Under these conditions Equation 8 predicts a linear relationship between the concentration of thallium and $(1/t_a)^{1/6}$.

A series of experiments was carried out to check this relationship with solutions of various concentrations of thallium, 1.06×10^{-3} M in mercuric chloride, 0.5 M in hydrochloric acid and 0.01% in polyacrylamide. Time t_a was measured on potential–time curves at -0.98 volt, where the hydrogen wave began to rise under the experimental condition. Some potential–time curves are reproduced in Fig. 8. The experimental relation between the concentration of thallium and $(1/t_a)^{1/6}$ is shown in Fig. 9, which indicates that the relationship represented by equation 8 holds when $(1/t_a)^{1/6}$ is not large, that is, when t_a is not too small. Apparently the deviation at small t_a values is related to the known fact that the Ilkovic relation does not hold at the beginning of the drop formation. A larger condenser current at small t may also be responsible for the deviation. It is worth mentioning that under the experimental conditions, thallium in a concentration as little as 10^{-5} M could be detected and determined in the presence of 10^{-3} M mercury. In such a mixture the detection of thallium in a concentration less than 2×10^{-5} M is not possible in the conventional polarographic method. The chronopotentiograms of thallium in Fig. 8 indicate that the chronopotentiometric method promises to be a sensitive means for the detection and determination of a second constituent in the presence of a large excess of another constituent which is reduced at a less negative potential. Note that the chronopotentiogram of thallium is clearly visible in curve 3 of Fig. 9. The possibilities of the chronopotentiometric method at the dropping mercury electrode are being studied in this Laboratory by Dr. S. Bruckenstein.

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[CONTRIBUTION FROM THE LEWIS FLIGHT PROPULSION LABORATORY]

The Preparation and Properties of Nitrosyl Azide

BY HAROLD W. LUCIEN

RECEIVED OCTOBER 4, 1957

Evidence for the formation of nitrosyl azide from reaction of sodium azide and hydrazoic acid with nitrosyl chloride, nitrosyl hydrogen sulfate and nitric acid at temperatures below −30° has been obtained. This evidence includes physical properties, decomposition studies and inferences made from infrared absorption spectra. Nitrosyl azide is an unstable yellow compound which decomposes even at temperatures as low as −50° to form nitrous oxide and nitrogen.

Since the initial preparation of hydrazoic acid in which Curtius[1] treated hydrazine with acidified nitrite solutions, several attempts have been made to verify the hypothesis that nitrosyl azide is an unstable by-product of the reaction. When these reagents are combined, the products are nitrous oxide, nitrogen, hydrazoic acid and ammonia. The nature of the products obtained and their relative amounts depend on the reaction conditions.[2–4] It was speculated that the hydrazoic acid which forms undergoes reaction with nitrous acid to form nitrosyl azide. The nitrosyl azide is unstable and immediately decomposes to form nitrous oxide and nitrogen. All attempts to prepare nitrosyl azide have resulted in the formation of equimolar quantities of nitrous ozide and nitrogen.[2,5–9]

The present approach to the synthesis of nitrosyl azide was to operate at lower temperatures than those which have been previously used and to select reagents suitable for use under these conditions. This study involved an investigation of the products which resulted from the reactions between sodium azide and nitrosyl chloride, sodium azide and nitric acid, sodium azide and nitrosyl hydrogen sulfate and nitrosyl hydrogen sulfate and hydrazoic acid at temperatures below −30°.

Experimental

Materials.—Nitrosyl chloride (Matheson) was fractionated twice on a vacuum line at −60 to −55° and the middle three-fifths fraction was used in these experiments. Sodium azide was obtained from the Matheson Co., Inc. Nitrosyl hydrogen sulfate and hydrazoic acid were prepared by standard procedures.[10]

Apparatus.—Experiments were conducted in a vacuum system located behind 5/8 inch Plexiglas shields in a well ventilated hood. Among other necessary components, the vacuum system consisted of a reaction vessel, six low-temperature U-tubes for fractionation, apparatus for measuring exact volumes, a gas density balance and melting point apparatus.

Analyses.—Molecular weights were determined with a gas density balance as well as from the mass of a given volume at a known temperature and pressure. Calibrated copper–constantan thermocouples were used with a potentiometer to measure the temperature, and melting points were observed by a technique described by Stock.[11] Infrared spectra were obtained on a recording spectrophotometer using a cell with sodium chloride prisms. The light path was 6.75 cm.

It was necessary to exercise due precaution against explosions in all the reactions investigated. Successful preparations were obtained only when the reagents were slowly mixed at the lowest practical temperature and gradually allowed to warm to the desired reaction temperature. Gradual and sudden pressure increases as well as explosions were encountered during fractionation procedures and the

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(2) H. Thiele, *ibid.*, **41**, 2681 (1908).

(3) F. Sommer and H. Pincas, *ibid.*, **49**, 259 (1916).

(4) A. Seel and T. Schwabel, *Z. anorg. allgem. Chem.*, **274**, 169 (1953).

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(7) T. Werner, *Proc. Roy. Soc.* (*London*), **28**, 257 (1911).

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(9) T. Goyal, *Agra Univ. J. Research*, **4**, 17 (1955).

(10) H. S. Booth, Editor-in-Chief, "Inorganic Syntheses," Vol. I, 1st Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1939, pp. 55, 78.

(11) A. Stock, *Ber.*, **50**, 156 (1917).

measurement of physical properties. Sections of the equipment were shattered at least once in each reaction type except in those experiments in which ether was used as a solvent or anhydrous sodium azide was used. Of seven attempts to treat sodium azide with nitrosyl hydrogen sulfate, only two were completely successful. There was an almost comparable record for the reaction of white fuming nitric acid and sodium azide.

The Reaction of Sodium Azide and Nitrosyl Chloride.—Sodium azide was placed in the reaction vessel and after the vessel had been evacuated to about 10^{-3} mm., freshly fractionated nitrosyl chloride was condensed on the salt with the aid of liquid nitrogen. These reagents were used in approximately stoichiometric quantities (1.3 g., 0.02 mole of sodium azide and of nitrosyl chloride) and using each reagent in excess. When the desired quantity of nitrosyl chloride had been transferred, the liquid nitrogen bath was replaced by one at the desired temperature and the reaction vessel was closed off from the rest of the vacuum line. The reagents were allowed to react at several temperatures from −70 to 0°. Bath temperatures were maintained to within three degrees of the desired temperature. Reaction times varied from four hours to seven days. The nitrosyl chloride was periodically condensed in the reaction vessel and the non-condensable product allowed to expand into a section of the vacuum line for characterization. After the reaction had been in progress for the desired time, the reddish-orange condensable residue was transferred to the first U-tube for fractionation. Individual fractions passed from this first trap through two additional traps maintained at the fractionation temperature. The fraction ultimately was condensed in a fourth trap at liquid nitrogen temperature. Two products were fractionated from unreacted nitrosyl chloride. Nitrous oxide was identified on the basis of molecular weight, vapor density and melting point determinations. The second yellowish-red product (20–25 mg.) was characterized as nitrosyl azide: m.p. −66 to −59°; v.p. 60 mm. at −58°.

Anal. Calcd. for N_4O: mol. wt., 72.04; N, 77.79. Found: mol. wt., 71.01; N, 76.41. The non-condensable gas was identified as nitrogen from molecular weight and density measurements.

This reaction was also allowed to take place at atmospheric pressure. Sodium azide (1.3 g., 0.02 mole) was placed in a tube which had a side arm extending downward inside the tube to within approximately 2 cm. of the bottom. The tube was fitted with a condenser with a spiral inner tube (8 cm. long × 3 cm. o.d.) about which coolant at approximately −60° flowed. The open end of the condenser was connected to two U-traps in series. Dry nitrogen gas was circulated about the open end of the second trap to prevent the condensation of moisture and oxygen in the apparatus while the reaction products were being collected. The two U-traps were surrounded by liquid nitrogen baths for the purpose of trapping products which were not stopped by the condenser. Nitrosyl chloride (1.3 g., 0.02 mole) was condensed on the sodium azide with the aid of a liquid nitrogen bath. The mixture was warmed to −50 to −45° at which temperature the reaction proceeded for two days. During this time, there occurred an evolution of gas from the orange-red mixture. The products were then transferred to the vacuum line for separation and analysis. Results were similar to those in which the reaction occurred at reduced pressure. Analysis of the fraction (18 mg., 2%) suspected to be nitrosyl azide consisted of mol. wt., 71.22; N, 76.37; m.p. −60 to −58°; and v.p. 200 mm. at −32°.

A similar group of experiments was conducted to observe the effect of water on the reaction. These were done in the vacuum line, at atmospheric pressure, and in sealed tubes at −60 to −50° for one to four days. The water was introduced by allowing the sodium azide to stand overnight in contact with the atmosphere or by the addition of a drop of water to dry sodium azide prior to use. The mixture of sodium azide and nitrosyl chloride at liquid nitrogen temperature was warmed gradually to the desired temperature over a three-hour period. The presence of water resulted in very vigorous reactions which made it necessary to quench frequently the reaction by cooling with liquid nitrogen and to release periodically the non-condensable product. No attempt was made to interrupt the reactions in the sealed tubes. These reactions yielded products similar to those obtained under anhydrous conditions; however, the amounts were increased. The products were separated and analyzed as above, and these data were obtained for the nitrosyl azide fraction (70–80 mg., 5%): v.p. 20 mm. at −68°; N, 75.09; mol. wt., 71.94.

The Reaction of Sodium Azide with Nitric Acid.—A dropping funnel was attached to the inlet tube described above for the experiments done at atmospheric pressure. Nitric acid (5 ml., 70%) was added dropwise at a rate of about one drop every two minutes to 1.3 g. of sodium azide at liquid nitrogen temperature. After a 2.5 to 3 hr. warm up period, the light mixture was allowed to stand at −35° to −30° for 8 to 24 hr. A lively evolution of gas appeared throughout the course of the reaction period. The products were then transferred to the vacuum line, separated and analyzed. Sodium azide was similarly treated with approximately molar excesses of (1) a 1:1 mixture of concentrated nitric and sulfuric acids, (2) nitrosyl hydrogen sulfate in concentrated sulfuric acid and (3) white fuming nitric acid. Physical constants and analyses compared well with those for products obtained from reactions with nitrosyl chloride. Physical constants also were used to identify other products.

The Reaction of Hydrazoic Acid and Nitrosyl Hydrogen Sulfate in Ether.—A 10% solution of hydrazoic acid in ethyl ether (15 ml.) was cooled to −50° to −60° and a mixture of nitrosyl hydrogen sulfate in concentrated sulfuric acid (20 ml.) was added over a period of 2.5 hr. The mixture was maintained at bath temperature for four days during which time gas was liberated slowly. The reaction vessel was then attached to the vacuum line, cooled to liquid nitrogen temperature and evacuated. A 5 ml. head fraction was allowed to fractionate into receivers on the vacuum line where it was refractionated several times until vapor pressure measurements indicated that ethyl ether was eliminated from the condensable products. Nitrous oxide, nitrosyl azide and nitrogen dioxide were identified among the products on the basis of physical constants. Results are given in Table I.

The Decomposition of Nitrosyl Azide.—A freshly isolated sample of nitrosyl azide was transferred to a section of the vacuum line and at liquid nitrogen temperature, the sample, a yellow solid, was evacuated to approximately 10^{-3} mm. The liquid nitrogen bath was replaced by a bath at about −30° which resulted in the complete volatilization of the sample. Under these conditions, the pressure was 237 mm. This bath was removed and the sample was allowed to stand at room temperature for 1.5 hr. When the gas was again cooled to −30°, the pressure was 462 mm. Upon further cooling with liquid nitrogen, a white solid condensed and the residual pressure was 226 mm. The non-condensable gas was assumed to be nitrogen on the basis of molecular weight determinations.

Calcd. for N_2: mol. wt., 28.02. Found: mol. wt., 29.00, 28.97.

The condensed white solid was found to exert a pressure of 234 ml. at −30° and was identified as nitrous oxide on the basis of its melting point, vapor pressure and molecular weight.

Calcd. for N_2O: mol. wt., 44.02 (v.p. 10 mm. at −128.7°, 100 mm. at 110.3°; m.p. −90.9°). Found: mol. wt., 43.92, 43.97; v.p. 11 mm. at −129°, 103 mm. at −110°; m.p. −90° to −89°.

The infrared spectra of representative samples from each of the procedures were recorded and compared. All spectra were taken at approximately 140 mm. pressure and showed similar absorption patterns. The absorption bands at 2340 and 1850 cm.$^{-1}$ have been identified with the nitrosyl ion[12] and those at 2180 and 1350 cm.$^{-1}$ with azides.[13] Three spectra representing the decomposition of nitrosyl azide over a period of 45 minutes were obtained. The initial spectrum was recorded on a sample of nitrosyl azide. Two additional spectra were obtained on the same sample after 15 and 30 minute intervals. During this time, characteristic absorption bands for nitrosyl azide disappeared and bands which could be identified with nitrous oxide appeared. The latter spectrum is similar to that obtained in a recent study.[14]

The vapor pressure of nitrosyl azide can be represented

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TABLE I

PROPERTIES OF NITROSYL AZIDE OBSERVED IN VARIOUS PROCEDURES

Chemical reaction → Property measured	$NOCl + NaN_3$ (anhydrous)	$NOCl + NaN_3$ (trace of water)	HNO_3(70%) + NaN_3	HNO_3/H_2SO_4(1:1) + NaN_3	HNO_3 wh. fum. + NaN_3	$NOSO_2OH + NaN_3$	$NOSO_2OH + HN_3$
Vapor pressure, mm. (°C.) log $p = 7.306 - 1215.6/T$	200(−32) 60(−58)	20(−68) 30(−66)	30(−61) 31(−67) 70(−50)	40(−61) 37(−62)	35(−60) 37(−60)	70(−51) 30(−62) 42(−60) 205(−30)	37(−62) 60(−50) 37(−61)
M.p. (°C.)	−66 to −59	−60 to −58	−58 to −56	−59 to −55	−60 to −57	−60 to −58	−59 to −57
Nitrogen anal.: calcd. for N_4O; 77.79	76.41	75.09	75.93	75.12	75.93		
Mol. wt.: calcd. for N_4O; 72.04	71.0	71.9		71.8	71.5	70.7	71.5
Yield (%)	1	5	4	5	1	6	5
Other gaseous products Note: N_2O and N_2 common to all preparations			NO_2, N_2O_3 HN_3	NO_2, HN_3	NO_2, HN_3	NO_2, HN_3	NO_2, HN_3

by log $p = 7.306 - 1215.6/T$ where p is in mm. and T is in degrees Kelvin. The extrapolated boiling point is 1.5°; the heat of vaporization is 5.6 kcal./mole; the Trouton constant is 20.2. The extrapolated boiling point was in good agreement with that which one might expect. Nitrosyl chloride and nitrosyl bromide boil at −6.5°[15] and −2°,[16] respectively. The melting point −60° to −57° falls between those for the corresponding chloride, −64.5°[12] and bromide, −55.5°.[13]

Discussion

Nitrosyl azide is a yellow compound of marked instability. It was possible to prepare this compound by several procedures; however, the amounts obtained were small. The low yields are attributed to its instability and to the slow and incomplete reactions by which it was prepared. Yields based on sodium azide did not exceed about 6%. The yields of the various reactions decreased in the order: $NOHSO_4 + NaN_3 > NOCl + NaN_3$ (moist) $> H_2SO_4/HNO_3(1:1) + NaN_3 > HNO_3(70\%) + NaN_3 > HN_3 + NOHSO_4 > NOCl$(anhyd.) $+ NaN_3$. Although low, yields from $NaN_3 + NOCl$ were increased almost threefold by adding water to the extent of about 60 mg./ml. of NOCl. Excessive quantities of water resulted in reactions which were difficult to control and primarily involved the hydrolysis of nitrosyl chloride. Improvement in the yield could also be obtained by using molar excesses of sodium azide with nitrosyl chloride and in all procedures by operating at the lowest practicable temperature. No significant difference in yield of nitrosyl azide was observed between the preparations in the vacuum system and those at atmospheric pressure; however, vacuum line experiments were simpler from a manipulative standpoint.

The characterization of nitrosyl azide was based on conventional analytical data as well as a study of its decomposition into nitrous oxide and nitrogen and infrared studies. The observation that the compound quantitatively decomposes into equimolar quantities of nitrous oxide and nitrogen not only assisted in identifying nitrosyl azide but also corroborated the results of previous speculations.[5-7]

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(16) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. I, Longmans, Green Co., New York, N. Y., 1940, pp. 619–620.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STEVENS INSTITUTE OF TECHNOLOGY]

Radiation Induced Decomposition of Lead Nitrate[1]

BY EVERETT R. JOHNSON

RECEIVED OCTOBER 31, 1957

Lead nitrate decomposes under γ-radiation to yield nitrite ion and oxygen in the stoichiometric ratio 1:1. As the radiation proceeds the yield of oxygen appears to fall off to a steady-state ratio of 2:1. The yield of nitrite ion is decreased by heating at 60° but not the oxygen yield.

The radiation induced decomposition of lead nitrate has been studied by Cunningham and Heal,[2a] and Hochanadel and Davis.[2b] The specific purpose in both papers was to attempt to explain the difference in yields (G-values) found, when several nitrates are decomposed by ionizing radiation. Hochanadel and Davis assumed the radiation induced decomposition of lead nitrate to be as indicated in equation 1

$$Pb(NO_3)_2 \rightsquigarrow Pb(NO_2)_2 + O_2 \qquad (1)$$

No gas analysis was performed by these authors and since the yield of nitrite ion was proportional to dose they believed that the above reaction was occurring. It has been found, however, that the radiation induced reaction of lead nitrate is much more complex and cannot be expressed by the simple equation 1 above.

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(1) Research supported by the AEC Contract No. AT(30-1)1824.

(2) (a) J. Cunningham and H. G. Heal, *Nature*, **179**, 1021 (1957); (b) C. J. Hochanadel and T. W. Davis, *J. Chem. Phys.*, **27**, 333 (1957).