[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BOSTON UNIVERSITY]

Amine Salts of N-Nitroamines

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The aminolysis of ethyl N-nitro-N-alkylcarbamates has been shown to be a general reaction suitable for the formation of substituted ammonium salts of N-nitroamines. These compounds may be used for the identification of amines and N-nitroamines and the reaction is also useful for the identification of N-nitrocarbamates. The conductances of five of these salts were determined.(2)

N-Nitro derivatives of primary amines have been prepared by the ammonolysis of N-nitrocarbamates using aqueous or alcoholic ammonia(3) or dry ammonia gas.

TABLE I

PROPERTIES OF AMINE SALTS OF N-NITROAMINES

Amine	Nitroamine	Formula	Analyses, % Calcd.	Analyses, % Found	M.p., °C.
Cyclohexyl	Isopropyl	$C_9H_{21}O_2N_3$	N, 20.7	20.5, 20.4	190–110
Isopropyl	Isopropyl	$C_6H_{17}O_2N_3$	C, 44.2	44.5, 43.8	93–94
			H, 10.4	10.2, 10.8	
Morpholine	Isopropyl	$C_7H_{17}O_3N_3$	C, 44.0	43.8, 43.8	70–71
			H, 8.9	9.1, 9.3	
Piperazine[a]	Isopropyl	$C_{10}H_{24}O_4N_6$	C, 40.8	40.9, 41.0	114
			H, 8.85	9.22, 9.06	
n-Butyl[b]	Isopropyl	$C_7H_{19}O_2N_3$	N, 23.7	23.2, 23.4	46–47
Di-*n*-butyl[c]	Isopropyl	$C_{11}H_{27}O_3N_3$	N, 18.0	17.6, 17.5	65–66
Morpholine	Benzyl	$C_{11}H_{17}O_3N_3$	N, 17.5	17.2, 17.2	90
Isobutyl	Cyclohexyl	$C_{10}H_{23}O_2N_3$	N, 19.3	19.0, 18.9	110–111
Morpholine	α-Phenylethyl	$C_{12}H_{19}O_3N_3$	N, 16.6	16.5	109-110
Cyclohexyl	Cyclohexyl	$C_{12}H_{25}O_2N_3$	N, 17.3	17.8	152–153
Morpholine	Ethyl	$C_6H_{15}O_3N_3$	N, 23.7	23.1	54–55
Morpholine	*o*-Dicyclohexyl	$C_{16}H_{31}O_3N_3$	N, 13.4	12.9, 12.9	107–108
Morpholine	Dodecyl	$C_{16}H_{35}O_3N_3$	N, 13.2	12.8, 12.7	60–61
Morpholine	Octadecyl	$C_{22}H_{47}O_3N_3$	N, 10.5	10.2, 10.3	79–80
Morpholine	*t*-Butyl	$C_8H_{19}O_3N_3$	N, 20.4	20.9	67–68
Morpholine	*n*-Propyl	$C_7H_{17}O_3N_3$	N, 22.0	21.4	85–86
Ethylenedi-	Isopropyl	$C_8H_{24}O_4N_6$	C, 35.8	35.8, 35.8	110
Morpholine	Ethylenedi-	$C_{10}H_{24}O_6N_6$	C, 37.0	36.5, 36.4	145–147
			H, 7.41	6.90, 8.02	
Isopropyl	Ethylenedi-	$C_8H_{24}O_4N_6$	N, 31.7	31.2, 31.5	157–159
Isopropyl	1,6-Hexanedi-	$C_{12}H_{32}O_4N_6$	N, 25.9	25.9, 25.8	117–118

[a] Reaction carried out in absolute ethyl alcohol and reaction mixture then poured into ether to cause precipitation. [b] Made by mixing the nitroamine with the amine without any solvent. [c] This salt was made by dissolving the nitrocarbamate in ligroin and adding the amine.

Since primary and secondary amines should react similarly with nitrocarbamates

$$RN(NO_2)COOR' + 2R''NH_2 \longrightarrow R''NHCOOR' + [RN(NO_2)]^-(R''NH_3)^+$$

it follows that the identification of the substituted ammonium N-nitroamine and the substituted carbamate would completely characterize an N-nitrocarbamate. Both of these products were identified in the aminolysis of ethyl N-nitro-N-isopropylcarbamate with (a) cyclohexylamine and (b) isopropylamine.

Furthermore, N-nitroamines react readily with primary and secondary amines to form salts which are suitable for identification of either N-nitroamines or amines.

An interesting comparison of the melting points of dicarboxylic acids and dinitroamines with the same number of methylene groups is shown in Table II.

TABLE II

MELTING POINTS OF DINITROAMINES AND DICARBOXYLIC ACIDS

Acid	No. of CH_2 groups	M.p., °C. acid	M.p., °C. dinitroamine
Succinic	2	190	174–176[a]
Glutaric	3	97.5	74–75[b]
Adipic	4	153	163[c]
Pimelic	5	105	59–60[d]
Suberic	6	144	106–107

[a] A. P. N. Franchimont and E. A. Klobbie, *Rec. trav. chim.*, **7**, 17 (1888). [b] A. P. N. Franchimont and E. A. Klobbie, *ibid.*, **7**, 347 (1888). [c] M. P. J. Dekkers, *ibid.*, **9**, 97 (1890). [d] A. P. N. Franchimont and E. A. Klobbie, *ibid.*, **7**, 352 (1888).

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(1) Abstracted from a portion of the dissertation submitted by Howard M. Curry in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) For detailed figures order Document 3295 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.05 for photocopies (6 × 8 inches) readable without optical aid.

(3) A. P. N. Franchimont and E. A. Klobbie, *Rec. trav. chim.*, **7**, 343 (1888); [4,5] and also by ammonolysis of N-nitroamides using aqueous ammonia.[6]

(4) J. C. A. S. Thomas, *ibid.*, **9**, 69 (1890).

(5) H. Van Erp, *ibid.*, **14**, 26 (1895).

(6) H. Umbgrove and A. P. N. Franchimont, *ibid.*, **16**, 385 (1897); **17**, 270 (1898).

The electrical conductances of isopropylammonium isopropyl-N-nitroamine, isopropylamine, isopropyl-N-nitroamine, potassium isopropyl-N-nitroamine, isopropylammonium chloride, morpholinium isopropyl-N-nitroamine, diisopropylammonium N,N'-dinitroethylenediamine, morpholinium dodecyl-N-nitroamine and di-*n*-butylammonium isopropyl-N-nitroamine were determined. The last two salts were not sufficiently soluble in water and their conductances were determined in absolute ethyl alcohol.

Experimental

Morpholinium Isopropylnitroamine.—Five grams (0.06 mole) of morpholine was dissolved in 50 cc. of ether, and 5 g. (0.05 mole) of isopropyl-N-nitroamine was added dropwise. The reaction was observed to be exothermic, but in this case not violent enough to bring about ebullition of the solvent. Precipitation did not occur immediately. The mixture was set aside and after about ten minutes precipitation occurred rapidly. The crystals were removed by suction filtration, washed with two 20-cc. portions of ether, and dried in a vacuum desiccator over phosphorus pentoxide; weight, 9 g. (98%).

The salt was obtained as white flaky crystals which were very soluble in water and insoluble in ether. Aqueous solutions of this compound were found to be neutral to litmus, methyl orange and phenolphthalein.

***n*-Butylammonium Isopropyl-N-nitroamine.**—Since this compound could not be made to precipitate from ether or ligroin, it was necessary to prepare it by direct admixture of the reactants.

Accordingly 9.14 g. (0.088 mole) of isopropyl-N-nitroamine was placed in a test-tube immersed in an ice-bath and 6.41 g. (0.088 mole, 8.66 cc.) of *n*-butylamine was added. The temperature rose from 0 to 70° in about 30 seconds and then began to fall. On cooling, the mass solidified to fine crystalline plates coated with oil.

Ten grams of the product was stirred with 10 cc. of ligroin. As much of the solvent as possible was removed by suction and the sticky solid was dried in a vacuum desiccator containing anhydrous calcium chloride, sodium hydroxide pellets and thinly sliced paraffin for removal of ligroin.

The dried material weighed 3 g.

Identification of the Products of the Aminolysis of Ethyl N-Nitro-N-isopropyl Carbamate with Cyclohexylamine.—Ten grams (0.057 mole) of ethyl N-nitro-N-isopropylcarbamate was dissolved in 20 cc. of ether and a solution of 11.3 g. (0.117 mole) of cyclohexylamine was added slowly with vigorous stirring. External cooling was supplied by means of an ice-bath. After about five minutes the cyclohexylamine salt of isopropyl-N-nitroamine began to separate. The mixture was allowed to stand in the ice-bath for 30 minutes and the salt was then removed by suction filtration; weight 11.2 g. (94.5%), m.p. 109–110°.

The ethereal solution was washed twice with water to remove any unprecipitated salt. The ether was then evaporated leaving a brown oil which solidified on cooling. The product was crystallized from a mixture of alcohol and water yielding 6.1 g. (63%) of product melting at 46–47°. After drying in a vacuum desiccator over calcium chloride, the product was carefully recrystallized from ligroin. This yielded 2 g. of pure ethyl N-cyclohexylcarbamate, melting at 57°.[7]

Identification of the Products of the Aminolysis of Ethyl N-Nitro-N-isopropylcarbamate with Isopropylamine.—Fifty grams (0.284 mole) of ethyl N-nitro-N-isopropylcarbamate was dissolved in 100 cc. of ether and cooled in an ice-bath. Then 40 g. (0.678 mole) of isopropylamine was added with stirring over a period of five minutes. The salt separated during this process as a gelatinous mass. After standing in the ice-bath for about ten minutes, the salt was removed by suction filtration and washed twice with ether. The pure white isopropylammonium isopropyl-N-nitroamine weighed 40 g. (83.5%), m.p. 93–94°.

The filtrate was distilled on a steam-bath to remove the ether and the residual pale yellow oil was subjected to vacuum distillation. The liquid distilled at 66° at 10 mm. and had a refractive index, $n^{20}D$ of 1.4231, both properties being characteristic of ethyl N-isopropylcarbamate.[8]

Twenty grams of the isopropylammonium isopropyl-N-nitroamine was dissolved in 100 cc. of water and 50 cc. of concentrated hydrochloric acid was added. The mixture was then extracted with two 50-cc. portions of ether, the ether layer was dried over anhydrous magnesium sulfate and the ether was removed by distillation on the steam-bath, leaving 6 g. (47%) of a light yellow oil. The oil was identified as isopropyl-N-nitroamine by forming its morpholine salt, m.p. 70–71°. A mixed melting point with a known sample of morpholinium isopropylnitroamine showed no depression.

The aqueous layer remaining after the ether extraction was rendered alkaline with 50% potassium hydroxide solution. The mixture was then distilled on a steam-bath using a long condenser with a receiver cooled in ice. The distillate was redistilled, collecting only the material boiling up to 40°. The distillate was identified as isopropylamine by allowing it to react with phenyl isothiocyanate.[9] The melting point of the N-isopropyl-N'-phenylthiourea was 101°.

N,N'-Dinitro-1,6-diaminohexane.—Twelve and two-tenths grams of N,N'-dicarbethoxy-1,6-diaminohexane was refluxed for two hours with a solution of 15 g. of sodium hydroxide in 100 cc. of water. Acidification of the reaction mixture yielded 6.1 g. (85.3%) of crude solid N,N'-dinitro-1,6-diaminohexane with a m.p. of 103–105° (dec.). Recrystallization from an ethyl alcohol–water mixture raised the m.p. to 106–107°.

Anal. Calcd. for $C_6H_{14}N_4O_4$: C, 34.9; H, 6.80; N, 27.2. Found: C, 34.4, 34.6; H, 6.89, 6.82; N, 27.0, 27.2.

Electrical Conductances.—The conductivity cell was made from a 25-ml. pipet containing two platinum electrodes and with the tip bent through an angle of 180°. A small funnel was sealed to the tip of the pipet to facilitate introduction of the sample. The electrodes were coated with platinum black[10] and the measurements were made at 25° with a type RC conductivity bridge manufactured by Industrial Instruments, Inc. Due to rather large capacitance effects caused by the water in the thermostat, it was impossible to balance the bridge when the cell was immersed in the water. It was therefore necessary to raise the cell above the bath when making the actual measurement. However, there was no appreciable change in temperature during the short time required for this measurement.

The cell constant was determined with 0.0100 *N* solution of pure potassium chloride and was found to be 0.2360. Two different samples of distilled water were used having specific conductances of 3.9×10^{-6} ohm^{-1} and 2.15×10^{-6} ohm^{-1}, respectively. All specific conductances were corrected for the conductance of water.

From the data on electrical conductance and the ionic conductances given in the literature,[11] the values given in Table III were obtained.

TABLE III

Compound	Λ_0, ohms^{-1} cm.^{2}	K_a	K_b	K_h
Potassium iospropyl N-nitroamine	102			
Isopropyl-N-nitroamine	378	2.1×10^{-7}		
Isopropylammonium chloride	112			
Isopropylammonium hydroxide	234		3.8×10^{-4}[a]	
Isopropylammonium isopropyl-N-nitroamine	72			1.2×10^{-4}
Morpholinium isopropyl-N-nitroamine				2.0×10^{-2}

[a] G. Bredig, *Z. physik. Chem.*, **13**, 295 (1894), obtained a value of 5.3×10^{-4} at 25°.

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[8] H. M. Curry and J. P. Mason, THIS JOURNAL, **72**, 5043 (1951).

[9] Shriner and Fuson, "Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1944, p. 148.

[10] Daniels, Mathews and Williams, "Experimental Physical Chemistry," 3rd ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 368.

[11] Gladstone, "Textbook of Physical Chemistry," 2nd ed., D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 895.