392. *The Preparation and Heats of Combustion of Some Amine Nitrates.*

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The nitrates of mono-, di-, and tri-methylamine, mono-, di-, and triethylamine, ethanolamine, glycine, aniline, and benzylamine have been prepared, and their heats of combustion determined. The heats of solution of mono- and tri-methylamine nitrates in water have also been determined.

The object of the present work was to prepare a series of amine nitrates and examine the effect of alteration of structure on a variety of their physical properties. Unfortunately the work was not completed, and only the heat of combustion of all the salts prepared was determined, as well as the heat of solution of two of them in water.

Early work on amine nitrates is due to Franchimont (*Rec. Trav. chim.*, 1883, **2**, 329), van Romburgh (*ibid.*, 1886, **5**, 246), and Walden (cf. *Chem. Centr.*, 1914, I, 1800). More recently, Willis (*Trans. Faraday Soc.*, 1947, **43**, 97) has prepared the nitrates of a number of cyclic bases, and determined their heats of combustion, but only one of the compounds investigated by him, aniline nitrate, has been studied by us.

Experimental.

Preparation of Amine Nitrates.—An aqueous solution of the base was neutralised with 70% nitric acid, the water removed by distillation *in vacuo*, alone and with alcohol, and the product recrystallised from absolute alcohol. M. p.s and analyses are given in Table I. The m. p.s are several degrees higher than those previously recorded, probably because many of the salts are very hygroscopic. No further comment is necessary, except for ethanolamine nitrate, which was prepared by Gabriel (*Ber.*, 1888, **21**, 2668) by saturating an aqueous solution of vinylamine with nitric acid, whereas we found that this precaution to prevent formation of the nitric ester is unnecessary, and that the pure nitrate can be formed if the temperature is kept below 10° during addition of nitric acid to an aqueous solution of ethanolamine. Aniline nitrate, for which we obtain a slightly different heat of combustion from that recorded by Willis (*loc. cit.*), was prepared as above, and a separate sample was prepared by treatment of aqueous aniline hydrochloride with silver nitrate solution, the final product being tested for absence of Ag^+ and Cl^-. Both samples gave the same heat of combustion.

TABLE I.

Nitrate.	M. p.	Found : N, %.	Calc. : N, %.
Methylamine	110·5—111·5°	29·9; 29·8	29·8
Dimethylamine	75·5— 76·5	26·0; 25·8	25·9
Trimethylamine	155 —156	22·9; 23·0	22·9
Ethylamine	Syrup	25·8; 25·9	25·9
Diethylamine	104 —105	20·5; 20·8	20·6
Triethylamine	113 —114	17·2; 17·1	17·1
Ethanolamine	52 — 53	22·6; 22·4	22·6
Glycine	145 —147 (d.)	20·3; 20·4	20·3
Aniline	(d.) ~182—184	17·6; 17·7	17·95
Benzylamine	137·5—138·5	16·4; 16·4	16·5

Heats of Combustion.—The heats of combustion were determined by using a Griffin–Sutton bomb calorimeter (*J. Sci. Instr.*, 1933, **10**, 286), temperature changes being measured on a B.S.S. 791 mercury-in-glass thermometer. The water equivalent of the system was found by the combustion of benzoic acid, obtained from the Bureau of Analysed Samples, Ltd., its heat of combustion at constant volume being taken as 6324 cals./g. in air.

Whenever possible the sample was made into a pellet, but some of the compounds examined did not give a firm pellet. In these cases the sample was weighed directly into the silica crucible in which it was held when in the bomb. The bomb was filled with oxygen to a pressure of 25 atmospheres. The ignition of the sample was facilitated by means of a paper fuse, hung over the platinum ignition wire so as to dip into the sample. For the fuse Whatman's No. 41 filter paper, dried at 110°, was used and a correction was applied for its known heat of combustion.

All the determinations were corrected for the heat of formation of oxides of nitrogen. This correction was generally very small, about −7 calories per g. of sample used.

The results obtained are given in Table II. An approximate figure for the standard deviation of the mean of duplicate determinations calculated from the differences between duplicates is ±8 calories. This of course does not take into account systematic errors of the determination or errors due to impurities in the sample, which, in view of the great hygroscopicity of the compounds, may be slightly greater than those usually experienced in this type of calorimetric work.

The temperature at which the determinations were carried out was about 16°.

From the observed heats of combustion, the heats of formation of the salts from the elements in their standard states at 298·16° K. were calculated, the values for the heats of formation of water and carbon dioxide given by Wagman, Kilpatrick, Taylor, Pitzer, and Rossini (*J. Res. Nat. Bur. Stand.*, 1945, **34**, 143) being used.

TABLE II.

Nitrate.	Heat of combustion, const. vol., water liq.; cals./g.	Heat of combustion, const. press., kcals./mole (mean).	Heat of formation, kcals./mole.
Methylamine (s)	2336, 2320	218·4	80·6
Dimethylamine (s)	3527, 3553	382·4	79·0
Trimethylamine (s)	4514, 4504	550·7	73·1
Ethylamine	3462, 3472	374·5	86·9
Diethylamine (s)	5055, 5038	687·4	98·7
Triethylamine (s)	6162, 6173	1013·6	97·3
Ethanolamine (s)	2614, 2613	323·8	137·6
Glycine (s)	1604, 1592	219·5	173·6
Aniline (s)	5080, 5104, 5098, 5095	795·1	42·5
Benzylamine (s)	5538, 5542	942·7	57·2

The heats quoted are $-\Delta H$ values.

Heats of Solution (with Dr. N. F. H. BRIGHT).—The heats of solution of mono- and tri-methylamine nitrate in water were determined by using an adiabatic calorimeter adapted from a design of Miles and Bullock (unpublished work). The following results were obtained :

	Q (soln.) (kcals./mole) in x moles of water.	x.
Methylamine nitrate	−5·33	846
	−5·28	506
	−5·31	313
Trimethylamine nitrate	−5·61	1248
	−5·54	635
	−5·56	429

These determinations were carried out at 29°. The heat of solution at infinite dilution, $-\Delta H^{\circ}_{29^{\circ}}$, may be estimated to be −5·3 kcals./mole for methylamine nitrate and −5·6 for trimethylamine nitrate.

DISCUSSION.

Willis (*loc. cit.*) gives the heat of combusion of aniline nitrate as 787·9 ± 0·7 kcals./mole, which does not agree very closely with our value of 795·1 kcals. The standard deviation of our result is about ±1·2 kcals., and the difference between the results is 7·2 kcals., or 0·9%. It is difficult to explain the discrepancy, but it may be that the lower result was due to the presence of a small amount of moisture in the sample.

It is possible to combine our value of the heat of formation of methylamine nitrate with its heat of solution, the heat of formation of the nitrate ion in solution, and the heats of solution and ionisation of methylamine, to arrive at a value for the heat of combustion of gaseous methylamine of 262·0 ± 1·5 kcals./mole (subsidiary data from " Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Stand., 1948). Bichowsky and Rossini (" The Thermochemistry of the Chemical Substances," New York, 1936) quote 258·1 and 261·4 kcals./mole. Our result is in good agreement with the higher of these, suggesting that it is the more reliable.

The analyses and combustions were carried out by the Analytical Department of Imperial Chemical Industries Limited, Nobel Division.

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