28. *Preparation and Properties of Methyldideuteramine.*

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When soluble compounds containing the amino- or imino-group are mixed with water containing deuterium oxide there is an interchange, resulting in partial substitution of deuterium for hydrogen in the amine groups. Quantitative measurements in these laboratories (unpublished : private communication) have shown that equilibrium is set up rapidly, and that in the case of methylamine hydrochloride the available deuterium distributes itself evenly between the two hydrogen atoms of the water and three out of six of the hydrogen atoms in the salt molecule. The repeated treatment of this with successive quantities of pure deuterium oxide must therefore lead to the formation of substantially pure methyldideuteramine deuterochloride ($CH_3{\cdot}ND_2,DCl$), from which the corresponding amine may be liberated.

Experimental.

The apparatus used in carrying out this transformation is shown in the figure. The tube *A* containing a quantity of 99·5% pure deuterium oxide sealed in a vacuum was opened by the vacuum capillary opener *S*, and its contents distilled into *C*. Methylamine hydrochloride (0·6 g.) which had been recrystallised from absolute alcohol was introduced into *E*, which was attached to the apparatus by a ground joint. Quantities of 0·65, 0·73, 0·70, 0·68, and 0·55 c.c. of deuterium oxide were then measured out in turn in the graduated tube *B*, and distilled into the methylamine hydrochloride by cooling *E* in liquid air. This deuterium oxide was in each case allowed to melt in *E* with the tap *T* closed, and was warmed at 30—35° for 30 minutes, after which the residual heavy water, which had become diluted with ordinary water liberated in the interchange, was distilled back into *D*.

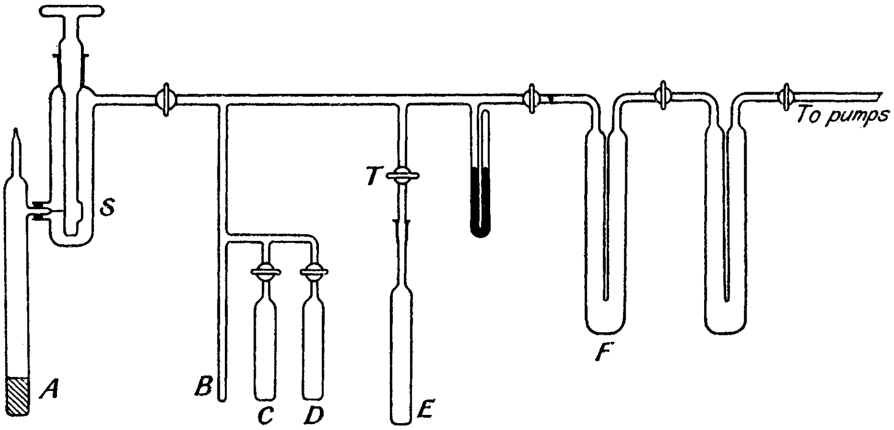
Calculation shows that, the deuterium oxide being assumed to be 99·5% pure, the above treatment should suffice for the replacement of 99·2% of the replaceable hydrogen in the methylamine hydrochloride used. After admission of dry air into *E*, excess of freshly ignited lime was introduced, and the mixture of lime and amine hydrochloride was heated at

150—200° in a vacuum. The amine evolved was collected over lime in the U-tube *F*, which was cooled in liquid air, dried by prolonged contact with lime, and then transferred to the vacuum fractionation apparatus, in which mercury valves were used in place of taps (Stock, *Ber.*, 1917, **50**, 989).

In order to remove any trace of ammonia which might be present, the amine was distilled in a vacuum from a bath at — 90° (which retains traces of water, carbon dioxide, and less volatile impurities) to two condensers, maintained severally at — 110° to — 115° and at — 190°. The amine condensed almost quantitatively in the former, ammonia and any other similarly volatile impurities passing over to the latter.

This process was repeated, and the middle fraction further fractionated by distillation into two main fractions. These fractions and the original main fraction gave vapour-pressure curves which were identical over the whole range from — 60° to — 10°, and afforded strong evidence, therefore, that all these fractions were pure methyldideuteramine.

Measurement of Vapour Pressure.—This was carried out in accordance with the well-known method of Stock (*loc. cit.*) in an appendage to the vacuum apparatus (isolated at will by a mercury valve), consisting of a thin-walled quill tube connected with a mercury manometer of about 10 mm. bore mounted on a glass mirror scale, which could be read to 0·2 mm. or less. Temperatures were measured by means of two vapour-pressure thermometers containing severally ammonia (— 60° to — 40°) and sulphur dioxide (— 50° to — 10°).



In making a measurement, the methylamine container and the bulb of the vapour-pressure thermometer were fixed side by side and then cooled by bringing up around them a bath of about 2 l. of acetone–carbon dioxide mixture contained in a large Dewar vessel, and previously brought to approximately the desired temperature and thoroughly stirred. The mercury gauges were then read until the pressures reached minimum values, which gave a direct comparison of the absolute vapour pressures of the amine and the ammonia or sulphur dioxide at the same temperature. The temperature was then deduced from standard values of vapour pressure for the thermometric liquids.

For the purposes of comparison, a sample of pure methylamine was prepared from hydrochloride which had been thrice recrystallised from alcohol. This was distilled twice with fractional condensation, and finally fractionally distilled from a bath at — 78° and separated into three main fractions. These gave identical vapour-pressure curves, whence it is inferred that the material was homogeneous and presumably pure.

In the temperature range — 10° to — 65°, 34 readings were taken of the vapour pressure of methyldideuteramine and 38 readings from methylamine. Sufficient of these data are given in Table I to enable curves to be plotted.

The vapour pressures of methyldideuteramine are consistently less than those of methylamine by an amount which varies from 5·4 mm. at — 60° to 31·8 mm. at — 10°, but these substances could be separated only by an extremely tedious process of fractionation at low temperatures.

The b. p.'s of methylamine and its *N*-dideutero-derivative read from the log p–$1/T$ graph were — 6·1° and — 5·1° respectively. Extrapolation of the vapour-pressure curves gave values of — 6·2° ± 0·1° and — 5·2° ± 0·1° respectively. The value for methylamine is higher than that, — 6·60°, recorded by Felsing and Thomas (*Ind. Eng. Chem.*, 1929, **21**, 1269).

TABLE I.

Temp.	V. p., NH_2Me, mm.	Temp.	V. p., ND_2Me, mm.	Temp.	V. p., NH_2Me, mm.	Temp.	V. p., ND_2Me, mm.
− 9·8°	644·7	−10·75°	588·2	−30·45°	224·7	−29·2°	225·9
−13·8	536·6	−12·9	530·4	−36·4	158·2	−35·15	158·7
−16·0	480·1	−17·4	425·3	−42·9	105·7	−41·2	109·0
−21·05	373·2	−19·8	376·2	−47·0	80·8	−48·8	65·5
−24·4	312·9	−23·25	312·8	−50·4	64·0	−50·3	59·0
				−57·6	38·3	−60·5	27·7

A comparison of the vapour pressures read from smoothed curves based on these observations is given in Table II.

TABLE II.

Temp.	−60°	−50°	−40°	−35°	−30°	−25°	−20°	−15°	−10°
V. p. of NH_2Me, mm.	31·6	66·0	127·5	174·0	231·2	304·0	392·2	505·0	640·8
V. p. of ND_2Me, mm.	26·2	60·4	118·0	161·4	216·0	283·8	371·2	480·0	609·0
Diff., mm.	5·4	5·6	9·5	12·6	15·2	20·2	21·0	25·0	31·8

The m. p.'s of the two compounds were determined by a series of direct observations of the melting of small samples condensed in a thin-walled quill tube attached to the vacuum apparatus. A stirred 2-litre alcohol–ether bath cooled by means of liquid nitrogen was used, and the melting temperature was observed with the bulb of a carbon dioxide vapour-pressure thermometer in close proximity to the sample. The beginning and end of melting could be sharply observed, and the whole transition from white opaque solid to clear liquid took place within a range of about 0·2°. The average melting temperature is therefore definite within ± 0·1°. The m. p.'s of methylamine and methyldideuteramine thus found were — 93·1° and — 89·2°, respectively.

The differences in physical properties between the two compounds are comparable with those observed for a number of other corresponding hydrogen and deuterium compounds. The purity of the specimen used was naturally limited by that of the deuterium oxide available (*viz.*, 99·5%), but it seems doubtful whether amine prepared with 100% pure deuterium oxide would give data sensibly different from those here recorded.

Absorption Spectrum of Methyldideuteramine.—The absorption spectrum was photographed on a Hilger small quartz spectrograph (E. 4), a quartz absorption cell, 10 cm. long, and Ilford Q plates being used. The light source was a hydrogen discharge tube (5000 v., 0·15 amp.), and copper and iron arc comparison spectra were superposed on the absorption spectra. The positions of the centres of the bands were measured on large-scale enlargements of the original negatives, the arc lines being used for reference standards. The error of measurement does not exceed ± 2 A. and in many cases is believed to be less than ± 1 A.

Table III contains measurements of the principal bands of methyldideuteramine. Those of methylamine have already been described (Emeléus and Jolley, J., 1935, 1612; Henri and Lasareff, *J. Chim. physique*, 1935, **32**, 353).

TABLE III.

λ (A.).	ν (cm.$^{-1}$).	$\Delta\nu$(cm.$^{-1}$).		λ (A.).	ν (cm.$^{-1}$).	$\Delta\nu$(cm.$^{-1}$).	
2412	41460			2169	46100		
2387	41890		590	2165	46190		520
2378	42050	540		2145	46620	560	
2357	42430		485	2139	46750		550
2351	42535		515	2120	47170	560	
2323	43050		540	2114	47310		580
2294	43590		520	2100	47620		
2267	44110		530	2094	47750	550	
2240	44640		550	2089	47860		510
2217	45110			2072	48260		
2213	45190	530	450	(2063)	48470		590
2191	45640		462	(2053)	48710		
2169	46100	550		2047	48850		
2165	46190						

The absorption spectrum of methyldideuteramine consists of bands extending from 2410 A. to the limit of transmission of quartz. Certain of the bands at the longer wave-lengths appear to have sharp heads and to be degraded towards the violet, but in general they are diffuse. A microphotometer trace was taken from a plate obtained at a pressure of 2·5 mm. and gave indications of many weak bands in addition to those measured and recorded in Table III. There is indeed no doubt that the spectrum is complex, and the use of instruments of much higher dispersion will be necessary before a vibrational analysis can be attempted.

A general comparison of the absorption spectra of methyldideuteramine and methylamine shows that they are totally different. The bands are differently spaced and the agreement of a few values for the wave-lengths of bands is clearly fortuitous. The measurements in Table III show a constant frequency difference of about 530 cm.$^{-1}$. Deviations from this mean are such as would arise from an error of 1—2 A. in measuring the positions of the bands, except in the neighbourhood of 2200 A., where uncertainty arises probably because of confusion between bands of the two main systems and those of the subsidiary systems. There are at least two series of bands which overlap, giving some of the bands the appearance of being double.

The frequency difference of 530 cm.$^{-1}$ probably corresponds to the value of 650 cm.$^{-1}$ which was first observed by Herzberg and Kolsch in the absorption spectrum of methylamine (*Z. Elektrochem.*, 1933, **39**, 572). The origin of this characteristic vibrational frequency is not clear, but it appears to be paralleled by the differences between the observed frequencies for deuterium cyanide (570·2 cm.$^{-1}$; Bartunek and Barker, *Physical Rev.*, 1935, **48**, 516; Dadieu and Klopper, *Wiener. Anz.*, 1935, 95) and for hydrogen cyanide (712 cm.$^{-1}$; Adel and Barker, *Physical Rev.*, 1934, **45**, 277; Herzberg and Spink, *Proc. Roy. Soc., A*, 1934, **147**, 434). This question has been discussed by Henri and Lasareff (*loc. cit*). Our present observations are insufficient to decide between the alternative explanations which have been suggested.

The general method here described for preparing deuteramines is being applied to isolate and examine other compounds of this type.

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