AN INFRARED STUDY OF TRIMETHYLAMINE OXIDE, ITS HYDRATE, AND ITS HYDROCHLORIDE¹

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ABSTRACT

The infrared spectra of trimethylamine oxide, its hydrate, and its hydrochloride in the solid state were measured over the range 300 to 3500 cm^{-1} to ascertain the nature of the bonds in these compounds. From the observed stretching frequencies, 937 cm^{-1} for N—O and 945 cm^{-1} for C—N, the corresponding bond lengths are calculated to be 1.44 and 1.50 Å in agreement with X-ray and electron diffraction data. Both these frequencies remain unchanged in the hydrochloride most of the evidence points to an ionic constitution. In both the hydrate and the hydrochloride the hydrogen bonds are particularly strong presumably because of the formal charges.

INTRODUCTION

Trimethylamine oxide (CH₃)₃NO offers the classical example of the so-called "coordinate link," an essentially covalent bond between two atoms with opposite formal charges. It was first pointed out by Pauling (1) that the distance between the atoms thus bonded, viz. N⁺ and O⁻, should not be affected appreciably by the electrical charges. Due to absence of other complicating factors, such as resonance among different valence bond structures, trimethylamine oxide is a suitable molecule to test this hypothesis. A first determination by electron diffraction (2) gave a N-O bond length of 1.36 Å, exactly the sum of the then accepted values (1) for the single-bond covalent radii of the N and O atoms. However, this result now appears inconclusive because, (a) the radial distribution method cannot resolve the very close C—N and N—O peaks and, (b) in the various models used for the visual comparison method, the N-O bond length was varied only between 1.30 and 1.40 Å since there is no obvious reason why this bond should be much longer than the sum of the covalent radii. In the meantime the latter parameters were found to require a sizable upward revision-to 0.74 Å for both atoms (3). This prompted a reinvestigation of the electron diffraction pattern of trimethylamine oxide (4). Preliminary results (5) indicated a longer N-O bond (1.44 Å) than the original one, and a C—N bond length (1.49 \AA) just a little over the sum of the (revised) covalent radii. These two values have been confirmed by a recent X-ray study of the crystalline hydrochloride (6), which gives 1.424 Å for the N—O bond and 1.50 Å for the average of the C-N bond lengths.

The first spectroscopic investigations of trimethylamine oxide were done in Raman effect. Edsall (7) studied the hydrochloride in aqueous hydrochloric acid solution; from the marked resemblance with the spectrum of tertiary-butyl alcohol he concluded to the existence of a trimethylhydroxyl ammonium ion $[(CH_3)_3NOH]^+$. Later Goubeau and Fromme (8) measured the spectra of the oxide dissolved in methanol (Table I). Also by comparison with the spectra of tertiary-butyl alcohol they assigned the band at 947 cm⁻¹ to the N—O stretching frequency and estimated the corresponding force constant to lie between 4 and 5×10^5 dynes cm⁻¹. An exploratory infrared study of the crystalline solid carried out in this laboratory (9) revealed some 10 bands between 700 and 3000 cm⁻¹; there also, a band at 943 cm⁻¹, one of the strongest, was assigned to

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(CH ₃) ₃ NO (8)		(CH ₃) ₃ NO.HCl (7)		
	Frequencies (in cm ⁻¹)	Relative intensities	Frequencies (in cm ⁻¹)	Relative intensities
	244	0		
	304	1/2	382	3
	413	1		
	439	1		
	494	1	500	2
	705	1		
	759	5	754	7
	947	4	947	7
	984	0		
	1029	0		
	1135	1	1132	2
	1281	1	1263	2
			1412	2
	1453	3	1449	7
	1593	0		
			1658	1 (water)
			2104	1
			2186	1
			2426	0
			2597	2
			2674	1/2
			2811	3
			2886	3
	2960	3	2974	10
	3031	4	3043	10

			TABLE I			
Raman	spectra	of	trimethylamine	oxide	and	its
		h	vdrochloride			

the N—O bond. While this work was in progress we came across two other communications on the same subject (10, 11) both relating in fact to the hydrate, as we shall see below.

EXPERIMENTAL

The sample of trimethylamine oxide was prepared by oxidation of a 25% aqueous solution of trimethylamine with 5% hydrogen peroxide (12). Repeated crystallizations in methanol gave needle crystals of the dihydrate, from which the anhydrous oxide was obtained by gentle heating under reduced pressure (13). The powder, resublimed twice, was placed in an evacuable absorption cell fitted with rock salt windows. By means of an electric heating tape a thin film of the solid was deposited on the windows. After recording of the spectra, air was admitted in the absorption cell, whereupon the film became hydrated fairly quickly. However, if the film was too thick, complete hydration was very slow. Upon hydration the white, powdery film became transparent. For comparison the spectra of dihydrate crystals were also obtained by the KBr pellet technique.

The same method was used for the hydrochloride, prepared by addition of hydrochloric acid to an aqueous solution of trimethylamine oxide. The crystals, purified by recrystallization, melted at 217–218° C with some decomposition. Two spectrometers were used: a Perkin–Elmer, Model 112, with NaCl and CsBr optics, and a Beckman, Model IR-4. Numerous attempts to secure the spectrum of the amine oxide in the vapor state were unsuccessful. A short (10 cm) glass absorption cell and a long-path (1 m) metal cell were tried in succession. Because of the low volatility of the oxide the sample had to be heated to about 180° C to produce measurable absorption. However, at that temperature the vapor decomposed rapidly and reacted with the salt windows.

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DISCUSSION

In interpreting the spectra of trimethylamine oxide (Fig. 1) it is convenient to consider



FIG. 1. Infrared spectra of the hydrated (A) and anhydrous (B) trimethylamine oxide.

the CH₃ groups as single atoms R of mass 15. The resulting XY₃Z type of molecule is of $C_{3\nu}$ symmetry, with six fundamental frequencies all active in infrared and Raman. For further simplification frequencies above 1200 cm⁻¹ (Table II) may be ignored here as they arise either from combination tones or from vibrations in the CH₃ groups. The latter are already well known from analysis of the spectra of trimethylamine (14, 15) and similar molecules. Assignment of the various fundamentals of the R₃NO molecule is best made by correlation with those of the isoelectronic tetramethyl ammonium ion R₄N⁺ (15). As shown in Table III the two symmetrical vibrations ν_1 and ν_2 of that ion have practically the same frequencies in the oxide, ν_2 and ν_6 . On the other hand the two triply degenerate vibrations ν_3 and ν_4 of RN₄⁺ are split in the oxide molecule into one non-degenerate and one doubly degenerate vibration: viz. ν_3 at 955 cm⁻¹ splits into a doublet at 937 cm⁻¹ and 945 cm⁻¹, and ν_4 at 455 cm⁻¹, into a pair at 490 and 472 cm⁻¹.

Present assignment of the infrared frequency at 937 cm⁻¹ (missing from the spectra of trimethylamine) to the N—O stretching mode follows that of the strong Raman shift at 947 cm⁻¹ (8). Apparently it was not feasible in the latter spectra to separate the two very close stretching frequencies ν_1 and ν_4 . Even in this work the doublet could be clearly resolved only in fairly thick samples and with the maximum resolving power available. Gallais and his co-workers (10) have reported a strong band at 1060 cm⁻¹ which they assigned to ν_4 . No significant absorption could be detected at that frequency in repeated recordings of our spectra of both the oxide and the hydrate (Table II); none was found either in an independent investigation of the latter compound (11). Since no experimental details were given by the French authors on preparation and purity of their samples it is not possible to account for that result. At any rate it is quite certain from the near identity of their reported spectra for trimethylamine oxide and its hydrate

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TABLE II Infrared spectra of trimethylamine oxide, its hydrate, and its hydrochloride

(CH ₃) ₃ NO	(CH ₃) ₃ N	(CH ₃) ₃ NO . HCl		
This work	This work	Gallais (10)	This work	
378 vs	381 vs			
472 vs	475 vs			
490 vs	490 vs			
	620 vs		620 w	
757 s	757 s	756 vw	758 vs	
765 sh	767 sh	773 vw 795 vw		
	852 m			
	893 m			
937 vs	937 s		939 s	
945 s	950 vs	950 s	950 vs	
		1020 s		
		1060 w		
1135 w	1125 m	1120 m	1122 m	
		1170 w		
1256 vs	1244 s	$1244 \mathrm{s}$	1255 s	
		1265 w		
		1320 vw		
		1342 w		
1390 m	1395 ni		1395 m	
1405 m				
	1440 sh		1432 w	
1458 s	1456 vw	1466 s	1453 vw	
1488 s	1475 s		1468 m	
			1530vs	
	1620 w			
$1668 \mathrm{w}$	1662 sh			
	1690 s			
1868 w	1868 w			
2175 w	2192 w			
2285 w	2275 w		2400 1	
			2460 sh	
			2015 VS	
			2070 VS	
00.40	0077		2790 s 2020	
2940 m	2975 m		2930 m	
3012	0100		3030 W	
	3180 w			
	3330 s			
	4100 w			

TABLE III Fundamental frequencies of the $R_4 N^+$ ion and the $R_3 NO$ molecule

	(CH ₃) ₄ N ⁺			(CH ₃) ₃ NO			
ν_1	(<i>a</i> ₁)	752 cm ^{−1}		ν2	(<i>a</i> ₁)	757 cm ⁻¹	sym. C-N stretch. non-deg.
ν_2	(<i>e</i>)	372 cm ⁻¹		ν_6	(<i>e</i>)	378 cm ⁻¹	⊥ asym. CNC bend. doubly deg.
ν_3	(f_2)	955 cm ¹	·	ν1	(a_1)	937 cm ⁻¹	∥ sym. N—O stretch. non-deg.
			+	V 4	(<i>c</i>)	$945 {\rm ~cm^{-1}}$	⊥ asym. C—N stretch. doubly deg.
ν_4	(f_2)	$455 { m cm^{-1}}$	<u></u> →	ν_3	(a_1)	490 cm~1	sym. ONC bend. non-deg.
			+	νā	(<i>e</i>)	$472 \mathrm{~cm^{-1}}$	\perp asym. $\widehat{\mathrm{OCN}}$ bend. doubly deg.

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that they were actually working with the same compound, namely the latter, in both cases. Indeed, the partial pressure of water vapor over the hydrate is less than 2.5 mm Hg at room temperature (16) so that unless special precautions are taken, as described above, atmospheric humidity almost always will be sufficient to hydrate completely the very hygroscopic amine oxide.

An attempt was made to calculate from the above frequencies the two bond force constants f_{N-0} and f_{C-N} . Equations of a valence force systems for a tetrahedral XY₃Z molecule (17) were used assuming force constants for bending modes to be one-tenth of those for stretching modes. Unique values could not be obtained, but only the following estimates.

	f (×10 ⁻⁵ dyne cm ⁻¹)	r (Å)
N-O C-N	3.8 to 4.8 3.1 to 3.4	$_{1.44\pm0.03}^{1.44\pm0.03}_{1.51\pm0.01}$

The bond lengths are from application of Badger's rule. These values agree exactly with the results of the more recent electron diffraction (5) and X-ray diffraction measurements (6). From comparison with other molecules such as NH_2OH , HNO_2 , etc. (5) it is obvious that the N—O "co-ordinate link" in trimethylamine oxide has roughly the same length as a "normal" N—O single bond as predicted by Pauling. The relationship suggested by Schomaker and Stevenson (18) also yields a N—O bond length (1.435 Å) very close to the present result; for the C—N bond, however, it gives a slightly shorter distance (1.465 Å) than the experimental value, although the difference is still within the limits of uncertainty of the latter. On the contrary Pauling had predicted for that bond an appreciable shortening (about 0.03 or 0.04 Å) from the normal single-bond length.

The spectrum of the hydrate, or more correctly the dihydrate, is shown in Fig. 1A and the principal frequencies are listed in Table II. Essentially identical spectra were obtained with the two kinds of samples used, viz. thin hydrated films and KBr pellets. Since, in addition, they agreed closely with the results of an independent investigation over the NaCl range (11) there is little doubt about the identity of the compound studied. As may be gathered by comparison, the spectrum of the dihydrate bears strong resemblance to that of the anhydrous oxide; particularly the N-O stretching band which retains the same frequency, 937 cm^{-1} . (The reversed intensity ratio with the C—N band at 950 cm^{-1} may be due to hydrogen bonding.) From this it is safe to infer the molecular nature of the dihydrate crystal. Indeed, the trimethylhydroxide ammonium ion $[(CH_3)_3NOH]^+$ suggested before (7, 10) would normally have a somewhat different N—O stretching frequency from the above. Furthermore, one would expect for that ion an OH bending frequency and a low-lying OH wagging frequency not found in our spectra. The O—H stretching mode cannot, obviously, yield any conclusive evidence, being indistinguishable from that in H₂O. Lüttke found a slightly lower value (3236 cm⁻¹) than that reported here, but the nearness of the C—H stretching frequencies makes these figures rather uncertain.

On the other hand all the new features in the spectra of the dihydrate may be accounted for satisfactorily in terms of vibrations of the H₂O molecules. Besides a strong O—H band at 3 μ , of which there is no trace in the anhydrous oxide, the broad, rather weak band centering around 1690 cm⁻¹ must belong to ν_2 , the bending mode. This frequency

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is appreciably higher than in pure water, 1650 cm^{-1} (19), which may be due to loss of symmetry of that mode because of unequal hydrogen bonds. In all probability one of the H atoms of each water molecule is hydrogen bonded to the O atom of trimethylamine oxide; now it is conceivable that the negative formal charge on the latter atom enhances its attraction for the proton, hence a strengthening of hydrogen bonds. The same explanation holds for the three separate broad bands at 893, 852, and 620 cm⁻¹ attributable to the three libration modes of H₂O molecules. In pure water these appear to merge into a single broad band with center at about 710 cm⁻¹ in the liquid and at 800–850 cm⁻¹ in ice (19). Formation of especially strong hydrogen bonds between the two kinds of molecules may be linked with the great stability of the dihydrate as mentioned above. Finally, it is worth recalling here that the low electrical conductivity of aqueous solutions of trimethylamine oxide has long ago been interpreted as proof of non-ionization of the dihydrate (20).

On the contrary, the infrared spectrum of the hydrochloride (Fig. 2) shows some



FIG. 2. Infrared spectrum of trimethylamine oxide hydrochloride, (CH₃)₃NO.HCl.

significant differences from those of the oxide and the dihydrate. True, the C-N and N—O stretching frequencies are unchanged (939 and 950 cm⁻¹) contrary to expectation for an ionic compound. (In hydroxylamine (21), for instance, the N-O frequency at 926 cm^{-1} is shifted to 1000 cm^{-1} in the hydrochloride.) However, the appearance of new, strong bands, notably at 1530 cm⁻¹ and around 2600 cm⁻¹, is certainly due to OH vibrations of the $[(CH_3)_3NOH]^+$ species. Very strong hydrogen bonds between that ion and the chloride anion must be responsible for the rather high OH bending frequency and, correspondingly, for the low OH stretching frequency. Rérat (6) has deduced an ionic structure for the hydrochloride on the basis of his X-ray data, particularly (a) the measured O-Cl distance (2.94 Å), which is definitely shorter than the sum of the van der Waals radii (3.2 Å), and (b) the near tetrahedral (110.4°) NOCl angle. Yet it should be pointed out that these features are equally compatible with a molecular structure since (a) there is no reason a priori why the over-all distance in O-H ... Cl should be any different from that in O...H—Cl and (b) hydrogen bonds have a tendency to become oriented along the direction of lone-pair orbitals (22). Thus sp^3 hybridization of the oxygen orbitals could account as well for the observed NOCI angle.

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RÉSUMÉ

On a étudié les spectres infrarouges de la triméthylaminoxyde, de son hydrate et son chlorhydrate afin de déterminer la nature de ces composés. La fréquence des vibrations N-O (937 cm⁻¹) et C-N (945 cm⁻¹) permet d'évaluer la longueur de ces liaisons à 1.44 Å et 1.50 Å respectivement en bon accord avec les résultats d'études récentes par diffraction des rayons X et des électrons. Le spectre du dihydrate indique qu'il s'agit d'un composé moléculaire, tandis que le chlorhydrate est très probablement ionique. Dans ces deux composés les charges nominales conduisent à des liaisons hydrogène particulièrement fortes.

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