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Characteristics of the mass spectra of some aliphatic amine *N*-oxides

The mass spectra of eight amine oxides have been studied because their parent amines are common structural features of drugs. The eight compounds have been prepared by standard methods and their behaviour in an LKB 9000S mass spectrometer has been studied at different temperatures. Compounds were introduced into the mass spectrometer using the insertion probe unheated, heated to 50° or heated to 100°. The temperature of the ion source was maintained at 250° and this resulted in the quartz tip of the probe being heated as soon as it was inserted into the source. Consequently, when it was desired to obtain spectra at the lowest possible temperature and when the probe was unheated, spectra were scanned immediately after probe insertion. At other probe temperatures spectra were scanned when the temperature of the probe heater indicated the appropriate value.

Features of the spectra of the amine oxides, together with limited data on the spectra of the corresponding amines, are listed in Table 1. Six of the eight amine oxides gave a molecular ion when the probe was unheated and the abundance of this ion was markedly reduced when the probe was heated to 50°. At a probe temperature of 100°, no molecular ion was observed for any of the compounds, due, presumably, to thermal degradation to the parent amine. Using an unheated probe, those compounds giving a molecular ion were the cyclic amine oxides (1 to 5) and *NN*-dimethylaniline-*N*-oxide (8). In the former case losses of 1, 16 and 17 mass units resulted in abundant ions and such losses appear to be characteristic. The loss of unit mass is probably associated with the formation of the imonium ion of the amine oxide, the loss of 16 mass units to the loss of oxygen whilst the M-17 ion is likely to be the imonium ion of the amine. Support for these proposals may be found by comparing the relative abundances of the M-16 and M-17 peaks of the oxides (1–5) with the abundances of the M and M-1 peaks of the corresponding amines.

NN-Dimethyl-2-phenylethylamine-*N*-oxide (6) gave no molecular ion, even with the probe unheated, but had abundant ions at *m/e* 104 (100%) and 61 (76%), ions which correspond to styrene and dimethylhydroxylamine respectively, and which are the expected products of Cope elimination (Cope & Le Bel, 1960) *NN*-Dimethyl-

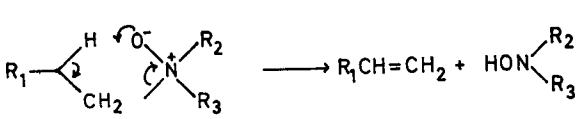

Table 1. *Abundance of ions in the mass spectra of some* N-*oxides and their parent amines.*

	Probe temp. A = ambient	% abundance relative to the base peak					
		Spectra of *N*-oxides				Spectra of corresponding amines	
		M	M−1	M−16	M−17	M	M−1
(1) 1-Methyl pyrrolidine-1-oxide	A	63	27	88	100	29	52
	50°	39	13	87	100		
(2) 1-Methyl piperidine-1-oxide	A	100	30	81	92	85	98
	50°	20	18	96	100		
(3) 4-Methyl morpholine-4-oxide	A	18	10	90	81	92	100
	50°	<2	<2	43	18		
(4) 1-Methyl hexamethylene imine-1-oxide	A	27	35	100	98	33	46
	50°	<2	<2	67	50		
(5) 1-Methyl heptamethylene imine-1-oxide	A	25	31	24	57	24	55
	50°	<2	<2	9	22		
(6) *NN*-Dimethyl-2-phenylethylamine-*N*-oxide	A	<2	<2	<2	<2	<2	<2
	50°	<2	<2	<2	<2		
(7) *NN*-Dimethyl-3-phenylpropyl-amine-*N*-oxide	A	<2	<2	18	2	18	1
	50°	<2	<2	28	39		
(8) *NN*-Dimethylaniline-*N*-oxide	A	14	<2	100	98	36	87
	50°	<2	<2	67	100		

1. Abundance values are not reported for the spectra recorded when the probe was heated to 100° as in most cases thermal decomposition was extensive.
2. In the spectra of *NN*-dimethyl-2-phenylethylamine-*N*-oxide the base peak at *m/e* 104 is so dominant that the tabulated peaks have negligible abundance. The spectrum of the parent amine has no significant M or M−1 peaks.

3-phenylpropylamine-*N*-oxide (7) also gave no molecular ion peak, and the fragmentation pattern differs from that of *NN*-dimethyl-2-phenylethylamine-*N*-oxide (6). The spectrum of (7) had ions of low abundance corresponding to the expected products of Cope elimination and the spectrum was very similar to that of the parent amine: it had no prominent features characteristic of the other amine oxides.

In summary, cyclic aliphatic amine oxides may be characterized by mass spectrometry providing that the probe temperature is kept as low as possible.

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