Mass Spectrometry of Sydnones, Sydnonimines and 5-Imino-oxatriazoles

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Mass spectrometry of mesoionic compounds had not been reported before a recent communication¹⁾ on some sydnones. The present authors have independently studied on the fragmentations of some twenty derivatives of sydnones (I-V), sydnonimines (VI-XXI) and 5-imino-oxatriazoles (XXII-XXIV) upon electron impact.

The highest mass peaks of the hydrochlorides are not molecular peaks of the salts (M') but of the bases ($M' - HCl : M$). These bases cleave generally in 3 steps with successive eliminations of $NO \cdot$, CR_3 and NXR_2 . Base peaks of these compounds examined were mostly due to the substituents (R_1 , R_2 or R_3). Minor fragment peaks containing the mesoionic rings were sometimes observed; $M - C_5H_{10}$ in I, $M - C_3H_6$ and $M - C_3H_7$ in VIII, $M - (CH_3)_2CH$ and $M - C_6H_{10}$ in XVI,

$M - C_3H_6$ in XVII, $M - CH_3$ and $M - (CH_3 + C_6H_{10})$ in XIX, and $M - OC_2H_5$ in XXI.

The fragment ions arising through elimination of $NO \cdot$ from 3-phenyl- or 3-amino-sydnones were more abundant than those from 3-alkylsydnones, probably owing to resonance stabilization of the $M - NO \cdot$ species as following;

The fragment peaks due to $M - HNO$ were observed in the spectra of the imines (VI-XVII) whereas not in the sydnones (I-V) and rarely in the N-acyl-sydnonimines (XVIII-XXI). N-Deuterio derivative of (XVI) gave a $M - DNO$ peak at m/e 178 instead of the $M - HNO$ peak. Therefore origin of the hydrogen transferred must be the 5-imino group. The $M - 30$ peak of (XI) can be assigned not to $M - CH_2O$ but to $M - NO \cdot$ since expected peaks at m/e 131 and m/e 104 due to further successive eliminations of $NO \cdot$ and HCN are not observed.

Apart from the peak at m/e 113 due to $M - \dot{N}O - HCN$, (XIV) exhibited an additional peak at m/e 114 owing to $M - NO - CN$ fragment, which was observed in the spectrum of N-morpholino-N-nitrosoaminoacetonitrile (XXV). Therefore 5-imino hydrogen in (XIV) seems to mi-

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Table 1. Mass Spectra[†] of Sydnones (I-V), Sydnonimines (VI-XXI) and 5-Imino-oxatriazoles (XXII-XXIV).

	R ₁	Structures		R ₃	M	-NO·	-CR ₃	R ₁	m/e (Relative intensities)				Miscellaneous					
		R ₂	XR ₂						From R ₁ , R ₂ , R ₃									
I	C ₆ H ₁₃	CH	O		170 (5)	140 (—)	112 *	85 *	57 (12)	55 (8)	43 (100)	41 (26)	100 ^{a)} (2)	97 ^{b)} (1)				
II	C ₆ H ₅	"	"		162 (16)	132 (10)	104 *	77 *	51 (40)									
III	Cyclohexyl	"	"		168 (14)	138 (1)	110 (4)	83 *	55 (100)	67 (8)	41 (70)	39 (24)						
IV	(CH ₃) ₂ N	"	"		129 (4)	99 *	71 (55)	44 *	42 (90)	43 (94)	28 (100)							
V	Morpholino	"	"		171 (2)	141 (26)	113 (5)	86 (20)	56 (100)	42 (15)								
VI	CH ₃	"	NH · HCl		99 (53)	69 (5)	42 (100)						68 ^{f)} (2)					
VII	C ₂ H ₅	"	"		113 (64)	83 (18)	56 (64)	29 (40)	28 (100)				82 ^{f)} (3)					
VIII	C ₄ H ₈	"	"		141 (35)	111 (1)	84 (26)	57 (95)	42 (60)	41 (100)			99 ^{c)} (18)	98 ^{d)} (23)	69 ^{e)} (49)			
IX	C ₆ H ₅	"	"		161 (8)	131 *	104 *	77	51 (24)				130 ^{f)} (8)					
X	C ₆ H ₅ (CH ₂) ₂	"	"		189 (2)	159 (3)	132 (5)	105 (13)	104 (30)	91 *	65 (14)	77 (7)	51 (6)	158 ^{f)} (2)				
XI	CH ₃ O · C ₆ H ₄	"	"		191 (3)	161 *	134 *	107 *	77 *	51 (33)	30 (66)		160 ^{f)} (10)					
XII	Cyclohexyl	"	"		167 (13)	137 (1)	110 (6)	83 (99)	67 (28)	55 (100)	41 (40)							
XIII	(CH ₃) ₂ N	"	"		128 (38)	98 (58)	71 (50)	44 (90)	43 (100)	42 (90)	28 (90)		97 ^{f)} (40)	59 ^{g)} (40)				
XIV	Morpholino	"	"		170 (4)	140 (24)	113 (2)	86 (20)	56 (65)	42 (86)	28 (100)		139 ^{f)} (22)	114 ^{h)} (2)	101 ^{g)} (76)			
XV	Morpholino	CCH ₃	NH · HCl		184 (19)	154 (10)	127 *	86 *	56 (39)	42 (100)			101 ^{g)} (5)	153 ^{f)} (3)				
XVI	Cyclohexyl	CCH(CH ₃) ₂	"		209 (17)	178 ^{f)} (1)	152 (4)	83 (80)	55 (100)	41 (53)	43 (40)		166 ⁱ⁾ (1)	163 ^{j)} (1)	135 ^{k)} (3)	127 ^{l)} (8)	97 ^{m)} (8)	70 ⁿ⁾ (68)
XVII	(CH ₃) ₂ CH	CC ₆ H ₅	"		203 (16)	172 ^{f)} (3)	146 (8)	43 (40)	77 (22)	51 (10)			161 ^{c)} (11)	157 ^{o)} (4)	117 ^{p)} (31)	104 ^{q)} (100)		
XVIII	Morpholino	CH	NCHO · HCl		198 (14)	168 (12)	113 (8)	86 (18)	56 (100)	42 (20)	29 (40)	28 (50)	140 ^{r)} (40)					
XIX	Cyclohexyl	"	NCOCH ₃ · HCl		209 (35)	179 (—)	110 (—)	83 *	55 (75)	67 (86)	41 (18)	43 (100)	194 ^{s)} (4)	137 ^{t)} (62)	112 ^{u)} (11)			
XX	Morpholino	"	NCOC ₆ H ₅ · HCl		274 (1)	244 (4)	113 (—)	86 (2)	56 (5)	105 *	77 (100)	51 (30)	139 ^{f)} (1)					
XXI	"	"	NCO ₂ C ₂ H ₅		242 *	212 (9)	113 (2)	86 *	56 (42)	42 (100)			197 ^{v)} (4)	168 ^{w)} (6)	140 ^{x)} (44)	101 ^{g)} (4)		
XXII	C ₆ H ₅	N	NH · HCl		162 *	132 (4)	105 (6)	77 *	51 (100)				131 ^{f)} (2)					
XXIII	o-CH ₃ · C ₆ H ₄	"	"		176 (2)	146 (6)	119 *	91 *	65 (100)				145 ^{f)} (2)					
XXIV	p-Cl · C ₆ H ₄	"	"		196 (2)	166 (10)	139 (28)	111 *	75 (100)				165 ^{f)} (6)					
XXV		N · N(NO)CH ₂ CN			170 (—)	140 (13)	114 ^{h)} (8)	86 *	56 (16)	42 (64)	28 (90)		139 ^{f)} (26)					

†) With a Hitachi RMU-6D double-focusing mass spectrometer, direct inlet system, ionizing energy of 70 eV, ion source temperature below 150 °C, evaporation temperature below decomposition temperature of each compound.

- a) M·C₅H₁₀ b) m/e 112·CH₃ c) M·C₅H₆ d) M·C₃H₇ e) m/e 99·NO· f) M·HNO g) R₁NH h) m/e 140·CN i) M·R₂
j) m/e 178·CH₃ k) m/e 178·R₂ l) M— m) m/e 127·NO· n) m/e 152— o) m/e 172·CH₃ p) C₆H₅CHCNH
q) C₆H₅CNH r) m/e 168·CO s) M·CH₃ t) M·(NO·+CH₂CO) u) M·(CH₃+) v) M·OC₂H₅ w) m/e 212·CO₂
x) m/e 168·C₂H₄

*: Metastable peak.

grate partially to the carbon at 4 position during the measurement.

A fragment peak at m/e 101 arising from (XIV) and (XV) is assigned to iminomorpholium ion. The 5-N-deuterio derivative of (XV) gave a peak at m/e 102 instead of the peak at m/e 101. 3-Dimethylaminosydnonimine (XIII) showed a fragment peak of $(CH_3)_2 N^+ = NH$ at m/e 59, whereas sydnones and sydnonimines with 5-N-acyl or 3-alkyl did not undergo such a fragmentation. Therefore these fragments will be formed by migration of the 5-N-hydrogens to the nitrogen at 3 position. The much abundance of these species will be caused by high stability of the quarternary ammonium structures.

The ethyl group in (XXI) seems to migrate to 5N with eliminating carbon

dioxide after expulsion of NO . The hydrogens of 5N-formyl in (XVIII) and 5N-acetyl in (XIX) transfer also to the 5N with eliminations of CO and CH_2CO , respectively. A 5N-benzoyl derivative (XX) did not show such a migration.

Fragmentations of 5-imino-oxatriazoles (XXII-XXIV) resemble to those of sydnonimines.

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Reference

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