MASS SPECTROMETRIC FRAGMENTATION OF THE PROTONATED SYDNONES UNDER CHEMICAL IONIZATION

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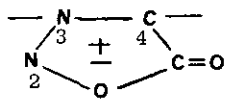
Abstract--The chemical ionization spectra of twenty protonated sydnones were measured by using methane as a reagent gas. The intense fragmentation reaction takes place from the rupture of the sydnone ring by losing of HNO and CO molecules except for 3-benzylsydnones. The benzylsydnones yield the benzylic (tropylium) cations as the base peak. The NH_4^+ protonated 3-phenylsydnone results in $[M+1]^+$ $[M+H+NH_3]^+$ and $[M+H+2NH_3]^+$ as the principal peaks without any significant fragmentations.

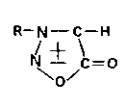
During the recent decades, the chemistry of the sydnone has been studied in some extent, such as nucleophilic substitution[1], metalation[2], functionalization via metalation.[3] Among those, the reactions are taking place at the position 4 (carbon atom). This suggests position 4 is bearing a partial negative charge



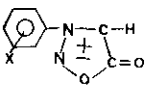
and is ready for those reactions occurring. The work dealing with EI-MS has been also carried out.[4] In general, the major fragmentation route is the elimination of an NO and a CO molecules from sydnone rings except for the series of 3-benzylsydnones, where the benzylic (tropylium) ions are the base peak. On the other hand, the theoretical calculation[5] and the acid hydrolysis[6] provide another information to support position 2 (nitrogen atom) bearing partial negative charge. Both of proposals are well supported by the experimental results. In the present study, we used CH_4 gas under electron impact producing CH_5^+ as the reagent to protonate a series of sydnones. This protonation method always takes place at stronger basic atom with higher proton affinity.[7] It can be a sensitive and easy way to detect the protonation site from the fragment ions because of the lack of the solvent effect in the gas phase. From this work, we expect to provide more accurate information for the charge distribution on the sydnone rings.

RESULTS AND DISCUSSION

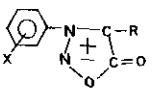
The reactions generally occuring in the CI-MS include the protonation, the proton-abstraction and the alkylation. In this work, the protonation products are the most important and their fragmentation products dominate the spectra. The site of protonation is determined by the nature of atoms or functional groups in the mole-



R



X



X R

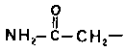
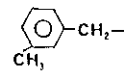
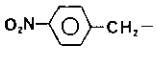
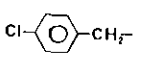
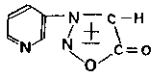
R		X		X	R	
t-Bu-	(I)	H-	(VII)	H-	Cl	(XIII)
	(II)	p -CH_3-	(VIII)	H-	Br	(XIV)
	(III)	p -EtO-	(IX)	H-	I	(XV)
	(IV)	p -Cl-	(X)	H-	CH_3	(XVI)
	(V)	p -Br-	(XI)	p -CH_3-	CH_3	(XVII)
	(VI)		(XII)	H-	CH_2OH	(XVIII)
				p -Br-	CH_2OH	(XIX)
				p -Br-	CH_2OAc	(XX)

Table I. Chemical Ionization Mass Spectra of Compounds I-XX.[a]

I. 143(73)(M+1) 87(26) 57(100).
II. 169(100)(M+1) 87(38) 83(59).
III. 144(100)(M+1) 116(11) 114(5) 85(28).
IV. 191(3)(M+1) 105(100).
V. 222(-)(M+1) 194(29) 175(3) 174(6) 163(6) 136(100).
VI. 195(2)(M+1) 125(100).
VII. 163(100)(M+1) 135(4) 131(9) 103(25) 85(19) 77(7).
VIII. 177(100)(M+1) 147(7) 146(3) 119(32) 118(13) 91(16).
VIII.[b] 211(7) 194(100) 177(22) 163(5).
IX. 207(100)(M+1) 179(4) 177(3) 176(6) 149(13) 148(15) 121(3).
X. 197(100)(M+1) 169(10) 167(4) 139(12) 138(11).
XI. 241(100)(M+1) 210(5) 183(11) 182(15).
XII. 164(100)(M+1) 136(6) 134(11) 133(4) 106(10) 105(19).
XIII. 197(100)(M+1) 139(10) 138(37) 105(10) 77(19) 69(14).
XIV. 241(100)(M+1) 211(3) 210(4) 182(32) 106(33) 105(10) 77(27).
XV. 289(100)(M+1) 259(5) 230(44) 162(9) 132(11) 77(10).
XVI. 177(100)(M+1) 119(11) 118(83) 106(6) 77(4).
XVII. 191(100)(M+1) 133(93) 120(8) 91(10).
XVII.[b] 225(6) 208(100) 191(4) 149(4) 132(5).
XVIII. 193(39)(M+1) 175(100) 135(39) 134(19) 117(9) 106(6) 77(3).
XIX. 271(100)(M+1) 253(21) 212(53) 195(28) 183(22) 182(11) 77(4).
XX. 329(3)(M+1) 270(20) 269(100) 195(5) 182(3).

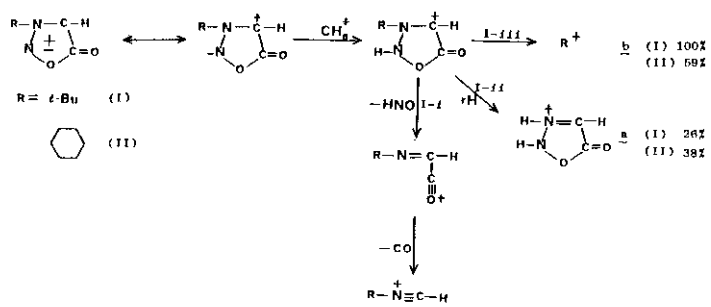
a. methane reagent gas was used.
b. ammonia reagent gas was used.

cule, such as their proton affinity. This meso-ionic compound, sydnones, contains more than one active site which could be protonated. The result from the competitive protonation will be deducted from their fragment ions based on the information obtained from EI-MS of the similar compounds. The CI-MS of twenty compounds, summarized in Table I, were measured. In order to discuss fragmentation of those compounds, they are divided into three classes as 3-alkylsydnones, 3-arylsydnones and 3-phenyl-4-substituted sydnones.

3-Alkylsydnones:

The characteristic ion in the CH_4 CI-MS of an extensive series of alkanes has been reported as abundent $[M-1]^+$ ions because of hydride abstraction is more feasible rather than protonation.[8] The protonation of 3-cyclohexyl- and 3-t-butylsydnones (I, II) results in $[M+1]^+$, $[M+2-R]^+$ and R^+ ions with the absence of $[M-1]^+$ ions. By comparison of this data with the general trend of alkanes, it is presumed that the protonation is occurring at sydnone rings. The fragmentation leading to lose of an HNO molecule suggests that the protonation site is at position 2 (nitrogen atom). The protonation of position 2 and following fragmentation can be depicted in Scheme I. The formation of $[M+2-R]^+$, a, must involve the cleavage of R-N bond with the positive charge retained at the ring accompanied by a hydrogen atom transfer from the alkyl group to the sydnone ring (I-ii). This cleavage also results in alkyl cation b (I-iii). A weaker peak of cyclohexyl ion could be accounted for by the formation of less stable secondary cation.

Scheme I

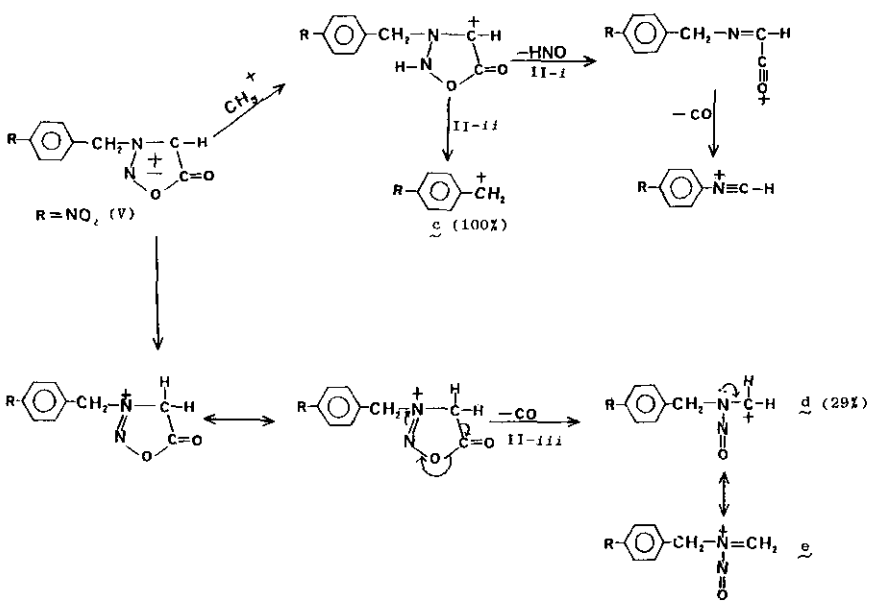


The functionalized alkylsydnones (III-VI) contain an additional site for protonation. This can complicate the spectra in some extent. The intensities of the protonated benzylsydnone ion $[M+1]^+$ are very weak. The major reaction channel primarily leads to benzylic type ion c (II-ii) as in the case of the simple alkylbenzene.[9] The protonation can take place either at phenyl ring or at sydnone ring. However, there is only one way to produce benzylic cation, i.e. sydnone ring with heterolytic cleavage.

Although the nitro group is the fragmentation center in the nitro-compounds,[10] it is also expected to complicate the spectrum of protonated compound V. The major fragment ions can also be rationalized as previous compounds in Scheme II. The formation of m/z 194, d, (29%) must involve a process with rupture of a CO molecule. Loss of a CO molecule to initiate the fragmentaion is the first observation from CI-MS as well as EI-MS in the series of sydnones. In order to lose

CO from [M+1]$^+$ ion, the protonation site should be different, If the phenyl ring accepts a proton from CH_5^+, the fragmentation of sydnone ring should follow the EI mode by losing of NO prior to CO. Therefore, the alternative process must take place where protonation at position 4 followed by the loss of CO resulted in the positive charge at nitrogen atom (II-iii). The resultant cation can be stabilized by the lone pair electrons on the nitrogen atom to form ion e as illustrated in Scheme II.

Scheme II



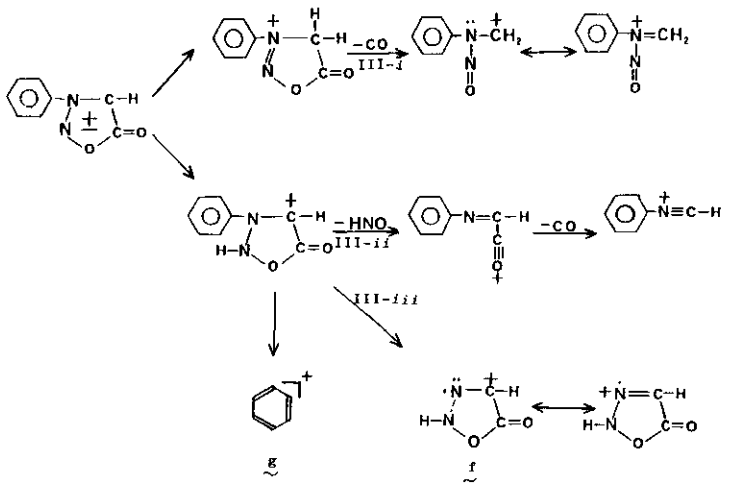
3-Arylsydnones:

In the CI-MS of the aromatic molecules, including polycyclic aromatics show only [M+1]$^+$.[9] According to this, the protonated phenyl ring of 3-arylsydnones would give no competitive fragmentation reaction between protonated phenyl ring and the sydnone rings. However, the chemistry of protonated substituents on the phenyl ring depends upon their nature. In general, splitting between two rings occurs only in a small extent because of strong bonding energy between two aromatic rings resulting in [M+1]$^+$ peaks with moderate intensities, and therefore, the loss of HNO and CO molecules is still a major reaction pathway.

The competition between phenyl ring and sydnone ring to accept a proton from CH_5^+ can be deducted from the CI-MS of 3-arylsydnone. The protonated sydnone ring will result in losing an HNO and a CO molecules (vide supra). On the other hand, protonated phenyl ring doesn't lead to the fragmentation of phenyl ring, but to the cleavage of sydnone ring with loss of an NO and a CO molecules as in the EI fragmentation mode. Actually, the loss of an HNO and a CO is the major fragmentation pathways in this series of compounds. This suggests that the protonation at sydnone ring is predominant and the loss of a CO molecule prior to the elimination of an HNO is observed in the CI-MS of this series of compounds. The fission of

two rings can be either homolytic process to yield f (19%) or a heterolytic process to yield phenyl cation g (7%) as shown in Scheme III.

Scheme III



The migration of the phenyl ring from position 3 to position 4 was suggested under acid hydrolysis.[6] In the gas-phase reaction the protonation is believed to be at position 2, which leads to the atom in the position 4 bearing the positive charge. The phenyl ring can also undergo a possible migration. However, there is no clear evidence to support this.

In the electron-releasing substituted phenylsydnones the rupture of [M+1]$^+$ by the loss of CO and NO molecules is equally important as the loss of HNO and CO molecules. Protonated phenyl alkyl ether is suggested to eliminate alkene forming the protonated phenol ion.[11] The CI-MS of 3-(p-ethoxyphenyl)sydnone (IX) displays the small [M+1-28]$^+$ (4%) fragment ion. The loss of 28 amu can be due to loss of either of C_2H_4 or CO molecule. If the loss of 28 amu involves the elimination of ethylene, there will be an additional loss of 28 amu for the fragmentation process of the sydnone ring. The lack of such fragmentation suggests that the fragment ion of [M+1-28]$^+$ results from the fragmentation of the sydnone ring rather than from the ethoxyl group.

The spectra of protonated arylsydnones containing the electron-attracting group (i.e. Cl, Br) are similar to other arylsydnones except for the relative intensity of [M+1-28]$^+$ ions. The fragmentation center is the sydnone ring rather than the halogen atoms. The importance of loss of CO molecule suggests that the protonation site at position 4 becomes significant by the influence of the electron-attracting groups.

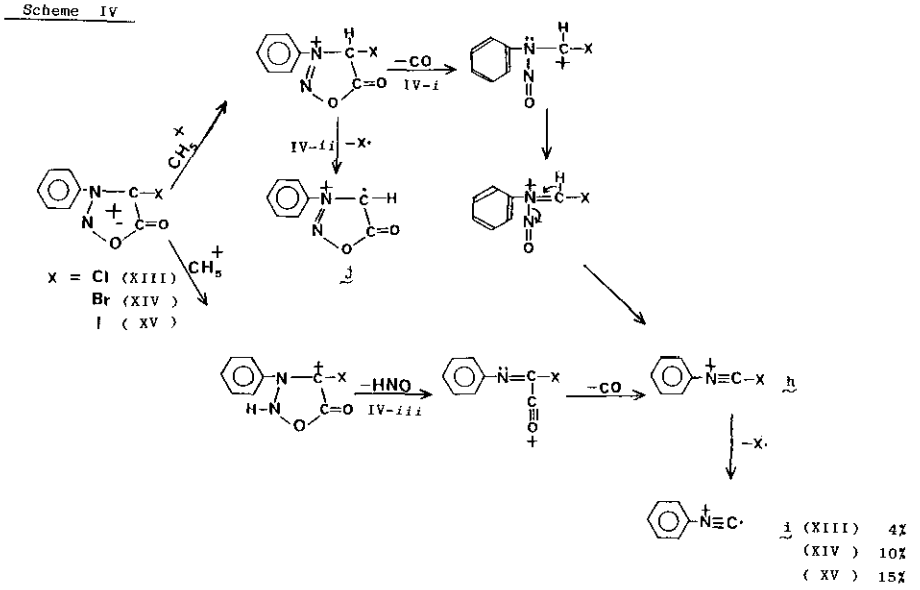
The fragmentation mode of protonated 3-pyridylsydnone (XII) is the same as that of 3-phenylsydnone (VII).

4-Substituted 3-phenylsydnones:

From the previous discussion, we already know that the phenyl ring tends to keep intact in the CI-MS. But it is expected that there are more fragmentations for the third series of compounds because substituents at position 4 of the sydnone ring contain the heteroatom bearing lone pair electrons. In some cases those heteroatoms are of high proton affinity[14] and are suggested to abstract proton from CH_5^+ resulting in significant [M+1]$^+$ ion.

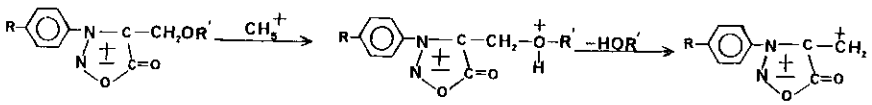
The cleavage of C-X (X=Cl, Br, I) bond from 4-halo-3-phenylsydnones takes place only in $C_6H_5\overset{+}{N}\equiv C-X$ ion h (IV-i) rather than in the sydnone ring directly. The intensities of the resultant $C_6H_5N=C^+$ i depend upon the bonding energy of C-X. The relative intensities of $C_6H_5N=C^{+\cdot}$ are 15%, 10%, and 4% in 4-I (XV), 4-Br (XIV), and 4-Cl (XIII), respectively. The weak carbon-iodine bond yields [M+1-I]$^+$ ion j (9%) (Scheme IV). Both reaction pathways in Scheme IV are some of the few examples of formation of an odd-electron product in the proton transfer chemical ionization.

Scheme IV



The protonated 4-hydroxymethylenesydnones (XVIII, XIX) behave like the combination of an alcohol and the sydnone ring. The significant [M+1-18]$^+$ ion suggests that the dehydration takes place at the protonated hydroxyl group, but not at sydnone ring. The methylene cation k resulting from the dehydration of protonated XVIII and XIX is believed to be stabilized by the meso-ionic ring as in the benzylic system. The relative intensities of [M+1-18]$^+$ significantly change from compound XVIII to XIX (Scheme V). This reaction is controlled by the substituent on phenyl ring. The bromine atom destabilizes the methylene cation through the resonance effect resulting in low population of ion k.

Scheme V



R	R'		k
H	H	100	74
Br	H	100	21
Br	Ac	3	100

Acetylation of compound XIX gave compound XX. The fragmentation of protonated compound XX resulted in loss of CH_3COOH as the the base peak. This is due to higher proton affinity of acetoxyl group. Bromine atom does not reduce the intensity of the fragment ion k as in the case of hydroxymethylated compounds (XVIII, XIX) (Scheme V). The elimination of a carboxyl group became possible and energetically feasible because the protonation step is sufficiently exothermic leading to further fragmentation to yield $[M+1-60]^+$. [13]

The intense fragmentation of CH_4 CI-MS suggests that the proton transfer process is a highly exothermic reaction. We investigated the fragmentation of NH_3 CI-MS. The NH_3 CI-MS displays major peaks $[M+1]^+$, $[M+18]^+$ as well as $[M+35]^+$ without further significant fragmentation. The high proton affinity of ammonia results in relatively low exothermic reaction. The intense $[M+1]^+$ or NH_3 adduct ions without fragmentation indicate the high proton affinity (@ 946 KJ/mol) of the sydnone rings.

CONCLUSION

The protonation in the gas-phase might be better way to study the nature of these mesoionic compounds. From our study of protonation of sydnones in the gas-phase, based on the fragmentation patterns, we believe that the major protonating site is at position 2 (nitrogen atom) and the minor is at position 4 (carbon atom). In most cases, the negative charge is more likely to locate at position 2. The electron-attracting substituent of a phenyl ring enhances the drawing the electron away from the nitrogen atom and further decreases the electron density on that nitrogen atom (position 2). This observation is consistent with theoretical calculations and supports the proposed mechanisms of the acid hydrolysis as well. That confirms the dual properties of this mesoionic compounds.

The migration of the phenyl ring from position 3 to 4 in the acid hydrolysis of phenylsydnone had been suggested. But no evidence for this was observed. This forbidden process might be caused by the rigid planar character of sydnone ring that prevents the interaction pf $p_{(phenyl)}$-$p^*_{(carbon\ cation)}$ in the reaction intermediate or by alternating electron distribution of phenyl ring between positions 2 and 4 through a hyperconjugative resonance.

The CI-MS often gives a stable molecular protonated ion $[M+1]^+$. The labile

sydnone ring undergoes intense fragmentation in CI-MS under substantial influence of the substituent of the sydnone rings. Those features can be useful for the identification of the compound. The substantial fragmentation in the CH_4 CI-MS could be due to high exothermic reaction during the proton transfer process. Only $[M+1]^+$, $[M+18]^+$ and $[M+35]^+$ were observed in the NH_3 CI-MS which suggests the high proton affinity of the sydnone rings. This evidence further supports the suggestion that the protonation site of this series by CH_5^+ will be at sydnone ring rather than on the substituents.

EXPERIMENTAL

The CI mass spectra were obtained on a JEOL model JMS-DX 300 double focusing mass spectrometer. Samples were introduced via a direct insertion probe; source temperature was kept at 75°C. The trap current for the 220 eV CI mass spectra was regulated at 300 μA while the accelerating voltage was maintained at 3 kV. A variable leak inlet was used to regulate a methane or an ammonia reagent gas pressure of 5.0×10^{-4} torr.

Previously published procedures were used for the preparation of 3-t-butylsydnone I;[20] 3-cyclohexylsydnone II;[15] 3-(aminocarboxymethyl)sydnone III;[24] 3-(m-methylbenzyl)sydnone IV;[20] 3-(p-nitrobenzyl)sydnone V;[21] 3-(p-chlorobenzyl)sydnone VI;[15] 3-phenylsydnone VII;[16] 3-p-tolylsydnone VIII;[15] 3-(p-ethoxyphenyl)sydnone IX;[17] 3-(p-chlorophenyl)sydnone X;[15] 3-(p-bromophenyl)sydnone XI;[18] 3-pyridylsydnone XII;[19] 3-phenyl-4-chlorosydnone XIII;[1b] 3-phenyl-4-bromosydnone XIV;[1b] 3-phenyl-4-iodosydnone XV;[25] 3-phenyl-4-methylsydnone XVI;[22] 3-(p-tolyl)-4-methylsydnone XVII;[23] 3-phenyl-4-hydroxymethylsydnone XVIII;[26] 3-(p-bromophenyl)-4-hydroxymethylsydnone XIX;[26] and 3-phenylsydnonylmethyl acetate XX.[26]

ACKNOWLEDGEMENTS

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