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Chemical Ionization Mass Spectrometry of Bifunctional Compounds. The Behaviour of Bifunctional Compounds on Protonation

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Positive-ion chemical ionization mass spectra were measured for simple bifunctional aromatic compounds of the type p-$XCH_2C_6H_4CH_2Y$, where $X = NH_2$, $NH(CH_3)$ and $N(CH_3)_2$ and $Y = OH$ and OCH_3. For each compound, essentially only three peaks of ions, $[MH]^+$, $[MH - XH]^+$ and $[MH - YH]^+$, appeared. The *B/E* constant linked-scan spectra showed that the stable non-decomposing $[MH]^+$ had the proton only on the nitrogen-containing functional group. From these data, the relative amounts of total protonation, the ratio of *N*- and *O*-protonation and the fraction of fragmenting $[MH]^+$ can be calculated. The ease of protonation (protonation susceptibility) and the reactivity (fragmentation capability) of the respective functional groups are discussed.

INTRODUCTION

Positive-ion chemical ionization mass spectrometry (CIMS) has been widely used in various fields of organic chemistry. The scope and limitations of this ionization method,[1–12] the characteristics of CI fragmentations[13,14] and the behaviour of even-electron organic cations in the gas phase[15–20] are well documented. However, the precise mechanistic investigation of fragmentation reactions from the physical organic point of view has been initiated only recently.[21–30] The aim of our work is to re-examine fragmentation rules in CIMS in general, and to establish the trend of bond fission of multifunctional compounds in particular. This paper describes a detailed study of the behaviour of some simple bifunctional organic compounds toward protonation.

We first selected a series of aromatic compounds of the type p-$XCH_2C_6H_4CH_2Y$, where $X = NH_2$, $NH(CH_3)$ and $N(CH_3)_2$ and $Y = OH$ and OCH_3. These compounds are suitable for our purposes for several reasons: (i) the carbon skeleton is simple and symmetric and thus eliminates any possible, unnecessary structural factors in interpreting the observed data, (ii) the central part of the compound is a very rigid benzene ring skeleton, which provides little chance for two functional groups X and Y to interact each other, e.g. proton bridging or intramolecular proton transfer between them is sterically improbable, (iii) one saturated carbon atom (CH_2) is inserted between the functional group and the benzene ring, which excludes the direct conjugative interaction between X and Y through the aromatic nucleus, and (iv) very facile fragmentations at both functional groups from the protonated molecule are expected because of the benzylic stabilization of positive charge in fragment ions.

The only disadvantage conceivable for this type of compound is a direct involvement of aromatic π-electrons as a proton acceptor. However, as far as fragmentations in normal and metastable ion spectra are concerned, we have had no indication of the interference from the protonation on the benzene nucleus of our compounds.

EXPERIMENTAL

Synthesis of compounds

Compounds **1**–**6** were synthesized by standard procedures from commercially available starting materials. p-Aminomethylbenzyl alcohol (**1**) was prepared by reduction of p-cyanobenzaldehyde with sodium tetrahydroborate followed by diborane reduction of the cyano group.

Acetylation of **1** with a limited amount of acetic anhydride in acetic acid gave an *N*-acetyl compound, the hydroxyl group of which was then protected as the tetrahydropyranyl ether. Methylation with methyl iodide and sodium hydride in tetrahydrofuran (THF) afforded the corresponding *N*-methyl compound, which was then treated with hydrochloric acid to remove both the *N*-acetyl and the *O*-tetrahydropyranyl protective groups to give **2**. The Eschweiler–Clarke reaction of **1** with formaldehyde and formic acid yielded the *N*,*N*-dimethyl compound **3**.

Methylation of p-cyanobenzyl alcohol with methyl iodide and sodium hydride in THF, followed by diborane reduction, yielded p-aminomethylbenzyl methyl ether (**4**). Similar treatment of **4** as for **1** gave **5** and **6**. All compounds were purified as their crystalline hydrochlorides. (Supplementary material for detailed synthetic procedures for **1**–**6** is available on request.)

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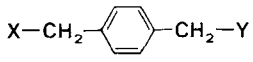

Compound	X	Y
1	NH_2	OH
2	$NH(CH_3)$	OH
3	$N(CH_3)_2$	OH
4	NH_2	OCH_3
5	$NH(CH_3)$	OCH_3
6	$N(CH_3)_2$	OCH_3

Mass spectra

Normal CI mass spectra were measured with a Shimadzu LKB 9000A mass spectrometer/GCMS-PAC-90 computer system. The source pressure was checked with an MKS Baratron Type 221A manometer. The spectra were recorded at a source temperature of 190 °C and an accelerating voltage of 3.5 kV. The total emission current was 120 μA and the electron energy 150 eV. Solid samples of hydrochlorides of **1–6** were introduced directly from a solid insertion probe.

Linked-scan mass spectra were measured on a Hitachi M-80A mass spectrometer on-line with an M-003 data system under the following conditions: accelerating voltage, 3 kV; electron energy, 100 eV; emission current, 100 μA; source temperature, 190 °C. Collisional activation in the first field-free region was performed by using helium as the collision gas, leading to a reduction of the main beam intensity of 30%.

Normal methane CI mass spectra of **1–6** are given in Table 1. Essentially only three peaks of ions appeared for each compound: $[MH]^+$, $[MH - XH]^+$ and $[MH - YH]^+$.

Calculation of thermochemical critical energy

The thermochemical critical energy (E^N) of the C—N bond cleavage shown in Table 5 was estimated by calculating the difference in the standard heats of formation of the protonated molecule and the corresponding fragments.

Standard heats of formation of neutral species, not available in a recent compilation,[31] were approximated by the well known Franklin's additivity rule.

The proton affinity (PA) of each functional group was estimated from published values for monofunctional compounds:[31] benzyl alcohol 789, benzylamine 907 and *N*,*N*-dimethylbenzylamine 954 kJ mol^{-1}. Since these values are very similar to those for the corresponding ethyl compounds (i.e., ethanol 788, ethylamine 908 and *N*,*N*-dimethylethylamine 952 kJ mol^{-1}), the PA of the methoxyl group of compounds **4–6** was estimated to be 822 kJ mol^{-1} (PA of ethyl methyl ether = 822 kJ mol^{-1}) and that of the *N*-methylbenzylamino group of **2** and **5** to be 932 kJ mol^{-1} (methylethylamine 932 kJ mol^{-1}).

Standard heats of formation of fragment ions were calculated by using the previously reported method.[32] The heat of formation of the reference cation, the *p*-methylbenzyl cation, was taken as 837 kJ mol^{-1}.[31]

Table 1. Normal methane CI mass spectra of compounds 1–6

No.	Compound X	Compound Y	Relative intensity of peaks (%) $[MH]^+$	$[MH - XH]^+$	$[MH - YH]^+$	Total
1	NH_2	OH	2	40	58	100
2	$NH(CH_3)$	OH	6	32	62	100
3	$N(CH_3)_2$	OH	11	22	67	100
4	NH_2	OCH_3	2	53	45	100
5	$NH(CH_3)$	OCH_3	9	41	50	100
6	$N(CH_3)_2$	OCH_3	19	27	54	100

RESULTS AND DISCUSSION

Site of protonation

The first question one might raise in interpreting the spectra of bifunctional compounds is where the proton from the reactant ion will reside in the protonated molecule. From experimental results for monofunctional compounds, it is clear that the protonation usually occurs with high efficiency only when the proton transfer process is exothermic.[33] Consequently, one can assume that, when a substrate molecule has two functional groups X and Y that can accommodate a proton from the reactant ion $[RH]^+$, both functional groups are protonated if $PA(X) > PA(R)$ and $PA(Y) > PA(R)$, but only one functional group, e.g. X, is protonated selectively if $PA(X) > PA(R) > PA(Y)$.

For **1–6**, the estimated proton affinity of each functional group is in the range from about 789 (OH) to 822 kJ mol^{-1} (OCH_3), and from about 907 (NH_2) to 954 kJ mol^{-1} ($N(CH_3)_2$).[31] Therefore, if methane (PA = 551 kJ mol^{-1})[31] is used as a reagent gas, both *N*- and *O*-functional groups can be protonated, whereas with ammonia (PA = 854 kJ mol^{-1}) only the *N*-functional group would be protonated.

It should also be noted that the protonated molecules formed are not necessarily stable enough to be observed. Some of them are vibrationally excited and may subsequently decompose. The term 'fragmenting $[MH]^+$' has been proposed.[34]

Local bond weakening on protonation

It appears that protonation will give rise to internal excitation of a given molecule and thus cause a loss of labile groups even when they are located at positions remote from the site of protonation. However, bond cleavages often seem to be triggered by the formal positive charge arising from the protonation of the functional group. It has already been shown that this is actually the case.[34]

For **1–6**, the local bond weakening on protonation can be demonstrated by three lines of evidence. First, we calculated the bond index differences between protonated and neutral molecules by the semi-empirical molecular orbital method. The bond weakening was shown to take place around the functional group on which the protonation occurs, and this may cause a cleavage of that part of the molecule. The detailed results of calculation will be reported elsewhere.

Secondly, in deuterated isobutane-mediated CI mass spectra, the fully methylated compound **6**, which has no exchangeable active hydrogen atoms, clearly showed an $[MD - CH_3OD]$ peak. The alternative

$[MD - CH_3OH]$ peak did not appear at all in the spectrum. This result indicates that the deuterium atom from the reactant ion was first attached to the ether oxygen atom and was eliminated as methanol from that part of the molecule. If the *N*-deuterated counterpart is a precursor ion of this fragmentation, the elimination of CH_3OD is not expected because direct transfer of a deuterium atom from N to O is improbable.

More direct and unequivocal evidence was obtained by combining selective protonation and collision-induced dissociation (CID) of these compounds. By using ammonia as reagent gas, we can protonate only the *N*-containing groups and thus produce the protonated molecule of a sole structure. The metastable ion spectra of this *N*-protonated molecule obtained by using the *B/E* constant linked-scan technique together with collision-induced dissociation clearly showed that from **4**, for instance, the $[MH - NH_3]^+$ ion was formed exclusively and the $[MH - CH_3OH]^+$ ion was not formed at all (Table 2). Consequently, it is evident that, when the protonation occurs at the amino group, the only fragmentation observed is the elimination of that amino group even if the protonated molecule is sufficiently energized. Therefore, we can conclude that the bond cleavage in CI fragmentations is responsible for *the effective* bond weakening by protonation on an appropriate position of the substrate molecule.

Relative amounts of protonated species

On the basis of local bond weakening on protonation discussed above, we can assume that for our compounds $[MH - amine]^+$ ions originate only from the *N*-protonated molecule and $[MH - ROH]^+$ ions only from the *O*-protonated counterpart. Surprisingly, metastable ion spectra mediated by isobutane or even methane showed that the observed fragmentation of stable protonated molecules involved only the elimination of ammonia or methylated ammonia, even under collisionally activated conditions (Table 2). This result indicates that all of the stable, non-decomposing $[MH]^+$ ions from our compounds are *N*-protonated species.

Since the strong $[MH - ROH]$ peak appeared in the normal spectrum with methane or isobutane, the above result also suggests that, when the protonation occurs at the *O*-functional group of our compounds, the resulting species are not stable enough to be observed and subsequently decompose to give $[MH - ROH]^+$ ions, whereas *N*-protonated species either survive as $[MH]^+$ or decompose to afford only $[MH - amine]^+$ ions.

We can now calculate the relative amounts of incipient *O*- and *N*-protonation from the observed normal spectral data. Since essentially only three peaks of ions, $[MH]^+$, $[MH - amine]^+$ and $[MH - ROH]^+$ appeared in each spectrum, initial *O*-protonation is equivalent to the abundance of the $[MH - ROH]^+$ ion, whereas *N*-protonation corresponds to the sum of the abundances of $[MH]^+$ and $[MH - amine]^+$ ions.

In order to analyse the protonation behaviour of the compounds more clearly, the methane-CI spectral data in Table 1 were recalculated in the following manner. We can assume that the protonation probability is virtually constant if the structure of the functional group is the same. Thus, if we take the data for **1** as a standard, the amount of initial *O*-protonation on OH should be constant, and should have the values of 58% also for **2** and **3**. In a similar way, the amount of initial *N*-protonation for **4** should be the same as that for **1**, and has a value of 42% instead of 55%. Then, the initial *O*-protonation of **4** becomes 34% instead of 45%, and this value may also be applicable to **5** and **6**. The recalculated data are given in Table 3. The relative peak intensity ratios of ions $[MH]^+$, $[MH - amine]^+$ and $[MH - ROH]^+$ for a respective compound are, of course, the same as those in Table 1, but the total abundance of ions is not normalized to 100%. Therefore, the values in Table 3 roughly reflect the actual relative abundance of the ions formed in the ion source.

As can be seen from Table 3, the initial *O*-protonation is constant for **1**, **2** and **3**, as assumed because of the same functional group structure, but the initial *N*-protonation decreases as the number of *N*-methyl groups increases. This is the reverse order of the *PA* values of these functional groups. This is also the case for **4**, **5** and **6**. Essentially the same trend was found between OH and OCH_3 for constant *N*-functional groups when the values for **1** and **4**, for **2** and **5**, and for **3** and **6** were compared. The amount of initial protonation on OCH_3 is smaller than that on OH, despite the larger *PA* value of the former.

Longevialle *et al.*[21] have already pointed out the similar apparent lack of correlation between relative protonation ratios and *PA* values of functional groups in isobutane CI spectra of conformationally rigid, *trans*-diaxial amino alcohols: the ratio of protonation cross-

Table 2. Linked-scan mass spectra of $[MH]^+$ ions of compounds 1, 4 and 6[a]

			Relative intensity of peaks (%)					
			B/E constant linked-scan			CID-*B/E* constant linked-scan		
Compound	Neutral lost	*m/z*	CH_4	i-C_4H_{10}	NH_3	CH_4	i-C_4H_{10}	NH_3
1	NH_3	121	—	—	4	—	—	19
	H_2O	120	—	—	[b]	—	—	[b]
4	NH_3	135	7	5	5	21	38	25
	CH_3OH	120	[b]	[b]	[b]	[b]	1	[b]
6	$NH(CH_3)_2$	135	4	2	2	12	17	14
	CH_3OH	148	[b]	[b]	[b]	[b]	1	[b]

[a] The intensity of monitored precursor ion $[MH]^+$, was taken as 100%.
[b] Less than 1%.

Table 3. Corrected relative intensity of peaks (methane)

No.	Compound X	Compound Y	Relative intensity of peaks (%) $[MH]^+$	$[MH-XH]^+$	$[MH-YH]^+$	Initial *N*-protonation (%)	Initial *O*-protonation (%)	Total protonation (%)
1	NH_2	OH	2	40	58	42	58	100[a]
2	$NH(CH_3)$	OH	6	30	58	36	58	94
3	$N(CH_3)_2$	OH	10	19	58	29	58	87
4	NH_2	OCH_3	2	40	34	42	34	76
5	$NH(CH_3)$	OCH_3	6	28	34	34	34	68
6	$N(CH_3)_2$	OCH_3	12	17	34	29	34	63

[a] Compound **1** was taken as an arbitrary standard.

section of NH_2 and OH is approximately 55/45 and that of $N(CH_3)_2$ and OH is 39/61.

It is of interest that the extent of initial *N*-protonation is essentially the same if the structure of the *N*-functional group is the same, as is assumed for *O*-functional groups, when the data for **2** and **5** and for **3** and **6** are compared. The amount of total protonation also shows a regular tendency, the value being the largest for **1** (no *N*- or *O*-methyl group) and the smallest for **6** (fully methylated). This is simply because the methylation of either NH_2 or OH functions make the protonation on that group difficult.

When we examined the data for the isobutane CI spectra, essentially the same conclusion regarding the protonation behaviour was obtained (Table 4).

Protonation susceptibility of functional groups

The above data show the relative ease of protonation of a particular functional group within a molecule. The order in methane CI spectra appears to be $OH > NH_2 > NH(CH_3) = OCH_3 > N(CH_3)_2$, with a seemingly fortuitous coincidence of values between $NH(CH_3)$ and OCH_3 (Table 3). In the isobutane CI spectra, the two *O*-functional groups (OH and OCH_3) shifted two positions down in the sequence to give the order $NH_2 > NH(CH_3) = OH > N(CH_3)_2 > OCH_3$ (Table 4).

These results also indicate the dependence of the protonation selectivity of a reactant ion on the protonation exothermicity. When a very strong Brønsted acid such as CH_5^+ is used as a reactant ion, the protonation exothermicity is very large, and the protonation takes place effectively at any functional groups, regardless of their *PA*.

For our compounds, intramolecular proton exchange between X and Y in protonated molecules would not occur for steric reasons. Direct intermolecular proton exchange between X and Y may not be expected either, since the protonated molecule cannot collide with the substrate but actually collides only with the reagent gas molecule R in the ion source because of the much lower concentration of the former than the latter. The collision of the initially formed, excited protonated molecule with R (reagent gas) would not effectively lead to any back-donation of the proton to R if the *PA* of R is much smaller than that of the substrate, as is the case for CH_4. Thus, under these conditions, proton exchange equilibrium is not attained among protonated molecules.

When the protonation exothermicity decreases, e.g. for NH_4^+, partial, if not complete, exchange of the proton among protonated molecules would occur, since the probability of proton removal through the collision of R possibly increases, i.e. the reagent gas molecule R can act to some extent as a proton carrier among protonated molecules. In this case, the protonation selectivity is considered to be relatively high. For our compounds, for example, only the amino function is protonated by NH_4^+.

Fraction of *N*-protonated fragmenting $[MH]^+$

As was discussed above, all the *O*-protonated species of our compounds decompose immediately to afford $[MH - ROH]^+$ ions, whereas a certain fraction of *N*-protonated species can decompose to give $[MH - \text{amine}]^+$ ions. The data in Table 5 show that the fraction of these fragmenting $[MH]^+$ ions in total *N*-protonation decreases as the number of *N*-methyl group increases. The trend appears to be correlated

Table 4. Corrected relative intensity of peaks (isobutane)

No.	Compound X	Compound Y	Relative intensity of peaks (%) $[MH]^+$	$[MH-XH]^+$	$[MH-YH]^+$	Initial *N*-protonation (%)	Initial *O*-protonation (%)	Total protonation (%)
1	NH_2	OH	45	18	37	63	37	100[a]
2	$NH(CH_3)$	OH	33	5	37	38	37	75
3	$N(CH_3)_2$	OH	31	1	37	32	37	69
4	NH_2	OCH_3	44	19	25	63	25	88
5	$NH(CH_3)$	OCH_3	32	4	25	36	25	61
6	$N(CH_3)_2$	OCH_3	31	1	25	32	25	57

[a] Compound **1** was taken as an arbitrary standard.

Table 5. Effects of *N*-functional group on fragmenting $[MH]^+$

No.	Compound X	Compound Y	Fraction of fragmenting *N*-protonated $[MH]^+$ (%) CH_4	Fraction of fragmenting *N*-protonated $[MH]^+$ (%) $i\text{-}C_4H_{10}$	Estimated critical energy, E^N (kJ mol^{-1})	ΔE^N [a] (kJ mol^{-1})	Estimated *PA* of *N*-functional group (kJ mol^{-1})	ΔPA[a] (kJ mol^{-1})
1	NH_2	OH	95	29	121	0	907	0
2	$NH(CH_3)$	OH	83	13	172	51	932	25
3	$N(CH_3)_2$	OH	66	3	211	90	954	47
4	NH_2	OCH_3	95	30	120	0	907	0
5	$NH(CH_3)$	OCH_3	82	11	172	52	932	25
6	$N(CH_3)_2$	OCH_3	59	3	211	91	954	47

[a] Relative to the NH_2 group of compounds 1 and 4.

with the thermochemically estimated critical energy (E^N) of the C—N bond cleavage (Table 5).

The protonation exothermicitiy, which is considered to be an important energy source for fragmentation, is merely a maximum internal energy that the protonated molecule may possess. Several hundred collisions with reagent gas molecules of this initially formed excited $[MH]^+$ in the ion source may result in the dissipation of a certain proportion of this excess energy and, therefore, the average internal energy of the protonated molecule tends to shift to the lower energy side.

In Fig. 1, the area under the $P(E)$ curve represents the amount of initial *N*-protonated species. Now, if the *PA* of the *N*-functional group becomes larger as the number of *N*-methyl group increases, the protonation exothermicity will be larger and, accordingly, the range of the $P(E)$ curve will be wider by the *PA* difference (ΔPA) of the *N*-functional groups. On the other hand, the area under the curve must be smaller because of the inhibitory effect of *N*-methyl groups on protonation (see above). Further, the critical energy of the fragmentation, E^N, becomes larger as the number of *N*-methyl groups increases, and this energy increment (ΔE^N) exceeds the ΔPA for our compounds. The net result should be a decrease in the fraction of the fragmenting $[MH]^+$ ions, as is observed, if we assume that the proportion of the energy dissipation is similar for each compound.

Since the *PA* of the eliminated amino compounds, NH_3, $NH_2(CH_3)$ and $NH(CH_3)_2$, increases in this order, the above result appears to be an extended version of Field's suggestion[35] for the reactivity of monofunctional compounds, that the extent of fragmentation is inversely proportional to the *PA* of the eliminated group if the residual structure of the substrate is the same. Therefore, one can conclude that in a pair of *para*-substituted aromatic compounds of the type $XCH_2C_6H_4CH_2Y$ and $X'CH_2C_6H_4CH_2Y$, the less basic functional group, e.g. X, can be cleaved more easily than the more basic X′ at constant Y in our compounds. However, this relationship seems to be valid only when the structural difference between X and X′ is relatively small, e.g. between OH and OCH_3, or among a series of methylated amino groups. The conclusion is, therefore, not justified for compounds where a large structural change of functional groups is involved.

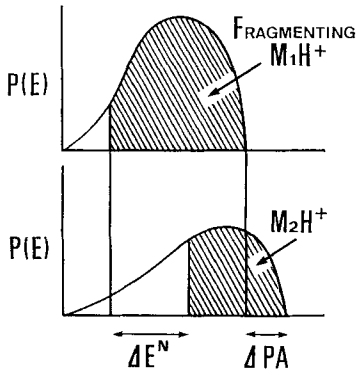

Figure 1. Schematic representation of $P(E)$ *vs.* E curves for two different protonated molecules. The shaded area corresponds to the fragmenting $[MH]^+$ ion of each compound.

Fragmentation capability of functional groups

One of the most important problems in the spectra of bifunctional compounds is how to predict the relative fragmentation capabilities of particular functional groups within a molecule. In terms of quasi-equilibrium theory (QET) the quantity of fragment ions depends largely on the $P(E)$ and $k(E)$ curves of the precursor ion, and a complete treatment of this subject will be reported in detail in a forthcoming paper. Here we shall describe only qualitatively some general features of fragmentations.

In the present series of compounds, **3** is situated in a particular position in that the peak intensity ratio [MH − amine]/[MH − ROH] is the smallest ([MH − XH]/[MH − YH] in Tables 1 and 3). This is due to the fact that the *N*,*N*-dimethylamino group can be cleaved least favourably among the three *N*-functional groups examined, whereas the hydroxyl group can fragment more easily than the methoxyl group. Compound **4**, on the other hand, is the another extreme, in which the fragmentation of the *N*-functional group takes place most readily but that of the *O*-functional group is suppressed. The amount of fragmentation of the unsubstituted primary amino group in **4** is even larger than that of the methoxyl group in the methane CI spectrum ([MH − amine]/[MH − ROH] = 1.18).

The result for **4** is surprising, since both reported and our unpublished data indicate that the amino group is almost always less reactive than the methoxyl group. In fact, a similar treatment of data for the isobutane CI spectra shows that the primary amino group can frag-

ment less favourably than the methoxyl group (Table 4). Hence the apparent reactivity of both functional groups in **4** under methane CI conditions should be regarded as an exception. Consequently, as far as compounds **1–6** are concerned, the reactivity sequence of the functional groups within a molecule would be in the order OH > $OCH_3 \gtrsim NH_2 > NH(CH_3) > N(CH_3)_2$. This order seems to be related to the *PA* values of these groups.

From these results, we can conclude that the less basic functional group is cleaved more easily even from bifunctional compounds. A useful corollary is that the fragmentation takes place more favourably from the protonated molecule that has a proton at a less basic site. For monofunctional compounds, a similar relationship has already been pointed out,[36,37] but only when competing and/or consecutive fragmentations are not significant.

The only requirement for the substrate for the present relationship to be valid is that the two functional groups are structurally independent as in **1–6**. This implies that, before the fragmentation, the intramolecular interaction between these two groups should be excluded (e.g. the proton bridging in $[MH]^+$ is not formed) and that, after the fragmentation, there is no strong interaction of one functional group with the developing positive charge in the fragment ion (e.g. the direct conjugation or neighbouring group participation, etc., is not operative). The type of bond cleavages would also be an important factor. For our compounds, both functional groups can be cleaved competitively by simple bond fission, at least formally, without any rearrangement.

CONCLUSION

In order to predict qualitatively the positive-ion mass spectral pattern of a given compound under chemical ionization conditions, it is necessary to know where the protonation occurs and where and to what extent the fragmentation takes place on the resulting protonated molecule. This work has elucidated several factors in the protonation and fragmentation of, at least, simple bifunctional compounds. Since the behaviour of protonated molecules in the ion source is of increasing importance for secondary ion mass spectrometry and fast atom bombardment mass spectrometry, we hope to generalize the trend of bond fission discussed here to some other compounds under other conditions, and to provide a detailed insight into the chemistry in a mass spectrometer.

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