Ammonium Adduct Ion in Ammonia Chemical Ionization Mass Spectrometry. Formation of Adduct Ion.

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The mechanism of formation of ammonium adduct ion, $[M+NH_4]^+$, observed in ammonia chemical ionization mass spectra, was examined by using a selected set of compounds. It was found that the adduct ion is formed preferentially when the proton affinity of the substrate molecule is close to that of ammonia.

1. Introduction

Ammonia chemical ionization mass spectrometry has recently been widely used to characterize various compounds including complex natural products.¹⁾ However, no systematic investigation has been carried out on the ammonium adduct ion, $[M+NH_4]^+$, often observed in the spectrum, though several papers have been published in the steroid field.²⁻⁴⁾ We therefore initiated a series of work to clarify the factors affecting the formation, structure, and fragmentations of this ammonium adduct ion. The present paper describes the nature and the necessary condition for the adduct ion formation.

2. Mechanism of Ammonium Adduct Ion Formation

Ammonium ion, NH_4^+ , or its cluster ion, $(NH_3)_nNH_4^+$, is considered to be a reactant ion in ammonia chemical ionization mass spectrometry. When these ions interact with the substrate molecule M in the ion source, the hydrogen-bonded complexes are initially formed (Scheme 1). At first approximation, this is considered to be a bimolecular process without intervention of any other species, and the complexes are therefore formed isoenergetically and are in the vibrationally excited state (see the hatched areas in Fig. 1). This implies that the most of the heat of reaction for the process is retained on the complexes.

If the proton affinity (P. A.) of the substrate M is larger than the P. A. of ammonia, the complexes rapidly collapse into $[MH]^++NH_3$, because the dissociation

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Scheme 1.

Fig. 1. Schematic potential energy diagram for ammonium adduct ion formation.

channel to this direction may have a small energy barrier, which is well overcome by the excess energies of the complexes (Fig. 1, a). Consequently, there would be only little chance for these complexes to be stabilized collisionally.

On the other hand, if the P. A. of the substrate is very small, the initially formed complexes would decompose back into M

+ NH_4^+ or, more simply, the complexes would hardly be formed (Fig. 1, b).

Between these extremes, there would be a case in which deactivation of the complexes by the collision with ammonia takes place effectively and gives rise to the stable adduct ion $[\text{M}+\text{NH}_4]^+$. Consideration of Fig. 1 suggested that the formation of the adduct ion would be pronounced

when the P.A. of the substrate is close to the P.A. of ammonia itself, since the shape of the potential energy diagram of Fig. 1 becomes more or less symmetrical in that situation. It is therefore expected that the ammonium adduct ion is formed favorably in a relatively narrow range of P.A. of the substrate molecule.

3. Results and Discussion

In order to substantiate the above mechanism of formation of $[M + NH_4]^+$, we have selected a set of compounds that have a different P.A. but have a similar boiling point (B.P.) (Table I), and compared the intensity of $[M + NH_4]^+$ and $[MH]^+$ peaks in ammonia chemical ionization mass spectra.

Table I. Selected Compounds Used for the Study

Compounds	P.A. ⁵⁾	B.P.	<i>m/z</i>	
	(kJ/mole)	(°C)	$[M + NH_4]^+$	$[MH]^+$
Benzyl alcohol (1)	781	205	126	109
Dihexyl ether (2)	826	208	204	187
Acetophenone (3)	850	202	138	121
<i>p</i> -Toluidine (4)	885	200	125	108
<i>N</i> -Ethylaniline (5)	924	205	139	122

When the spectrum of each compound was measured separately, data shown in Table II were obtained. Essentially no fragment ion peaks were observed under the present experimental condition. As would be expected, the intensity of $[MH]^+$ peak relative to that of $[M + NH_4]^+$ becomes larger as the P.A. of the substrate increased. The tendency is particularly remarkable for those compounds whose P.A.'s are larger than ammonia (P.A. 846 kJ/mole). The similar trend has also been reported for a series of long chain aliphatic com-

pounds⁶⁾ and steroid ketones⁷⁾ (Table III).

On the contrary, the $[M + NH_4]^+$ peak appeared for compounds whose P.A.'s are smaller than ammonia. This indicates that the collisional deactivation of the initially formed complexes occurred in a certain extent in these cases. However, the absolute intensity of the peak must be low because of the facile dissociation of the complexes to $M + NH_4^+$ as discussed above.

Table II. Relative Peak Intensity Ratio of $[M + NH_4]^+$ vs. $[MH]^+$

Compounds	$[M + NH_4]^+$	$[MH]^+$
Benzyl alcohol (1)	99%	1%
Dihexyl ether (2)	99	1
Acetophenone (3)	90	10
<i>p</i> -Toluidine (4)	38	62
<i>N</i> -Ethylaniline (5)	5	95

To compare the absolute intensity of $[M + NH_4]^+$ and $[MH]^+$ peaks among these compounds, the equimolar amount of each compound was taken together and the spectrum of this mixture was measured. This technique provides relative capabilities of ion formation under the same ion source condition. The boiling point differences of each compound are rather small (within the range of 10°C) and this serves to avoid any possible source of errors on peak intensity due to the vaporization efficiency. The *m/z* values of $[M + NH_4]^+$ and $[MH]^+$ peaks differ from one another (see, Table I), and we can easily characterize each peak as $[M + NH_4]^+$ or $[MH]^+$ for these compounds in the spectrum of the mixture.

The observed intensities of $[M + NH_4]^+$ and $[MH]^+$ peaks are plotted against the P.A. of each compound, the intensity of $[MH]^+$ peak of *N*-ethylaniline being arbi-

trary taken as 100 %. As is seen from Fig. 2, the intensity of $[MH]^+$ peak increases with P.A., whereas the intensity of $[M+NH_4]^+$ peak shows a maximum value when the sample is acetophenone.

The P.A.'s of both benzyl alcohol (1) and dihexyl ether (2) are smaller than ammonia, and consequently, the proton transfer process, $M + NH_4^+ \rightarrow [MH]^+ + NH_3$, does not occur effectively. For acetophenone (3), *p*-toluidine (4), and *N*-ethylaniline (5), the P.A. is larger than ammonia and is increasing in the order (3) < (4) < (5). This is reflected by the monotonous increase of $[MH]^+$ intensities.

On the other hand, the intensity of the ammonium adduct ion, $[M + NH_4]^+$, has a maximum at acetophenone (3). The result implies that only when the substrate molecule has a similar P.A. to ammonia, as for acetophenone (3), the initially formed complexes survive long enough, and their collisional stabilization can effectively compete either with decomposition to $[MH]^+ + NH_3$, or with dissociation back into the starting materials, $M + NH_4^+$. The long life time of the complexes would also provide a better chance to convert the structure of the adduct ion of acetophenone (3) to a protonated carbinolamine.⁸⁾ The present results can therefore be accounted for, at

Table III. Peak Ratio of $[M+NH_4]^+$ vs. $[MH]^+$

Compounds ^{6,7)}	P.A. (kJ/mole)	Peak Ratio	
		$[M+NH_4]^+$	$[MH]^+$
$CH_3(CH_2)_9CH_2CH_2OH$	791	98%	2%
$CH_3(CH_2)_9COOH$	795	93	2
$CH_3(CH_2)_9COOCH_3$	858	89	11
$CH_3(CH_2)_9OCOCH_3$	866	33	67
$CH_3(CH_2)_9NHCOCCH_3$	874	29	71
$CH_3(CH_2)_9NH_2$	900	3	97
854	95	5
> 854	15	85

Fig. 2. Peak intensity vs. proton affinity.

● Intensity of $[M+NH_4]^+$ ○ Intensity of $[MH]^+$

Numbers 1 - 5 refer to the compounds shown in Table I.

least qualitatively, by the processes depicted in Scheme 1. By using compounds with limited range of P.A. the similar argument has been presented recently.⁹⁾

4. Conclusion

The ammonium adduct ion, $[M+NH_4]^+$, in ammonia chemical ionization mass spectra is formed favorably in the case of compounds whose P.A.'s are close to that of ammonia. The mechanism of this adduct ion formation is represented in Scheme 1, where the initially formed complexes are stabilized by collision with ammonia in the ion source. Since the hydrogen bond plays an important role in these complexes,¹⁰ it also appears that a lone pair of electrons at the basic site of a substrate molecule is a necessary prerequisite for formation of $[M+NH_4]^+$ ions. Finally, it is quite instructive to note in the present context that the largest hydrogen-bonding stabilization is obtained in protonated mixed dimers $[B_1HB_2]^+$ when the basicities of B_1 and B_2 are equal.¹¹

5. Experimental

All spectra were recorded on a Shimadzu LKB 9000 A mass spectrometer at reagent gas (NH_3) pressure of 0.1 Torr. The sample was introduced through an inlet system with a reservoir heated approximately at 190°C. The ion source temperature was kept at 240–250°C. All data were based on an average of at least three scans.

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Keywords

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