

Fragmentation Reactions of Adduct Ions $[M+CH_3CO]^+$ of Isomeric Phenylenediamines

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Abstract: The dissociation routes of the adduct ions $[M+CH_3CO]^+$ formed by ion-molecule reaction of isomeric phenylenediamines with acetyl ion from acetone under chemical ionization condition were investigated by using collision-induced dissociation (CID) technique performed at ion kinetic energies of 40eV. The adduct ions are intermediate ion-neutral complexes.

Keywords: Collision-induced dissociation, phenylenediamine, ion-neutral complex.

Acetone has been used as a chemical ionization (CI) reagent gas in a conventional ion source and found to produce numerous reagent ions, which react with different classes of compounds to form a variety of adduct ions, mostly used to gain molecular masses, stereochemical structure information, to assist in the differentiation of various isomers and also to give characteristic reaction with different functional groups¹⁻⁵. Intramolecular functional group interactions play important roles in the dissociation reactions of gas-phase ions^{6,7}.

The adduct ions $[M+CH_3CO]^+$ formed by ion-molecule reactions of isomeric phenylenediamines with ion system of acetone under chemical ionization condition were studied. In order to obtain the structure of the adduct ions, their collision-induced dissociation (CID) mass spectra were obtained. The product ions of $[M+CH_3CO]^+$ of isomeric phenylenediamines are listed in **Table 1**.

Table 1. The CID result reactions of $[M+A]^+$ ($[M+A_d]^+$) from isomeric phenylenediamines

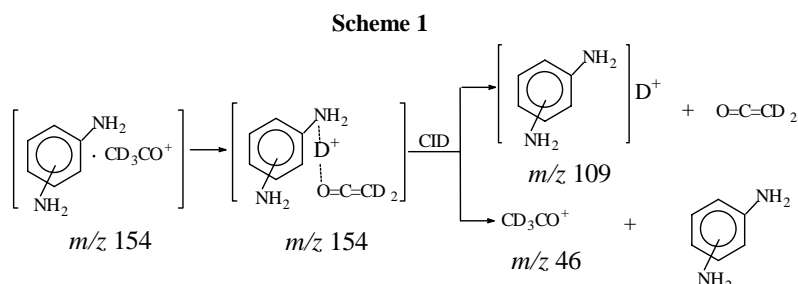
Compound	Parent ion $[M+A]^+$ (or $[M+A_d]^+$)	product ion		
		$[M+H]^+$ ($[M+D]^+$)	A^+ (A_d^+)	$[M+A-H_2O]^+$ $[M+A_d-H_2O]^+$
1	m/z 151(m/z 154)	m/z 109(m/z 110)	m/z 43(m/z 46)	m/z 133(m/z 136)
2	m/z 151(m/z 154)	m/z 109(m/z 110)	m/z 43(m/z 46)	
3	m/z 151(m/z 154)	m/z 109(m/z 110)	m/z 43(m/z 46)	

Notes: **1**, **2**, **3**, A, A_d stand for *ortho*-phenylenediamine, *meta*-Phenylenediamine and *para*-Phenylenediamine, CH₃CO, CD₃CO, respectively.

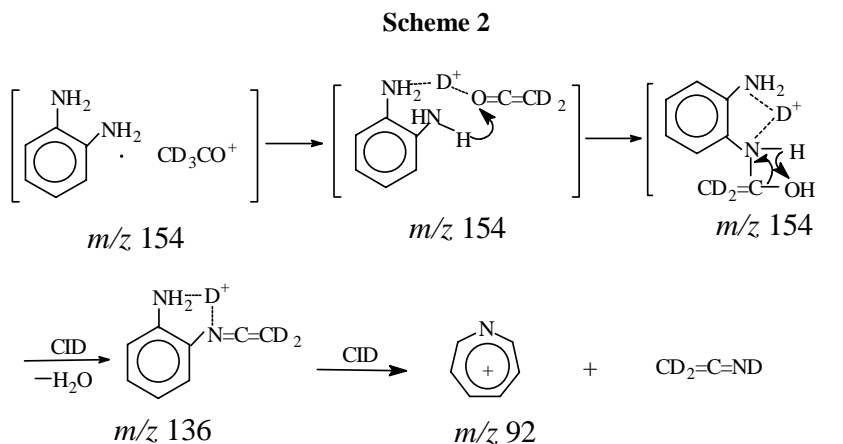
Adduct ions $[M+CD_3CO]^+$ formed by ion-molecule reactions of isomeric phenylene-diamines with deuterium-labeled acetone as chemical ionization reagent could dissociate to produce the fragmentation ions, such as $[M+D]^+$, $[CD_3CO]^+$, $[M+CD_3CO-OH_2]^+$ (shown in **Table 1**)

Based on the data in **Table 1**, we find that common fragment pathways for adduct ions $[M+CH_3CO]^+$ and $[M+CD_3CO]^+$ from isomeric phenylenediamines are to produce protonated molecule (*m/z* 109 or *m/z* 110) and acetyl ions (*m/z* 43 or *m/z* 46). During the

dissociation process, H^+ or D^+ transferred from acetyl ion (or deuterium-acetyl ion) to phenylenediamines molecule to form protonated molecule (or $[M+D]^+$), other fragmentation pathway was to produce the acetyl ions (m/z 43 or m/z 46). The product ions show that the fragmentation reaction involved an intermediate ion-neutral complex. Their dissociation reaction mechanism of $[M+CD_3CO]^+$, which fragment to produce the protonated molecule and acetyl ion, is shown in **scheme 1**.



The different dissociation routes of the corresponding *ortho* isomer is that $[M+CH_3CO]^+$ and $[M+CD_3CO]^+$ ions could produce fragment ions m/z 133 and 136, and loss of 18amu neutral species, respectively. The fragment ions of m/z 133 and 136 further fragment to give ions m/z 92, and loss of 41amu, 44amu neutral species, respectively. The fragmentation mechanism of the adduct ion $[M+CD_3CO]^+$ is shown in **scheme 2**. This reaction is similar to the reductive alkylation reaction of amine.



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