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楊秋華 5/29

行政院國家科學委員會補助專題研究計畫成果報告

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離子阱串聯質譜儀的正/負化學游離法之應用

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Characterization of Phthalic Anhydride and Related Compounds by Negative-ion Chemical Ionization and Collisional Activated Dissociation in an External Source Ion Trap Mass Spectrometer

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Abstract

GCQ is the first commercial benchtop ion trap mass spectrometer capable of performing negative ion analysis. A series of halogenated phthalic anhydrides and their derivatives were examined by GCQ, and it was found that since these halogenated compounds possess higher electron affinities, a resonance electron capture process can form negative ions in GCQ easily. Low-energy collisionally activated dissociation can further dissociate precursor ions. From these fragments, the structure of ions can be determined. Therefore, such experiments using GCQ can provide information about negative ions that cannot be detected by a traditional internal ionization ion trap mass spectrometer. In this study, the differentiation of isomers is discussed, and the CAD spectra obtained from methane and oxygen as reagent gases are compared.

Introduction

The subject of negative ions has intrigued traditional mass spectrometry for several decades [1-28], but because the ion trap mass spectrometer (ITMS) which utilizes internal ionization could not perform negative ion analysis, there have been few reports about its use in the past [29-32]. The reason for this dearth of information is that when 70 eV electrons are used, electron capture does not form negative ions efficiently. However, ever since 1996 when the first commercial ion trap mass spectrometer with an external source, Finnigan GCQ, appeared on the market, we have been able to detect negative ions with the conversion dynode (± 15KV). Already GCQ has been reported to possess excellent MS/MS capability in Positive Chemical Ionization (PCI) [33, 34], and the source temperature and reagent gas pressure effect on the PCI and Negative Chemical Ionization (NCI) have been evaluated [34, 35]. In this study, we used the GCQ ion trap to characterize an array of phthalic anhydrides and related compounds with methane and oxygen as reagents using a combination of Negative Chemical Ionization and collisionally activated dissociation (CAD) techniques. The structures of phthalic anhydrides and related compounds are shown in Figure 1. In fact, while none has been done with the ITMS, some structurally related compounds have been characterized by traditional mass spectrometers

in a couple of studies [16, 17] in which, for example, CAD of the molecular anion of phthalic anhydride yielded fragment ions which resulted from the elimination of CO, CO_2 and C_2O_3 [17]. GCQ presents us with certain advantage in the study of NCI and it can provide valuable information about negative ions, which until now could not be detected by a traditional internal ionization ITMS. We will discuss these advantages and, we will also compare the CAD results we obtained by using methane and oxygen as reagent gasses.

Experimental Method

All experiments were carried out in an external source ion trap mass spectrometer (Finnigan MAT GCQ) [33-36]in which NCI was used with methane and oxygen as the reagent gases. The instrument was operated in the mass selective instability mode. The pressures of He buffer gas and NCI reagent gases were 1 mtorr and 4×10^{-4} torr, respectively. The pressure in the ion source region was 100 mtorr measured by a convectron gauge. Ion source temperature was 200°C. Ionization times were set using automatic gain control (AGC). The ion injection time (from source to mass analyzer) was 0.3-25 msec. Collisional experiments were performed by applying a supplementary tickle voltage to the endcaps of the ion trap at $q_z = 0.225$. The collisional activation time was 15 msec. Signal width for selection of the parent ions was from 0.5-1 amu; the collision energy for fragmentation of the parent ions was from 1-3 V. Samples were introduced to the ion source region via a temperature controlled direct insertion probe (DIP) to assist the desorption of the sample. The probe tip was heated to a temperature of 150°C to 300°C at a speed of 80-100°C/min. Spectra were acquired from 50 to 650 amu at a rate of 0.5 s/scan. The identification of all isotope peaks was achieved using "isoform 1.02" software. All compounds were purchased from Aldrich Chemical Company (Milwaukee, WI) except 3,4,5,6-tetrabromophthalimide which was obtained from Alfa Chemical Company (Ward Hill, MA) and 4,5-difluorophthalic anhydride which was purchased from Merck Chemical Company (Darmstadt, Germany).

Results and discussion

Negative Chemical Ionization spectra using methane as reagent gases

NCI spectra typically produce much lower signals than the PCI spectra in the traditional mass analyzer. However, in GCQ, we found that NCI can also produce as intense signals as PCI [33, 34]. GCQ software prints a total ion count at the top of the spectrum as "RIC". In the NCI of GCQ, the negative ionization mode is also very sensitive to the cleanliness of the ion source. Traditionally, methane has been used as the most common reagent gas in many NCI applications [14, 15, 21, 23, 25, 27, 28]. Table 1 lists NCI spectra of all compounds using methane as a reagent gas at the ion source temperature of 200^{0}C. The formation of the NCI products includes the molecular anion, fragment ions, dimeric ions and the ions due to impurities. The intensities of the fragments and dimeric ions are typically quite small compared with the molecular anion or $[M-H]^-$. The largest dimeric ion is $[2M-HCl]^-$ of 4, 5-dichlorophthalimide (73%). To compare the NCI spectra of phthalic anhydride derivatives with that of the phthalimide derivatives, the proton abstraction reactions for phthalimide derivatives were observed typically, because the trace amount of water or oxygen in GCQ lead to the formation of the OH^- ion, which then reacted with the hydrogen atom on the amide. One typical example of this process can be seen in Scheme 1, which shows the probable mechanism for the formation and CAD of $[M-H]^-$ of phthalimide. Since only the OCN^- ions at m/z 42 were produced, this mechanism could be confirmed by CAD results. Regarding phthalic anhydride derivatives, since they do not possess a hydrogen on the oxygen atom, the base peaks are mainly M^- ions except for the 3, 4, 5, 6-tetrabromophthalic anhydride and the 3, 4, 5, 6- tetrabromo-2-sulfobenzoic acid cyclic anhydride, both of which produced $[M-Br]^-$ as the base peaks due to the easily elimination of the Br atom. For bromo-substituent compounds, the base peaks were either $[M-Br]^-$ (3, 4, 5, 6-tetrabromophthalic anhydride) or $[(M-H)-Br]^-$ (3, 4, 5, 6-tetrabromophthalimide). This finding proves that the Br atom is more easily eliminated than Cl atom. In addition, for fluoro-substituent compounds, no F^- ions were ever observed. We only found small neutral losses of HF. When comparing the NCI spectra of the 3, 4, 5, 6-

tetrabromophthalic anhydride with that of 3, 4, 5, 6- tetrabromo-2-sulfobenzoic acid cyclic anhydride, fragment ions such as $[M-CO_2-SO_2]^-$, $[M-Br_2]^-$, $[M-CO_2-SO_2-Br]^-$ or Br_2^- ions were only observed for the latter. Since no fragment ions could be observed in either phthalic anhydride or phthalimide, the halogen-substituent effect would be the main factor for determining the formation of the fragment ions. When comparing the NCI spectra of 4,5-dichlorophthalic anhydride (see Figure 2) with that of 3,6-dichlorophthalic anhydride (see Figure 3), although both spectra were obtained using methane as the reagent gas, several higher chlorinated additional compounds including m/z 324 ($[2M-CO_2-CO-HCl]^-$ ion, 5%), m/z 288 (1%) and m/z 252 ($[M-H+Cl]^-$ ion, 5%) could be observed, and they were observed in the NCI spectra of 3,6-dichlorophthalic anhydride only. The presence of trace amounts of reactive species such as oxygen and water in GCQ can also complicate the NCI spectra in GCQ. For example, the ions at m/z 233, and 198 ($[M+OH]^-$ and $[M+OH-Cl]^-$, Figure 2) could only be observed in 4,5-dichlorophthalic anhydride. That the formation of these ions could only be observed in the methane-spectrum but not in the oxygen-spectrum for NCI of 4,5-dichlorophthalic anhydride suggests the presence of some impurity caused by the anion of phthalic acid formed by hydrolysis rather than an ion formed during the gas phase [35]. The NCI spectra of really pure samples of the two isomers should not show any appreciable differences in GCQ.

Comparison of the CAD results for Negative Chemical Ionization spectra using methane and oxygen as reagent gases.

The CAD technique was applied to the adduct ions, molecular anion, $[M-H]^-$, and fragment ions to investigate the structural information of NCI products. Tables 2 and 3 list CAD findings on the ions formed by NCI using methane and oxygen as reagent gases. Both involved neutral loss spectra of the NCI ions, demonstrating typical fragmentation processes. However, three main differences could be observed. First, NCI spectra with oxygen as the reagent for some halogenated compounds in the GCQ typically produced some oxygenated ions ($[M-X+O]^-$, where X = Cl or Br). The $[M-Cl/Br+O]^-$ ion was formed because the neutral molecule (M) reacted

with some oxygen ions in a nucleophilic reaction [35]. CAD of these ions eliminates CO or CO_2 typically. Second, more fragment ions were produced in the CAD of oxygen-spectra than the CAD of methane-spectra. CAD of M^- of 3,4,5,6-tetrafluorophthalic anhydride using oxygen as reagent gas, for example, produced many more fragment ions than the one using methane as the reagent for the same compound (see Scheme 2). Third, one oxygen atom may quickly attach to the fragment ions during the CAD processes that use oxygen as the reagent. For example, CAD of 3,4,5,6-tetrachlorophthalic anhydride and 3,4,5,6-tetrabromophthalic anhydride produce the base peaks at $[M-Cl+O]^-$ and $[M-Br+O]^-$, respectively.

Differentiation of isomers by GCQ

Isomer differentiation by traditional mass analyzer is difficult [14, 27, 28]. However, it can be easily achieved by GCQ since GCQ possesses excellent tandem mass capability [33, 34]. In fact, isomer differentiation can be done uniquely by GCQ by combining NCI with its MS/MS capability. One example of isomer differentiation is that for the NCI of 4,5-difluorophthalic anhydride from that of 3,6-difluorophthalic anhydride in this study in which both NCI spectra were obtained using methane as the reagent. The NCI spectra for both isomers could be easily differentiated since 3,6-difluorophthalic anhydride produces two characteristic ions at m/z 276 ($[2M-CO_2-CO-HF]^-$ ion, 6%) and m/z 112 ($[M-CO_2-CO]^-$ ion, 8%) while 4,5-difluorophthalic anhydride produces two characteristic ions at m/z 320 ($[2M-CO_2-HF]^-$ ion, 5%) and m/z 201 ($[M+OH]^-$ ion, from the impurity, 6%). CAD of the M^- ions of these two isomers also had different results. CAD of the M^- ions of 3,6-difluorophthalic anhydride produces the ion mainly at m/z 112 through the loss of one CO_2 and CO molecules while CAD of the M^- ions of 4,5-difluorophthalic anhydride only produces one ion at m/z 156 through the elimination of one CO molecule.

Conclusion

In this study, we found an external ionization ion trap mass spectrometer to have excellent NCI capability. Additionally, we found that the use of pure oxygen and methane as NCI reagent

gases in GCQ gave it good sensitivity. These novel experiments provide valuable information regarding past NCI studies that could not be performed by a traditional internal ionization ITMS. We have found combining NCI with CAD in GCQ to be a very useful analytical technique. Moreover, because of its excellent sensitivity in NCI and tandem mass capability, GCQ is also ideal for trace analysis of target compounds in complex mixtures.

Acknowledgments

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Captions

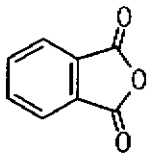
Figure 1. structures of phthalic anhydride and its structural related compounds.

Figure 2. NCI spectra of 4,5- dichlorophthalic anhydride.

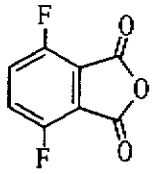
Figure 3. NCI spectra of 3,6- dichlorophthalic anhydride.

Scheme 1. Proposed mechanism for formation and CAD of $(M-H)^-$ of phthalimide.

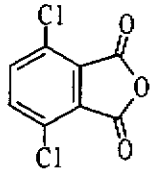
Scheme 2. Proposed product structure for CAD of M^- of 3,4,5,6-tetrafluorophthalic anhydride using oxygen as reagent gas.



Phthalic anhydride



3,6-Difluorophthalic anhydride



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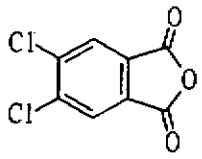
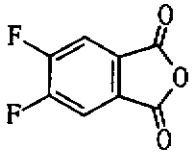
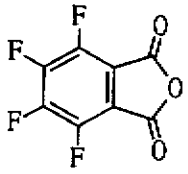


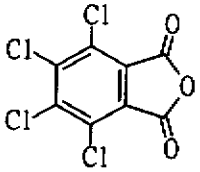
4,5-Dichlorophthalic anhydride



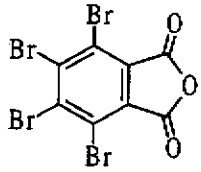
4,5-Difluorophthalic anhydride



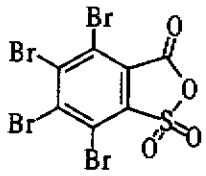
Tetrafluorophthalic anhydride



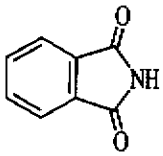
Tetrachlorophthalic anhydride



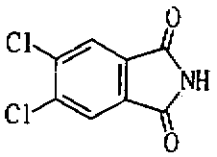
Tetrabromophthalic anhydride



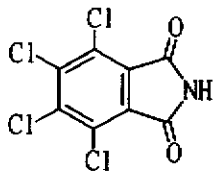
Tetrabromo-2-sulfobenzoic acid cyclic anhydride



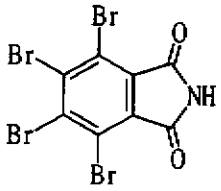
Phthalimide



4,5-Dichloro phthalimide

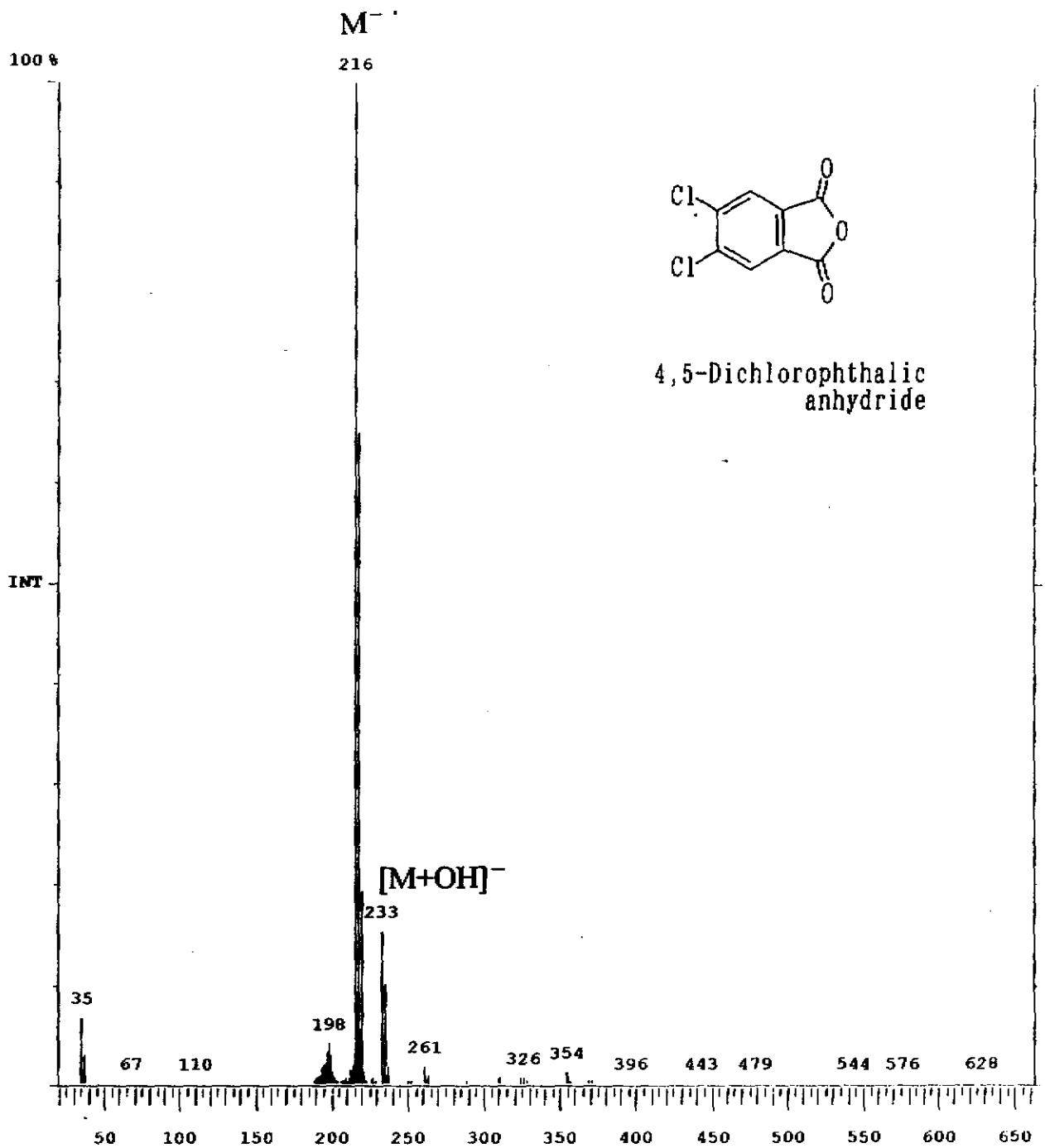


3,4,5,6-Tetrachloro phthalimide



3,4,5,6-Tetrabromo phthalimide

Figure 1.


M⁻·
100 %
216
INT
[M+OH]⁻
233
35
198
261
67
110
326
354
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443
479
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628
50
100
150
200
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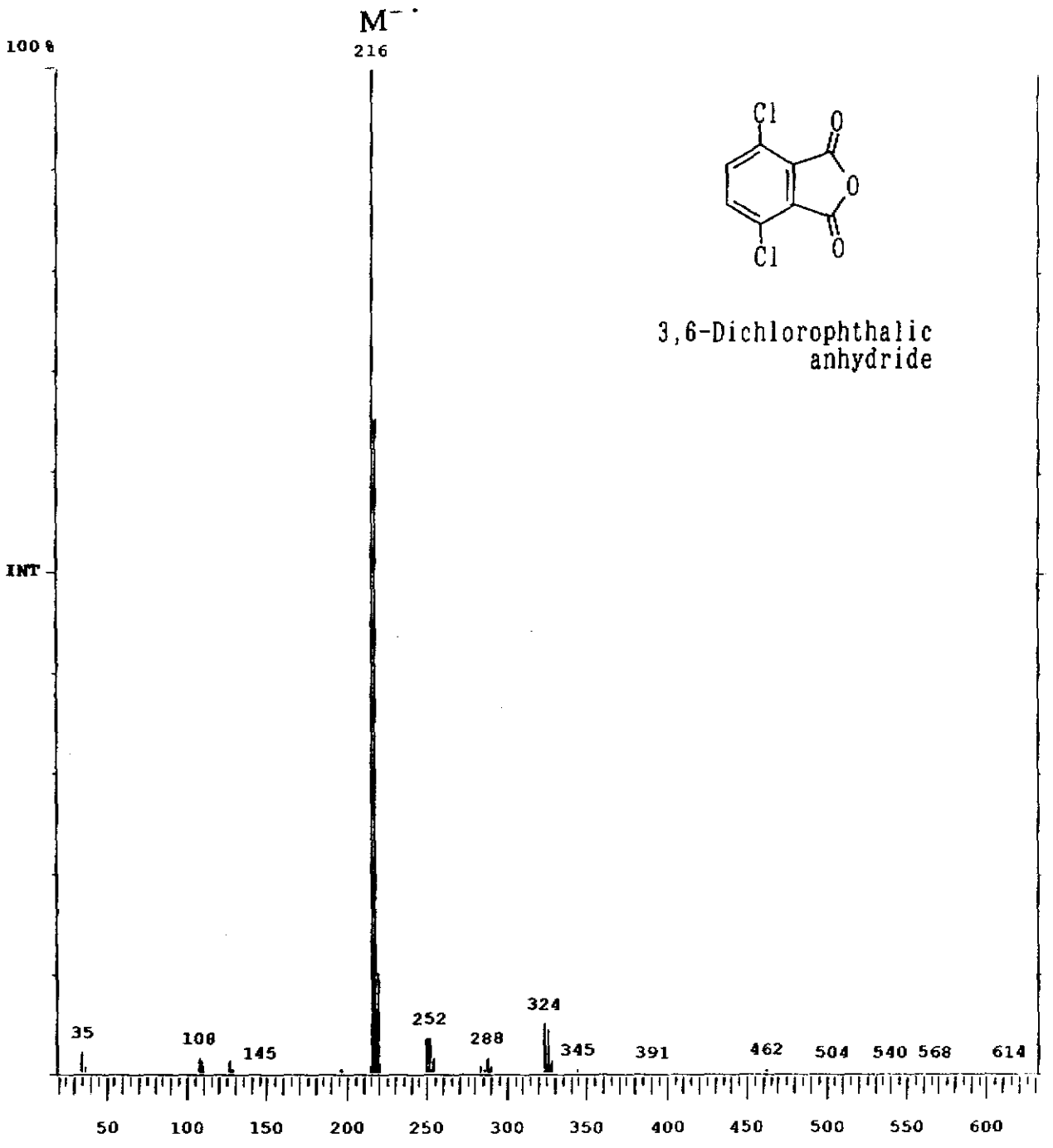
600
650
Cl
Cl
O
O
O
4,5-Dichlorophthalic
anhydride

Figure 2


M⁻·
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100 %
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Cl
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3,6-Dichlorophthalic
anhydride
35
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288
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345
391
462
504
540
568
614
50
100
150
200
250
300
350
400
450
500
550
600

Figure 3

Phthalic anhydride (148)	$M^{-\cdot}$ 100%
3,6-Difluorophthalic anhydride (184)	$[2M-CO_2-CO-HF]^-$ (276,6%) $M^{-\cdot}$ 100% $[M-CO_2-CO]^-$ (112,8%)
3,6-Dichlorophthalic anhydride (217)	$[2M-CO_2-CO-HCl^{35}]^-$ (326,3%) $[2M-CO_2-CO-HCl^{37}]^-$ (324,3%) 288, 1% $[M-H+Cl^{35}]^-$ (252,3%) $[M-H+Cl^{37}]^-$ (250,3%) $M^{-\cdot}$ 100% Cl^- (37,1%) Cl^- (35,3%)
4,5-Difluorophthalic anhydride (184)	$[2M-CO_2-HF]^-$ (320,5%) $[M+OH]^-$ (201,6%) $M^{-\cdot}$ 100%
4,5-Dichlorophthalic anhydride (217)	$[2M-CO_2-HCl^{35}]^-$ (354, < 1%) $[2M-CO_2-CO-HCl^{35}]^-$ (326, < 1%) $[2M-CO_2-CO-HCl^{37}]^-$ (324, < 1%) $[M+OH]^-$ (233,18%) $M^{-\cdot}$ 100% $[M+OH-Cl^{35}]^-$ (198,4%) $[M+OH-Cl^{37}]^-$ (196,2%) Cl^- (37,3%) Cl^- (35,3%)
Tetrafluorophthalic anhydride (220)	$M^{-\cdot}$ 100%
Tetrachlorophthalic anhydride (286)	$M^{-\cdot}$ 100% Cl^- (37,43%) Cl^- (35,100%)
Tetrabromophthalic anhydride (464)	$M^{-\cdot}$ 20% $[M-Br^{79}]^-$ (385,95%) $[M-Br^{81}]^-$ (383,100%) Br^- (81,83%) Br^- (79,80%)
Tetrabromo-2-sulfobenzoic acid	

	$M^{-\cdot}$ <1%
	$[M-Br^{79}]^-$ (421,93%)
	$[M-Br^{81}]^-$ (419,100%)
	$[M-CO_2-SO_2]^-$ (392,40%)
	$[M-Br^{79}Br^{79}]^-$ (342,6%)
	$[M-Br^{79}Br^{81}]^-$ (340,15%)
	$[M-Br^{81}Br^{81}]^-$ (338,9%)
	$[M-CO_2-SO_2-Br^{79}]^-$ (313,13%)
	$[M-CO_2-SO_2-Br^{81}]^-$ (311,12%)
	$Br^{81}Br^{81-}$ (162,12%)
	$Br^{79}Br^{81-}$ (160,14%)
	$Br^{79}Br^{79-}$ (158,6%)
	Br^- (81,77%)
	Br^- (79,64%)
Phthalimide (147)	$[M-H]^-$ (146,100%)
4,5-Dichlorophthalimide (216)	$[2M-HCl^{35}]^-$ (396,73%)
	$[2M-HCl^{37}]^-$ (394,69%)
	$[2M-HCl^{35}-HCl^{35}]^-$ (360,6%)
	$[2M-HCl^{35}-HCl^{37}]^-$ (358,12%)
	$[M-H]^-$ 100%
	$[M-H-HCl^{35}]^-$ (181,10%)
	$[M-H-HCl^{37}]^-$ (179,38%)
	Cl^- (37,11%)
	Cl^- (35,21%)
3,4,5,6-Tetrachlorophthalimide (285)	$[2M-HCl^{35}]^-$ (534,10%)
	$[2M-HCl^{37}]^-$ (532,10%)
	$[2M-HCl^{35}-HCl^{35}]^-$ (498,1%)
	$[2M-HCl^{35}-HCl^{37}]^-$ (496,2%)
	$M^{-\cdot}$ 100%
	$[M-HCl^{35}]^-$ (249,82%)
	$[M-HCl^{37}]^-$ (247,65%)
	$[M-HCl^{35}-Cl^{35}]^-$ (214,<1%)
3,4,5,6-Tetrabromophthalimide (463)	$[2M-HBr^{79}]^-$ (846,<1%)
	$[2M-HBr^{79}-HBr^{81}]^-$ (764,<1%)
	$M^{-\cdot}$ 12%
	$[M-HBr^{79}]^-$ (383,93%)
	$[M-HBr^{81}]^-$ (381,100%)
	$[M-HBr^{79}-Br^{79}]^-$ (304,3%)
	$[M-HBr^{79}-Br^{81}]^-$ (302,5%)

[M+HBr+Br$^-$]	(300,27%)
Br^-	(81,50%)
Br^-	(79,50%)

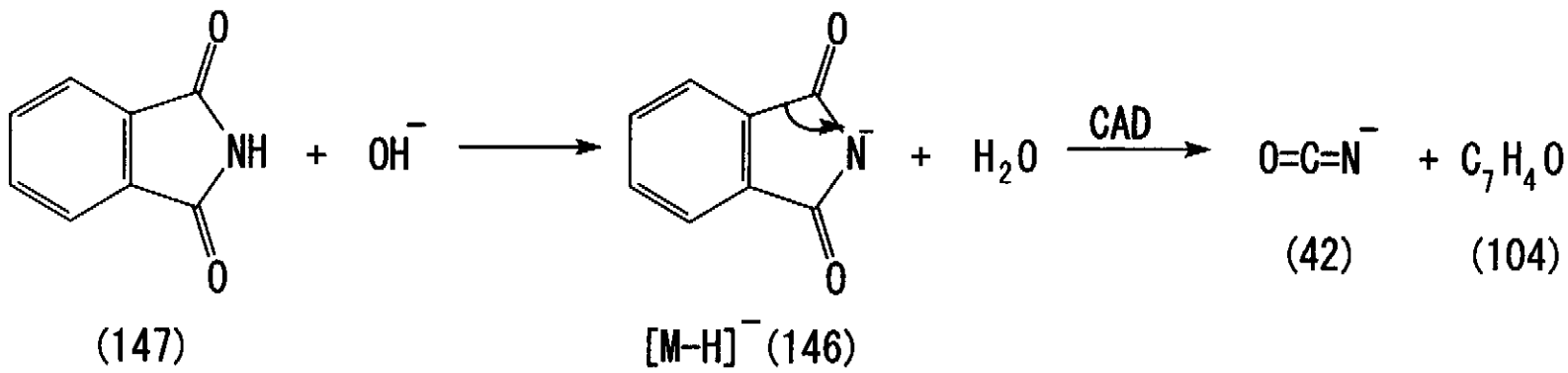
Compound	Isolation	Fragment ions
3,6-Difluorophthalic anhydride (184)	$[2M-CO_2-CO-HF]^-$(276)	$-CO_2$ (232,100%)
		$-(CO_2+CO)$ (204,5%)
	$M^{-\cdot}$(184)	$-(CO_2+CO)$ (112,100%)
		96 4%
		76 7%
	$[M-CO_2-CO]^-$(112)	76 100%
4,5-Difluorophthalic anhydride (184)	$[2M-CO_2-HF]^-$(320)	-CO (292,70%)
		$-(CO_2+CO)$ (248,100%)
	$[M+OH]^-$(201)	$-CO_2$ (157,100%)
		$-2CO_2$ (113,55%)
	$M^{-\cdot}$(184)	-CO (156,100%)
		$-(CO_2+CO)$ (112,6%)
4,5-Dichlorophthalic anhydride (217)	$[M+OH]^-$(233)	$-CO_2$ (189,100%)
	$M^{-\cdot}$(217)	$-Cl^{35}+O$ (199,36%)
		$-Cl^{37}+O$ (197,100%)
	$[M+OH-Cl^{35}]^-$(198)	-CO (170,100%)
		$-(CO_2+CO)$ (126,29%)
Tetrafluorophthalic anhydride (220)	$M^{-\cdot}$(220)	-27 (193,7%)
		$-(CO_2+CO)$ (148,100%)
		$C_4F_4^-$ (124,8%)
		$C_4F_2^-$ (86,4%)
Tetrachlorophthalic anhydride (286)	$M^{-\cdot}$(286)	-CO (242,3%)
		$-Cl^{35}Cl^{35}$ (216,23%)
		$-Cl^{35}Cl^{37}$ (214,100%)
		Cl^- (35, 100%)
		Cl^- (37, 13%)
Tetrabromophthalic anhydride (464)	$M^{-\cdot}$(464)	$-Br^{79}$ (385,73%)
		$-Br^{81}$ (383,100%)
Tetrabromo-2-Sulfobenzoic acid cyclic anhydride (500)	556	$-CO_2$ (512,100%)
	$M^{-\cdot}$(500)	$-CO_2$ (456,50%)
		$-Br^{79}+O$ (437,50%)
		$-Br^{81}+O$ (435,100%)
		$-Br^{79}$ (421,24%)
		$-Br^{81}$ (419,23%)

		-($Br^{79}Br^{79}$+O) (358,4%)
		-($Br^{79}Br^{81}$+O) (356,7%)
		-($Br^{81}Br^{81}$+O) (354,4%)
		-(SO_2+CO_2+Br^{79})+O (329,9%)
		-(SO_2+CO_2+Br^{81})+O(327,9%)
		-(SO_2+CO_2+Br^{79}) (313,4%)
		-(SO_2+CO_2+Br^{81}) (311,4%)
	[M-Br^{79}]$^-$(419)	-SO_2 (355,20%)
		-(SO_2+CO_2) (311,100%)
	[M-CO_2-SO_2]$^-$(392)	-Br^{79} (313,80%)
		-Br^{81} (311,100%)
		239 8%
		$Br^{79}Br^{79-}$ (162,17%)
		$Br^{79}Br^{81-}$ (160,50%)
		$Br^{81}Br^{81-}$ (158,22%)
	[M-CO_2-SO_2-Br^{79}]$^-$(313)	$Br^{79}Br^{81-}$ (160,3%)
		Br^- (81,100%)
		Br^- (79,20%)
Phthalimide (147)	[M-H]$^-$(146)	NCO^- (42,100%)
4,5-Dichloro phthalimide (216)	[2M-HCl^{37}]$^-$(394)	-HCl^{35} (358,100%)
	[2M-HCl^{35}-HCl^{37}]$^-$(358)	-CO (330,80%)
		-Cl^{35} (323,100%)
	[M-H]$^-$(215)	-HCl^{35} (179,100%)
	[M-H-HCl^{37}]$^-$(179)	-Cl^{35} (144,100%)
3,4,5,6-Tetrachloro phthalimide (285)	[2M-HCl^{35}]$^-$(534)	-HCl^{35} (498,100%)
		-HCl^{37} (496,90%)
		-(HCl^{35}+CO) (470,80%)
		-(HC^{37}+CO) (468,55%)
	[2M-HCl^{35}-HCl^{37}]$^-$(496)	-CO (468,100%)
	$M^{-\cdot}$ (285)	-HCl^{35} (249,100%)
		-HCl^{37} (247,83%)
		-(HCl^{35}+Cl^{35}) (214,8%)
		-(HCl^{35}+Cl^{37}) (212,6%)
	[M-HCl^{35}]$^-$(249)	-Cl^{35} (214,66%)
		-Cl^{37} (212,100%)
3,4,5,6-Tetrabromo phthalimide (462.7)	$M^{-\cdot}$ (463)	-HBr^{79} (383,100%)
		-HBr^{81} (381,92%)
		-(HBr^{79}+Br^{79}) (304,7%)
		-(HBr^{79}+Br^{81}) (302,22%)

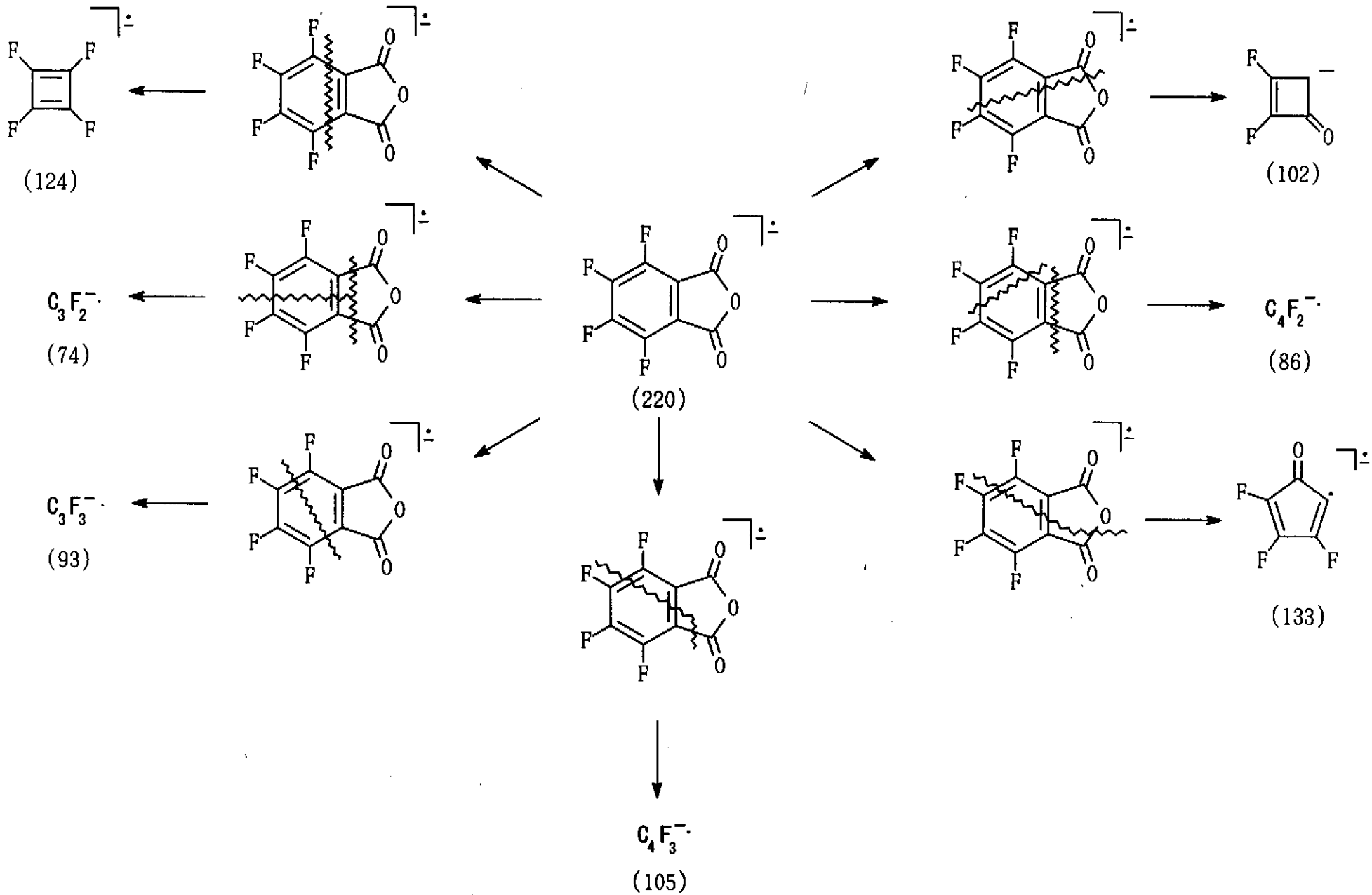
	-(HBr +Br) (300,11%)
$[M\text{-}HBr^{81}]^-$(381)	$-Br^{79}$ (302,100%)
$[M\text{-}HBr^{79}\text{-}Br^{81}]^-$(302)	$-HBr^{79}$ (222,100%)

Table 3. CAD results of ECD by using oxygen as reagent

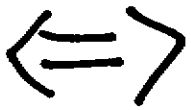
Compound ions	Isolation	Fragment
4,5-Dichlorophthalic anhydride (217)	$[M\text{-}Cl^{35}+O]^-$(197)	$-CO_2$ (153,100%) $-(CO_2+CO)$ (125,41%)
Tetrafluorophthalic anhydride (220)	$M^{-\cdot}$	$C_5F_3O^-$ (133,73%) $C_4F_4^-$ (124,57%) $C_4F_3^-$ (105,71%) $C_4F_2O^-$ (102,41%) $C_3F_3^-$ (93,22%) $C_4F_2^-$ (86,100%) $C_3F_2^-$ (74,8%)
Tetrachlorophthalic anhydride (286)	$M^{-\cdot}$	$-Cl^{35}+O$ (267,100%) $-Cl^{37}+O$ (265,49%) $-(Cl^{35}+CO_2)+O$ (223,4%) $-(Cl^{37}+CO_2)+O$ (221,1%)
	$[M\text{-}Cl^{35}+O]^-$(267)	$-CO_2$ (221,100%) $-(CO_2+CO)$ (193,28%)
Tetrabromophthalic anhydride (464)	$M^{-\cdot}$	$-Br^{79}+O$ (401,100%) $-Br^{81}+O$ (399,42%) Br^- (81,7%) Br^- (79,6%)
	$[M\text{-}Br^{81}+O]^-$(399)	-45 (354,100%) $-(CO_2+CO)$ (327,35%)



Scheme.1



Scheme. 2



Ion-Molecule Reactions and Collisional Activated Dissociation of Tricyclic Antidepressants in an External Source Ion Trap Mass Spectrometer

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