REGULAR PAPER

Discrimination of Isomers of Dichlorobenzene Using Charge Inversion Mass Spectrometry

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Chlorinated aromatic compounds are well-known environmental pollutants and their toxicity often depends dramatically on the chlorine substitution pattern within a homological group. Analysis of extremely toxic environmental pollutants such as dioxins requires high sensitivity, typically in the parts-per-trillion (ppt) range. Mass spectrometry (MS), being the most sensitive of analytical methods, has been used for pollutant analysis, but conventional mass spectrometry alone cannot be used for isomer-specific analysis of these toxic chemicals. In this work, we investigated the possibility of discriminating among the isomeric precursors of chlorinated aromatic compounds by charge inversion mass spectrometry using an MS/MS instrument. Charge inversion mass spectra using Cs, K, and Na targets were measured for $C_6H_4Cl_2^+$ ions produced from the ortho-, meta-, and para-isomers of dichlorobenzene ($C_6H_4Cl_2$). The charge inversion mass spectra were found to display a clear dependence on the nature of the isomeric precursors for each of the targets used. The clear discrimination among the isomers of dichlorobenzene achieved using charge inversion mass spectrometry in the present work indicates that most of the $C_6H_4Cl_2^+$ ions obtained by electron impact retain the structure of the parent molecules, demonstrating the potential utility of this technique for isomer-selective microanalysis of various pollutants.

1. Introduction

Polychlorinated aromatic compounds are well-known environmental pollutants,[1]-[10] and the position isomers of these compounds vary greatly in acute toxicity and biological activity.[1]-[3] Since some isomers of these compounds are extremely toxic, such as poly-chlorinated dibenzo-p-dioxines (PCDD's), and poly-chlorinated dibenzofurans (PCDF's), much effort has been devoted to developing rapid, sensitive and specific analytical methods for analysis of these compounds.[11]-[35] There have been numerous reports published describing the analysis of environmental samples for PCDD's and PCDF's, all using mass spectrometry as the detection method because of its high detection efficiency. Since high resolution gas chromatographic methods can separate structural isomers,[15]-[19] and high resolution mass spectrometry[14], [20] offers advantages in selective detection in the presence of substantial background interference, the combination of gas chromatography and high resolution mass spectrometry (HRGC-HRMS) has been used widely for analysis of chlorinated aromatic environmental pollutants.[14] However, analysis of a single sample using capillary gas-chromatography requires several minutes. Various mass spectrometry/mass spectrometry (MS/MS) methods have been reported[21]-[26] that enable more rapid and sensitive analysis.

Most chlorinated aromatic environmental pollutants are volatile and can be ionized by electron impact (EI)

for mass spectrometry.[12] The mass spectra of o-, m-, and p-$C_6H_4Cl_2$, which are worldwide pollutants,[8]-[10] appear in Mass Spectral Data.[27] The EI mass spectra measured in our laboratory are identical with those appearing in Mass Spectral Data, and there are no differences between the spectra of o-, m-, and p-$C_6H_4Cl_2$.[28] The possibility of isomer-selective ionization has been demonstrated by Resonance-Enhanced Multi-Photon Ionization spectra of isomeric poly-chlorinated aromatic compounds.[29] Safe et al.[28] suggested that there was incomplete chlorine randomization in trichlorobenzenes and polychlorinated biphenyl's (PCB's) on the basis of ion kinetic energy spectra, but this was not the case for dichlorobenzenes. Buser[30]-[32] indicated that the mass spectra of the two groups of hexa-chlorinated dibenzo-p-dioxines (HCDD's) containing two, three, and four chloro substituents on each side of the molecules showed significant differences in the low mass range. Levy and Oswald[33] reported that structural isomers of PCB's containing three ortho chloro substituents display a relatively intense $[M-Cl]^+$ fragment. Correlations between the structural isomers of PCB's and tetra-chlorinated dibenzo-p-dioxines (TCDD's) and decomposition of metastable ions have also been reported.[34], [35] On the other hand, randomization of hydrogen atoms in mono-substituted benzenes[36]-[38] and chlorine atoms in mono-substituted chlorobenzenes[39] have been reported except dissociation with rearrangement in ortho structures.[40], [41] Therefore, it is very difficult to differentiate between the isomers of chlorinated aromatic compounds using EI mass spectrometry. While most isomers of PCDD's, PCDF's, and PCB's are not distinguishable clearly using conventional mass spectrometry,[12] mass spectrometry is, nevertheless, the most rapid and sensitive instrumental analytical method, and so differentiation of isomers using some form of

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mass spectrometry would be an extremely useful tool for environmental analysis.

Through the use of charge inversion mass spectrometry using an alkali metal target, we have been able to distinguish clearly between the isomers of $C_3H_4^{+42}$ and $C_2H_2^{+ . [13]}$ Charge inversion studies using the thermometer molecule $W(CO)_6^{[44]}$ and partially deuterated methanol[45] demonstrated that this discrimination between the isomers was a result of the reaction mechanism involving neutral species formed *via* neutralization followed by dissociation into neutral fragments. In the present work, the possibility of using charge inversion mass spectrometry for microanalysis of environmental pollutants was investigated by attempting to differentiate the structural isomers of dichlorobenzene.

2. Experimental

The MS/MS instrument used in this work comprises a double focusing mass spectrometer as MS-I to mass-separate precursor ions, a 3 cm long target chamber, and a cylindrical electrostatic analyzer (ESA) as MS-II to mass-analyze secondary ions.[12] Positive precursor ions were formed by electron impact ionization, and accelerated to 3 keV kinetic energy. The detector was a 10 kV post-acceleration secondary electron multiplier, which could detect both positive and negative ions upon application of a suitable polarity. In our charge inversion mass spectrometer, mass-selected positive ions are made to collide with alkali metal targets, and the resulting negative ions formed upon two electron transfer are mass analyzed. Neutralization, dissociation and negative ion formation take place in the target chamber filled with alkali metal vapor. CID spectra were measured by mass-analyzing positive ions exiting the target chamber, by changing the polarity of

MS-II and the detector. Both the charge inversion mass spectra and the CID spectra measured were independent on the electron impact energy between 30 eV and 70 eV. The spectra shown in this work are those measured at 70 eV impact energy. *Ortho-*, *meta-*, and *para*-dichlorobenzene (98%, Wako, Japan) were used as received.

3. Results and Discussion

Figure 1 shows the charge inversion mass spectra and collision induced dissociation (CID) spectra obtained using a K target for $C_6H_4^{35}Cl_2^-$ ions obtained from *o-*, *m-*, and *p*-$C_6H_4Cl_2$ by electron impact (EI). The $C_6H_4^{35}Cl_2^+$ ions of $m/z = 146$, which gives rise to the strongest peak in the EI spectra, were selected as precursor ions for all of the spectra in Fig. 1. In the charge inversion spectra shown in Figs. 1(a), (b), and (c), the peaks associated with Cl^- ions at $m/z = 35$ and $C_6H_4Cl^-$ ions at $m/z = 111$ are dominant. The weak peaks associated with $C_6H_n^-$ ($n = 1-3$) are also observed at $m/z = 73-75$. In the *o*-$C_6H_4Cl_2$ spectrum of Fig. 1(a), the peak at $m/z = 35$ is larger than that at $m/z = 111$, and in the *m*-$C_6H_4Cl_2$ spectrum of Fig. 1(b) the peak at $m/z = 35$ is smaller than that at $m/z = 111$. In the *p*-$C_6H_4Cl_2$ spectrum of Fig. 1(c), the peak at $m/z = 35$ is much smaller than that at $m/z = 111$. In summary, the difference among the charge inversion mass spectra of the structural isomers is the intensity of the Cl^- peak relative to the $C_6H_4Cl^-$ peak.

In the CID spectra shown in Figs. 1(d), (e), and (f), the non-dissociative $C_6H_4^{35}Cl_2^-$ peaks at $m/z = 146$ are by far the strongest. In each of these CID spectra, the $C_6H_4Cl^-$ peaks ($m/z = 111$) resulting from loss of a Cl atom are the most dominant dissociative peaks. The peaks at $m/z = 75$ are associated with $C_6H_3^+$ ions resulting from loss of one H atom and two Cl atoms. The
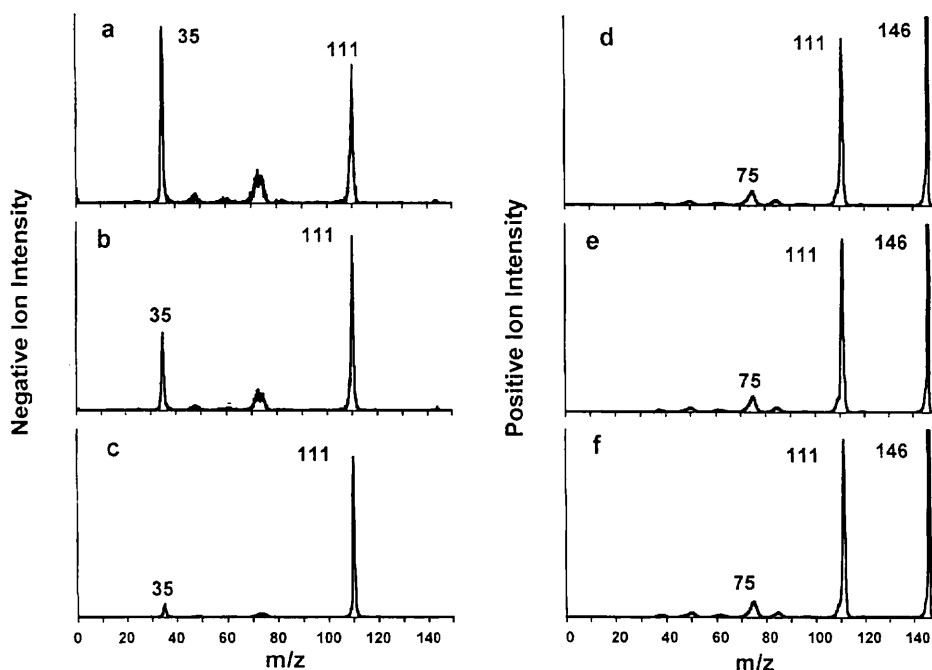

Fig. 1. Charge inversion mass spectra of $C_6H_4Cl_2^+$ ions of *o-*, *m-*, and *p*-dichlorobenzene, denoted by (a), (b), and (c), respectively and collision induced dissociation (CID) spectra of $C_6H_4Cl_2^+$ ions of *o-*, *m-*, and *p*-dichlorobenzene, denoted by (d), (e), and (f), respectively. The discrimination among structural isomers is seen clearly in the charge inversion mass spectra, whereas no differences among the isomeric compounds are observed in the CID spectra.

profiles of the observed peaks arising from dissociation of the precursor ions are similar for each of the structural isomers. The ions of $m/z=75$ and $m/z=111$ are also observed as major peaks in the EI spectra. The similarity between the EI and the CID spectra implies that dissociation of positive ions in EI and CID gives identical fragment ions for each of the structural isomers of poly-chlorinated benzenes, and the isomers cannot be differentiated from one another.

Discrimination among the isomers of dichlorobenzene is clearly achieved in the charge inversion mass spectra, whereas differences in the CID spectral profiles for the isomers are not observed. The collision conditions including the precursor ion intensities, the target densities and the collision energy of the charge inversion spectra of Figs. 1(a), (b), and (c) are identical with those of the CID spectra of Figs. 1(d), (e), and (f), respectively. The only difference between the charge inversion spectra and the CID spectra is the polarity of the ions that are analyzed and detected. The discrimination of the isomers in the charge inversion spectra measured under identical conditions to the CID spectra indicates that the precursor ions obtained from the structural isomers retain their own structures. At the same time, the difference between the charge inversion and the CID implies that the dissociation of neutral species is much more structure dependent than that of cations.

Charge inversion mass spectra of o-, m-, and p-$C_6H_4Cl_2^+$ ions using Cs and Na targets are shown in Fig. 2. Differentiation among the isomeric $C_6H_4Cl_2^+$ ions is clearly achieved not only for K target but also for both Cs and Na targets. As shown in Figs. 2(a) and (b), the peaks at $m/z=111$ in the spectra of the o- and m-$C_6H_4Cl_2$ using a Cs target are broad. The breadth of these peaks is caused by piling of the peak associated with $C_6H_3Cl^-$ ions $(m/z=110)$ resulting from the loss of HCl. In the spectra obtained using Cs targets, the peak

at $m/z=35$ predominates for o- and m-$C_6H_4Cl_2$ as shown in Figs. 2(a) and (b), whereas the peak at $m/z=111$ is the most intense for p-$C_6H_4Cl_2$ as shown in Fig. 2(c). In the spectra obtained using Na targets shown in Figs. 2(d), (e), and (f), the peak at $m/z=111$ is dominant for each of the isomeric precursor ion, and the intensities of the peaks at $m/z=111$ relative to the peaks at $m/z=35$ are dependent on the isomeric precursor ions. The differences seen with each of the targets used demonstrates that charge inversion mass spectrometry using alkali metal targets can provide a clear differentiation among the cations of isomers whose CID and EI spectra are similar. As shown from the results of studies on the thermometer molecules $W(CO)_6$[44] and partially deuterated methanol,[45] the excited neutral are formed via near resonant neutralization in the charge inversion mass spectrometry using alkali metal targets. Since the neutralization process was the near resonant, the energy level of the formed neutral was lower than the level of the precursor positive ions by an amount equal to the ionization energy of targets. The dissociation in the charge inversion mass spectrometry occurred from this energy-selected neutral species. Therefore, the discrimination in the charge inversion spectra was attributed to the isomer-dependent dissociation pattern of energy selected neutrals.

Figure 3 shows heats of formation of o-, m-, and p-$C_6H_4Cl_2$ and their parent ions. The thermochemical values are from ref. 46. Since the neutralization step in the charge inversion process occurs via near-resonant electron transfer,[44, 45] the energy levels of the formed neutral species should be lower than the level of the precursor cation by an amount equal to the ionization energy of the target. Ionization energies of Cs, K, and Na are 3.894, 4.341, and 5.139 eV, respectively.[47] The energy levels associated with the resonant processes are also shown as dotted lines in Fig. 3. The resonant
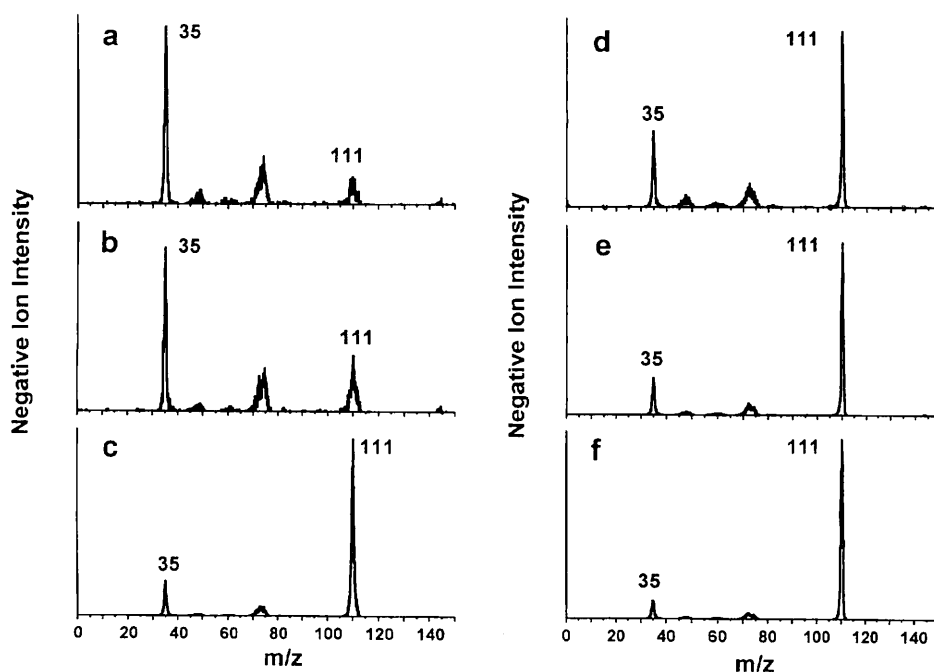

Fig. 2. Charge inversion mass spectra of $C_6H_4Cl_2^-$ ions of o-, m-, and p-dichlorobenzene, denoted by (a), (b), and (c) using Cs target, respectively, and those by (d), (e), and (f) using Na target, respectively.
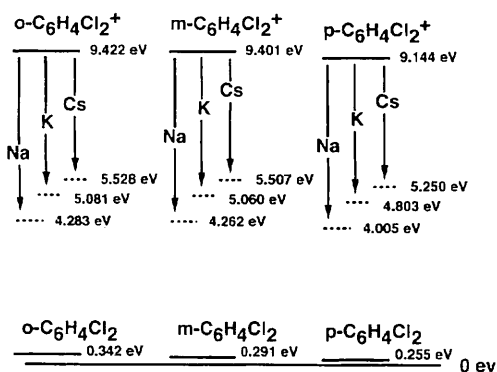
Fig. 3. Heats of formation of *o*-, *m*-, and *p*-dichloro-benzene, and the parent ions in electron volts. The thermochemical data are taken from ref. 46. The values shown next to the dotted lines are the energy values predicted near-resonant neutralization.

levels for each target decrease in the order Cs, K, and Na.

The relative intensity of the Cl^- peak to that of the $C_6H_4Cl^-$ peak in the charge inversion spectrum of the *o*-$C_6H_4Cl_2$ precursor with the Cs target is the highest, as shown in Fig. 2(a), of all the charge inversion spectra measured in this work. The relative intensities of the Cl^- peaks to the $C_6H_4Cl^-$ peaks decrease with increasing ionization energies of the targets for each of the precursor ions. Furthermore, for each of the targets used, the relative intensities decrease in the order, *ortho*, *meta*, and *para* isomers. For these combinations of precursors and targets, the relative intensities of the Cl^- peaks to the $C_6H_4Cl^-$ peaks are in the same order as the internal energies of the neutral intermediates, as shown in Fig. 3. The order of the relative intensities of the Cl^- peak to the $C_6H_4Cl^-$ peak for each of the precursor ions can be explained by the internal energies of the neutral intermediates from the agreement of the order of the relative intensities with the internal energies shown in Fig. 3. However, the relative intensity for the *p*-$C_6H_4Cl_2^-$ precursor ion with the Cs target (Fig. 2(c)) is smaller than that for the *o*-$C_6H_4Cl_2^+$ precursor ion with the Na target (Fig. 2(d)). This order do not agree with that of internal energies shown in Fig. 3. Therefore, the order of the relative intensities cannot be explained solely by the magnitude of the internal energies of the neutral intermediates.

Charge inversion mass spectrometry is an MS/MS method and is no more complex than CID, which is used widely in conventional mass spectrometry, because the only difference between the charge inversion and CID measurement is the polarity of the detected ions. Whereas CID is a single collision process, charge inversion is a two-collision process that consists of near-resonant neutralization, spontaneous dissociation of the excited neutral, followed by anionization of the fragment neutral. The average time interval between neutralization and anionization was estimated to be 0.3 μs from the velocity of the precursor ions and the length of the target chamber. The excited neutrals dissociated faster than this time interval. The charge inversion spectra were measured under the transmis-

sion of precursor ions between 10% and 50%. The relative intensities of the peaks observed in the charge inversion spectra were independent on transmission of precursor ions. Though the target pressure in the target chamber was not measured directly, the order of the target pressure was able to be estimated from the transmission. Cross sections of the near-resonant electron transfer in various combinations of precursors and targets were reported as about 10^{-14} cm^2.[18]-[50] Using this cross section and the length of the target chamber, the target pressure of alkali metal targets in the charge inversion mass spectrometry was estimated to be 10^{-3} and 10^{-4} Torr order for the transmission of 10% and 50%, respectively. This pressure was the same order for high energy CID using rare gas target. The total efficiency of the charge inversion process is estimated to be about one order of magnitude smaller than the CID process.

The reason why the relative intensities of $C_6H_4Cl^-$ ions to Cl^- ions in the charge inversion spectra depend on the isomeric precursors, is examined. The negative ion intensity is determined by the abundance of the neutrals and the cross section of electron transfer between the neutral and the target. While the ion intensity is directly proportional to the neutral abundance, the relative intensities of the negative ions are not as same as the neutral abundance, due to different cross section of the electron transfer. If the reaction pathway of the excited $C_6H_4Cl_2^*$ is only fragmentation to C_6H_4Cl and Cl, the C_6H_4Cl and Cl have equal abundance for any isomeric precursors, because these fragments are complementary. Other reaction pathways are observed in the charge inversion spectra. The $C_6H_3Cl^-$ ions associated with loss of HCl from $C_6H_4Cl_2^*$ are observed for *ortho*- and *meta*-precursors with a Cs target as shown in Figs. 2(a) and (b) and for *ortho*-precursor with a K target as shown in Fig. 1(a). The peaks observed at $m/z = 74-76$ in both Figs. 1 and 2 are associated with $C_6H_n^-$ $(n = 2-4)$ ions resulting from loss of two Cl atoms. These dissociation processes of the excited $C_6H_4Cl_2^*$ compete each other. Since the relative importance of these competing dissociation processes may depend on the isomeric precursor and the internal energy, the dependence of the relative intensities of $C_6H_4Cl^-$ ions to Cl^- ions on the isomeric precursors is rationalized. Another possibility of the dependence of relative intensity on the precursors is associated with the structure of C_6H_4Cl radicals. If the structures of C_6H_4Cl radicals depends on the precursor, negative ion intensities of $C_6H_4Cl^-$ ions vary because the cross section to negative ion formation may depend on the structure of neutral radicals. In order to certify this possibility, the calculation of the structure of these radicals and isomerization barriers is needed. Since the reason for the dependence of the relative intensity is not clearly elucidated, for the present, the precise experiment combined with the calculation will be tried.

The precise analysis of environmental pollutants is currently performed using a combination of capillary gas chromatography and high-resolution mass spectrometry, requiring about thirty minutes for a single sample analysis.[14] A sample can be analyzed within one minute using charge inversion mass spectrometry.

In order to measure many environmental pollutants, any reduction in analysis time is significant. PCDD's, PCDF's, and PCB's have many isomers, and these isomers may dissociate into many fragments. Using different targets, these isomers may be differentiated on the basis of the relative intensities of peaks in the charge inversion mass spectra of the many fragments. Therefore, we believe that this technique is capable of providing a method for rapid isomer analysis of PCDD's, PCDF's, and PCB's.

Acknowledgments

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