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# Isomer effect in the branching ratio of anions for thermal electron attachment to chlorinated phenols

Seiko Nakagawa*

*Tokyo Metropolitan Industrial Technology Research Institute Radiation Laboratory, 2-11-1, Fukazawa, Setagaya-ku, Tokyo 158-0081, Japan*

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## Abstract

The temperature dependence of the formation of negative ions from chlorinated phenols was studied. For all compounds, $Cl^-$ was produced and the intensity of the chloride ion increased with the increasing number of Cl atoms present in the molecule. For some of them, $(M-HCl)^-$, $(M-H)^-$, and $M^-$ (M: parent molecule) were also observed. The intensities of the fragment ions such as $Cl^-$ and $(M-HCl)^-$, increased with the increasing temperature, though that of the parent anion decreased. There may be two mechanisms to produce $(M-HCl)^-$. One is the HCl elimination of the hydroxylic hydrogen atom and the *ortho*-Cl atom. The other is the HCl elimination followed by the migration of the hydroxylic hydrogen atom to the *ortho* position for the 3,4- and 3,5-dichlorophenols. The branching ratio of $[(M-HCl)^-]/[Cl^-]$ depends on the length of the H–Cl bond of the intermediate for the former mechanism.

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*Keywords:* Negative chemical ionization; Chlorinated phenol; Isomer effect; Branching ratio; Temperature dependence; Electron affinity

## 1. Introduction

Chlorinated phenols are known for their toxicity especially as endocrine disrupters [1], though they have been used as herbicides and insecticides or produced as by-products of the chemical industry in the past. They are the origin of polychlorinated dibenzo-*p*-dioxins in reactors, especially incinerators. Based on these aspects, it is necessary to develop an effective method for the degradation of chlorinated phenols.

Several techniques involving photolysis and radiolysis for the degradation of chlorinated phenols have been investigated [2,3]. Several conditions have been studied depending on the types of solvents, pH, the presence of catalysts and radical scavengers, etc. There will be at least two reasons for their complicated reaction mechanisms. One is that the liberation of H in the hydroxyl base easily occurs in the aqueous system. Another is that chlorinated phenols react with at least three types of species: H atoms, OH radicals, and electrons. In these reactions, dissociative electron attachment is one of the important processes. The efficiency of the dechlorination and the degradation process also depends on the position of the chlorine substitution. This means that it is important to determine the produced anions from the electron attachment depending on the types of chlorinated phenols for the development of an effective degradation method.

While there are several reports on halogenated benzenes regarding the electron attachment process, only a few reports about chlorinated phenols are available. Recently, Deinzer's group studied the negative ions produced from chlorinated dibenzofurans [4a] and dibenzodioxins [4b] by negative chemical ionization (NCI) and electron absorption spectrum (EAS) measurements. They found that the signal intensity of the fragment ion ($Cl^-$) increased with the increasing number of chlorine atoms in the molecule. The parent anions were observed for the molecule having more than three chlorine atoms. However, they have not yet studied chlorinated phenols. Muftakhov et al. observed the EAS of 4-chlorophenol and found fragment ions, $Cl^-$ and $(M-H)^-$ (M: parent molecule), which were produced when the electrons with an energy of 1.0 eV are attached to the molecule [5]. There is no information on anions produced from the electron attachment process for other chlorinated phenols.

In this report, we studied the temperature dependence (423–573 K) of the negative ion formation of chlorinated

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* Tel.: +81-3-3702-3116; fax: +81-3-3703-9768.
*E-mail address:* Nakagawa.Seiko@iri.metro.tokyo.jp (S. Nakagawa).

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phenols (2-chlorophenol (*o*-ClP), 3-chlorophenol (*m*-ClP), 3,4-, 3,5-, 2,3-, 2,4-, 2,5-, and 2,6-dichlorophenols (DCP), and 2,3,4-, 2,4,6-, 2,3,6-, 2,3,5-, and 2,4,5-trichlorophenols (TCP)) by negative chemical ionization mass spectrometry (NCIMS). We also studied the molecular orbital calculations to determine the production mechanism of the fragment anions.

## 2. Experimental

Chlorinated phenols and isopropyl alcohol used as the solvent were supplied by Tokyo-Kasei and Wako-Junyaku, respectively, and were used as received. Our experimental apparatus has been previously described in detail [6]. Fig. 1 shows the ion-source apparatus. Electrons are provided from the filament. The temperature of the ion source is measured with a Pt sensor. Some electrons are collected by the repeller to measure the concentration of electrons and the filament current is controlled in order to maintain a constant concentration. Samples are introduced from downstream of the filament into the ion source chamber through the capillary interface. Electrons, whose energy is 200 eV, are produced and thermalized by collisions with isobutane.

The energy of the electrons may be widely distributed. However, to confirm that the energy of the electron is thermalized at the incident temperature, the following experiment was carried out with $C_2Cl_4$. It is reported that the thermal electron attachment for $C_2Cl_4$ led to the $Cl^-$ formation [7]. If the intensity of the $Cl^-$ ion from $C_2Cl_4$ remained constant by changing the flux of isobutane, the electrons should be thermalized. The pressure of the mass analytical tube was monitored by an ion gauge and increased with the increasing flux of isobutane. The intensity of the $Cl^-$ ion from $C_2Cl_4$ was almost constant when the monitored pressure was greater than $2.5 \times 10^{-5}$ Torr. Because we measured the ion intensity at the pressure of $2.5 \times 10^{-5}$ to $3.0 \times 10^{-5}$ Torr, most of the electrons should be thermalized [6].

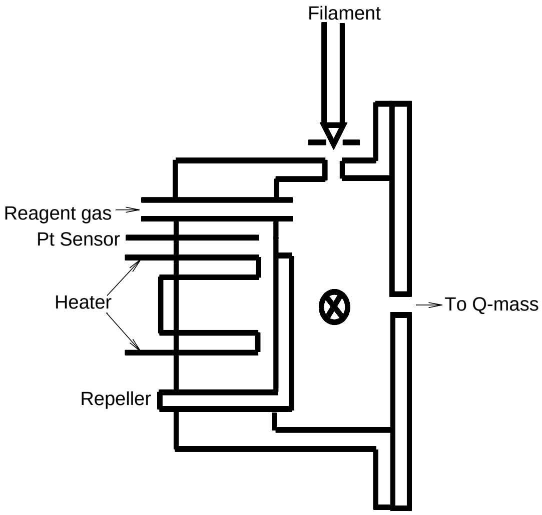

Fig. 1. Schematic diagram of the ion-source apparatus. Electrons are provided with the filament. The temperature of the ion source is measured with Pt sensor. Some electrons are corrected to the repeller to measure the concentration of electrons and the filament voltage is controlled to keep the concentration constant.

The pressure of the mass analytical tube was maintained at $2.5 \times 10^{-5}$ to $3.0 \times 10^{-5}$ and $1.0 \times 10^{-6}$ to $2.0 \times 10^{-6}$ Torr with and without isobutane, respectively. The main gas in the reaction volume was isobutane and the contribution of nitrogen or oxygen could be neglected. The produced anions were mass selected by the quadruple pole mass filter (Q-mass in Fig. 1) and detected by the electron multiplier. The chemical ionization mass spectra were taken using a Shimadzu QP1100EX GC-MS equipped for negative chemical ionization. The anions of isobutane were not observed under the experimental conditions. The observed anions were produced from the attachment of electrons thermalized by collisions with isobutane, and not from the electron transfer from the isobutane anion. The instrument was tuned using the NCI mass spectra of tris(perfluorobutyl)amine (TPFBA) at 523 K and the conditions were maintained throughout the measurements.

A gas chromatograph was operated in the split mode with a wide bore capillary column to provide in-line purification of the samples. The carrier gas was Helium which was pumped in at the capillary interface. The samples were diluted with isopropyl alcohol in 1/100, 1/50, and 0.2–1.0 mol% for TCP, DCP, and the mono-chlorinated phenols, respectively, and 0.4–1.5 μl of them was injected. The samples were separated from the solvent through the capillary column. A single peak due to the electron attachment to the sample gas was observed in the chromatogram with no extraneous peaks or interference. The temperature of the GC column was kept at 423 K for *o*-ClP, at 453 K for 2,3-, 2,4-, 2,5-, 2,6-DCP and *m*-ClP, and at 473 K for 3,4-, 3,5-DCP and TCP so that the retention time for all the chlorinated phenols could be maintained at about 3.0 min.

The temperature of the reaction volume was controlled by a computer. When the temperature was changed, the ion source was allowed to equilibrate for 30–60 min. The mass spectra were obtained via a personal computer. The ion abundance was obtained from the integrated sums of all the isotopic masses of the ions.

## 3. Results and discussion

### *3.1. The temperature dependence of the formation of negative ions*

The total ion chromatogram (TIC) and mass spectra at each time were obtained. We can observe the ion chromate of each ion from the TIC. Fig. 2 shows the TIC and mass spectrum at the peak of the TIC obtained for 2,3,4-TCP where the ion source temperature was 423 K. The observed ions were $Cl^-$, $(M - HCl)^-$ (the HCl loss from the parent ion), and $M^-$ (M: parent molecule). The

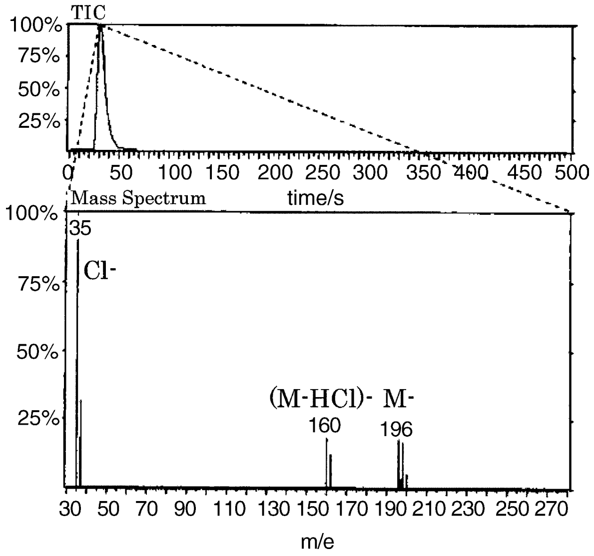

Fig. 2. Total ion chromate (TIC) and negative chemical ionization (NCI) mass spectrum at the peak of TIC for 2,4,5-TCP where the ion source temperature was 423 K.

chlorine atom has two isotopes ($^{35}$Cl and $^{37}$Cl) and its natural abundance is 3:1, which is in good agreement with the intensity ratio of the two $Cl^-$ peaks observed in Fig. 2. Because $(M - HCl)^-$ and $M^-$ produced from TCP have two and three Cl atoms, the relative isotopic ratio $^{35}Cl^{35}Cl$:$^{35}Cl^{37}Cl$:$^{37}Cl^{37}Cl$ in the $(M - HCl)^-$ and $^{35}Cl^{35}Cl^{35}Cl$:$^{35}Cl^{35}Cl^{37}Cl$:$^{35}Cl^{37}Cl^{37}Cl$:$^{37}Cl^{37}Cl^{37}Cl$ in the $M^-$ should be 9:6:1 and 27:27:9:1, respectively. The relative signal intensities between the isotopes for $(M - HCl)^-$ and $M^-$ in Fig. 2 are in good agreement with the expected isotopic ratio except for $^{37}Cl^{37}Cl$ of $(M - HCl)^-$ and $^{37}Cl^{37}Cl^{37}Cl$ of $M^-$, whose signal intensities were too low to be observed.

The intensity of the ion was summed around the peak area and was proportional to the injection quantity of the sample (0.4–1.5 μl). The intensity of each ion per $10^{-7}$ mol of the sample was calculated by the least-squares method. The branching ratio was obtained as the relative intensity of the ions. The temperature of the ion source chamber was changed and the intensity of the ions was measured by the same method.

To check whether the temperature of the sample molecule was the same as that of the electrons, the temperature of the capillary interface was changed. The temperature of the interface was maintained at 100 K lower than that of the ion source. If the sample gas passed through the interface at a lower temperature and was not heated enough in the ion source chamber, the intensity and the relative ratio of the ions should be influenced. The intensity and the relative ratio of ions did not change, indicating that the temperature of the electrons should be almost the same as that of the sample molecules in the reaction chamber.

The mainly observed ion was $Cl^-$ for all measured compounds and the signal intensity of the chloride ion increased with the increasing number of Cl atoms present in the molecule. The signal intensity of $Cl^-$ increased in the order 2,3,4- < 2,4,5- < 2,3,5- < 2,3,6- ≈2,4,6-TCP, 3,4- ≈2,5- < 2,4- < 2,6 < 2,3- ≈3,5-DCP, and *m*- < *o*-ClP. $(M - HCl)^-$ and $(M - H)^-$ (M: parent molecule) were also observed for TCP and DCP. The signal intensity of $(M - H)^-$ was not high and the branching ratio, $(M - H)^-/Cl^-$, was less than 0.05 for all the chlorinated phenols. The signal intensity of $(M - HCl)^-$ increased in the order 2,3,4- < 2,3,6- ≈2,4,6- < 2,3,5- ≈2,4,5-TCP and 2,4- < 2,5- ≈2,6- < 3,4- < 2,3- < 3,5-DCP, though the branching ratio, $(M - HCl)^-/Cl^-$, was less than 0.05 for 2,4- and 2,6-DCP.

For 2,3,4- and 2,4,5-TCP, $M^-$ was observed at a temperature lower than 523 K and the branching ratio $M^-/[Cl^- + (M - Cl)^-]$ was greater than 0.05 at temperature lower than 473 K. For the other TCPs, $M^-$ was observed at lower than 473 K and no $M^-$ was observed for DCP, *o*-ClP and *m*-ClP. The result that the parent anions were observed for the molecules having more than three chlorine atoms is similar to the chlorinated dibenzofurans and dibenzodioxins [4]. The electron affinity of these chlorinated compounds increases with the increasing number of chlorine atoms in the molecule. The signal intensity of the fragment ions, $Cl^-$ and $(M - HCl)^-$, increased with the increasing temperature, while that of the parent anion decreased. The decreasing ratio of the parent ions is greater than the increasing ratio of the fragment ions. This result agrees with that of $C_6F_5X$ (X = Cl, Br, I) [8]. Dissociative electron attachment and electron detachment from the parent anion will competitively occur at higher temperatures.

$Cl^-$ was the only observed ion for *o*-ClP and *m*-ClP at the same concentration of the sample as the other chlorinated phenols. $(M - H)^-$ was also observed at the higher concentration, though the branching ratio of $(M - H)^-/Cl^-$ was less than 1/1000. The signal intensity of the $Cl^-$ from the mono-chlorinated phenol was less than 1/100 for TCP and 1/10 for DCP. Muftakhov et al. measured the electron attachment spectra of 4-ClP and reported that the fragment anions, $Cl^-$, and $(M - H)^-$ were produced from the electron attachment process with an energy of around 1.0 eV [5]. Thermal electron attachment would not occur for *o*-ClP and *m*-ClP in the same manner as 4-ClP.

### 3.2. Reaction mechanism

Chlorinated phenols will react with electrons as follows:

$$M + e^- (\sim 0\,\mathrm{eV})(+R) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} M^- \xrightarrow{k_2} (M - Cl) + Cl^-$$

$$\xrightarrow{k_3} (M - HCl)^- + HCl \xrightarrow{k_4} (M - H)^- + H$$

$$\text{Negative ion} + P^+ \xrightarrow{k_N} \text{Products}$$

$$e^- + P^+ \xrightarrow{k_r} \text{Products}$$

where $P^+$ is a positive ion and R is the reagent gas.

The sample gas should be spread over the ion source chamber ejected from the capillary interface. Electrons were constantly provided from the filament. We can assume a steady state condition of electrons supplied by the ion source just like radiolysis in a cell. When electrons whose energy was 200 eV were thermalized by collisions with isobutane, positive ions of isobutane were produced for a high concentration of isobutane. The monitoring pressure at the mass analytical tube did not increase by the introduction of the sample molecules, indicating that the concentration of the sample should be less than that of isobutane. Therefore, the concentration of electrons and positive ions of isobutane should be much greater than that of the negative ions produced from the sample. The concentration of positive ions and electrons would remain constant during the measurement. These assumptions lead to the results that $k_{N'}[P^+] = k_N =$ constant and that the rate ($k_r$) of the electron-ion recombination reaction should be maintained constant during the measurement.

The instrumental constant includes the interaction volume, ion draw-out efficiency, ion lens and mass spectrometer transmission efficiencies and ion detection efficiency of the electron multiplier. If measurements are carried out with the same experimental setup, the ion lens and mass spectrometer transmission efficiencies or ion detection efficiency should be the same for all the measurements. However, the absolute value of the ion draw-out efficiency would depend on the type of sample. When ions with a higher translational energy are produced, they could not be focused as well like the same type of ions with a lower energy [9]. Because we discussed that the branching ratio of $[(M - HCl)^-]/[Cl^-]$ and the production mechanism of each fragment ion would not significantly differ among the DCPs and TCPs, the relative difference in the ion draw-out efficiency and the instrumental constants should be regarded as almost the same for all the compounds studied.

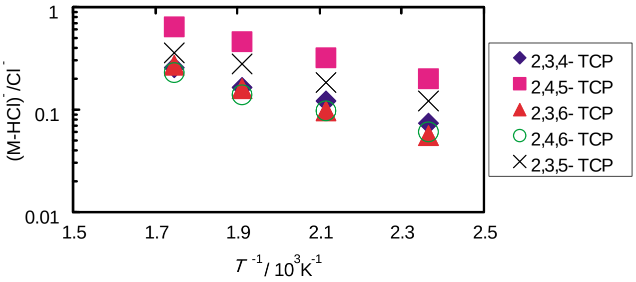

Fig. 3. The temperature dependence of the branching ratio, $(M - HCl)^-/Cl^-$, for TCP.

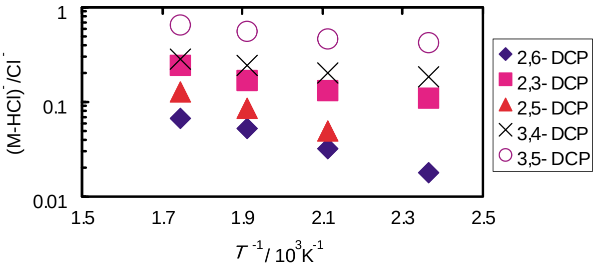

Fig. 4. The temperature dependence of the branching ratio, $(M - HCl)^-/Cl^-$, for DCP.

The reaction rate constant could be described as $k = A\exp(-E/RT)$, where $A$ is a pre-exponential factor and $E$ is the apparent activation energy. Therefore, the branching ratio of the fragment ions, $[(M-HCl)^-]/[Cl^-]$, can be expressed as $[(M - HCl)^-]/[Cl^-] \propto A_3/A_2 \exp(-(E_3 - E_2)/RT)$, where $A_2$ and $A_3$ are pre-exponential factors, and $E_2$ and $E_3$ are activation energies for the reaction generating $Cl^-$ and $(M-HCl)^-$, respectively. Figs. 3 and 4 show the temperature dependence of the branching ratio of $[(M-HCl)^-]/[Cl^-]$ for TCP and DCP, respectively. The slope of the plot should depict the difference between the activation energy of the reaction to produce $(M-HCl)^-$ and that for $Cl^-$, $(E_3-E_2)$. The intercept denotes the ratio of the Arrhenius pre-exponential factor for the formation of $(M - HCl)^-$ and $Cl^-$, $A_3/A_2$. Table 1 lists the values of $(E_3 - E_2)$ and $A_3/A_2$ obtained from Figs. 3 and 4. For TCP, the value of $(E_3 - E_2)$ is found to be almost the same, revealing that the activation energy of the reaction intermediate leading to $(M - HCl)^-$ should almost be the same for the TCPs. The relative production ratio is related to $A_3/A_2$. The $A_3/A_2$ value increased in the order of 2,3,4- < 2,3,5- ≈2,4,6- < 2,4,5- ≈2,3,6-TCP.

Fig. 5 represents the temperature dependence of the branching ratio of $M^-/[Cl^- + (M - HCl)^-]$ for 2,3,4- and 2,4,5-TCP. The parent anion was observed only at the lowest temperature (423 K) for the other TCPs. Though the branching ratio of 2,4,5-TCP was lower than that of 2,3,4-TCP, the trend in the temperature dependence of the branching ratio between them is almost the same. This means that the parent anions should dissociate into fragment ions with almost the same probability for the two TCPs. $M^-/[Cl^- + (M - HCl)^-]$ extrapolated at 300 K in Fig. 5 for 2,3,4- and 2,4,5-TCP was estimated to be greater

Table 1
The difference between the activated energy of the production of $(M - HCl)^-$ and $Cl^-$: $(E_3 - E_2)$, the ratio of the Arrhenius parameter: $A_3/A_2$, and the strength between the *ortho*-Cl and the H of –OH

| | $E_3 - E_2$[a] (eV) | $A_3/A_2$[b] | $r$(H–Cl) (Å) |
|---|---|---|---|
| 2,3,4-$C_6Cl_3H_2OH$ | 0.165 ± 0.013 | 7.59 ± 2.23 | 2.056 |
| 2,3,5-$C_6Cl_3H_2OH$ | 0.150 ± 0.007 | 8.19 ± 1.55 | 2.041 |
| 2,3,6-$C_6Cl_3H_2OH$ | 0.205 ± 0.013 | 18.0 ± 4.0 | 2.048 |
| 2,4,5-$C_6Cl_3H_2OH$ | 0.159 ± 0.004 | 17.4 ± 0.17 | 2.029 |
| 2,4,6-$C_6Cl_3H_2OH$ | 0.177 ± 0.017 | 8.52 ± 2.5 | 2.052 |
| 2,6-$C_6Cl_2H_3OH$ | 0.180 ± 0.004 | 2.99 ± 0.37 | 2.007 |
| 2,3-$C_6Cl_2H_3OH$ | 0.105 ± 0.003 | 1.97 ± 0.25 | 2.034 |
| 2,5-$C_6Cl_2H_3OH$ | 0.215 ± 0.004 | 11.2 ± 1.72 | 1.993 |
| 3,4-$C_6Cl_2H_3OH$ | 0.060 ± 0.001 | 0.95 ± 0.20 | – |
| 3,5-$C_6Cl_2H_3OH$ | 0.060 ± 0.001 | 2.21 ± 0.52 | – |

[a] The difference between the activated energy of the production of $(M - HCl)^-$ and $Cl^-$.

[b] The ratio of the Arrhenius parameter for $(M - HCl)^-$ formation and for $Cl^-$ formation.

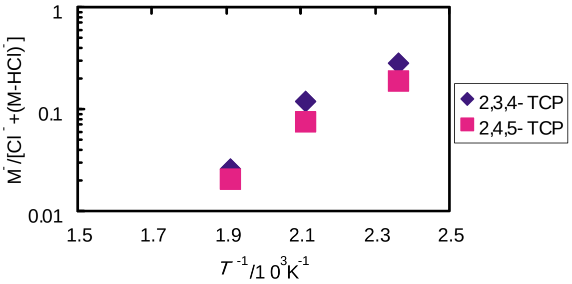

Fig. 5. The temperature dependence of the branching ratio, $M^-/[Cl^- + (M - Cl)^-]$, for 2,3,4- and 2,4,5-TCP.

than 20, indicating that the relative intensity of the parent anions ($M^-$) should be 20 times greater than that of the fragment ions ($Cl^-$ and $(M - HCl)^-$) and the parent anions should be relatively stable at room temperature. This fact is one of the reasons why it is difficult to degrade chlorinated phenols by an electron transfer reaction [3d].

### 3.3. Dynamics of HCl elimination

The $A_3/A_2$ value in Table 1 shows that the amount of $(M - HCl)^-$ is several times greater than that of $Cl^-$ at the high-temperature limit. Moreover, the value of $A_3/A_2$ depends on the molecule. For TCP, the reaction dynamics of the intermediate leading to $(M - HCl)^-$ will be similar, because the value of $E_3 - E_2$ is almost the same. The expected structure of the common intermediate for the HCl elimination from TCPs should be the loss of hydroxylic hydrogen and the *ortho*-Cl. The H atom loss and the Cl atom loss should not separately occur because the signal intensities of $(M - H)^-$ and $(M - Cl)^-$ were much lower than that of $(M - HCl)^-$. The most appropriate mechanism for the HCl elimination should be the HCl molecular loss of the hydroxylic hydrogen atom and the *ortho*-Cl atom. It is expected that a similar mechanism will take place to produce $(M - HCl)^-$ for 2,3-, 2,5-, and 2,6-DCP, which possesses the *ortho*-Cl atom. On the other hand, the HCl elimination of the hydroxylic hydrogen and the *ortho*-Cl cannot occur for 3,4- and 3,5-DCP, since these molecules do not possess the *ortho*-Cl atom. Otherwise, not only formation of $(M - HCl)^-$ was observed for 3,4- and 3,5-DCP, but also the branching ratio of $[(M - HCl)^-]/[Cl^-]$ became greater than those of 2,4-, 2,5-, and 2,6-DCP.

To interpret these phenomena, we propose the process in which the hydroxylic hydrogen atom can migrate to the *ortho* position to produce $C_6Cl_2H_4O^-$, the cyclohexadienone-type anion. Subsequently, the elimination of the H atom at the *ortho* location and the Cl atom at the *meta* position will then take place. The mechanism should be similar for 3,4- and 3,5-DCP, because their values of $E_3 - E_2$ are almost the same. The value of $A_3/A_2$ for 3,5-DCP is two times greater than that of 3,4-DCP. This means that the probability for the elimination of HCl based on the H atom migration for 3,5-DCP should be twice that for 3,4-DCP. For 3,4-DCP, two rotational isomers (*cis* and *trans*) exist, and in the *trans* isomer, the subsequent HCl elimination with the hydroxylic H atom migration cannot occur. This is a reasonable scenario based on the experimental result.

To estimate the reactivity for the production of $(M - HCl)^-$, we have calculated the structure of the intermediates for both reaction processes using the Gauusian98 program [10]. The B3LYP/D95 method, whose accuracy is reasonable for its cost, was used to optimize the structures.

For the case of the HCl molecular elimination, the *ortho*-Cl atom is situated nearer to the hydroxylic hydrogen atom than the neutral molecule. We can postulate that the nearer the *ortho*-Cl is to the H atom, the easier the HCl elimination occurs. The bond length between the *ortho*-Cl and the hydroxylic hydrogen is listed in the far right column of Table 1. The value becomes greater in the order of 2,4,5- < 2,3,5- < 2,3,6- < 2,4,6- < 2,3,4- for TCP and 2,5- < 2,6- < 2,3- for DCP. This result almost corresponds to the order of the value $A_3/A_2$ of TCP and DCP, that is, the branching ratio of $[(M - HCl)^-]/[Cl^-]$ is greater and the bond length of H–Cl is the shortest for 2,4,5-TCP and 2,5-DCP among the derivatives. On the other hand, the branching ratio of $[(M - HCl)^-]/[Cl^-]$ is the smallest and the bond length of H–Cl is the longest for 2,3,4-TCP and 2,3-DCP among the derivatives. The hydrogen bonding between the hydroxylic hydrogen atom and the *ortho*-Cl was studied by comparison of the fluorescence excitation spectrum and resonance enhanced multiphoton ionization excitation spectrum measurements of *o*-ClP [11]. It is reasonable that the HCl elimination from the hydroxylic hydrogen atom and the *ortho*-Cl atom should take place for the chlorinated phenol anions.

For 3,4- and 3,5-DCP, the structure of the intermediate, the cyclohexadienone-type anion, was optimized by the molecular orbital calculations. The energy of the intermediate was less than that of the parent anion for both molecules. This suggests that the HCl elimination through the cyclohexadienone-type anion should be appropriate for 3,4- and 3,5-DCP. On the contrary, unimolecular HF and HCl loss as from the fluorinated phenol cation [12] and chlorinated phenol cation [13] was observed by mass-analyzed ion kinetic energy (MIKE) spectrometry. A ring-walk mechanism of the fluorine and the chlorine atom was proposed. The activation energy of the chlorine atom ring-walk from *m*-$ClP^+$ was calculated to be approximately 2.1 eV. However, we cannot optimize the structure obtained by the ring-walk chlorine atom mechanism in the case of chlorinated phenol anions. This result reveals that the migration of the hydroxylic hydrogen in the chlorinated phenol anion should take easily place to give rise to the HCl elimination.

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