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On the structure of negative ions formed by dissociative electron attachment by monochlorophenol molecules*

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The energetics of negative ion formation by resonant dissociative electron attachment by *o*-, *m*-, and *p*-chlorophenol molecules was studied. The structures of some fragment ions and their neutral partners were established. Hidden rearrangement processes leading to the formation of oxy anions by the detachment of chlorine atoms from molecular ions were found. The O—H bond dissociation energies for *o*-, *m*-, and *p*-chlorophenol molecules were 3.74±0.11, 3.72±0.17, and 3.94±0.11 eV, respectively.

Key words: mass spectrometry, negative ions, resonant dissociative electron attachment; monochlorophenols, chlorobenzene, phenol; rearrangement processes, oxy anions.

Chloroaromatic compounds, especially chloro-substituted derivatives of dibenzo-*p*-dioxin, are characterized by toxicity, capability of accumulating in organisms, and enhanced stability, being dangerous for humans, animals, and environment.[4] Therefore, researchers faced such urgent problems as the development of sensitive and selective methods for determination of these substances and methods of their neutralization. Mass spectroscopic methods of studying ecotoxicants and some methods of their neutralization by the electron beam treatment (see, *e.g.*, Refs. 5 and 6) are based on the interaction of molecules with electrons.

The purpose of this work is to study the decomposition of *p*- (PCP), *m*- (MCP), and *o*-chlorophenol (OCP) molecules under conditions of resonant dissociative electron attachment (DEA) with moderate energies (E_e = 0—15 eV) in the gas phase.[7]

Experimental

Experiments were carried out on an MI-1201 magnetic sector mass spectrometer modified for the generation and detection of negative ions (NI).[8] The ion source of the instrument was equipped with a trochoidal electron monochromator,[9] which formed an electron beam with the energy resolution $\Delta E_{1/2}$ = 0.15—0.20 eV in an energy interval of 0—15 eV at an electron current of ~150—250 nA. The MCP, PCP, and OCP samples (Aldrich, purity ≥98%) were introduced into an ionization chamber with a temperature of 100 °C through a liquid and gas sample inlet system at T = 50 °C. The NI appearance energies (E_{app}) were measured using effective yield curves (EYC) according to a previously described procedure.[10] The procedure of measurement of the relative DEA cross sections (σ_{DEA}) will be described elsewhere.

Results and Discussion

Mass spectra of NI of chlorophenol isomers under DEA conditions: qualitative comparison. The mass spectra of all studied compounds contain peaks of the $[M - H]^-$, $[M - 2 H]^-$, $[M - 2 H - Cl]^-$, $[M - H - Cl]^-$, $[M - Cl]^-$, and Cl^- negative ions (Fig. 1). Peaks of molecular NI were not detected, which indirectly indicates a negative electron affinity of these molecules.

The energies of the EYC maxima (E_{max}) for the series of chlorophenol isomers differ insignificantly. However, the intensities of peaks vary in a wide range (see Fig. 1), which can make a basis for a method of isomer identification. Note that PCP and MCP cannot be identified under the conditions of GC analysis due to close retention times, and their EI mass spectra of positive ions are virtually indiscernible.[11]

The mass spectra of NI formed under DEA from phenol and chlorobenzene are presented in Fig. 2 for comparison.

The mass spectra of NI of the chlorophenol isomers contain peaks of the $[M - H]^-$ ions; their EYC at low energies (0—3 eV) are similar in shape, and the energies of maxima are close to each other (see Fig. 1). The peak of the $[M - H]^-$ ion with a similar shape of EYC is also observed in the mass spectrum of phenol (see Fig. 2, *a*)

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[*] This work continues the cycle of works[1—3] on thermochemistry of negative ions.

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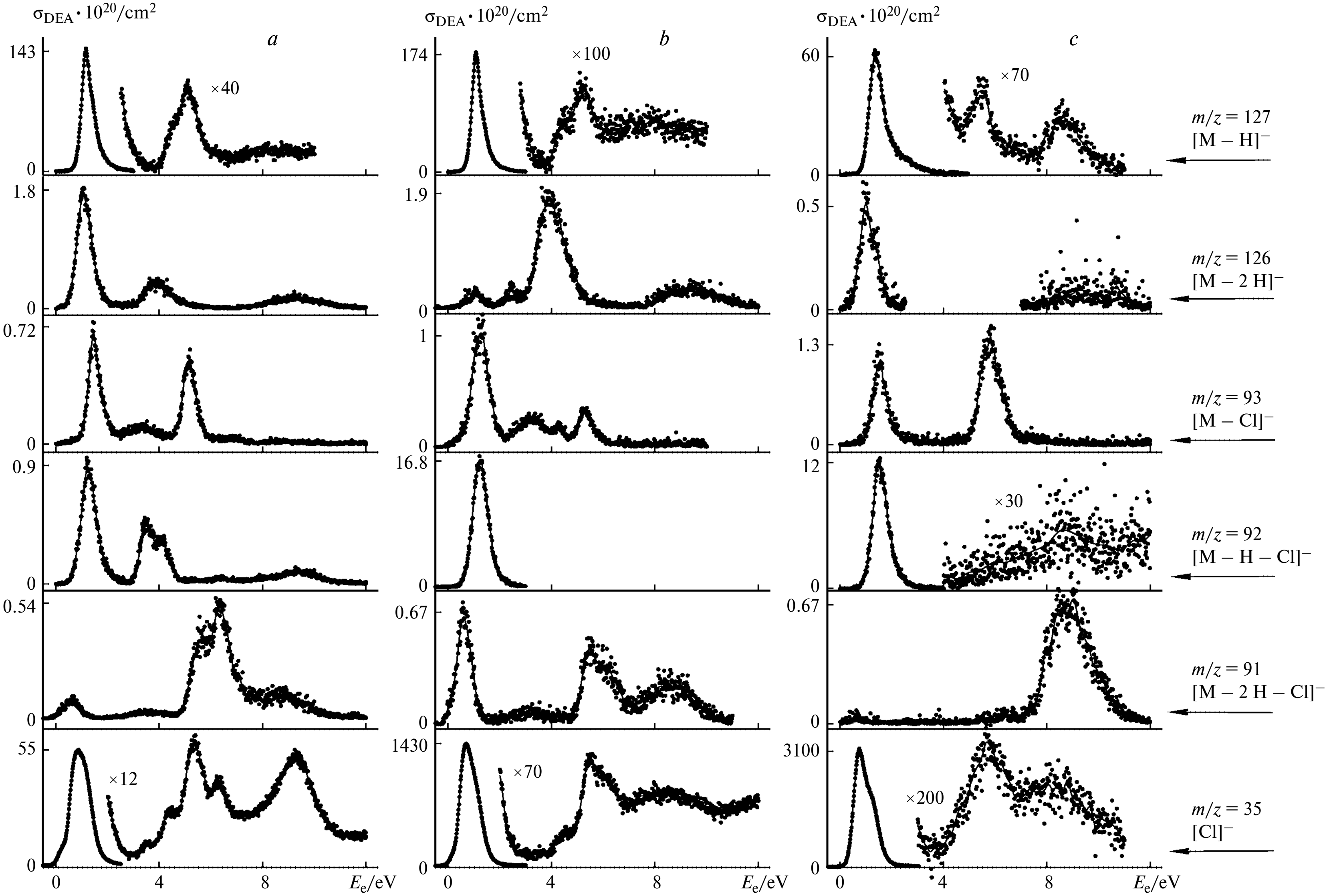


Fig. 1. Mass spectra of NI under the DEA conditions for *p*- (*a*), *m*- (*b*), and *o*-chlorophenol (*c*) in the 0—12 eV interval.

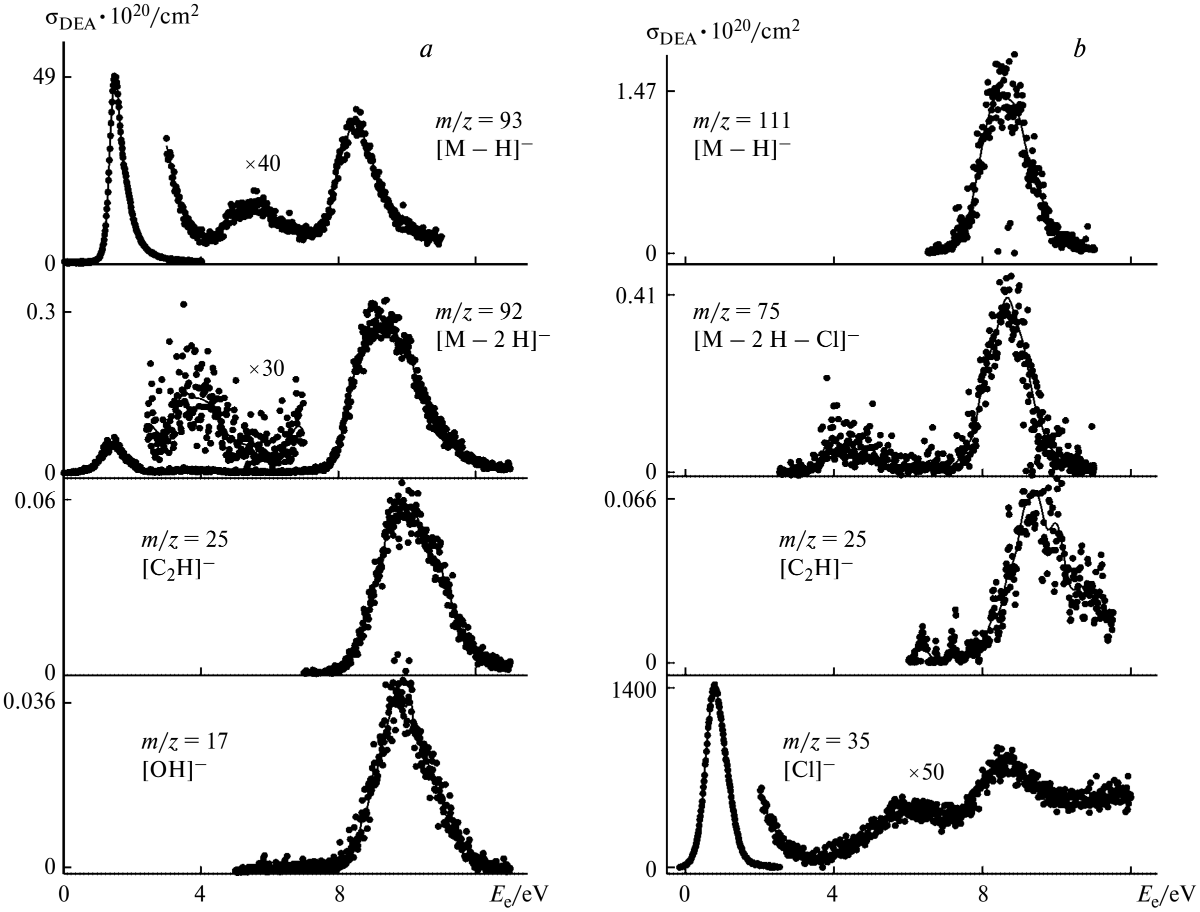


Fig. 2. Mass spectra of NI under the DEA conditions for phenol (*a*) and chlorobenzene (*b*) in the 0—12 eV interval.

but it is absent from the mass spectrum of chlorobenzene (see Fig. 2, *b*). Therefore, the formation of these ions is related to the OH group in the structure of phenol molecules. We have previously shown[12] that the $[M - H]^-$ ions are formed from pentachlorophenol (C_6Cl_5OH), whose benzene ring contains no H atoms. This indicates that the H atom is detached from the OH group. Analysis of the EYC suggests that in the medium-energy region (3—7 eV) the $[M - H]^-$ ions are also formed due to the O—H bond cleavage (Fig. 3). In the high-energy region (above 7 eV), the absence of maxima in the EYC of the $[M - H]^-$ ions and their presence in the EYC for chlorobenzene (see Fig. 2, *b*) suggest that the formation of the NI under discussion in this region is caused by the H atom detachment from the aromatic ring for all studied phenols.

In the case of phenols, the $[M - 2\,H]^-$ and $[M - HCl]^-$ ions (*cf.* Figs. 1 and 2) are also formed involving the H atom of the hydroxy group, because the mass spectrum of chlorobenzene does not contain peaks corresponding to these ions (see Fig. 2, *b*). On the contrary, the formation of the $[M - 2\,H - Cl]^-$ ions is not probably related to the presence of the hydroxy group in the molecules, because the peaks of these ions are present in the mass spectra of both chlorophenols and chlorobenzene (*cf.* Figs. 1 and 2, *b*).

The intense peaks of the $[M - H]^-$ and Cl^- ions in the mass spectra of chlorophenols agree with two rules of formation of NI mass spectra under the DEA conditions[13]:

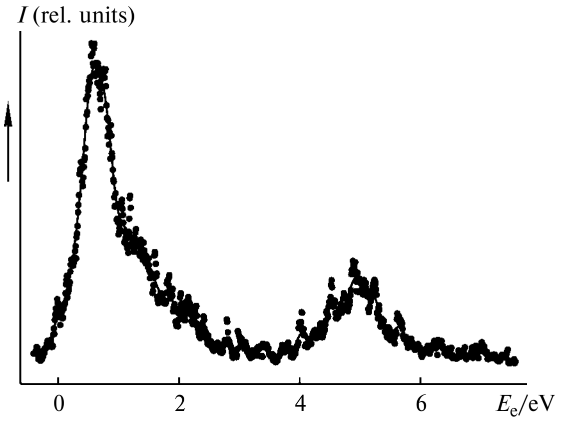


Fig. 3. Effective yield curve of the $[M - H]^-$ NI from pentachlorophenol.

(1) NI, whose respective neutral species have a higher electron affinity (E_{ea}), are predominantly formed, which occurs, in fact, in our case (see E_{ea} for the Cl atom and chlorophenoxyl radicals in Table 1); (2) NI that appear due to the simple bond cleavage are preferentially formed.

Table 1. Thermochemical data ($\Delta H_f°$, E_{ea}, and D) for some substituted benzene derivatives and their fragments

Compound or fragment	Parameter	Refs.
	$\Delta H_f°$	
PhOH	-96.4 kJ mol^{-1}	14
	-23.1 ± 0.1 kcal mol^{-1} = = -96.65 kJ mol^{-1}	15
	-96.4 ± 0.9 kJ mol^{-1}	16
	-93.0 kJ mol^{-1}	17
PhO$^{\bullet}$	11.6 ± 2.3 kcal mol^{-1} = = 48.53 kJ mol^{-1}	15
	54.0 ± 6.0 kJ mol^{-1}	18
H	217.998 kJ mol^{-1}	19
H_2	0	
p-ClC_6H_4OH	-119.1 kJ mol^{-1}	14
p-$OHC_6H_4^{\bullet}$	37.4 kcal mol^{-1} = = 156.48 kJ mol^{-1}	17
p-$OHC_6H_4^-$	11.1 kcal mol^{-1} = = 46.44 kJ mol^{-1}	17
m-ClC_6H_4OH	-135.4 kJ mol^{-1}	14
m-$OHC_6H_4^{\bullet}$	37.2 kcal mol^{-1} = = 155.64 kJ mol^{-1}	17
m-$OHC_6H_4^-$	8.6 kcal mol^{-1} = = 35.98 kJ mol^{-1}	17
o-ClC_6H_4OH	-122.7 kJ mol^{-1}	14
Cl	29.0 kcal mol^{-1} = = 121.33 kJ mol^{-1}	20
HCl	-22.1 kcal mol^{-1} = = -92.47 kJ mol^{-1}	20
	E_{ea}	
PhO$^{\bullet}$	2.253 ± 0.006 eV = = 217 ± 0.6 kJ mol^{-1}	21
Cl	348.5750 ± 0.0026 kJ mol^{-1}	22
p-$ClC_6H_4O^{\bullet}$	2.58 ± 0.10 eV = = 248.93 kJ mol^{-1}	23
m-$ClC_6H_4O^{\bullet}$	2.57 ± 0.16 eV = 247.97 kJ mol^{-1}	23
o-$ClC_6H_4O^{\bullet}$	2.59 ± 0.10 eV = = 249.90 kJ mol^{-1}	24
Ph$^{\bullet}$	99 kJ mol^{-1}	25
	D	
PhO—H	377 ± 13 kJ mol^{-1}	26
	86.8 ± 2.2 kcal mol^{-1} = = 363.17 ± 9.20 kJ mol^{-1}	15

Note. Measuring units accepted in original articles and units used by researchers in practice (eV) were transformed into the units of International System of Units using the following coefficients recommended by CODATA[27]: 1 eV = 96.4853 kJ mol^{-1}, 1 kcal mol^{-1} = 4.184 kJ mol^{-1}.

However, the third rule (concerning symmetry correlation of electronic states of parent NI and daughter fragments) for the $[M - H]^-$ and Cl^- ions is inappropriate in the formulation given in Ref. 13. The formation of the $[M - H]^-$ ions from phenol and PCP has been considered by us in general outline previously.[12,28] The spectroscopic features of NI formation from the chlorophenol isomers will be considered in more detail elsewhere. Thus, the aforementioned rule for formation of NI mass spectra is not rigid and finally formulated.

Other channels of chlorophenol decomposition obey requirements of any of three rules listed above, due to which they are less intense. Indeed, the composition of the neutral partners of the $[M - 2\,H]^-$, $[M - 2\,H - Cl]^-$, and $[M - H - Cl]^-$ ions indicates complicated structural transformations in the molecular framework, which contradicts the requirements given by the second rule.

Energetic approach to establishment of structures of NI and their neutral partners. The formation of NI during DEA by AB molecules can be described by the energy balance equation[7]

$$E_{app}(A^-) = D(A\text{—}B) - E_{ea}(A^{\bullet}) + E^{*}, \qquad (1)$$

where $E_{app}(A^-)$ is the appearance energy of the A^- ions, D(A—B) is the energy of the A—B bond homolytic cleavage, $E_{ea}(A^{\bullet})$ is the electron affinity of the $A^{\bullet}$ fragment, and E^* is an excessive energy of DEA including the energy of fragment excitation and their kinetic energy. The D and E_{ea} values can be presented through standard enthalpies of formation ($\Delta H_f°$) of species by the following correlations:

$$D(A\text{—}B) = \Delta H_f°(A^{\bullet}) + \Delta H_f°(B^{\bullet}) - \Delta H_f°(AB), \qquad (2)$$

$$E_{ea}(A^{\bullet}) = \Delta H_f°(A^{\bullet}) - \Delta H_f°(A^-). \qquad (3)$$

The structures of DEA products (NI and their neutral partners) are established by comparison of the experimentally measured appearance energy of NI ($E_{app}{}^{exp}$) with the calculated value ($E_{app}{}^{calc}$), assuming some certain structure (the latter should be close to $E_{app}{}^{exp}$). Equation (1) is applicable only to DEA processes near the energy threshold of a certain monomolecular decomposition, when the reactants and reaction products are in the ground electron states and their vibrational and kinetic energies can be neglected. The E^* value can be non-negligible for ions formed at energies much higher than the threshold.

Ions $[M - H]^-$ from chlorophenol isomers. The threshold of $[M - H]^-$ ion formation from phenol by the simple O—H bond cleavage is $E_{app}{}^{calc}(PhO^-) = D(PhO\text{—}H) - E_{ea}(PhO^{\bullet}) = 363.17 - 217 = 146.17$ kJ mol^{-1} = 1.51 eV (calculation by Eq. (1) with insertion of Eq. (2) gives 1.497 eV (see Table 1 and published data[12])). This value insignificantly exceeds the experimental value $E_{app}{}^{exp} = 1.29\pm0.05$ eV (Table 2) and virtually coincides with the

Table 2. Experimental energy parameters (the lowest appearance energy (E_{app}) and the energy of the corresponding peak maximum (E_{max})) of peaks of negative ions in the mass spectra of phenol, *o*-, *m*-, and *p*-chlorophenol, and chlorobenzene*

Ion	PhOH		*o*-ClC$_6$H$_4$OH		*m*-ClC$_6$H$_4$OH		*p*-ClC$_6$H$_4$OH		PhCl	
	E_{app}	E_{max}	E_{app}	E_{max}	E_{app}	E_{max}	E_{app}	E_{max}	E_{app}	E_{max}
	eV									
$[M - H]^-$	1.29	1.49	1.05	1.35	1.01	1.15	1.03	1.16	7.7**	8.6
$[M - 2H]^-$	0.90	1.40	0.55	1.00	0.58	1.04	0.73	1.05	—	—
$[M - Cl]^-$	—	—	1.09	1.50	0.83	1.25	1.15	1.45	—	—
$[M - HCl]^-$	—	—	1.10	1.49	0.85	1.30	0.85	1.25	—	—
$[M - 2H - Cl]^-$	—	—	7.40	8.80	0.28	0.59	0**	0.65**	3.7	4.3**
$[Cl]^-$	—	—	0.40	0.70	0.40	0.65	0.46	0.75	0.49	0.74
$[OH]^-$	8.5	9.8	—	—	—	—	—	—	—	—
$[C_2H]^-$	8.5	9.8	—	—	—	—	—	—	7.8	9.4**

* The errors of determination of E_{app} and E_{max} are 0.05 (in the energy region ≤1.5 eV) and 0.1 eV (in higher-energy regions).

** Difficult to determine with an appropriate accuracy.

maximum of the $[M - H]^-$ NI peaks, which is equal to 1.49 eV (see Table 2). This indicates the near-threshold character of formation of these ions.

The effective yield curves of the $[M - H]^-$ ions from the chlorophenol isomers at 0—3 eV are non-symmetrical in shape and demonstrate a sharp slope at the low-energy side (see Fig. 1) similar to that for phenol (see Fig. 2, *a*). A fine vibrational structure, whose origin was explained by the pre-dissociative mechanism, has previously been observed in the high-energy shoulder of these EYC for phenol and some its chloro-substituted derivatives (PCP and pentachlorophenol).[12] It is most likely that the formation of the $[M - H]^-$ ions from PCP, MCP, and OCP in this region is restricted from the bottom by an energy threshold, as it takes place for phenol. In this case, the "true" left slope of the EYC should be vertical (see Fig. 1), if a slight "diffusion" of the EYC shape due to the "hot" band effect and the limited instrumental energy resolution are ignored.

Using Eq. (1), which contains $E_{max}([M - H]^-)$ (see Table 2) instead of $E_{app}([M - H]^-)$ due to the above concepts, we can obtain the O—H bond dissociation energies (D(O—H)) for the chlorophenol isomers: 3.74±0.11 (PCP), 3.72±0.17 (MCP), and 3.94±0.11 eV (OCP) (published data on the O—H bond dissociation energies for the chlorophenol isomers are unavailable). The D(O—H) value obtained for OCP is somewhat higher than those for two other isomers, which can be explained by the possible formation of an intramolecular hydrogen bond, whose energy, according to different estimations, is 0.06—0.1 eV.[29]

Ions $[M - H - Cl]^-$ and $[M - 2H]^-$. Peaks of the $[M - H - Cl]^-$ ions are observed in the mass spectra of many chloroaromatic compounds,[30—32] and the formation of the $[M - 2H]^-$ ions is characteristic of polycyclic oxygen-containing compounds.[33,34] At the same time, data on the structure of similar fragments are few. According to the published data,[35] peaks of the odd-electron negative ions (radical anions) are of low intensity in the NI mass spectra under the DEA conditions. This also concerns the peaks of the $[M - H - Cl]^-$ and $[M - 2H]^-$ ions in the mass spectra of the compounds of the series under discussion (see Figs. 1 and 2, *a*).

The mass spectra of positive ions of isomeric chlorophenols also contain peaks of the $[M - HCl]^+$ ions, which, as shown in experiments with a deuterium label in the hydroxy groups, are formed involving the H atom of the OH group.[36] The relative intensity of the $[M - HCl]^+$ peaks in the MIKE (mass-analyzed ion kinetic energy) spectra increases in the series PCP < MCP < OCP (note that the mass spectra of NI exhibit the same tendency, at least for the low-energy $[M - HCl]^-$ peak of PCP and MCP (see Fig. 1)). Therefore, it was proposed that the Cl atom can migrate over the benzene ring, and the closer the Cl atom to the OH group initially, the higher the intensity of the $[M - HCl]^+$ ion. The respective mechanism was named "ring-walk" (see Ref. 36 and works cited therein). Bromophenols are not characterized by the detachment of HBr molecules from either positive[36] or negative ions,[37] which is probably related to a low mobility of the Br atom due to its big mass.

It can only be suggested that the $[M - H - Cl]^-$ and $[M - 2H]^-$ ions (at least in the low-energy region) appear due to the detachment of the HCl and H_2 molecules rather than the individual H and Cl atoms or two H atoms. This is confirmed by the energetic concepts. It has previously[34] been shown that the rearrangement detachment of the H_2 fragment is energetically more favorable by the bond energy value $D(H—H) \approx 436$ kJ mol^{-1} than the detachment of two individual H atoms.

We have recently[34] shown that H_2 detachment under DEA by ecdysteroid molecules affords the pseudo-molecular $[M - H_2]^-$ ions with the system of conjugated double bonds, which is impossible for unsaturated aromatic systems. For example, the mass spectrum of chlorobenzene contains no $[M - H_2]^-$ peak at all (see Fig. 2, *b*), and in the spectrum of benzene the low-intensity peak of the $C_6H_4^-$ ions was found only in the high-energy region[37] and, most likely, corresponded to the detachment of two H atoms.

The $[M - H_2]^-$ ions from phenol and $[M - HCl]^-$ from chlorophenols have the same structure. In order to check this assertion, below we present the thermochemical estimation of the difference between the E_{app} values for the $[M - H_2]^-$ ions from phenol and $[M - HCl]^-$ from the chlorophenol isomers, assuming their structural identity in peaks of the low-energy region (according to Eqs. (1) and (2)):

$$\begin{aligned}\Delta E_{app} &= E_{app}([M - H_2]^-/PhOH) - \\ &- E_{app}([M - HCl]^-/ClC_6H_4OH) = [\Delta H_f^\circ(H_2) + \\ &+ \underline{\Delta H_f^\circ(St)} - \Delta H_f^\circ(PhOH) - \underline{\underline{E_{ea}(St)}}] - [\Delta H_f^\circ(HCl) + \\ &+ \underline{\Delta H_f^\circ(St)} - \Delta H_f^\circ(ClC_6H_4OH) - \underline{\underline{E_{ea}(St)}}],\end{aligned}$$

where St is the proposed (unknown) structure, and mutually annihilated terms are singly and doubly underlined. Whence

$$\begin{aligned}\Delta E_{app} &= [\Delta H_f^\circ(H_2) - \Delta H_f^\circ(HCl)] + [\Delta H_f^\circ(ClC_6H_4OH) - \\ &- \Delta H_f^\circ(PhOH)],\end{aligned}$$

being 0.69, 0.56, and 0.73 eV for OCP, MCP, and PCP, respectively (the data in Table 1 were used).

Thus, according to the calculation, the appearance energy of the $[M - H_2]^-$ NI from phenol should be by 0.56—0.73 eV higher than the appearance energy of the $[M - HCl]^-$ ions from chlorophenols. However, the experimentally determined E_{app}^{exp} values almost coincide (see Table 2): $E_{app}^{exp}([M - H_2]^-/PhOH) = 0.9$ eV, $E_{app}^{exp}([M - HCl]^-)$ from *o*-, *m*-, and *p*-chlorophenols are 1.10, 0.85, and 0.85 eV, respectively, *i.e.*, the assumption that the structures of these ions are identical is invalid.

Ions $[M - Cl]^-$. No peaks of the $[M - Cl]^-$ ions were observed in the mass spectrum of chlorobenzene, which is probably related to a relatively low electron affinity of the phenyl radical ($E_{ea}(Ph^\bullet) = 99$ kJ mol^{-1}, see Table 1) compared to that for the Cl atom ($E_{ea}(Cl) = 348.575$ kJ mol^{-1}) and agrees with the rule (1) (see above).

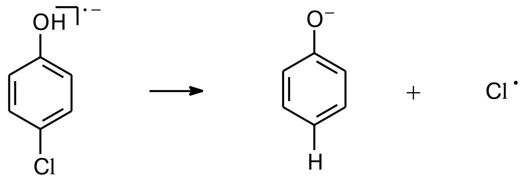
The estimate of the energy balance of monomolecular decomposition shows that the threshold of $[M - Cl]^-$ NI formation from PCP due to the simple C—Cl bond cleavage is 2.97 eV (according to Eqs. (1)—(3) with insertion of the values in Table 1), and that for MCP is 3.03 eV. Published data for OCP are insufficient but we propose a close value. Thus, the $[M - Cl]^-$ ions from PCP in the energy region higher than 2.97 eV (see Fig. 1) can be formed by the simple C—Cl bond cleavage. However, the EYC of the $[M - Cl]^-$ NI ions of all chlorophenol isomers contain a peak lying below this threshold (see Fig. 1 and Table 2), and the experimentally determined appearance energies for these ions from PCP, MCP, and OCP are 1.15, 0.83, and 1.09 eV, respectively (see Table 2).

This observation can be explained accepting that the neutral $[M - Cl]^\bullet$ species have a high E_{ea} value (according to Eq. (1)). The phenoxyl radical is characterized by the high electron affinity (2.25 eV, see Table 1). The consideration of the energetics of decomposition of the molecular NI from PCP with the H atom migration from the OH group to the site of Cl atom detachment (Scheme 1, Table 1) demonstrates the value

$$\begin{aligned}E_{app}^{calc}(PhO^-) &= \Delta H_f^\circ(PhO^\bullet) + \Delta H_f^\circ(Cl) - \\ &- \Delta H_f^\circ(p\text{-}ClC_6H_4OH) - E_{ea}(PhO^\bullet) = \\ &= 48.53 + 121.33 - (-119.1) - 217 = \\ &= 71.96 \text{ kJ mol}^{-1} \approx 0.75 \text{ eV},\end{aligned}$$

which satisfies $E_{app}^{exp} = 1.15$ eV.

Scheme 1



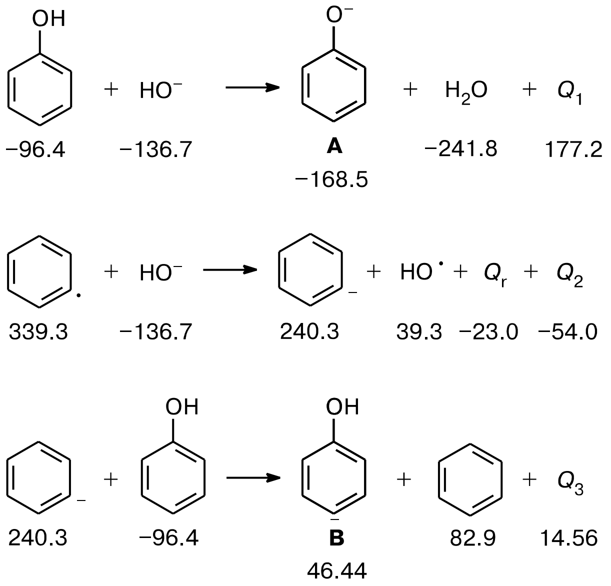
Thus, the $[M - Cl]^-$ ions from PCP in the low-energy region have likely the structure of oxy anion **A** rather than carbanion **B** (Scheme 2). This conclusion can also be extended to MCP and OCP. For them $E_{app}^{calc}([M - Cl]^-) = 0.91$ and 0.78 eV, respectively, within the errors of calculation ($\geq$0.1 eV) and our measurements (0.05 eV) also agree with the experimental values ($E_{app}^{exp} = 0.83$ and 1.09 eV).

The main states of the quasi-equilibrium theory of mass spectra also favor the oxy anion structure of the $[M - Cl]^-$ ions from the chlorophenol isomers. According to these states, ions with a higher relative thermodynamic stability are formed under other equivalent conditions. The series of equations of isodesmic reactions composed from the published data[20,38] (see Scheme 2) shows that structure **A** from PCP is by $Q_1 - Q_2 + Q_3 = 245.8$ kJ mol^{-1} (by 2.5 eV) more stable than structure **B**. Thus, the oxy anion structure **A** satisfies the experimental observation of the low-energy peaks of the $[M - Cl]^-$ ions from chlorophenols by all energetic criteria (E_{app}^{calc} and thermodynamic stability).

The low cross section of $[M - Cl]^-$ ion formation compared to that for the complementary Cl^- NI is related to the more complicated (rearrangement) route of appearance of these ions and to the lower electron affinity of the phenoxyl radical compared to that of the Cl atom.

We have earlier established similar hidden rearrangement processes of oxy anion formation for DEA by mol-

Scheme 2



Note. The series of isodesmic reactions for comparison of the thermodynamic stabilities of NI structures **A** and **B** (numbers designate ΔH_f° of molecules, radicals, and NI (in kJ mol^{-1}), and Q_r shows the stability of the OH^- species relatively to $OH^\bullet$ (see Ref. 20)).

ecules of the chloro-substituted dibenzo-*p*-dioxin derivatives.[3] Probably, rearrangements during resonant electron attachment are more general contrary to the common opinion,[7] which can be formulated as follows. Since NI have a short lifetime compared to the time of electron autodetachment, rearrangements have no time to occur. The rearrangement processes found on the basis of the energetic approach indirectly indicate sufficiently long lifetimes of NI, comparable with the period of oscillatory motions in molecules. As shown in this work, the factor of time is significant for the formation of NI mass spectra under DEA conditions: NI peaks formed by the rearrangement route are much less intense than peaks of ions appeared by the simple bond cleavage. The energetics also plays an important role in these processes.

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