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Experimental and theoretical investigation of gas phase complexes between chloride ion and some chloroethenes

Alessandro Bagno, Anna Donò, Silvia Martinucci, Cristina Paradisi*, Gianfranco Scorrano

Centro Studi Meccanismi di Reazioni Organiche del CNR, Dipartimento di Chimica Organica-Università di Padova, v. Marzolo 1, 35131 Padova, Italy

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Abstract

Analysis of the negative ions produced from trichloroethene (TCE) and *Z*-1,2-dichloroethene (*Z*-1,2-DCE) in air at atmospheric pressure in an APCI source revealed the occurrence of the corresponding complexes with chloride ion. In contrast, under the same experimental conditions no such complexes were detected for *E*-1,2-dichloroethene (*E*-1,2-DCE) and tetrachloroethene (PCE). A bracketing approach and competition experiments produced the following Cl^--affinity scale: *Z*-1,2-DCE > TCE > PCE, *E*-1,2-DCE, benzene (39.3 kJ mol^{-1}). The results of collision induced dissociation experiments on these (Cl^-) (M) complexes suggest rather weak bonding interactions. Quantum chemical calculations at the DFT Becke3-LYP level (B3LYP/6-311+G(d,p)//6-31+G(d)) support this conclusion [the calculated binding energy (kJ mol^{-1}) are: 58.6, 56.1, 43.5, and 15.1 for *Z*-1,2-DCE, TCE, *E*-1,2-DCE and PCE, respectively]. The calculations also show that such complexes are planar, with an almost linear $C–H \cdots Cl^-$ arrangement in the case of TCE and *E*-1,2-DCE. In contrast, *Z*-1,2-DCE binds Cl^- via both hydrogens to give a symmetric complex. A similar geometry is also predicted for the very weakly bound (Cl^-)(PCE) complex. (Int J Mass Spectrom 179/180 (1998) 349–357) © 1998 Elsevier Science B.V.

Keywords: Chloroethenes-chloride ion complexes; Gas phase chloride ion clusters; Chloride ion affinity-scale; APCl of chloroethenes; Calculated binding energies for chloroethenes-chloride ion complexes

1. Introduction

Despite the great diffusion of chloro-substituted ethenes in many different areas of application and the very large number of scientific papers in the recent literature dealing with their properties, reactivity, and analysis, surprisingly little is known of the gas phase ion chemistry of such compounds. And yet, chloroethenes, some of which are listed among the most diffuse and difficult to remediate organic pollutants (VOCs) in the atmosphere, are volatile and readily ionized. As part of our research in the field of nonthermal plasma induced decomposition of volatile atmospheric pollutants, we are investigating the ionic species which are produced from selected VOCs in air at ambient pressure in a APCI (atmospheric pressure chemical ionization) source [1,2]. APCI sources, which are commonly used as interfaces in HPLC-MS instrumentation, employ corona discharges for the production of ions. Corona discharge in a gas at ambient pressure

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* Corresponding author. E-mail: Paradisi@mail.chor.unipd.it

Dedicated to Professor Fulvio Cacace for his outstanding contributions to gas-phase ion chemistry.

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generates a plasma in which the mean energy of the electrons is much higher than the average translational energy of the other species (molecules, radicals, and ions), which remain virtually at room temperature. Hence the terms nonthermal or nonequilibrium are used to denote such plasmas. The application of nonthermal plasma based technologies for the abatement of VOCs is being presently pursued as an alternative to traditional methods of removal [1, 3]. Since the energy cost associated with the production of the plasma goes mainly into the production of energetic electrons, which induce decomposition of the pollutant, rather than into the indiscriminate heating of the bulk gas mixture, nonequilibrium plasma based technologies appear especially suited for treatment of large volumes of gaseous streams containing pollutants in low concentration, as is often the case with industrial VOC-contaminated emissions.

Earlier results from this laboratory have shown that the negative ion chemistry of trichloroethene (TCE) in air at atmospheric pressure is dominated by the Cl^- ion and its complexes with neutral molecules of TCE and water [2]. Chloride is produced presumably via electron attachment or charge transfer (a value of 0.40 ± 0.22 eV was recently determined for the electron affinity of TCE [4]) and dissociation.

The interest in gas phase ion–molecule complexes has produced in recent years a large body of binding energies and affinity scales. In addition, with the aid of computational analysis, useful information has emerged about structures and bonding interactions of many such complexes. Specifically, the energetics and structures of gas phase anionic complexes of halide ions (X^-) with many different neutrals (M) Brønsted and Lewis acids, have been examined experimentally, by means of equilibria studies [Eqs. (1) and (2)] carried out in high ion-source pressure and FT-ICR mass spectrometers, as well as theoretically. The literature covering complexes of the halide ions was recently reviewed [5].

$$X^- + M \rightarrow (MX)^- \tag{1}$$

$$(MX)^- + M' \rightarrow M + (M'X)^- \tag{2}$$

Much attention was spent in examining clusters with benzene and substituted benzenes. The insaturation of these molecules renders, in principle, plausible covalent binding interactions resulting from nucleophilic attack of the anion to the ring. However, while covalent σ-adducts are predicted for a limited number of F^- complexes (notably with hexa- and pentafluoro benzenes [6]), for most halide-benzenes complexes the bonds are largely electrostatic and involve in-plane H-bonding to a ring hydrogen. Such is the case, for example, for the complexes of Cl^- and Br^- with benzene and several mono- and disubstituted benzenes [7]. For the gas-phase complex of Cl^- with benzene a binding energy, defined as $-\Delta H°$ of reaction (1), of 39.3 kJ mol^{-1} was determined experimentally in a pulsed beam mass spectrometer, in reasonable agreement with the theoretically calculated value of 35.1 kJ mol^{-1} [8]. Such relatively low binding energy is consistent with the proposed H-bonded structure. In contrast, a much larger binding energy (115.1 kJ mol^{-1}) was determined for the covalently bound complex of F^- with C_6F_6 [9].

To the best of our knowledge, Cl^- affinity data are not available for ethene and the chloroethenes. It was, therefore, of interest to examine the behavior of such an important class of compounds with regard to their binding properties towards chloride. The present account reports our experimental results obtained in a study conducted at atmospheric pressure in air using an APCI source coupled with a quadrupole mass analyzer. Use of atmospheric pressure ionization mass spectrometry for the study of ionic clusters was pioneered and critically reviewed a few years ago by Grimsrud and Zook [10]. While the establishment of an equilibrium condition for ion–molecule reactions, such as complexation [Eq. (1)], is readily achieved within an atmospheric pressure ion source, generally this equilibrium state is perturbed by ion sampling prior to mass analysis [10]. In the study reported here, we used a bracketing approach to compare the Cl^- binding ability of different chloroethenes under as homogeneous as possible experimental conditions. The investigation also involved quantum mechanical calculations of the Cl^--chloroethene complexes. These were carried out at the DFT Becke3-LYP level (B3LYP/6-311+G(d,p)//6-31+G(d)) and provided binding energies and structures. In view of recent studies [11,12] on the mechanisms for nucleophilic substitution at vinylic carbons (concerted versus stepwise), it was of particular interest to evaluate the covalent carbanionic adducts resulting from Cl^- nucleophilic attack onto the double bond.

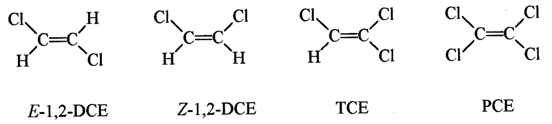

Chart 1.

2. Experimental

A TRIO 1000 II instrument (Fisons Instruments, Manchester, UK) was used, equipped with a Fisons APCI source. A schematic of this source and of the experimental setup used for the introduction of vaporized samples was given in a previous publication [2]. The ion source is kept at near atmospheric pressure by flowing a stream of buffer gas (synthetic air in the present investigation) at 4000–5000 mL/min introduced through the nebulizer line, a capillary of ~2 mm i.d. The final length (~1 cm) of the nebulizer line is wrapped externally with a heating wire, which controls the temperature of the APCI source. Vapors of liquid analytes, as the chloroethenes used in the present investigation, are stripped from a small reservoir by an auxiliary flow of buffer gas. The flow is adjusted to such a value (typically 20–45 mL/min) as to obtain a concentration of the analyte in the APCI source of 500–600 ppm_V. Two such lines are available on this instrument and merge into a capillary (i.d. = 0.3 mm) which enters the APCI source running coaxially inside the nebulizer line. The concentration of analyte in the ion source is determined by quantitative GC analysis of aliquots of accurately measured volume withdrawn from the source outlet line through a septum with a gas tight syringe mounted on a Hamilton inert gas sampling valve. These samples were analyzed with a Varian 3600 gas chromatograph equipped with a flame ionization detector and a 3 mm × 2 m glass column packed with 10% SP-1000 on Supelcoport 80/100. Quantitative determinations were obtained by means of calibration curves constructed using analyte/buffer mixtures of known composition, as detailed before [2].

The needle electrode for corona discharge was kept at 3000 V. Ions leave the source through an orifice, ca 50 μm in diameter, in the counter electrode (the "sampling cone," held at 0–150 V relative to ground), cross a region pumped down to ca. 10^{-2} Torr and, through the orifice in a second conical electrode (the "skimmer cone," kept at ground potential), reach the low pressure region hosting the focusing lenses and the quadrupole analyzer. It was shown earlier that CID (collision induced decomposition) experiments can be usefully carried out in the intermediate pressure region between sampling and skimmer cones by the proper adjustment of ΔV, the difference between their potentials [2]. In all our experiments spectra are recorded at several different values of ΔV ranging from the lowest possible value (1–10 V) necessary to achieve an acceptable signal to noise ratio up to 150 V. Each experiment also includes a preliminary analysis of the background spectra, again at several different values of ΔV, prior to the introduction of the analyte.

The chloroethenes were commercial products of high purity and were used as received. High purity synthetic air was used as background gas, with a specified H_2O impurity of less than 5 ppm. Before conducting an experiment at 300 °C, the nebulizer was kept at 300–400 °C for a couple of hours and the inlet lines were heated with the help of a heating gun.

3. Results and discussion

3.1. Experimental observation of complexes of chloride ion with chloroethenes in an APCI source

The following chloroethenes were examined with regard to the negative ions produced in air at atmospheric pressure in the APCI source: *E*- and *Z*-1,2-dichloroethene (*E*-1,2-DCE and *Z*-1,2-DCE), trichloroethene (TCE) and tetrachloroethene (PCE) (Chart 1).

All four compounds display a common pattern of reactivity, both at 30 and at 300 °C, which involves production of Cl^- to such an extent that all ions due to the "background" (mainly $O_2^{-\cdot}$, $O_3^{-\cdot}$ and, to a

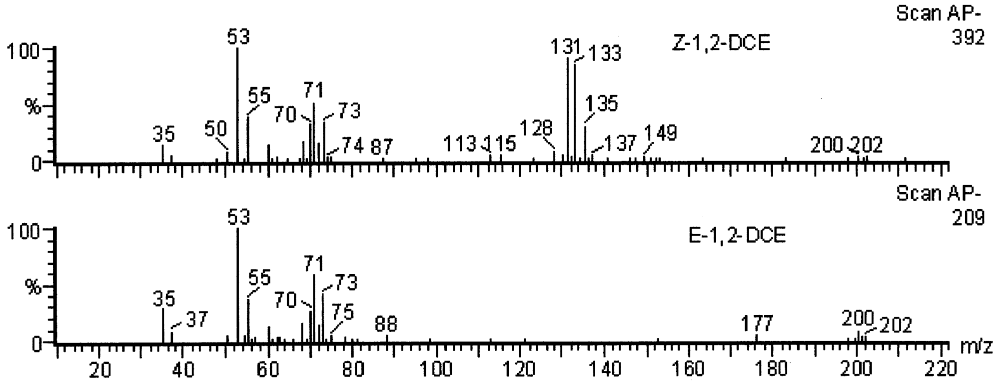

Fig. 1. APCI negative ion spectra of *E*- and *Z*-1,2-DCE in synthetic air at 300 °C recorded with a ΔV of 5 V.

lesser extent $(NO)_2^-$, and their hydrates) become minor contributors to the spectra. In no instance could we detect the analyte (M) radical anion, $M^{-\cdot}$, nor, for the hydrogen containing compounds, the deprotonated species $[M\text{-}H]^-$. It appears, therefore, that the negative ion chemistry of the chloroethenes involves one-electron reduction, either via electron attachment or charge transfer, leading to dissociation. These observations are consistent with those reported earlier for TCE [2]. The negative spectra recorded at low values of ΔV include signals due to Cl^- complexes with water and also, for some of the analytes, with M. In this respect, we have found, the reactivity of the chloroethenes varies significantly from one to another, pointing to different affinities for the chloride ion. Thus, under similar experimental conditions (temperature, pressure and concentrations of analyte, M, and of water—*vide infra* for this last parameter), TCE and *Z*-1,2-DCE produce significant amounts of anionic products of composition $(Cl^-)M$, whereas PCE and *E*-1,2-DCE do not. These qualitative observations are very reproducible. Most remarkable is the different ability to bind Cl^- displayed by the two geometric isomers of 1,2-dichloroethene. Fig. 1 reports typical negative ion spectra of *Z*- and *E*-1,2-DCE recorded under the same experimental conditions. Common major signals observed in both spectra are attributed to Cl^- (*m*/*z* 35), $(Cl^-)H_2O$ (*m*/*z* 53), $(Cl^-)(H_2O)_2$ and $(Cl^-)HCl$ (both at *m*/*z* 71, but with different isotopic patterns) and Cl_2^- (*m*/*z* 70). In addition to these, a very strong signal, in fact the base peak in the spectrum, is observed for the *Z* isomer, due to the species $(Cl^-)M$ at *m*/*z* 131, showing the characteristic isotopic pattern due to 3 chlorine atoms. This species is not detected in the spectrum of the *E* isomer.

Similar observations were made in experiments conducted at a source temperature of 30 °C. At this temperature higher aggregates, $(Cl^-)(M)_2$ $(Cl^-)(H_2O)(M)$ and $(Cl^-)(M)_3$, are observed for those analytes which bind chloride, namely, TCE [2] and *Z*-1,2-DCE.

A few competition experiments were also performed at 300 °C by introducing, through independent inlets, two neutrals into the APCI source and allowing them to compete for Cl^-. A first set of experiments aimed at establishing a relative scale of chloride affinities for the chloroethenes under investigation: pairs of competing partners included TCE and *Z*-1,2-DCE and TCE and *E*-1,2-DCE. Each pair was examined in mixtures of different relative concentrations of the two partners, ranging from 0.1 to over 10. In all such experiments only one cluster species was observed, a different one for the two cases, namely, the (Cl^-)(*Z*-1,2-DCE) cluster for mixtures of TCE and *Z*-1,2-DCE, and the (Cl^-)(TCE) for mixtures of TCE and *E*-1,2-DCE. These results establish the following qualitative Cl^--affinity scale: *Z*-1,2-DCE $>$ TCE $>$ *E*-1,2-DCE.

It was obviously of interest to anchor the above qualitative scale to some established Cl^--affinity value and we made an attempt in this direction. To this end benzene (Cl^--affinity: 39.3 kJ mol^{-1} [8]) was used as reference in competition experiments with TCE and PCE. Again, the experiments were performed at 300 °C and with the reagents in different concentrations as specified above. In the former case only the (Cl^-)(TCE) complex was observed, a result suggesting that the Cl^--affinity of TCE is greater than 39.3 kJ mol^{-1}. When benzene/PCE mixtures were examined the observed species were neither the benzene nor the PCE Cl^--complexes, but only the hydrates $(Cl^-)(H_2O)$ and $(Cl^-)(H_2O)_2$.

One important aspect of our experimental conditions concerns the obvious presence of residual water, which can intervene as a "contender" for chloride ions. Clearly it would be desirable to know the water concentration in our experiments. It is well known, however, that the amount of residual water in an APCI source is difficult to control and quantify and that "traces" of water are sufficient to dominate the background spectra, especially the positive ion one. Notably, in "ultra high purity" N_2 or Ar, virtually all of the positive ions are accounted for by H_2O^+, H_3O^+, NO^+, $O_2^{+\cdot}$ and their clusters with water and N_2 or Ar [13]. A thorough investigation showed that it was possible to reduce if not eliminate the contribution to the background spectra due to ions derived from different ion–molecule reactions involving water only under "very dry" conditions, achieved after several weeks of baking at 400 °C [13]. Our own experience shows that, under given experimental conditions (source temperature and instrumental parameters) the spectra of the background are greatly influenced by the amount of water present in the source. The changes involve the size of the hydrates and their relative abundances. The reverse must, therefore, be true, i.e. if in two experiments the background spectra are very similar, the water concentration in the source must also be very similar. In conclusion, while we did not attempt to determine the amount of water present in our experiments, we took care in establishing uniform conditions throughout, by verifying the consistency of the background spectra prior to each new experiment. We therefore trust that water was present in reasonably constant concentration in all our experiments. Under this plausible hypothesis, the following Cl^--affinity scale can be deduced from our results: *Z*-1,2-DCE $>$ TCE $>$ PCE, *E*-1,2-DCE, benzene (39.3 kJ mol^{-1}).

Our data do not allow one to place H_2O (Cl^--affinity: 60.2 kJ mol^{-1} [14]) in the above scale. While it can be probably concluded that both PCE and *E*-1,2-DCE have lower chloride-affinities than water, more rigorous quantitative determinations would be necessary to find the correct location of water in the left-hand side of our scale.

A comment is due on the question of whether the ion complexes we detect in our experiments form under equilibrium conditions in the ion source or rather in the hydrodynamic expansion associated with ion sampling through the sampling cone orifice. Cluster growth, due to collisions and concomitant cooling, is typically observed in this stage preceding ion analysis [10,15]. The extent of cluster growth depends on the dimensions of the orifice, the temperature and the buffer gas used. Notably, experimental conditions were found under which no perturbation occurred, i.e. the ion population sampled and analyzed matched that expected at equilibrium [10]. Such conditions included use of He or H_2 as buffer gas, while use of N_2 produced obvious perturbations of the equilibrium distributions. It cannot, therefore, be excluded that the complexes observed in our experiments form during the ion-sampling stage rather than within the ion source and that we may be monitoring the result of competition for Cl^- by different neutrals (H_2O, M_1, and M_2) at, both a pressure and temperature which are significantly lower than in the ion source. Even if this were the case, the reproducibility and self-consistency of our observations and the good agreement with the results of the calculations described in the following section make us confident of the value of this experimental approach for the analysis of ion affinities.

A matter of interest concerns the type of bonding that holds these chloride–chloroethene complexes together. Collisional activation of these (Cl^-)(M) species results in loss of M to give Cl^-, the process occurring generally at rather modest values of ΔV (see Experimental section), typically 5–10 V. Higher values of ΔV are usually necessary to induce the rupture of covalent bonds [2]. Our CID results therefore suggest that, as is the case for most benzene–

Table 1
Electronic properties of chloroethenes

Property	*Z*-1,2-DCE[d]	*E*-1,2-DCE[e]	TCE[f]	PCE[g]
Dipole moment[a]				
μ_x	0	0	−0.863	0
μ_y	0	0	0.246	0
μ_z	1.944	0	0	0
Quadrupole moment[b]				
Θ_{xx}	−3.694	−1.629	3.597	−2.059
Θ_{yy}	−1.795	+4.650	−1.369	2.474
Θ_{zz}	+5.490	−3.022	−2.228	−0.416
Θ_{yz}	0	−2.028	−1.473	0
Polarizability[c]				
α_{xx}	29.658	29.613	63.853	41.427
α_{xy}	0	0	5.927	0
α_{yy}	65.395	42.899	81.941	85.688
α_{zz}	47.290	73.945	35.435	91.521
α_{yz}	0.000	12.280	0	0

[a] In Debye (1 D $= 3.33564 \times 10^{-30}$ C m).

[b] In Debye · Ångstrom (1 D Å $= 3.33564 \times 10^{-40}$ C m^2).

[c] In atomic units (1 au $= 4\pi\varepsilon_0 a_0^3 = 1.649 \times 10^{-41}$ J^{-1} C^2 m^2, the volume polarizability $\alpha' = \alpha/4\pi\varepsilon_0$ in 10^{-24} cm^3 can be calculated as α (au) $\times$ 0.148184.

[d] Molecule lying in the *yz* plane, CC bond parallel to the *y* axis.

[e] Molecule lying in the *yz* plane, CCl bonds parallel to the *z* axis.

[f] Molecule lying in the *xy* plane, CCl(H) bond approx. parallel to *y* axis; total dipole moment $\mu = 0.897$.

[g] Molecule lying in the *yz* plane, CC bond parallel to the *y* axis.

halide complexes, the interactions holding these adducts together are not covalent but rather electrostatic. Ab initio calculations were then carried out to address this question and to find explanations for the observed affinity trends, particularly for the striking difference between the *Z* and *E* isomers of 1,2-dichloroethene. The results of these calculations, presented in the following section, are consistent with the conclusions drawn from our experimental results and offer insight into the interactions holding these complexes together.

3.2. Quantum chemical calculations on the complex formation between chloride ion and chloroethenes

Complex formation between chloride ion and the chloroethenes *Z*- and *E*-1,2-DCE, TCE, and PCE has been theoretically investigated by means of quantum chemical calculations at the DFT Becke3-LYP [16] level, using the 6-31+G(d) basis set for geometry optimization and 6-311+G(d,p) for energy (B3LYP/6-311+G(d,p)//6-31+G(d)). Calculations were carried out with the Gaussian 94 suite of programs [17]. The results of such calculations provide data for electronic properties, structures and binding energies.

3.3. Electronic properties

Electronic properties of chloroethenes, i.e. dipole (μ), quadrupole (Θ) moments and polarizabilities (α) are collected in Table 1.

For *Z*-1,2-dichloroethene the dipole moment vector is aligned with the bisector of the CC bond, as required by symmetry, the positive end pointing away from the chlorine atoms, as does the largest positive component of Θ (Θ_{zz}). This orientation renders the approach of a negatively charged species favorable along that direction. The polarizability is largest along the CC bond. *E*-1,2-dichloroethene obviously has no dipole moment. For this molecule the largest positive component of Θ (Θ_{yy}) is approximately aligned with the CH bonds, and there is also a substantial negative component aligned with the CCl bonds. The polarizability is largest along CCl bonds. In both cases, the moment corresponding to the π

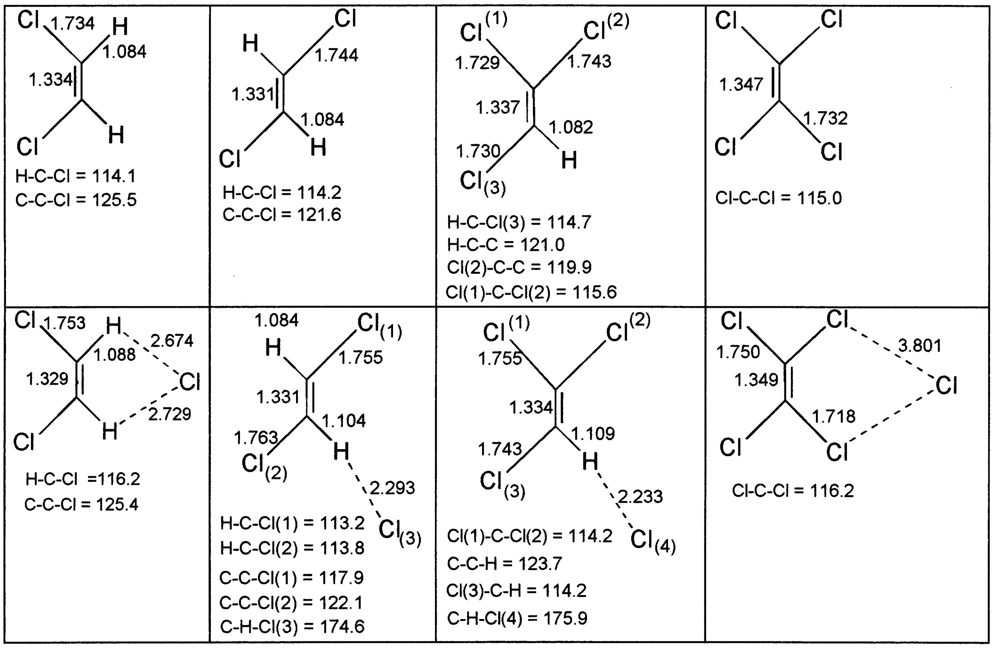

Chart 2.

system axis (Θ_{xx}) is negative, i.e. unfavorable for the approach of Cl^-.

Trichloroethene (TCE) has a smaller dipole moment than *Z*-1,2-dichloroethene. The Θ_{xx} component is positive and directed approximately along the line connecting H–C–C–Cl(trans), whereas both Θ_{yy} and Θ_{zz} are negative. As for the dichloroethenes, the moment along the π system axis is negative. Polarizability is largest in the molecular plane.

For tetrachloroethene (PCE) two opposite Θ components are found: a positive one in-plane, bisecting the CC bond, and a negative one along the π system. Polarizability is largest in the molecular plane. Hence, in this case the approach of a negative ion should be favored in the molecular plane, although all ends are individually negative.

3.4. Structures and binding energies

The calculated structures of the complexes of Cl^- with the investigated chloroethenes are shown in Chart 2, and binding energies are collected in Table 2.

Complexes with Cl^- interacting with the π system (above the molecular plane), as well as covalent adducts (e.g. $Cl_2CH{-}CHCl^-$) do not seem to be stationary points on the potential energy surface, geometry optimization leading to the corresponding planar complex. The geometry of binding is quite different for the two isomeric dichloroethenes, the *Z* preferring a symmetric complex via both hydrogens, the *E* an almost linear C–H · · · Cl arrangement. This result, as well as the instability of π complexes, agrees with the above considerations concerning the direction of molecular quadrupole moments. Interestingly, the *Z* isomer binds the chloride ion more strongly than the *E* does, by ~16.7 kJ mol^{-1}.

The structure and binding energy of the trichloroethene-Cl^- complex are similar to those of the dichloroethenes. In contrast, tetrachloroethene binds Cl^- much more weakly. The structure of such (Cl^-)(PCE) complex is similar to that of *Z*-1,2-dichloroethene but with a longer Cl · · · Cl distance, and agrees with the predictions made from the analysis of quadrupole moments.

4. Conclusions

The simple instrumental apparatus used in the present investigation performed remarkably well in

Table 2
Energetics of complex formation of chloride ion with chloroethenes

Species	Energy[a]	ZPE[b]	ΔE[c]	ΔE[d]	ΔE[e]
Cl$^-$	−460.3037076	—	—	—	—
Z-1,2-DCE	−997.8596617	89.87	—	—	
Cl$^-$ complex	−1458.1857631	90.17	−58.6	−58.2	−59.0
E-1,2-DCE	−997.8592745	89.04	—	—	—
Cl^{-1} complex	−1458.1796062	89.41	−43.5	−43.1	−44.8
TCE	−1457.4741589	65.10	—	—	—
Cl$^-$ complex	−1917.7991876	64.94	−56.1	−56.1	−57.3
PCE	−1917.085347	40.21	—	—	—
Cl^{-1} complex[f]	−2377.394771	40.21	−15.1	−15.1	−15.1

[a] In hartrees at the B3LYP/6-311+G(d,p)//6-31+G(d) level.

[b] Zero-point vibrational energy, in kJ mol^{-1} at the B3LYP/6-31+G(d) level.

[c] $\Delta E = E(\text{complex}) - [E(\text{Cl}^-) + E(\text{chloroethene})]$, in kJ mol^{-1}.

[d] Including unscaled ZPEs.

[e] With BSSE correction (no ZPE).

[f] One low negative frequency (-38 cm^{-1}).

experiments that allowed for the observation and study of some chloride–chloroethene complexes. Such complexes are of considerable interest both for the extension of the available Cl$^-$-affinity scales to include so far unreported ethene derivatives and also for their involvement in gas-phase nucleophilic substitution reactions of vinylic substrates [11,12]. The behavior of the chloroethenes of interest was examined under as uniform as possible experimental conditions, so as to compare their relative abilities to bind Cl$^-$ by means of a bracketing approach. The following experimental Cl$^-$-affinity scale was established in competition experiments: *Z*-1,2-DCE $>$ TCE $>$ *E*-1,2-DCE, PCE. Through use of reference compounds, namely benzene and water, always present as background, it was also possible to anchor the above scale to known affinity data and conclude that the Cl$^-$-affinity of both *Z*-1,2-DCE and of TCE must be larger than 39.3 kJ mol^{-1}, probably in the same range as that of water (60.2 kJ mol^{-1}), while the Cl-affinities of *E*-1,2-DCE and PCE must be less than 60.2 kJ mol^{-1}. Such relatively low binding energies are consistent with the results of CID experiments which show the lability of such (Cl$^-$)(M) complexes towards dissociation into Cl$^-$ and M. The results of quantum chemical calculations also agree with the conclusion that the complexes under study are rather weakly bound. The calculated energies for those chloride–chloroethene complexes which were observed experimentally agree well with the estimates made from those experiments. Particularly useful are, clearly, calculated binding energy data for those complexes which are inaccessible under our experimental conditions because of the interference of water. Thus, the calculations show that PCE binds chloride much more weakly than any of the H-containing members of the family. This result is the direct consequence of the type of bonding in these chloride–chloroethene complexes. They all have planar structures in which Cl$^-$ interacts with either one (TCE and *E*-1,2-DCE) or two hydrogens (*Z*-1,2-DCE), or, in the case of PCE, much more loosely with one Cl substituent. The experimentally observed greater tendency of the *Z* relative to the *E* isomer of 1,2-DCE to complex Cl$^-$ is, thus, nicely accounted for by the bridged structure, indicated by the calculations, involving a bifurcated H-bond. A similar type of interaction was proposed for the I$^-$-benzene complex [8]. Interestingly, no stationary points could be located on the potential energy surfaces for complexes in which Cl$^-$ interacts with the π system of the ethene, nor for the covalent adducts resulting from nucleophilic addition, which were found to collapse to the planar complexes of Chart 2. These observations, as well as the obtained structures and binding energies, agree with those made in a study of the potential energy surface for the substitution reaction of chloroethene with Cl^- for which no two-step pathway via a carbanion intermediate was found [11]. The calculations indicated that substitution is a concerted reaction which proceeds via in-plane backside attack on C with inversion of configuration, the transition state laying 136.5 kJ mol^{-1} above the original stable complex [11]. It would be interesting to probe experimentally the calculated energy surface by verifying whether a specifically labeled complex, say the complex between $^{37}Cl^-$ and TCE, could, upon suitable activation, undergo nucleophilic substitution and release $^{35}Cl^-$.

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