Symmetry Control in Bond Cleavage Processes: Dissociative Electron Attachment to Unsaturated Halocarbons**

Rainer Dressler, Michael Allan*, and Edwin Haselbach*

Dedicated to Professor Tino Gäumann on the occasion of his 60th birthday

Abstract: Dissociative electron attachment (DEA or DA) to chlorobenzene, benzyl chloride, *o*-, *m*- and *p*-tolyl chloride, vinyl chloride, and allyl chloride has been investigated, including an analysis of the kinetic energy content of the fragments, i.e. hydrocarbon radical and $\mathrm{Cl}^{\ominus}$. Electron transmission (ET) spectroscopy is simultaneously employed to reveal the properties of the initial temporary molecular anions. The results suggest that for all systems the incident electron is captured into a low-lying π^*-orbital. If the C—Cl bond lies in the nodal plane of the π-system the symmetry of the ground state fragments does not correlate with the initial anion resonance of $^2\Pi$-symmetry. Predissociation offers a mechanism to yield these products but sufficient time remains to channel the excess energy into various internal degrees of freedom of the products, resulting experimentally in less kinetic energy release. Alternatively, if the C—Cl bond does not lie in the nodal plane of the π-system, adiabatic correlation between initial and final species in their ground states is obtained. The initial anion is formed in a repulsive state and $\mathrm{Cl}^{\ominus}$ appears experimentally with considerable kinetic energy. The present results thus offer clear-cut experimental indications for symmetry control in bond cleavage processes.

The events which occur during the collision of a free electron with an isolated molecule in the gas phase have received much attention in the past 20 years. This renaissance of the electron scattering field has been initiated by the discovery that short-lived negative ions, also called resonances, may appear as intermediates in such collisions[1]. A knowledge of the properties of such resonances is of crucial importance to an understanding of their subsequent fate which determines phenomena in e.g. astrochemistry, laser plasmas, and magnetohydrodynamics[2]. Furthermore an increasing number of industrial chemical processes make use of electron-impact induced association or dissociation reactions, commonly termed «electron curing»[3].

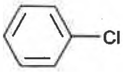
Halogenated hydrocarbons have become a major threat to the environment and the search for economic ways of eliminating the halogen atoms has thus stimulated much basic research[4]. The well known process

$$\mathrm{RHal} + e^{\ominus} \rightarrow \mathrm{R}^{\odot} + \mathrm{Hal}^{\ominus}$$

offers an attractive procedure of dissociatively reducing them to less toxic substances including an inert halogen anion. Since anaerobic bacteria apparently also possess the potential for this reaction, much work is currently devoted to elucidate its mechanism in detail[5].

Considerable electrochemical work has been done on halogen elimination in solution. Electrochemical methods can contribute to the study of solvent effects on the reaction rates and, if the radical anion lives longer than 10^{-9} s, to the determination of the lifetimes of the unstable species[6,7]. The internal energy distribution of the product molecular anion, as well as the reduction potential dependence of the reaction rates are, however, difficult to obtain with such measurements. Dissociative electron attachment (DA) spectroscopy including the kinetic energy analysis of the product anion thus offers a unique possibility to examine the dissociation mechanism of the isolated short-lived radical anion and to interpret the findings in the light of theoretical considerations.

We now report DA processes in the unsaturated halocarbons chlorobenzene (**1**), benzyl chloride (**2**), vinyl chloride (**3**), and allyl chloride (**4**). DA in **1** has already been investigated[10]. For **2** an efficient DA process with thermal electrons has been noticed in a γ-irradiated organic matrix[11]. Our spectra of this compound will show that the cross section becomes even larger at non-thermal electron energies. The DA to **3** has also previously been reported[12], while no data on the DA to **4**, as well as on any ion kinetic energy measurements of the compounds **2** and **4** are known to us.



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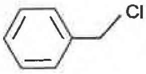

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In DA to saturated halocarbons, the electron is captured into a σ-orbital of the C—Cl bond and causes its dissociation. This type of process has been studied theoretically on the prototype molecules HCl[8] and halogenated methanes[9]. In the case of unsaturated compounds, however, the electron may also be accomodated in a π^*-orbital before dissociation takes place. Symmetry considerations assuming the molecule to remain planar during the C—Cl bond cleavage speak against this mechanism if adiabatic formation of the ground state products is envisaged, but the large DA-band observed at the energy of the π^*-resonance, known from electron transmission spectroscopy, supports the notion of the formation of an intermediate radical anion of $^2\Pi$-symmetry.

Thus, from the previous results of DA to chloroethylenes, and from calculations and electron transmission studies[13,14] it was concluded that the electron is accomodated in a π^*-orbital before dissociation[12]. In our work, all four systems are shown to produce $\mathrm{Cl}^{\ominus}$ efficiently via the capture of the incident electron into the lowest unoccupied π^*-orbital. A distinct difference, however, exists in the partitioning of the excess energy between those compounds, in which the chlorine atom and the π-system are *directly* linked, and those, in which they are *separated* by a methylene group. Characteristic differences in the dissociative breakdown of the anions of benzyl chloride and chlorobenzene were in fact predicted almost 20 years ago on the basis of the symmetries of the initial anion state and the final states of the dissociation products[15].

Experimental

The dissociative attachment instrument has been described earlier[16]. A quasi-monoenergetic (about 0.06 eV fwhm) electron beam is prepared using a trochoidal monochromator[17]. The beam then collides with a static gas in a target chamber. Negative ions are extracted through a slit from the chamber at 90° with respect to the electron beam and are energy analysed by

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a 90° cylindrical condenser and associated ion optics. The ions are then either directly detected to obtain high-resolution ion-yield curves, or are passed into a commercial double-focusing magnetic sector mass filter to give lower resolution but mass selected curves.

The trochoidal monochromator allows the measurement of processes at electron energies very close to 0 eV with the same beam intensity as at higher energies. Thus, this energy selecting device has an important advantage over pure electrostatic systems in the investigation of chloro compounds which often yield $Cl^{\ominus}$ upon collisions with 0 eV electrons.

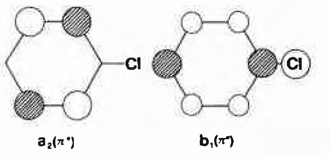
The resolution in the ion kinetic energy measurements is limited by thermal broadening[18]. This broadening becomes considerable at ion energies above 100 meV. Furthermore, the observed shape of the ion kinetic energy curves depends on the transmission function of the ion optics for different ion energies. This function is consistent with a $1/E_{kin}$ drop of the ion extraction efficiency for the present instrument[16,19]. In our communication the conclusions are based on the qualitative differences between the ion kinetic energy spectra in a series of compounds, the knowledge of the true curve-shapes therefore not being essential. The ion energy spectra shown in the figures were not corrected for the effect of the transmission function. The electron energy was calibrated on the $O^{\ominus}/CO_2$ threshold at 3.988 eV.

Results

Fig. 1 shows the electron energy dependence of the zero energy $Cl^{\ominus}$ yield from **1** and the ion kinetic energy spectra taken at 0.7 eV and 1.1 eV incident energies. The 0.75 eV DA band is in agreement with previous work[10,20,21], but some differences still exist in the region of weak signal-intensities below 0.5 eV[20,21].

The C–Cl dissociation energies found in the literature indicate that the $Cl^{\ominus}$ threshold must lie close to 0 eV. We observe a weak peak at 0 eV, and the $Cl^{\ominus}$ yield does not drop to zero at energies above 50 meV. Similar peaks at zero energy have been observed in a number of saturated halocompounds such as $Cl^{\ominus}/CH_3Cl$[22], $Cl^{\ominus}/CCl_4$ and $Cl^{\ominus}/CFCl_3$[23], and were interpreted as the onset of an s-wave scattering process with attachment cross section proportional to $E_{in}^{-1/2}$[23]. Except for our lower resolution, the peak we observe at zero energy in **1** is similar to the one reported for the saturated halogenated methanes[23]. We may thus describe this peak as arising from the direct capture of the electron into a C–Cl σ*-orbital, the mechanism of dissociation being similar to that described for the prototype saturated compounds[8,9].

The $Cl^{\ominus}$ yield increases sharply at energies above 300 meV. At this energy a shape resonance in the transmission spectrum is observed, which was assigned to the $\tilde{X}\ {}^2A_2$ state of the molecular anion[24]. Two anion states are expected to be formed at these energies by the capture of an electron into the $a_2(\pi^*)$ and $b_1(\pi^*)$ lowest unoccupied orbitals:



The transmission curve in Fig. 1, recorded with the present instrumentation, shows that the rise in $Cl^{\ominus}$ signal coincides with the decrease of the transmitted current, and thus with the attachment cross section. We can therefore associate the intense DA band with the capture of the incident electron into the low-lying π*-orbitals. The existence of a shoulder in the DA energy dependence at 1.1 eV may indicate the location of the second state $\tilde{B}\ {}^2B_1$. The ion kinetic energy spectra show that only zero energy $Cl^{\ominus}$ is produced from the DA event at this energy.

Fig. 2 shows the energy dependence of the $Cl^{\ominus}$ yield from **2** and the ion kinetic energy distributions measured at the incident energy locations indicated with a,b,c, and d. In contrast to **1**, $Cl^{\ominus}$ appears with considerable kinetic energy from this molecular anion. The analyser was adjusted to accept 400 meV ions for the energy dependence measurement. The ion signal intensity from **2** is similar to the one observed in **1**. Considering the $1/E_{in}$ drop of the apparatus sensitivity, one may estimate the $Cl^{\ominus}$ DA cross section of **2** to be one to two orders of magnitude larger than the corresponding cross section for **1**.

As $Cl^{\ominus}$ cross sections from compounds without π-bonding such as CH_3Cl in general only reveal a peak at zero energy[22], we may conclude, that the high $Cl^{\ominus}$ cross section at non-thermal electron energies in **2** is due to the capture of the electron into the low-lying π*-orbitals. From the approximate C–Cl dissociation

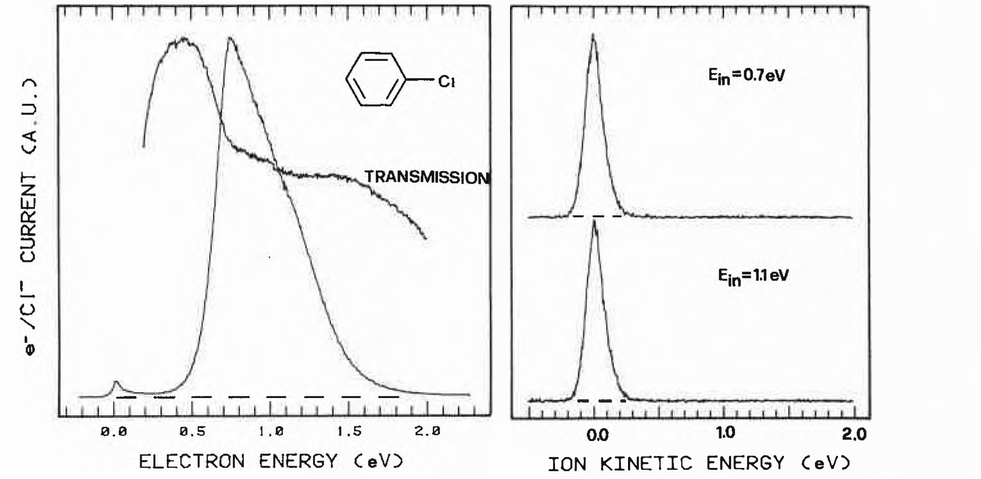


Fig. 1. $Cl^{\ominus}$ yield and ion kinetic energy distributions from dissociative electron attachment to chlorobenzene **1** *at low incident electron energies. The transmission curve (not derivative) indicates the position of the shape resonances associated with the capture of an electron into the unoccupied π*-orbitals.*

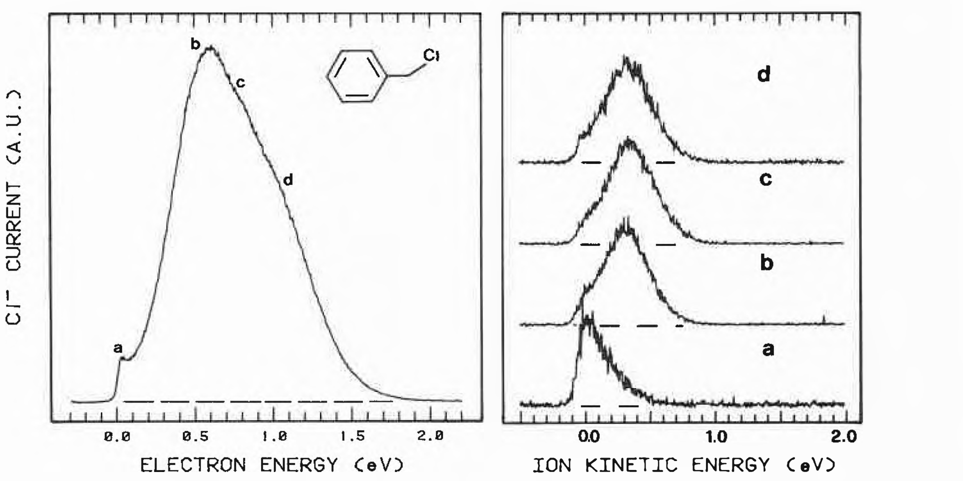


Fig. 2. Incident electron energy dependence of $Cl^{\ominus}$ yield and ion kinetic energy spectra of benzyl chloride **2**. *The letters a, b, c, and d stand for the incident energies E_{in} = 0, 0.5, 0.8, and 1.1 eV, respectively. The curve on the left was obtained with the ion analyser adjusted to accept 0.4 eV ions.*

energy of 3.0 eV[25] we can expect the threshold for the production of $Cl^{\ominus}$ from **2** to be at about −0.6 eV. At an incident electron energy of 0.5 eV we thus have an excess energy of 1.1 eV, and with $\beta = 0.28$[26], the highest possible kinetic energy of $Cl^{\ominus}$ would be 0.79 eV. Approximately 40% of the available excess energy therefore appears as kinetic energy of the fragments.

Fig. 3 compares the energy dependence of the $Cl^{\ominus}$ yield and the ion kinetic energy spectra of **3** and **4**. The $Cl^{\ominus}$ cross section of **4** is estimated to be one to two orders of magnitude greater than that in the vinyl system **3**. In analogy with the aromatic systems, $Cl^{\ominus}$ appears with very little kinetic energy from **3**, but with a considerable amount from **4**. From the 3.5 eV C−Cl dissociation energy of vinyl chloride[25], one would expect the treshold to be above 0 eV. Our spectrum shows a weak peak at 0 eV, similar to the one observed in **1**. We therefore conclude that the threshold lies little below 0 eV. At $E_{in} = 1.4$ eV, the ion kinetic energy of 100 meV indicates that more than 80% of the excess energy is absorbed as internal energy by the vinyl fragment. If we assume the threshold energy of **4** to be similar to that of **2**, we see that at $E_{in} = 0.8$ eV about 60% of the excess energy is channeled to translational energy of the fragments. The data are summarized in Table 1.

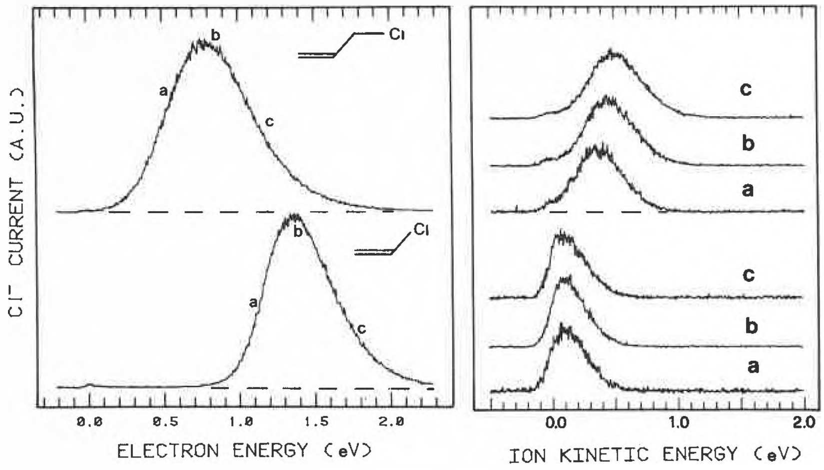


Fig. 3. Energy dependence of $Cl^{\ominus}$ yield and ion kinetic energy spectra of vinyl chloride **3** *and allyl chloride* **4**. *The letters a, b, and c stand for the incident energies $E_{in} = 1.1$, 1.4, and 1.8 eV, respectively in the case of* **3**, *and for $E_{in} = 0.5$, 0.85, and 1.8 eV, respectively in the case of* **4**. *In the energy dependence measurements, the ion energies were fixed at 0.1 and 0.4 eV for* **3** *and* **4**, *respectively.*

Table 1. Evaluation of ion kinetic energies obtained from dissociative electron attachment to **1**–**4**. The ion kinetic energies at the maxima of the distributions (E_{ion}) were obtained from the data corrected with respect to the extraction efficiency. E_{th} is the threshold energy for dissociation. E_{kin}/E_{ex} is the fraction of the excess energy partitioned to the translation energy of the fragments.

		E_{in} [eV]	E_{th} [eV]	E_{ion} [eV]	E_{kin}/E_{ex}
chlorobenzene	**1**	0.7	≈ 0	0	0
		1.1		0	0
benzyl chloride	**2**	0	≈ −0.6	0.2	0.45
		0.5		0.37	0.45
		0.8		0.4	0.40
		1.1		0.4	0.33
vinyl chloride	**3**	1.1	≈ 0	0.1	0.20
		1.4		0.1	0.16
		1.8		0.1	0.13
allyl chloride	**4**	0.4	≈ −0.6	0.35	0.65
		0.8		0.45	0.60
		1.2		0.5	0.52

Discussion

Summarizing the experimental observations, the following distinct patterns are found in the investigated compounds:

(i) In compounds where the Cl-atom is bound directly to the carbon π-system (and thus lies in the symmetry plane of the π-system), no kinetic energy release and smaller signal intensities are observed;

(ii) in compounds where the Cl-atom is separated from the carbon π-system by a CH_2-group (and is – by steric reasons – no longer in the above mentioned plane), a large kinetic energy release and larger signal intensities are found.

The explanation of the difference in internal energy of the neutral fragments may be based on symmetry considerations. The ground state fragments of **1**, phenyl-radical $C_6H_5^{\bullet}$ ($^2A_1$, or «$^2\Sigma$») and $Cl^{\ominus}(^1S)$ can only be correlated with a totally symmetric anion resonance, a feature already pointed out in[15]. The electron captured into a π*-orbital, however, yields a short-lived anion, whose wave function is antisymmetric with respect to the molecular plane. We shall call this temporary negative ion a «$^2\Pi$»-resonance. If this initial state is correlated with a dissociation continuum yielding $Cl^{\ominus}$ (^1S), the phenyl-radical fragment must have also $^2\Pi$-symmetry. This is shown with schematic potential curves in Fig. 4. The $^2\Sigma$-$^2\Pi$ excitation energy (2.34 eV) of the phenyl-radical was taken from[27]. We can thus expect the predissociation via the σ*-resonance to be the only energetically possible way of dissociation. In order for predissociation to be feasible, the symmetry of the resonance must be lowered by eliminating the molecular plane of symmetry. Molecular distortions such as the excitation of the C−Cl bond out-of-plane wagging motion, could create the necessary interaction between the states involved. A similar mechanism has been involved in the dissociative attachment to **3**[13] and is based on the theoretical findings that the $^2\Pi$-ethylene anion is unstable with respect to out-of-plane tortional motions about the double bond[14].

Two qualitative reasons may thus be given for the zero $Cl^{\ominus}$ kinetic energy in the dissociative attachment to **1**:

(i) The excess energy must be transformed into the excitation of vibrational deformation modes to enable dissociation;

(ii) the predissociation mechanism implies a – relatively speaking – longer dissociation time, thus allowing for the efficient distribution of the excess energy among the various vibrational degrees of freedom of the molecule.

The fact that $Cl^{\ominus}$ appears with small, yet observable kinetic energy in **3** (as opposed to **1**) can be associated with the higher excess energy and with the smaller number of vibrational degrees of freedom of the vinyl fragment, among which the excess energy can be distributed.

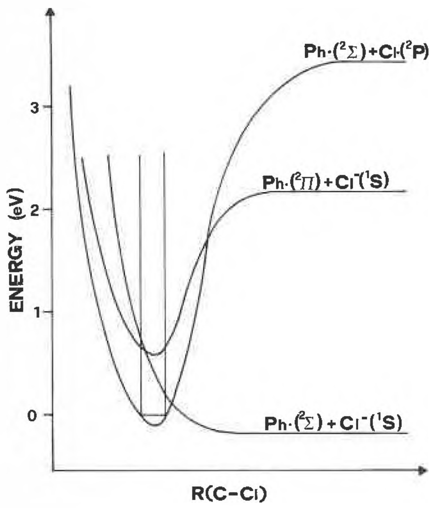


Fig. 4. Approximate potential energy curves of the ground state and the low-lying anion states of chlorobenzene **1**. *The molecule is assumed to remain planar during the dissociation of the C−Cl bond.*

In the benzyl chloride system **2**, the C–Cl bond is not fixed in the plane of the π-system. Molecular models indicate that by steric reasons this bond is strongly rotated out of plane. The C–Cl σ^*-bond orbital is thus able to mix with the π^*-orbitals of the benzene ring, becoming part of the π^*-system. This is visualized in the energy dependence of the $Cl^{\ominus}$ yield of **2** in Fig. 4, where no distinct separation between a $^2\Sigma$- and a $^2\Pi$-DA resonance can be made as in the case of **1**. The anion of **2** can thus directly dissociate, i.e. the electron is directly captured into a repulsive state. Here, no interactions between a discrete non-dissociative level and a dissociation continuum determine the lifetime of the resonance with respect to dissociation, which is therefore expected to proceed rapidly. There is also less time for the distribution of the excess energy among the vibrational degrees of freedom which remains localized in the dissociating coordinate. Consequently, a considerable fraction of excess energy will appear as translational energy of the fragments.

This explanation of the different DA characteristics observed in unsaturated halocarbons was supported by the measurement of the ion kinetic energy of $Cl^{\ominus}$ from *o*-, *m*-, and *p*-tolyl chloride. The recorded spectra are shown in Fig. 5. No major difference between the spectra of the *m*- and *p*-tolyl compounds in comparison with the benzyl compound **2** can be seen. *o*-Tolyl chloride, however, reveals a distinct reduction of the ion kinetic energy. The steric interaction between the Cl-atom and the methyl group is expected to favour a conformation with the C–Cl bond now situated in the plane of the π-system, thus interrupting the interaction between the π-system and the σ^*-orbital of the C–Cl bond with respect to **2**. The dissociation takes therefore more time which allows the excess energy to be more efficiently channeled into the various vibrational modes of the tolyl lattice.

Conclusion

The results of the present work suggest, that in DA to unsaturated halocarbons the fragment $Cl^{\ominus}$ is most efficiently produced through the capture of the incident electron into a low-lying unoccupied π^*-orbital. The $Cl^{\ominus}$ yield is highest when the C–Cl bond does not lie in the nodal plane of the π-system, thus permitting the interaction between this bond and the π-system. The temporary negative ion is then formed in a repulsive state and $Cl^{\ominus}$ appears with considerable kinetic energy.

If the C–Cl bond is directly linked to the π-system, i.e. if it lies in the nodal plane of the π-system, the symmetry of the ground states of the fragments no longer permit their formation adiabatically by direct dissociation of the initial anion resonance of $^2\Pi$-symmetry. A predissociation mechanism necessitating a distortion of the molecular anion can nevertheless account for its decay into ground state fragments. However, in this case, sufficient time remains to channel the excess energy primarily into the various vibrational modes of the organic moiety, resulting in less kinetic energy release of the fragments.

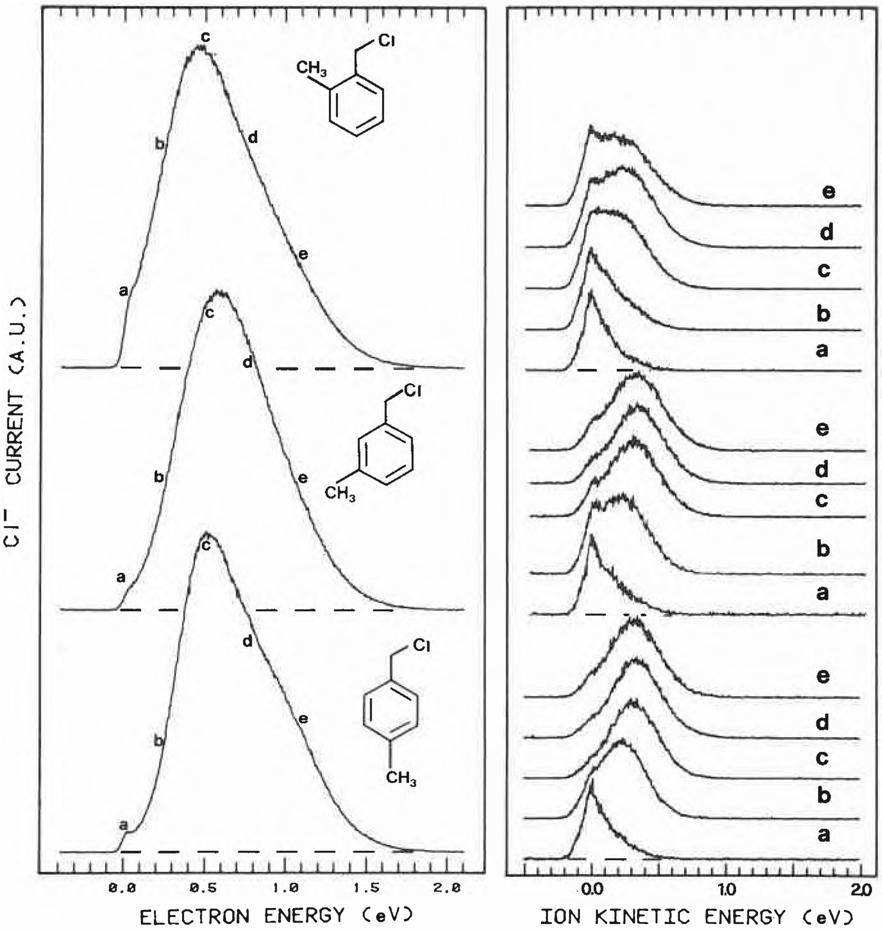


Fig. 5. $Cl^{\ominus}$ yields and ion kinetic energy spectra of o-, m-, and p-tolyl chloride. The energy dependence of the lower two compounds was taken with the ion analyser adjusted to accept 0.3 eV ions. In the ortho-compound, the energy dependence of the production of 0.2 eV ions is displayed. The letters a, b, c, d, and e stand for the incident energies E_{in} = 0, 0.25, 0.5, 0.8, and 1.1 eV, respectively.

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