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Assignment of the first photoelectron band of the CH_3CHCl radical using ab initio quantum mechanical calculations

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Abstract. HeI photoelectron spectra have been recorded for the reaction of atomic fluorine with ethyl chloride at different reaction times. A structured band associated with a short-lived primary reaction product has been recorded with adiabatic and vertical ionization energies of (7.84 ± 0.02) and (8.18 ± 0.02) eV respectively. An average vibrational separation of $(680 \pm 30)\ cm^{-1}$ was observed in this band. Comparison between the experimental vertical and adiabatic ionization energies and ionization energies computed for $CH_3CHCl\ (X^2A)$ and $CH_2CH_2Cl\ (X^2A)$ at different levels of theory led to the assignment of the observed first photoelectron band to the ionization of $CH_3CHCl\ (X^2A)$. The observed vibrational structure was assigned to excitation of the C–Cl stretching mode in $CH_3CHCl^+(X^1A)$.

Keywords: Radical – Photoelectron – Vertical ionization energy – Adiabatic ionization energy

Introduction

The radicals obtained on the loss of a hydrogen atom from stable molecules such as ethyl chloride are of considerable interest as they are reaction intermediates in combustion and thermochemical processes [1, 2]. Two isomeric 1-chloroethyl and 2-chloroethyl radicals may be formed as primary products from the reaction of fluorine atoms with ethyl chloride (reactions in Eqs. 1, 2). The ethyl radical may also be formed on the loss of a chlorine atom from ethyl chloride according to the reaction in Eq. (3).

$$F + CH_3CH_2Cl \rightarrow CH_3CHCl + HF \tag{1}$$

$$F + CH_3CH_2Cl \rightarrow CH_2CH_2Cl + HF \tag{2}$$

$$F + CH_3CH_2Cl \rightarrow CH_3CH_2 + FCl \tag{3}$$

The radicals obtained from the reactions in Eqs. (1), (2) and (3) have been the subjects of a number of experimental and theoretical investigations [3, 4, 5, 6, 7, 8].

A preliminary study of these radicals produced as primary products from the $F + CH_3CH_2Cl$ reaction by photoelectron spectroscopy [3] gave a product band centered at an ionization energy of (8.10 ± 0.05) eV. This band was tentatively assigned to the ionization of CH_2CH_2Cl obtained from β-hydrogen abstraction from CH_3CH_2Cl [3].

In the $F + CH_3CH_2Cl$ reaction, three primary reaction products are possible, CH_3CHCl, CH_2CH_2Cl and CH_3CH_2, and experiments to determine the heats of formation of these radicals have been carried out to estimate their relative stabilities [4, 5, 6]. The most reliable and recent values have been obtained by Holmes and Lossing [9] as (80.8 ± 8.0) and $(95.3 \pm 8.0)\ kJ\ mol^{-1}$ for CH_3CHCl and CH_2CH_2Cl, respectively. These values were obtained in an electron impact study of some precursor molecules such as $ClCH_2CH_2COCH_3$ and $ClCH_3CH_2OH$. The heat of formation of the ethyl radical has been measured as $(116.3 \pm 2.5)\ kJ\ mol^{-1}$ [6]. These results imply that the 1-chloroethyl radical is energetically stabler than the 2-chloroethyl radical.

Ab initio self-consistent-field (SCF) molecular orbital calculations have also been performed on the 2-chloroethyl radical [8, 10] and the 1-chloroethyl radical [8, 10, 11] and the effect of the basis set on the computed equilibrium geometries has been examined. The computed energies obtained by Zheng and Phillips [8] at the UMP2/6-311G(p,d) and the B3LYP/6-311++G(3df,3pd) levels

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for the CH_3CHCl and CH_2CH_2Cl radicals in their ground electronic states at their computed minimum-energy geometries clearly indicate that the CH_3CHCl radical is lower in energy than the CH_2CH_2Cl radical by about 15 and 16 kJ mol^{-1}, respectively.

Separate ab initio calculations have been performed for CH_3CHCl^+ and $CH_2CH_2Cl^+$ at their computed minimum-energy geometries [12]. These calculations using different basis sets showed that in all cases the 1-chloroethyl singlet closed-shell cation is stabler than the 2-chloroethyl singlet closed-shell cation.

1-Chloroethyl and 2-chloroethyl radicals have also been the subjects of some experimental investigations [13, 14]. Reaction of the Cl atom with C_2H_5Cl and C_2D_5Cl has been the subject of some kinetic studies over the temperature range 280–367 K [13]. In this work product analysis was carried out for CH_3CHCl_2, $ClCH_2CH_2Cl$ and their deuterated analogues by flame ionization gas chromatography. The results obtained confirmed the general trend of chlorine atom attack being faster at a substituted carbon atom. This implies that in the $Cl + C_2H_5Cl$ reaction the rate of α-hydrogen abstraction is greater than that of β-hydrogen abstraction. Chloroethyl radicals have also been the subjects of extensive studies by electron spin resonance spectroscopy in solution [15, 16, 17]. Electron spin resonance spectra have been recorded for the 2-chloroethyl radical in solution by Bowles et al. [17]. It was concluded that the 2-chloroethyl radical has a preferred conformation in which the C–Cl bond is eclipsed by the *p* orbital containing the unpaired electron on the radical center.

The aim of this work was to study the radical generated in the $F + CH_3CH_2Cl$ reaction by HeI photoelectron spectroscopy and to assign the first photoelectron band of the radical by comparison between the computed values of the vertical and adiabatic ionization energies and the corresponding experimental values. Owing to the vibronic nature of the transitions observed in the first photoelectron band, the other aim was to assign the vibrational structure to the excitation of a given vibrational mode on ionization.

Experimental

Photoelectron spectroscopy

All the photoelectron spectra obtained in this work were recorded using HeIα radiation (21.22 eV) on a single-detector photoelectron spectrometer designed to study short-lived species in the gas phase [18]. To study the $F + CH_3CH_2Cl$ reaction, fluorine atoms were generated by a microwave discharge (2.45 GHz) of 5% molecular fluorine in flowing helium. C_2H_5Cl (BDH Chemicals, purity more than 99%) was liquid at room temperature and a commercial sample was used in all cases. The reagent mixing distance above the photon beam could be varied in the range 0–10 cm and the band attributed to a short-lived reaction product was observed at the optimum mixing distance of 7 mm above the photon beam. The typical resolution under the operating conditions as measured for argon (full width at half maximum) using HeIα radiation was 25–30 meV. For the $F + C_2H_5Cl$ reaction, the band associated with a primary reaction product was calibrated using the HeIα spectrum of methyl iodide.

Computational details

In this work ab initio calculations were performed for the 1-chloroethyl and 2-chloroethyl radicals and their low-lying cationic states using different basis sets at SCF and MP2(full) level of theory. These calculations were also carried out using a density functional method in the form of B3LYP.All theoretical calculations were carried out using 6-311G**, 6-311+G** and 6-311++G** basis sets. Mulliken population analyses of the converged SCF wave functions were also carried out for the 1-chloroethyl and 2-chloroethyl radicals and their singlet closed-shell ionic states.

For the CH_3CHCl and CH_2CH_2Cl radicals and their low-lying cationic states, the geometries computed at different levels of theory were of point group C_1. At the optimized geometries, the ground electronic configurations for the 1-chloroethyl and 2-chloroethyl radicals were computed as

$$(14a)^2(15a)^2(16a)^2(17a)^1 \quad CH_3CHCl(X^2A),$$
$$(14a)^2(15a)^2(16a)^2(17a)^1 \quad CH_2CH_2Cl(X^2A).$$

For both CH_3CHCl (X^2A) and CH_2CH_2Cl (X^2A), ionization from the (17*a*) level gives rise to a ^1A closed-shell cationic state, whereas ionization from the (16*a*) level results in two ionic states, a ^1A open-shell and a ^3A open-shell.

Hartree–Fock SCF calculations were performed on the singlet and triplet ionic states and it was found that the singlet closed-shell ionic state is lower lying energetically than the singlet open-shell and the triplet open-shell ionic states and therefore in chloroethyl radicals, the ground ionic state is the X^1A closed-shell state.

The values of the first vertical and adiabatic ionization energies of the radical were then computed using the singlet closed-shell ionic states. In order to take the effect of electron correlation into account, calculations were also carried out at the MP2(full) level of theory.

The values of the vertical and adiabatic ionization energies of the observed first photoelectron band of the radical were computed via ΔSCF, ΔMP2(full) and ΔB3LYP calculations using 6-311G**, 6-311+G** and 6-311++G** basis sets.

Results and discussion

The photoelectron spectrum obtained for the reaction of F atoms with CH_3CH_2Cl recorded at a mixing distance

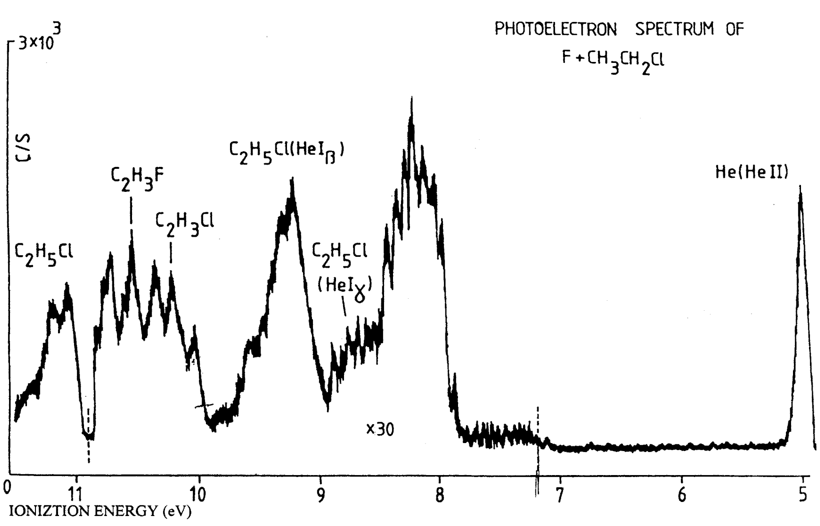

Fig. 1. HeI photoelectron spectrum obtained for the reaction of F atoms with ethyl chloride at a mixing distance of 7 mm above the photon beams

of 7 mm above the photon beam over the ionization energy range 4.5–12.0 eV is shown in Fig. 1. An expanded spectrum of this region calibrated using the HeIα spectrum of methyl iodide is shown in Fig. 2.

In Fig. 1, the sharp band at the apparent ionization energy of 4.99 eV is associated with the ionization of He atoms from the He lamp by HeII radiation. Also the ionization energy band at 11.0–12.0 eV (vertical ionization energy 11.06 eV) arises from the first photoelectron band of C_2H_5Cl [19]. The bands in the 9.5–11.0 eV regions (vertical ionization energies 10.18 and 10.57 eV) are assigned to vinyl chloride and vinyl fluoride [19] as secondary reaction products. Also present are features in the 9.0–10.0- and 8.4–9.0 eV regions, and these are assigned to the C_2H_5Cl ionized with HeIβ and HeIγ radiation, respectively. As well as these features, a structured band was observed in the 7.8–8.5-eV region, which showed maximum intensity at a reagent mixing distance of 7 mm above the photon beam.

The vertical and adiabatic ionization energies of the CH_3CHCl band in Fig. 2 were measured as (8.18 ± 0.02) and (7.84 ± 0.02) eV, respectively. The band centered at (8.18 ± 0.02) eV in Fig. 2 shows a regular vibrational structure with an average vibrational spacing of (680 ± 30) cm^{-1}. When the heats of formation of CH_3CHCl and CH_2CH_2Cl [9] are combined with the heats of formation of F, HF, and C_2H_5Cl [20], the heats of the reactions in Eqs. (1) and (2) can be calculated as(-158.6 ± 4.0) and(-143.5 ± 12.0) kJ mol^{-1}, respectively. The heat of the reaction in Eq. (3) can be estimated [6, 20] as (98.7 ± 12.0) kJ mol^{-1}. Hence for the $F + C_2H_5Cl$ reaction, the reaction in Eq. (1) is clearly more exothermic than the reactions in Eqs. (2) and (3) and presumably is rapider. This implies that in the $F + C_2H_5Cl$ reaction, the CH_3CHCl radical is the dominant primary reaction product, and this supports the experimental results obtained, before and the first photoelectron band centered at (8.18 ± 0.02) eV in Figs. 1 and 2 can be assigned to the ionization of CH_3CHCl (X^2A).

This conclusion is supported by the quantum mechanical calculations carried out in this work. The computed values of the first vertical ionization energies of CH_3CHCl (X^2A) and CH_2CH_2Cl (X^2A) via ΔSCF,

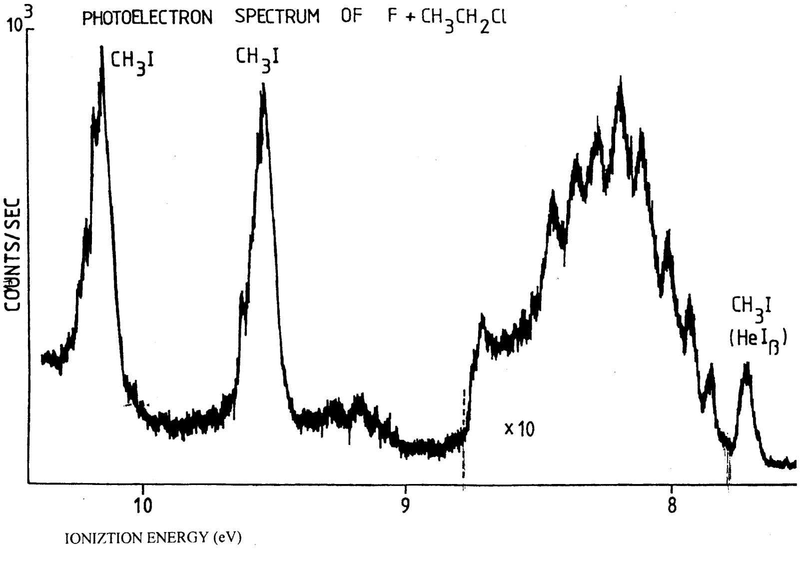

Fig. 2. Expanded scan of the 7.5–10.5-eV ionization energy region showing the first band of CH_3CHCl calibrated with the HeIα spectrum of methyl iodide

Table 1. Computed first vertical ionization energies (*VIEs*) of CH_3CHCl (X^2A) and CH_2CH_2Cl (X^2A)

Ionization	Basis set	ΔSCF (VIE) /eV	ΔMP2(full) VIE/eV	Δ(B3LYP) VIE/eV	Exp. VIE/eV
$CH_3CHCl(X^2A)$	6-311G**	8.14	8.11	8.27	8.18 ± 0.02
$CH_3CHCl(X^2A)$	6-311 + G**	8.23	8.10	8.26	8.18 ± 0.02
$CH_3CHCl(X^2A)$	6-311 + + G**	8.23	8.10	8.26	8.18 ± 0.02
$CH_2CH_2Cl(X^2A)$	6-311G**	8.83	9.16	9.32	8.18 ± 0.02
$CH_2CH_2Cl(X^2A)$	6-311 + G**	8.80	9.15	9.32	8.18 ± 0.02
$CH_2CH_2Cl(X^2A)$	6-311 + + G**	8.80	9.16	9.31	8.18 ± 0.02

Table 2. Computed first adiabatic ionization energies (*AIEs*) of $CH_3CHCl(X^2A)$ and $CH_2CH_2Cl(X^2A)$

Ionization	Basis set	ΔSCF (AIE)/eV	ΔMP2(full) AIE/eV	Δ(B3LYP) AIE/eV	Exp. AIE/eV
$CH_3CHCl(X^2A)$	6-311G**	7.67	7.61	7.91	7.84 ± 0.02
$CH_3CHCl(X^2A)$	6-311 + G**	7.65	7.61	7.91	7.84 ± 0.02
$CH_3CHCl(X^2A)$	6-311 + + G**	7.65	7.62	7.91	7.84 ± 0.02
$CH_2CH_2Cl(X^2A)$	6-311G**	7.81	7.54	8.07	7.84 ± 0.02
$CH_2CH_2Cl(X^2A)$	6-311 + G**	7.80	7.54	8.06	7.84 ± 0.02
$CH_2CH_2Cl(X^2A)$	6-311 + + G**	7.80	7.54	8.10	7.84 ± 0.02

ΔMP2(full) and ΔB3LYP calculations are summarized in Table 1.

The computed values of the vertical ionization energies in Table 1 for CH_3CHCl (X^2A) via ΔSCF, ΔMP2(full) and ΔB3LYP using different basis sets are in very good agreement with the experimental value of (8.18 ± 0.02) eV and clearly indicate that the structured band observed in the photoelectron spectrum of the $F + C_2H_5Cl$ reaction can be assigned to ionization of the $CH_3CHCl(X^2A)$ radical.

The results of the computed values of the first adiabatic ionization energies of CH_3CHCl and CH_2CH_2Cl at different levels of theory and basis set are shown in Table 2.

These values suggest that at the SCF level of theory, the computed adiabatic ionization energy of CH_2CH_2Cl is in better agreement with the corresponding experimental value, whereas the ΔMP2(full) and ΔB3LYP computed adiabatic ionization energies for $CH_3CHCl(X^2A)$ are in better agreement with the experimental value of (7.84 ± 0.02) eV in Table 2. As the width of the first photoelectron band of the radical is about 1 eV, suggesting a large geometry change upon ionization, it seems that the position of the first adiabatic ionization energy can be unobservable because of the poor Franck–Condon overlap. Also owing to the exothermic reaction of F atoms with C_2H_5Cl, it is possible that vibrationally excited radicals are formed, leading to a hot band in the observed photoelectron spectrum. Although mixing-distance studies were performed in this work to show whether the measured onset of the first photoelectron band is the adiabatic ionization energy position or not, a clear conclusion cannot be made as to which radical the computed adiabatic ionization energies favor. When all the themochemical evidence and computational values of the vertical ionization energies are taken into account, it can be clearly concluded that the first photoelectron band observed in the $F + C_2H_5Cl$ reaction should be assigned to the ionization of the $CH_3CHCl(X^2A)$ radical.

The results of Mulliken population analyses performed on the converged SCF wave functions of $CH_3CHCl(X^2A)$ and $CH_2CH_2Cl(X^2A)$ and their singlet closed-shell ionic states show a loss in electron density from C_1 and Cl on ionization [21]. As the half-filled molecular orbital in $CH_3CHCl(X^2A)$ is antibonding in character in the C_1–Cl direction, it is expected that a decrease in the C_1–Cl bond length will be observed on ionization. The equilibrium geometry of $CH_3CHCl(X^2A)$ computed in this work at B3LYP/6-311 + + G** and MP2(full)/6311 + + G** levels have C_1–Cl bond lengths of 1.735 and 1.717 Å, respectively The corresponding values of the C_1–Cl bond length of the optimum geometry of $CH_3CHCl^+(X^1A)$ were computed as 1.635 and 1.612 Å, respectively.

Although the C–Cl vibrational frequency for CH_3CHCl is not known experimentally, the C–Cl stretching frequency in CH_3CH_2Cl has been measured as 677 cm^{-1} [22]. Owing to the results obtained in this work the vibrational structure observed in the first photoelectron band of CH_3CHCl with a vibrational spacing of (680 ± 30) cm^{-1} can be assigned to the excitation of the C–Cl stretching mode in the ion.

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