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REGULAR ARTICLE

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Assignment of the first photoelectron band of $CH_3CHBr(X^2A)$ using ab-initio and density functional theory (DFT) computational calculations

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Abstract HeI photoelectron spectra have been recorded for the reaction of atomic fluorine with ethyl bromide at different reaction times. A structured band associated with a short-lived primary reaction product has been recorded at a mixing distance of 12 mm above the photon beam. The adiabatic and vertical ionization energies of this band was measured as 7.78 ± 0.01 and 8.05 ± 0.01 eV, respectively . The average vibrational separation of $700 \pm 30\,cm^{-1}$ was observed in this band. Vertical ionization energies were computed in this work for $CH_3CHBr(X^2A)$ and $CH_2CH_2Br(X^2A)$ via ΔSCF, ΔMP2 (full) and Δ(B3LYP) levels of theory using different basis sets. Mulliken population analysis and force constant calculations have also been carried out for CH_3CHBr (X^2A) and $CH_2CH_2Br(X^2A)$ and their singlet cationic states. Comparison between the experimental vertical ionization energies and the corresponding values computed for CH_3 CHBr (X^2A) and $CH_2CH_2Br(X^2A)$ at different levels of theory led to the assignment of the observed first photoelectron band to the ionization of $CH_3CHBr(X^2A)$. The observed vibrational structure was assigned to the excitation of C–Br stretching mode in $CH_3CHBr^+(X^1A)$.

1 Introduction

The radicals studied in this work obtained from the F + C_2H_5Br reaction are of considerable interest as they are reactive intermediates in combustion and thermo chemical processes [1,2]. Two isomeric 1-bromoethyl and 2-bromoethyl radicals may be generated as primary products from the reaction of fluorine atoms with ethyl bromide according to the reactions (1) and (2). Ethyl radical may also be formed on loss of bromine atom from ethyl bromide according to the reaction (3).

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$$F + CH_3CH_2Br \rightarrow CH_3CHBr + HF \quad (1)$$

$$F + CH_3CH_2Br \rightarrow CH_2CH_2Br + HF \quad (2)$$

$$F + CH_3CH_2Br \rightarrow CH_3CH_2 + FBr \quad (3)$$

The radicals obtained from reactions (1), (2) and (3) have been the subjects of a number of experimental and theoretical investigations [3–7]. For the F+C_2H_5Br reaction, it would be useful to consider the heats of formation of the reaction products obtained on hydrogen atom abstraction to examine their relative stabilities. The heats of formation of the CH_2CH_2Br and CH_3CHBr have been measured by Holmes and Lossing [3] and also examined by other workers [4–6]. In the electron impact studies of Homes and Lossing on selected precursor molecules such as $BrCHCH_3COOH$ and $BrCH_2CH_2COOH$, the heats of formation of 1-bromoethyl and 2-bromoethyl radicals [3] were measured as 114.2 ± 8.0 and $135 \pm 8.0\,kj/mol$ respectively. Also the heat of formation of the ethyl radical [7] has been measured as $116.3 \pm 8.0\,kj/mol$. Comparison of these values shows that the 1-bromoethyl radical is more stable than both the 2-bromoethyl radical and the ethyl radical. Ab-initio molecular orbital calculations have also be performed for the CH_3CHBr and CH_2CH_2Br radicals by Phillips [8] at different levels of theory. The results obtained on the calculated energies clearly indicate that at UMP2/6-311G(d, p) and B3LYP/6-311++G (3df, 3pd) levels of theory, 1-bromoethyl radical is more stable than 2-bromoethyl radical. Other experimental evidence also supports this conclusion [5].

For example the competitive photobromination of C_2H_5Br has been studied over the temperature range 310–370 K and it was concluded that Br atom attack occurs almost exclusively at the substituted site [5]. It was therefore concluded that the 1-bromoethyl radical is the only primary reaction product in the F + C_2H_5Br reaction [5]. This conclusion was also supported by the results obtained for the F + C_2H_5OH [9] and F + C_2H_5Cl reactions [17] studied previously that the F atom attack occurs at the substituted site. However, there are a few reports of systematic ab-initio calculations or experimental/spectroscopic studies on the bromine- and/or iodine- substituted ethyl radicals [10,11]. Recently, it has been observed that a transient resonance Raman spectrum of photoproducts produced from the A band of 1-bromo-2-iodoethane in cyclohexene solution [8,11].This transient resonance Raman spectrum is probably due to bromoethyl radicals generated from the primary photo dissociation of 1-bromo-2-iodoethane [11]. Also an ab-initio study has been reported for CH_2CH_2Br using a multireference double excitation configuration interaction (MRD-CI) methodology [12] and this investigation focused on examining the potential energy surface for a possible bridging or shuttling motion of the Br atom between the two carbon atoms [12].

The aim of this work was to study the radicals generated as primary products in the $F+CH_3CH_2Br$ reaction and assign the observed first photoelectron band as well as its vibrational structure with the aid of computational calculations.

2 Experimental section

All the photoelectron spectra obtained in this work were recorded using HeI_α radiation (21.22 eV) on a single detector photoelectron spectrometer designed to study short-lived species in the gas-phase [13]. To study the short-lived primary products formed in the $F+CH_3CH_2Br$ reaction, fluorine atoms were generated by a microwave discharge (2.45 GHz) of 5% molecular fluorine in flowing helium. C_2H_5Br (Aldrich Chemical Ltd. 99%) were liquid at room temperature and commercial samples were used in all cases. In order to monitor the concentration of the radicals generated in the $F + C_2H_5Br$ reaction, the reagent mixing distance could be varied in the range 0–10 cm above the photon beam. For the $F + CH_3CH_2Br$ reaction studied in this work, the band attributed to short-lived primary reaction product was observed at the optimum mixing distance of 12 mm above the photon beam. Typical resolution under operating condition as measured for argon (FWHM) using HeI_α radiation was 25–30 meV. For the $F + CH_3CH_2Br$ reaction studied in this work, the band associated with the radical was calibrated using the first photoelectron band of ethyl bromide recorded with HeIα and HeI_β radiation.

3 Computational calculations

In this work ab-initio calculations were performed for the 1-bromoethyl and 2-bromoethyl radicals and their singlet closed-shell cationic states using different basis sets at SCF, MP2 (full) levels of theory. These calculations were also carried out using density functional method in the form of B3LYP with different basis sets. All calculations were performed 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 above radicals and their singlet ionic states.

At the optimized geometries, the ground electronic configurations for the 1-bromoethyl and 2-bromoethyl radicals were computed as:

$......(23a)^2(24a)^2(25a)^2(26a)^1 \quad CH_3CHBr(X^2A)$

$......(23a)^2(24a)^2(25a)^2(26a)^1 \quad CH_2CH_2Br(X^2A)$

For both the $CH_3CHBr(X^2A)$ and $CH_2CH_2Br(X^2A)$, ionization from the (26a) level gives rise to a ^1A closed shell ionic state, whereas ionization from the (25a) level result 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 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 in bromoethyl radicals, the ground ionic state is the X^1A closed-shell state. The values of the first vertical and adiabatic ionization energies (AIEs) of the radicals were then computed using the singlet closed-shell ionic states.

In order to take the effect of electron correlation into account, calculations were carried out at MP2 (full) level of theory using different basis sets. The values of the vertical ionization energies of the observed first photoelectron band of the radicals were computed via ΔSCF, ΔMP2 (full) and Δ(B3LYP) levels of theory, while the values of the first AIEs were computed via ΔSCF and ΔMP2 (full) levels of theory.

4 Results

The photoelectron spectrum obtained for the reaction of F atoms with ethyl bromide recorded at a mixing distance of 12 mm above the photon beam over the ionization energy range 5.0–11.0 eV is shown in Fig. 1. An expanded spectrum of this band calibrated using the first photoelectron band of ethyl bromide recorded with HeI_α and HeI_β radiation is shown in Fig. 2.

In Fig. 1, the bands in the 10.0–11.0 eV ionization energy region (vertical ionization energy 10.30 ± 0.01 and 10.62 ± 0.01 eV respectively have been assigned to ethyl bromide [14].

The band in 9.5–10.0 eV ionization energy was assigned to vinyl bromide [15] which is a secondary reaction product. Also present in Fig. 1, are two features in the 8.2–9.0 eV ionization energy region (apparent vertical ionization energies of 8.43 and 8.75 eV, respectively), which are assigned to the HeI_β component of the first photoelectron band of ethyl bromide. The other feature in Fig. 1, a band in the 7.5–8.5 eV ionization energy regions shows a maximum in intensity at a reagent mixing distance of 12 mm above the photon beam.

An expanded scan of the 7.5–8.5 eV ionization energy region is shown in Fig. 2. The vertical and AIEs of the band labeled as C_2H_4Br have been measured as 8.05 ± 0.01 and 7.78 ± 0.01 eV respectively, when averaged over 25 spectra. Also shown in Fig.2 are bands associated with ethyl bromide, which were used to calibrate the band assigned to the C_2H_4Br radical.

Regularly spaced vibrational components were observed in this band with average spacing of $700 \pm 30 cm^{-1}$. On increasing the mixing distance of 12 mm above the photon beam, the intensity of this band decreased. In fact this band was only observed at reagent mixing distances of less than

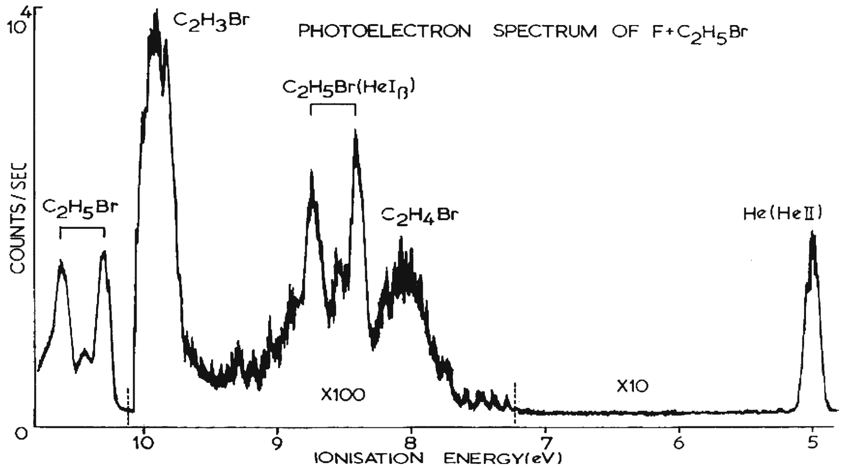

Fig. 1 HeI photoelectron spectrum obtained for the $F{+}C_2H_5Br$ reaction at a mixing distance of 12 mm above the photon beam

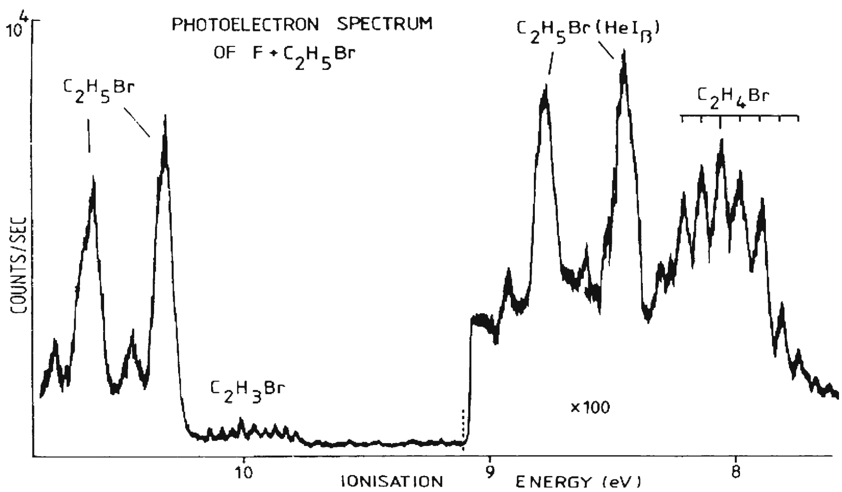

Fig. 2 Expanded scan of 7.5–8.5 eV ionization energy regions showing the first band of CH_3CHBr calibrated with the first photoelectron band of CH_3CH_2Br recorded with HeI_α and HeI_β radiation

5.0 cm above the photon beam. At mixing distances greater than 5.0 cm, the first band of C_2H_4Br completely disappeared and strong bands due to vinyl bromide [15], bromine atoms [14], hydrogen bromide [14] and HF [14] were observed.

No photoelectron bands were observed for vinyl fluoride [14], BrF [16] and CH_3CHBrF although vinyl bromide was thought to be generated from decomposition of vibrationally excited CH_3CHBrF. The assignment of the C_2H_4Br band associated with a short-lived primary product generated in the $F + C_2H_5Br$ reaction will be presented in the Discussion section.

5 Discussion

In the $F{+}C_2H_5Br$ reaction, a band centered at $8.05{\pm}0.01$ eV ionization energy was assigned to a short-lived primary reaction product. As for the other $F + C_2H_5X$ (X=OH, Cl) reactions studied previously [9, 17] it would be useful to compare the heats of reactions (1) to (3) in this work. The heat of reaction (1) can be calculated as -163.6 ± 9.0 kj/mol, when the heats of formation $\Delta H°_{f298}$ of F [18], HF [18], C_2H_5Br [19] and CH_3CHBr [3] are taken into account. Also using the heat of formation of CH_2CH_2Br [3] in combination with the heats of formation $\Delta H°_{f298}$ of F, C_2H_5Br [19] and HF [18] leads to the determination of the heat of reaction (2) as -142.7 ± 9.0 kj/mol. Finally, the heat of formation $\Delta H°_{f298}$ of the ethyl radical [7] can be combined with the heat of formation of F, BrF [16] and C_2H_5Br [19] to give the heat of reaction (3) as -140.6 ± 9.0 kj/mol. Hence on this basis it can be seen that reaction (1) is more exothermic than reactions (2) and (3). Therefore it can be concluded that the band with vertical ionization energy of 8.05 eV in Figs. 1 and 2, associated with a short-lived primary product can be assigned to ionization of CH_3CHBr. Also on the basis of kinetic studies of the reaction of ethyl radical with ethyl bromide [5] in which product analysis was performed using gas chromatography, it was found that the 1-bromoethyl radical was formed much more rapidly than the 2-bromoethyl radical. Also the

Table 1 Computed first vertical ionization energies of $CH_3CHBr(X^2A)$ and $CH_2CH_2Br(X^2A)$ using different levels of theory and basis set

Ionization	Basis set	ΔSCF VIE/eV	ΔMP2 (full) VIE/eV	Δ(B3LYP) VIE/eV	Experimental VIE/eV
$CH_3CHBr(X^2A)$	6-311G**	8.17	8.08	8.15	8.05 ± 0.01
$CH_3CHBr(X^2A)$	6-311+G**	8.17	8.06	8.18	8.05 ± 0.01
$CH_3CHBr(X^2A)$	6-311++G**	8.17	8.06	8.17	8.05 ± 0.01
$CH_2CH_2Br(X^2A)$	6-311G**	8.57	8.83	9.01	8.05 ± 0.01
$CH_2CH_2Br(X^2A)$	6-311+G**	8.58	8.86	9.04	8.05 ± 0.01
$CH_2CH_2Br(X^2A)$	6-311++G**	8.58	8.85	9.04	8.05 ± 0.01

Table 2 Computed first adiabatic ionization energies (AIEs) of $CH_3CHBr(X^2A)$ and $CH_2CH_2Br(X^2A)$ using different levels of theory and basis sets

Ionization	Basis set	ΔSCF AIE/eV	ΔMP2 (full) AIE/eV	Exp. AIE/eV
$CH_3CHBr(X^2A)$	6-311G**	7.66	7.68	7.78 ± 0.01
$CH_3CHBr(X^2A)$	6-311+G	7.66	7.70	7.78 ± 0.01
$CH_3CHBr(X^2A)$	6-311++G**	7.66	7.70	7.78 ± 0.01
$CH_2CH_2Br(X^2A)$	6-311G**	7.56	7.31	7.78 ± 0.01
$CH_2CH_2Br(X^2A)$	6-311+G**	7.56	7.34	7.78 ± 0.01
$CH_2CH_2Br(X^2A)$	6-311++G**	7.56	7.34	7.78 ± 0.01

results of competitive photobromination of C_2H_5Br suggest that bromine atom attack occurs almost exclusively at the α–carbon atom to produce 1-bromoethyl radical. Hence it can be concluded that the observed first photoelectron band with vertical ionization energy of 8.05 ± 0.01 eV should be assigned to the ionization of CH_3CHBr radical.

The photoelectron spectra obtained in this work for the $F + C_2H_5Br$ reaction showed photoelectron bands assigned to vinyl bromide [15], HF [14] and Br atom [14]. It is interesting that no bands associated with BrF [16] were observed under any reaction condition. Therefore the possible mechanism for the $F + C_2H_5Br$ reaction, which is consistent with these experimental observations, is as follows:

$$F + CH_3CH_2Br \rightarrow CH_3CHBr + HF$$
$$CH_3CHBr + F \rightarrow [CH_3CHBrF]^*$$
$$[CH_3CHBrF]^* \rightarrow CH_2{=}CHBr + HF$$
$$[CH_3CHBrF]^* \rightarrow CH_2{=}CHF + HBr$$
$$HBr + F \rightarrow Br + HF.$$

The first photoelectron band of vinyl fluoride (vertical ionization energy 10.57 eV) was not observed [20] due to overlap with a much more intense band associated with C_2H_5Br recorded with HeI_α radiation.

This conclusion has been supported by the computational calculations carried out in this work. The computed values of the first vertical ionization energies of $CH_3CHBr(X^2A)$ and $CH_2CH_2Br(X^2A)$ via ΔSCF, ΔMP2 (full) and Δ(B3LYP) calculations have been summarized in Table 1.

The computed values of the first vertical ionization energies for $CH_3CHBr(X^2A)$ and $CH_2CH_2Br(X^2A)$ in Table 1, via ΔSCF, ΔMP2 (full) and Δ(B3LYP) using different basis sets are in good agreement with the corresponding experimental VIE value of 8.05 ± 0.01 eV and clearly indicate that the structured band observed in the photoelectron spectrum associated with a short-lived species can be assigned to the ionization of the $CH_3CHBr(X^2A)$ radical in agreement with the conclusions reached before [9, 17].

The results of the computed values of the first AIEs of $CH_3CHBr(X^2A)$ and $CH_2CH_2Br(X^2A)$ at ΔSCF and ΔMP2 (full) levels of theory using different basis sets have been summarized in Table 2.

As can be seen from Table 2, the computed first AIEs of $CH_3CHBr(X^2A)$ at ΔSCF and ΔMP2 (full) levels of theory are in good agreement with the corresponding experimental AIEs of 7.78 eV. However, as the width of the first photoelectron band of the radical in Figs. 1 and 2 is about 1 eV, suggesting a large geometry change upon ionization, it seems that the position of the first AIE can be unobservable because of the poor Franck–Condon overlap. Also due to the exothermic reaction of F atoms with ethyl bromide, it is possible that vibrationally excited radicals are formed leading to hot band in the observed photoelectron spectrum. Although mixing distance studies have been performed in this work to show whether the measured onset of the first photoelectron band is the AIE position or not, it seems that a clear conclusion cannot be made that the computed AIEs favor which radical. When all the thermo chemical evidences as well as computed values of VIEs are taken into account, it can be clearly concluded that the first photoelectron band observed in the $F + C_2H_5Br$ reaction should be assigned to the ionization of the $CH_3CHBr(X^2A)$ radical.

The results of Mulliken population analyses performed in this work on the converged SCF wave functions of CH3CHBr (X^2A) and $CH_2CH_2Br(X^2A)$ and their singlet closed-shell cationic states show a loss in electron density from C_1 and Br on ionization in agreement with the conclusion reached before [9]. As the half-filled molecular orbital in CH_3CHBr (X^2A) is anti-bonding in character in the C_1–Br direction, it is expected that a decrease in the C_1–Br bond length will be observed on ionization. The equilibrium geometry of CH_3CHBr (X^2A) computed in this work shows a decrease in the C_1–Br distance upon ionization.

Although the C–Br vibrational frequency in CH_3CHBr is not known experimentally, the C–Br vibrational frequency in CH_3CHBr has been computed in this work as 676 cm^{-1} at SCF/6-311++G** level. The C–Br vibrational frequency in $CH_3CHBr^+(X^1A)$ has been computed in this work as 705 cm^{-1}. This increase in vibrational frequency upon ionization is consistent with the anti-bonding nature of the half-filled molecular orbital in $CH_3CHBr(X^2A)$. The C–Br vibrational frequency in CH_2Br has been measured as 693 cm^{-1} [21,22]. Therefore by analogy with the results obtained for the F + C_2H_5Cl reaction [17] and the results of Mulliken population analyses as well as force constant calculations carried out in this work, the vibrational structure observed in the first photoelectron band of CH_3CHBr with average vibrational spacing of 700 ± 30 cm^{-1} can be assigned to the excitation of C–Br stretching mode in the ion.

References

1. Hucknal DR (1985) Chemistry of hydrocarbon combustion, Chapman and Hall, New York
2. Nonhebel DC, Tedder JM, Watson JC (1997) Radicals, Cambridge University Press, Cambridge
3. Holmes JL, Lossing FP (1988) J Am Chem Soc 110:7343
4. Tscheuikow-roux E, Salmon DR (1987) J Phys Chem 91:699
5. Jung KH, Choi YS, Yoo HS, Tschuikow-roux E (1988) J Phys Chem 90:1816
6. Wang KT, Armstrong DA (1969) Can J Chem 47:4183
7. Holmes JL, Lossing FP, Maccoll A (1988) J Am Chem Soc 110:7339
8. Zheng X, Phillips DL (2000) J Phys Chem A 104:1030
9. Dyke JM, Lee EPF, Zamanpour Niavaran MH (1977) J Phy Chem A 101:373
10. Pakansky J, Koch W, Miller MD (1991) J Am Chem Soc 113:317
11. Zheng X, Phillips DL (1999) J Chem Phys 110:1638
12. Engel B, Peyerimhoff SP (1986) TEOCHEM 31:59
13. Dyke JM, Jonathan N, Morris A (1979) In: Brundle RC, Baker AD (eds) Electron Spectroscopy, vol 3 Academic. London
14. Kimura K, Katsumata S, Achiba V, Yamazaki T, Iwata S (1981) Handbook of HeI photoelectron spectra of fundamental organic molecules
15. Chadwick D, Frost DS, Katrib A, McDowell CA (1972) Can J Chem 50:2642
16. Colnourn EA, Dyke JM, Fayad NK, Morris A (1978) J Elect Spect Relt Phen 14:443
17. Zamanpour MHN, Hadidsaz F (2004) Theor Chem Acc 112:277
18. Stull DR, Prophet H (1971) JANAF thermo chemical tables, 2nd edn
19. Stull DR, Western EF, Sinke GC (1969) The chemical thermodynamics of organic compounds, Wiley, New York
20. Lake RF, Thompson H (1970) Proc Roy Soc Lond A 315:323
21. Smith DW, Andrews L (1971) J Chem Phys 55:5295
22. Shimanouchi T (1972) Table of molecular vibrational frequencies, vol I