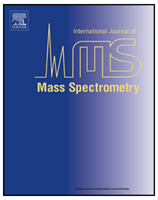
International Journal of Mass Spectrometry 378 (2015) 134–142

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms



Iodine atom loss kinetics in internal energy selected 1-iodoalkane cations by imaging photoelectron photoion coincidence spectroscopy

Tyson G. Rowland [a], Sampada Borkar [a], Andras Bodi [b], Bálint Sztáray [a,*]

[a] Department of Chemistry, University of the Pacific, Stockton,CA 95211, United States
[b] Molecular Dynamics Group, Paul Scherrer Institut, Villigen 5232, Switzerland

A R T I C L E I N F O

Article history:
Received 4 June 2014
Received in revised form 8 July 2014
Accepted 8 July 2014
Available online 30 July 2014

Keywords:
Dissociative photoionization
PEPICO
Quantum chemistry
Iodoalkane
Transition state
Dissociation kinetics

A B S T R A C T

Imaging photoelectron photoion coincidence (iPEPICO) spectroscopy has been used to determine 0 K appearance energies for the unimolecular dissociation reactions of several energy selected straight chain alkyl iodide cations $1\text{-}C_nH_{2n+1}I^+ \rightarrow C_nH_{2n+1}{}^+ + I^\bullet$, ($n = 3$–7). The 0 K appearance energy of iodine atom loss, yielding in fact the 2-alkyl radical cation up to $n = 6$, was determined to be 9.836 ± 0.010, 9.752 ± 0.010, 9.721 ± 0.010, 9.684 ± 0.010 and 9.688 ± 0.015 eV in $1\text{-}C_3H_7I$, $1\text{-}C_4H_9I$, $1\text{-}C_5H_{11}I$, $1\text{-}C_6H_{13}I$, and $1\text{-}C_7H_{15}I$, respectively. In 1-iodohexane and the smaller molecules, these correspond to the transition state along the 1-iodoalkane cation → 2-iodoalkane cation reaction path, and can be used in conjunction with isodesmic reaction energies to determine the reverse barriers to dissociative photoionization. The small kinetic shift is indicative of little H tunneling during isomerization. Directly computed reverse barriers show that run-of-the-mill computational approaches are of limited use when applied to open shell systems containing period 5 elements. Hindered rotors were found to play a minor role in the internal energy distribution and the dissociation rate constants.

1. Introduction

It has been documented both experimentally [1,2] and, more recently, by quantum chemical calculations [3–7] that halogen–carbon bond strengths decrease with increasing halogen atom size from F > Cl > Br > I. The fragileness of the C–I bond has been put to good use in producing short-lived radicals for gas-phase experiments and in synthetic chemistry [8,9]. Iodine's outstanding leaving group character in the presence of a nucleophilic reactant makes it an attractive ligand in S_N2 type substitutions [10]. The dissociation of a carbon–iodine bond, however, is not always just a simple bond-breaking reaction, as Rosenstock et al. recognized three decades ago. Even though the potential well in the 1-iodopropane cation is less than 60 kJ mol^{-1} deep, the fragment ion is not the 1-propyl cation, but rather the 2-propyl cation, after isomerization [11]. Thus, however weak the C–I bond may be, alternative reaction paths to simple bond rupture may still arise even in barely bound ionic systems.

Recent advances in quantum chemistry have made calculating thermochemical properties of small molecules and ions more accessible, while also contributing to more accurate and complete thermochemical data [12–17]. Iodine-atom loss was found to be accompanied by different translational energy distributions in diiodoethylene and diiodoethane cations [18]. Preliminary calculations and a more detailed exploration [19] of the potential energy surface of $C_2H_4I_2{}^+$ illustrated the computational challenges, notably the role of spin–orbit coupling in describing open shell systems containing iodine. Dissociative photoionization experiments using photoelectron photoion coincidence (PEPICO) spectroscopy are one of the few ways to measure dissociative photoionization onsets with an accuracy approaching 1 meV (0.1 kJ mol^{-1}) in favorable cases [20–22], which, by providing benchmark values, can contribute to quantum chemical methods development for experimentally and computationally challenging systems.

It is in this regard that the dissociative photoionization of 1-iodoalkanes are of particular interest. In C–I bond breaking dissociative photoionization reactions, both products, i.e., the closed shell organic fragment ion and the iodine atom, may be reasonably well known and no open shell species is involved in the reaction energy to challenge theory. However, as will be shown later, straight chain 1-iodoalkanes yield 2-alkyl cations over an isomerization transition state, the energy of which can be accurately measured in PEPICO experiments. This means that the measured activation barriers shall be useful computational benchmarks for transition state calculations. Along with the

---

* Corresponding author. Tel.: +1 209 946 2654.
E-mail address: bsztaray@pacific.edu (B. Sztáray).

http://dx.doi.org/10.1016/j.ijms.2014.07.028
1387-3806/© 2014 Elsevier B.V. All rights reserved.

adiabatic ionization energies, also available experimentally for molecules with little geometry change upon ionization, they provide accurate and rare experimental anchor points for computational chemistry.

In this study, we performed imaging PEPICO (iPEPICO) experiments to study I loss in 1-$C_3H_7I^+$ through 1-$C_7H_{15}I^+$. The iodine-atom loss threshold in the dissociative photoionization of the two smaller iodoalkanes, iodomethane and iodoethane, has been reported previously using iPEPICO and a TPEPICO experiment, respectively [23,24]. These studies, along with literature thermochemistry data on the dissociative photoionization energy of iodopropane, have established accurate thermochemical onsets, which can be used in conjunction with isodesmic reaction energy calculations involving closed-shell species, $RH + R'^+ \rightarrow R^+ + R'H$ and $RI + R'H \rightarrow RH + R'I$ to obtain the threshold of I loss from longer chain alkanes.

Rosenstock et al. [11] reported the dissociative ionization threshold dissociative photoionization onset (E_0) for the iodine atom loss in 1-propyl iodide to be 9.84 ± 0.01 eV. This energy is in a Frank–Condon gap of the photoelectron spectrum, which makes non-threshold ionization experiments difficult. They also found the parent molecular ion to be metastable, and reported that the dissociation is accompanied by significant kinetic energy release (KER). They concluded that the main reason for the metastability of the parent ion could be an overall reverse barrier to dissociation, and the formation of the more stable 2-propyl instead of the 1-propyl cation. Therefore, they could only determine an upper limit to the heat of formation of the 1-$C_3H_7^+$ cation, at 822 ± 5, and 805 ± 5 kJ mol^{-1} at 0 K and 298 K, respectively. Based on the kinetic energy release, they also determined the 0 K heat of formation of 2-$C_3H_7^+$ to be 816.2 ± 4 kJ mol^{-1}. In a similar study, Brand and Baer looked at the kinetic energy release distribution of I-loss alkyl cations from 1- and 2-iodopropane ions using the PEPICO technique [25]. From kinetic energy release data, they confirmed that the product of iodine-loss dissociation from 1-$C_3H_7I^+$ is the 2-propyl cation, and that the isomerization of 1-$C_3H_7I^+$ to 2-$C_3H_7I^+$ takes place prior to dissociation. At higher internal energies, however, the direct dissociation to 1-$C_3H_7^+$ was suggested to be faster than the isomerization channel, thus, outcompeting the rearrangement process yielding 2-$C_3H_7^+$.

Oliveira et al., from the same group [26], reported the 0 K threshold for $1\text{-BuI} \rightarrow Bu^+ + I + e^-$ as 9.74 ± 0.02 eV. The study concludes that the dissociation proceeds via a reverse barrier, even though the kinetic energy release is relatively small, but the onset energies from the 1-haloalkanes cannot be used to derive the heat of formation of the 2-butyl cation. Similarly to the case of iodopropane, they conclude that 1-iodobutane dissociates into the 2-butyl isomer cation by H atom transfer before the iodine atom leaves. They propose the following mechanism:

$$CH_3CH_2CH_2CH_2X^+ \rightarrow CH_3CH_2CHXCH_3{}^+ \rightarrow CH_3CH_2C^+HCH_3 + X \tag{1}$$

supported by low-level ab initio calculations.

Park et al. have used vacuum-ultraviolet mass-analyzed threshold ionization (MATI) to study 1-propyl and 1-butyl iodide and discussed their thermochemistry at length. They reported 0 K appearance energy of I loss in 1-propyl iodide to be 9.8332 ± 0.0017 eV [27]. The metastable ion dissociation spectrum obtained with a double focusing mass spectrometer was used to estimate the dissociation rate constant of 1-iodopropane ion in the threshold region to be 10^4–10^5 s^{-1}[27]. Because the 1-propyl and cyclopropane isomer cations are significantly higher in energy, this study agrees that the dissociation occurs by isomerization to the 2-iodopropane cation, with subsequent dissociation of this species into the 2-propyl cation. The analogous result on 1-iodobutane was a 2-butyl cation appearance energy at $E_0(2\text{-Bu}^+) = 9.7544 \pm 0.0045$ eV [28], in good agreement with the PEPICO study of Oliveira et al. [26]. So far, there are no published studies that report dissociative ionization thresholds of iodopentane, iodohexane, or iodoheptane.

With respect to neutral thermochemistry of iodoalkanes, Mortimer et al. [29] reported $\Delta_f H_{298K}(1\text{-PrI}) = -29.7 \pm 7.5$ kJ mol^{-1} by calorimetry, while Stull et al. [30] later gave $\Delta_f H_{298K}(1\text{-PrI}) = -30.5$ kJ mol^{-1}. A thermochemical review of iodoalkyl species by Richard and Gaona [31] reports $\Delta_f H_{298K}$ values of −27.8, −48.5, −60.1, −89.7, and −110.3 kJ mol^{-1} for 1-PrI, 1-BuI, 1-PenI, 1-HexI, and 1-HepI, respectively, taken partly from the literature and partly derived by using group additivity calculations [32]. Benson and Amano reported $\Delta_f H_{298K}(1\text{-BuI}) = -50.2$ kJ mol^{-1} using the CH_2 additivity rule [33].

Adiabatic ionization energies (IE_{ad}) are needed to convert dissociative photoionization thresholds to potential energy well depths, i.e., activation energies in the cation. In propyl iodide, photoelectron spectroscopy (PES) was used to obtain IE_{ad} as 9.26 ± 0.01 eV [34–36] and more recently as 9.25 eV by Novak et al. [37], and as 9.28 eV by Luo and Pacey [38]. Studies on butyl iodide confirm a decreasing IE_{ad} trend with most photoelectron spectroscopy (PES) studies agreeing on an IE_{ad} value of 9.23 ± 0.01 eV [25,34,35,37,39], while the PEPICO study by Oliveira et al. [26] yielded $IE_{ad} = 9.21 \pm 0.01$ eV. The IE_{ad} of pentyl iodide was found to be 9.18 ± 0.01 [34], 9.20 [35], and 9.22 eV [37] from photoelectron spectroscopy. For hexyl iodide, Boschi and Salahub [35] established an IE_{ad} of 9.20 eV, while Novak [37] lists 9.19 eV, both by PES. The only heptyl iodide IE study by Novak et al. [37] reports 9.17 eV as the IE_{ad}.

2. Experimental

Samples 1-C_3H_7I and 1-C_4H_9I were purchased from TCI America, 1-$C_5H_{11}I$ and 1-$C_6H_{13}I$ from Sigma–Aldrich, and 1-$C_7H_{15}I$ from Alfa Aesar. All samples were marked as over 98.0% purity and used without further purification. Experimental data were collected at the VUV beamline [21] of the Swiss Light Source, Paul Scherrer Institut, on the Imaging Photoelectron Photoion Coincidence (iPEPICO) endstation. Detailed description of the instrument and technique can be found elsewhere [20,40–43] and only a brief overview is given here. The gas-phase sample was effusively introduced into the ionization region at room temperature through a 30 cm long, 6 mm o.d. Teflon tube. The typical pressure in the experimental chamber was $1–7 \times 10^{-6}$ mbar during measurements. Monochromatic synchrotron radiation was used to ionize the sample in a less than 2 × 2 mm interaction region. The photon energy was calibrated using Ar autoionization lines, 11s′ at 15.7639 eV and 12s′ at 15.7973 eV [44], in first and second order. A constant 120 V cm^{-1} electric field accelerates the photoelectrons and photoions in opposite directions. The electrons are velocity map imaged onto a Roentdek DLD40 position sensitive delay-line detector with kinetic energy resolution better than 1 meV at threshold. Photoions are space focused and detected in delayed coincidence by a Jordan TOF C-726 microchannel plate detector after being analyzed by a two-stage Wiley–McLaren time-of-flight mass spectrometer with a 5.5 cm long first and a 1 cm long second acceleration region and a 55 cm drift region. The multiple-start/multiple-stop data acquisition technique eliminates signal paralysis and allows for measurements at high ionization rates [45]. The non-threshold, "hot", electron contamination of the threshold electron signal at the center of the image was approximated by and subtracted based on the average count rate in a ring area surrounding the center spot of the detector [40]. Photoions were thus internal energy selected by correlating only the ions that were in delayed coincidence with the corrected threshold electron signal.