Full Length Article

Electron impact ionization of 1-propanol

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A R T I C L E   I N F O

A B S T R A C T

Experimental measurements of the cations created in electron impact ionization have been undertaken for the primary isomer of propanol using a Hidden Quadrupole Mass Spectrometer (EPIC 300), with a mass resolution of 1 amu. The mass spectra recorded at an incident electron energy of 70 eV reveals the relative probability of forming 50 different cations, by either direct ionization or dissociative ionization. Individual partial ionization cross sections (PICS) for 31 different cations were measured for the first time in this work, for the incident electron energy range from 10 to 100 eV. Also, appearance energies (AEs) and Wannier exponents for the 16 most intense cations formed in electron collisions with 1-propanol are reported. Where possible, those results are compared to those from an earlier investigation. Total Ionization Cross Sections (TICS) were also obtained from the sum of the measured PICS, for nearly all cations measured, and are compared to relevant data reported in the literature. In addition, as a part of this study, theoretical TICS were calculated using the Binary-encounter Bethe (BEB) and independent atom model with screening corrected additivity rule (IAM–SCAR) methods. Good agreement between current measured and calculated TICSs and corresponding earlier results was typically found.

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1. Introduction

In an era of globalization, which is marked by a rapid expansion in industrialization, the indiscriminate use of petroleum-based fuels is the object of many discussions. These discussions have observed that those resources are finite, are rapidly decreasing, and their price is steeply increasing [1,2]. Furthermore, their intensive use in many areas produces environmental degradation [3], which probably leads to climate change and global warming [1]. As a result, in order to control the demand for fossil fuels and to reduce the environmental hazards, governmental and industrial sectors are giving tremendous attention into research that uses bio-origin fuels as potential alternative energy sources [4]. The chemical and biological synthetization, and studies of their thermodynamic properties, of the first four aliphatic alcohols (methanol, ethanol, propanol and butanol) indicates some features that suggest they might be used in internal combustion engines [5,6]. However,

these alternative alcohol fuels must initially be better understood and optimized, in order to realize their most efficient operating conditions, in such engines for complete combustion and highest energy release [7]. In the internal combustion engine, the ignition of a plasma [8] and also the residual products created by that plasma, such as positive ions, can be characterized by their Total and Partial Ionization Cross Sections (TICS and PICS). The accurate determination of the cations formed and also their ionization and fragmentation energies, namely the Ionization Energies (IE) and Appearance Energies (AEs), is an important basis for an understanding of many electron impact phenomena, such as the processes present in an ignition system.

Electron impact ionization is a phenomenon that can be efficiently investigated using mass spectrometry, which may produce new information not only about the variety of the cations formed but also reveal their Total and Partial ICSs [9]. Although for a few decades researchers have been studying electron impact ionization of atoms and molecules, there is still much to be done in order to have a complete and reliable data base for many molecules. Indeed, up to now, absolute ICS for all energetically open scattering channels have been measured for only a very few molecules

[10]. There has been a significant amount of studies for electron impact of methanol and ethanol, as was noted in Ref. [9] and references therein. Theoretical and experimental investigations of the Total Ionization Cross Sections for electron impact were reported by references [9,11–17], while Partial Ionization Cross Sections were reported by references [9,14–18]. Appearance energies (AEs) for methanol and ethanol were much less studied, and were reported by only a few authors [9,18–20]. Nonetheless, these studies have produced important information for modeling the use of those alcohols as biofuels. However, there is not much information in the literature on electron collisions with 1-propanol [12–14,18,21–24]. Khakoo et al. [21] reported experimental and calculated differential cross sections for elastic scattering of low energy electrons by 1-propanol, for selected impact energies ranging from 1 to 100 eV. Their measurements were carried out using the relative-flow method, and the calculations employed two different implementations of the Schwinger multichannel variational method including polarisation effects. Hudson et al. [14] reported experimental and calculated absolute TICSs for propanol, for electron impact energies ranging from 16 to 200 eV and for all its isomers. Their experimental data were obtained using a linear transmission apparatus, while the calculated results were obtained using a Deutsch-Märk (DM) additivity method, the Binary Encounter Bethe (BEB) method and a polarisation model. More recently, Bull et al. [23] reported theoretical absolute total electron impact ionization cross-section data, and polarizability parameters, for 65 polyatomic molecules, including 1- propanol. Their data were produced using the empirical polarizability correlation and BEB models, and the functional group additivity approximation. Takeuchi et al. [24] investigated the fragmentation mechanisms of 1-propanol by low energy electron impact, specifically for energies in the range 8–25 eV, and also generated potential energy curves calculated using *ab initio* MO methods. Beside that theoretical study, their 1-propanol experimental work used a Hitachi RMU-6 M mass spectrometer to obtain total positive ion abundances. Rejoub et al. [18] measured absolute partial and total cross sections, for electron-impact ionization of 1-propanol from threshold to 1000 eV, for groups of cations with similar mass, by using a time-of-flight mass spectrometer. Finally, Williams and Hamill [22] measured AEs and bond dissociative energies for 1-propanol using a retarding potential difference (RPD) method in their mass spectrometer. They found the onsets for production of the $C_3H_7O^+$ cation (m = 59 amu) at 10.93 eV and a slope change at 14.07 eV.

This paper is an extension of our previous work [9], where we investigated electron impact ionization of methanol and ethanol. We report here a study of electron impact ionization and ionic fragmentation of 1-propanol, using mass spectroscopy, where we measured for the first time the PICS for individual ionic fragments, over the energy range 10–100 eV. Adding up the PICS, which were normalised to an absolute scale, we also obtained an absolute TICS. Corresponding theoretical BEB and IAM – SCAR TICS were also calculated as a part of this study. In addition, AEs for a range of cations formed in electron collisions with 1-propanol are reported. The mass spectrum obtained reveals the relative probability of forming the various cation fragments by either direct ionization, as well as dissociative ionization, using incident electrons of 70 eV. For many of the mass values more than one cation fragment is possible, thus making the assignment of each peak observed a little more difficult. In these cases, the appearance energy helps us to determine the identity of the fragments recorded. Finally, PICS for a group of cations of 1-propanol were compared to the only previously published data from Rejoub et al. [18].

The structure of the remainder of this paper is as follows. In Section 2 we describe the experimental methods and analysis procedures, and our theoretical TICS calculations, while in Section 3 the mass spectra, PICS and TICS, as well as the AEs we determined are presented and discussed. Finally, some conclusions from this investigation are summarised in Section 4.

2. Experimental methods, analysis procedures and theory details

The experimental apparatus has been described in some detail in a previous article [9], so that only a brief description need be given here. The electron impact ionization experiments with 1-propanol have been performed using a Hiden Analytical [25] quadrupole mass spectrometer (QMS), fitted with a RF head capable of measuring masses up to 300 amu (EPIC 300) and with 1 amu resolution. This apparatus has an ionization stage and so can be operated in a residual gas analysing (RGA) mode, which was applied in this work. The internal ionization source is used to create ions by electron impact ionization. The ions created are most likely to arise from the uniform background of target molecules, which effused from a needle positioned perpendicular to the axis of the mass filter and below the entrance to the ionization stage. In these studies an electron current of 20 µA and operating pressures of 1–1.5 × 10⁻⁶ Torr were used. No mass dependence of the QMS over the mass range studied in this work was found, as was investigated in some detail in our previous work [9]. The behavior of our apparatus was checked by measurements of the PICS for Argon, Ar^+, over the energy range from 10 to 100 eV. That data was compared to the corresponding results from Rejoub et al. [26], obtaining excellent agreement [9], thereby demonstrating that appropriate tuning of all the parameters of the spectrometer had been achieved.

The samples of 1-propanol were degassed by several freeze-pump-thaw cycles before the vapour was admitted into the chamber using a needle valve (MLV-22 [27]). The gas handling lines were heated to ~40 °C, to prevent condensation of the vapour along the lines, and so yield a stable operating pressure, although the vacuum vessel itself did not require heating and remained at the temperature of the air-conditioned laboratory, *i.e.*, 22 °C. The vapour pressure of 1-propanol was calculated to be 17.39 Torr, using the Antoine Equation [9], where the constants employed were A = 5.31384, B = 1690.864 and C = −51.804 [28].

The mass spectra for 1-propanol, as well as the residual background, were recorded on several separate days spanning this study. After the background signal was subtracted from the mass spectra, the average spectrum was normalised to the most intense peak. The results from this process are shown in Fig. 1 and Table 1. The standard deviation on the relative cations abundances were determined after that normalization process. The recorded mass spectrum at 70 eV, as well as the PICS at 70 eV, were set on an absolute scale, using the sum of the PICS for the various groups of cations corresponding to those reported by Rejoub et al. [18]. Note that the absolute data of Rejoub et al. at 70 eV was determined by an interpolation of the data they reported at 60 eV and 80 eV. The error bars in our mass spectrum and in the PICS were obtained by the mean square root of the square of the statistical error on our measurements, added to the square of the total error of the Rejoub et al. [18] measurements. A sum of the absolute PICS for all the cations subsequently yields the absolute TICS, with its errors being the mean square root of the square of statistical errors as well as inheriting the uncertainty in the absolute measurements of Rejoub et al. [18] that we used in the normalization.

The production of ion fragments as a function of the incident electron energy can be described by the Wannier Law (Eq. (1)). From measurements of near-threshold PICS curves, the ionization energy of the parent ion and the AEs of the others cation fragments can be obtained as fitting parameters of the Wannier Law, convoluted with the experimental instrument response function. Here we employ a Gaussian function as the instrument response func-