Electron impact ionization of glycolaldehyde

Sylwia Ptasińska, Stephan Denifl, Paul Scheier, Tilmann D. Märk *

Institut für Ionenphysik, Leopold Franzens Universität Innsbruck, Technikerstr. 25, A-6020 Innsbruck, Austria

Abstract

Positive ion formation upon electron impact ionization of the monomeric and dimeric form of glycolaldehyde is studied with high electron energy resolution. In the effusive neutral beam of evaporated monomeric glycolaldehyde some ions with a mass larger than the monomer indicate the presence of weakly bound neutral dimers. The yield of all ions that originate from the electron impact ionization of these neutral dimers exhibit a strong temperature dependence that can be interpreted as being due to the formation of dimers via three body collisions and thermal decomposition of the dimeric form back into monomers at higher temperatures. Ion efficiency curves are measured and analyzed for the 10 most abundant product cations of monomeric glycolaldehyde. The appearance energies of the parent ion signals of the monomer and dimer of glycolaldehyde (10.2 and 9.51 eV, respectively) are lower than the appearance energy of the parent cation of the more complex sugar deoxyribose that was recently determined to be 10.51 eV.
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1. Introduction

The properties of glycolaldehyde ($C_2H_4O_2$) in various states were the subject of several investigations including infrared and Raman spectroscopy [1], X-ray diffraction, microwave spectroscopy [2], proton magnetic resonance [3] and mass spectrometry [4] in the 1970s. This sugar was observed as a product in the radiolysis of methanol [5]. The discovery of glycolaldehyde in the interstellar cloud Sagittarius B2(N) [6] and its formation as a secondary atmospheric photooxidation product [7] has triggered a renewed interest in this molecule [8–10]. Glycolaldehyde has a planar HOC−COH skeleton with two out-of-plane hydrogen atoms, where the carbonyl and hydroxyl groups are arranged *cis* to each other, thus allowing a five member ring with intermolecular hydrogen bond to be formed [11]. This structure is considered to be of special interest because the hydroxyaldehyde group is a constituent of many molecules. Several of these compounds are important biochemicals, e.g.,

the carbohydrates or sugars (e.g., glucose and deoxyribose) of which glycolaldehyde is the simplest possible member. In the solid state, glycolaldehyde exists generally in a crystalline dimeric form [12]. However, in solution or during heating, it dissociates into different dimeric and monomeric forms [13].

From a fundamental point of view, glycolaldehyde is a good model for studying intermolecular bifunctional interactions and, particularly, their effect on protonation or complexation energetics. In the present study the threshold energies of the most abundant product cations formed upon electron impact ionization of gas phase monomeric glycolaldehyde are determined with high electron energy resolution. In addition, some threshold energies have been measured for ions produced via electron impact ionization of a dimeric glycolaldehyde sample. The data obtained for the monomer and dimer of glycolaldehyde are compared with the appearance energy of deoxyribose, a more complex sugar of DNA that was studied recently with the same instrument [14].

2. Experimental setup and data analysis

The present experimental setup consists of a high resolution hemispherical electron monochromator (HEM)

* Corresponding author. Tilmann D. Märk is also adjunct professor at the Department of Plasma Physics, Comenius University, SK-84248 Bratislava, Slovakia. Tel.: +43 512 5076240; fax: +43 512 5072932.
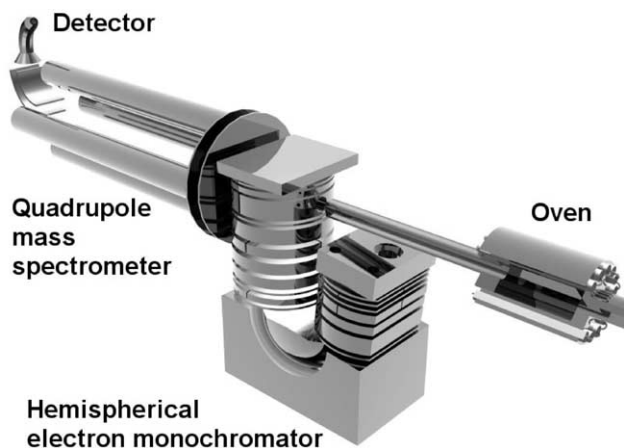*E-mail address:* tilmann.maerk@uibk.ac.at (T.D. Märk).

Fig. 1. Schematic view of the experimental setup.

in combination with a quadrupole mass spectrometer. A schematic view of this apparatus is given in Fig. 1. The HEM was described in detail in an earlier publication [15]. The electron beam is produced with a filament with a typical energy spread of 700 meV. While the highest achievable energy resolution of the electron beam with this instrument is around 35 meV (FWHM) with an electron current of 1 nA [16], we typically worked with a resolution of 110 meV (FWHM) and beam currents of 10 nA to ensure sufficiently high ion signals in the near-threshold region. Monomeric glycolaldehyde with a melting point of about 366–369 K, according to the specifications, obtained from ICN Biomedicals is used. The dimeric glycolaldehyde, purchased from Fluka, contains a mixture of stereoisomers and melts between 353 and 363 K depending on the stereoisomeric composition. A molecular beam of glycolaldehyde is produced by heating 25 mg of the crystalline powder in a copper oven up to a temperature of 340 K, measured by a Pt100 resistor. The volume of the oven is 1.57 cm^3. The pressure in the vacuum chamber under working conditions reaches a value up to 7.5×10^{-4} Pa. The cations formed by electron impact ionization of glycolaldehyde are extracted by a weak electric field into a quadrupole mass filter. After mass analysis the ions are detected by a channeltron type secondary electron multiplier operated in an ion counting mode. The yield of all product ions is recorded as a function of the electron acceleration voltage in an energy range from about 3 eV below to 4 eV above the threshold.

By fitting a Wannier type threshold function $f(E)$ [17] to the measured ion efficiency curves it is possible to determine the appearance energies of all cations formed by electron impact ionization of glycolaldehyde (for more details concerning this method see [18,19]).

$$f(E) = b \quad \text{if} \quad E < AE_1 \tag{1a}$$

$$f(E) = b + c(E - AE_1)^{p_1} \quad \text{if} \quad AE_1 < E < AE_2 \tag{1b}$$

$$f(E) = b + c(E - AE_1)^{p_1} + d(E - AE_2)^{p_2} \quad \text{if} \quad E > AE_2 \tag{1c}$$

The parameter b describes a possible constant background. In the fitting algorithm the parameters c, d, AE_1, AE_2, p_1 and p_2 are varied until an optimum overall agreement of the trial function $f(E)$ with the data is reached. With this approach, both the poly-atomic Wannier exponents p_i and the threshold energies AE_i ($i = 1, 2$) can be extracted from the experiment. Before and after each measurement of a product ion of glycolaldehyde the electron energy scale is calibrated relative to the well-known ionization threshold of Ar, which was admitted into the chamber as a background gas.

3. Results and discussion

A mass spectrum of the cations formed by electron impact ionization of the monomeric glycolaldehyde sample at an electron energy of 70 eV is shown in Fig. 2. The most abundant cations in the mass range between 10 and 70 Da are labeled in the mass spectrum: $C_2H_5O_2^+$ (61 Da), $C_2H_4O_2^+$ (60 Da), $C_2H_3O^+$ (43 Da), CH_4O^+ (32 Da), CH_3O^+ (31 Da), CHO^+ (29 Da) and CH_3^+ (15 Da). H^+ (1 Da) and H_2^+ (2 Da) were measured, using a different high frequency head of the quadrupole spanning a mass range of only 0–512 Da that has an increased transmission for low mass ions. With a few exceptions, our mass spectrum is in good agreement with one in the NIST database [20]. The peaks at 61 and 43 Da are much weaker in the NIST mass spectrum. The ion with a mass of 43 Da corresponds to $C_2H_3O^+$ and is most likely formed via the loss of a water molecule (dehydration) from protonated glycolaldehyde [21,22], see also the identification of this reaction using a MIKE technique by Bouchoux et al. [8]. Dehydration is a well known process for more complicated sugar molecules (e.g., deoxyribose [14]).

The most abundant fragment cations of glycolaldehyde (see Fig. 2) are CH_3O^+, CH_4O^+ and CHO^+. Two of these ions, i.e., CH_3O^+ and CHO^+, can be formed by a simple splitting of the parent molecule. In the present mass spectrum the yield of the protonated glycolaldehyde $C_2H_5O_2^+$
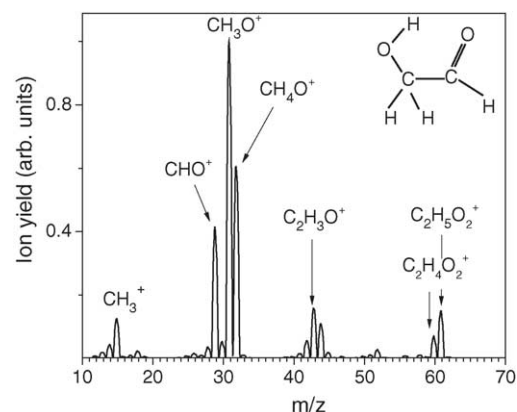

Fig. 2. Mass spectrum obtained by electron impact ionization of monomeric glycolaldehyde (see the molecular structure included top right) at the electron energy of 70 eV. The temperature in the oven is set to 320 K.