Electron impact ionization of glycolaldehyde

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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)

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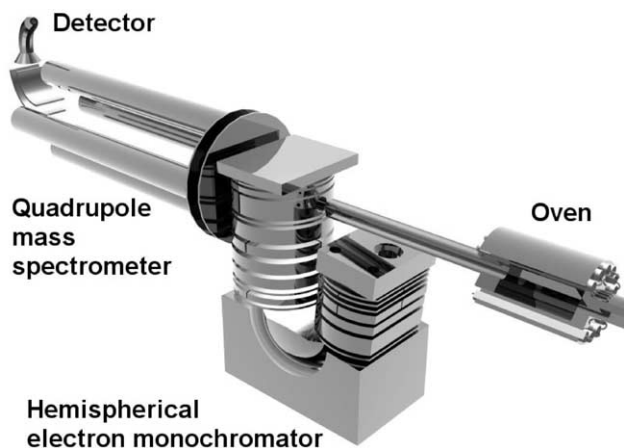*E-mail address:* tilmann.maerk@uibk.ac.at (T.D. Märk).

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 $C_2H_5O_2^+$
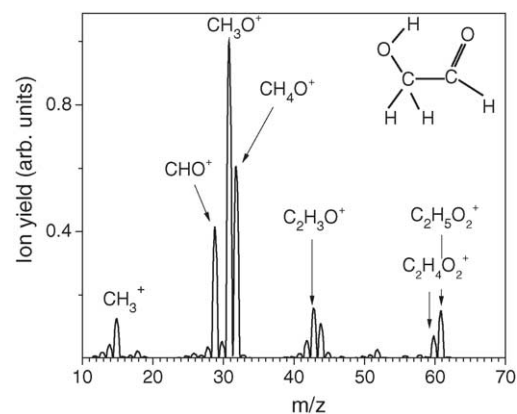

Fig. 2. Mass spectrum obtained by electron impact ionization of monomeric glycolaldehyde (see the molecular structure included top right) at the electron energy of 70 eV. The temperature in the oven is set to 320 K.

(61 Da) produced via electron impact ionization of the evaporated monomeric sample is higher than that of the parent ion $C_2H_4O_2^+$. In principle protonation of glycolaldehyde is possible at both, the carbonyl or hydroxyl oxygen atoms. Protonation at the carbonyl site leads to a more stable structure via formation of an internal hydrogen bond. Although the proton forms a covalent bond with the hydroxyl oxygen atom this kind of protonated glycolaldehyde is much less stable [8]. The proton affinities of the carbonyl and hydroxyl oxygen determine this difference in the stability of the two isomeric forms.

Information about the origin of the dimer ions and the protonated monomer ions produced by electron impact ionization of the evaporated monomeric sample is deduced from the study of the temperature dependence of the ion currents of several ions for these two samples. In the case of the dimeric sample all ions exhibit rather similar (exponential) dependences on the temperature (Fig. 3, lower panel). In contrast, for the monomeric sample the temperature dependence of ions that originate from a neutral dimer complex differs substantially from an exponential function. Moreover, it is interesting to note that for the monomeric sample the total ion yield increases by about a factor of 5 whereas in the case of the dimeric sample the ion yield increases by almost a factor of 8 for a 10 K temperature rise. According to the specifications from the
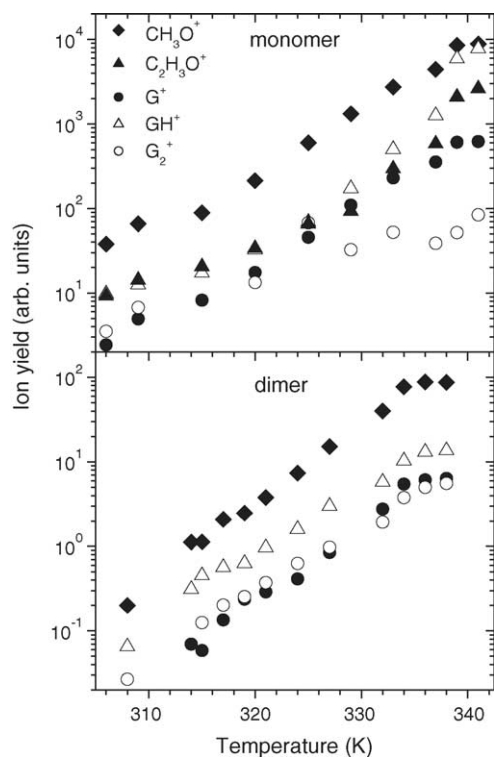
manufacturer the present monomeric sample contains exclusively glycolaldehyde monomers. However, the presence of the dimer cation and fragment ions larger than the monomer prove that under the present conditions either the effusive beam of glycolaldehyde contains already neutral dimers (maybe produced via three body association reactions in the oven) and/or that these ions are produced via ion molecule reactions in the ions source. The different temperature dependence of these ions originating from the monomeric and dimeric sample indicates a different formation process.

Ion efficiency curves are measured near the threshold for all ions designated in the mass spectrum shown in Fig. 2 and also for H_2^+ and H^+. The appearance energies (AEs) are determined using the fit procedure described above. Figs. 4 and 5 show the ion efficiency curves and the corresponding fit functions for the parent monomer and parent dimer cations and eight fragment ions obtained from a sample of monomeric glycolaldehyde (see also AE values in Table 1).

Fig. 3. Ion yield of the monomer (G^+, solid circle), dimer (G_2^+, open circle), protonated monomer (GH^+, open triangle) and its fragment $C_2H_3O^+$ (solid triangle) and the most abundant fragment CH_3O^+ (solid diamond) plotted as a function of the oven temperature for a monomeric sample (upper panel) and a dimeric sample (lower panel).
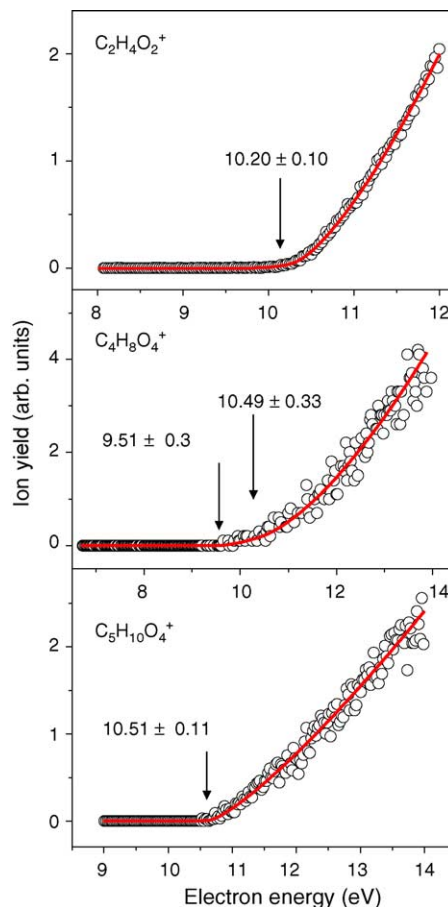

Fig. 4. Ionization efficiency curves near the threshold region for parent cations formed by electron impact of the monomeric (a) and dimeric sample of glycolaldehyde (b) and deoxyribose (c) leading to the cations $C_2H_4O_2^+$, $C_4H_8O_4^+$ and $C_5H_{10}O_4^+$, respectively. The measured data are shown as open circles whereas the fit curves (derived by the fitting procedure described in text) are shown as solid lines. The positions of the AEs are indicated by the arrows.
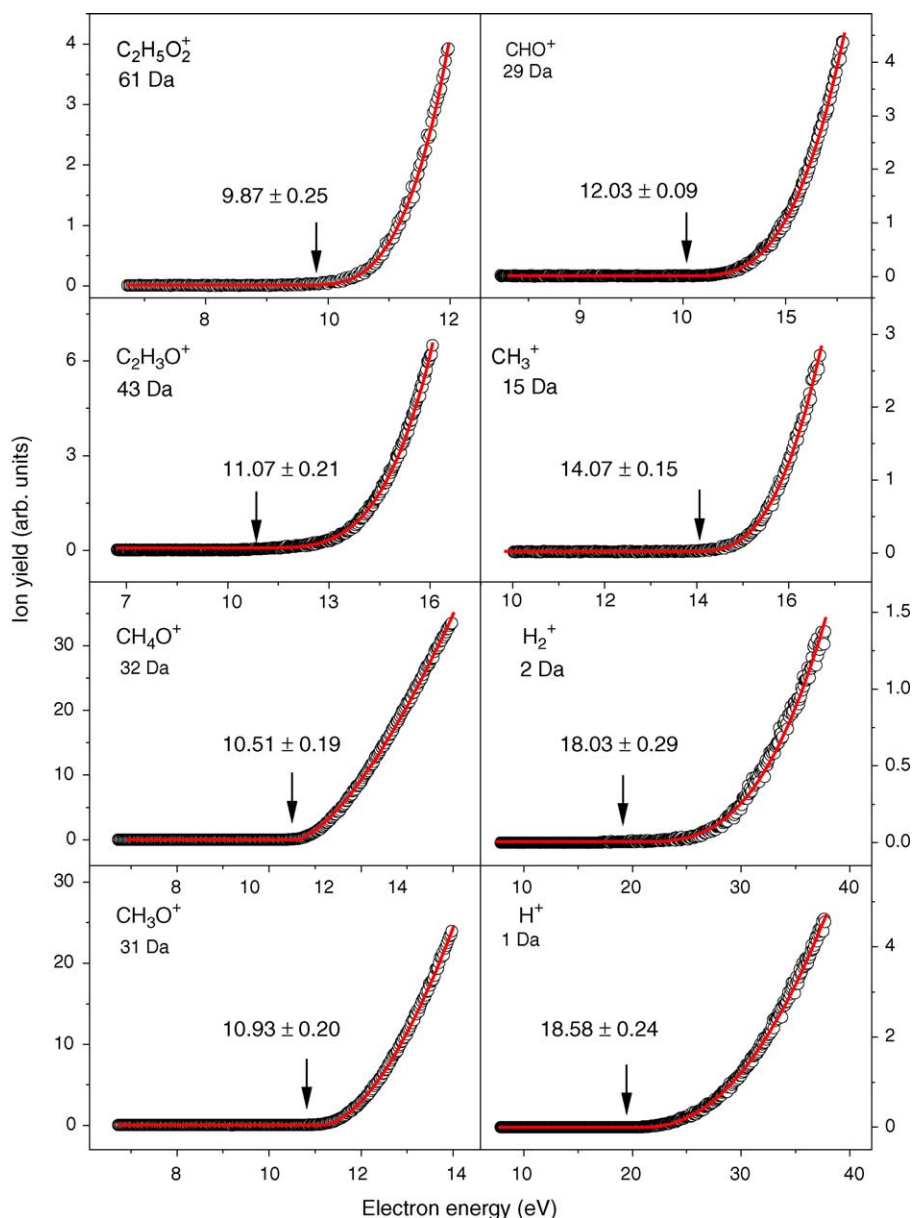
Fig. 5. Ionization efficiency curves near the threshold region for protonated glycolaldehyde and fragment cations: $C_2H_5O_2^+$, $C_2H_3O^+$, CH_4O^+, CH_3O^+, CHO^+, CH_3^+, H_2^+ and H^+ measured by electron impact ionization of a monomeric glycolaldehyde sample. The temperature in the oven is set to 320 K.

Table 1
Appearance energies for cations produced by electron impact on monomeric glycolaldehyde

Cation produced by electron impact on glycolaldehyde	Mass (Da)	Present AE value (eV)
$C_2H_5O_2^+$	61	9.87 ± 0.25
$C_2H_4O_2^+$	60	10.20 ± 0.10
$C_2H_3O^+$	43	11.07 ± 0.21
CH_4O^+	32	10.51 ± 0.19
CH_3O^+	31	10.93 ± 0.20
CHO^+	29	12.03 ± 0.09
CH_3^+	15	14.07 ± 0.15
H_2^+	2	18.03 ± 0.29
H^+	1	18.58 ± 0.24

The appearance energy values given in the figures represent mean values derived from several independent measurements. The error is calculated from the standard deviation of the single AE determination. For the ionization energy (IE) of the parent ion a value of 10.20 ± 0.10 eV is obtained. This is in good agreement with a previously published value of 10.26 ± 0.03 eV obtained by electron impact [23]. Fig. 4 shows a comparison of the ionization behavior close to the threshold of the parent ions of three different structures of sugar (besides the monomeric form of glycolaldehyde this graph contains the dimeric form of glycolaldehyde and deoxyribose—$C_5H_{10}O_4$). The monomer of glycolaldehyde has the simplest structure and it is a building block of other more complex sugar molecules. The ion efficiency curve

of the glycolaldehyde dimer shows two thresholds and thus the data are fitted with Eq. (1c). The first threshold is determined with 9.51 ± 0.3 eV and a second onset is found at 10.49 ± 0.33 eV. The uncertainty of the second onset is rather large as a result of the poor statistics of this measurement caused by the low ion intensity. The presence of two onsets can be explained by the existence of different forms of glycolaldehyde dimers. FTIR spectroscopy indicates that glycolaldehyde dimers exist in three different structures, i.e., two cyclic and one acyclic form [24]. According to this study heating transforms cyclic glycolaldehyde dimers via a ring opening into the acyclic form of a dimer that can recycle back into one of the two cyclic structures. Surprisingly the IE of the parent ion of deoxyribose, the most complex form of the three kinds of sugar, has the highest IE value (10.51 ± 0.11 eV [14]). The parent cation of the monomeric glycolaldehyde, $C_2H_4O_2^+$, can also be observed using the dimeric sample of glycolaldehyde and the deoxyribose sample. The apparent ionization energies measured for the reaction channels are 10.29 ± 0.16 and 11.28 ± 0.16 eV [14] for the dimeric glycolaldehyde and the deoxyribose sample, respectively. The appearance energy of the monomer cation from the dimeric sample is with 10.29 eV within the error bars equal to the ionization energy of the monomeric sample (10.2 eV). This is very likely the result of neutral monomers being present in the effusive beam of the dimeric sample. In contrast, the formation of $C_2H_4O_2^+$ from deoxyribose needs substantially more energy, i.e., in this case the furanose ring has to be broken to produce this fragment ion.

The two most abundant product ions with masses of 31 and 32 Da have threshold values of 10.93 ± 0.20 and 10.51 ± 0.19 eV, respectively. The AEs of these two cations, CH_3O^+ and CH_4O^+, are in good agreement with previously published values of 10.86 ± 0.05 and 10.42 ± 0.05 eV, respectively [25]. The formation of CH_4O^+ via CO release of monomeric glycolaldehyde requires a substantial rearrangement in comparison to the CH_3O^+ fragment that can be formed via a simple bond cleavage. Surprisingly a lower AE is observed for the more complicated reaction channel. This could indicate that at low electron energies the CH_4O^+ fragment is formed from a dimeric neutral precursor.

The AE value of the CH_3^+ cation is determined to be 14.07 ± 0.15 eV. Intermolecular rearrangement is necessary to produce this fragment via electron impact ionization of monomeric glycolaldehyde. The thresholds for the formation of H_2^+ and H^+ are observed above 18 eV.

The threshold region of the ion efficiency curve of the protonated glycolaldehyde is shown in Fig. 5 and exhibits a smooth onset located at an electron energy of 9.87 ± 0.25 eV. This value is about 0.3 eV higher than the ionization energy of the dimer cation. The threshold energy for the $C_2H_3O^+$ ion that is most likely formed via dehydration of the protonated glycolaldehyde has a value of 11.07 ± 0.21 eV. Besides this measurement at 333 K the AE of $C_2H_5O_2^+$ has also been determined at 343 K. For this higher temperature the AE value is shifted by about 0.93 eV towards lower electron energies,

which makes it even lower than the ionization energy of the dimer.

4. Summary

In the present work positive ion formation via electron impact ionization is presented for monomeric and dimeric samples of glycolaldehyde. In the case of the dimeric sample the ion yield of all product ions shows the same temperature dependence, i.e., an exponential increase as a function of the temperature. For the monomeric sample, however, all product ions possibly originating from neutral dimers that were formed during the evaporation process show a characteristic temperature dependence that differs from an exponential growth, i.e., at a temperature of 325 K the dimer parent ion does not increase with rising temperature and the protonated monomer and its dehydrated fragment product increase much stronger with the temperature than the rest of the ions. At the same time the appearance energy for the protonated glycolaldehyde drops by almost 1 eV and reaches at a temperature of 343 K a value that is even slightly lower than the ionization energy of the dimer. Another surprising result is the fact that the ionization energies for both, the monomer and dimer parent cations are lower than the ionization energy for the parent deoxyribose ion.

Acknowledgment

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