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Detection of gaseous oxygenated hydrocarbons in upper tropospheric and lower stratospheric aircraft borne experiments

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In memory of Werner Lindinger.

Abstract

Atmospheric oxygenated hydrocarbons (OHCs), including acetone, were measured at altitudes between 8.5 and 12.5 km using an aircraft-based chemical ionization mass spectrometer (CIMS) instrument equipped with an ion trap (IT) mass spectrometer. The IT-CIMS instrument offers a high mass resolution. It also provided a unique opportunity to carry out fragment ion investigations of mass selected ions, which greatly improved our ability to identify trace gases. Furthermore, in the IT, water molecules are “boiled off” from hydrated ions which simplifies core ion identification and greatly reduces the risk of masking of product ions by reagent ions. Acetone could be unambiguously identified in the upper troposphere (UT)/lower stratosphere (LS) by a combination of isotope and fragment ion investigations. A protonated molecule B with mass $m = 73$ could for the first time be detected in the UT/LS by CIMS due to the absence of the otherwise masking reagent ion $H^+(H_2O)_4$ ($m = 73$). The atmospheric volume mixing ratio (VMR) of the molecule B ($m = 72$) is about 150 pptv in the UT and decreases very steeply above the local tropopause indicating that B has a shorter lifetime than acetone. In the UT, the abundance ratio of B and acetone was found to be around 0.3. Additional observed molecules have mass 86 and 100. (Int J Mass Spectrom 223–224 (2003) 733–741)

Keywords: Oxygenated hydrocarbons; Acetone; UT

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1. Introduction

Oxygenated hydrocarbons (OHCs) have previously been detected in the upper troposphere (UT) and lower stratosphere (LS). Among the OHCs, two classes of carbonyls are of considerable importance in the atmosphere, ketones and aldehydes. These atmospheric carbonyl compounds are both, directly emitted by antropogenic and biogenic sources and photochemically produced from hydrocarbons [2]. The observed OHCs include acetone ($(CH_3)_2CO$), formaldehyde (H_2CO), methanol (CH_3OH), ethanol (C_2H_5OH), formic acid (HCOOH), and acetic acid (CH_3COOH) [1,3,8–10,13]. Their photolysis is considered to be a major source of free radicals and can even become the predominant radical source in the UT. Among these OHCs, acetone turned out to be most abundant reaching atmospheric volume mixing ratios (VMRs) of up to about 4 ppbv in the UT. Due to its large abundance, acetone may have a substantial influence on UT chemical processes. Acetone acts as a source of HO_2, organic acids, and PAN

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and thereby also may influence UT ozone-formation [1,9].

UT acetone has originally been detected by our group using chemical ionization mass spectrometry (CIMS) building on protonation of acetone by reaction with $H^+(H_2O)_n$ reagent ions in a flow tube reactor [5]. Unambiguous identification was also achieved by our group by fragment ion mass spectrometry using a CIMS instrument equipped with a triple quadrupole mass spectrometer. The latter allowed to make fragment ion studies of mass selected protonated acetone [7]. Considering the potentially important role of UT OHCs, it is interesting to search for additional so far undetected OHCs. Their speciation, identification, and quantification is necessary in order to understand and assess their contribution to the production of photo-oxidants and thus learn more about the photo-oxidation cycles in the upper troposphere.

The present paper reports on a search of UT OHCs using a novel aircraft-based CIMS instrument equipped with a quadrupole ion trap (IT) mass spectrometer which allows to make improved fragment ion studies and isotope analyses of mass selected ions and thereby allow unambiguous identification of OHCs.

2. Experimental

The instrument termed IT-CIMS which was developed and built by our group is composed of five major components (Fig. 1): (a) IT, (b) ion flow reactor (IFR), (c) ion source (IS), (d) sampling line (SL) and (e) isokinetic air-intake (AI). Component IT was taken from a commercial Finnigan-LCQ which we have modified. The isokinetic AI was used in order to avoid anisokinetic oversampling of volatile atmospheric trace substances contained in cloud elements or large aerosol particles. Upon some unintended heating of the sample air flow in the SL and IFR volatile substances may evaporate from cloud elements or large aerosole particles. Such vapors of aerosol particle origin would erroneously be identified as atmospheric gaseous species.

Atmospheric air enters the IFR (inner diameter: 4 cm) and due to ram pressure passes the IFR within about 30 ms. The total gas pressure in the IFR was typically around 200–300 hPa.

Note that trapping in the IT of externally produced ions requires damping of the ion motion in the *z*-direction by collision with He-atoms in the IT

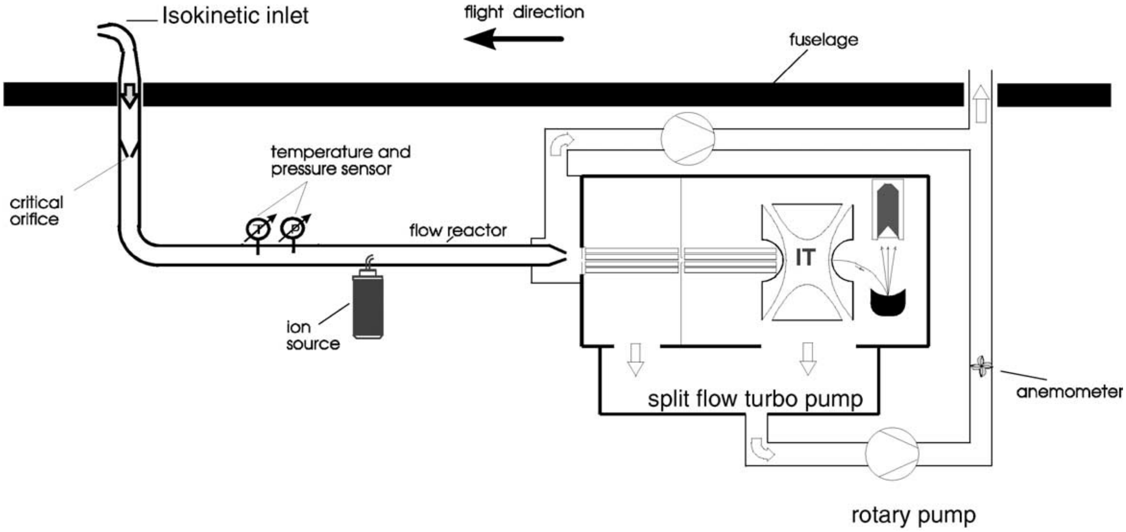

Fig. 1. Schematic view of the experimental setup. Atmospheric air enters the flow reactor through an isokinetic inlet and a critical orifice. Ions produced in the ion source react with trace gases in the flow reactor and are detected in the IT.

(typically present at a pressure of 1 mTorr). Thereby, weakly bound cluster ions like $H_3O^+(H_2O)_3$ experience collision-induced dissociation (CID) and loose ligand molecules. For example $H_3O^+(H_2O)_3$ (73 amu) is "boiled down" mostly to H_3O^+. This allows the detection of H^+MEK (Methyl Ethyl Ketone, 73 amu) without the risk of masking by $H_3O^+(H_2O)_3$ (see above). Also various other cases of masking are avoided. Particularly at m equal to 37, 55, 91, 109, 127, and 145 corresponding to $H_3O^+(H_2O)_n$ ions.

Atmospheric trace gases with sufficiently large proton affinity (PA) react in the IFR with reagent ions ($H_3O^+(H_2O)_n$ with n mostly around 3–4) via:

$$H_3O^+(H_2O)_n + X \rightarrow HX^+(H_2O)_{n-1} + H_2O. \quad (1)$$

Both product and educt ions enter the differentially pumped (pump: two stage turbomolecular pump with a pumping speed of 125/200 L/s) IT-vacuum chamber via an inlet orifice (diameter: 0.15 mm). By the action of two octapole lenses (OP1, OP2), the inflowing ions are guided into the IT. After an ion sampling time of typically 20–50 ms, ions are expelled from the trap in the mass selective instability mode [11] and ultimately detected by a conversion dynode multiplier system. Thereby, an ion mass spectrum is created within 40 ms. Hence, the over-all time resolution of the IT-CIMS measurements in the MS-mode is 60–90 ms.

During the flight, the IT-CIMS was alternatively operated in a positive or negative ion mode. In addition, a fragment ion mode (MS^2-mode) was occasionally employed for ion identification. In this mode, the kinetic energy of mass selected trapped ions (usually H^+X) is sufficiently raised and energetic collisions of these ions with He-atoms in the trap may result in ion fragmentation. For a given H^+X ion, several fragmentation channels may exist each having a defined probability of occurrence.

The data to be reported here were obtained during two flights of our IT-CIMS instrument. The first took place on February 4, 1998 on board of the research jet aircraft "Learjet," the flight path extended from Kiruna (68°N, Sweden) to Hohn (54.5°N, Germany). During the flight, a peak altitude of 12 km was reached. Both UT and LS air masses were probed. IT-CIMS data (positive ions) were obtained at altitudes between 8 and 12 km around 08:30–09:00 h UT. The second flight took place on September 21, 1998 on board of the research jet aircraft "Falcon," the flight path extended from München (Germany) to Bologna (Italy). During the first flight, the mass range was limited to a lower mass cut off of $m_{\mathrm{min}} = 50$ amu which could be reduced to $m_{\mathrm{min}} = 15$ amu in the second flight. MS^2 spectra shown in the following are, therefore, from flight 2 as they show additional fragment ions in the mass range 15–50 amu.

3. Results and discussion

Fig. 2 shows a positive ion mass spectrum obtained by the IT-CIMS instrument in the UT around 10 km altitude during flight 1. The spectrum starts only at $m = 50$ and extends to $m = 200$. Therefore, the spectrum does not contain the reagent ion H_3O^+ ($m = 19$). Six major mass peaks ($m = 59$, 73, 87, 117, 131, 145) are present. Among these, 59 is largest and can be attributed to the ion $H^+(CH_3)_2CO$ (protonated acetone). Previous UT measurements with our Linear Quadrupole Mass Spectrometer (LQ-MS) instrument have already found that $H^+(CH_3)_2CO(H_2O)_n$ ions are the most abundant product ions [1,13]. As mentioned before, H_2O-ligands are "boiled off" in the ion trap of the IT-CIMS instrument and, therefore, only the unhydrated product ion of the type $H^+(CH_3)_2CO(H_2O)_n$ ($n = 0$) should be present.

Our present experiment offers three additional observations which strongly support the identification of the ion 59 as $H^+(CH_3)_2CO$ (Ac). These are: (a) the heavy isotopomer of $H^+(CH_3)_2CO$ ($m = 60$) which contains one C^{13} atom; (b) a fragment ion mass spectrum of trapped 59, (c) the presence of mass 117 $H^+((CH_3)_2CO)_2$.

Concerning (a) an ion ($m = 60$) is clearly noticeable and the measured abundance ratio of the ions 60 and 59 is 0.034. In comparison, the expected ratio for the $H^+(CH_3)_2CO$ ions with m equal to 60 and 59 is 0.033. Hence, the measured ratio indicates that each

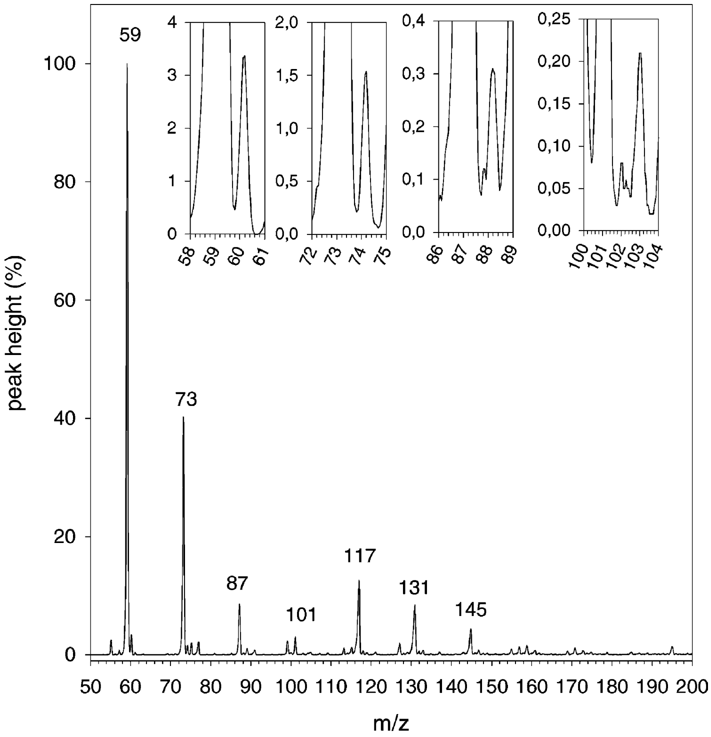

Fig. 2. Mass spectrum of positive ions obtained at 10 km altitude by the aircraft borne IT-CIMS instrument. Insert panels show enlarged portions of the spectrum including ionic isotopomers containing the ^{13}C isotope.

of the ions 59 and 60 contains three C-atoms. This strongly supports an identification as $H^+(CH_3)_2CO$. Note that in our previous measurements with the LQ-CIMS instrument mass number 60 was masked by $H^+CH_3CN(H_2O)$. Therefore, an isotope analysis was previously not possible. Concerning (b) a fragment ion mode spectrum of the trapped ion 59 was obtained by IT-CIMS in the UT (Fig. 3; top panel). The spectrum which was obtained during flight 2 contains only the parent ion 59 but no fragment ion. This is characteristic for $H^+(CH_3)_2CO$ as was demonstrated in a laboratory experiment (Fig. 3, middle panel). By contrast, protonated propanal which also has $m = 59$ shows pronounced fragmentation in the laboratory experiment (Fig. 3, bottom panel). Hence, the UT ion 59 is certainly not protonated propanal but most likely protonated acetone. Concerning (c) the presence of $H^+((CH_3)_2CO)_2$ ($m = 117$) supports the view that 59 is a protonated molecule with $m = 58$. The ion 117 is formed in the IFTR by reaction of $H^+(CH_3)_2CO(H_2O)_n$ with $(CH_3)_2CO$.

Considering H^+W_n (W = water) conversion to $H^+((CH_3)_2CO)W_{n-1}$ and further conversion to $H^+((CH_3)_2CO)_2W_{n-2}$ (rate coefficients 2.04×10^{-9} cm^3 s^{-1}) the measured $R = 0.13$ for $H^+((CH_3)_2CO)_2/H^+((CH_3)_2CO)_1$ is consistent with an atmospheric acetone concentration of 5×10^9 cm^{-3}. The latter corresponds to a VMR of about 500 pptv at 10 km altitude. In comparison, typical acetone VMRs previously measured by our group using LQ-CIMS instruments were mostly around 500–1000 pptv [1,13].

The second most abundant ion in Fig. 2 has $m = 73$. This ion also seems to be a protonated molecule (hereafter termed molecule **B**) as indicated by the presence of the cluster ion $H^+(CH_3)_2CO\mathbf{B}$ ($m = 131$). The ion 73 also has at most three C-atoms as indicated by the ion 74. Unfortunately, no fragment ion study of the ion 73 was made in the UT.

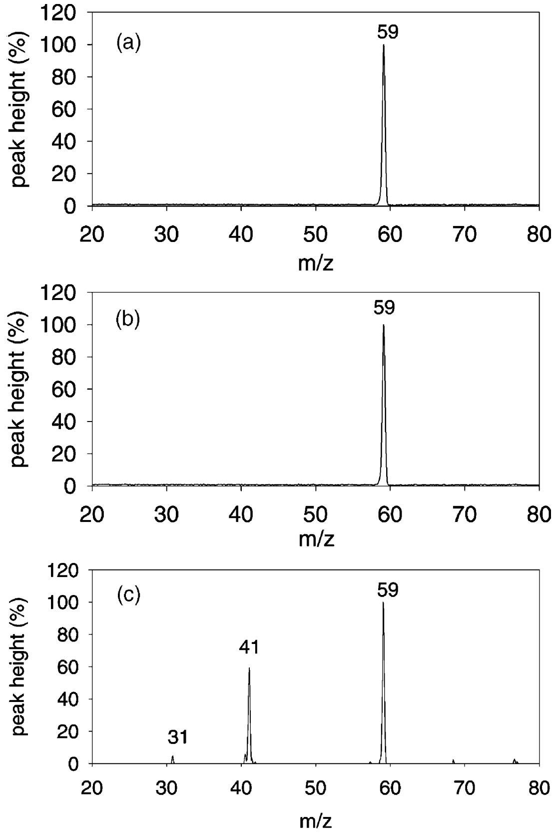

Fig. 3. Mass spectrum of positive ions obtained by the IT-CIMS instrument when operated in the fragment ion mode when only parent ions with $m = 59$ were trapped. Panel (a): 10 km altitude; panel (b): protonated acetone in a laboratory experiment; panel (c): protonated propanal in a laboratory experiment.

It seems worth noting that in our UT measurements with LQ-CIMS instruments a protonated molecule **B** with mass $m = 73$ could not be detected since it was heavily masked by the reagent ion $H^+(H_2O)_4$ ($m = 73$). The ion 73 may at least in principle also be $H_3O^+(H_2O)_3$. However, as discussed above this is very unlikely since $H_3O^+(H_2O)_3$ suffers from very marked CID inside the IT. This is also clearly indicated by our present flight-data namely by the near absence of $H^+Ac(H_2O)$. Note that the energy required for removing one H_2O is nearly the same (about 19 kcal/mol) for H^+AcH_2O and $H_3O^+(H_2O)_3$. Hence, the abundance ratios $H_3O^+(H_2O)_3/H_3O^+(H_2O)_2$ and H^+AcH_2O/H^+Ac should be about the same. By contrast, however the measured ratios are 13.6 and 0.06, respectively. This argues very strongly against an identification of 73 as $H_3O^+(H_2O)_3$!

Fig. 4 shows as function of altitude measured peak heights for the ions 73 and 59. The 59 profile decreases above about 10 km the level of the local tropopause. The latter is indicated by the O_3-data. Since the total peak height of $H^+(H_2O)_n$ reagent ions (not measured by the IT-CIMS but previously measured by our LQ-CIMS) is nearly constant between 10 and 13 km, the decrease of 59 reflects the decrease of the acetone VMR. In fact, previous LQ-CIMS experiments of our group have observed a decrease of the acetone VMR above the local tropopause. This decrease is due to acetone-photolysis (acetone lifetime ∼16 days [9]) and slow vertical exchange above the tropopause.

The peak height of the ion 73 (Fig. 4) decreases even more steeply than 59 above the tropopause. This indicates that the molecule **B** is most likely an atmospheric molecule of tropospheric origin whose lifetime is markedly shorter than the lifetime of acetone. An identification of **B** has to await an UT fragment ion study of the ion 73. Aircraft borne Proton Transfer Reaction Mass Spectrometry (PTRMS) measurements (for working principle, see [6]) over Surinam reported by Williams et al. [12] also showed a mass peak 73 which was ascribed to MEK by the authors. This would imply that the ion 73 has to contain four C-atoms which is not consistent with our isotope study (the ratio of ion 74 to ion 73 is 0.37 and should be 0.44 for a **B** containing four C-atoms). Candidates for **B** containing only three C-atoms are: acrylic acid ($CH_2CHCOOH$) and methyl glyoxal (CH_3COCHO).

The peak height ratio of the ions 73 and 59 is about 0.3 in the UT. This suggests that the abundance ratio is also around 0.3. If so, the atmospheric VMR of the gas **B** would be around 150 pptv in the UT. An estimate of the atmospheric lifetime of **B** may be made from the decrease of **B** above the local tropopause. Since **B** decreases more steeply above the tropopause than acetone, it has a shorter atmospheric lifetime than acetone. From the slopes in Fig. 4, one can derive a ratio of 0.25 for the lifetimes of **B** and acetone, respectively. Taking an average lifetime of 16 days for

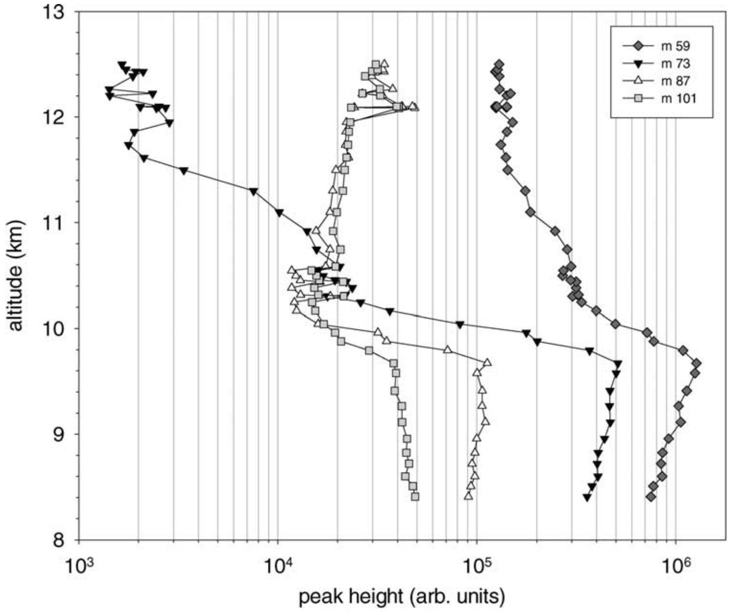

Fig. 4. Height profiles of mass peak heights of ions with mass numbers 59, 73, 87, and 101. The local tropopause is at ~10,500 m.

acetone, this gives a mean lifetime of about 4 days for compound **B** between 10 and 13.5 km.

The ion 87 which is also observed in LQ-CIMS measurements is the third most abundant ion in Fig. 2. Most likely, it is a protonated molecule **C** as indicated by the presence of $H^+(CH_3)_2CO$**C** ($m = 145$). We have made an UT fragment ion study of the ion 87 (Fig. 5) which indicates five fragment ions (69, 55, 45, 43, 37) which seem to be formed by abstraction of H_2O; O_2, S, or CH_3OH; C_3H_7, CH_2CO, or HNCO; C_2H_4O, CHS, respectively. Assuming the parent ion to be composed of three C-atoms plus H- and O-atoms, the neutral fragments 18, 32, 44, and 50 are H_2O, O_2, CO_2, and $H_2O + O_2$. The remaining neutral fragment 42 may be C_2H_2O. If so, the ion 87 would contain three O-atoms which would identify the molecule **C** as $C_3H_2O_3$ (carbonic acid or cyc-(HOC=COHC)=O). If so, the ion 87 contains at least one and perhaps even two O-atoms. The measured peak height profile of the ion 87 (Fig. 3) behaves quite differently compared to 59 and 73 above the tropopause where it is nearly constant with increasing altitude. Near and below the tropopause 87 behaves similar to 73. Hence, the overall behavior of the ion 87 profile is puzzling. Below about 10.3 km, the ion 87 behaves as if the molecule **C** would be an atmospheric molecule of tropospheric origin which has a shorter lifetime than acetone. Above about 10.3 km, the ion 87 behaves as if the molecule **C** would be a contaminant at these heights which desorbs from the inner wall of the IFTR.

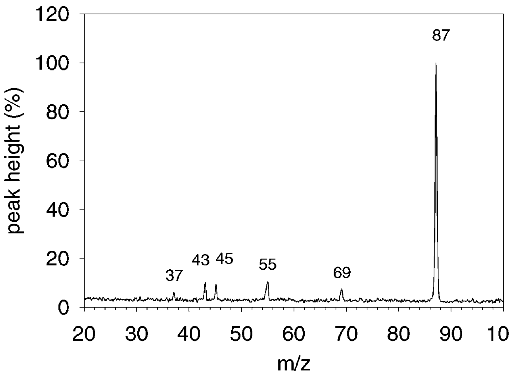

Fig. 5. Fragment ion mass spectrum of the ion with $m = 87$ obtained by the IT-CIMS in flight.

The ions 99 and 101 which are also observed in LQ-CIMS measurements have mass peaks which are

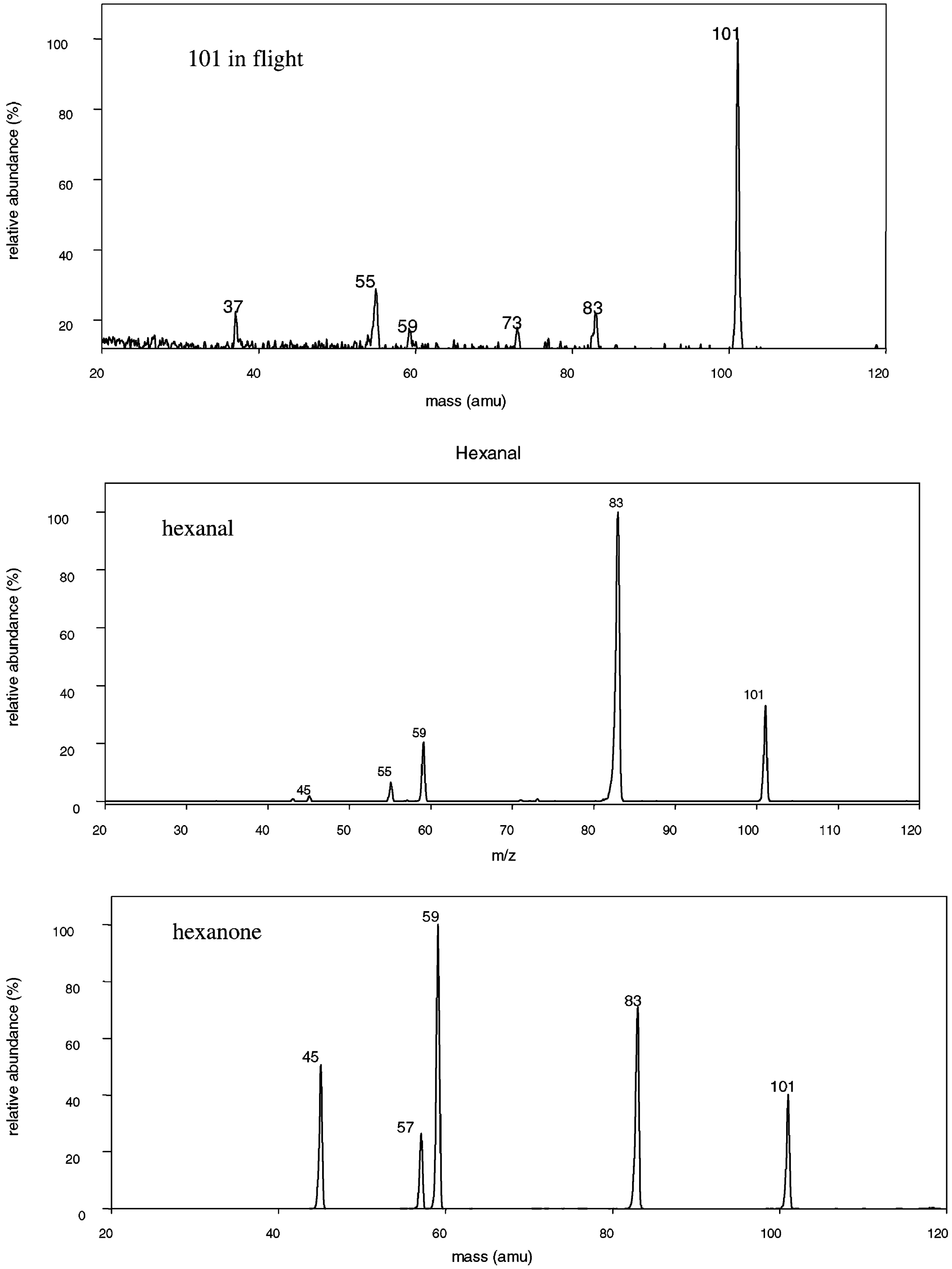

Fig. 6. Fragment ion mass spectrum of the ion with $m = 101$ obtained by the IT-CIMS in flight.

still far above the background of the spectrum shown in Fig. 2. Ions consistent with $H^+(CH_3)_2CO$**D** (**D** has mass 98) and $H^+(CH_3)_2CO$**E** (**E** has mass 100) having *m* equal to 157 and 159 are also present in Fig. 2. Hence, the ions 99 and 101 also seem to be protonated molecules (**D** and **E**). An UT fragment ion spectrum has been obtained for the ion 101 (Fig. 6, upper panel). Here, five major fragment ions (83, 73, 59, 55, 37) are present. These seem to be formed by abstraction of H_2O; C_2H_4 or CO; CH_2CO or C_3H_6; C_2H_5OH, NO_2, or CH_2S; SO_2 or $(CH_3OH)_2$, respectively. If so, the ion 101 would contain at least one and perhaps two O-atoms. PTRMS measurements at Sonnblick [4] attributed the mass 101 to *n*-aldehydes. However, laboratory fragment ion studies with the IT-CIMS instrument made by our group clearly showed that the UT ion 101 is not protonated hexanal (Fig. 6, mid panel) or hexanone (Fig. 6, lower panel). The fragmentation pattern of both hexanal and hexanone show fragments which are not present in the atmospheric fragmentation of ion 101 (45, 43 for hexanal and 57, 45 for hexanone) and neither of them shows a fragment with mass 37. In addition, the relative intensities of the fragments which appear for all compounds is markedly different. This makes clear that the atmospheric compound **D** does not include hexanal or hexanone. The altitude profile of the peak height of the ion 101 (Fig. 3) is somewhat similar to that of the ion 87. Hence, the stratospheric branch of the abundance profile again suggests that in the LS molecule **E** may be a contaminant. However, in the UT and tropopause region, molecule **E** behaves like a gas of tropospheric origin.

Additional IT-CIMS measurements in the UT and in the laboratory are necessary for an identification of the molecules **D** and **E**. The same is true for additional minor ions (55, 70, 77, 89, 113, 115, 127, 155, 161, 169, 171, 195) whose mass peaks are clearly noticeable in Fig. 2.

4. Summary and conclusions

Various gaseous OHCs have been detected in UT/LS aircraft-borne experiments using a novel CIMS instrument equipped with an IT mass spectrometer. High levels of these compounds may have a significant impact on radical chemistry, since they will constitute an important source of HO_x radicals through photolysis by natural sunlight.

The most abundant gaseous OHC detected is acetone which was identified by isotope and fragment studies. In the UT, the acetone VMR was around 500 pptv. In the LS, the acetone VMR decreased steeply which can be explained in terms of photolysis and slow vertical exchange.

Other observed abundant trace gas species (**B**, **C**, and **D**) which have mass numbers 72, 86, and 100 also seem to be UT OHCs. Of these species, **B** behaves like an atmospheric species of tropospheric origin having a lifetime which is about four times shorter than that of acetone. Species 87 and 100 behave like an atmospheric gas in the UT but in the LS seem to behave like a contaminant. Future UT/LS IT-CIMS measurements should include also fragment ion studies of the ion 73.

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