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# Mass and Collision Cross-Section Determination Using a Low-Vacuum Mass Spectrometer

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**A simple low-vacuum mass spectrometer (LVMS) operating in the milliTorr pressure range was developed. The instrument resolves masses by time-of-flight measurements and employs a high-gain, fast-response detector that can operate at these pressures. This instrument allows simultaneous determination of mass and collision cross sections of the ions with the bath gas. Here we demonstrate the LVMS's abilities to determine total collision cross sections for the collisions of organic ions with three background gases, He, $N_2$, and $SF_6$. As a demonstration of the system capabilities, the unimolecular interconversion of photochemically produced $C_7H_7^+$ to the tropylium ion structure is investigated.**

Mass spectrometric techniques are extensively used to determine the masses of gas-phase ions. However, structural information cannot be directly retrieved from the mass determination, and in some cases, additional characterization must be performed. This additional information is often obtained from measurements of fragmentation patterns, spectroscopy, and reactivity data. Typically, the need to obtain multidimensional information requires larger and/or expensive apparatus. Here we present a low-vacuum mass spectrometer (LVMS) that provides both mass and structural information but is inexpensive and compact in size.

In mass spectrometry, where ions with different isomers are present in a sample, physical parameters such as collision cross sections and mobilities can provide the missing structural information. Collision cross sections can be measured by classical scattering experiments using high-pressure collision cells[1] or using complicated mass spectrometric techniques such as a double-focusing sector mass spectrometer,[2] triple-quadrupole mass spectrometer,[3] or the flowing afterglow selected ion drift tube technique.[4] These experiments usually require relatively complicated experimental setups. Although the mass of ions, cluster ions, and proteins cannot be directly obtained from ion mobility spectrometry (IMS), this technique has been very successful in providing information about their structure and collision cross sections.[4−9] However, classical ion mobility spectrometers usually suffer from low resolution and sensitivity mainly due to the lack of high-gain detectors and space charge limitation. Recently new methods have been introduced to overcome those resolution[7,10,11] and sensitivity problems in IMS.[12] To introduce mass resolution to IMS instruments, they are often coupled to quadrupole or time-of-flight (TOF) mass spectrometers that increase the complexity of the experimental setup.

The LVMS presented here uses a new approach for simple mass and cross-section measurements. This spectrometer is a linear time-of-flight instrument that operates at low vacuum, in the milliTorr pressure range. Mass information is obtained from the TOF spectra, and collision cross sections are deduced from the measurements of the ion beam attenuation as a function of the bath gas pressure in the field free drift region. Therefore, both mass and structural information can be obtained in a single, simple apparatus. The requirement of high ion sensitivity and flight time resolution is achieved by using a microsphere plate (MSP) as the ion's detector. This detector provides sensitivity and excellent time response that were not available before in instruments that operated at high pressures such as IMS. We present measurements of the mass and total collision cross sections for benzene and methylated benzene cations with three different gases, using this new system. In addition, we provide evidence for the isomerization of $C_7H_7^+$ ions to a cyclic form, the tropylium ion structure.

## EXPERIMENTAL SECTION

The LVMS consists of a linear time-of-flight tube, shown in Figure 1. A single chamber houses the two-stage ion optics, the flight tube, and the ion detector. The field free drift tube is 25 cm long and has a diameter of 50 mm. A longer tube for increasing the mass resolution could easily be incorporated into the instrument. The chamber has several inlets to introduce the target gas and the sample gas. A calibrated Baratron capacitance manometer

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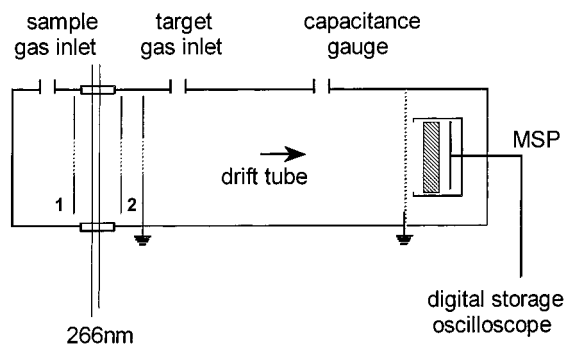(12) Hoaglund, C. S.; Valentine, S. J.; Clemmer, D. E. *Anal. Chem.* **1997**, *69*, 4156.

**Figure 1.** Schematic representation of the LVMS. A 266-nm laser pulse produces the ions. The drift tube's inner diameter is 50 mm, and the extraction lenses have 8-mm-diameter mesh in the center for the extraction of ions. The drift tube can be easily changed between 25 and 50 cm length, with just O-ring sealing between the different parts. Typical applied voltages are 970 and 700 V on electrostatic lenses 1 and 2, respectively. These voltages accelerate the ions to ~750 eV; 3.3 kV is applied to the MSP.

(100 mTorr full range) is mounted directly onto the tube, providing absolute determination of the pressure in the drift tube.

Toluene, *p*-xylene, and benzene were introduced into the cell through a side inlet. No change in the total pressure of the instrument was observed upon injection of the measured gases. All substances were used as purchased (purity >99%).

The fourth harmonic (266 nm) of a Nd:YAG laser (Spectra Physics, GCR-100) was used to ionize the sample molecules. These compounds are easily ionized by a two-photon ionization at 266 nm to give ions in their ground electronic state. Care was taken to use low laser intensities (40 $\mu$J cm$^{-2}$ in a 8-ns pulse), which avoids fragmentation and higher order multiphoton ionization processes that lead to ion fragmentation. This consideration was especially important for toluene, which may be resonantly ionized at this wavelength. Low laser intensities are also essential to keep the ion intensity low enough to avoid broadening of the signal due to ion−ion repulsion. All the ions appear at their respective masses based on the TOF equation. By mildly focusing the laser beam, ionization of *p*-xylene was used to produce the $C_7H_7^+$ ion, at mass 91.

An advantage of this instrument is the small and compact pumping system. The pumping system consists of a mechanical pump (Varian SD-450) and a small Turbo pump (Varian V-70). The mass spectra were obtained at different pressures of the target gas, typically averaged over 250 laser shots directly on a digital oscilloscope (LeCroy 9361). In the present experiments, the pressure ranged from 0.01 to 1.2 mTorr. The base pressure in the flight tube was below the measuring range of the Baratron (0.01 mTorr). At the lower pressures, a mass resolution of $m/\Delta m$ = 100 can be obtained.

The key to the operation of the LVMS is the ability to amplify the ion signal at relatively high chamber pressure. This was achieved by using the MSP (El Mul, Yavne, Israel). The MSP[13] is fabricated by sintering an array of glass beads, forming an irregularly packed porous disk, ~1-mm thick. Ions impinging on the front surface emit secondary electrons. A high-voltage field accelerates these electrons between the beads, and amplification is achieved by emission of secondary electrons upon further
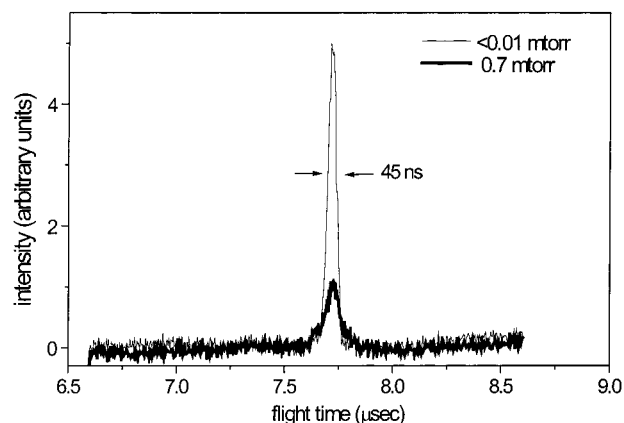
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**Figure 2.** Mass spectra of toluene at two different pressures of the $N_2$ target gas: <0.01 (the Baratron's detection limit) and 0.7 mTorr.

collisions with the glass beads. The complex path of the electrons between the glass beads inhibits ion feedback, which is the mechanism that limits the operation of regular MCPs at these pressures. The MSP can operate well at these high pressures with an amplification of $10^5$ and a time response in the nanosecond range.[14−16]

## RESULTS AND DISCUSSION

Figure 2 shows typical time-of-flight spectra for toluene in an $N_2$ bath gas using a 25-cm drift tube. Unit mass resolution is readily achieved over the mass range of interest. The peak width at half-maximum is ~45 ns, and the flight time is ~7.7 $\mu$s. Part of the peak width arises from the photoionization pulse length (~8 ns). Further increase in the peak width arises from thermal broadening and from inhomogeneity of the electric fields. When the gas pressure in the tube is increased, the ion signal is attenuated. This attenuation is attributed to scattering of molecules from the beam by collisions with the background gas. Figure 2 illustrates how the signal changes when the pressure increases from 0.01 to 0.7 mTorr.

When a collimated beam of ions travels through a collision cell of length $l$ that contains a target gas with a number density $n$, the intensity of the beam is reduced as some of the ions are deflected out of the beam due to collisions with the bath gas. Hence, the signal at the detector obeys the following relation[2,17]

$$I_l/I_0 = e^{-n\sigma_T l} \tag{1}$$

Where $I_0$ is the initial beam intensity, $I_l$ is the intensity of the beam at length $l$, and $\sigma_T$ is the total collision cross section, which is the sum of all processes that lead to depletion of molecules from the beam: scattering, charge transfer, and collision-induced dissociation. Figure 3 shows the dependence of the ion signal on the pressure of $N_2$ background gas for the four ions studied. The linear dependence of log $I_l$ on the pressure is evident. From the

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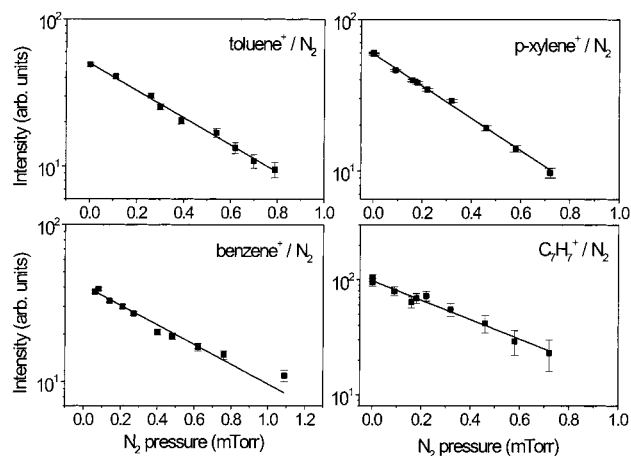
**Figure 3.** Ion signal peak height as a function of $N_2$ pressure in the drift tube for positively charged toluene, benzene, and p-xylene and for $C_7H_7^+$. Collision cross sections are directly calculated from the slope of such graphs.

slope of these graphs, it is possible to extract the total cross section for the ion−molecule collisions.

In the present measurement technique, deflected ions either do not appear at the detector at their appropriate arrival time or they appear as a broadening of the mass signal, i.e., as a long time tail in the TOF signal. Such broadening in time-of-flight peaks has been investigated theoretically and shall not be discussed here.[18] Accordingly, the peak amplitude of the signal at the lowest pressure is taken to be the intensity of the unscattered ions ($I_0$). In this work, only the decrease in the signal height was considered and we did not relate to the peak area. This approach is equivalent to applying a velocity discrimination on the signal that corresponds to those molecules that did not undergo any interaction with the bath gas and therefore did not change their velocity, i.e., with $\Delta v = 0$. Because this approach treats only the unscattered molecules, it largely eliminates a problem of detecting scattered molecules (multiple collisions, collisions with the walls, etc.) at continuously changing detection solid angle. In this evaluation, collisions in the acceleration zone are ignored. The discrimination against ions that undergo energy loss also ensures that the amplification of the MSP, which is a function of impact energy, is the same for all ions. Last, for the pressure range used in the present experiments, the mean time between collisions is in the microsecond time scale. Consequently, the ionization process, which is confined to the ionization laser's pulse width (∼8 ns), is not affected by collisions with the background gas. Pressure quenching of the ionization process and consequent effects on the evaluation of our data can therefore be ruled out.

Table 1 presents the total cross sections obtained for the collisions of the four ions studied with three background molecules, at a collision energy of $E_{kin} = 750$ eV. The results show the expected trend of larger cross section when a methyl group is added to the aromatic ring or when the ions collide with larger target gas molecules. This trend in cross section was also observed in earlier determinations of relative collision cross sections.[2,19] The absolute cross section obtained for benzene, 11.5 Å$^2$ (at $E_{kin} =$

**Table 1. Total Collision Cross Section (in Å²) Measured at Kinetic Energy of 750 eV for Three Different Target Gases**

|  | He | N₂ | SF₆ |
|---|---|---|---|
| $C_6H_6^+$ | 11.5 ± 1.1 | 17.9 ± 1.2 | 30.7 ± 2.3 |
| $C_7H_8^+$ | 18.5 ± 2.1 | 26.6 ± 1.0 | 41.5 ± 3.1 |
| $C_8H_{10}^+$ | 19.2 ± 2.1 | 30.5 ± 0.71 | 44.2 ± 0.4 |
| $C_7H_7^+$ | 15.5 ± 2.1 | 24.2 ± 1.8 | 33.7 ± 2.2 |

750 eV), is larger than the available literature value of 6.82 Å$^2$. This latter value was measured in collision cell experiments using He as target gas and at a kinetic energy of $E_{kin} = 8$ keV.[19] The difference between the two measurements may be explained by the lower kinetic energy used in the present set of experiments. In addition, our analysis includes only molecules that do not change momentum. This is in contrast to the collision cell experiment,[19] in which no velocity selection was used and all ions of a specific mass that arrived at the detector were included in the analysis. The present approach necessarily results in larger, and probably more accurate, collision cross sections. As expected, the values obtained here are still considerably smaller than the cross sections, $\sigma = 50.26$ Å$^2$, calculated based on van der Waals radii.[4] To the best of our knowledge, no other data exist in the literature on total collision cross sections for the collision pairs studied here and at comparable kinetic energies.

The noise observed in the data presented in this work originates from fluctuations in the ionization process. The accuracy of the cross-section measurements is subject to known TOF measurement techniques and to the accuracy of pressure determination in the instrument.

The values shown in Table 1 demonstrate that it is possible to determine differences in molecular structure applying the LVMS. As an example of this property of the system, we considered the isomerization of $C_7H_7^+$, which is the main fragment from the 2 + 1 photon ionization of p-xylene. The isomerization from the photochemically produced $C_7H_7^+$ ion to the tropylium structure of $C_7H_7^+$ has been studied in earlier work using electron impact ionization.[20,21] From these earlier works, it is not known whether isomerization may occur after photoinduced abstraction of a methyl group from p-xylene cations. The structure of the $C_7H_7^+$ ion, which is photochemically produced, is expected to have a collision cross section almost equal to that of the toluene cation. The dipoleless cyclic 7-ring structure of the $C_7H_7^+$ tropylium ion is expected to have a different cross section. The collision cross section of $C_7H_7^+$ (see Table 1) was determined from the set of mass spectra that used p-xylene sample gas and the higher laser flux for ionization. For all the different target gases that we used, the $C_7H_7^+$ cross section is significantly smaller than that of toluene, suggesting that a large fraction of the $C_7H_7^+$ species undergoes isomerization to the tropylium structure. This result is in agreement with electron impact $^{13}$C-labeling study of Grotemeyer[21] and consistent with the work of van Houte et al., who concluded that ions with cyclic structures have distinctly lower total cross sections than corresponding ions with noncyclic structure.[19]

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## CONCLUSIONS

The present work demonstrates the ability of the LVMS to operate as a time-of-flight mass spectrometer at low vacuum and in addition to provide total collision cross sections of ions with a background gas. We have used this instrument to show that a large fraction of the $C_7H_7^+$ ions formed by photofragmentation of p-xylene has a cyclic structure. Without changes in the instrument, the collision cross sections may be determined at various ion kinetic energies.

The low-vacuum instrument presented here offers several advantages: it provides mass information that is not available in IMS while at the same time it enables determination of collision cross sections of ions with various gases. This combination of information is usually difficult to achieve by a simple and inexpensive system that employs a small and inexpensive pumping system (no differentially pumped detection chamber is required with the presently used detector). Inclusion of simpler ionization sources (such as a radioactive source), the small physical size, and the minimal pumping requirements are particularly appealing for field analytical applications and present the attractive possibility of adding mass determination to atmospheric pressure instruments, such as ion mobility spectrometers.