

Examination of Hydroxyl Polycyclic Aromatic Hydrocarbon Isomers Using Time of Flight Mass Spectrometry

Qin Chen*, Juan Suro, Peter B. Kelly

Department of Chemistry, University of California, Davis, Davis ,CA95616, USA

Key Words

Time of flight mass spectrometry
Polycyclic aromatic hydrocarbons
Photochemistry

Introduction

Determination of toxicity and health effects associated with particulate matter requires chemical speciation of the aerosol. Particulate matter formed by combustion processes contain a wide variety of polycyclic aromatic hydrocarbons (PAH) and their derivatives. PAH derivatives, such as nitro-PAHs, have significantly larger biological activity than unsubstituted PAHs. Exposure of the particulate matter to NO_x , SO_x , and photochemical atmospheric processes can produce substituted PAHs. Aromatic sulfonates have been studied as a contaminant in association with municipal waste water.[1] However, little is known about the possible effects of these hydrophilic aromatic sulfonates on the environment or about their degradation in the atmosphere.

Analytical tools for the qualitative and quantitative determination of highly water-soluble aromatic anions at the trace levels in aerosols have not been available. Currently, liquid chromatography is the most commonly used technique for detecting highly polar aromatics. However, liquid chromatographic methods require a large sample size and multiple runs [2][3].

Laser Desorption Ionization Time-of-Flight Mass Spectrometry (LDIMS) has proven to be an effective method for detection of trace levels of polycyclic aromatic hydrocarbons (PAHs) and PAH derivatives [4][5] in airborne particulate matter. This paper discusses the use of LDIMS to examine two naphthalene sulfonate isomers (1-naphthol-4-sulfonic acid and 1-naphthol-3-sulfonic acid) and nitro-naphthanol isomers to study the structural information as well as possible photochemical reactions from the mass spectra.

Experimental

Two isomers: sodium salt of 1-naphthol-4-sulfonic acid (1,4-SNS) and sodium salt of 1-naphthol-3-sulfonic acid (1,3-SNS) were chosen for study. Both were purchased from TCI America (Portland, Oregon) and used without further purification. Each compound (10 mg) was dissolved in 1 ml methanol, and was mixed with 9 ml ethyl acetate. The solution was applied directly to the sample surface (20mm^2) of an aluminum probe and crystallized on the surface after normal air drying.

All the mass spectra were obtained using our custom built time-of-flight mass spectrometer. The sample probe was introduced into the instrument through a fast pump-down load-lock antechamber. Our previous papers provide a detailed description of the instrument [4].

A pulsed ultraviolet laser with the wavelength of 266nm was used for desorption and ionization. The 8 ns duration ionization pulses were produced by attenuating the fourth harmonic of a Spectra-Physics Quanta Ray DCR-3Nd:YAG laser. The laser energy was $\sim 0.8 \times 10^7 \text{W/cm}^2$ at the focus. Each mass spectrum is the sum of fifty-five laser shots at a 5 Hz repetition rate.

The ion source optics are composed of the repeller, the extractor and accelerator plates based on Wiley-McLaren design. Switching the polarity on the ion source plates can produce mass spectra of either positive or negative ions. In the positive ion mode, the potentials on each ion optics are: 7500v on the repeller, 2470v on the extractor, with the

accelerator and flight tube at ground potential. A microchannel plate (MCP) detector is set at the end of the 96 cm flight tube. A fast high-voltage transistor switch (HTS50-06 from Eurotek, Germany) is used to provide a 271 ns delay between the creation of the ions with the laser pulse and the application of the high voltage for extraction of the ions. The delayed extraction of the ions allowed time for prompt decay of metastable ions and yielded improved resolution.

Results and Discussion

The mass spectra of the two isomers given in Fig. 1 have several features in common. In negative mode (Fig. 1a and 1b), both isomers show a molecular peak with mass 246 and $[M-Na]^+$ peak with mass 223. The $[M-SO_3Na]^+$ anion with mass 143 is most intense because the carbon-sulfur bond is easily broken in the ionization process [6].

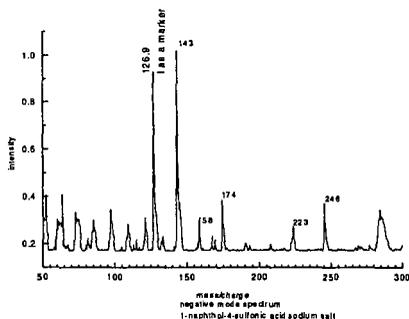


Fig. 1a

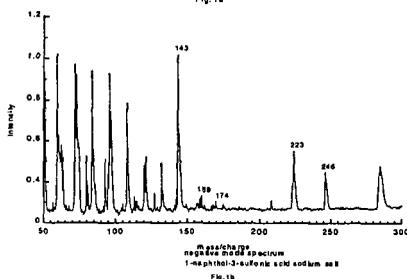
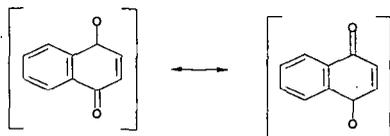
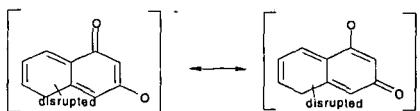


Fig. 1b

On the other hand, the two isomers did exhibit characteristic fragment ions in negative mode. The mass 158 anion is more stable in 1,4-SNS than in 1,3-SNS. The mass 158 anion is assigned as the naphthalene quinone anion, $[M-SO_2Na-H]^+$, following a dissociation path similar to that reported by Binkley et al. [7]. The sulfonate anions can rearrange in the gas phase reaction and form phenoxide ions. The enhanced signal intensity for the 1,4 isomer is driven by the charge delocalization. The 1,3 isomer cannot delocalize the negative charge as effectively.

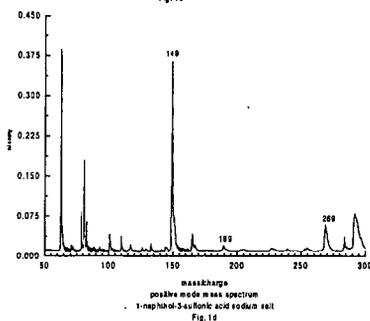
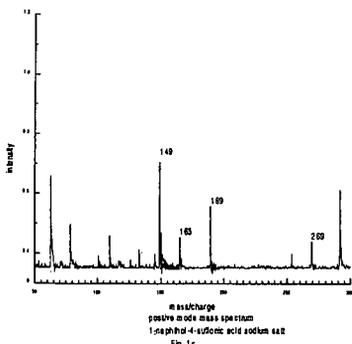


The 1,4-SNS forms quinone structure in which the negative charge is well distributed in the highly conjugated system



In 1,3-SNS the conjugate system is disrupted, therefore, the negative charge can not distribute as well as in 1,4-SNS. Therefore, the 158 anion is more stable in 1,4-SNS than in the 1,3-SNS.

Neither isomer forms a stable molecular positive ion, however diagnostic fragment ions are observed in Fig. 1c and 1d. Several sodium adduct ions are observed. The mass 269 peak, formed by association of Na^+ with the sulfonic acid salt, $[\text{M}+\text{Na}]^+$, is observed for both isomers. The Na^+ cation is the most intense peak due to the high vapor pressure of sodium and the low ionization potential.



The differences in the structure of the two isomers yields a difference in the positive ion spectra as well. The mass 189 cation is more intense in 1,4-SNS than in 1,3-SNS. The observation of Brykov et al. [8] that the 1,4 isomer can photochemically re-arrange in condensed phase or as a dimer pair to produce the 1,2 SNS isomer opens the possibility for a pathway that would produce the 189 cation. The 1,2 SNS isomer can form an epoxide adduct with Na^+ ions of mass 189.

Conclusion

In summary, the study of the 1,4-SNS and 1,3-SNS isomers provide new understanding of the fragmentation of the radical ions formed from hydrocarbon sulfates in gas phase. It demonstrates that slight change of molecular structure can cause differences in ion stability. The fragmentation pathways observed in mass spectrometry suggest that formation of naphthalene sulfonic acid in acidic sulfate aerosol droplets can lead to formation of naphthalene quinones by ultraviolet photochemistry.

Acknowledgment

This work was supported by the NIEHS Superfund Basic Research Grant P42ES-04699 and the California Air Resources Board.

References

- [1] B. Altenbach, W. Giger, *Analytical Chemistry* **1995** (67) 2325-2333
- [2] M. J. Cugat, F. Borrell, M. Calull, *Chromatographia* **1997**(46) 204-208

- [3] L.A. Gundel, J.M. Daisey, D. Schuetzle, *J. Environ. Sci. Technol.* **1993**(27)2112-2119
- [4] D.Z. Bezabeh, T.M. Allen, E.M. Mclauley, P.B. Kelly, A.D. Jones, *Journal of the American Society of Mass Spectrometry*, **1997**, 8(6)630-636
- [5] D.Z. Bezabeh, A.D. Jones, L.L. Ashbaugh, P.B. Kelly *Aerosol Science and Technology* **1999** 30(3)288-299
- [6] B. Zhong, R.W. Binkley, *Journal of Carbohydrate Chemistry* **1998** 17(6) 823-834
- [7] R. W. Binkley, T.W. Flechtner, M.J. Tevesz, W. Winnk, B. Zhong *Organic Mass Spectrometry* **1993**(28) 769-772
- [8] A. Brykov, L. Rikenglz, etc *Journal of Microwave Power and Magnetic Energy* **1999**, 34(2), 73-78
- [9] A. Brykov, L.I. Rikenglaz, I.V. Tselinskii *Journal of Russian Applied Chemistry* **1997** (70) 1855-1860