

Supporting Information

Epoxide Formation from Heterogeneous Oxidation of Benzo[a]pyrene with Gas-phase Ozone and Indoor Air

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Direct Analysis in Real Time-Mass Spectrometry (DART-MS) Analysis of BaP. In order to determine the epoxide yield from BaP/O₃ reaction, the BaP levels before and after high ozone oxidation were quantified using DART-MS. Upon completion of the oxidation experiment, the BaP on the glass tube was extracted with 20 mL of THF. 100 μ L of the extracted solution was diluted into 50 mL DCM for DART-MS analysis. The remaining solution was then derivatized with NAC for the evaluation of epoxide generation. The details of the DART-MS technique employed in the present investigation are described in our earlier publication.¹ Briefly, home-made Teflon capillary holders were used to mount 10 glass melting point capillaries with their bottom ends sealed. 1 μ L of the BaP solution was deposited onto the sealed end of the capillary tube. After the solvent evaporated, the capillary holder was then placed on a motorized linear rail, located between the DART ion source (IonSense Inc., Saugus, MA) and a Vapor Interface (IonSense Inc.), that brought the sample to the MS. The moving speed of the rail was 0.3 mm/s. Helium (3.0 L/min at 500°C) was used in the DART source, and mass spectra were acquired using a JMS-T100LC time-of-flight mass spectrometer (JEOL USA Inc., Peabody, MA) with mass resolution of approximately 6000 at a mass-to-charge ratio (m/z) 600.

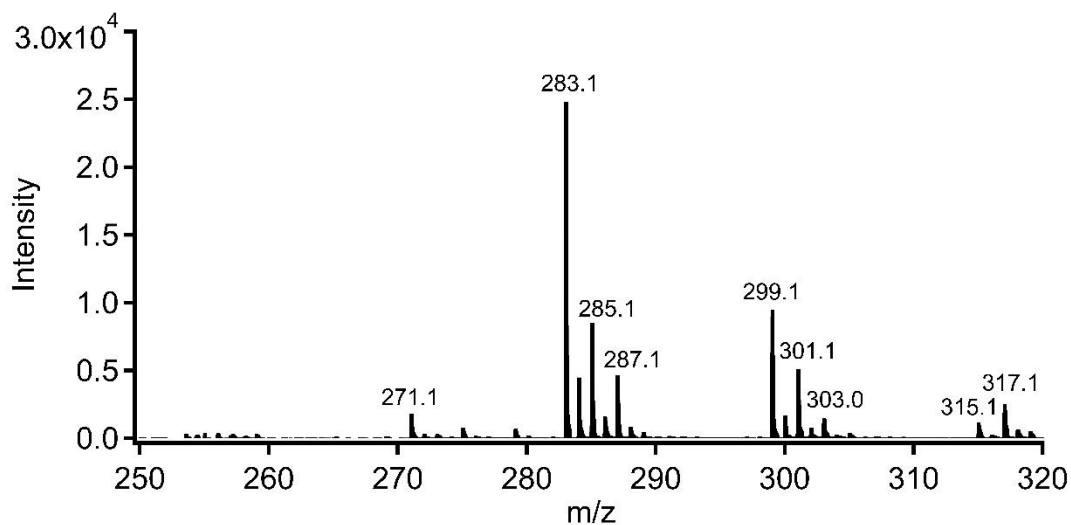
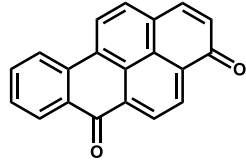
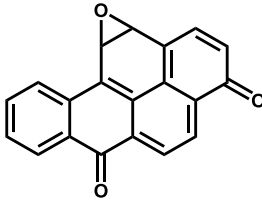
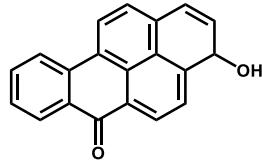
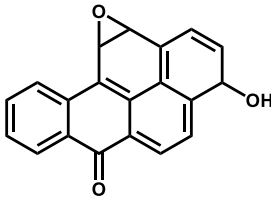
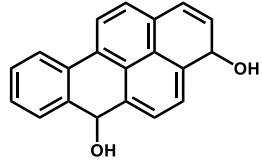
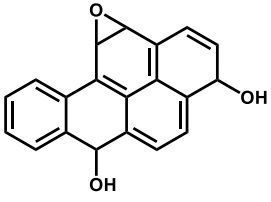
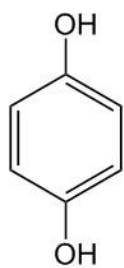


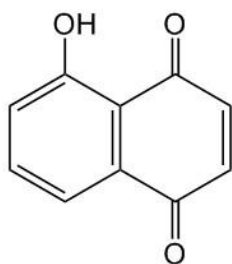
Figure SI-1. Mass spectrum for the products from ozonolysis of BaP

Table SI-1. Possible identities of the products from ozonolysis of BaP obtained by DART-MS

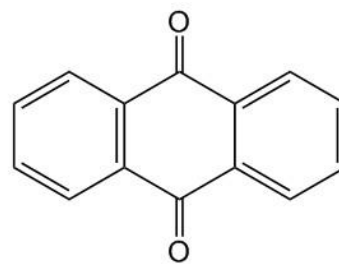
m/z	Identity	m/z	Identity
283	 and isomers	299	 and isomers
285	 and isomers	301	 and isomers
287	 and isomers	303	 and isomers



Benzene-1,4-diol



5-Hydroxy-1,4-naphthalenedione



Anthraquinone

Figure SI-2. Selected products from aromatic hydrocarbons oxidation.

Mass spectrometer parameters

A) MS parameters

Capillary (kV)	1.5
Source Temperature (°C)	150
Desolvation Temperature (°C)	500
Cone gas flow (L/hr)	150
Desolvation gas flow (L/hr)	800
Collision gas flow (mL/min)	0.15
Nebuliser gas flow (Bar)	5.20

B) MS/MS experiment

Compound	Parent (<i>m/z</i>)	Daughter (<i>m/z</i>)	Dwell time (s)	Cone voltage (V)	Collision energy (eV)
NAC-BPDE or NAC-rev BPDE	464	317	0.010	34	8
Mono epoxide	430	283	0.010	34	8

C) Neutral loss scan experiment

Neutral loss	Mass range (<i>m/z</i>)	Scan duration (s)	Collision energy (eV)
147	250 to 650	0.116	20

LC chromatographic separation parameters**i.) Kinetex 2.6 μm C18 100 \AA , 2.1 \times 50 mm,
Phenomenex**Column temperature ($^{\circ}\text{C}$): 40Mobile phase A: 0.1% ammonium hydroxide in Milli-Q H_2O

Mobile phase B: Methanol

Injection volume (μL): 2**LC gradient, total run time 8 min**

Time (min)	Flow rate (mL/min)	%A	%B	Curve
Initial	0.5	90	10	6
0.50	0.5	90	10	6
5.00	0.5	50	50	6
5.50	0.5	50	50	6
5.60	0.5	90	10	6
7.00	0.5	90	10	6

**ii) CSH Fluoro Phenyl, 1.7 μm , 130 \AA , 2.1 \times 50 mm,
Waters**Column temperature ($^{\circ}\text{C}$): 40Mobile phase A: 0.1% Formic acid in Milli-Q H_2O

Mobile phase B: Acetonitrile

Injection volume (μL): 2**LC gradient, total run time 9 min**

Time (min)	Flow rate (mL/min)	%A	%B	Curve
Initial	0.5	90	10	6
0.50	0.5	90	10	6
7.00	0.5	60	40	6
7.10	0.5	10	90	6
7.50	0.5	10	90	6
7.60	0.5	90	10	6
8.00	0.5	90	10	6

References

1. Zhou, S.; Forbes, M.W.; Abbatt, J.P.D. Application of direct analysis in real time-mass spectrometry (DAR-MS) to the study of gas-surface heterogeneous reactions: focus on ozone and PAHs. *Anal. Chem.*, **2015**, *87*, 4733-4740.