



Experimental study of photooxidation products of ethylbenzene

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Abstract

Smog chamber experiments were performed to investigate the composition of products formed from photooxidation of aromatic hydrocarbon ethylbenzene. Vacuum ultraviolet photoionization mass spectrometer and aerosol time-of-flight mass spectrometer were used to measure the products in the gas and particle phases in real-time. Experimental results demonstrated that ethylphenol, methylglyoxal, phenol, benzaldehyde, and 2-ethylfurane were the predominant photooxidation products in both the gas and particle phases. However, there were some differences between detected gas phase products and those of particle phase, for example, 2-ethylfurane, ethylglyoxylic acid, nitroethylbenzene, 3,4-dioxopentanal and ethyl-nitrophenol were only existing in the particle-phase. The possible reaction mechanisms leading to these products were also discussed and proposed.

Key words: ethylbenzene; secondary organic aerosol; smog chamber; desorption/ionization; reaction mechanism

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Introduction

Ethylbenzene is an important constituent of aromatic hydrocarbons, also a harmful environmental pollutant and toxicant in atmosphere (Tanaka and Samukawa, 1996; Trost et al., 1997). Besides its toxicity to humans, conversion of ethylbenzene in the atmosphere can play a significant role in the increase of tropospheric ozone as well as in the formation of secondary organic aerosol (SOA) (Odum et al., 1997; Jang et al., 2002; Atkinson and Arey, 2003; Seinfeld and Pankow, 2003), which are known to be harmful to human health and ecosystem (Annmarie et al., 1993; Pilinis et al., 1995; Schwartz et al., 1996). As emissions of ethylbenzenes are concentrated in urban areas, the formation of SOA becomes an acute problem.

In the past decade, the studies on reaction mechanism and degradation products of photooxidation of ethylbenzene are of particular interest (Ohta and Ohyama, 1985; Forstner et al., 1997; Huang et al., 2007). The gas phase products were collected using cryogenic trapping system or solid phase adsorbent tubes, then samples were flash heated and injected onto the head of the gas chromatograph column. The SOA particles formed from the photooxidation of ethylbenzene were usually collected using filters or impactor plate and samples were prepared using chem-

ical extraction. Molecular composition of SOA particles could be analyzed by gas chromatograph/mass spectrometer (GC-MS) (Forstner et al., 1997; Jang et al., 2004). However, there are some disadvantages in GC/MS, for example, possible secondary chemical reactions or loss of semivolatile compounds associated with traditional aerosol sampling onto a filter or impactor plate, or with multi-step chemical treatments.

From the mid 1990s, real-time laser mass spectrometry has been remarkably developed, offering new opportunities for on-line studying gaseous and particulate matters (Suess and Prather, 1999; Nemet et al., 2004). However, for the high laser intensity required to desorb and ionize the gaseous products, organic ions generated will readily absorb multiple UV photons resulting in massive fragmentation (Gloaguen et al., 2006). Thus, for gaseous products, new “soft” ionization methods necessarily minimize the fragmentation in the mass spectra. As we all know, synchrotron radiation provides vacuum ultraviolet light and soft X-rays which are used for a wide range of analytical techniques (Elder et al., 1947; Codling and Madden, 1965). However, to the best of our knowledge, synchrotron radiation has not been used for detecting the ethylbenzene photooxidation gaseous products. And our laboratory has demonstrated that aerosol time-of-flight mass spectrometry (ATOFMS) can be used to measure the

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size and chemical composition of toluene SOA particles in real-time (Huang et al., 2007). Therefore, in this article, the photooxidation of ethylbenzene was initiated by hydroxyl radical (OH·) in the home-made smog chamber, vacuum ultraviolet photoionization mass spectrometer (PIMS) using synchrotron radiation. ATOFMS were employed to detect the photooxidation products.

1 Experimental method

1.1 Vacuum ultraviolet photoionization mass spectrometry (VUV-PIMS)

The experimental apparatus have been described previously (Wang et al., 2007; Liu et al., 2009). In brief, we performed vacuum ultraviolet photoionization mass spectrometry (VUV-PIMS) measurements on the atomic and molecular physics beamline with the supersonic expansion molecular beam/a reflectron time-of-flight mass spectrometer (RTOFMS) system at National Synchrotron Radiation (NSRL) in Hefei, China. Photon energies in the region of 7.5–22.5 eV with a resolving power of 5000 at 15.9 eV, and a photon flux of 10^{12} photons/sec were selected with a grazing-incidence SGM monochromator employing a grating of 370 grooves/mm and a slit width of 80 μm . For calibration of the photon energies, we used the photoionization spectrum of Ne, N₂, Ar, Kr and Xe.

Figure 1 shows a schematic diagram of the experimental configuration. The gaseous sample was introduced by a supersonic expansion through a continuous beam nozzle with an orifice of 70 μm diameter from the molecular beam chamber into the differential chamber through a $\varnothing 1$ mm skimmer. A secondary skimmer collimates the molecular beam to enter the ionization chamber where the sample molecular beam intersected the monochromatized synchrotron radiation beam at 70 mm from the nozzle. A reflectron time-of-flight mass spectrometer (RTOFMS) was employed for the VUV photoionization/fragmentation studies. The ions were taken out of the photoionization region by a pulse extraction field triggered with a pulse generator (DG 535 SRS, Stanford Research Systems, Inc., Canada) and detected by a microchannel plate (MCP) detector. The ion signal was recorded by a multiscaler P7888 (FAST Comtec., Germany) after it was amplified with preamplifier VT120C (EG&G, ORTEC, Oak Ridge, Tenn., USA).

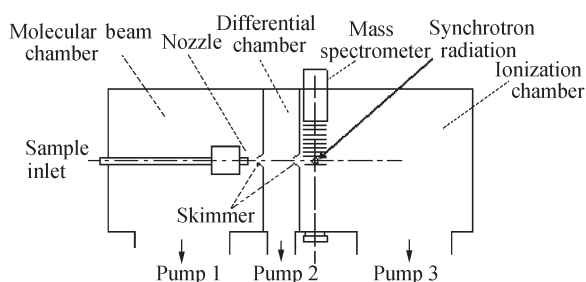


Fig. 1 Schematic of the tunable vacuum ultraviolet photoionization mass spectrometer.

1.2 Aerosol time-of-flight mass spectrometer (ATOOFMS)

Aerosol time-of-flight mass spectrometer includes three distinct regions: (1) an aerosol introduction interface, which includes three adjustable stages of differential pumping; (2) a light scattering region for particle detection and velocity/size determination; and (3) a linear-time-of-flight mass spectrometry for single particle composition analysis (Xia et al., 2004a, b). Figure 2 shows a simplified drawing, highlighting key instrumental features, and provides a reference for a general overview of instrument operation. Particles were introduced into the instrument through a converging nozzle. The nozzle was separated from a skimmer and the region was mechanically pumped to a pressure of 266 Pa. The expansion of molecules in this region accelerated the particles to velocities dependent on their aerodynamic size. A secondary skimmer allows for differential pumping to reach the pressures needed to operate the mass spectrometer and collimates the particle beam by removing particles that do not follow a straight trajectory through the nozzle. Particles then entered a light scattering region where they encountered two red continuous-wave, diode-pumped lasers separated by a known distance. The lasers were positioned perpendicular to one another and orthogonal to the particle beam. For each laser, an arrangement of optics was used to focus the laser beam to a spot that intersects the particle beam. A particle passing through each laser beam scattered light which was collected by an ellipsoidal mirror and focused onto a photomultiplier tube (PMT) detector. The PMTs sent pulses to an electronic timing circuit that measured the time required for the particle to travel the known distance between the two scattering lasers. The distance and the particle time-of-flight were used to calculate the particle velocity. An external size calibration used particles of known size to relate the velocity to a physical aerodynamic diameter. Then the circuit begins a countdown to the time when the particle reaches the center of the ion source region of a mass spectrometer. At this time, the circuit sent a signal to fire a pulsed excimer KrF laser at 248 nm having an average power density of 10^6 W/cm² and a pulse length 2.5 ns. Upon absorption of the laser pulses, the particle was heated in a rapid fashion, desorbing and ionizing individual molecules from the particle. The resulting positive ions were mass analyzed in a linear time-

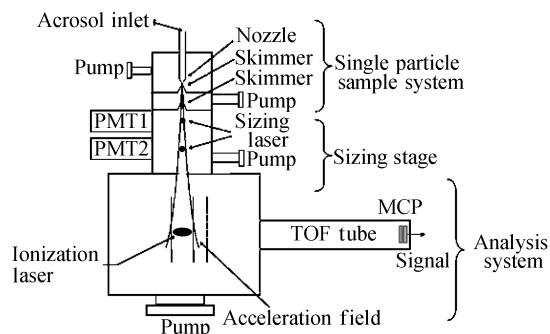


Fig. 2 Schematic of the aerosol time-of-flight (TOF) mass spectrometer. PMT: photomultiplier tube; MCP: microchannel plate.

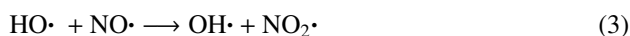
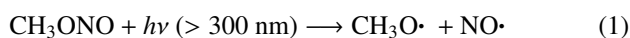
of-flight mass spectrometer. For each particle analyzed, the size was obtained through the particle velocity and the corresponding particle composition was determined through the positive ion mass spectra.

1.3 Smog chamber experiment

Ethylbenzene (> 99%) was obtained from Sigma-Aldrich Chemistry Corporation, Germany. Sodium nitrate (> 99%) and methanol (> 99%) were purchased from The Third Reagent Manufactory (Tianjin, China), and nitrogen oxide (99.9%) from Nanjing Special Gas Factory, China.

Methyl nitrite was synthesized by the dropping sulfuric acid into a methanol solution of sodium nitrate. Their reaction products passed through saturated sodium hydroxide trap to remove the traces of sulfuric acid, and were dried by passing through a calcium sulfate trap and collected using a condenser of liquid nitrogen at 77 K. The methyl nitrite was purified using a vacuum system of glass.

Photooxidation of ethylbenzene was performed using UV-irradiation of ethylbenzene/CH₃ONO/NO/air mixtures in our home-made smog chamber (Hao et al., 2005). Prior to start each experiment, the chamber was continuously flushed with purified laboratory compressed air for 20 min, and evaluated to a vacuum of 10⁻¹ Pa by a mechanical pump. The compressed air was processed through three consecutive packed-bed scrubbers containing, in order, activated charcoal, silica gel and a Balston DFU[®] filter (Grade BX), to remove the trace of hydrocarbon compounds, moisture and particles. Ethylbenzene was sampled by a micro liter injector and injected directly into the chamber. NO and methyl nitrite were expanded into the evacuated manifold to the desired pressure through Teflon lines, and introduced into the smog chamber by a stream of purified air. The whole system was completely shrouded from light with a black polyethylene tarpaulin. Hydroxyl radicals were generated by the photolysis of methyl nitrite in air at wavelengths longer than 300 nm (Atkinson et al., 1981). The chemical reactions leading to the formation of the OH• radical are as follows:



The initial concentration of ethylbenzene, CH₃ONO and NO was 10, 100 and 20 ppm, respectively, at the end of reaction. The products produced by the photooxidation were analyzed by the VUV-PIMS and ATOFMS connected directly to the chamber using a Teflon line.

2 Results and discussion

2.1 Photoionization of gaseous products

The photoionization mass spectrum of air and gaseous mixture before the photooxidation of ethylbenzene at the wavelength of 72.9 nm is shown in Fig. 3a. It is known to all that, air is made up of oxygen, nitrogen, and few water vapor, therefore, it is not surprised that, the photoionization mass spectrum of air contains the mass peak *m/z* 18, 28,

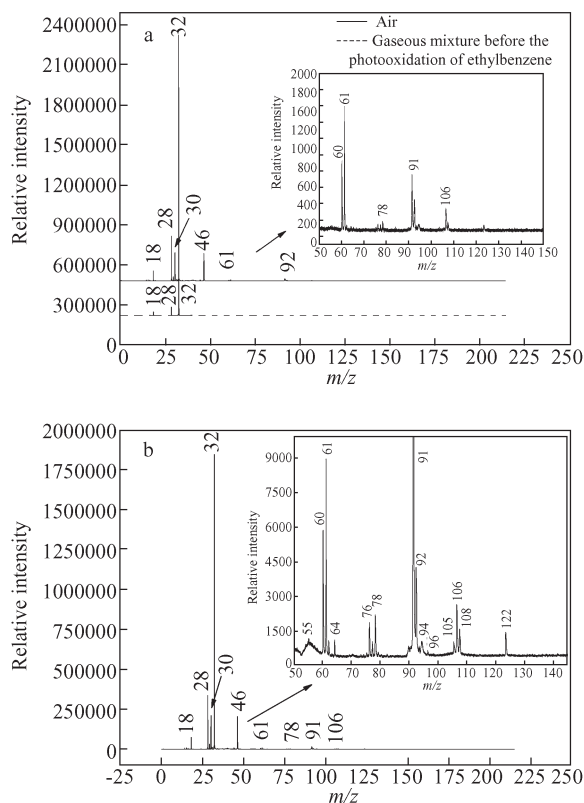


Fig. 3 Photoionization mass spectra of the photooxidation of ethylbenzene at the wavelength of 72.9 nm. (a) mass spectra of air and gaseous mixture before the photooxidation; (b) mass spectra of gaseous products formed from photooxidation.

and 32. Compared with the photoionization mass spectrum of air, the photoionization mass spectrum of the gaseous mixture before the photooxidation of ethylbenzene, adds the mass peaks including *m/z* 30 as the reagent NO, *m/z* 46 as NO₂, *m/z* 61 as methyl nitrate (CH₃ONO), *m/z* 106 as ethylbenzene, and *m/z* 78 and 91 as the fragment ion of ethylbenzene (benzene ion and benzylium ion). Therefore, no product was formed before the photooxidation.

Photoionization mass spectra of gaseous products formed from photooxidation of ethylbenzene at the wavelength of 72.9 nm is shown in Fig. 3b. Compared with the photoionization mass spectrum of gaseous mixture before the photooxidation of ethylbenzene, photoionization mass spectra of gaseous products adds the mass peaks *m/z* 55, 64, 76, 72, 94, 96, and 122, which means that some products are formed after the photooxidation. Each ratio of mass to charge corresponds to a different compound molecule. Table 1 lists the *m/z*, and molecular structures of speculated products from photooxidation of ethylbenzene.

Table 1 Molecular structures of speculated gaseous products from photooxidation of ethylbenzene

<i>m/z</i>	Products	Formula	Ref. and comment
72	Methylglyoxal	CH ₃ COCHO	Tentatively identified
94	Phenol	C ₆ H ₅ OH	Forstner et al., 1997
96	2-Ethylfuran	C ₄ H ₃ OCH ₂ CH ₃	Tentatively identified
106	Benzaldehyde	C ₆ H ₅ CHO	Forstner et al., 1997
122	Ethylphenol	C ₈ H ₉ OH	Forstner et al., 1997

However, m/z 55, 60 and 64 represent some unidentified compounds. From our experimental results and discussion mentioned above, it is shown that in these molecules and radicals detected using PIMS, some of them are produced from H-atom abstraction of the ethyl group of ethylbenzene and others from OH addition to the benzene ring in the ethylbenzene reaction. The chemical compositions identified in gas phase can also be divided into aromatic ring-retaining products (benzaldehyde and phenol), non-aromatic ring-reserved products (2-furaldehyde), and ring-opening carbonyl products (methyl glyoxal).

2.2 Laser desorption/ionization (LDI) mass spectra of ethylbenzene SOA particles

According to the design principles on the measuring system of particle diameter, timing circuit, and laser desorption/ionization setup of ATOFMS, its time of flight mass spectroscopy is only obtained from those particles of secondary organic aerosol, whose diameter has been measured. The positive laser desorption/ionization mass spectra of SOA particles are shown in Fig. 4. It can be seen that each piece of mass spectrum corresponds to an aerosol particle, and the diameter and chemical composition might be different from each other.

The software that was compiled in Visual C++ was developed by our laboratory. Using this software, we can get the total number (N_0) of mass spectra of the experiment of ethylbenzene. Additionally, the number (n) of mass

spectra including a defined ratio of m/z can be picked out the total number (N_0) of mass spectra. The ratio of n to N_0 is defined as η ($\eta = n/N_0$). For example, $N_0 = 1650$, and $n = 281$ for mass spectra including $m/z = 94$, $\eta = 17\%$. Table 2 lists main mass spectra peaks, possible fragment ions, and the molecular structures of speculated products from photooxidation of ethylbenzene.

Photochemical oxidation of ethylbenzene is mainly initiated by hydroxyl radicals $\text{OH}\cdot$. The OH-ethylbenzene reaction results in the minor H-atom abstraction from the ethyl group and major OH addition to the aromatic ring (about 90%) (Atkinson and Arey, 2003). Under atmospheric conditions, the OH-ethylbenzene adduct reacts with O_2 to form the oxygenated organic compounds or NO_x to yield nitrated organic compounds. These photooxidation products can also be divided into semivolatile organic compounds (ethylphenol, methylglyoxal, phenol, 2-furaldehyde), and nonvolatile organic compounds (ethylglyoxylic acid, nitroethylbenzene, and ethyl-nitrophenol). Nonvolatile organic compounds have very low vapor, and can only exist in the particle phase (Table 2). Semivolatile organic compounds can result in SOA formation through the self-nucleation process or the gas/particle partitioning on preexisting particulate matter (Odum et al., 1997). Therefore, it is not surprised to find that ethylphenol, methylglyoxal, phenol, benzaldehyde, and 2-ethylfuran are the predominant photooxidation products in both the gas and particle phases.

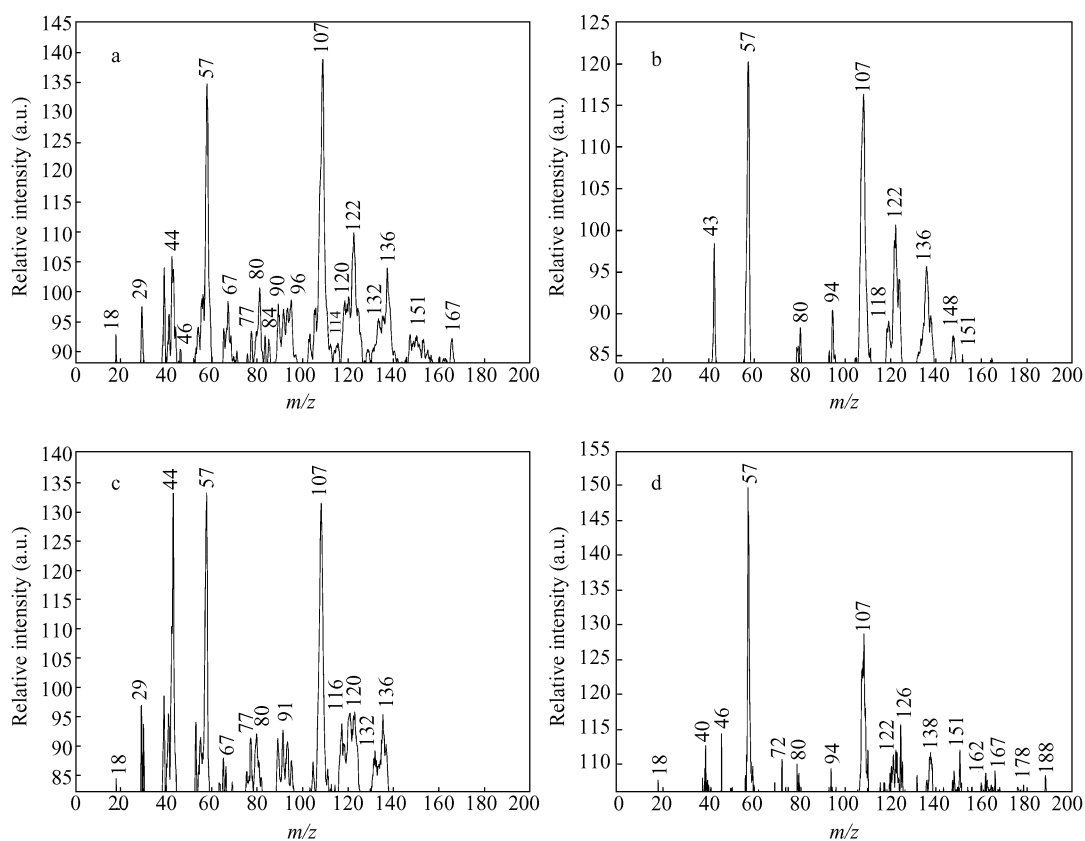


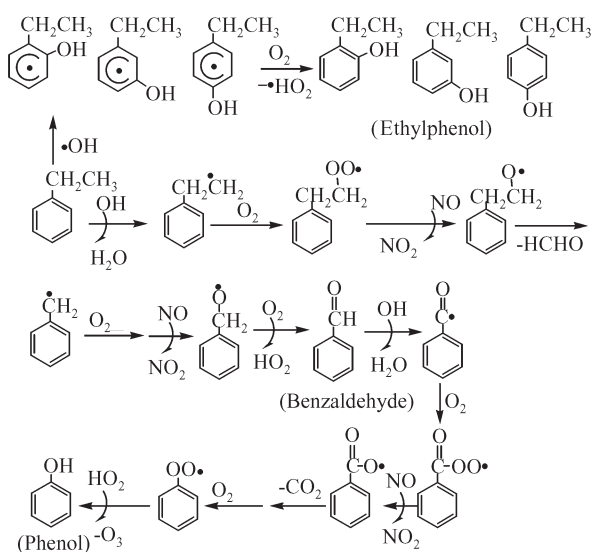
Fig. 4 Laser desorption/ionization time-of-flight mass spectra and size of four individual xylene SOA particles after two hours photooxidation. Aerosol diameter: (a) 0.72 μm ; (b) 1.16 μm ; (c) 2.03 μm ; (d) 1.84 μm .

Table 2 Molecular structures of identified SOA products from photooxidation of ethylbenzene

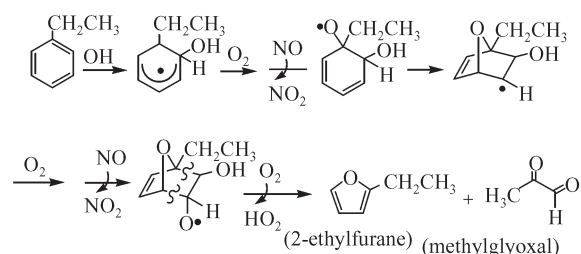
Observed M. ⁺ (<i>m/z</i>)	η (%)	Possible fragment ions (<i>m/z</i>)	Products	Formula
72	25	HCOCO ⁺ (57)	Methylglyoxal	CH ₃ COCHO
94	17	C ₆ H ₅ ⁺ (77)	Phenol	C ₆ H ₅ OH
96	6	C ₄ H ₃ O ⁺ (67)	2-Ethylfuran	C ₄ H ₃ OCH ₂ CH ₃
102	10	H ₂ O ⁺ (18), CO ₂ ⁺ (44) CH ₃ CH ₂ O ⁺ (57)	Ethylglyoxylic acid	CH ₃ CH ₂ COCOOH
106	14	HCO ⁺ (29), C ₆ H ₅ ⁺ (77)	Benzaldehyde	C ₆ H ₅ CHO
114	15	HCOCO ⁺ (57)	3,4-Dioxopentanal	CH ₃ CH ₂ COCOCOH
122	16	C ₆ H ₅ ⁺ (77)	Ethylphenol	C ₈ H ₉ OH
151	7	NO ₂ ⁺ (46), C ₆ H ₅ ⁺ (77)	Nitroethylbenzene	C ₈ H ₉ NO ₂
167	5	NO ₂ ⁺ (46), C ₆ H ₅ ⁺ (77)	Ethyl-nitrophenol	C ₈ H ₈ OHNO ₂

Possible mechanisms leading to the ethylbenzene photooxidation products are depicted in Figs. 5 and 6. As well as toluene, the OH initiated photooxidation reaction of ethylbenzene is depicted in Fig. 6, illustrating the abstraction/addition pathway. OH abstracts a hydrogen atom from the methyl group, and the oxygen molecule adds to the radical. This peroxy radical can react with NO to form an alkoxy radical and NO₂ (Forstner et al., 1997). This alkoxy radical can crack to form formaldehyde and benzyl radical. Benzyl radical may react with O₂ to benzyl peroxy radical, which can react with NO to form an alkoxy radical and NO₂. Oxygen can abstract a hydrogen atom from the alkoxy radical to form benzaldehyde, which can further be reacted to form benzoic acid and phenol and to propagate the radical chain reaction. Figure 6 also outlines this suggested mechanism leading to phenol.

Similar to toluene-OH adduct reactions, the addition of OH to the ring results in ethyl hydroxycyclohexadienyl radicals, a path estimated to be 90% of the OH-ethylbenzene reaction. Most products in ethylbenzene photooxidation result in subsequent reactions of the ethyl hydroxycyclohexadienyl radical, comprising both ring-retaining species and ring-fragmentation species. As shown in Fig. 5, OH can add to ethylbenzene in the ortho, meta, and para positions, with the ortho position energetically favored. The ethyl hydroxycyclohexadienyl radicals

**Fig. 5** Proposed reaction mechanisms leading to the formation of aromatic retaining products.

may react with O₂ to form three different ethylphenol (Forstner et al., 1997). And ortho ethyl hydroxycyclohexadienyl radical through reaction with O₂ and NO, leading to the formation of alkoxy radicals (Jang and Kamens, 2001). Methylglyoxal, 2-ethylfuran and 2-furaldehyde can be produced via a bridged oxide intermediate on a bicyclic intermediate from alkoxy radicals, as shown in Fig. 6.

**Fig. 6** Proposed reaction mechanisms leading to the formation of nonaromatic retaining products.

3 Conclusions

A laboratory study was carried out to investigate the gaseous and particulate products from photooxidation of ethylbenzene in the smog chamber. The vacuum ultraviolet photoionization mass spectrometer using synchrotron radiation and aerosol time of flight mass spectrometer were employed to simultaneously detect the composition of the gaseous and particulate products, respectively. Ethylphenol, methylglyoxal, phenol, benzaldehyde, and 2-ethylfuran are the predominant photooxidation products in both the gas and particle phases. This will provide new information for discussing ethylbenzene photooxidation reaction mechanism.

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