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# Chemical analysis of aged benzene secondary organic aerosol using aerosol laser time-of-flight mass spectrometer

**Mingqiang Huang · Yuehong Lin · Xianying Huang · Xingqiang Liu · Changjin Hu · Xuejun Gu · Weixiong Zhao · Li Fang · Weijun Zhang**

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**Abstract** Secondary organic aerosol (SOA) from the photooxidation of aromatic compounds is a very complex mixture containing products with a different chemical nature that are dependent on aging processes. Aging of SOA particles formed from OH-initiated oxidation of benzene was investigated in a home-made smog chamber in this study. The chemical composition of aged benzene SOA particles were measured using aerosol laser time-of-flight mass spectrometer (ALTOFMS) coupled with Fuzzy C-Means (FCM) clustering algorithm. Experimental results showed that nitrophenol, dinitrophenol, nitrocatechol, dinitrocatechol, 6-oxo-2,4-hexadienoic acid, 2,4-hexadiendioic acid, 2,3-dihydroxy-6-oxo-4-hexenoic acid, 2,3-epoxy-4-hexendioic acid, 2,3-epoxy-4,5-dihydroxy-hexanedioic acid and high-molecular-weight (HMW) components were the predominant products in the aged particles. Compared to offline method such as liquid chromatography mass spectrometry (LC-MS) measurement, the real-time ALTOFMS detection approach coupled with the FCM data processing algorithm can make cluster analysis of SOA successfully and provide more information of products. The present results also indicate that benzene SOA aging proceeds through the oxidation of the internal double bond of ring-opened products, phenolic compounds, and acid-catalyzed heterogeneous reactions of carbonyl products. The possible reaction mechanisms leading to these aged products were also discussed and proposed.

**Keywords** Benzene · Secondary organic aerosols · Laser desorption/ionization · Fuzzy clustering (FCM) algorithm · Aging mechanism

M. Huang · Y. Lin · X. Huang
College of Chemistry & Environment, Minnan Normal University, Zhangzhou 363000, China

M. Huang · X. Liu
Department of Environmental Science and Engineering, Tan Kah Kee College, Xiamen University, Zhangzhou 363105, China

C. Hu · X. Gu · W. Zhao · L. Fang · W. Zhang (✉)
Laboratory of Atmospheric Physico-Chemistry, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031, China
e-mail: wjzhang@aiofm.ac.cn

## 1 Introduction

Benzene is the simplest aromatic compound and is released into the atmosphere by human activities (Li et al. 2014). Besides the toxicity to humans, conversion of benzene in the atmosphere can play a significant role in the formation of secondary organic aerosol (SOA) (Martín-Reviejo and Wirtz 2005; Borrása and Tortajada-Genarob 2012; Wang et al. 2013), which are known to be harmful to human health and ecosystem (Russell and Brunekeef 2009; Baltensperger 2010; Wang et al. 2012; Tiwari et al. 2014). As shown by the previous studies that the SOA formation from the gas-phase oxidation of benzene tends to take place in the first few hours after emission, SOA can continue to age chemically over its atmospheric lifetime (Rudich et al. 2007; Andreae 2009). Not only the chemical composition changes as SOA ages, but also the physical and chemical properties of aerosol particles such as the volatility, hygroscopicity, toxicity, and the optical properties will change (Tritscher et al. 2011; Sareen et al. 2013).

Limited information is available on the oxidation processes that form the molecular basis of aromatic SOA aging processes. Loza et al. (2012) carried out long-photoirradiation (about 36 h) laboratory chamber experiments to investigate the photooxidation of m-xylene, and reported the rate of increase of the O/C ratio to be 0.0012 $h^{-1}$ during SOA aging. Recently, Sato et al. (2012) measured the chemical structure of aged SOA from the photooxidation of benzene and 1,3,5-trimethylbenzene in the presence of $NO_x$ using liquid chromatography/time-of-flight mass spectrometry (LC/TOF-MS), and observed aged products such as nitrophenol, caroboxylic acid and oxocarboxylic acids. However, for the LC/TOF-MS measurements sampling with Teflon membrane filter followed by extraction with methanol is therefore necessary. It is labor intensive and prone to artifacts.

We have measured SOA formed from the photooxidation of aromatic compounds using aerosol laser time-of-flight mass spectrometer (ALTOFMS) and reported that ALTOFMS is a useful tool to reveal the formation and transformation processes of SOA particles (Huang et al. 2007, 2013a). Very recently, Fuzzy C-Means (FCM) algorithm to classify the mass spectra of large numbers of SOA particles obtained by ALTOFMS have been developed by our group (Huang et al. 2013b). In this study, we focus on the chemical characterization of major products that are formed upon formation of benzene SOA and subsequent aging through OH-initiated reactions in the presence of $NO_x$. The use of ALTOFMS offers the advantage in that it allows the detection of the size and chemical composition of aged SOA in real-time, whereas the use of FCM algorithm is suitable for extracting out potential aerosol classes. The spectra patterns of aged SOA particles determined by FCM are interpreted in detail and tentative structures for them are proposed taking into account that they are formed through photooxidation of benzene. Also, the possible reaction mechanisms leading to these aged products were also proposed.

## 2 Experimental

### 2.1 Smog chamber experiment of benzene SOA aging

Aging of benzene SOA was performed using UV-irradiation of benzene/$CH_3ONO$/NO/ air mixtures in an 850 L sealed collapsible polyethylene smog chamber (Huang et al. 2013a). After chamber purification, 2.0 μL/L benzene, 20.0 μL/L $CH_3ONO$, 2.0 μL/L NO were injected into the chamber, mixed with the pre-existing purified air. Then the chamber was filled with the purified air to 850 L full volume. 4 Black lamps were turned on and the

photooxidation reaction was initiated. OH radicals were generated by the photolysis of $CH_3ONO$ in air at wavelengths longer than 300 nm (Atkinson et al. 1981). The time series of the OH concentration was estimated assuming that aromatic hydrocarbon decreased by the reaction with OH radicals, where the rate constants used for calculations were taken from Aschmann et al. (2006). In the experiment, the OH concentration reached a maximum immediately after the start of irradiation and then decreased with time, but the OH concentration maintained $>5\times10^5$ molecules $cm^{-3}$ during irradiation. This indicates that particles and vapors in the reaction chamber were continuously oxidized during irradiation. After 24 h photooxidation, the aged benzene SOA particles are analyzed continuously using the ALTOFMS connected directly to the chamber using a Teflon line.

## 2.2 Aerosol laser time–of–flight mass spectrometer (ALTOFMS)

The ALTOFMS setup has been described in detail previously (Huang et al. 2007, 2013b). Particles are introduced into the instrument through the aerodynamic lens and undergo a supersonic expansion. The particles are accelerated to a terminal velocity that is proportional to their diameter. The particles then enter a sizing region where they pass through two continuous wave laser beams. After being sized, the particle travels to the ion source region of a time-of-flight mass spectrometer. Chemical species in the particle are desorbed/ionized, using the pulsed output from an ultraviolet laser, and separated and detected using a time-of-flight mass spectrometer equipped with multichannel plate (MCP) for ion detection.

Each mass spectrum contains 4096 data points, corresponding to ion signal intensity. The particle mass spectra are calibrated using software which was developed by our laboratory and compiled in Visual C++. A list containing the area and exact mass-to-charge ratio of all peaks in each particle mass spectrum is generated. Peaks less than 10 arbitrary units above the baseline on a 256-unit scale or with areas of less than 30 arbitrary units are rejected (Guo et al. 2008). Each revised spectrum is then converted to a normalized 300-point vector, each point representing one mass unit. Then the positive ion mass spectra of a single particle are described as 300-dimensional data vectors using the ion masses as dimensions and the ion signal peak areas as values. The data vectors of all particles measured are written into a classification matrix. Each spectrums data is stored as one row in this matrix.

## 2.3 Fuzzy c-means algorithm (FCM) clustering criteria

The method for clustering the data matrix is based on the Fuzzy c-means algorithm (FCM) (Bezdek 1981). The preprocessing algorithm is coded and compiled in Visual C++ and then linked with the data acquisition software. The FCM is an iterative method starting the calculation with random class centers to find a substructure in the data. The procedure works in such a way that finally similar objects (particle spectra) have a minimum distance between their corresponding data vectors. Basically, FCM calculates fuzzy partition matrix to group some of the data points into k clusters. And the membership coefficients $u_{ik}$ of each particle $i$ to each class center $k$ are determined. The class centers and membership coefficients provide for a detailed characterization of all the measured particles. Each class center can be represented as "mean" mass spectra pattern. This provides for the characterization of the mean chemical composition of the particle class.

The important problem accompanying the application of the Fuzzy c-means algorithm is the choice for the optimum cluster number (Hinz et al. 1999). The first step in determination of this optimum cluster number is to estimate an upper limit of the number of clusters, $C$max. Classification vectors for cluster numbers between 2 and $C$max are computed by the FCM

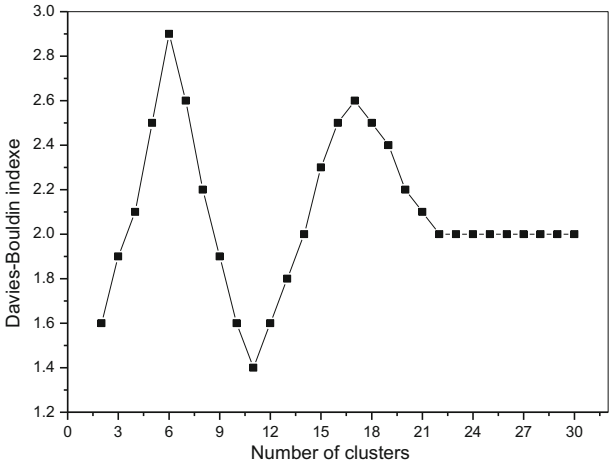


**Fig. 1** The clustering number was evaluated using Davies-Bouldin index for aged benzene SOA particles

method as described above. To select the optimum cluster number among different partitions, each of these can be evaluated using Davies–Bouldin (DB) index. It is defined as:

$$DB = \frac{1}{n}\sum_{i=1,j\neq i}^{n} \max\left\{\frac{\sigma i + \sigma j}{d(c_i, c_j)}\right\}$$

where n is the number of clusters, $\sigma_i$ is the average distance of all patterns in cluster i to their respective cluster center $c_i$, $\sigma_j$ is the average distance of all patterns in cluster j to their respective cluster center $c_j$, and $d(c_i,c_j)$ is the distance of cluster centers $c_i$ and $c_j$. Small values of DB correspond to clusters that are compact, and whose centers are far away from each other. Consequently, the number of clusters that minimizes DB is taken as the optimal number of clusters.

## 3 Results and discussion

### 3.1 Classification of aged benzene SOA particles spectra

According to the design principles on the measuring system of particle size, timing circuit, and laser desorption/ionization setup of ALTOFMS, the particle's mass spectrum is only acquired from the one whose diameter has been measured (Huang et al. 2007, 2013b). For the fuzzy cluster analysis of 5217 pieces of single particle mass spectra of aged SOA particles, we set the FCM initial clustering number (n) from 2 to 30, fuzzy degrees parameter (m) to 2, the biggest cycles for 500, and the precision of the clustering to 0.1. Clustering is first started with the investigation of the smallest quantitative variance for the classification result at different initial n. Then the classification result is used to calculate the Davies-Bouldin index. The clustering number leading to the smallest Davies-Bouldin index is the best cluster solution. Figure 1 shows different Davies-Bouldin indexes when n changes from 2 to 30. The Davies-Bouldin index has the minimum value at $n=11$, suggesting the aged SOA particles can be clustered into 11 classes. The spectra patterns determined as the cluster centers of these eleven classes are shown in Fig. 2. The patterns are displayed in analogy to real time-of-flight mass spectra as

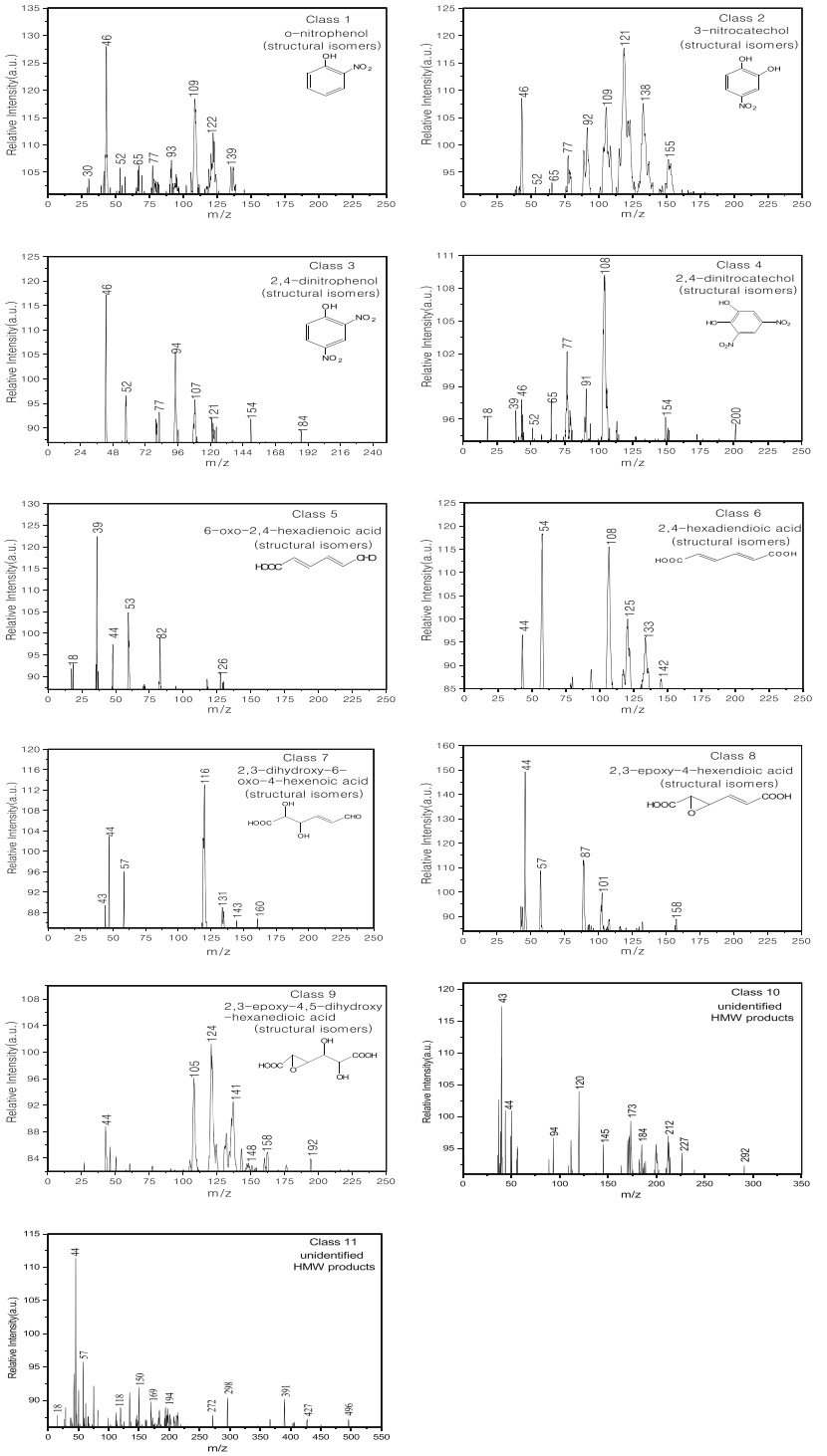


**Fig. 2** Representative spectra patterns of aged benzene SOA particles determined by FCM

positive ion "signals", with the signal intensities representing the vector components of the cluster center, which are similar to the mass spectra of aromatic SOA particles shown in our previous study (Huang et al. 2007; 2013b).

### 3.2 Chemical composition and mechanism of aged benzene SOA particles

The first to fourth class represented molecules with benzene ion at m/z 77 ($C_6H_5^+$), and the fragments at m/z 65 ($C_5H_5^+$), 52 ($C_4H_4^+$), 39 ($C_3H_3^+$), and thereby were identified as aromatic ring retaining products (Silva and Prather 2000). Also, these classes showed the characteristic cleavage fragments at m/z 46 ($NO_2^+$), and was tentatively considered as nitrogenated organic compound (Alfarra et al. 2006). The first class was identified as o-nitrophenol (or other structural isomers), where we observed a parent mass at m/z 139 ($C_6H_5NO_3^+$), and three separate ions at m/z 122($C_6H_3NO_2^+$), m/z 109($C_6H_5O_2^+$) and m/z 93($C_6H_5O^+$) (Sato et al. 2012). The second class was observed to have parent mass at m/z 155 ($C_6H_5NO_4^+$), and fragment ions at m/z 138 ($C_6H_4NO_3^+$), m/z 121 ($C_6H_3NO_2^+$), m/z 109 ($C_6H_5O_2^+$), and m/z 92 ($C_6H_4O^+$). It was tentatively identified as 3-nitrocatechol (or other structural isomers) (Sato et al. 2012). The third class represented particle with the maximum m/z 184 ($C_6H_4N_2O_5^+$), accompanied by m/z 154 ($C_6H_4NO_4^+$), m/z 121 ($C_6H_3NO_2^+$), m/z 107 ($C_6H_3O_2^+$), m/z 92 ($C_6H_4O^+$) mass peaks, so it was classified to be 2,4-dinitrophenol (or other structural isomers). An analysis to the fourth class observes the relative intensities of the parent mass m/z 200 ($C_6H_4N_2O_6^+$), and three ion signals of m/z 154 ($C_6H_4NO_4^+$), m/z 108 ($C_6H_4O_2^+$) and m/z 91($C_6H_3O^+$). A tentative identification of this compound was 2,4-dinitrocatechol (or other structural isomers) (Sato et al. 2012).

The formation of the first-generation oxidation of phenol has already been reported in a number of benzene chamber studies (Martín-Reviejo and Wirtz 2005; Borrása and Tortajada-Genarob 2012; Wang et al. 2013). As proposed by Henry and Donahue (2012), SOA aging includes OH-radical oxidation of the first-generation oxidation products. As proposed by Atkinson and Arey (2003), OH-phenol reaction results in H-atom abstraction from the hydroxyl group and OH addition to the aromatic ring which are depicted in Fig. 3. The phenoxy radical formed from abstraction pathway can then react with $NO_2$ to form a variety of nitro phenolic compounds. The positions of the alkoxy radical determines where $NO_2$ adds to the ring. OR group on an aromatic ring are ortho- and para-directing, with OR more strongly activating. Hence, $NO_2$ adds ortho and para to the oxygen in the phenoxy radical. This step leading to o-nitrophenol is outlined in Fig. 3, with these identified aged benzene SOA products boxed. Also shown in Fig. 3 are further reactions of o-nitrophenol with OH and $NO_2$ to yield 2,4-dinitrophenol, another species detected in aged benzene SOA. OH adds to phenol in the ortho, meta, and para positions, with the ortho position energetically favored (Atkinson and Arey 2003). Oxygen can abstract a hydrogen atom from the ortho phenol-OH adduct to form catechol. Similar to phenol reactions, OH can react with the catechol to abstract an H-atom from the hydroxyl group to form hydroxyl phenoxy radical. This radical can then react with $NO_2$ to form 3-nitrocatechol and 2,4-dinitrocatechol as shown in Fig. 3.

The fifth class represented particle with strong ion signal of m/z 44 ($CO_2^+$), accompanied by m/z 18 ($H_2O^+$) mass peak and was identified as organic acid (Alfarra et al. 2006). Also, this class presented the parent ion at m/z 126 ($C_6H_6O_3^+$), characteristic cleavage fragments at m/z 82 ($C_5H_6O^+$), m/z 53 ($C_4H_5^+$) and m/z 39 ($C_3H_3^+$), so it was classified to be 6-oxo-2,4-hexadienoic acid (or other structural isomers) (Sato et al. 2012). The sixth class displayed the parent mass at m/z 142 ($C_6H_6O_4^+$), and fragment ions at m/z 125 ($C_6H_5O_3^+$), m/z 108 ($C_6H_4O_2^+$), m/z 54 ($C_4H_6^+$), and m/z 44 ($CO_2^+$). It was tentatively identified as 2,4-hexadiendioic acid (or other structural isomers) (Sato et al. 2012). The seventh class was

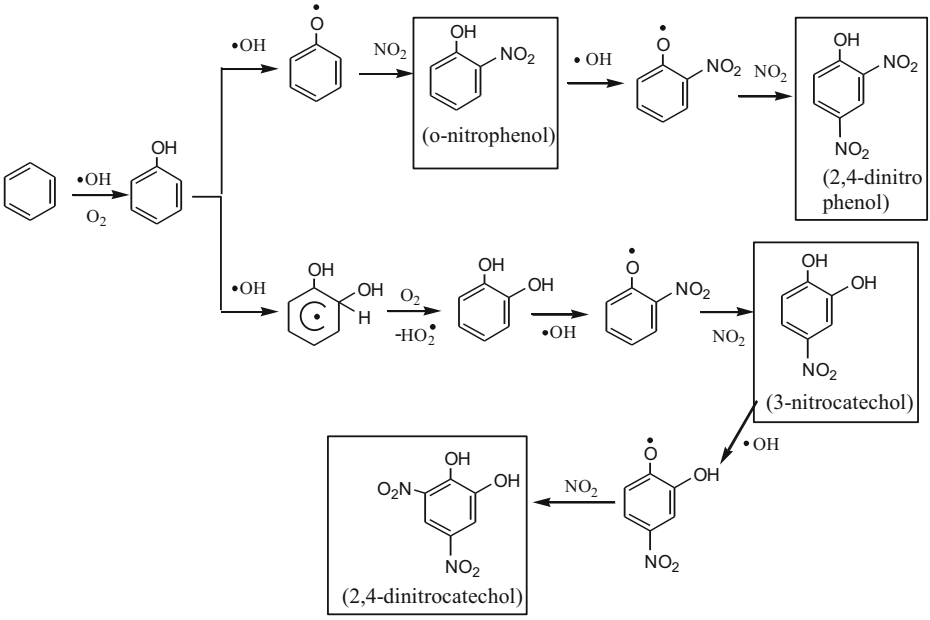


**Fig. 3** Proposed aging mechanism leading to the formation of nitrogenated organic compounds

identified as 2,3-dihydroxy-6-oxo-4-hexenoic acid (or other structural isomers), as we observed a parent mass at m/z 160 ($C_6H_8O_5^+$), and five separate ions at m/z 44($CO_2^+$), m/z 90($C_3O_3H_6^+$), m/z 102($C_4O_3H_6^+$), m/z 118($C_4O_4H_6^+$) and m/z 154($C_7O_4H_6^+$) (Sato et al. 2012).

The major fraction of total benzene SOA mass is believed to comprise ring-opened products from aromatic hydrocarbons. Dialdehydes, like 6-oxo-2,4-hexadienal is produced as ring-opened products from the reaction of benzene with OH radicals (Martín-Reviejo and Wirtz 2005; Borrása and Tortajada-Genarob 2012; Wang et al. 2013). OH abstracts a hydrogen atom from the carbonyl group, and oxygen adds to the radical. This peroxy radical can react with $HO_2$ (or $RO_2$) to form the 6-oxo-2,4-hexadienoic acid directly, or it can react with NO to form an alkoxy radical and $NO_2$. As shown in Fig. 4, this alkoxy radical can abstract a hydrogen from another aldehyde molecule to yield the 6-oxo-2,4-hexadienoic acid and to propagate the aging reaction (Forstner et al. 1997; Sato et al. 2012). 6-oxo-2,4-hexadienoic acid may undergo the following OH-radical oxidation shown in Fig. 4 to produce 2,4-hexadiendioic acid, or reacts with OH-radical, $O_2$ and NO to form $NO_2$ and 2,3- dihydroxy-6-oxo-4-hexenoic acid.

The eighth class was observed to have parent mass at m/z 158 ($C_6H_6O_5^+$), and fragment ions at m/z 101 ($C_4H_4O_3^+$), m/z 87 ($C_3H_3O_3^+$), m/z 58 ($C_2HO_2^+$) and m/z 44 ($CO_2^+$). It was tentatively identified as 2,3-epoxy-4-hexendioic acid (or other structural isomers) (Sato et al. 2012). The ninth class has a parent mass m/z 192 ($C_6H_8O_7^+$) and five ions m/z 158 ($C_6H_6O_5^+$), m/z 148($C_5H_8O_5^+$), m/z 141($C_6H_5O_4^+$), m/z 124 ($C_6H_4O_3^+$) and m/z 105 ($C_3H_5O_4^+$). A tentative identification of this compound was 2,3-epoxy- 4,5-dihydroxy-hexanedioic acid (or other structural isomers) (Sato et al. 2012). Epoxide product, like 2,3-epoxy-6-oxo-4-hexenal has already been detected in benzene chamber study by Yu and Jeffries (1997). Similar to dialdehydes, epoxide products can undergo subsequent aging by OH radicals shown in Fig. 5 to form oxocarboxylic acids, 2,3-epoxy-4-hexendioic acid. Oxocarboxylic acids may continue

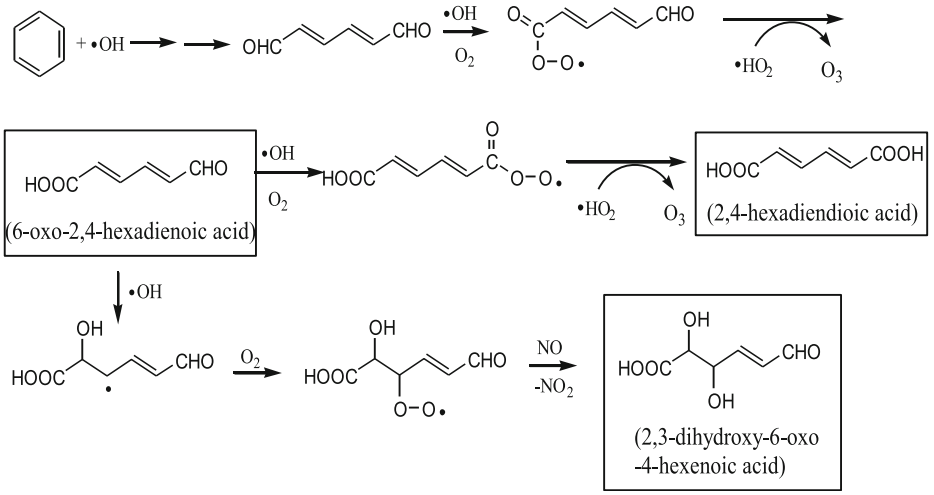


**Fig. 4** Proposed aging mechanism leading to the formation of oxocarboxylic acid products

to react with OH-radical, $O_2$ and $HO_2$-radical to form ozone and 2,3-epoxy-4,5-dihydroxy-hexanedioic acid as shown in Fig. 5.

As proposed by Gao et al.(2004), the products of SOA can be divided into low-molecular-weight (LMW, MW <250 Da) and high-molecular-weight (HMW, MW >250 Da) components. The former nine classes products belong to LMW components, while the 10th to 11th classes have m/z greater than 250, the 11th class with maximum m/z up to 500, indicating that HMW components are present in aged benzene SOA particles. As shown in Fig. 6, dialdehydes such as glyoxal, butenedial, 6-oxo-2,4-hexadienal, and 2,3-epoxy-6-oxo-4-hexenal are produced as ring-opened products from the reaction of benzene with OH radicals (Martín-Reviejo and Wirtz 2005; Borrása and Tortajada-Genarob 2012; Wang et al. 2013). These products, as well as second or higher generation products formed from subsequent oxidation, are absorbed onto existing particles. Some second or higher generation products

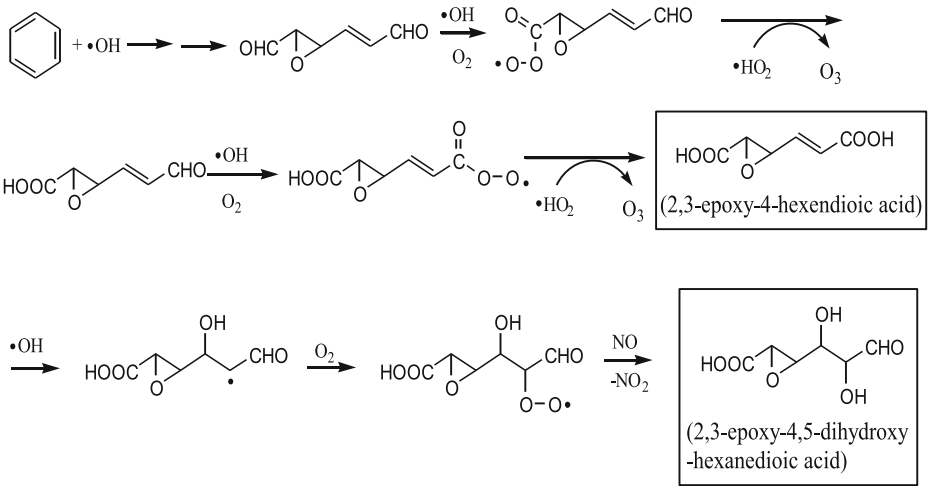


**Fig. 5** Proposed aging mechanism leading to the formation of epoxide products

have both carbonyl and hydroxy groups. In the particle phase, HMW components are formed from carbonyl hydration, hemiacetal formation, acetal formation, carbonyl polymerization, and aldol condensation (Jang et al. 2002; 2004; Gross et al. 2006).

### 3.3 Comparison with LC-MS studies

Sato et al. (2012) have used LC-MS to detect the products of aged benzene SOA formed from irradiating benzene/$CH_3ONO$)/$NO_x$/air mixtures for about 11 h. Nitrogenated organic compound, oxocarboxylic acid, epoxide product are observed as major aging products. Similar to Sato et al. (2012), the aged benzene SOA were also formed from photooxidation of benzene/$CH_3ONO/NO_x$/air mixtures, but the photooxidation time is 24 h, which is longer than that of Sato et al. (2012). Besides nitrogenated organic compound, oxocarboxylic acid, epoxide product, HMW components with maximum m/z up to 500 were detected by ALTOFMS. As we know, the LC-based methods provide important data for most compounds formed in aging experiments. However, due to their high polarity, HMW components cannot be measured with

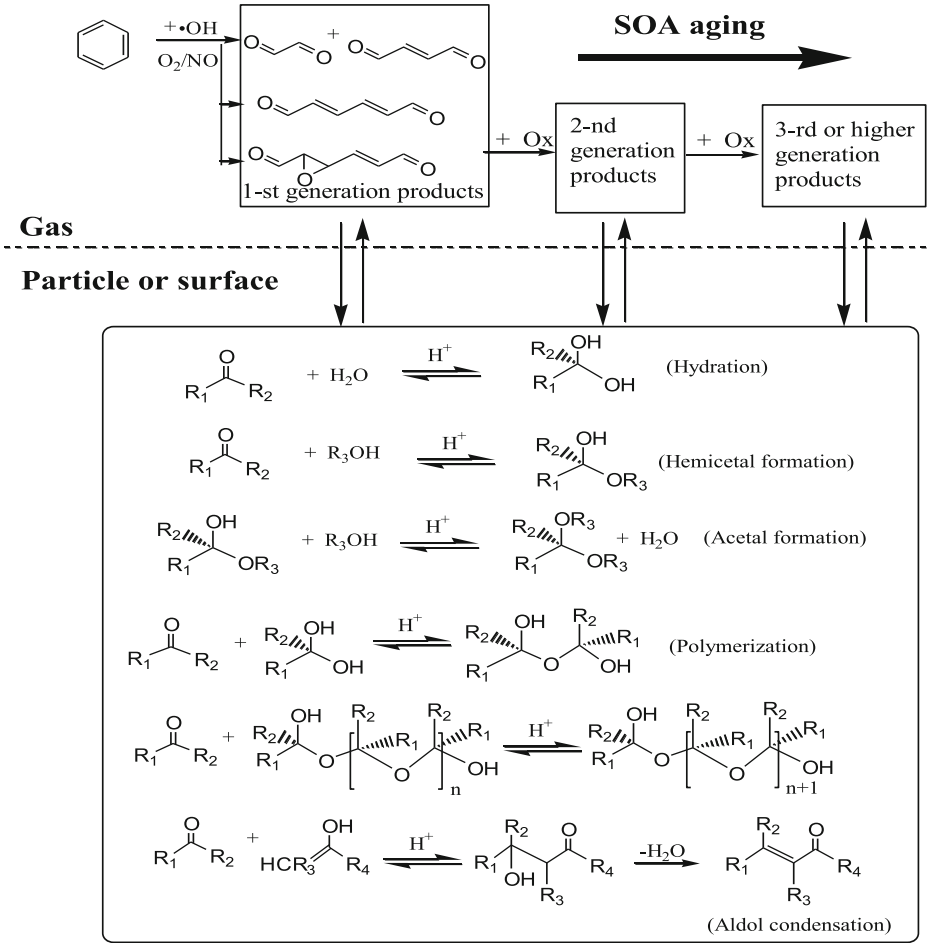


**Fig. 6** Proposed aging mechanism leading to the formation of high-molecular-weight products

this method (Hamilton et al. 2003). Sampling with filters followed by extraction for the LC measurements is therefore necessary. This method is labor intensive and prone to artifacts. In the sample handling process sample evaporation may occur which will result in the loss of some chemical components. Compared to offline method of LC-MS, the real-time detection by ALTOFMS coupled with an FCM data processing approach can overcome these shortcomings and obtain more product information.

As shown by Sato et al. (2012), benzene SOA aging proceeds through the oxidation of the internal double bond of ring-opened products and oxocarboxylic acid formation resulting from the OH-initiated oxidation of the carbonyl group. Organic nitrogen-containing products formation from phenolic compounds is initiated by reactions with OH radicals, and react with $NO_2$ subsequently (Sato et al. 2012). Our work extended the photooxidation time to 24 h, and the results strongly suggest that HMW components with maximum m/z up to 500 are present in aged benzene SOA particles, indicating that chemical compositions of SOA have been modified continually upon aging. Since carbonyls and carboxylic acid are present in SOA particles formed from benzene, HMW components are formed from the acid-catalyzed heterogeneous reactions (Jang et al. 2002; 2004; Gross et al. 2006).

## 4 Conclusion

We were able to clearly identify distinct chemical classes of aged benzene SOA particles using the ALTOFMS system for data acquisition and fuzzy clustering for data analysis. The Fuzzy c-means algorithm has been proved to be the appropriate algorithm to process these kinds of mass spectra data. Definition of the most useful number of clusters can be performed by combination of a set of criteria that are evaluated by the data handling program. The method gives rise to detailed chemical information about the detected single particles and the determined particle classes. Some important aged products such as nitrogenated organic compound, oxocarboxylic acid, epoxide product and high-molecular-weight compounds can be measured. This demonstrates that ALTOFMS is a useful tool to reveal the aging processes of SOA particles in smog chambers.

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