Analysis of the Ozonation Products of Phthalic Acid in Water Using Combined High-performance Liquid Chromatography - Mass Spectrometry*

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Several aromatic intermediates formed in the reaction of ozone with phthalic acid in water can be identified using combined HPLC - MS. The mass spectra obtained are simple and fragments providing useful mass information are usually observed. A degradation scheme for phthalic acid by ozonation is proposed.

Keywords: *Ozonation products analysis; phthalic acid - water; high-performance liquid chromatography - mass spectrometry; salicylic acid - water*

Ozone is a powerful oxidant used as a disinfectant in drinking water treatment plants. It is also known to be capable of oxidising most organic compounds to smaller and more easily biodegraded molecules. The identification of the primary oxidation products is necessary in order to evaluate their properties, especially their toxicity. Rice[1] and Gilbert[2] have presented excellent reviews on the chemistry of ozonation and the reaction of ozone with organic compounds in aqueous solutions.

Phthalate esters, which are extensively used as plasticisers, have been detected in rivers and lakes.[3,4] Their widespread presence in the environment has generated great concern about their possible health hazards.[5,6] Phthalate esters are specified by the US Environmental Protection Agency (EPA) as priority pollutants[7]; however, their behaviour with respect to ozone in water is almost unknown. This is due, to a large extent, to the limitations of the analytical methods available until now.

Recent developments in the coupling of high-performance liquid chromatography and mass spectrometry[8-13] have overcome the main analytical problem, which is the limited information about identity given by the detectors usually associated with HPLC. We have applied this new technique to the study of the intermediates resulting from the ozonation of aqueous solutions of phthalic acid as the simplest model phthalate. The acid was chosen rather than an ester because of the low solubility of the latter in water. A study of the reactions taking place on the aromatic ring of this simple molecule is necessary as a basis for the subsequent elucidation of those involving substituents and esters.

Experimental

Ozonation of Phthalic Acid

Ozone was generated from air by electrical discharge in a Trailigaz 76 laboratory ozoniser, and bubbled at the base of a Pyrex reactor, containing 80 mg of analytical-reagent grade phthalic acid (Prolabo) dissolved in 1 l of Millipore-purified water. The ozonation procedure was carried out at room temperature for 60 min with an average ozone production rate of 0.75 mg min^{-1}. These conditions correspond to the oxidation of approximately 50% of the initial amount of phthalic acid. A 20-ml volume of this ozonised solution was concentrated to 1 ml in a rotary evaporator at 40 °C for subseqeuent HPLC - MS analysis.

HPLC - MS Analysis

The HPLC system was a Hewlett-Packard 1084B with a solvent programmer and a variable-volume injector. A 100-µl volume of the concentrated ozonised solution of phthalic acid was injected into a 10-µm LiChrosorb RP-8 column (250 × 4 mm i.d.).

The eluents were (A) water, adjusted to pH 2.7 with concentated HCl, and (B) acetonitrile. A 20-min linear

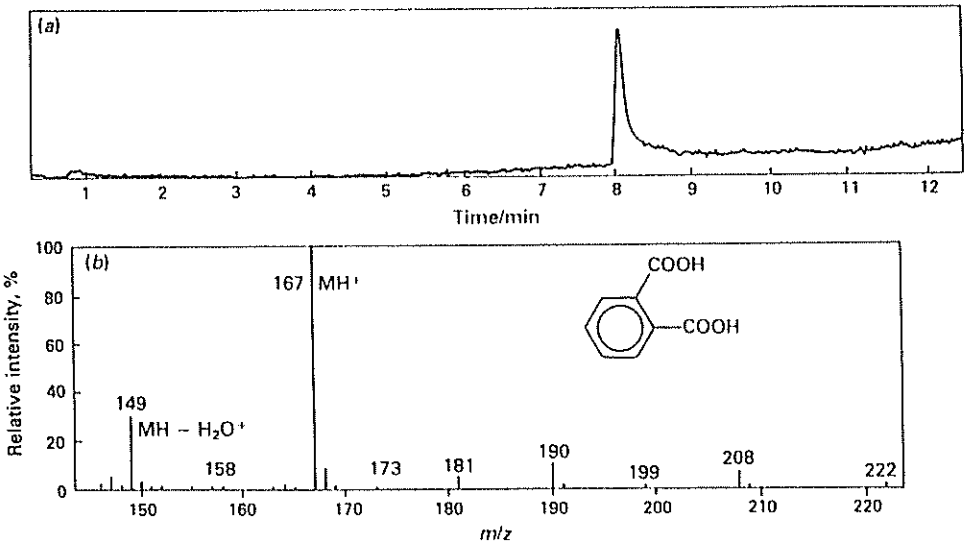

Fig. 1. (*a*) Chromatogram of the total ion current and (*b*) the mass spectrum of the phthalic acid peak

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elution gradient from 5 to 70% of acetonitrile was run at a flow-rate of 1 ml min^{-1}.

The HPLC - MS interface was a Hewlett-Packard direct liquid insertion probe[13] with splitting ratio of 1:100 so that, with a flow-rate of 1 ml min^{-1}, approximately 10 µl min^{-1} of the mobile phase enter the mass spectrometer source. As the evaporated solvent is present in an excess, it acts as a chemical ionisation reactant gas.

The mass spectrometer used was Hewlett-Packard 5958B linked to an HP 100 computer system; the source temperature was 150 °C and the ionising voltage was 70 eV. The spectra were recorded over a mass range of 145–300 a.m.u., at a scan

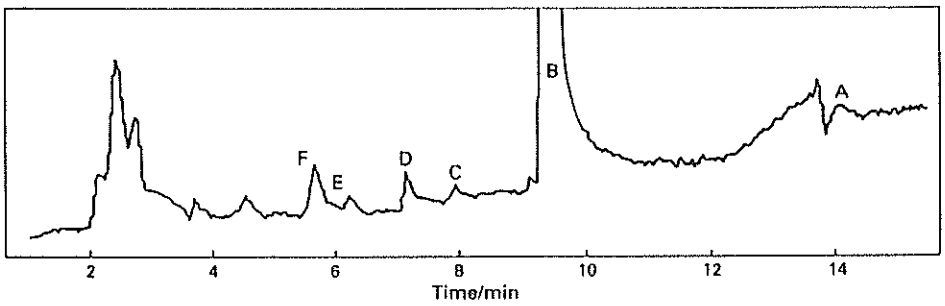

Fig. 2. Total ion current chromatogram of an ozonised solution of phthalic acid. Peaks: A, salicylic acid; B, phthalic acid; C, 3-monohydroxyphthalic acid; D, 4-monohydroxyphthalic acid; and peaks E and F, unidentified

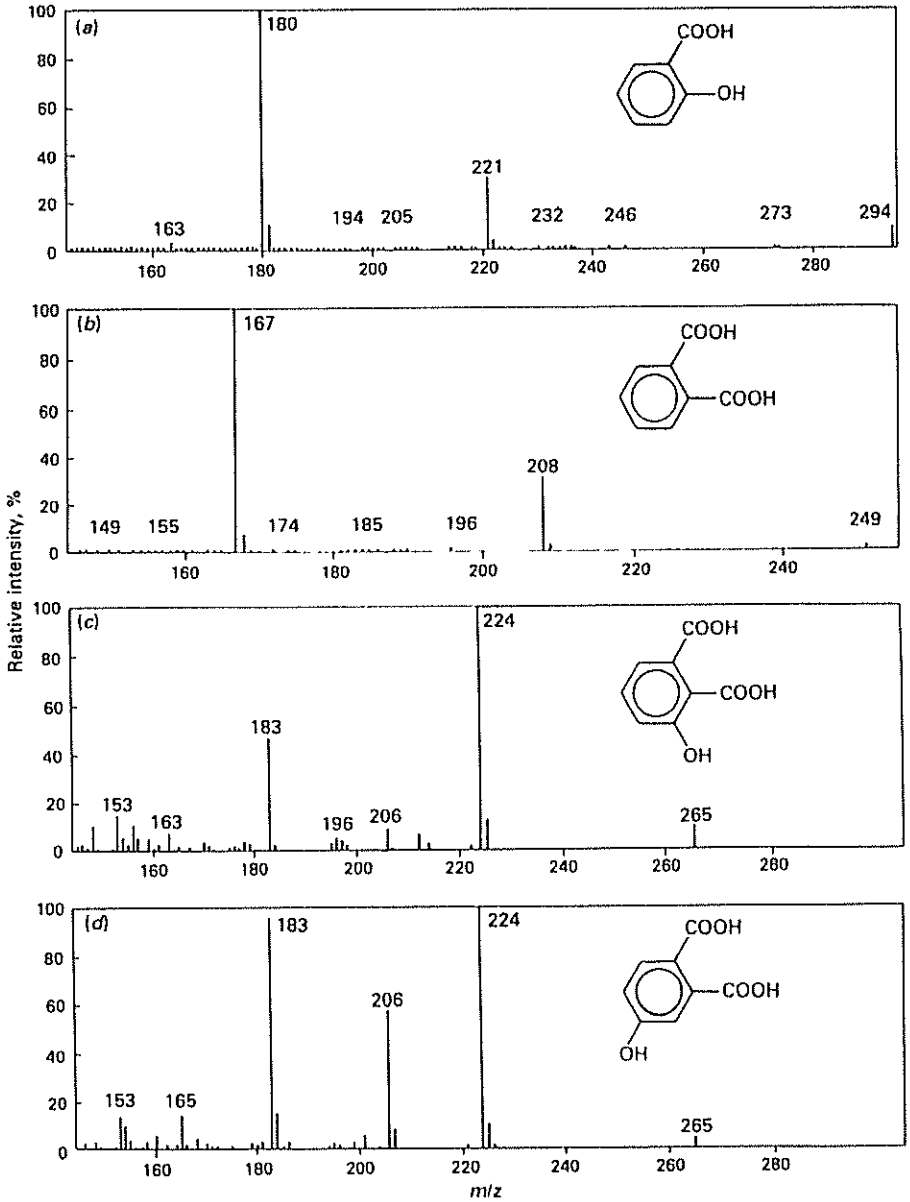

Fig. 3. Mass spectra of (*a*) salicylic acid (peak A, Fig. 2); (*b*) phthalic acid (peak B); (*c*) 3-monohydroxyphthalic acid (peak C); and (*d*) 4-monohydroxyphthalic acid (peak D)

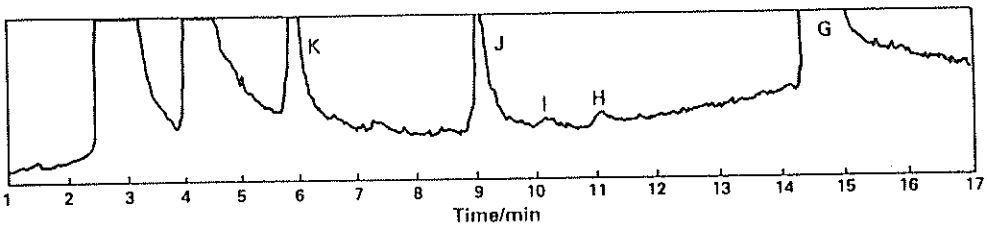

Fig. 4. Chromatogram of the total ion current of an ozonised solution of salicylic acid. Peaks: G, salicylic acid; H, 2,5-dihydroxybenzoic acid; I, 2,6-dihydroxybenzoic acid; J, *cis,cis*-muconic acid; and K, probably a muconic acid isomer

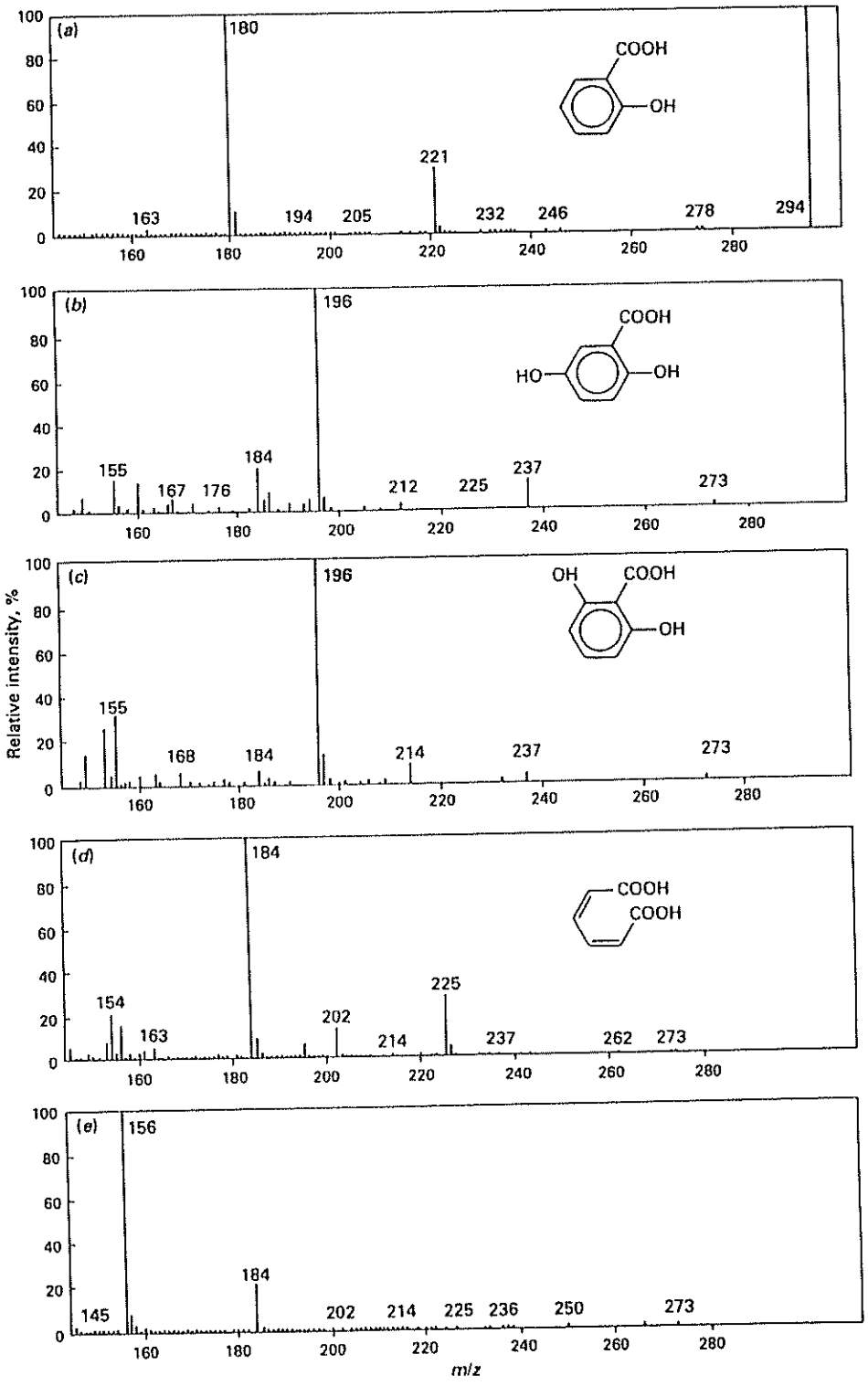

Fig. 5. Mass spectra of (*a*) salicylic acid (peak G); (*b*) 2,5-dihydroxybenzoic acid (peak H); (*c*) 2,6-dihydroxybenzoic acid (peak I); (*d*) *cis,cis*-muconic acid (peak J); and (*e*) probably a muconic acid isomer (peak K)

rate of 2 a.m.u. s^{-1}. The mass spectrum of each peak was taken at its summit with subtraction of the base-line spectra at the beginning and the end of the peak.

Results and Discussion

In a preliminary investigation, a solution of phthalic acid was injected in order to study the types of ions formed using acetonitrile - water as eluent/chemical ionisation reagent gas.

The chromatogram obtained from the total ion current and the mass spectrum corresponding to the phthalic acid peak are shown in Fig. 1. This mass spectrum shows the quasi-molecular ion (MH^+) at *m/z* 167 and a fragment corresponding to the loss of H_2O at *m/z* 149. The ions observed at 190 and 208 result from the addition of acetonitrile (41 a.m.u.) with and without the elimination of water, respectively.

The over-all increase of 15 a.m.u. to give the peak observed in the mass spectrum of phthalic acid at *m/z* 181 would suggest a reaction involving the elimination of HCN (27 a.m.u.) after the addition of acetonitrile to the molecule. This phenomenon was observed by Henion[11] but not explained. The interpretation of the different mass spectra obtained from the analysis of the ozonised solution was based on the chemical ionisation spectrum observed for phthalic acid, *i.e.*, addition of acetonitrile, elimination of water, etc.

The total ion current chromatogram showing the HPLC separation of the ozonised solution of phthalic acid is shown in Fig. 2. The HPLC conditions were chosen to give a good separation of the aromatic oxidation products and this results in a poor separation of the polar products observed in the beginning of the chromatogram. The mass spectra of these early peaks show that they are obviously mixtures. Generally, these products are short-chain acids and aldehydes resulting from ozone rupture of the aromatic ring. They have already been extensively studied and are known to be very similar for most aromatic compounds and so are of less interest than the primary aromatic oxidation products, which are eluted later.

Fig. 3(*a*) gives the mass spectrum of peak A, which indicates the relative molecular mass of salicylic acid (138), the ions at *m/z* 180 and 221 being $(M + H + 41)^+$ and $(M + H + 41 + 41)^+$, respectively. The quasi-molecular ion $(M + H)^+$ for salicylic acid at *m/z* 139 could not be scanned by mass spectrometry as the background noise due to the solvent was very important in this region so the scanning was started at 145 a.m.u. However, some specific ions could be detected below this level and by means of the individual ion mass chromatogram corresponding to *m/z* 139 we were able to demonstrate the presence of this fragment at the retention time of salicylic acid. The second mass spectrum in Fig. 3(*b*) is that of peak B, which corresponds to phthalic acid. The two mass spectra in Fig. 3(*c*) and (*d*) indicate the relative molecular mass of monohydroxyphthalic acid (182), displaying its quasi-molecular ion $(M + H)^+$ at *m/z* 183, while the ions at *m/z* 224 and 265 result from the addition of one and two molecules of acetonitrile. The elimination of H_2O associated with the addition of acetonitrile gives the ion at *m/z* 206. The lack of abundant ion peaks in the mass spectra obtained for peaks E and F in Fig. 2, except for a base peak at *m/z* 156, means we do not have sufficient information to identify the corresponding molecules.

By subsequent ozonation of salicylic acid and analysis of the ozonised solution by HPLC - MS (Fig. 4) we were also able to identify two isomers of dihydroxybenzoic acid (relative molecular mass 154) [Fig. 5 (*b*) and (*c*)], and tentatively identify two others as muconic acid isomers (relative molecular mass 142) [Fig. 5 (*d*) and (*e*)]. The identifications of salicylic acid, 4-hydroxyphthalic acid, 2,6-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid and *cis,cis*-muconic acid were confirmed by co-injection using authentic standards. 3-Hydroxyphthalic acid is not available commercially, but is the only other possible monohydroxyphthalic acid isomer.

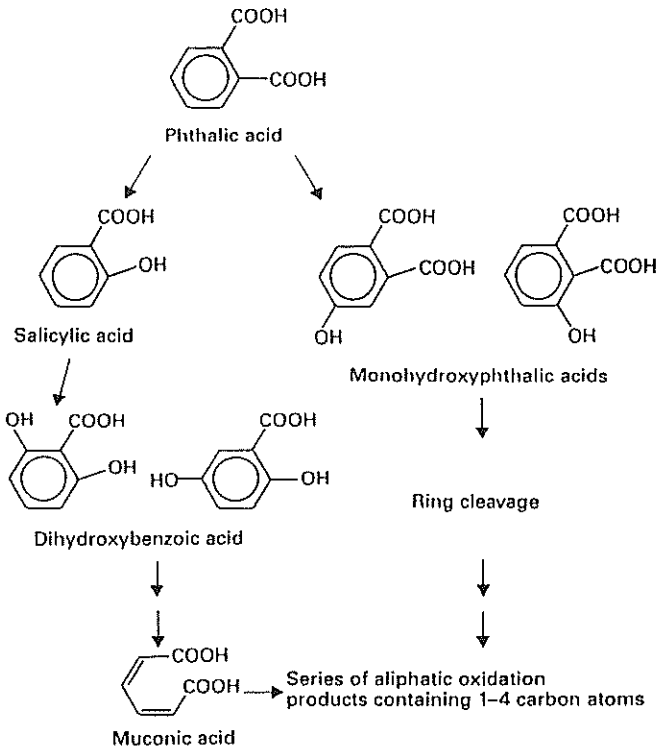

Fig. 6. Degradation scheme for phthalic acid, by ozonation in aqueous solution

From these results we are able to propose a degradation scheme for phthalic acid by ozonation in aqueous solution (Fig. 6) involving two main reaction pathways, the first being hydroxylation of the aromatic ring, leading to the formation of monohydroxyphthalic acids, and the second decarboxylation of a carboxyl group to give salicylic acid and dihydroxybenzoic acids after hydroxylation of the salicylic acid. These two oxidation patterns are associated with ring cleavage to give muconic acids and a series of very polar short-chain oxidation products.

Conclusion

The technique of combined reversed-phase HPLC - MS is useful for the analysis of model water samples containing a limited number of unknown organic pollutants, and where a reasonable separation of the products is possible. This technique avoids such procedures as extraction and derivatisation, and can complement gas chromatography - mass spectrometry for the analysis of non-volatile or thermolabile compounds.

The sensitivity of the system is reduced by the small amount of the total eluate (1%) that enters the mass spectrometer source. The concentration of the 4-hydroxyphthalic acid, for example, was about 2.5 μg ml^{-1} in the ozonised solution. It was necessary to concentrate this solution 20-fold in order to observe a distinct signal in the total ion current chromatogram. Efforts must be made towards improving sensitivity, increasing the mass spectrometry fragmentation and addition reaction data for the various commonly used liquid chromatography solvent systems and mass spectrometry working parameters.

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