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Atmospheric chemistry of benzene oxide/oxepin

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The atmospheric chemistry of benzene oxide/oxepin, a possible intermediate in the atmospheric oxidation of aromatic hydrocarbons, has been investigated in a large volume photoreactor at 298 K and atmospheric pressure using *in situ* FTIR spectroscopy for the analysis. Rate coefficients of $(10.0 \pm 0.4) \times 10^{-11}$ and $(9.2 \pm 0.3) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} have been determined for the reaction of benzene oxide/oxepin with OH and NO_3 radicals, respectively. Reaction with OH radicals produces almost exclusively the (*E*,*Z*)- and (*E*,*E*)-isomers of hexa-2,4-dienedial, whereas reaction with NO_3 produces (*Z*,*Z*)-hexa-2,4-dienedial and unidentified organic nitrates. Phenol has been observed as a major product of the thermal decomposition, visible and UV photolysis of benzene oxide/oxepin. The results are discussed in conjunction with the oxidation mechanisms of aromatic hydrocarbons. The major atmospheric sinks of benzene oxide/oxepin will be reaction with OH radicals and photolysis and, under smog chamber conditions with high NO_2 concentrations, also reaction with NO_3.

Tropospheric photooxidant formation, mainly in the form of ozone, is now recognised as one of the most important environmental problems in the industrialised world. It can occur on urban, suburban and rural scales. In Germany, for example, the public is regularly warned when the ozone concentration in urban areas reaches 90 ppb (180 µg m^{-3}). Ozone and other photooxidants are formed in a complex series of reactions initiated by the sunlight-induced oxidation of precursor emissions of volatile organic compounds (VOCs) and of nitrogen oxides ($NO_x = NO + NO_2$).[1]

In recent years, considerable effort has been expended in generating computer models which accurately describe tropospheric oxidation processes and are able to predict reliably the extent of photooxidant formation. Such models are the principal tools used by policy makers for testing emission-reduction strategies aimed at reducing ozone formation in problem areas. Reliable chemical oxidation mechanisms for the precursor VOCs are a prerequisite for the successful implementation of these models. One of the most serious problems with the VOC oxidation mechanisms employed in the chemical modules of current models is the speculative nature of the degradation mechanism for aromatic hydrocarbons.[2] According to model calculations, using these, presently, uncertain and doubtful mechanisms, aromatic hydrocarbons could account for up to 40% of the photooxidant formation in urban areas.[3] This places aromatic hydrocarbons among the most important classes of hydrocarbons emitted into the urban atmosphere. The most important aromatic hydrocarbons in this respect are benzene and the methylated benzenes (toluene and the xylene and trimethylbenzene isomers).

The degradation mechanisms presently used to represent the atmospheric oxidation of aromatic hydrocarbons do not adequately describe many of the experimental observations. The primary fate of aromatic hydrocarbons in the atmosphere is reaction with OH radicals. For methylated benzenes, this reaction can proceed by two pathways, abstraction of an H-atom from a methyl side-group and addition of OH to the aromatic ring. The abstraction pathway accounts for *ca.* 10% of the overall decay and leads to the formation of benzaldehyde derivatives.[4] This minor pathway is well understood and will therefore not be discussed here. Therefore, Fig. 1 only shows the addition pathway, and the methyl groups present in the atmospherically important methylated aromatic hydrocar-

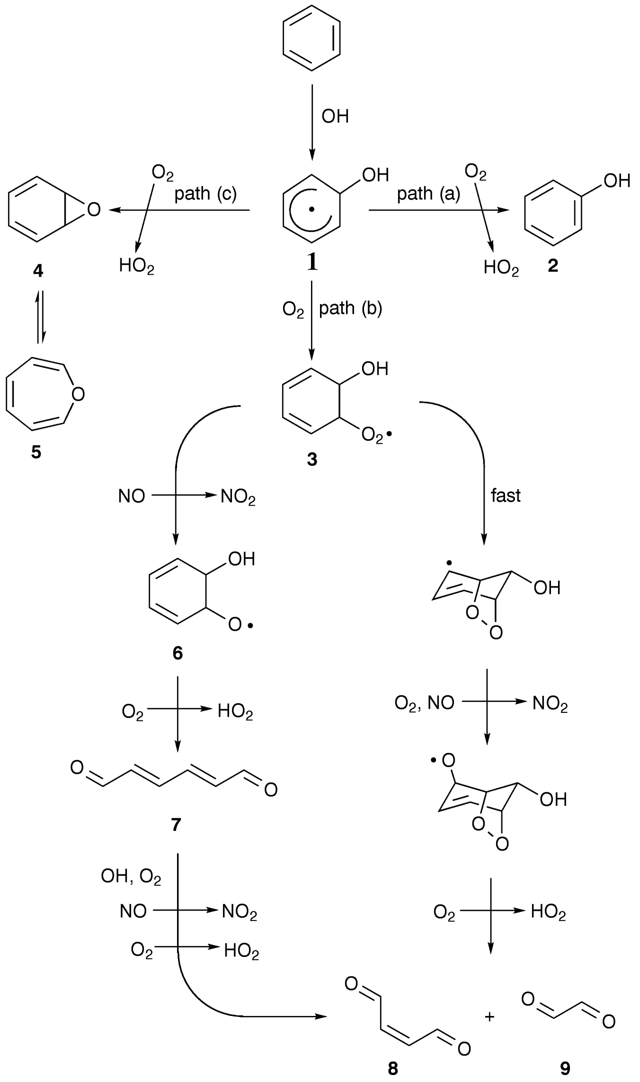


Fig. 1 Postulated pathways for the addition channel in the OH-initiated oxidation of aromatic hydrocarbons. Methyl groups have been omitted for clarity.

bons (toluene, xylenes, trimethylbenzenes) have been omitted for simplicity.

As shown in Fig. 1, the addition pathway results in the formation of a hydroxycyclohexadienyl radical, **1**, also termed aromatic-OH-adduct. This adduct has been well characterised and is now known to react primarily with O_2 under atmospheric conditions, although in smog chamber studies conducted in the presence of NO_x, reaction with NO_2 can also be important.[5] The products of both these reactions, however, are not yet established. Concerning the fate of the adduct *via* reaction with O_2, two pathways have been postulated as depicted in Fig. 1 [paths (a) and (b)]. Here, we propose an alternative route proceeding from **1**, shown as path (c) in Fig. 1.

There are conflicting results in the literature concerning the importance of path (a) leading to the formation of phenol/methylated phenols **2**. The high yields reported in some studies[6] are undoubtedly due to the experimental conditions employed, which are now known to influence the yields of hydroxylated aromatic hydrocarbons in the photooxidation of aromatic hydrocarbons.[7] However, this cannot explain the discrepancies in every case. The observation of 'prompt' HO_2 formation in flash photolysis/resonance fluorescence studies of the OH oxidation of aromatic hydrocarbons[8] was previously taken as evidence for path (a). However, the yields of prompt HO_2 formation found for benzene and toluene are near unity. If this reaction pathway were operative, this would require the formation of equivalent yields of phenols. Despite uncertainties regarding the yields of phenolic compounds, literature data[4] do not support the contention that path (a) is major, and suggest that alternative pathways must exist for fast HO_2 radical production.

Hydroxycyclohexadienyl peroxyl radicals, **3**, can be formed by addition of O_2 to **1**. A recent theoretical study[9] showed that such an addition would primarily occur at the *ortho*-position of **1**. This is in contrast to the analogous reaction in solution, where addition at the *para*-position is thought to be dominant.[10] **3** could then further react to give the shorter-chain dicarbonyl compounds **8** and **9** observed in the photooxidation of aromatic hydrocarbons.[11] One postulated pathway for this reaction, involving O_2 bridging, is shown in the right-hand column of Fig. 1. From two recent theoretical studies,[12,13] the allylically stabilised 1,3-bridged adduct plotted in Fig. 1 is thought to be the most stable cyclisation product.

3 might also react with NO to give hydroxycyclohexadienyloxyl radicals **6** which, in turn, can ring open to give muconaldehyde derivatives **7**, these are unsaturated 1,6-dicarbonyls. Indirect evidence for the formation of unsaturated 1,6-dicarbonyls was obtained some time ago[14] and, recently, their formation in the photooxidation of an aromatic hydrocarbon has been conclusively proved[15] using gas chromatography/ion trap mass spectrometry.

Although the assumption of peroxyl radical formation from the reaction of **1** with O_2 can explain the final products observed in the atmospheric oxidation of aromatic hydrocarbons, no experimental evidence has yet been found to support the intermediacy of **3** despite extensive efforts. For example, studies have shown that addition of NO to the system, which efficiently converts peroxyl radicals to oxyl radicals, has no significant effect on the kinetics or the product distribution of the reaction.[7] Further, no evidence has been found, even at low temperatures, for the existence of a peroxy nitrate, a typical reaction product from the addition of NO_2 to peroxyl radicals.[16] In addition, peroxyl radical formation cannot explain the prompt HO_2 observed by Siese *et al.*,[8] since, if it were a major pathway, HO_2 formation would occur with a considerable time-delay further down the oxidation chain, caused by the reduction of a peroxyl radical with NO to give an oxyl radical and NO_2, see Fig. 1.

The alternative pathway proposed for the reaction of **1** with O_2 in this work [path (c), Fig. 1] involves the formation of arene oxides, *i.e.* benzene oxide **4**/oxepin **5** or its methylated derivatives. These compounds were suggested as intermediates in the photooxidation of *o*-xylene as early as 1984 by Shepson *et al.*[17] but have since received no further attention. Shepson *et al.* found an unidentified compound of molecular formula $C_8H_{10}O$ in their experiments with *o*-xylene, concluded that it could not be a dimethylphenol and suggested 1,6-dimethylbenzene oxide.

Arene oxides are believed to be primary metabolites of aromatic hydrocarbons in biological systems. In the metabolism of benzene there is substantial, though only indirect, evidence for the formation of benzene oxide/oxepin, which may contribute to the carcinogenicity and other toxicities attributed to this compound.[18] For several polycyclic aromatic hydrocarbons (PAHs), the corresponding arene oxides have been positively identified as the primary metabolites. The formation of 1,2-naphthalene oxide from naphthalene by liver microsomes was shown as early as 1968.[19] Subsequently, arene oxides were identified as metabolites of several other PAHs.[20,21]

A mechanism postulating the formation of arene oxides in the gas phase can explain some of the uncertainties and contradictions currently associated with the initial steps in the photooxidation of aromatics, notably the formation of prompt HO_2 and the variation of the yields of phenolic products in the OH-initiated oxidation of aromatic hydrocarbons. In order to assess whether benzene oxide/oxepin derivatives are candidates for intermediacy in the atmospheric photooxidation of aromatic hydrocarbons, benzene oxide/oxepin has been synthesised as a model compound and selected aspects of its atmospheric chemistry investigated. The kinetics and products of the reactions of this compound with OH and NO_3 radicals, as well as its thermal stability and photochemistry, have been studied in a large-volume photoreactor. Apart from a very rudimentary study by Nojima *et al.*,[22] which was conducted under conditions not representative of the troposphere, no investigation of the atmospheric chemistry of benzene oxide/oxepin has previously been carried out.

Experimental

The kinetic and product studies were carried out at (298 ± 3) K in a 1080 L quartz reaction chamber using long-path *in situ* FTIR spectroscopy to monitor reactants and products. The reactor is equipped with a White mirror system, allowing a total optical path length of 579.2 m for the FTIR. The vessel is surrounded by 32 low-pressure mercury lamps ($\lambda_{max} = 254$ nm) and 32 superactinic fluorescent lamps ($320 < \lambda/\text{nm} < 480$, $\lambda_{max} = 360$ nm). Further details of the experimental set-up can be found elsewhere.[23] The UV spectrum of benzene oxide/oxepin was recorded in a 480 L Duran glass reaction chamber fitted with an FTIR and a UV spectrometer (SPEX, focal length 2 cm) with a diode array detector (PAR 1412). The optical pathlengths were 51.6 and 39.12 m for the FTIR and UV spectrometers, respectively. All the IR spectra were recorded with a spectral resolution of 1 cm^{-1}. The substances were injected directly into the evacuated chambers using calibrated gas-tight syringes. Calibrations were performed by injecting weighed amounts of the substances into the evacuated reaction chambers in a flow of dry nitrogen.

The NO_3 radical reactions were conducted at a pressure of 800 mbar of synthetic air. All other experiments were conducted at total pressures of 1000 mbar. The photolysis of methyl nitrite–NO mixtures in synthetic air was employed as the OH radical source,[24] NO_3 radicals were generated by thermal decomposition of N_2O_5, which was synthesised by reacting NO_2 with ozone. Typical starting concentrations for all reactants were in the range $(2.5\text{–}5) \times 10^{13}$ molecules cm^{-3}.

The relative rate technique was used for the determination of the rate coefficients of the reactions of OH and NO_3 radicals with benzene oxide/oxepin. The rate coefficient for reaction with OH radicals was determined relative to reaction with (*E*)-but-2-ene ($k_{\mathrm{OH}+(E)\text{-but-2-ene}} = 6.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}).[25] The NO_3 kinetic experiments were performed relative to 2-methylbut-2-ene ($k_{\mathrm{NO_3}+2\text{-methylbut-2-ene}} = 9.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}).[26] The decay of benzene oxide/oxepin and the reference hydrocarbon are determined by the following rate laws:

$$-\frac{\mathrm{d[oxepin]}}{\mathrm{d}t} = k_1[\mathrm{OH\ or\ NO_3}][\mathrm{oxepin}] + k_3[\mathrm{oxepin}] \tag{I}$$

$$-\frac{\mathrm{d[reference]}}{\mathrm{d}t} = k_2[\mathrm{OH\ or\ NO_3}][\mathrm{reference}] + k_4[\mathrm{reference}] \tag{II}$$

where k_1 and k_2 are the bimolecular rate coefficients (in units of cm^3 molecule^{-1} s^{-1}) for the reaction of oxepin and the reference hydrocarbon with OH or NO_3 radicals, and k_3 and k_4 are the first-order rate coefficients (in s^{-1}) for wall, thermal decomposition and/or photolysis loss of oxepin and the reference, respectively. Upon integration, eqns. (I) and (II) can be rearranged to give:

$$\ln\frac{[\mathrm{oxepin}]_{t_0}}{[\mathrm{oxepin}]_t} - k_3(t - t_0) = \frac{k_1}{k_2}\ln\frac{[\mathrm{reference}]_{t_0}}{[\mathrm{reference}]_t} - k_4(t - t_0) \tag{III}$$

The wall and photolysis losses were negligible for both the references employed and thus the term $k_4(t - t_0)$ reduces to zero in eqn. (III). Wall, thermal and photolysis losses for benzene oxide/oxepin were non-negligible in the kinetic experiments and thus the correction term $k_3(t - t_0)$ had to be applied in the analysis of the kinetic data. The appropriate k_3 values for the OH and NO_3 kinetic determinations were measured in separate experiments, as described in the Results section. The values were found to remain constant not only within an individual experiment but also from experiment to experiment, *i.e.* fluctuations due to possible changes in the reactor surface and light intensity are minor. Plots of $\{\ln([\mathrm{oxepin}]_{t_0}/[\mathrm{oxepin}]_t) - k_3(t - t_0)\}$ against $\ln([\mathrm{reference}]_{t_0}/[\mathrm{reference}]_t)$ should yield a straight line of slope k_1/k_2 and zero intercept.

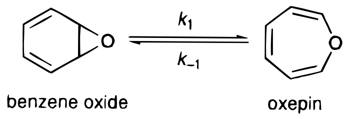
All the errors quoted represent two standard deviations and therefore account for experimental scatter only. Additional errors, *e.g.* due to uncertainties in the rate coefficients of reference compounds, are not included.

Benzene oxide/oxepin was prepared as described by Gillard *et al.*[27] and further purified by Kugelrohr distillation. The resulting fluorescent clear-yellow liquid was 95–98% pure benzene oxide/oxepin (^{1}H NMR), the impurities consisted largely of phenol, from thermal rearrangement of benzene oxide, with minor contributions from bromobenzene. Phenol formation could be minimised by adding small quantities of potassium carbonate to the flask containing the purified compound. The presence of bromobenzene did not have any effect on the experiments owing to its very low reactivity.[25] The levels were also too low to make any measurable contribution to the UV spectrum of benzene/oxepin. Therefore, no effort was made to purify the benzene oxide/oxepin samples further.

Results and Discussion

Equilibrium benzene oxide/oxepin and FTIR and UV spectra

Benzene oxide is known to be in rapid equilibrium with its monocyclic isomer, oxepin.[28]



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The equilibrium constant, *K*, for this reaction can be calculated from the Gibbs energy, Δ*G*, using the thermodynamic equation: $\ln K = -\Delta G/RT$. The energy change in the conversion of benzene oxide to oxepin has been calculated by various groups.[29–32] According to most of these theoretical calculations, the equilibrium is somewhat shifted towards oxepin in the gas phase, though entropy effects have usually been ignored. In the studies where entropy effects were explicitly calculated, it was concluded that they are dominant and result in a shift of the equilibrium towards oxepin.[29] Vogel and Günther[28] measured Δ*G* of the benzene oxide/oxepin tautomerism in solution and also found that entropy effects dominated. Thus it would appear reasonable to conclude that the equilibrium is indeed shifted towards oxepin in the gas phase.

The temperature dependences of the rate coefficients for the forward reaction, k_1, of benzene oxide to oxepin and k_{-1} for the back reaction have been determined by Vogel and Günther[28] using ^{1}H NMR spectroscopy in CF_3Br–pentane (2 : 1) solution. Extrapolation of the values, obtained in this way, to room temperature, gives an equilibrium lifetime of *ca.* 0.2 μs. The FTIR spectrometers used in the present study have a time resolution of *ca.* 1 s. The UV spectrometer was operated at exposure times of 60–90 s. Thus, even when the equilibrium lifetime in the gas phase is significantly higher than that in solution, the isomerisation of the benzene oxide initially formed in the proposed mechanism must still be several orders of magnitude faster than the time resolution of the spectrometers used. Therefore, the IR and UV spectra presented below do not show unique benzene oxide and oxepin bands but, rather, 'mixed absorptions' due to the constant interconversion of these two isomers. Another important consequence of the fast equilibrium is that the subsequent decay of benzene oxide in the atmosphere would affect the equilibrium mixture with oxepin, not just the benzene oxide postulated to be formed from $\mathbf{1} + O_2$ initially. The authors, therefore, believe that the data presented here are indeed relevant for atmospheric conditions, provided the new mechanism is valid.

Fig. 2 shows the gas-phase FTIR spectrum of benzene oxide/oxepin in the range 1700–700 cm^{-1}, with the inset showing the spectral region 3150–2950 cm^{-1}. For the most intense band (736 cm^{-1}), an absorption cross-section of $(4.2 \pm 0.3) \times 10^{-19}$ cm^2 molecule^{-1} has been determined. The spectral features can be assigned as follows. The absorption band around 3052 cm^{-1} is typical for the stretching vibrations

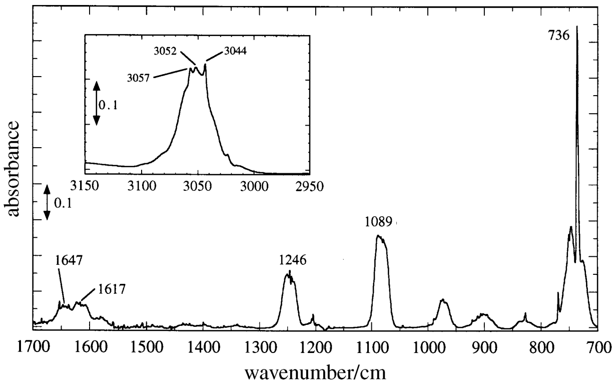


Fig. 2 Gas-phase FTIR spectrum of benzene oxide/oxepin in the range 1700–700 cm^{-1}. The inset shows the spectral region 3150–2950 cm^{-1}.

of CH bonds. The bands at 1647 and 1617 cm^{-1} correspond to the stretching vibration of the conjugated C=C double bonds. Absorptions at 1246 cm^{-1} are in a region typical for the C—O stretch of both epoxides and vinyl ethers. The band at 1089 cm^{-1} occurs in a spectral region where vinyl ethers typically exhibit strong absorptions. The very intense absorption at 736 cm^{-1} is due to the CH out-of-plane deformation of the (*Z*) double bonds. Other, weaker bands in the spectrum cannot be unequivocally assigned.

Fig. 3 shows the gas-phase UV–VIS spectrum of benzene oxide/oxepin in the range 230–480 nm. It exhibits a broad, featureless absorption showing a maximum at 270 nm with an absorption cross-section of 1.14×10^{-18} cm^2 $molecule^{-1}$. The spectrum is very similar to that obtained by Vogel and Günther in isooctane solution, where a benzene oxide/oxepin ratio of 30 : 70 was found.[28] This similarity can be taken as a further indication that, in the gas phase, oxepin is present in higher concentrations than benzene oxide. A further noteworthy similarity exists between the UV–VIS spectrum of benzene oxide/oxepin and the UV spectrum of a transient in the reaction of benzene with O (^3P) atoms.[33] This suggests that the intermediate observed in this system might indeed be benzene oxide/oxepin, as suggested by the authors.

Thermal stability of benzene oxide/oxepin

A first-order kinetic decay of benzene oxide/oxepin was observed in the reactor. From the decay a gas-phase lifetime of benzene oxide/oxepin in the reactor of (5.0 ± 0.3) h has been determined. The measured decay is a combination of loss to the reactor wall and isomerisation of benzene oxide/oxepin. The only product observed was phenol. The loss rate of phenol to the reactor wall has been measured and found to obey first-order kinetics. This indicates that once phenol has reached the wall it remains attached to the surface and does not re-enter the gas phase. This supports the premise that phenol is being produced solely from isomerisation of benzene oxide/oxepin, a process which is well known from solution-phase studies.[28] Using the known wall loss of phenol, it has been estimated, from a simulation of the results with a computer model, that the observed decay of benzene oxide/oxepin is a 50 : 50 combination of wall loss and isomerisation. This allows a value of *ca.* 3×10^{-5} s^{-1} to be deduced for the thermal decomposition rate of benzene oxide/oxepin at (298 ± 3) K.

Photolysis of benzene oxide/oxepin

On using the low-pressure mercury lamps, benzene oxide/oxepin was rapidly photolysed. The photolysis obeyed first-order kinetics and gave a lifetime of (53 ± 4) s; a kinetic plot of the experimental data is shown in Fig. 4. The main products were phenol, CO, unidentified ketene and carbonyl compounds and very low yields of butenedial and maleic anhydride. From an analysis of the results, taking into account wall losses of both phenol and benzene oxide/oxepin, the yields of phenol and CO have been estimated to be 45 and 20% (molar basis), respectively. The ketene exhibited absorption maxima at 2135 and 2127 cm^{-1} and may possibly be the same compound observed by Jerina and co-workers in the photolysis of a thin film of benzene oxide/oxepin at 77 K.[34] This group proposed a reaction scheme similar to that outlined in Fig. 5 to explain the formation of both the ketene, **10**, and phenol, **2**. In contrast to the present study, they did not observe formation of any carbonyl compounds, presumably owing to the absence of molecular oxygen in their system.

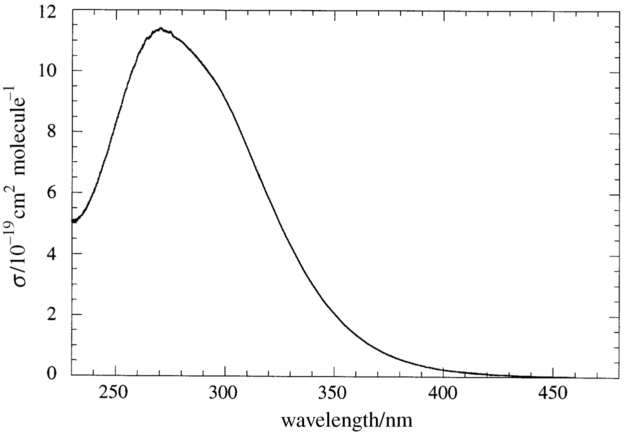


Fig. 3 Gas-phase UV spectrum of benzene oxide/oxepin. The spectrum is very similar to that obtained by Vogel and Günther in isooctane solution[28] indicating a slight shift of the equilibrium towards oxepin.

Other products observed in the gas-phase photolysis of benzene oxide/oxepin with the low-pressure mercury lamps included very low yields of (*E*)- and (*Z*)-butenedial and maleic anhydride. These are very probably products of the OH radical reaction of benzene oxide/oxepin, as described in detail below. In this particular case, the formation and subsequent photolysis of H_2O_2, formed from the recombination of HO_2 radicals produced in the photolysis of benzene oxide/oxepin, is probably the major source of the OH radicals.

Photolysis of benzene oxide/oxepin with the superactinic fluorescent lamps ($320 < \lambda/nm < 480$, $\lambda_{max} = 360$ nm) was fairly slow and the experimental data showed a high degree of scatter. However, assuming first-order kinetic decay, a lifetime

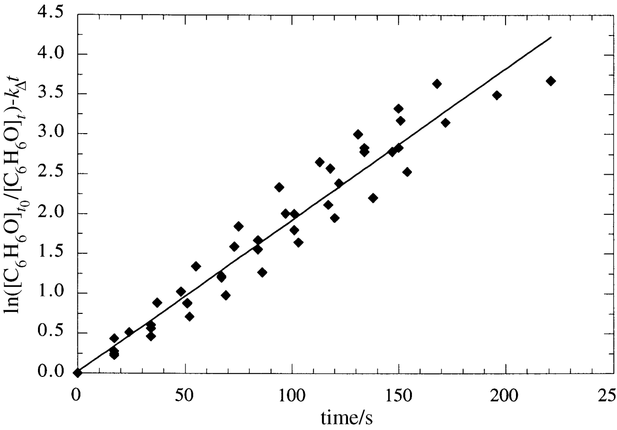


Fig. 4 First-order kinetics plot of the experimental data of the photolysis of benzene oxide/oxepin using low-pressure mercury lamps

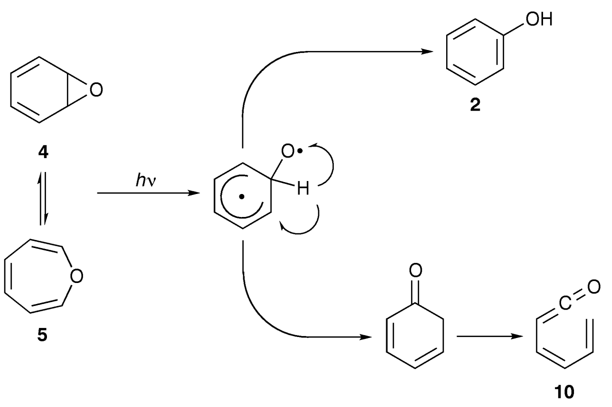
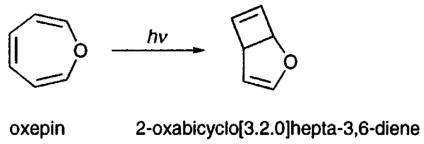


Fig. 5 Possible mechanism for the formation of a ketene in the gas-phase photolysis of benzene oxide/oxepin. A similar scheme has been proposed by Jerina and co-workers[34] for the liquid phase.

of (93 ± 10) min was determined for benzene oxide/oxepin under these conditions, a plot of the experimental data is shown in Fig. 6. The photolysis resulted in the formation of phenol, CO and unknown ketene and carbonyl compounds. An analysis of the data, which takes into account wall loss of both benzene oxide/oxepin and phenol, results in a yield of (53 ± 10)% for the phenol channel in the photolysis. The ketene IR absorption was identical to that observed from photolysis with the low-pressure mercury lamps, though the yield was significantly lower. The carbonyl absorption was also very similar, small differences observed being probably due to slight over- or under-estimations of the subtraction factors of the reference spectra of the various carbonyl compounds which were present in low yields in both photolysis systems.

In addition to the products mentioned above, very small amounts of (*E*,*E*)-hexa-2,4-dienedial and maleic anhydride were also identified. As was the case in the UV photolysis, these are probably products of the reaction of benzene oxide/oxepin with OH radicals produced in side-reactions in the system.

Fig. 7 shows the residual IR spectrum obtained from the photolysis of benzene oxide/oxepin with the superactinic lamps, after subtraction of the absorptions of benzene oxide/oxepin and all identified products. Apart from the ketene and carbonyl bands mentioned above, intense bands in the fingerprint and the CH bond stretching regions are visible, which were not observed in the photolysis with the low-pressure mercury lamps. These bands are probably due to 2-oxabicyclo[3.2.0]hepta-3,6-diene, a well known product of the oxepin photolysis in solution with light in the visible region of the electromagnetic spectrum:[28,35]



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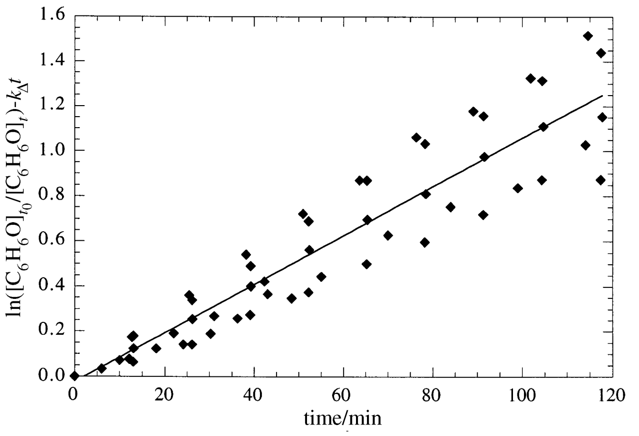

Fig. 6 First-order kinetics plot of the experimental data of the photolysis of benzene oxide/oxepin using the superactinic fluorescent lamps

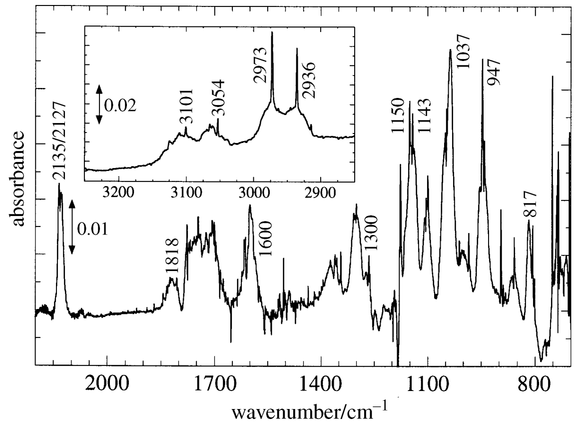

Fig. 7 Residual product spectrum obtained after 2 h irradiation with the superactinic lamps, after subtraction of the absorptions of all identified compounds. The bands centred around 2130 and 1720 cm^{-1} have also been observed in the UV photolysis. Most of the other bands are probably due to 2-oxabicyclo[3.2.0]hepta-3,6-diene.

The photolysis frequency for benzene oxide/oxepin under atmospheric conditions can be estimated from the experiments using the superactinic lamps. This is accomplished by adjusting the value obtained in the reactor to atmospheric conditions by multiplication with the factor: factor = J_{NO_2} (atmosphere)/J_{NO_2} (in the reactor) = (8.5 ± 0.5) × 10^{-3} s^{-1}/(2.7 ± 0.2) × 10^{-3} s^{-1} = 3.15. The atmospheric noontime NO_2 photolysis frequency of J_{NO_2} = (8.5 ± 0.5) × 10^{-3} s^{-1} is typical for July 1 clear sky conditions at a latitude of 40° N. This estimation technique gives a photolysis frequency of $J_{\text{oxepin}} = (5.6 \pm 0.6) \times 10^{-4}$ s^{-1} for benzene oxide/oxepin which corresponds to an atmospheric lifetime of (30 ± 3) min under the chosen conditions.

Another way to estimate upper limits for atmospheric photolysis frequencies is to calculate them from UV–VIS absorption cross-sections, assuming a photolysis quantum yield of unity.[36,37] This procedure leads to a significantly larger photolysis frequency for benzene oxide/oxepin of $J_{\sigma,\text{ oxepin}} = 3.3 \times 10^{-3}$ s^{-1} which corresponds to a photolytic lifetime of only 5.1 min. This is nearly an order of magnitude lower than the estimate from the chamber experiment. The lower photolysis frequency from the chamber studies suggests that the photolysis quantum yield for benzene oxide/oxepin is probably significantly lower than unity.

Despite the uncertainty in the absolute value of the photolysis frequency, the experiments indicate that, under atmospheric conditions, the photolysis lifetime of benzene oxide/oxepin will be short and photolysis will be an important sink for this compound.

OH kinetic studies

The reaction rate coefficient for the reaction of benzene oxide/oxepin with OH radicals was obtained using the competitive kinetic technique relative to reaction with (*E*)-but-2-ene. In Fig. 8, the kinetic data obtained are plotted according to eqn. (III) using a value of $k = 5.6 \times 10^{-5}$ s^{-1} for the first-order losses of benzene oxide/oxepin to the wall or through photolysis. From the data, a rate coefficient $k_{OH} = (10.0 \pm 0.4)$

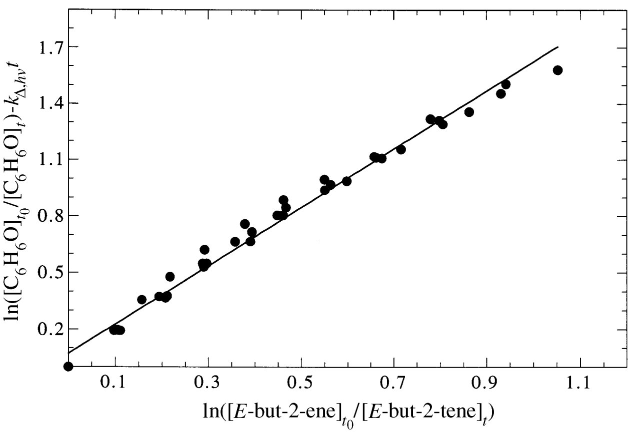

Fig. 8 OH kinetic data for benzene oxide/oxepin, as described in the text

$\times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was obtained for the reaction of OH with benzene oxide/oxepin, which is close to the gas kinetic limit. Assuming a 12 h average OH radical concentration[38,39] of 1.6×10^6 molecules cm^{-3}, a tropospheric lifetime for benzene oxide/oxepin due to reaction with OH radicals of $\tau_{OH} = (105 \pm 4)$ min can be calculated. From a comparison with similar, but non-oxygenated, conjugated alkenes such as 1,3,5-cycloheptatriene ($k_{OH} = 9.74 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) and cyclohexa-1,3-diene ($k_{OH} = 16.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}), a very fast OH radical reaction was expected for this compound.[25]

The very fast reaction observed for benzene oxide/oxepin with OH radicals suggests that addition of OH to one of the double bonds is the dominant process. The rate coefficient determined is *ca.* two orders of magnitude larger than that for benzene with OH and *ca.* one order of magnitude larger than that for toluene and the xylene isomers. This difference can be ascribed to the non-aromatic nature of the conjugated double bonds in benzene oxide/oxepin.

OH product studies

A typical concentration–time profile for benzene oxide/oxepin and the identified products of its reaction with OH radicals is displayed in Fig. 9. The gas-phase FTIR absorption cross-sections used to calculate the concentrations of the hexa-2,4-dienedials have been redetermined using a considerably improved method. The new values represent a significant improvement over the estimates published in an earlier paper from this laboratory.[24] For (*E*,*E*)-hexa-2,4-dienedial, an absorption cross-section of $\sigma_e = (4.00 \pm 0.14) \times 10^{-18}$ cm^2 molecule^{-1} has been determined at 1716 cm^{-1}, for (*E*,*Z*)-hexa-2,4-dienedial, a value of $\sigma_e = (2.68 \pm 0.16) \times 10^{-18}$ cm^2 molecule^{-1} was obtained at 1709 cm^{-1}. No data on the IR absorption cross-sections for (*E*)-butenedial exist in the literature, therefore, a carbonyl absorption cross-section of $\sigma_e = 9.3 \times 10^{-19}$ cm^2 molecule^{-1} has been used to calculate its concentration. This value was determined for acrolein, a structurally similar compound, in this laboratory.

The major products of the OH-initiated oxidation of benzene oxide/oxepin are the (*E*,*Z*)- and (*E*,*E*)-isomers of hexa-2,4-dienedial, **7**. Based on the above absorption cross-sections, a combined yield of (*E*,*Z*)- and (*E*,*E*)-hexa-2,4-dienedial of (105 ± 10)%C was derived from the experiments. The yields have been corrected for the further reaction of the hexa-2,4-dienedials with OH radicals according to the method published by Tuazon and co-workers.[40] This shows that the muconaldehydes are formed in nearly quantitative yield and that any additional reaction channels, *e.g.* formation of the multifunctional compounds proposed by Bartolotti and Edney,[9] must be minor.

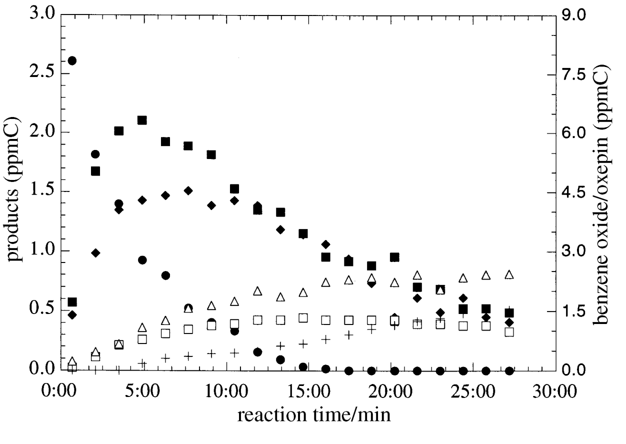

Fig. 9 Concentration–time profiles for the products identified in the OH-initiated oxidation of benzene oxide/oxepin: (●) benzene oxide/oxepin, (■) **7c**, (◆) **7b**, (□) (*E*)-butenedial , (Δ) glyoxal, (+) maleic anhydride. Note the different scales for benzene oxide/oxepin and its oxidation products.

The formation of the hexa-2,4-dienedials can be explained by the mechanism outlined in Fig. 10. The OH radical can attack at the C(2) position of the oxepin isomer. This site is expected to be favoured because it leads to a pentadienyl radical further stabilised by the ring oxygen. This oxepin-OH adduct is expected to undergo ring fragmentation to give an acyclic delocalised radical which can react with molecular oxygen, yielding HO_2 and hexa-2,4-dienedial, **7**. The muconaldehydes can also be formed by addition of OH to the C(3) position of the benzene oxide isomer. The resulting benzene oxide-OH adduct, a propenyl radical, might then ring-fragment at the epoxy group, yielding a hydroxycyclohexadienyl oxyl radical. This intermediate could then undergo a second ring fragmentation to give the same acyclic delocalised radical postulated to arise from fragmentation of the oxepin-OH adduct, see Fig. 10.

It is extremely difficult to speculate on which of these pathways might be dominant. However, the expected greater stability of a pentadienyl-type radical (the oxepin-OH adduct), compared to a propenyl-type radical (the benzene oxide-OH adduct) seems to favour the route starting from oxepin. The possible shift in the benzene oxide/oxepin equilibrium towards oxepin (see above) might be taken as a further indication for a dominance of this route.

From the observed product distribution, it is not possible to say whether (*Z*,*Z*)-hexa-2,4-dienedial, **7a**, is formed initially, or whether the ring-opened benzene oxide/oxepin-OH adduct undergoes isomerisation into the thermodynamically more stable (*E*,*Z*)- and (*E*,*E*)-forms. The latter pathway would lead to the direct formation of **7b** and **7c** from the reaction of O_2 with this radical. **7a** has not been conclusively identified among the products formed in the OH-initiated oxidation of benzene oxide/oxepin. However, this isomer is known to isomerise quickly under the experimental conditions,[24,41] so that its steady state-concentration might have been too low to be detectable by the techniques employed.

In Fig. 11, product spectra of the OH-initiated oxidation of benzene oxide/oxepin are shown, together with reference spectra of the most important products. Note that spectrum (a) and the reference spectra (b) and (d) are scaled down by a factor of three to allow for easier comparison. It is clear from

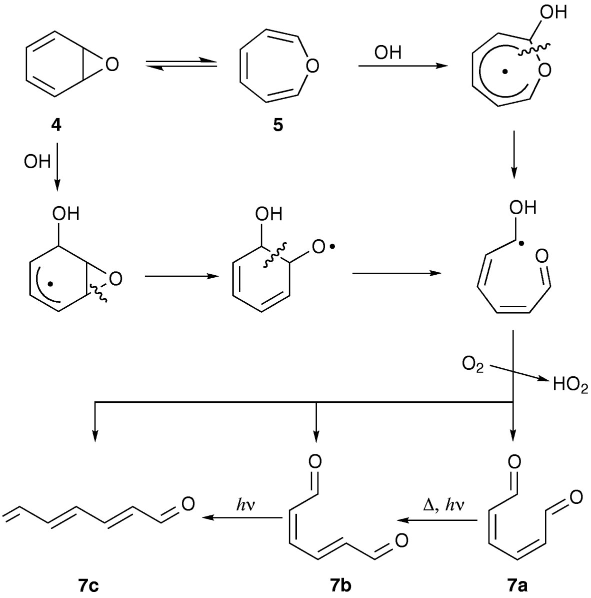

Fig. 10 Possible mechanisms for the OH-initiated oxidation of benzene oxide/oxepin, explaining the observed products

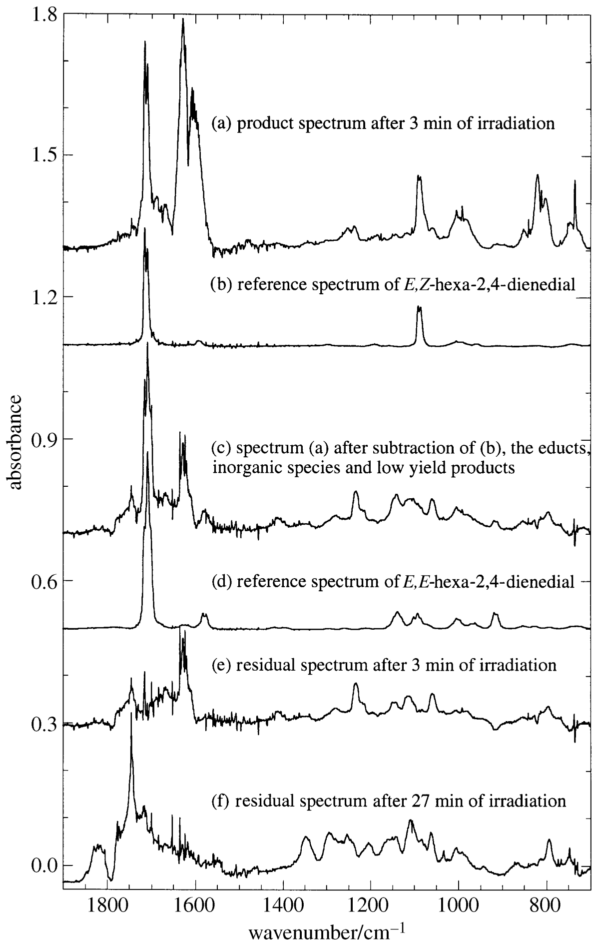

Fig. 11 Product spectra of the OH-initiated oxidation of benzene oxide/oxepin. The spectra clearly indicate that **7b** and **7c** are the main products. Note that spectrum (a) and the reference spectra (b) and (d) are scaled down by a factor of three for clarity.

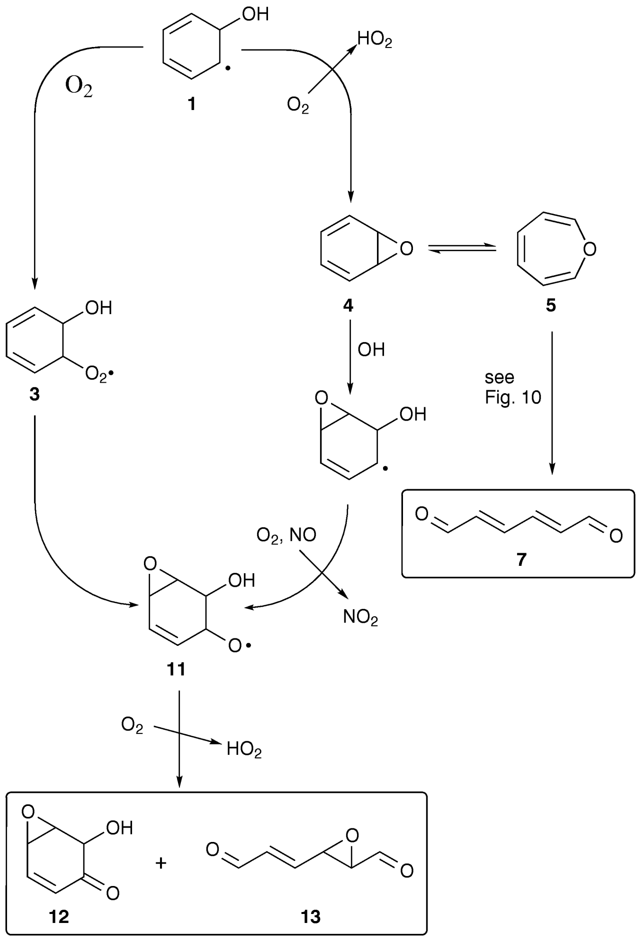

Fig. 12 Possible mechanisms for the formation of **12** and **13** from further reactions of **1**. In the left-hand column, the mechanism recently proposed by Bartolotti and Edney[9] is plotted, the right-hand column shows the mechanism proposed in the present work. Methylated derivatives of compounds plotted in boxes have been observed as photooxidation products of toluene,[15] see text for details. The new mechanism proposed here can explain the formation of these compounds.

Fig. 11 that **7b** and **7c** are the main products of the reaction. The other intense bands visible in spectrum (a) are mainly due to NO_2, methyl nitrite and benzene oxide/oxepin. Spectrum (e) shows the residual absorptions after subtraction of reference spectra of all identified products, the spectrum being recorded after 3 min of irradiation. An analogous spectrum, recorded after 27 min irradiation, is shown in Fig. 11(f). This last spectrum is identical to the residual spectrum obtained in the OH-initiated oxidation of **7b** published in an earlier paper.[24] The evident differences in the residual spectra recorded at different reaction times indicate that a short-lived intermediate species is being formed in comparably low yield. It might be speculated that these are the hydroxyepoxycyclohexenones, **12**, or epoxymuconaldehydes, **13**, proposed by Bartolotti and Edney.[9] Methylated derivatives of such compounds have recently been identified in the photooxidation of toluene, though their yields are highly uncertain.[15] Possible mechanisms for the formation of these compounds are outlined in Fig. 12. Bartolotti and Edney proposed the formation of a hydroxyepoxycyclohexene oxyl radical, **11**, from intramolecular rearrangement of the (short-lived) radical **3**, which in turn was formed by addition of molecular oxygen to **1**. **11**, however, could also be formed by the OH-initiated oxidation of benzene oxide, **4**, and would be in direct competition with the oxidation of benzene oxide/oxepin which leads to muconaldehydes. As indicated in Fig. 12, an OH radical might add to one of the double bonds of benzene oxide, the resulting adduct could then add O_2 to give a peroxyl radical, which can be subsequently converted to give **11**, as proposed by Bartolotti and Edney. This radical can then ring open to give products such as **12** or **13**.

A further possibility is that the observed intermediates are photooxidation products of 2-oxabicyclo[3.2.0]hepta-3,6-diene, a photolysis product of oxepin (see above). However, due to the rapid nature of the OH reaction compared to photolysis under the experimental conditions, this seems unlikely. 2-Oxabicyclo[3.2.0]hepta-3,6-diene could only be formed in low yields, and any secondary product of this compound would have to be comparably stable to be detectable in the photooxidation of benzene oxide/oxepin. This is in contrast to the rapid decay of the intermediate observed in the experiments on the OH-initiated oxidation of benzene oxide/oxepin.

NO_3 kinetic studies

The kinetic data from studies on the reactions of NO_3 with benzene oxide/oxepin are plotted in Fig. 13. A value of $k_{NO_3} = (9.2 \pm 0.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} was obtained. This is similar in magnitude to that obtained for other conjugated cyclic dienes, *e.g.* cyclohexa-1,3-diene and cyclohepta-1,3-diene.

NO_3 product studies

7a and unidentified nitrates have been observed as products of the reaction of nitrate radicals with benzene oxide/oxepin. Fig.

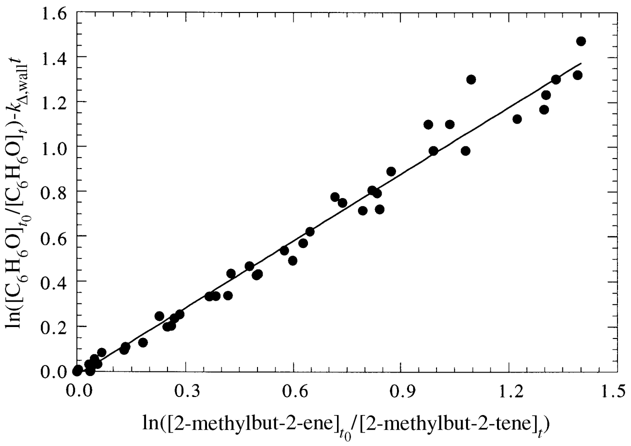

Fig. 13 Kinetic data for the reaction of NO_3 radicals with benzene oxide/oxepin

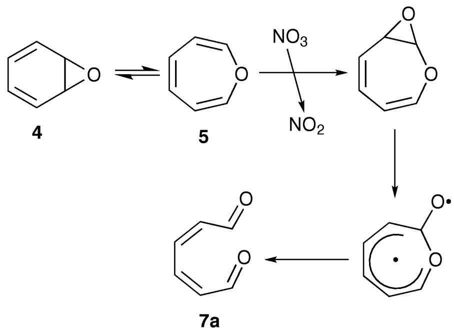

Fig. 15 Possible mechanism for the formation of **7a** in the reaction of benzene oxide/oxepin with NO_3 radicals. Davies and Whitham proposed a similar mechanism for the reaction of benzene oxide/oxepin with peracids in solution.[43]

14 shows spectra obtained during the reaction of benzene oxide/oxepin with NO_3. Spectrum (a) is a product spectrum of the reaction in which only absorptions due to NO_y and benzene oxide/oxepin have been subtracted. The area around 1600 cm^{-1}, where NO_2 exhibits its most intensive absorption band, has been replaced by a straight line, since this compound was present at concentrations well outside the applicability of the Lambert–Beer law. Spectrum (b) is a reference spectrum of **7a** published in an earlier paper.[24] From the similarity of absorption bands it is evident that **7a** is being formed in the reaction of benzene oxide/oxepin with NO_3 radicals. A possible formation mechanism is outlined in Fig. 15. This mechanism is similar to that postulated for the reaction of peracids with benzene oxide/oxepin in solution.[43] The postulated intermediate, 2,3-epoxyoxepin, rapidly undergoes ring opening leading to **7a**. The exact yield of **7a** is uncertain since a determination of its gas-phase FTIR absorption cross-section was not possible, owing to the fast thermal rearrangement of this compound into the more stable (*E*-*Z*)-form. A rough estimate, however, can be made by assuming **7a** to have the same carbonyl absorption cross-section as **7c**. A value of 25%C is thus obtained for the formation yield of **7a** from the reaction of benzene oxide/oxepin with NO_3 radicals. The remaining absorptions, after subtraction of (b) from (a), are depicted in Fig. 14(c). Strong absorption bands in the approximate regions 1700 ± 50, 1290 ± 20 and 800 ± 50 cm^{-1}, as are present in spectrum (c), are characteristic for compounds containing nitrate and peroxynitrate functional groups.[44] In the region above 1700 cm^{-1}, absorptions from carbonyl groups can also be present. Since the reaction of NO_3 radicals with hexa-2,4-dienedials is slow,[24] these carbonyl/nitrate compounds stem entirely from reaction with benzene oxide/oxepin and represent the major fraction of the reactions products. It is obvious from the product spectrum that more than one product is present. The exact identity of the products has not yet been established. However, from the known chemistry of the reactions of NO_3 radicals with alkenes[45] multifunctional organic nitrate compounds are expected, *e.g.* unstable unsaturated nitrooxyperoxynitrate-type compounds, unsaturated nitrooxy-aldehydes or -ketones and possibly also unsaturated dinitrate and hydroxynitrate compounds. Product analyses are planned to determine the identity and yields of the various organic nitrate compounds.

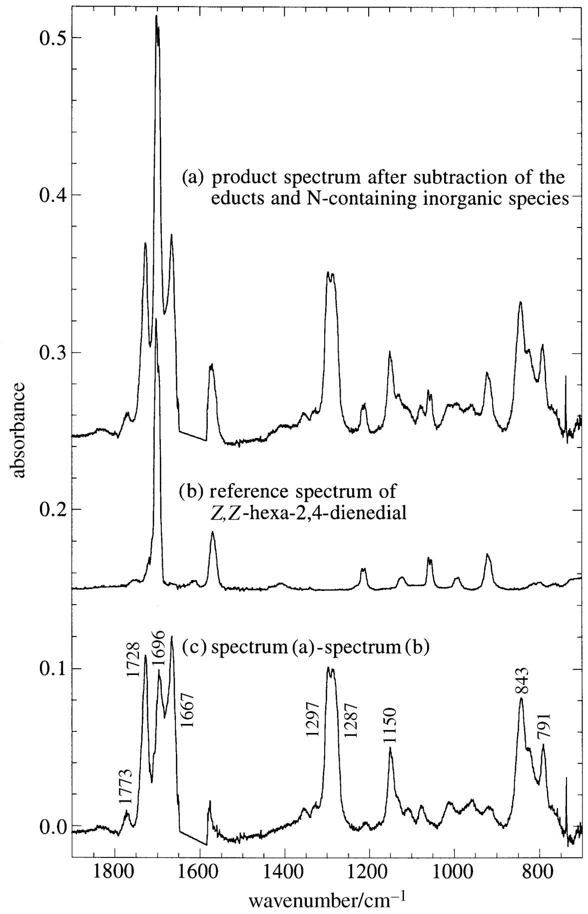

Fig. 14 FTIR product spectra obtained during the reaction of benzene oxide/oxepin with NO_3 radicals. The absorptions due to **7a** are clearly visible.

Possible implications for laboratory investigations and the atmosphere

The emphasis of the work on the newly postulated benzene oxide/oxepin mechanism was twofold. One aim was to establish whether the oxidation of benzene oxide/oxepin is so rapid that this compound might have eluded detection in earlier product studies on the atmospheric oxidation of benzene and, consequently, also the detection of its methylated derivatives in studies of the oxidation of other aromatic hydrocarbons. The other was to see if the photooxidation of benzene oxide/oxepin leads to the products which have been observed in reaction chamber studies of the photooxidation of benzene. In the following discussion, benzene oxide/oxepin is employed as a model substance to represent not only the benzene oxidation but also its methylated derivatives, which may be formed in the oxidation of other aromatic hydrocarbons.

Apart from a tentative assignment by Shepson and coworkers,[17] the intermediate formation of derivatives of benzene oxide/oxepin has not yet been reported in mechanistic studies on the photooxidation of aromatic hydrocarbons. However, the present work has shown that benzene oxide/oxepin reacts rapidly with OH radicals and is also rapidly photolysed. This high reactivity of benzene oxide/oxepin compared to aromatic hydrocarbons will make the identification of benzene oxide/oxepin derivatives extremely difficult in both direct and photoreactor product studies of the photooxidation of aromatic hydrocarbons.

The rapid nature of the equilibrium between benzene oxide and oxepin has important implications for its atmospheric chemistry. If the proposed mechanism for the OH-initiated oxidation of benzene is valid, benzene oxide will be formed initially. However, because of the rapid equilibrium between benzene oxide and oxepin, all further reactions will involve both isomeric species.

The major product of the thermal decomposition and both the UV and visible photolysis of benzene oxide/oxepin is phenol. In sharp contrast, the major products of the OH-initiated oxidation of benzene oxide/oxepin are unsaturated 1,6-dicarbonyls (hexa-2,4-dienedials), whose further reaction leads to 1,2- and unsaturated 1,4-dicarbonyls. Thus, the intermediacy of benzene oxide/oxepin or its derivatives in the oxidation of benzene and other aromatic hydrocarbons can account for the formation of hydroxylated aromatics, unsaturated 1,4-dicarbonyls and α-dicarbonyl products, all of which have been identified in laboratory experiments as important oxidation products of aromatic hydrocarbons.

Since thermal rearrangement and especially photolysis, but not the OH-radical reaction of benzene oxide/oxepin leads to the formation of phenol, the ratio $k_{\mathrm{oxepin}}[\mathrm{OH}]$ to the photolysis frequency under the prevailing light conditions, in laboratory studies as well as in the atmosphere, will play an important role in determining the product yield ratio, especially with regard to phenol formation. Under atmospheric conditions, OH radical reaction and/or photolysis will be the major sinks for benzene oxide/oxepin, thermal decomposition being much too slow to be of any atmospheric significance. For example, taking a 12 h average OH radical concentration of 1.6×10^{6} molecules cm^{-3} gives a loss rate, due to reaction with OH, of $1.6 \times 10^{-4}\ \mathrm{s}^{-1}$ which can be compared with the estimated photolysis frequency of $(5.6 \pm 0.6) \times 10^{-4}\ \mathrm{s}^{-1}$ determined for 40° N latitude for noon July 1. Although the precise photolysis frequency is presently very uncertain, it is still obvious from the values that, in the atmosphere, both OH reaction and photolysis will be important. The relative importance of the pathways will probably be a strong function of the solar irradiance. In laboratory chamber experiments the OH radical concentration can be highly variable ranging from lows of several 10^{6} to well over 10^{7} molecules cm^{-3}. This fact might explain the large degree of scatter in the formation yields of phenolic compounds published in the literature for the oxidation of aromatic hydrocarbons.

One of the main reasons for investigating the reaction of benzene oxide/oxepin with $\mathrm{NO_3}$ radicals was to assess its potential as a possible NO_y sink in the oxidation of aromatic hydrocarbons. In aromatic hydrocarbon–NO_x photooxidation systems studied in photoreactors, a large fraction of the reacted NO_x remains unaccounted for. It was not clear from earlier studies whether this was a chamber artefact or a true loss due to chemical reactions in the system. Recent investigations in the large-scale EUPHORE photoreactor facility in Valencia, Spain support the proposal that the loss is very probably chemical in nature.[46] However, the reactions resulting in the 'NO_y deficiency' have still not been identified. In some models of photooxidant formation in smog chambers, the reaction of phenol/methylated phenols with $\mathrm{NO_3}$ is used as a daytime sink for NO_y in order to regulate the NO_x levels.[47] In smog-chamber experiments, nitrate radical reactions can become very important if high concentrations of NO_x are employed. Because the reaction of benzene oxide/oxepin with $\mathrm{NO_3}$ radicals is so fast, it can be expected to have a similar effect on the concentration of NO_x in the photooxidation of aromatic hydrocarbons as the nitrate radical reaction of phenols currently used, but with very different products. In the atmosphere, however, daytime nitrate radical concentrations are too low to constitute a significant sink, with the possible exception of highly polluted areas. At nighttime, when $[\mathrm{NO_3}]$ can be higher, benzene oxide/oxepin is not expected to be formed from aromatic hydrocarbons due to the very low OH radical levels.

In the present studies on the OH-initiated photooxidation of benzene oxide/oxepin, much higher OH radical concentrations (up to 3×10^{8} molecules cm^{-3}) were produced than are normally observed from the oxidation of alkenes under otherwise identical experimental conditions, indicating that this compound is a potentially copious radical source in photooxidation systems.

Conclusions

In summary, the reaction of OH radicals with aromatic hydrocarbons produces hydroxycyclohexadienyl radicals, the fate of which is presently unknown. Several mechanisms have been proposed for the loss of these radicals but these do not adequately explain all the experimental observations. In the present study, the reaction of $\mathrm{O_2}$ with hydroxycyclohexadienyl radicals to form benzene oxide/oxepin (or derivatives) and $\mathrm{HO_2}$ radicals has been postulated as an alternative mechanism for the photooxidation of aromatic hydrocarbons.

The investigations on the atmospheric chemistry of the postulated intermediate for benzene, benzene oxide/oxepin, have shown that its further oxidation, which involves primarily photolysis and reaction with OH radicals, results in the formation of phenol **2**, Hexa-1,4-dienedials **7**, unsaturated 1,4-dicarbonyls **8** and α-dicarbonyls **9**, the yields of which will be strongly dependent on the relationship between the OH radical level and ambient light conditions. It has also been suggested that the very fast reaction of $\mathrm{NO_3}$ radicals with benzene oxide/oxepin might be responsible for the 'NO_x deficiency' observed in the atmospheric oxidation of aromatic hydrocarbons.

A mechanism involving the intermediate formation of a benzene oxide/oxepin derivative in the oxidation of aromatic hydrocarbons is more consistent with experimental observations than previously proposed mechanisms. However, for validation of the mechanism positive identification of the occurrence of benzene oxide/oxepin derivatives in aromatic hydrocarbon photooxidation systems is necessary.

Financial support by the BMBF, the NERC and the EC is gratefully acknowledged.

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Paper 6/06152D; *Received* 6*th September*, 1996