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Product Study of the OH Radical and Cl Atom Initiated Oxidation of 1,3-Dioxane

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The products of the hydroxyl (OH) radical and chlorine (Cl) atom initiated oxidation of 1,3-dioxane are determined under various reaction conditions in a 50 L teflon reaction chamber using FTIR spectroscopy for analysis. The major products detected in all experiments are (2-oxoethoxy)methyl formate, formic acid and methylene glycol diformate with average molar yields of 0.50 ± 0.05 , 0.41 ± 0.02 and 0.03 ± 0.01 respectively for the OH initiated oxidation in the presence of NO_x. The yields of these products do not vary significantly with O₂ partial pressure or oxidising agent (OH or Cl). However, the

1. Introduction

Ethers are widely used as fuel additives and solvents. The release of these volatile organic compounds (VOCs) into the atmosphere is likely to contribute to the formation of ozone and other components of photochemical smog, particularly in urban areas.^[1] In order to understand and evaluate the impact that these compounds will have on the environment, a detailed understanding of the kinetics and mechanisms for their atmospheric degradation is required.

The main atmospheric fate of saturated ethers following their release into the atmosphere is reaction with hydroxyl (OH) radicals in the gas-phase.^[1,2] Numerous laboratory studies have been conducted on linear and branched ethers and there now exists a relatively large database on the kinetics and mechanisms for their atmospheric reactivity.^[2] However, the cyclic ethers have received less attention. Although the kinetics of the OH reactions with cyclic ethers has been investigated in detail,^[3,4] mechanistic studies have only been reported for 1,4dioxane,^[5,6] 1,3-dioxolane,^[7] 1,3,5-trioxane^[8] and tetrahydrofuran.^[2] Ballesteros et al.^[9] have also investigated the kinetics and mechanisms for the reaction of chlorine (Cl) atoms with tetrahydropyran. The aim of this work is to investigate the atmospheric oxidation mechanism for another cyclic ether, 1,3-dioxane. Experiments have been performed using both OH radicals and CI atoms to initiate the oxidation process in the presence and absence of nitrogen oxides (NO_x). The results are used to derive an atmospheric degradation mechanism for 1,3-dioxane and also provide further insights into the reactivity of the oxygenated alkoxy radical intermediates.

Experimental Section

Experiments were performed at 298 ± 2 K and a total pressure of 760 ± 10 torr of mixtures of ultra-pure nitrogen and oxygen in a

yield of formic acid decreased by at least a factor of two in the absence of NO_x . The results of these experiments are used to elucidate a simplified gas-phase atmospheric degradation scheme for 1,3-dioxane and also provide valuable information on the atmospheric fate of the cyclic and linear alkoxy radicals produced in these and similar reactions. The available experimental data suggests that the relative importance of the competing pathways (reaction with O_2 and ring opening by C–C or C–O bond fission) is a strong function of the ring strain in the cycloalkoxy radicals.

collapsible 50 L teflon reaction vessel. A detailed description of the apparatus and the general experimental procedures is provided elsewhere.^[10,11] Measured amounts of reactants were flushed from calibrated pyrex bulbs into the reaction vessel by a stream of ultrapure nitrogen. The reactor was then filled to its full volume with mixtures of N₂ and O₂ and the contents were allowed to mix for at least 30 min prior to initiation of the reactions. For hydroxyl radical initiated oxidation, photolysis of either O₃/H₂O mixtures, H₂O₂ or CH₃ONO were used as the radical precursor. Ozone was produced by passing zero-grade oxygen through an ozone generator (Monitor Labs) directly into the reaction vessel at a flow of 1 Lmin^{-1} for 10 min. Water, (0.5 mL) triply distilled was injected directly into the chamber. The generation of OH radicals was initiated by the use of 10 lamps (Philips TUV 15W) with an intensity maximum at 254 nm. [Eqs. (1) and (2)]

$$O_3 + h\nu(\lambda = 254 \text{ nm}) \rightarrow O(^1\text{D}) + O_2 \tag{1}$$

$$O(^{1}D) + H_{2}O \rightarrow OH + OH$$
⁽²⁾

Photolysis of H_2O_2 (0.1 mL, 30 wt %) was also initiated with the Philips TUV lamps. [Eq. (3)]

$$H_2O_2 + h\nu \ (\lambda = 254 \text{ nm}) \rightarrow OH + OH$$
 (3)

Methyl nitrite was made by adding a solution of sulfuric acid (50% in triply distilled water) to a saturated solution of methanol under nitrogen. The products of this reaction were carried by a stream of nitrogen through a solution of sodium hydroxide, to remove excess acid, and calcium chloride to remove water and unreacted

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methanol. The methyl nitrite was collected at 178 K and stored in the dark. Photolysis of methyl nitrite was achieved through the use of 5 "sun" lamps (Philips TL 20/09) and 5 "black" lamps (Philips TL 20/08). [Eqs. (4)–(6)]

$$CH_3ONO + h\nu \ (\lambda = 300 - 450 \text{ nm}) \rightarrow CH_3O + NO \tag{4}$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO \tag{5}$$

$$HO_2 + NO \rightarrow OH + NO_2$$
 (6)

Generation of Cl atoms was achieved by photolysis of Cl_2 using a combination of the "sun" and "black" lamps. [Eq. (7)]

$$Cl_2 + h\nu \ (\lambda = 300 - 450 \text{ nm}) \rightarrow Cl + Cl \tag{7}$$

A Mattson Polaris FTIR spectrometer was used to obtain concentration-time profiles for reactants and products at regular intervals during the experiments. The contents of the chamber were sampled into an evacuable 2 L cell containing a multi-pass White mirror arrangement mounted in the cavity of the spectrometer. Prior to sampling, the cell was evacuated using a rotary pump. Spectra were recorded using a 6.5 m pathlength over the wavelength range 500–3500 cm⁻¹ with a resolution of 2 cm⁻¹. The spectra were derived from 128 co-added spectra using Mattson FIRST[™] software. Reactants and products were identified by comparison of the FTIR spectra with those of authentic samples. Reference spectra and calibration curves were obtained by expanding measured pressures of pure compounds into the cell. Complex spectra were analysed by successively subtracting absorption bands in the reference spectra of known compounds.

The chemicals used Herein, their manufacturer and stated purity were: 1,3-dioxane (Aldrich, 97%), hydrogen peroxide (Aldrich, 30wt% in water), chlorine (Aldrich > 99.5%), nitric oxide (Aldrich, 98.5%), carbon monoxide (Aldrich, 99%), 1,3,5-trioxane (Aldrich, > 99%), formic acid (Aldrich, 99.5%). Two of the expected atmospheric oxidation products of 1,3-dioxane, (2-oxoethoxy)methyl formate and 1,3-dioxan-2-one, were not commercially available and had to be synthesised. (2-Oxoethoxy)methyl formate (HC(O)O-CH₂OCH₂C(O)H), was synthesised according to the literature.^[12] Glycerol formal was added to p-tosyl chloride in pyridine to make 5-tosyl oxy-1,3-dioxane. Concentrated hydrochloric acid was then added to this mixture and heated gently. The mixture was distilled under vacuum to produce 4H-[1,3]-dioxine as the remaining colourless liquid. Ozone was then passed over this at a flow rate of 1 Lmin⁻¹ for 2 h and the resulting mixture was an oily yellow liquid, which was confirmed to be HC(O)OCH2OCH2C(O)H by FTIR spectroscopy. 1,3-Dioxan-2-one was synthesized according to the method of Searles et al.^[13] Dimethyl carbonate and sodium 1,3-propanediol were added to a round bottom flask and heated to 353 K until the sodium was dissolved. The reaction mixture was then heated to 403 K and after 30 min the temperature was raised to 443 K. The mixture was distilled under vacuum and then placed on a rotary evaporator to remove any excess ethanol. The residue was dissolved in benzene, washed with water and dried over CaCl₂. The benzene was then removed in vacuo and the resulting colourless liquid was distilled and identified as 1,3-dioxan-2-one (purity > 99%) by NMR and FTIR spectroscopy.

2. Results

The hydroxyl radical and chlorine atom initiated oxidation of 1,3-dioxane was studied at various partial pressures of O_2 in the presence and absence of NO_x and at a temperature of 298 ± 2 K and atmospheric pressure. Details of the initial experimental conditions are provided in Table 1. FTIR spectra from one of the experiments are shown in Figure 1. The following species were detected and quantified in all experiments; (2-ox-oethoxy)methyl formate [HC(O)OCH₂OCH₂C(O)H], formic acid (HCOOH), carbon monoxide (CO) and methylene glycol difor-



Figure 1. FTIR spectra obtained for a 1,3-dioxane/Cl₂/air mixture: a) before photolysis, b) after 12 min photolysis and after successive subtraction of c) 1,3-dioxane, d) HC(O)OH and CO, e) HC(O)OCH₂OCH₂C(O)H, HCI and CO₂, and f) HC(O)OCH₂OC(O)H.

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Precursors ^a	[1,3-dioxane]ª	[O ₂] ^b	[NO]ª	Y(HC(O)OCH ₂ OCH ₂ C(O)H) ^c	Y(HC(O)OH) ^c	Y(HC(O)OCH₂OC(O)H) ^c
O ₃ (50); H ₂ O (5000)	133	152		0.51±0.03	0.14±0.02	0.06±0.01
H ₂ O ₂ (2000)	123	23	60	0.52±0.05	0.38 ± 0.02	0.03 ± 0.01
CH ₃ ONO (100)	51	23	20	0.47 ± 0.04	0.43 ± 0.02	0.03 ± 0.01
Cl ₂ (120)	124	23		0.64±0.03	0.24 ± 0.01	0.03 ± 0.01
Cl ₂ (120)	125	152		0.62±0.04	0.23 ± 0.03	0.02 ± 0.01
Cl ₂ (120)	114	760		0.59 ± 0.04	0.22 ± 0.02	0.03 ± 0.01
Cl ₂ (90)	126	23	60	0.52 ± 0.09	0.40 ± 0.03	0.03 ± 0.01
[a] Mixing ratio in ppmV. [b] Partial pressure in Torr. [c] Y(product) indicates the observed yield of the product. Errors quoted are twice the standard devia- tion and represent precision only.						

mate, $[HC(O)OCH_2OC(O)H]$. Although two of these products, (2-oxoethoxy)methyl formate and methylene glycol diformate, possess very similar FTIR spectra, as indicated by spectra d and e in Figure 1, there are distinguishable differences in the absorption bands in the 1600–1800 cm⁻¹ and 1000–1200 cm⁻¹ regions to enable satisfactory subtraction of the spectra. One of the expected products, 1,3-dioxan-2-one, was not detected in any of the FTIR spectra and it should be noted that in all experiments, the residual spectrum, arising from subtraction of all known reactants and products contained very few absorption features, thus indicating that all major products had been accounted for.

Representative concentration-time and product yield plots are shown in Figures 2 and 3 respectively. The concentration of HC(O)OCH₂OC(O)H was determined using the FTIR product



Figure 2. Concentration-time profile for the Cl atom initiated oxidation of 1,3-dioxane (124 ppmV) in purified air at 760 ± 10 Torr and 298 ± 2 K.

spectrum generated from the Cl atom initiated oxidation of 1,3,5-trioxane in the presence of NO_x and assuming a 100% yield.^[8] The yield plots for HC(O)OCH₂OCH₂C(O)H, HC(O)-OCH₂OC(O)H and HCOOH are linear indicating that these compounds are primary products of the reaction and are not removed to any significant extent during the timescale of the experiments. Their yields were determined from a linear least squares fit of the data for reactant conversions < 50%. As indicated in Figure 3, the formation of CO shows a non-linear re-



Figure 3. Product yield plot for the Cl atom initiated oxidation of 1,3-dioxane (124 ppmV) in purified air at 760 ± 10 Torr and 298 ± 2 K.

sponse at longer reaction times, thereby indicating that it is most likely a secondary product.

3. Discussion

The observed product distributions can be used to elucidate the importance of various possible reaction pathways for the photooxidation of 1,3-dioxane. Hydroxyl radicals or Cl atoms can abstract a hydrogen atom from one of three possible reaction sites in 1,3-dioxane. Three alkyl radicals may be produced which react with O₂ to produce the corresponding peroxy radicals and, in the presence of NO_x react to form the corresponding alkoxy radicals. The possible reaction pathways for these three alkoxy radicals (**I**, **II** and **III**) in the presence of NO_x are shown in the reaction schemes given in Figures 4–6. These reaction schemes are based on the current knowledge on the reactivity of alkoxy radicals^[14] and, in particular, on the observed reactivity of cyclic alkoxy radicals produced during the atmospheric oxidation of cyclic ethers.^[2,5–9]

Previous studies of the atmospheric oxidation of ethers indicate that the reaction mainly proceeds by H-atom abstraction from a carbon atom in the α -position to the O atoms.^[2] The reaction scheme for this pathway is shown in Figure 4. Hydrogen atom abstraction from this site produces alkoxy radical I, which can react with O2 or decompose via cleavage of the C-C or C-O bond. Fission of the C-O bond is much less energetically favourable than cleavage of the C-C bond, and is unlikely to be important for this radical.^[2] The expected product of the reaction with O₂ is 1,3-dioxan-4-one. However, there was no evidence for the formation of this species in the FTIR spectra, even at high partial pressures of O2, indicating that, like the principal alkoxy radical produced during the photooxidation of 1,4-dioxane,^[5,6] cleavage of the C-C bond appears to be the sole reaction pathway. The resulting ring-opened radical is oxidised to the alkoxy radical la which can react with O₂ to form the major product, (2-oxoethoxy)methyl formate, undergo 1,5-H shift isomerisation and further oxidation to produce radical Ib, or decompose via C-C bond scission. The latter reaction yields the minor product methylene glycol diformate and formaldehyde. By analogy with the radical chemistry observed in the photooxidation of cyclohexane,^[15] radical **Ib** may undergo further isomerisation to produce hydroxy(2-oxoethoxy)methyl formate, though, the lack of an absorption band in the O-H stretching region at ca. 3600 cm⁻¹ indicates that this pathway is of minor importance. Alternatively, because it is of the general structure RC(O)OCH(O·)R', radical Ib may also undergo an $\alpha\text{-ester}$ rearrangement to produce RC(O)OH and the carbonyl radical R'(C·)O.^[14, 16] As shown in Figure 4, this reaction pathway would produce formic acid, CO₂ and glycolaldehyde. The α -ester rearrangement of radical **Ib** is therefore a possible source of the formic acid detected in these experiments. Although the co-product glycolaldehyde was not detected in the FTIR spectra, this compound is reactive towards both OH and Cl and may also be photolysed under the conditions employed in the experiments to produce formaldehyde and CO.[17,18] Formaldehyde was observed in most experiments but only at levels below the quantification limit - this compound is also

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Figure 4. Mechanism for the OH/Cl initiated oxidation of 1,3-dioxane in the presence of NO_x: attack at a $-CH_2$ - site in the α -position to an ether group.

expected to undergo rapid photolysis and reaction with OH and Cl to produce CO.^[19] Thus, the further reaction of glycolaldehyde and formaldehyde could be a possible source of CO, which was observed as a secondary product in these experiments.

As indicated in Table 1, the yield of formic acid increased by at least a factor of two when the atmospheric oxidation of 1,3dioxane was performed in the presence of NO_x. This suggests that the α -ester rearrangement of radical **Ib** is more important when the radicals were produced from the RO₂+NO reaction than via the self-reaction of peroxy radicals. A similar effect was observed Wallington et al.^[20] in the atmospheric oxidation of methyl formate and was attributed to the formation of vibrationally excited radicals in the RO₂+NO reaction.

Hydrogen atom abstraction from the $-CH_2-$ group in the β -position to both O atoms results in radical II, which may also undergo C-C bond cleavage or reaction with O₂, Figure 5. There is no evidence for the latter pathway from FTIR spectra. Cleavage of the C-C bond results in formation of radical IIa which cannot undergo isomerisation via a 1,5 H-atom shift or

an α -ester rearrangement. Reaction with O_2 to produce the major product (2-oxoethoxy)methyl formate is thus the most likely pathway. However, based on the fact that H-atom abstraction from the α -position is favoured^[2] and that there are two such sites in 1,3-dioxane, it seems likely that attack at the β -position only makes a minor contribution to the observed yield of (2-oxoethoxy)methyl formate.

Hydrogen atom abstraction from the -OCH₂Osite in 1,3-dioxane results in the production of alkoxy radical III, as shown in Figure 6. Reaction with O₂ and C-O bond cleavage are the only possible pathways for this radical, since C-C bond cleavage and isomerisation are not possible.^[14] The product of the reaction with O₂ is 1,3-dioxan-2-one, however, there was no evidence for the formation of this species by FTIR spectroscopy, indicating that this is a very minor pathway. Cleavage of the C-O bond produces radical Illa which can either react with O₂ to produce 3-oxopropyl formate or undergo C--C bond cleavage to eventually form 2-oxoethyl formate. Assuming that radical IIIa behaves in a similar manner to its analogue in the cyclohexane system, reaction with O₂ is expected to be an order of magnitude faster.[15] Again, there was no evidence for the formation of 3oxopropyl formate or 2-oxoethyl formate in the FTIR product spectra. It is possible that any absorption features due to these products were below the detection limits of the analytical method. On the other hand, because these compounds are very similar in structure to the major product, (2-oxoethoxy)methyl formate, they may also have very similar infrared absorption bands which could have been inadvertently subtracted out. In the absence of authentic reference



Figure 5. Mechanism for the OH/Cl initiated oxidation of 1,3-dioxane in the presence of NO_x: attack at the $-CH_2$ - site in the β -position to both ether groups.

3983



Figure 6. Mechanism for the OH/Cl initiated oxidation of 1,3-dioxane in the presence of NO_x: attack at the $-CH_2$ - site in the α -position to both ether groups.

spectra for 3-oxopropyl formate or 2-oxoethyl formate it is not possible to confirm this. Although the formation of these formates cannot be ruled out, they are highly unlikely to be major products since attack at the $-OCH_2O-$ site is only expected to contribute less than 20% to the overall reactivity of 1,3-dioxane,^[4,7].

A number of reaction parameters were varied during the set of experiments, as indicated in Table 1. The yields of the two main products were found to be slightly higher when Cl atoms were used to initiate the oxidation process, indicating that there may be a small difference in the relative proportions with which OH and Cl attack the three reactive sites in 1,3-dioxane. However, varying O₂ partial pressure had no noticeable effect on the product yields, indicating that, in particular, the formation of (2-oxoethoxy)methyl formate is not very sensitive to this parameter. The only significant effect is the observed increase in formic acid yields in the presence of NO_x, which has been explained above. In the absence of NO_x, the peroxy radicals can only react with each other or HO₂, Figure 7. The peroxy radical self-reactions can lead to the formation of alkoxy radicals or molecular products, while reaction with HO₂ normally produces hydroperoxides.^[1] The lack of hydroperoxide absorption bands in the FTIR spectra suggests that the RO₂ + HO₂ reactions did not lead to the formation of stable products or that the hydroperoxides underwent further reaction. Nevertheless, since the product yields are not greatly affected by NO_{x} , it appears that the major fate of the peroxy radicals in the absence of NO_x is via self-reaction to give the corresponding alkoxy radicals.



Figure 7. Mechanism for the OH/Cl initiated oxidation of 1,3-dioxane in the absence of NO_x: attack at a $-CH_2$ - site in the α -position to an ether group.

It is of interest to compare the reactivity of radicals I, II and III with other cyclic alkoxy radicals generated during the atmospheric degradation of cycloalkanes and other cycloethers. Under ambient conditions the cyclohexoxy radical produced from cyclohexane reacts directly with O₂ to give cyclohexanone with yields of 25-39% and by C-C bond cleavage leading to ring opening products.^[15,21-23] In contrast, cyclopentoxy and cycloheptoxy radicals almost exclusively react by ring opening, and the yields of the corresponding cycloalkanones are $<5\,\%.^{\scriptscriptstyle [15,21,23]}.$ Isomerisation of cycloalkoxy radicals is unlikely to be important due to steric limitations. The difference in the behaviour of the C_5-C_7 cycloalkoxy radicals can be rationalised in terms of ring strain energies. In this work, the ring strain energies for the cycloalkoxy radicals have been calculated from the difference in the experimentally reported enthalpies of formation in the gas phase at 298 K,^[24] and those estimated from the addition of the group contributions to $\Delta H_{\rm f}^{\rm o}$ obtained using thermochemical data from linear molecules.^[25] Using this methodology, the ring strain energy in the cyclohexoxy radical is close to zero and for the 5- and 7-membered cycloalkoxy radicals is approximately 25 kJ mol⁻¹. The lack of ring strain in the cyclohexoxy radical means that reaction with O₂ and C-C bond cleavage are competitive processes. However, as first discussed by Takagi et al., [21] the added ring strain in the C₅ and C₇ cycloalkoxy radicals lowers the enthalpy of the ring-opening pathway, leading to an approximate 100-fold increase in the rate coefficient for cyclopentoxy ring-opening compared to that for cyclohexoxy.

The presence of O atoms in the ring system causes an increase in the ring strain energy of the corresponding cylcoalkoxy radicals. For example, the C₆ cycloalkoxy radical produced via H-atom abstraction from the CH₂ groups α to the O atom in tetrahydropyran have an estimated ring strain energy of almost 5 kJ mol⁻¹. However this does not appear to represent a significant barrier as the radical reacts mainly with O₂ to form δ -valerolactone, with little evidence for ring opening.^[9] In contrast, the strained (≈ 20 kJ mol⁻¹) 5-membered ring cycloalkoxy radicals formed from tetrahydrofuran decompose mainly by C–C bond fission leading to ring opening and the production of alkyl radicals containing the formate group.^[2]

Using the method outlined above, the ring strain in the 6membered cyclic diethers 1,4-dioxane and 1,3-dioxane is calcu-



Figure 8. Proposed mechanism for the formation of methylene glycol diformate from the atmospheric oxidation of (2-oxoethoxy)methyl formate.

lated to be around 15 kJ mol⁻¹. The higher strain energy in these compounds makes reaction with O₂ considerably less favourable and ring opening is therefore the sole reaction pathway for the cycloalkoxy radicals. As outlined above, fission of the C--C bond is the dominant pathway. However, in cases where this pathway is not possible, for example, radical III, C–O cleavage is generally preferred over reaction with O₂. The sole cycloalkoxy radical produced during the atmospheric oxidation of 1,3,5-trioxane also undergoes C-O bond cleavage rather than reaction with $O_2^{[8]}$ and is thus consistent with the high strain energy of this triether (\approx 30 kJ mol⁻¹). In contrast, Sauer et al.^[7] reported that the cycloalkoxy radical generated by H-atom abstraction from the -OCH₂O- group in 1,3-dioxolane preferentially reacts with molecular oxygen to form a cyclic carbonyl compound, despite having an estimated ring strain energy of around 30 kJ mol⁻¹. This is the only instance where reaction with O₂ appears to be a favourable reaction pathway for the highly strained C₅ cycloalkoxy radicals.

4. Conclusions

The atmospheric oxidation of 1,3-dioxane generates (2-oxoethoxy)methyl formate and formic acid as major products with average molar yields of 0.50 ± 0.05 and 0.41 ± 0.02 respectively for the OH initiated oxidation in the presence of NO_x. Methylene glycol diformate is also observed a primary product with an average yield of 0.03 ± 0.01 . The yields of these products do not vary significantly with O₂ partial pressure or oxidising agent (OH or Cl). However, the yield of formic acid decreases

by at least a factor of two in the absence of NO_x. The results indicate that the principal mode of attack is H-atom abstraction from a carbon atom in the α -position to the O atoms followed by C–C bond cleavage of the resulting cycloalkoxy radical, leading to the formation of (2-oxoethoxy)methyl formate, formic acid and methylene glycol diformate. In the atmosphere, further oxidation of (2-oxoethoxy)methyl formate is expected to produce methylene glycol diformate and CO, Figure 8. Methylene glycol diformate is relatively unreactive towards OH radicals^[7] and is thus unlikely to participate in gasphase reactions in urban air masses. The eventual fate of this compound is likely to be uptake by atmospheric water droplets followed by further processing and rainout.

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