Atmospheric Oxidation of Ethers Under High and Low NO$_x$ Conditions

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Introduction

The photooxidation of diethyl ether (C$_2$H$_5$OC$_2$H$_5$) and diisopropyl ether, (CH$_3$)$_2$CHOCH(CH$_3$)$_2$, in the presence of NO$_x$ was studied at the European Photoreactor (EUPHORE) in May 1998. The main objective of the experiments was to validate the degradation mechanisms that are based on data obtained from laboratory photoreactor studies. For diisopropyl ether, the experiments provided product yield data that differed significantly from that obtained in conventional photoreactor studies. In order to elucidate further mechanistic information, the photooxidation of diisopropyl ether was studied again in July 1998 in the presence and absence of NO$_x$.

Experimental

Photooxidation studies of diethyl ether (DEE) and diisopropyl ether (DIPE) were performed in Chambers A and B of the EUPHORE facility. Both chambers had a volume of about 195,000 litres. For DEE, photooxidation was only performed in the presence of NO$_x$, whilst for DIPE, reactions were performed in the presence and absence of NO$_x$ using the photolysis of HONO and H$_2$O$_2$ as the source of hydroxyl radicals respectively. For the photoxidation of DIPE in the presence of NO$_x$, two experiments were performed;

(i)   "normal NO$_x$"conditions, where a single injection of *ca.* 150 ppb of NO was made at the start of the experiment

(ii)   "high NO$_x$" conditions, where several injections of NO were made during the first few hours of the experiment to ensure that NO was present throughout the whole reaction.

Measured volumes of gaseous and liquid samples were introduced into the chambers *via* a stream of purified air and H_2O_2 (30% w/w) was added using a nebulizer. Two mixing fans, housed in the chambers, were used to achieve rapid mixing of reactants. The loss of reactants and formation of products was monitored using FTIR spectroscopy (Nicolet Magna 550 spectrometer). Infrared spectra were obtained *in situ* by long-path absorption, with a resolution of 1 cm^{-1} and using pathlengths of 326.8 m (Chamber A) and 553.5 m (Chamber B). Additional quantitative analysis for experiments performed in Chamber B was provided by GC-PID and HPLC. The reactants and products were quantified using calibrated reference spectra which were obtained by introducing known volumes of materials into the chambers.

The concentration of reactants and products decreased through chemical processes and also due to leakage from the chambers. The leak rate was determined daily by adding an unreactive tracer gas (SF_6) and measuring its loss by FTIR spectroscopy. The temperature inside the chambers was continuously monitored by thermocouples and the intensity of sunlight was measured using the two $J(NO_2)$ radiometers located in Chamber A. Ozone and NO_x concentrations were continuously monitored using chemiluminescent analysers.

Results and Discussion

Diethyl ether (DEE)

The oxidation of DEE in the presence of NO_x at EUPHORE yielded ethyl formate (EF), C_2H_5OCHO, ethyl acetate (EA), $C_2H_5OC(O)CH_3$, and HCHO as products. Their yields are given in Table 1 together with the results obtained from similar experiments carried out in a ~ 50 L reaction vessel in our laboratory and available literature data. A simplified mechanism for the atmospheric oxidation of DEE in the presence of NO_x is shown in Scheme 1. Studies of the OH radical initiated oxidation of alkanes have shown that abstraction of a secondary hydrogen atom occurs around 95% of the time (Kwok and Atkinson, 1995). For simplification purposes, abstraction from the CH_3 group has been omitted from the mechanism shown in Scheme 1.

Table 1.   Summary of the product yields for the atmospheric oxidation of DEE.

Conditions	EF[a,b]	EA[a,b]	CH$_3$CHO[b]	Reference
Air/NO$_x$	0.72 ± 0.03	0.12 ± 0.01	not detected	This work (EUPHORE)
N$_2$/O$_2$ (3%)/H$_2$O$_2$/NO	0.79 ± 0.04	0.11 ± 0.04	not detected	This work (Dublin)
Air/CH$_3$ONO/NO	0.92 ± 0.06	< 0.05	< 0.05	Wallington and Japar, 1991
Air/HONO/NO$_x$	0.66 ± 0.14	0.04 ± 0.03	0.08 ± 0.02	Eberhard et al., 1993

[a] EF = C$_2$H$_5$OCHO ; EA = C$_2$H$_5$OC(O)CH$_3$
[b] errors are twice the standard deviation and represent precision only.

Scheme 1.   Simplified mechanism for the atmospheric oxidation of diethyl ether in the presence of NO$_x$.

ethyl acetate

ethyl formate   + CH$_3$·

HCHO

formaldehyde
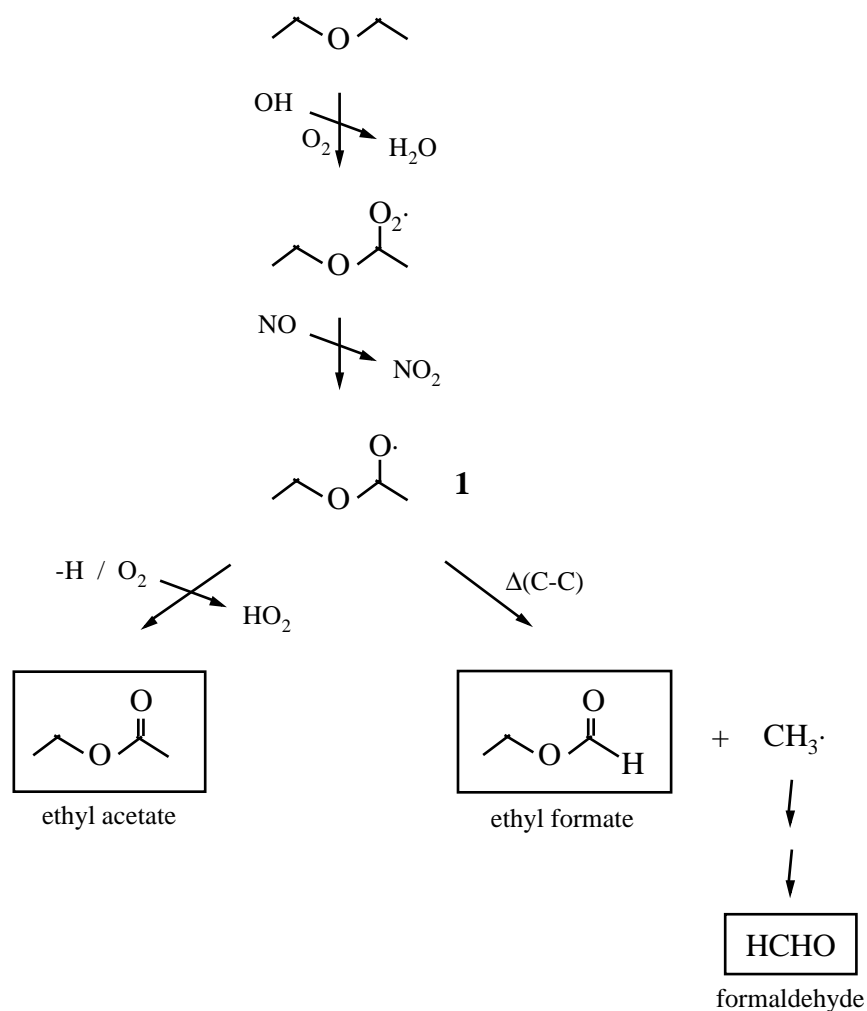
The sum of the yields of EF and EA are *ca.* 90% for each experiment. Since abstraction of a secondary hydrogen is expected to occur 95% of the time, this suggests that any other possible reactions of the alkoxy radical **1**, such as isomerisation, are of little importance. However, the residual IR spectrum contains weak bands in the C=O stretching region that may be due to products formed as a result of H-atom abstraction from the $-CH_3$ group (*e.g.* $C_2H_5OCH_2CHO$). A comparison of the results from the present study with those obtained in conventional laboratory studies is provided in Table 1. In all cases EF was identified as the major product. The EF yield calculated from this work is consistent with that determined in small reactor studies performed in our laboratory and that of Eberhard *et al.*, but somewhat lower than that determined by Wallington and Japar. Eberhard *et al.* also identified EA and CH_3CHO as primary products, but Wallington and Japar did not identify either of these products and set upper limits of 0.05 for their yields. The yield of EA obtained from this work is higher than that determined by Eberhard *et al.* CH_3CHO was not detected as a product in this work.

Diisopropyl Ether (DIPE)

The concentration-time profile for the reaction for DIPE under "normal NO_x" conditions is shown in Figure 1. Isopropyl acetate (IPAc), formaldehyde and acetone were all detected as products. Acetone is a relatively weak infrared absorber and was difficult to measure using FTIR spectroscopy. However, it was detected and quantified using GC-PID and HPLC. The rate of formation of the products, as reflected in the shape of their concentration-time profiles, is somewhat unusual. In the early stages of the experiment, whilst NO was present in relatively high concentration, only isopropyl acetate and formaldehyde were observed as products. However, as the concentration of NO decreased due to reactions with peroxy radicals, acetone began to form. Finally, under very low NO concentrations, acetone appeared to be the sole product. Clearly, two different regimes were involved in the reaction, which depended on the presence or absence of NO. In order to investigate these two regimes in isolation, experiments were carried out under "high NO_x" conditions and also in the absence of NO_x using H_2O_2 as the hydroxyl radical precursor. The products identified in the three experiments performed on DIPE are summarised in Table 2.

Table 2.   Summary of the products and their yields for the atmospheric oxidation of DIPE.

Conditions	Isopropyl acetate[a]	Acetone[a]	References
Air / "high NO$_x$"	1.01 ± 0.02	< 0.10	This work
Air / H$_2$O$_2$	< 0.03	1.05 ± 0.11	This work
Air / "normal NO$_x$"	0.89 ± 0.09 [b]	0.93 ± 0.13 [c]	This work
Air/CH$_3$ONO/NO	1.05 ± 0.06	Not detected	Wallington *et al.*, 1993

[a] errors are twice the standard deviation and represent precision only.
[b] in the presence of NO (9:00 - 12:00)
[c] in the absence of NO (13:00 - 15:50)

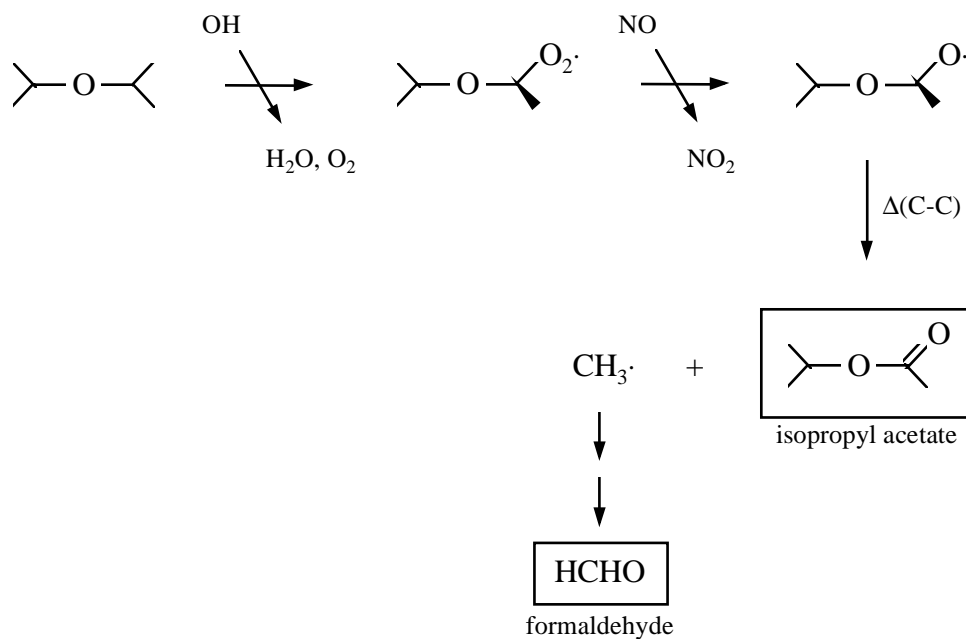**Scheme 2.**   Simplified mechanism for the atmospheric oxidation of diisopropyl ether in the presence of NO$_x$.
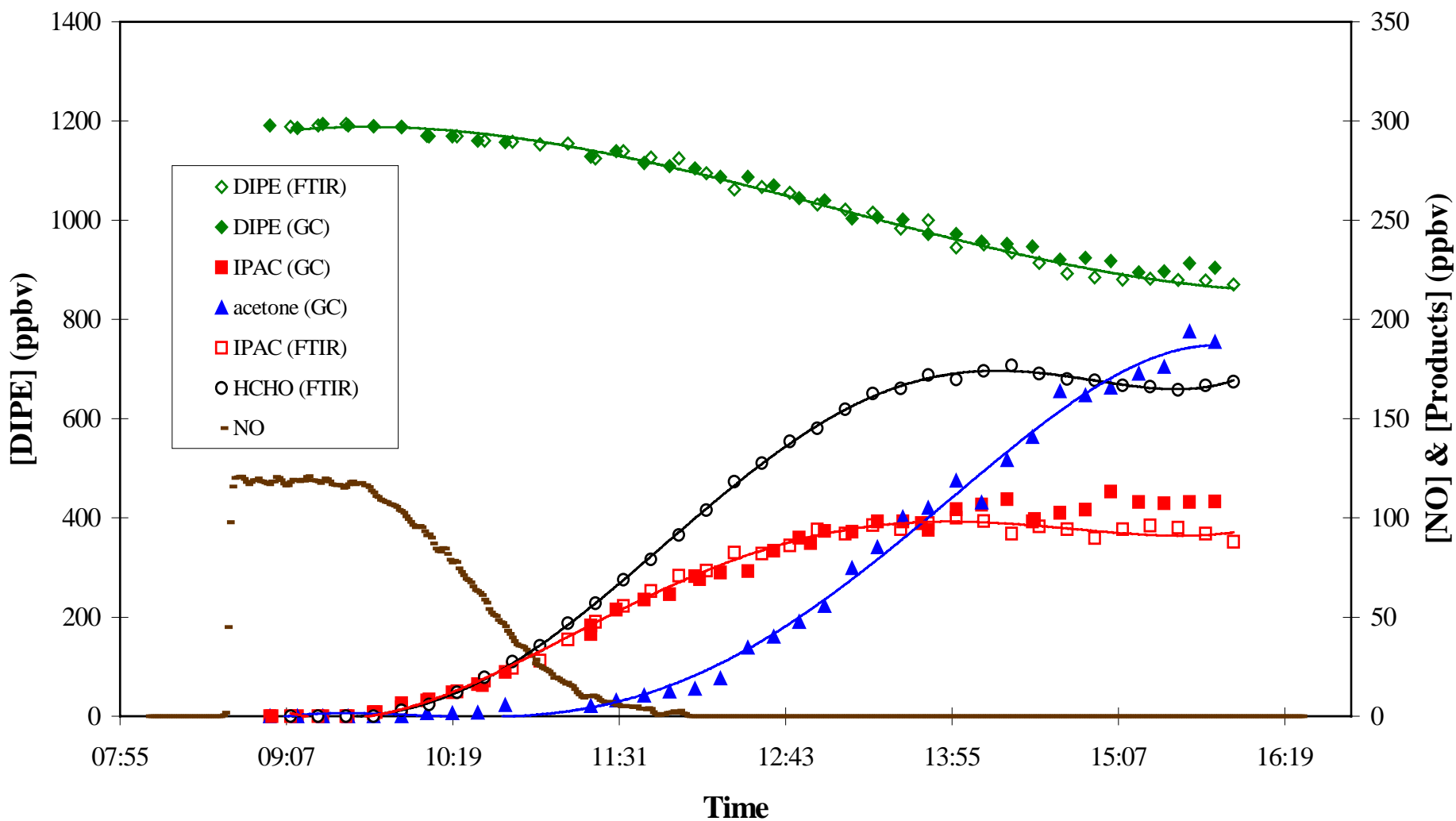
Figure 2. Concentration-time profile for the photooxidation of diisopropyl ether under "normal NO$_x$" conditions at EUPHORE.

For the experiment performed under "high NO$_x$" conditions, only trace amounts of acetone were detected and IPAc therefore accounted for virtually all of the DIPE lost due to reaction with hydroxyl radicals. Similarly during the initial hours of the "normal NO$_x$" experiment, the initial yield of IPAc was also high (0.89 ± 0.09). These data agree with the findings of the only previously published work on DIPE photooxidation (Wallington *et al.* 1993) and thus confirm the proposed mechanism, shown in Scheme 2. Hydroxyl radical attack is expected to occur about 80% of the time at the >CH− group (Kwok and Atkinson, 1995). As a result, H-atom abstraction from the −CH$_3$ group is omitted from Scheme 2 for simplification purposes.

For the experiment performed in the absence of NO$_x$ only trace amounts of IPAc were detected, whilst the yield of acetone was 1.05 ± 0.11. Similarly during the final hours of the "normal NO$_x$" experiment, the yield of acetone was also high (0.93 ± 0.13). Two possible decomposition routes that could lead to the formation of acetone are shown in Scheme 3. One possible route is through C−O bond cleavage of the alkoxy radical yielding acetone and another alkoxy radical, which will react with O$_2$ to form a second acetone molecule. The other route is *via* a hydroperoxy-peroxy radical reaction to form the hydroperoxide i-PrOC(OOH)(CH$_3$)$_2$. This hydroperoxide is similar in structure to 1-hydroxyalkyl hydroperoxides (HOCH(OOH)R) which are known to decompose to H$_2$O$_2$ and RCHO, (Kurth *et al.*, 1991). By analogy, i-PrOC(OOH)(CH$_3$)$_2$ could decompose to give isopropyl hydroperoxide and acetone.
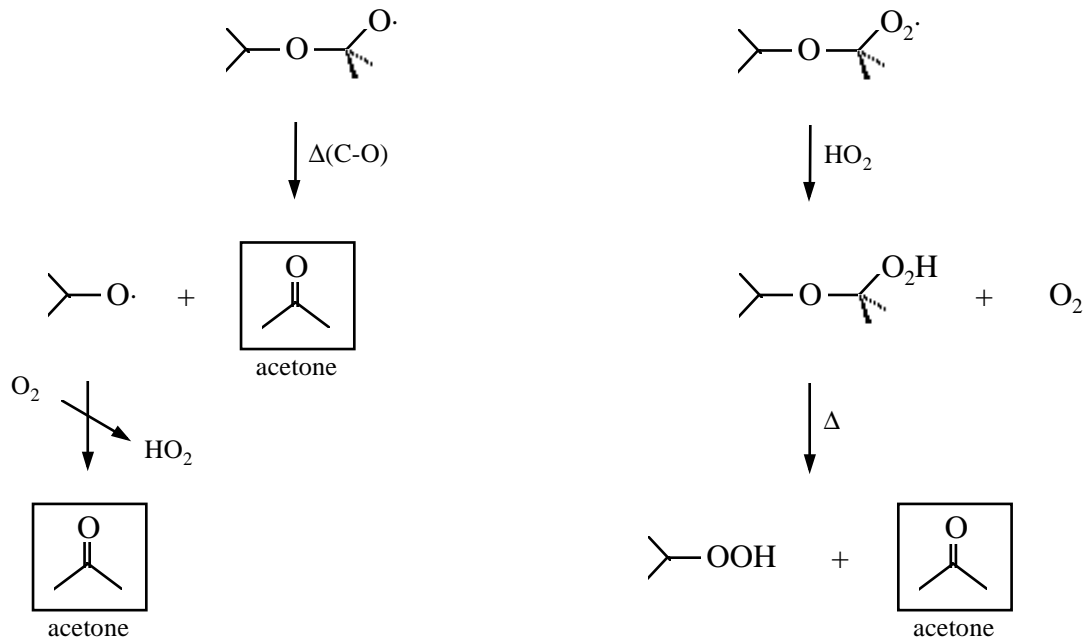
Scheme 3. Possible decomposition routes leading to the formation of acetone.

The hydroperoxide and alkoxy radical channels are expected to produce one and two molecules of acetone respectively for every molecule of DIPE consumed. Since the yield of acetone in the absence of NO_x was around 100% then it seems likely that the hydroperoxide channel was responsible for acetone formation. The HO_2 radicals required for this process to occur were formed by the reaction of H_2O_2 with OH radicals;

$$H_2O_2 + OH \rightarrow H_2O + HO_2$$
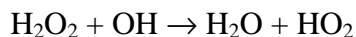
The hydroperoxide channel also produces isopropyl hydroperoxide. This species was not detected as a product by FTIR spectroscopy or GC-PID. However, it is possible that its absorption features were obscured by the strong bands due to H_2O_2 and that it decomposed on the separating column. In addition, isopropyl hydroperoxide could react with OH or undergo photolysis. In the latter case this would lead to the formation of another molecule of acetone. Further experimental work is planned in which HPLC will be employed for the detection of isopropyl hydroperoxide. This will therefore allow us to confirm or discount the proposed mechanism for its formation.

Acknowledgements

References

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