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The effect of oxygen pressure on the tropospheric oxidation of diethyl ether, H-atom elimination from the 1-ethoxyethoxy radical

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The simulated tropospheric oxidation of diethyl ether gave yields of the products ethyl formate, acetaldehyde and ethyl acetate in broad agreement with previous studies. However the effect of variation of oxygen pressure on the relative yields of ethyl acetate and ethyl formate disagrees with the prediction of the mechanism previously proposed. It is suggested that ethyl acetate is produced by the reaction $C_2H_5OCH(O)CH_3 \rightarrow CH_3COOC_2H_5 + H$ as well as by the reaction of the 1-ethoxyethoxy radical with oxygen.

Introduction

Because of the importance of ethers as industrial solvents and fuel additives, their tropospheric oxidation has received significant attention. Laboratory studies have been performed using oxidation initiated by OH radicals, to simulate tropospheric chemistry, and also initiated by chlorine atoms. Much previous work has been concerned with the evaluation of rate coefficients for the attack of OH on ethers. In the case of diethyl ether the rate coefficient data has been reviewed by Atkinson[1] and by Mellouki *et al.*[2] A number of studies of the products of simulated tropospheric oxidation of diethyl ether have been carried out.[3–5] Following the observation of ethyl formate, formaldehyde, acetaldehyde and ethyl acetate as reaction products the following reaction mechanism has been suggested.[5] It is assumed that attack by OH occurs almost exclusively at the secondary carbons.

$$C_2H_5OC_2H_5 + OH \rightarrow C_2H_5OCHCH_3 + H_2O \tag{1}$$

$$C_2H_5OCHCH_3 + O_2 \rightarrow C_2H_5OCH(O_2)CH_3 \tag{2}$$

$$C_2H_5OCH(O_2)CH_3 + NO \rightarrow C_2H_5OCH(O)CH_3 + NO_2 \tag{3}$$

$$C_2H_5OCH(O)CH_3 \rightarrow HCOOC_2H_5 + CH_3 \tag{4}$$

$$C_2H_5OCH(O)CH_3 \rightarrow CH_3CHO + C_2H_5O \tag{5}$$

$$C_2H_5OCH(O)CH_3 + O_2 \rightarrow CH_3COOC_2H_5 + HO_2 \tag{6}$$

$$C_2H_5OCH(O)CH_3 \rightarrow CH_2CH_2OCH(OH)CH_3 \tag{7}$$

The CH_3 is oxidised to produce formaldehyde. The isomerisation channel (7) is believed to be unimportant in this case.[5]

According to this scheme, ethyl formate and acetaldehyde are produced by decomposition of the 1-ethoxyethoxy radical, and ethyl acetate by reaction of 1-ethoxyethoxy with oxygen. In order to test this mechanism we have studied the simulated tropospheric oxidation of diethyl ether, and examined the ratio of the products ethyl acetate and ethyl formate as a function of the pressure of oxygen.

Experimental

Oxidation of diethyl ether was initiated by OH radicals generated by photolysis of methyl nitrite in the presence of NO and an excess of oxygen[3] and nitrogen. Typical pressures used (mTorr) were methyl nitrite 150, NO 340 and diethyl ether 900. The oxygen pressure was varied from 8 to 702 Torr and the total pressure made up to 703 ± 3 Torr with nitrogen. In some experiments oxidation was initiated by chlorine atoms generated by photolysis of molecular chlorine (150 mTorr). Similar pressures of NO, diethyl ether and oxygen to those used in the OH-initiated experiments were present and the mixtures again made up to about 705 Torr with nitrogen. Reactions were carried out in Pyrex vessels of volume 0.25 dm^3 thermostated at 293 ± 1 K and irradiated with light from a high pressure mercury lamp. Diethyl ether, acetaldehyde, ethyl formate and ethyl acetate in the irradiated mixtures were measured by GC using a Chrompack CP9001 series gas chromatograph with a temperature-programmed Porapak R column. The conversion of the ether was typically 20%. Under these conditions a good separation of these products and the unchanged diethyl ether was achieved and calibration graphs enabled estimations to be made with the errors shown in Tables 1 and 2.

Results and discussion

Reaction products

The reaction products detected by GC were ethyl formate, ethyl acetate and acetaldehyde. Formaldehyde has been shown to be a major product[5] but in our system it is also produced from the photolysis of methyl nitrite. Table 1 shows the yields (mol product/mol ether consumed) of the products

Table 1 Product yields[a] in different studies

Ref.	Ethyl formate	Ethyl acetate	Acetaldehyde
3	0.92 ± 0.06	< 0.05	< 0.05
4	0.84 ± 0.05	0.06 ± 0.01	0.10 ± 0.03
5	0.66 ± 0.14	0.04 ± 0.03	0.08 ± 0.02[b]
This work (OH initiated)	0.65 ± 0.05[c]	0.07 ± 0.03	0.13 ± 0.05
This work (Cl initiated)	0.79 ± 0.09	0.07 ± 0.01	0.11 ± 0.03

[a] mol product/mol ether consumed. [b] See text. [c] For consistency with previous work errors given are 2σ

Table 2 Effect of oxygen pressure on product yields

Oxygen pressure/Torr	Ethyl formate	Ethyl acetate	Acetaldehyde
8	0.67 ± 0.06	0.075 ± 0.007	0.10 ± 0.03
141	0.65 ± 0.05	0.070 ± 0.030	0.13 ± 0.05
350	0.64 ± 0.08	0.084 ± 0.007	0.16 ± 0.01
702	0.66 ± 0.06	0.100 ± 0.007	0.15 ± 0.02

for the mixtures nearest to tropospheric composition (142 Torr O_2, 562 Torr N_2). Results for both OH-initiated and Cl-initiated oxidations are shown, each being the mean of six runs. Conclusions of previous investigations are included for comparison.

The product yields in this work are in satisfactory agreement with previous studies notwithstanding the far higher reactant pressures used. It should be noted that the values quoted for ref. 5 are the fractions of the decomposition of 1-ethoxyethoxy proceeding by routes (4), (5), and (6), rather than the yields as defined above. Since the C_2H_5O radical produced in reaction (5) is partly converted to more CH_3CHO, the experimental yield of acetaldehyde was reduced in ref. 5 to obtain the fraction given.

Effect of variation of oxygen pressure

The mechanism shown earlier implies that the yield of ethyl acetate should depend on the pressure of oxygen. Product yields were measured in runs with various pressures of oxygen but with the same total pressure of 703 ± 3 Torr.

The results are shown in Table 2, in which each yield is the mean of the results of six runs. As can be seen in Fig. 1, increasing the oxygen pressure has little effect on the yield of the major product, ethyl formate, but causes some increase in acetaldehyde and in ethyl acetate. The increase in acetaldehyde can be attributed to an increase in the fractional conversion of C_2H_5O to CH_3CHO with increasing O_2. The increase in ethyl acetate is due to reaction (6). However, according to the mechanism given above, the ratio of the yields of ethyl acetate and ethyl formate should be directly proportional to the oxygen pressure. This ratio is shown in Fig. 2, and its weak dependence on oxygen pressure is clearly at odds with the mechanism.

To account for the discrepancy the mechanism requires modification either to make ethyl acetate production less dependent on oxygen, or the formation of ethyl formate more oxygen-dependent. The latter alternative might be achieved qualitatively by adding to the original mechanism reaction (8), the analogue of reaction (6) but with the formation of CH_3O_2 instead of HO_2.

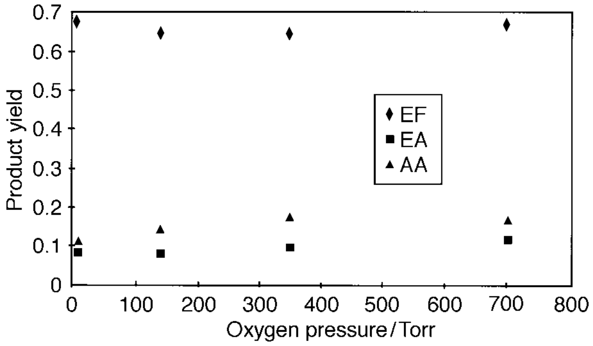


Fig. 1 Effect of oxygen pressure on product yields. EF, ethyl formate; EA, ethyl acetate; AA, acetaldehyde.

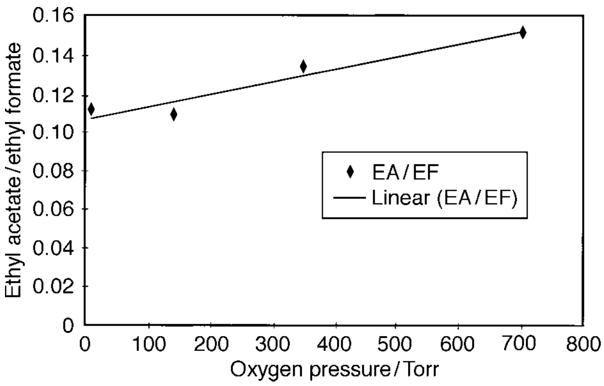


Fig. 2 Effect of oxygen pressure on the ratio of ethyl acetate to ethyl formate. EA, ethyl acetate; EF, ethyl formate.

$$C_2H_5OCH(O)CH_3 + O_2 \rightarrow HCOOC_2H_5 + CH_3O_2 \quad (8)$$

Quantitatively, however, this is unsatisfactory. A mechanism involving (4), (5), (6) and (8) would lead to a linear dependence of ethyl formate/ethyl acetate on the reciprocal of the oxygen pressure and this is not observed. Moreover, at very high oxygen pressures the ratio ethyl formate/ethyl acetate approaches k_8/k_6 and the value of about 6 seems improbable.

A more probable explanation is that there is a component of ethyl acetate formation which is independent of oxygen. The most likely process is the decomposition step (9), in which a hydrogen atom is ejected from 1-ethoxyethoxy.

$$C_2H_5OCH(O)CH_3 \rightarrow CH_3COOC_2H_5 + H \quad (9)$$

Step (9) is an alternative to step (4) which produces the major product ethyl formate by fission of a carbon–carbon bond.

For simple alkoxy radicals such as ethoxy and isopropoxy C–H fission is about 25 kJ mol^{-1} more endothermic than C–C fission.[6] Assuming similar Arrhenius A factors this would lead to C–C fission being more favourable by a factor in rate of 2.4×10^4.

For the C–C fission step (4) yielding ethyl formate however, the estimated enthalpy change is -2.5 kJ mol^{-1} and that for step (9) indicates it to be thermoneutral.[7] A difference of 2.5 kJ mol^{-1} would correspond to a factor of 2.74 in favour of step (4) over step (9).

The mechanism involving steps (4), (5), (6), and (9) predicts a linear dependence of ethyl acetate/ethyl formate on oxygen pressure in satisfactory agreement with the results in Fig. 2. The intercept is $k_9/k_4 = 0.11$ at 293 K, and $k_6/k_4 = 1.9 \times 10^{-21}$ cm^3 $molecule^{-1}$ is derived from the slope.

Reaction (9) should therefore be added to the original oxidation mechanism. The results indicate that under atmospheric conditions about 90% of the ethyl acetate is produced by reaction (9) rather than reaction (6). Support for this proposal is provided by evidence for the occurrence of the corresponding H-atom ejection from the methoxymethoxy radical reported by Jenkin *et al.*[8]

Estimates of the heats of formation of the methoxymethoxy and 1-ethoxyethoxy radicals using Benson's additivity rules suggest that both these radicals eliminate hydrogen with a low endothermicity. A further example is provided by the decomposition of the $HOCH_2O$ radical for which an enthalpy change of 13.4 kJ mol^{-1} has been given.[9] This decomposition has been invoked to explain the chain process producing H_2 in the photo oxidation of formaldehyde. Clearly the elimination of hydrogen atoms from these oxygenated alkoxy radicals may have a wider significance which cannot be ignored.

It has been suggested by a referee that the apparent weak dependence of the ethyl acetate/ethyl formate ratio on oxygen pressure could be due to the relatively high NO pressure used in this work and the consequent dominance of reactions (10) and/or (11) over reaction (6).

$$CH_3CH_2OCH(O)CH_3 + NO \rightarrow CH_3CH_2OCH(ONO)CH_3 \quad (10a)$$

$$\rightarrow CH_3CH_2OC(O)CH_3 + HNO \quad (10b)$$

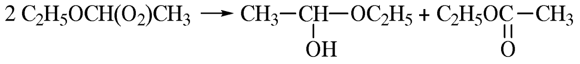
$$CH_3CH_2OCH(O)CH_3 + NO_2 \rightarrow CH_3CH_2OCH(ONO_2)CH_3 \quad (11a)$$

$$\rightarrow CH_3CH_2OC(O)CH_3 + HONO \quad (11b)$$

Table 3 Effect of nitric oxide pressure on the ethyl acetate/ethyl formate ratio

NO pressure/Torr	Ethyl acetate/ethyl formate
0.340	0.140
0.250	0.143
0.150	0.131
0.075	0.147
0.034	0.232

We have therefore carried out experiments in which the NO was varied at a constant oxygen pressure of 140 Torr. The results are given in Table 3 and show that the ratio ethyl acetate/ethyl formate is unchanged when the NO pressure is reduced from 0.340 to 0.075 Torr. Further reduction to 0.034 Torr produces an unexpectedly high value of ethyl acetate/ethyl formate. A possible explanation for this is that at very low NO pressures some contribution from the recombination of $C_2H_5OCH(O_2)CH_3$ radicals occurs which could yield extra ethyl acetate as in step (12).



$$2\,C_2H_5OCH(O_2)CH_3 \longrightarrow CH_3-\underset{\underset{OH}{|}}{CH}-OC_2H_5 + C_2H_5O\underset{\underset{O}{\|}}{C}-CH_3 \qquad (12)$$

This behaviour is also contrary to the suggestion that reactions (10) and (11) are significant under these conditions.

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