Hydroxyl-radical-initiated oxidation of isobutyl isopropyl ether under laboratory conditions related to the troposphere

Product studies and proposed mechanism

Konrad Stemmler, Wolfgang Mengon and J. Alistair Kerr^{†*}

EAWAG, Swiss Federal Institute for Environmental Science and Technology, ETH Zürich, CH-8600 Dübendorf, Switzerland

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The products formed by the hydroxyl-radical-initiated oxidation of the model ether, isobutyl isopropyl ether $[(CH_3)_2CHCH_2OCH(CH_3)_2]$, have been investigated by irradiating synthetic air mixtures containing the substrate, methyl nitrite, and nitric oxide at ppm levels in a Teflon bag reactor at room temperature. The decay of reactant and formation of products were monitored by gas chromatography, mass spectrometry and by HPLC. The molar yields of the major products (mol of product formed/mol of isobutyl isopropyl ether consumed) were as follows: acetone, 0.56 ± 0.04 ; isopropyl formate, 0.48 ± 0.03 ; isobutyl acetate, 0.28 ± 0.02 ; 2-hydroxy-2-methylpropyl acetate $[CH_3C(O)OCH_2C(OH)(CH_3)_2]$, 0.25 ± 0.1 . The molar yields of the minor products were as follows: isobutyraldehyde, 0.06 ± 0.05 ; isopropyl nitrate, 0.09 ± 0.06 ; 1,1,4-trimethyl-3-oxapentyl nitrate $[(CH_3)_2CHOCH_2C(CH_3)_2(ONO_2)]$, 0.07 ± 0.02 ; isopropyl isobutyrate $[(CH_3)_2CHC(O)OCH(CH_3)_2]$ ca. 0.01; and isobutyl formate, ca. 0.01. The major products are explained by a mechanism involving initial OH attack at the -CH- and $-CH_2-$ groups in the alkyl side chains of the ether followed by the subsequent reactions of the resulting carbon-centred, organic peroxy, and organic oxy radicals. The observed products, in conjunction with the proposed reaction pathways, account for a total yield of about 1.15, indicating that all the main routes are accounted for in the degradation of this ether. The major reaction pathways of the three principal organic oxy radicals are summarised as follows (percentage of overall reaction in brackets):

 $(CH_3)_2C(\dot{O})OCH_2CH(CH_3)_2 \rightarrow CH_3C(O)OCH_2CH(CH_3)_2 + \dot{C}H_3 \qquad (28\%)$ $(CH_3)_2CHOCH(\dot{O})CH(CH_3)_2 \rightarrow (CH_3)_2CHOC(O)H + \dot{C}H(CH_3)_2 \qquad (\leqslant 48\%)$ $(CH_3)_2CHOCH_2C(\dot{O})(CH_3)_2 \rightarrow (CH_3)_2\dot{C}OCH_2C(OH)(CH_3)_2 \qquad (25\%)$

This study supports the finding that organic oxy radicals generated from ethers and containing the structure RCH(O')OR undergo mainly decomposition by C—C bond cleavage, whereas those oxy radicals with the structure RCH(O')CH₂OR undergo preferential 1,5-H-atom transfer isomerisation reactions. The following rate coefficients $(10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ at room temperature for the reactions of OH radicals with the reactant and products have been determined by the relative rate technique: isobutyl isopropyl ether, 19.5 ± 0.4 ; isobutyl acetate, 6.0 ± 0.5 ; isobutyraldehyde, 25.8 ± 0.7 ; isopropyl formate, 2.1 ± 0.1 ; isopropyl isobutyrate, 6.5 ± 0.4 ; 1,1,4-trimethyl-3-oxapentyl nitrate, 16.5 ± 0.7 ; and 2-hydroxy-2-methylpropyl acetate, 9.5 ± 1.6 .

The mechanism of elementary reactions for the breakdown of volatile organic compounds in the troposphere is generally agreed^{1,2} to involve the initial formation of carbon-centred or alkyl radicals, mainly from attack of hydroxyl radicals on the organic molecule. These carbon-centred radicals are rapidly oxidised in air to the corresponding alkylperoxy radicals, which in a NO_x-containing atmosphere, principally react to generate NO₂ plus an oxygen-centred or alkoxy radical. The subsequent reactions of the alkoxy radicals, either directly with O₂, by decomposition or by isomerisation, give rise to the first generation of carbonyl compounds such as aldehydes, ketones, and esters, from the original organic compound. The relative rates of the reactions of the alkoxy radicals under atmospheric conditions consequently control the distribution of initial carbonyl products which are formed.

For hydrocarbon molecules such as alkanes and alkenes,² there is now a sufficient body of laboratory kinetic and thermodynamic data to enable the product distributions to be estimated *via* sets of empirical rules for the reactions of the hydrocarbon alkoxy radicals.³ In the case of oxygencontaining organic compounds, the data base for the reactions of the corresponding oxygen-containing alkoxy radicals is still too limited to develop the empirical approach.³ To provide more laboratory data on the atmospheric degradations of oxygen-containing compounds, detailed product and mechanistic studies of the atmospheric degradations of ethers⁴ and glycol ethers have been carried out.^{5,6}

In the present study we have extended this approach by investigating the mechanism of the atmospheric oxidation of a model ether, isobutyl isopropyl ether. This molecule contains two readily transferable tertiary C—H bonds together with a sufficiently large carbon skeleton to enable the resulting oxy radicals to undergo rapid isomerisation reactions.⁷ The detailed quantitative product studies, that we have undertaken, should provide further insight into the reactions, especially isomerisation, of oxygen-containing alkoxy radicals under atmospherically related conditions.

Experimental

Materials

The source or preparation of synthetic air, methyl nitrite and nitric oxide have already been described.⁵ Isobutyl isopropyl ether was prepared by reacting 0.5 mol sodium isopropylate

[†] Present address: School of Chemistry, University of Birmingham, Birmingham, UK B15 2TT. Fax: +44 121 472 8067. E-mail: a.kerr@bham.ac.uk.

and 0.5 mol isobutyl bromide at room temperature for three days. The reaction produced isopropyl alcohol and isobutylene as by-products. The reaction mixture was distilled twice and the remaining isopropyl alcohol was removed by refluxing with sodium for several hours followed by vacuum distillation. This purification procedure was repeated three times. The purity of the resulting isobutyl isopropyl ether was checked by GC-FID, GC-MS and NMR and found to be ca. 99%. Isopropyl isobutyrate was synthesised by refluxing a mixture of 0.4 mol isopropyl alcohol and 0.4 mol isobutyryl chloride for 3 h and was purified by distillation. The purity was found to be >99.5% (GC-FID, GC-MS). Isopropyl formate was prepared by refluxing a mixture of 0.2 mol isopropyl alcohol and 1 mol formic acid overnight. The mixture was neutralised with sodium hydrogen carbonate. The organic layer was separated and washed with an aqueous sodium hydrogen carbonate solution, dried with sodium sulfate and distilled. The purity of the product was found to be >99.5%(GC-FID, GC-MS). Isobutyl formate (purity >99%) was prepared by the same procedure as for isopropyl formate with isopropyl alcohol replaced by isobutyl alcohol. Isopropyl nitrate (>99% purity) was synthesised^{8,9} by esterification of 0.05 mol isopropyl alcohol with nitric acid in the presence of sulfuric acid at temperatures lower than 273 K. 2-Hydroxy-2methylpropyl acetate was synthesised as follows: a suspension of 0.66 mol 1,2-epoxy-2-methylpropane (isobutylene oxide) and 0.66 mol of ammonium acetate in 30 cm³ water was stirred under reflux for 5 h. A further 0.34 mol ammonium acetate was then added and the two-phase mixture was stirred for 10 h at 323 K to produce a homogeneous mixture, which was extracted twice with 200 cm³ diethyl ether. The ether extracts were washed with saturated aqueous sodium hydrogen carbonate solution, dried with sodium sulfate and vacuum distilled with a 30 cm Vigreux column. The product was checked with GC-FID, GC-MS and NMR and found to be 98% pure. The product 1,1,4-trimethyl-3-oxapentyl nitrate was produced by the reaction of 0.04 mol 2-hydroxy-1isopropoxy-2-methylpropane with N-nitrocollidinum tetrafluoroborate as described by Olah et al.¹⁰ The reaction converted only about 20% of the precursor alcohol into the nitrate, but the nitrate could be isolated by twice repeated liquid chromatography through a silica gel 60 (Merck) column $(2 \text{ cm} \times 40 \text{ cm})$, using gradient mixtures of pentane and diethyl ether. The product was confirmed by high resolution mass spectrometry and by NMR analysis and the purity was found to be ca. 97% (GC-FID). The precursor 2-hydroxy-1isopropoxy-2-methylpropane was synthesised by the reaction of 0.22 mol sodium isopropylate with 0.84 mol 1,2-epoxy-2methylpropane in 200 cm³ isopropyl alcohol. The mixture was refluxed for 8 h followed by the addition of 50 cm³ water, when the organic layer was separated and dried with sodium sulfate. The isopropyl alcohol was distilled off and the residue was fractionated by vacuum distillation with a 25 cm Vigreux column. The resulting product was >99% pure (GC-FID, GC-MS, NMR). An attempt was made to synthesise 1,1,4trimethyl-3-oxapentyl nitrite by esterification of 2-hydroxy-1isopropoxy-2-methylpropane with sodium nitrite in the presence of sulfuric acid as described by Noyes.11 The product could not be isolated by vacuum distillation or by liquid chromatography owing to the instability of this tertiary nitrite and the resulting two-component mixture contained about 40% of the nitrite along with the precursor alcohol, 2-hydroxy-1isopropoxy-2-methylpropane. The mixture was analysed by ¹H, ¹³C, ¹⁷O NMR spectroscopy and by high resolution mass spectrometry (GC-MS) to confirm the identity of the 1,1,4trimethyl-3-oxapentyl nitrite and was used in a qualitative photolysis experiment.

The following compounds were used without further purification, other than degassing by repeated thaw and freeze cycles under vacuum: isobutyl acetate (Fluka, *ca.* 99%), acetone (Fluka, >99.5%), dipropyl ether (Fluka, 99%), dibutyl ether (Fluka, >99.5%), isobutyraldehyde (Fluka, >99%) and acetic acid (Merck, 99.8%).

Apparatus

The relative rate coefficient measurements and the product studies were carried out in an experimental system which has been described previously^{4,7,12} and which is summarised here. Hydroxyl radicals were produced from the photolysis of methyl nitrite in air containing NO:

$$CH_3ONO + hv \rightarrow CH_3O + NO$$
 (1)

$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$
 (2)

$$HO_2 + NO \rightarrow OH + NO_2$$
 (3)

The experiments were performed at room temperature $(297 \pm 3 \text{ K})$ and at atmospheric pressure $(725 \pm 10 \text{ Torr})$ in a 200 dm³ Teflon bag reactor surrounded by 16 black lamps (Philips L20/05) which provide UV-radiation in the region of 350-450 nm. Reactant mixtures were prepared by sweeping measured amounts (capacitance manometer MKS Baraton 220 C) of isobutyl isopropyl ether and methyl nitrite vapours from a calibrated volume of a vacuum line into the Teflon bag with a stream of synthetic air. The bag was filled with up to 200 dm³ of synthetic air using mass flow controllers and a stopwatch and nitric oxide was added to minimise the formation of O_3 . Once the gas mixture was prepared, the bag was agitated and left to stand for about 0.5-1 h in the dark to allow the reactants to mix. The bag mixture was irradiated for up to 1.5 h during which time samples were periodically removed and analysed.

Relative rate coefficient measurements

The relative rate measurements of OH reactions with isobutyl isopropyl ether and with some of its observed products (TST) were each carried out in two separate experiments with either dipropyl ether or dibutyl ether as the reference substances (REF):

$$OH + TST \rightarrow products$$
 (4)

$$OH + REF \rightarrow products$$
 (5)

Assuming that there are no loss processes of the test (TST) and reference compound (REF) other than the reaction with OH radicals, the rate expressions for these processes are given by:

$$-d[TST]/dt = k_{TST}[OH][TST]$$
(I)

$$-d[REF]/dt = k_{REF}[OH][REF]$$
(II)

which can be integrated and combined to give the following equation:

$$\ln \left([TST]_0 / [TST]_t \right) = (k_{TST} / k_{REF}) \times \ln \left([REF]_0 / [REF]_t \right)$$
(III)

where the subscripts 0 and t indicate concentration at the beginning of the experiment and at time t respectively. A plot of $\ln ([TST]_0/[TST]_t)$ vs. $\ln ([REF]_0/[REF]_t)$ thus yields the rate coefficient ratio k_{TST}/k_{REF} . The bag mixture, initially containing the test and reference compounds, nitric oxide and methyl nitrite, was irradiated for up to 2 h during which time samples of the mixture were periodically removed via a 3 cm³ stainless steel loop and gas-sampling valve. The test and the

reference compounds were analysed by GC (Carlo Erba HRGC 5300) with a FID detector equipped either with a combination of a 30 m DB-XLB fused silica capillary column (J&W Scientific, 0.25 mm id, 0.25 μ m film) and a 25 m DB-5 fused silica capillary column (J&W Scientific, 0.25 mm id, 0.25 μ m film) or a 30 m DB-Wax fused silica column (J&W Scientific, 0.32 mm id, 0.25 μ m film) operated with temperature programming from 313 to 453 K.

Analyses of products

Not all of the products could be detected and quantified under the same analytical conditions and consequently several sets of experiments were carried out. A total of 12 quantitative experiments to measure the products of the OH-radical-initiated oxidation of isobutyl isopropyl ether were performed.

In experiments no. 1-3, the decay of the starting material, isopropyl isobutyl ether, and the formation of the major products, acetone, isopropyl formate and isobutyl acetate, were measured by GC-FID (Carlo Erba HRGC 5300). Vapour samples were injected via 3 cm³ gas sample loop on a combination of a 30 m DB-XLB and a 25 m DB-5 fused silica capillary column maintained at 313 K for 1 min and then heated to 453 K at the rate of 10 K min⁻¹. This column combination was necessary to resolve the signal peaks of methyl nitrate, isobutyraldehyde and isopropyl formate. To check further for interference arising from peak overlaps, this column combination was tested using a quadrupole mass spectrometer detector (Fisons MD800) which enables the measurement of specific signals for each compound. It was not possible to measure the minor product isobutyraldehyde under these conditions owing to interference from the methyl nitrate signal.

In experiments no. 4–7, the starting compound and the major products were again measured as described above. Additionally, the minor products isopropyl isobutyrate, isopropyl nitrate, and isobutyl formate were analysed by withdrawing a gas sample from the bag through a 3 cm³ sampling valve and injecting onto a DB-1701 capillary column (J&W Scientific, 30 m, 0.25 mm id, 1 µm film) with temperature programming from 313 to 433 K. The products were detected with a mass spectrometer (Fisons MD800, 70 eV electron impact ionisation) operated in the single ion mode, recording ions with $m/z = 71.0 \pm 0.2$, and 89.0 ± 0.2 for isopropyl isobutyrate; $m/z = 56.0 \pm 0.2$ and 60.0 ± 0.2 for isopropyl nitrate, during the elution period of each compound.

In experiments no. 7-9, isobutyl isopropyl ether and the major products were measured as described above and the minor carbonyl compound isobutyraldehyde was quantitatdetermined by derivatisation with 2,4-dinitroivelv phenylhydrazine (2,4-DNPH) followed by HPLC separation with a 250×4 mm id Zorbax ODS (5 µm particle size) column (Säulentechnik Knauer) using a three-component gradient solvent programme and a UV-VIS detector set to 360 nm.¹³ Samples of the gas mixture (2 dm³) were withdrawn from the bag at a flow rate of 0.5 $dm^3 min^{-1}$ through an impinger containing 4 cm³ of acidified 2,4-DNPH-acetonitrile solution cooled to 273 K.¹³ During this sampling procedure it was not possible to prevent small amounts of acetonitrile from entering the bag reactor which precluded the analysis of acetone by gas chromatography owing to co-elution.

In experiments no. 10-12, vapour samples were injected simultaneously via 3 cm³ sample loops into two gas chromatographs equipped with FID detectors. The first GC was fitted with a 30 m DB-Wax fused silica column to analyse the polar compounds 1,1,4-trimethyl-3-oxapentyl nitrate and 2hydroxy-2-methylpropyl acetate. Isobutyl isopropyl ether, which had a retention time of only 0.7 min on this column and was suspected of co-eluting with other rapidly eluted products, was analysed in the second GC containing a less polar DB-5 capillary column. Both GC columns were operated for 1 min at 313 K after injection and were then heated to 453 K with a heating rate of 20 K min⁻¹. In these three experiments the mixing ratios of NO and NO₂ were measured using a commercial chemiluminescent analyser (Thermo Environmental Instruments Model 42). The NO₂ mixing ratios were corrected for the contribution of methyl nitrite to the NO_x signal. The approximate mixing ratios of methyl nitrite were determined by GC–FID using the DB-5 capillary column as described above.

In all of the above analyses, the compounds were calibrated by preparing at least four bag mixtures containing standards in air at mixing ratios comparable to those in the experiments and by analysing with the same procedures as in the experiments to yield response factors obtained from a linear leastsquares fit of the data. For qualitative GC-MS analysis, vapour samples were preconcentrated on Tenax TA adsorption tubes followed by thermal desorption into a GC-MS as described previously.⁶

Results

Rate coefficient measurements

The rate coefficients of the OH radical reactions with isobutyl isopropyl ether, isobutyl acetate, isobutyraldehyde, isopropyl formate, and isopropyl isobutyrate were each determined in two separate relative rate measurements involving dipropyl ether as the reference compound and the DB-XLB-DB-5 GC column combination for chromatographic separation. The rate coefficients of 1,1,4-trimethyl-3-oxapentyl nitrate and 2hydroxy-2-methylpropyl acetate were each determined relative to dibutyl ether in two separate experiments involving the DB-Wax capillary column. The initial mixing ratios in the bag reactor were as follows: isobutyl isopropyl ether, 3.2 and 3.0 ppm; isobutyl acetate, 3.5 and 3.7 ppm; isobutyraldehyde, 3.1 and 3.2 ppm; isopropyl formate, 3.9 and 5.3 ppm; isopropyl isobutyrate, 3.3 and 2.9 ppm; 1,1,4-trimethyl-3-oxapentyl nitrate, 0.5 and 1.1 ppm; 2-hydroxy-2-methylpropyl acetate, 1.5 and 1.6 ppm; dipropyl ether, 2.8-5.4 ppm; dibutyl ether, 2.0-4.0 ppm; NO, 8.9-20 ppm; and methyl nitrite, 5.5-29 ppm. Typical ln-ln plots of the present data according to eqn. (III) are shown in Fig. 1 and 2 and the rate coefficient ratios derived from the slopes of linear least-square fits of the data are listed in Table 1. The error limits correspond to 95% confidence intervals. These rate coefficient ratios were converted to absolute rate coefficients on the basis of the evaluated values¹ for $k(OH + dipropyl ether) = 18.5 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ and $k(OH + dibutyl ether) = 28.8 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K and are shown in Table 1. In general, linear ln-ln plots with near zero intercepts and good reproducibility were observed for these competitive experiments. Both sets of data from the experiments competing 2hydroxy-2-methylpropyl acetate against dibutyl ether, however, revealed distinct curvature in their plots, as shown in Fig. 2. The possibility of GC interference from the products of the oxidation of dibutyl ether in the analysis of 2-hydroxy-2methylpropyl acetate was excluded, by the irradiation of a mixture of dibutyl ether, nitric oxide and methyl nitrite and analysis under the same conditions. However, interference from its own oxidation products cannot be ruled out. In addition, in the competitive experiments with 2-hydroxy-2-methylpropyl acetate, higher than normal methyl nitrite concentrations were employed to reduce the importance of wall loss processes compared to the loss via OH reaction. The resulting increased removal rates of 2-hydroxy-2-methylpropyl acetate and dibutyl ether reduced the number of analyses taken during the run (see Fig. 2). Finally, it should be pointed



Fig. 1 Sample plots of $\ln([TST]_0/[TST]_i)$ vs. $\ln([dipropyl ether]_0/[dipropyl ether]_i)$ for the reaction of OH with following test compounds (TST): (\blacktriangle) isobutyl isopropyl ether, (\bigcirc) isobutyl acetate, (+) isopropyl formate, (\triangledown) isopropyl isobutyrate and (\blacksquare) isobutyraldehyde



Fig. 2 Sample plots of $\ln ([TST]_0/[TST]_t)$ vs. $\ln ([dipropyl ether]_0/[dipropyl ether]_t)$ for the reaction of OH with the following test compounds (TST): (\blacksquare) 1,1,4-trimethyl-3-oxapentyl nitrate and (\bigcirc) 2-hydroxy-2-methylpropyl acetate

out that systematic errors in obtaining gas kinetic data for 2-hydroxy-2-methylpropyl acetate are likely to arise from the low volatility and polar nature of this compound which may cause it to be adsorbed on the surfaces of the reactor and of the analytical system.

Product measurements

The observed product mixing ratios were corrected for secondary removal by the OH radical according to the method of Atkinson *et al.*¹⁴ using the expressions:

$$F[\text{prod}] = f\Delta[\text{IBIPE}] \qquad (IV)$$

where

$$F = \left(\frac{k_{\text{IBIPE}} - k_{\text{prod}}}{k_{\text{IBIPE}}}\right) \times \left(\frac{1 - [\text{IBIPE}]_t / [\text{IBIPE}]_0}{([\text{IBIPE}]_t / [\text{IBIPE}]_0)^{k_{\text{prod}} / k_{\text{IBIPE}}} - [\text{IBIPE}]_t / [\text{IBIPE}]_0}\right)$$
(V)

 k_{IBIPE} and k_{prod} are the room temperature rate coefficients of the OH radical reactions with isobutyl isopropyl ether and with the given product and Δ [IBIPE] = [IBIPE]₀ - [IBIPE]_t, where [IBIPE] refers to the concentration of isobutyl isopropyl ether and the subscripts denote the time at which it was measured. The fractions of isobutyl isopropyl ether which form the given product, f, were derived by linear least-squares fits of the slopes of the data plotted according to eqn. (IV). The rate coefficients of the OH radical reactions needed to calculate the correction factors, F, which have been measured in this work are given in Table 1. The remaining OH rate coefficients are either taken from the literature or estimated using the structure activity relationship (SAR) of Kwok and Atkinson¹⁵ and are as follows: $k(OH + acetone) = 2.19 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298$ K (ref. 1), $k(OH + isopropyl nitrate) = 4.9 \times 10^{-13} \text{ cm}^3$ molecule⁻¹ s⁻¹ at 298 K (ref. 1), k(OH + isobuty)formate) = 4.55 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ at 298 K (SAR estimation¹⁵). The maximum values of the correction factors, F, (corresponding to the largest extent of the reaction) are given in the caption of Fig. 3 for the typical sets of results shown. In order to obtain an estimation of the error introduced via this correction procedure, the rate coefficients of isobutyl isopropyl ether and the products with the OH radical were varied simultaneously in the range of the errors given in Table 1 and the effects of these variations were included in the errors of the product yields in Table 2. For the two rate coefficients measured competitively against dibutyl ether, an additional variation range of $\pm 20\%$ was employed to account for systematic errors between the two different reference compounds utilised.

Table 1 Room temperature rate coefficients for reaction of OH radicals with oxygenated compounds determined in this study

		present study	literature data
compound	$(k_{\rm TST}/k_{\rm REF})^a$	$k^{a}/10^{-12} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}$	$k^{d}/10^{-12} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}$
isobutyl isopropyl ether isobutyl acetate isobutyraldehyde	$\begin{array}{c} 1.05 \pm 0.02^{b} \\ 0.32 \pm 0.03^{b} \\ 1.39 \pm 0.04^{b} \end{array}$	$\begin{array}{c} 19.5 \pm 0.4 \\ 6.0 \pm 0.5 \\ 25.8 \pm 0.7 \end{array}$	$ \begin{array}{r} 18.1 \pm 2.1^{e} \\ 27 \pm 5^{f} \\ 24.2 \pm 3.3^{g} \\ 46.3 + 7.4^{h} \end{array} $
isopropyl formate isopropyl isobutyrate 1,1,4-trimethyl-3-oxapentyl nitrate 2-hydroxy-2-methylpropyl acetate	$\begin{array}{c} 0.11 \pm 0.01^{b} \\ 0.35 \pm 0.02^{b} \\ 0.57 \pm 0.02^{c} \\ 0.33 \pm 0.06^{c} \end{array}$	$\begin{array}{c} 2.1 \pm 0.1 \\ 6.5 \pm 0.4 \\ 16.5 \pm 0.7 \\ 9.5 \pm 1.6 \end{array}$	_

^{*a*} Error limits are for 95% confidence intervals. ^{*b*} REF = dipropyl ether. ^{*c*} REF = dibutyl ether. ^{*d*} Errors are 2*s*. ^{*e*} Ref. 20. ^{*f*} Ref. 17. ^{*g*} Ref. 18. ^{*h*} Ref. 19.



Fig. 3 Plots of the mixing ratios, corrected for secondary reactions with OH radicals, of (●) acetone (F < 1.007), (▲) isopropyl formate (F < 1.08), (■) isobutyl acetate (F < 1.22), (○) isopropyl nitrate (F < 1.005), (□) isopropyl isobutyrate (F < 1.1, plot displaced by -0.01 ppm on the vertical axis), (△) isobutyl formate (F < 1.07), (▼) isobutyraldehyde (F < 1.43), (+) 1,1,4-trimethyl-3-oxapentyl nitrate (F < 2.15), (♦) 2-hydroxy-2-methylpropyl acetate (F < 1.61) against the mixing ratios of isobutyl isopropyl ether reacted with the OH radical

Not all of the identified products could be quantified in any given experiment. Thus, nine experiments (no. 1–9) were carried out to measure principally the formation of isobutyl acetate, isopropyl formate and acetone. In these experiments the initial mixing ratios of isobutyl isopropyl ether, methyl

Table 2 Corrected^a yields of the major products from the photo-
oxidation of isobutyl isopropyl ether

observed product	yleid
acetone isopropyl formate isobutyl acetate isobutyraldehyde isopropyl isobutyrate isobutyl formate isopropyl nitrate 1,1,4-trimethyl-3-oxapentyl nitrate 2-hydroxy-2-methylpropyl acetate	$55.8 \pm 4.2 \\ 47.7 \pm 3.2 \\ 28.3 \pm 1.7 \\ 5.5 \pm 4.7 \\ 0.84 \pm 0.32 \\ 0.59 \pm 0.77 \\ 8.70 \pm 5.7 \\ 7.1 \pm 1.5 \\ 25.2 \pm 9.6$

^{*a*} Corrected for secondary OH radical attack (see text). ^{*b*} Expressed as a percentage of isobutyl isopropyl ether reacted. ^{*c*} Error limits are for 95% confidence intervals and include the errors in the analytical responses of isobutyl isopropyl ether and the respective product, the scatter of the results and the worst case estimates of the errors in correcting for secondary OH reactions.

nitrite and NO were 3.0-4.3 ppm, 11-18 ppm, and 10-17 ppm, respectively. Fig. 3(a) shows typical yields of isobutyl acetate, isopropyl formate and acetone, corrected for secondary OH reactions, vs. the mixing ratios of isobutyl isopropyl ether removed by OH reaction during the course of the given experiment. In four experiments (no. 4-7) quantification of the minor products isopropyl nitrate, isopropyl isobutyrate and isobutyl formate was carried out and Fig. 3(b) shows typical yields of these compounds vs. the mixing ratios of isobutyl isopropyl ether removed by OH reaction for a given experiment. Three of these experiments (no. 7-9) above included measurements of the carbonyl product isobutyraldehyde via derivatisation with 2,4-dinitrophenylhydrazine (2,4-DNPH). Additionally, acetone was detected as the main carbonyl containing product, but no calibrations were carried out to quantify this compound by this analytical method. No additional unknown 2,4-dinitrophenylhydrazone derivatives were observed. For a typical experiment, a plot of the yield of isobutyraldehyde, corrected for secondary OH removal, vs. the amount of isobutyl isopropyl ether reacted is shown in Fig. 3(c).

In experiments no. 10-12 the mixing ratios of isobutyl isopropyl ether, 1,1,4-trimethyl-3-oxapentyl nitrate and 2hydroxy-2-methylpropyl acetate have been determined. Additionally several unknown minor products were observed, which were all thought to be formed by reactions of OH radicals with the first generation products, since their signals did not increase linearly with the amount of isobutyl isopropyl ether consumed. The most abundant of these secondary products was identified to be acetic acid using a liquid standard of this compound. The sources of acetic acid were found, by qualitative irradiations of methyl nitrite-NO-primary product mixtures, to be mainly the OH-initiated oxidation of 2hydroxy-2-methylpropyl acetate and, as a minor contribution, the secondary reactions of isobutyl acetate. The initial mixing ratios of isobutyl isopropyl ether, methyl nitrite and nitric oxide in the latter three experiments were 5.7-6.4 ppm, 13-15 ppm and 8-11 ppm respectively. A plot of the mixing ratios of 1,1,4-trimethyl-3-oxapentyl nitrate and 2-hydroxy-2-methylpropyl acetate, corrected for secondary OH removal, vs. isobutyl isopropyl formate removed during the irradiation for a typical experiment is shown in Fig. 3(d).

The overall results of all the experiments are summarised in Table 2, where the quoted values are weighted mean values of the results of the various experiments with error limits for 95% confidence intervals, derived as described by Cvetanovic *et al.*,¹⁶ including errors in the analytical responses, the scatter of the results and worst case estimates of the errors in correcting for secondary OH reactions.

Discussion

Rate coefficient determinations

To the best of our knowledge, of the OH rate coefficients that we have measured, there are literature data only for the reaction of isobutyraldehyde as listed in Table 1. The present room temperature rate coefficient is in good agreement with that data of Kerr and Sheppard¹⁷ and of Semmes *et al.*,¹⁸ and is in line with the evaluated rate coefficient of Atkinson²¹ of 27.4×10^{-12} cm³ molecule⁻¹ s⁻¹. On the other hand the values of Dóbé *et al.*¹⁹ and of Audley *et al.*²⁰ are factors of *ca.* 1.8 higher and *ca.* 1.4 lower respectively than our determination.

The present room temperature rate coefficient of isobutyl isopropyl ether with the OH radical can be compared to the corresponding literature data for diisopropyl and diisobutyl ethers, on the basis that the reactivity of ethers towards OH attack can be expressed as the sum of the independent contributions of both alkyl side chains.^{22,23} For diisopropyl ether, the rate coefficients of McLoughlin *et al.*²⁴ of 11.1×10^{-12} cm³ molecule⁻¹ s⁻¹, Mellouki *et al.*²⁶ of 9.79×10^{-12} cm³ molecule⁻¹ s⁻¹ and the relative and absolute data of Nelson *et al.*²⁷ of 11.3×10^{-12} cm³ molecule⁻¹ s⁻¹ are in excellent agreement and can be

combined to give an average value of ca. 10.6×10^{-12} cm³ molecule⁻¹ s⁻¹ at 298 K. For the reaction of diisobutyl ether with the OH radical, the only reported value is that of Bennett and Kerr,²⁸ *i.e.* $k = 26.1 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. Hence the average of the rate coefficients of diisobutyl and diisopropyl ethers with the hydroxyl radical gives an estimate of the rate coefficient of isobutyl isopropyl ether of ca. 18.4×10^{-12} cm³ molecule⁻¹ s⁻¹, which is in good agreement with the measured value reported here. This conclusion can be interpreted as giving support to the rate coefficient for diisobutyl ether reported by Bennett and Kerr,²⁸ although some of the values they reported for other ethers appear to have been underestimated.¹

Product analyses and proposed mechanisms

Reaction Schemes 1, 2 and 3 show proposed mechanisms for the breakdown of isobutyl isopropyl ether following the initial H-atom abstraction by the OH radical from the secondary and the two tertiary C—H groups in the molecule, including all the possible major channels. The observed products, upon which the proposed reactions are based, are highlighted in boxes. In most of these schemes the organic peroxy radicals produced by the reaction of the carbon-centred radicals with O_2 and all unobserved alkyl nitrates have been omitted for clarity.



Scheme 1

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Scheme 1 shows the reactions occurring after H-atom abstraction by the hydroxyl radical from the tertiary C-H bond of the isopropyl side chain in isobutyl isopropyl ether. The intermediate organic oxy radical 2 appears to decompose mainly via rupture of a C-C bond to form the principal product, isobutyl acetate and a methyl radical. An additional decomposition pathway, involving the rupture of the C-O bond, leads to the formation of acetone and the alkoxy radical 3, which is believed to lead mainly to isobutyraldehyde^{29,30} via reaction with oxygen. The relatively low yield of isobutyraldehyde, which can also be formed from another reaction in the oxidation of isobutyl isopropyl ether (see Scheme 2), indicates that the breakdown via C-O breakage is a minor channel of oxy radical 2. This is in agreement with the finding of Wallington *et al.*,²⁶ that the OH-radical-initiated oxidation of diisopropyl ether leads to isopropyl acetate (yield: $105 \pm 6\%$) as the only observed product, and therefore the intermediate 1-isopropoxy-1-methylethyl oxy radical $[(CH_3)_2C(O')OCH(CH_3)_2]$ does not react by C-O bond breaking. As a further possibly important reaction, oxy radical 2 may undergo isomerisation, via a six-membered ring transition state, involving the relatively weak tertiary C-H atom to produce the organic radical 6. The resulting tertiary oxy radical 7 is thought²⁹ to decompose mainly to form acetone and the organic radical 8, leading to the complex alkoxy radical 9. By analogy with oxy radicals derived from methyl ethers,^{31,32,33} [CH₃OCH₂(O') or (CH₃)₃COCH₂(O')], radical 9 is proposed to mainly undergo reaction with oxygen or C-H bond fission leading to the organic formate 10. This molecule is a hemiacylal which would certainly be unstable and might be expected to form acetone and formic acid, at least under the present analytical conditions. No formic acid

was observed by qualitative MS analyses of the bag mixtures, although formic acid was observable under the experimental conditions. As a kinetically less favourable reaction channel, oxy radical 7 may decompose to give the hemiacetal 11 and a methyl radical. Compound 11 would be expected to decompose to form acetone and hydroxyacetone during analysis, but the latter compound was not observed. Although the proposed reactions in Scheme 1 are complex and the products proposed following the potential isomerisation reaction are hypothetical and no standards of such unstable compounds can be synthesised, the high yield of isobutyl acetate (ca. 28% of isobutyl isopropyl ether removed) indicates that the major pathway of oxy radical 2 under atmospheric conditions is decomposition via C-C bond scission. Assuming that both the alkyl substituents in an ether molecule react independently towards OH attack, the contribution of the isopropyl side chain (q) to the total reactivity of isobutyl isopropyl ether is given by the expression:

$$q = \frac{0.5 \times k(\text{OH} + \text{diisopropyl ether}) \times 100}{k(\text{OH} + \text{isobutyl isopropyl ether})} \approx 27\% \quad \text{(VI)}$$

This percentage is close to the observed yield of isobutyl acetate, implying that this compound is the exclusive product from the reactions following H abstraction from the tertiary C-H bond in the isopropyl group of the ether.

Scheme 2 shows the proposed reactions following H-atom abstraction from the CH_2 group of the isobutyl side chain. The intermediate organic oxy radical **12** decomposes mainly via C-C bond breakage to form isopropyl formate and the isopropyl radical **13**, which can form isopropyl nitrate and the 2-propoxy radical, **14**, leading to acetone by a reaction with



Scheme 2



Scheme 3

oxygen.³⁴ Alternatively, oxy radical 12 may decompose via C-O bond rupture yielding isobutyraldehyde and a 2propoxy radical which again forms acetone. The relatively small amounts of the isobutyraldehyde, which may additionally be formed by other reactions in the degradation of this ether (Scheme 1), indicate that C-O bond rupture in oxy radical 12 is a minor channel, which is in agreement with previous atmospheric product studies of ether type com-pounds.^{4-6,26,31-33,36,37} This is substantiated by empirical methods for estimating the rate coefficients of alkoxy radical decomposition reactions,^{1,38} which relate estimated enthalpy changes^{39,40} to the activation energies of such processes. Thus the two potential pathways leading to the formation of isobutyraldehyde above, the decompositions of oxy radical 2 (Scheme 1) and oxy radical 12 (Scheme 2) via C-O bond rupture are both estimated to be ca. 46 kJ mol⁻¹ endothermic, whereas the enthalpy changes of the decomposition reactions of these radicals by C-C bond rupture are estimated to be *ca*. -23 and +2.7 kJ mol⁻¹ respectively. Thus, on the basis of these estimated enthalpy changes, the C-O bond fissions should be insignificant relative to the alternative C-C bond fissions in both oxy radicals. It is consequently unclear which pathway leads to the observed production of isobutyraldehyde. The reaction of the organic oxy radical 12 with oxygen, leading to a small amount of isopropyl isobutyrate, is significantly slower than the decomposition of this radical via

C-C bond breakage, under the experimental conditions. The relatively high yields of isopropyl nitrate may indicate that this compound was produced not only by the reaction of the isopropyl peroxy radical with nitric oxide as shown in Scheme 2, but also by the reaction of the isopropoxy radical with nitrogen dioxide:

$$(CH_3)_2CHO' + NO_2 + M \rightarrow (CH_3)_2CHONO_2 + M$$
 (6)

This reaction is believed to be insignificant at typical tropospheric NO₂ levels, in relation to the competing reaction of the isopropoxy radical with oxygen:¹

$$(CH_3)_2 CHO' + O_2 \rightarrow (CH_3)_2 C = O + HO_2$$
(7)

Under the present experimental conditions, the NO₂ mixing ratios built up from values near 0 ppm to *ca*. 10 ppm at the end of an experiment. The yields of isopropyl nitrate by this pathway were simulated for the conditions of experiments no. 10-12, based on the known rate coefficients of reactions (6) and (7),^{34,35} the given O₂ and NO₂ concentrations and estimated isopropoxy radical yields from the overall reaction (40– 60%). These calculated yields of isopropyl nitrate from reaction (6) corresponded roughly to half of the observed build up of isopropyl nitrate under the experimental conditions.

Scheme 3 shows the proposed reactions following a H-atom abstraction from the tertiary C-H bond of the isobutyl side





chain. The initial carbon-centred radical adds oxygen to form a peroxy radical, which further reacts with nitric oxide. The latter reaction leads partly to the formation of 1,1,4-trimethyl-3-oxapentyl nitrate, but the reaction produces mainly the organic oxy radical 15. This oxy radical is expected to undergo isomerisation via 1,5-H-atom shift by abstracting a H atom from the tertiary C-H centre in the isopropyl group of the ether. The resulting organic radical 16 is, by analogy with radical 1 (see Scheme 1), most likely to lead to the formation of 2-hydroxy-2-methylpropyl acetate via breakage of the C-C bond in the intermediate organic oxy radical 17. As shown in Scheme 3, oxy radical 15 may additionally decompose to produce acetone and radical 18. This radical leads to oxy radical 19 which, in line with the reactions^{31,32,33} of the oxy radicals CH₃OCH₂(O') or (CH₃)₃COCH₂(O'), will react predominantly with oxygen or by C-H bond fission to form isopropyl formate. The alternative decomposition reaction would lead to 1-isopropoxypropan-2-one and a methyl radical. A standard of 1-isopropoxypropan-2-one was not available but a reference mass spectrum of this compound is reported in the NIST mass spectra database and no equivalent mass spectrum was found in our analyses. Tests to establish the formation of 2-hydroxy-2-methylpropyl acetate by the above mechanism were carried out in qualitative experiments. Hydroxyl-radical-initiated reactions of the first generation product isobutyl acetate, in the presence of typical concentrations of formaldehyde found in the present experiments, did not produce the acetate, which could possibly have arisen from the bimolecular reaction³² of the long-lived tertiary oxy radical $CH_3C(O)CH_2C(O')(CH_3)_2$ with the labile C-H bonds in formaldehyde. However, the photolysis of 1,1,4-trimethyl-3oxapentyl nitrite in air, which leads⁷ to the initial formation of oxy radical 15, produced 2-hydroxy-2-methylpropyl acetate as a stable end product. The latter experiment was carried out, in the absence of a pure standard of 1,1,4-trimethyl-3-oxapentyl nitrite, with a gas mixture containing several ppm of this compound together with 2-hydroxy-1-isopropoxy-2-methylpropane (see Materials section) and 10 ppm nitric oxide. In this qualitative experiment two further products were observed and identified as acetone and isopropyl formate, believed to come from the decomposition of oxy radical 15.

The abstraction of H atoms from the four methyl groups in isobutyl isopropyl ether are expected to be slow processes. From the structure activity relationship (SAR) of Kwok and Atkinson¹⁵ the contribution of the four methyl groups to the total reactivity of isobutyl isopropyl ether towards OH attack can be calculated to be ca. 2% and consequently only minor products were expected from these channels. Scheme 4 shows the possible reaction sequences after H-atom abstraction from a methyl group of the isobutyl side chain. The intermediate primary oxy radical 21 may break down to form formaldehyde and the organic radical 22. This radical may be converted to the oxy radical 23 via oxygen addition and reaction with NO. Oxy radical 23 may isomerise via 1,5-H-atom shift to form radical 24 and subsequently oxy radical 25, which, by analogy with oxy radical 2 (see Scheme 1), is expected to produce mainly 1-acetoxy-2-hydroxypropane via decomposition. A reference mass spectrum of this compound is available in the NIST mass spectra database, but no equivalent mass spectrum was observed in our experiments. Oxy radical 23 may alternatively react with oxygen to produce 1isopropoxypropan-2-one, which was not observed by mass spectral analysis as stated above. Oxy radical 23 could also undergo two decomposition reactions as shown in Scheme 4. The decomposition product acetaldehyde was not observed by analysis of the gas mixtures via derivatisation with 2,4-DNPH followed by HPLC separation and comparison with a standard of the 2,4-DNPH hydrazone derivative of acetaldehyde. It seems unlikely that oxy radical 21 will isomerise via 1,4- or 1.6-H-atom shifts.

In Scheme 5, the OH attack occurs on a methyl group of the isopropyl side chain. The resulting organic oxy radical 27 may (i) react with oxygen to form the aldehyde 30, (ii) isomerise *via* a 1,5-H-atom shift to produce in the subsequent reactions mainly the respective formate or (iii) decompose to form

formaldehyde and the organic radical **28** which is thought to be the source of the observed minor product isobutyl formate.

Overall the proposed mechanism gives a reasonably quantitative account of the observed product distribution. The absence of major unknown peaks in our analyses and the fact that the observed products, in conjunction with the proposed mechanism, account for ca. $115 \pm 11\%$ of the isobutyl isopropyl ether removed, indicates that all the main routes are accounted for in the degradation of this ether. Furthermore, the proposed reaction mechanism for the formation of the major products is based entirely on established gas-phase reactions. Clearly the relatively high errors in the reported product yields do not rule out the possibility of additional minor pathways. One such additional source of error seems likely to involve the loss of the low vapour pressure products on the Teflon walls and on aerosols formed in the system. These loss processes were investigated by irradiating a typical bag mixture and following the decay of the concentrations of the products in the dark over a period of over 2 h. The observed trends in the analyses during this period were small. For the most critical compound, 2-hydroxy-2-methylpropyl acetate, a loss rate of ca. 3% h⁻¹ was observed and consequently no corrections were applied for this effect, which introduces a systematic error of < 3%. Under the irradiation conditions of the experiments, only the product 1,1,4trimethyl-3-oxapentyl nitrate revealed a measurable decay due to photolysis $[k = (2.6 \pm 0.6) \times 10^{-5} \text{ s}^{-1}]$ which was accompanied by the build-up of an unidentified product. No corrections for this loss process were applied.

One of the main objectives of the present study was to investigate isomerisation reactions in organic oxy radicals



Scheme 5

formed from ethers. Isopropyl isobutyl ether was chosen as a model compound for this product study for two reasons. Firstly, because the two tertiary C-H groups in this molecule will result in the formation of two structurally different types of oxy radicals; type I $[(CH_3)_2C(O)OCH_2CH(CH_3)_2]$, derived from the isopropyl side chain, has an alkoxy substituent in the α -position relative to the radical centre, whereas type II [(CH₃)₂HCOCH₂C(O')(CH₃)₂], from the isobutyl side chain, does not. Secondly, the two relatively labile tertiary C-H bonds in the ether are in positions which potentially facilitate the rapid isomerisation reactions of the resulting oxy radicals, via 1,5-H-atom transfers. In general, the OH-initiated oxidation of ethers is believed¹⁵ to generate mainly oxy radicals of type I, although we have recently shown⁶ that oxy radicals of type II can play an important role in the atmospheric oxidation of ethers with longer $(>C_3)$ alkyl side chains. The present study has confirmed that organic oxy radical types I and II react differently under atmospheric conditions. None of the observed products indicated any isomerisation reaction of the oxy radical of type I; thus, on the basis of the high yields of isobutyl acetate, oxy radical 2 undergoes mainly unimolecular decomposition via rupture of a C-C bond. Conversely the observed major product, 2-hydroxy-2methylpropyl acetate, indicates that for oxy radicals of type II (oxy radical 15 in Scheme 3) the 1,5-H shift is an important reaction under atmospheric conditions. The rate coefficient of this isomerisation reaction cannot be calculated from the present data, since the competitively produced decomposition products of oxy radical 15, acetone and isopropyl formate, also arise from the decay of oxy radical 12 (see Scheme 2). A recent product study of the OH-initiated photo-oxidation of 2-butoxyethanol⁶ came to a similar conclusion concerning the relative importance of isomerisation reactions and decompositions reactions for oxy radicals with the structures RCH(O')OR' and RCH(O')CH₂OR', respectively.

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