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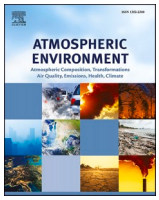

Atmospheric degradation of 2-Isopropoxyethanol: Reactions with Cl, OH and NO_3

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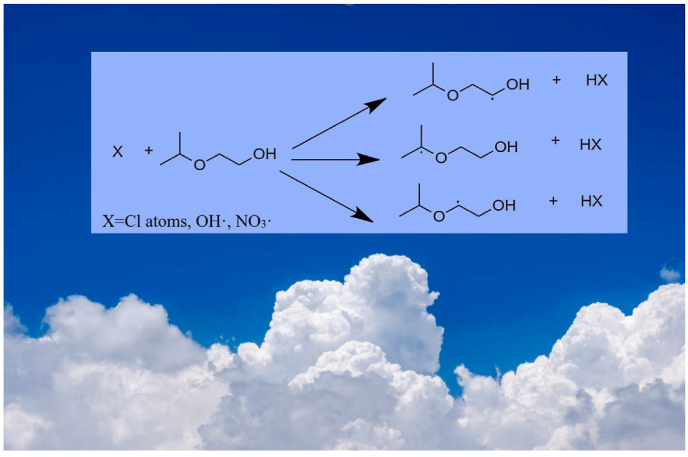
HIGHLIGHTS

- First kinetic data for the reaction of 2-iPE with Cl atoms and NO_3 radicals.
- High reactivity of hydroxyethers due to the presence of alcohol and ether groups.
- Mechanism proposed with the formation of carbonylic and multifunctional products.
- Short atmospheric lifetime with OH radicals, what implies a local impact.
- Importance of the products formed and its POCP.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of glycol ethers as solvents and chemical intermediates has increased markedly in recent years. Once released into the atmosphere, they can undergo degradation processes mainly by reactions with the atmospheric oxidants that can have significant effects on the environment. In this work, the kinetic and products study of reactions of 2-isopropoxyethanol (2-iPE, $(CH_3)_2CHOCH_2CH_2OH$) with OH and NO_3 radicals and Cl atoms have been performed using FTIR (Fourier Transform Infrared Spectroscopy) and GC-MS (Gas Chromatography/Mass Spectrometry) as detection techniques. The rate coefficients obtained were (units cm^3 $molecule^{-1}$ s^{-1}): $(2.18 \pm 0.15) \times 10^{-10}$, $(1.88 \pm 0.10) \times 10^{-11}$ and $(3.16 \pm 0.45) \times 10^{-15}$ for Cl, OH· and NO_3· reactions, respectively. The kinetic results obtained have been included in comparison tables of the general reactivity of hydroxy ethers to extract conclusions of the atmospheric behaviour of this type of compounds. The main products detected and

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quantified have been isopropyl formate, formaldehyde, 2-hydroxyethyl acetate and, in the case of NO_3· reactions, nitrated compounds. A reaction mechanism has been proposed according to the reaction products obtained. The calculated lifetimes have been determined and Global Warming Potential (GWP) and Photochemical Ozone Creation Potential ($POCP_E$) have been estimated, concluding, first, that the reaction with OH radicals is the main pathway of degradation of this and others glycol ethers in the atmosphere, second, that these compounds have GWP negligible and third, that they could have influence on ozone generation at local and regional level.

1. Introduction

Hydroxy ethers (glycol ethers) are bifunctional volatile organic compounds containing alcohol group and ether group in their structure. They are extensively used as solvents and chemical intermediates (Cheremisinoff, 2003; Sigma-Aldrich, 2022). The global market demand for glycol ethers reached a volume of 2.7 million metric tons in 2020 and continues to grow (Expert Market research EMR, 2022).

Due to the presence of glycol ethers in widely used industrial products, many sectors are concerned by professional exposure. The main effects observed in animals after repeated exposure were hematotoxicity, testicular toxicity and developmental effects (Cicolella, 2006). The general population can be exposed to the glycol ethers by using cleaning products, liquid soaps, and cosmetics (Sittig, 1985). Specifically, 2-iPE is used as a solvent, particularly in paints and lacquers and significant exposure can occur in spray painting and in brushing or rolling (Haz--map, 2022).

Once released into the troposphere, these compounds can undergo atmospheric degradation processes. Predominant processes are initiated by reaction with OH radicals, to a lesser extent by Chlorine atoms and by NO_3 radicals. The photolysis is not a significant removal process because ethers do not absorb significantly at wavelengths >200 nm (Atkinson, 2003). Only for unsaturated ethers, reaction with O_3 can be a competitive loss process. (Mellouki et al., 2015).

According to this, reported studies are mostly related to the reactivity of these compounds with OH radicals (Aranda et al., 2021; Aschmann and Atkinson, 1998, 1999; Aschmann et al., 2001, 2011; Barrera et al., 2017, 2019; Colmenar et al., 2020a,b; Dagaut et al., 1989; Hartmann et al., 1987; Kumar et al., 2021; Markgraf et al., 1999; Porter et al., 1997; Stemmler et al., 1996a, 1996b, 1997; Tuazon et al., 1998) and a few focused on NO_3· reactions (Aranda et al., 2021; Aschmann and Atkinson, 1998; Chew et al., 1998; Colmenar et al., 2020a,b; Harrison and Wells, 2012). Only recent works have addressed the study of reactivity with chlorine atoms. (Aranda et al., 2021; Barrera et al., 2017, 2019; Colmenar et al., 2020a,b). Given the little relevance of ozone reactions, there is to date only one published work (Aschmann and Atkinson, 1998).

Therefore, a detailed understanding of the kinetics and mechanisms of the atmospheric degradation of the glycol ethers group is necessary considering the potentially high emission rate and the variety of compounds used (Multigner et al., 2005). In the work presented here, rate coefficients, products studies and mechanistic aspects are determined and evaluated for the reactions of 2-iPE with OH and NO_3 radicals and with Cl atoms. The possible atmospheric implications have been evaluated according to the reaction products obtained, the lifetimes calculated, the Global Warming Potential (GWP) and the Photochemical Ozone Creation Potential ($POCP_E$). The results described here extend the information provided by previous works of our group (Aranda et al., 2021; Colmenar et al., 2020a,b) and allow to draw conclusions on the reactivity and the atmospheric behaviour of this type of bifunctional compounds to be used for correlations and atmospheric models.

2. Experimental section

2.1. Relative rate methodology

The relative method has been used for the determination of the rate coefficients. The integrated kinetic equation used has been:

$$\ln\left(\frac{[2-\mathrm{iPE}]_o}{[2-\mathrm{iPE}]_t}\right)=\frac{k_{2-\mathrm{iPE}}}{k_R}\ln\left(\frac{[R]_o}{[R]_t}\right) \quad (1)$$

Where $[2-\mathrm{iPE}]_o$, $[2-\mathrm{iPE}]_t$, $[R]_o$ and $[R]_t$ are the concentrations of the compound under study (2-iPE) and of the reference compound at times 0 and t, respectively. From the plots of $\ln([2-\mathrm{iPE}]_o/[2-\mathrm{iPE}]_t)$ versus $\ln([R]_o/[R]_t)$, a straight line is obtained with intercept zero and whose slope allows to determine the unknown rate coefficient of the compound, known that of the reference. Generally, the representation corresponds to some property proportional to the concentration.

2.2. Experimental systems

The experimental systems used to carry out the experiments have already been widely described in previous works (Aranda et al., 2021; Colmenar et al., 2020a,b). Briefly, for the kinetic and products studies, a cylindrical Pyrex glass reactor with a volume of 50 L was used, coupled to an FTIR (Fourier Transform Infrared Spectrophotometer) with a MTC/A (Mercury, Telluride, Cadmium) detector. The reactor was equipped with a multi-reflection white cell with a maximum optical path of 200 m. In addition, Gas chromatography coupled to a Mass Spectrometer with Time Of Flight analyzer (GC-MSTOF) was used to study the reaction products. Sampling was performed by solid phase microextraction (SPME) using a DVB/CAR/PDMS (divinylbenzene/carboxene/polydimethylxyloxane) fiber (collection time = 4 min) and subsequent desorption (during 2 min) in the injection port of the GC (desorption temperature = 250 °C). The capillary column used was an Equity™-1701 (30 m × 0.32 mm × 1 μm) semipolar fused silica. The chromatographic conditions were the following: injector 250 °C; interface 200 °C; oven initial temperature 40 °C during 4 min; ramp of 25 °C min^{-1} to 120 °C, held for 10 min, and second ramp of 20 °C min^{-1} to 200 °C held for 2 min. Once in the mass spectrometer, the sample was ionized by electron impact source (EI), analysed by the TOF, and detected.

2.3. Experimental procedure

The kinetic experiments consist of the reactions of the compound under study and the reference compounds with the three main atmospheric oxidants: OH and NO_3 radicals, and Cl atoms. These were generated in situ, as in previous works (Aranda et al., 2021; Colmenar et al., 2020a,b), by procedures described in the literature according to the following reactions:

For Cl: $Cl_2 + h\nu \rightarrow 2Cl\ \lambda = 360$ nm (R1)

For OH·: $CH_3ONO + h\nu \rightarrow CH_3O\cdot + NO\ \lambda = 360$ nm (R2)

$CH_3O\cdot + O_2 \rightarrow \cdot HO_2 + HCHO$ (R3)

$\cdot HO_2 + NO \rightarrow NO_2 + OH\cdot$ (R4)

For NO_3·: $N_2O_5 + M \rightarrow NO_2 + NO_3\cdot + M$ (R5)

The experiments were performed using nitrogen as carrier gas, except for the experiments with OH·, which were developed in air, since O_2 is necessary to generate the radical according to reaction 3. On the inside of the pyrex glass reactor, there are eight actinic lamps (Philips, TL-K 4W, Actinic BL) that emit in the region of 350–400 nm (λmax =

360 nm) to photolyze the reactants when necessary.

Thus, once the oxidant precursors, 2-iPE and reference compound were introduced into the Pyrex glass reactor (and lamps are switch on in the case of OH· and Cl experiments), the variation of the characteristic bands as a function of time was monitored by FTIR. The treatment of the spectra was carried out using the OMNIC program. The IR bands selected for the monitoring of reactant and the reference compounds have been: 3610 cm^{-1} (O–H stretch) and 1070 cm^{-1} (C–O stretch) for 2-iPE, 2740 cm^{-1} (C–H aldehyde stretch) for hexanal, 2750 cm^{-1} (C–H-aldehyde stretch) for propanal, 911 cm^{-1} (C–H out of plane bend) for 1-butene respectively.

For product studies, the same methodology was followed using air as carrier gas for all experiments and without the reference compounds.

Typical concentrations (in ppm) used in the experiments were as follows: 9–18 for 2-iPE and references, 19–24 for Cl_2, 17–35 for CH_3ONO, 17–23 for NO, 14–25 for N_2O_5. Conversion of 2iPE (%): 40–80 for Cl_2 experiments, 25–50 for OH· experiments and 8–16 for NO_3· experiments. Total pressure = 700 ± 9, temperature = 298 ± 2 K.

2.4. Materials

The purity and supplier company of the reagents used to carry out the experiments is specified below: 2-isopropoxyethanol (99%) and the reference compounds: hexanal (98%), propanal (97%), 1-butene (≥99%) and from Sigma Aldrich. The commercially available products: Isopropyl formate (98%) from Sigma Aldrich and 2-hydroxyethyl acetate (>60%) from TCI. The precursors of the radicals: methyl nitrite, CH_3ONO, synthesized in the laboratory in accordance with the method of Taylor et al. (1980). Dinitrogen pentoxide (N_2O_5) synthesized in the laboratory according to the procedure described by Schott and Davidson (1958). Cl_2 (99%) from Praxair. NO (98.5%) from Air Liquide, N_2O_4 (99.5%) from Fluka, N_2 (99.999%) and synthetic air (99.999%) from Praxair.

3. Results and discussion

3.1. Kinetic study

Previous experiments performed ensured that the variations of the IR bands were proportional to the variations of the concentrations of the reactants, verifying that the photolysis of the organics was a negligible process, that reactions with the walls of the reactor were no significant and that the IR bands selected for monitoring the variations of 2-iPE and the references didn't overlap with those of possible products.

Two or three reference compounds (R) were used in each case. An example of the plots obtained is shown in Fig. 1 for the reactions of Cl with 2-iPE. The slope of each line allows to calculate $k_{2\text{-iPE}}$, known that

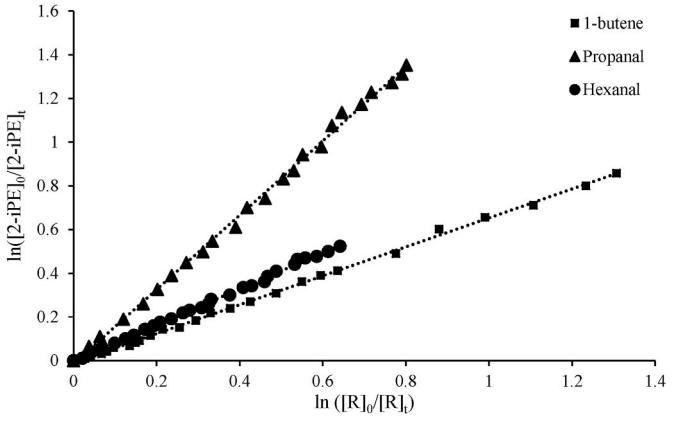


Fig. 1. Plot according to Eq (1) for the reaction of 2-iPE with Cl atoms with three reference compounds.

of the reference compound according to equation (1). Straight lines with zero intercept are obtained in all cases. The plots obtained for the reactions of 2-iPE with OH· and with NO_3· are shown in Figs. S1 and S2.

Table 1 summarizes the results from the kinetic studies. The total absolute error σ (k_{2iPE}) is calculated using the statistical errors from the regression analysis (σ_{slope}) and the quoted error in the value of the rate coefficient for the reference compound (σ_{kR}) according to the following equation:

$$\sigma(k_{2iPE}) = \sqrt{(k_R * \sigma_{pte})^2 + (pte * \sigma_{k_R})^2} \quad (2)$$

Where pte y σ_{pte} are the slope and the associated error, and k_R and σ_{k_R} are the reference coefficient and its error. The final values of the rate coefficients and the associated error were calculated as a weighted average.

The average rate coefficients obtained have been (in cm^3 $molecule^{-1}$ s^{-1}): (2.18 ± 0.15) × 10^{-10}, (1.88 ± 0.10) × 10^{-11} and (3.16 ± 0.45) × 10^{-15} for Cl, OH· and NO_3· reactions with 2-iPE, respectively. Our result is in perfect agreement with those obtained for OH radical reactions in a previous study using absolute and relative techniques (Table S1) (Porter et al., 1997). No previous data are available on the reactivity of 2-iPE with NO_3· or Cl atoms and therefore no comparison can be made. However, it is possible to analyse the obtained results by comparing them with those of other hydroxy ethers and, at the same time, to draw conclusions about the influence on the reactivity of the chemical structure. Thus, the rate coefficients determined in the literature for the reactions of hydroxy ethers with the atmospheric oxidants are compiled in Table S1. Values obtained here are of the same order of magnitude as those of other hydroxy ethers. In a previous work (Aranda et al., 2021) it

Table 1
Summary of relative rate coefficients and absolute rate coefficients for the reaction of 2-iPE with Cl atoms and OH and NO_3 radicals. k in units of cm^3 $molecule^{-1}$ s^{-1}. The rate coefficients used for the reference compounds are also listed in the table.

Reaction	Reference compound[d]	Run	$k_{2iPE}/k_{Ref}\pm2\sigma$	$k_{2iPE}\pm2\sigma$[a,b,c]
2-iPE + Cl[a]	1-butene	1	0.70 ± 0.01	2.10 ± 0.42
	k_{Cl} = 3.00 ± 0.60	2	0.70 ± 0.02	2.10 ± 0.42
		3	0.66 ± 0.01	1.99 ± 0.40
	Propanal	1	1.73 ± 0.05	2.16 ± 0.44
	k = 1.25 ± 0.25	2	1.90 ± 0.02	2.37 ± 0.48
		3	1.70 ± 0.04	2.12 ± 0.43
	Hexanal	1	0.83 ± 0.01	2.30 ± 0.46
	k = 2.79 ± 0.56	2	0,82 ± 0.01	2.29 ± 0.46
		3	0.82 ± 0.01	2.29 ± 0.46
	Weighted Average			**2.18 ± 0.15**
	SAR estimation			**2.11**
2-iPE + OH[b]	1-butene k = 3.10 ± 0.62	1	0.78 ± 0.02	2.43 ± 0.49
		2	0.77 ± 0.03	2.39 ± 0.49
		3	0.77 ± 0.02	2.40 ± 0.49
	Hexanal k = 2.85 ± 0.43	1	0.79 ± 0.03	2.25 ± 0.35
		2	0.72 ± 0.02	2.05 ± 0.32
		3	0.75 ± 0.02	2.14 ± 0.33
	Propanal k = 1.99 ± 0.30	1	0.80 ± 0.03	1.59 ± 0.25
		2	0.84 ± 0.06	1.67 ± 0.28
		3	0.82 ± 0.05	1.63 ± 0.27
		4	0.86 ± 0.02	1.70 ± 0.26
	Weighted Average			**1.88 ± 0.10**
	SAR estimation			**2.61**
2-iPE + NO_3·[c]	1-butene k = 13.00 ± 3.25	1	0.19 ± 0.07	2.44 ± 1.09
		2	0.35 ± 0.03	4.53 ± 1.21
		3	0.29 ± 0.06	3.71 ± 1.22
	Propanal k = 6.30 ± 2.52	1	0.39 ± 0.07	2.43 ± 1.07
		2	0.43 ± 0.03	2.68 ± 1.09
		3	0.50 ± 0.05	3.14 ± 1.29
		4	0.67 ± 0.07	4.20 ± 1.73
	Weighted Average			**3.16 ± 0.45**
	SAR estimation			**7.18**

[a,b,c]k is given in 10^{-10},$10^{-11}$and 10^{-15},also for the reference rate coefficient.[d]Values from McGillen et al., (2020).

was proposed that the rate coefficients with OH· of these series of compounds, increase with increasing chain length on both sides of the ether group. Thus, 2-iPE ($(CH_3)_2CHOCH_2CH_2OH$) rate coefficient determined here agrees with the expected trend when the chain on the ether side is increased (an average value is shown for each rate coefficient calculated from the data in Table S1, units cm^3 $molecule^{-1}$ s^{-1}):

$k_{2ME}(1.22 \times 10^{-11}) < k_{2EE}(1.77 \times 10^{-11}) < k_{2PE}(1.89 \times 10^{-11}) \approx \mathbf{k_{2\text{-}iPE}(1.88 \times 10^{-11})} < k_{2BE}(2.15 \times 10^{-11})$

Considering the increase of the chain in the side of the alcohol group, no rate coefficients of other propoxy ethers are available, except for propoxyethanol but no significant variation is observed comparing k_{2PE} with $k_{2\text{-}iPE}$.

In the case of the reactions with Cl, an increase in the rate coefficients is observed when the length of the hydrocarbon chain increases on both sides of the ether group, but there are few data to establish a clear trend. Furthermore, the reactions are very fast, close to the limit of collision theory:

$k_{2EE}(2.02 \times 10^{-10}) < \mathbf{k_{2\text{-}iPE}(2.18 \times 10^{-10})} < k_{1M2P}(2.28 \times 10^{-10}) < k_{3M1P}(2.66 \times 10^{-10}) < k_{1M2B}(2.79 \times 10^{-10}) < k_{3M1B}(2.95 \times 10^{-10}) < k_{3E1P}(3.41 \times 10^{-10})$

In the case of reactions with nitrate radical, although the number of data available is scarce, a rate coefficient of the same order as those obtained for 2 EE and 2BE has been obtained, with no clear dependence of the reactivity with increasing chain length.

Comparing the rate coefficients obtained here for 2-iPE with those corresponding to similar organic compounds but with one or no functionality (ether and alcohol) in their structure (Fan et al., 2020; Mellouki et al., 2004; Wilson et al., 2006), it is observed that the rate coefficient of 2-iPE is the highest, as shown below for OH· reactions:

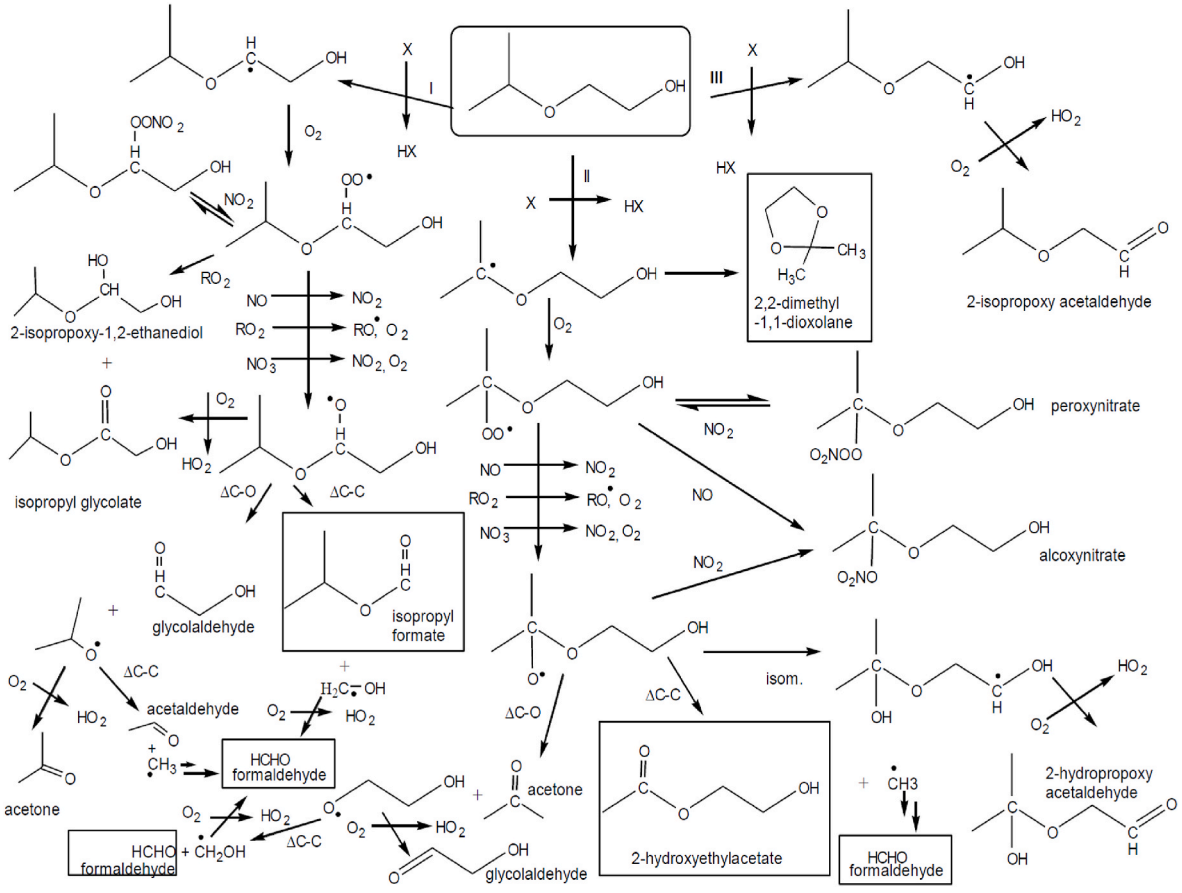
$k_{isopentane} = 3.65 \times 10^{-12}((CH_3)_2CHCH_2CH_3) < k_{ethyl\text{-}isopropylether} = 1.1 \times 10^{-11}((CH_3)_2CHOCH_2CH_3) < k_{3methylbutanol} = 1.4 \times 10^{-11}((CH_3)_2CHCH_2CH_2OH) < \mathbf{k_{2\text{-}iPE} = 1.88 \times 10^{-11}}$ $((CH_3)_2CHOCH_2CH_2OH)$

The activating effect of the two substituents on the reactivity is evident. The alcohol group activates the C–H bond in the α position carbon although previous studies also indicate the activating effect to the carbon in β and even in γ position (Barrera et al., 2019). The ether group also produces an increase in the reactivity of carbons directly attached to oxygen.

An estimation of the rate coefficients of 2-iPE with the atmospheric oxidants have been made using Structure-activity Relationships (SARs). The followed methodology is explained in the Supplementary information and, briefly, is based on the database of experimental kinetics coefficients available to estimate the reactivity factors F(R), for each functional group (R) depending on the type of carbon to which it is attached. The factors proposed by Calvert et al. (2011), have been used for Cl and OH radical reactions and the proposed by Kerdouci et al. (2014), for NO_3 radical reactions. The calculated values are presented in Table 1. Rate coefficients very similar to the experimental ones have been obtained in the estimations with Cl atoms and OH radicals. However, NO_3· calculations are overestimated (an estimated value twice the experimental one), probably due to the uncertainty in the reactivity factors used, as the authors themselves indicate (Kerdouci et al., 2014).

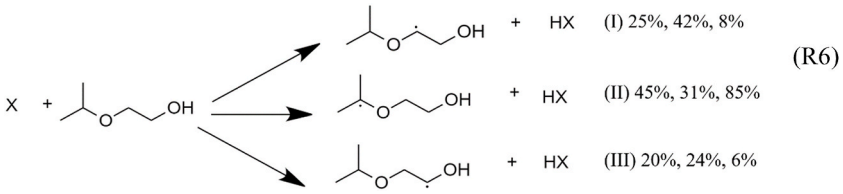
3.2. Mechanism and products

The procedure followed has been to initially establish a proposed mechanism (Scheme 1) in accordance with the principles of atmospheric reactivity and previous studies, and later to carry out the verification of



Scheme 1. The proposed mechanism of the reactions of 2-iPE with the atmospheric oxidants (OH and NO_3 radicals, and Cl atoms). Identified compounds are framed (except for nitrated compounds, also identified in the reactions with NO_3 radicals).

the mechanism from the products obtained experimentally. The reaction is initiated by the attack of the oxidant to one of the carbons of the molecule and the abstraction of a hydrogen atom forming the alkyl radical, that evolves generating mainly carbonyl products such as esters, hydroxyesters, hydroxyaldehydes, alkoxyaldehydes and alkoxyketones. There are six possible pathways for hydrogen abstraction, but according to the SAR calculations (supplementary information), only three ways of attack (H-abstraction from the α carbons with respect to the alcohol or ether groups) have significant contribution in the overall reaction and are shown below.



(R6)

(R6)

X = Cl atoms, OH·, NO_3· and the percentages shown in the reaction correspond to this order.

As can be seen in Scheme 1, the alkyl radical formed reacts with oxygen to form 2-isopropoxy acetaldehyde in route III or to form peroxy radical in routes I and II.

The peroxy radical formed in route I reacts on one hand, with NO and subsequent unimolecular decomposition C–O to glycolaldehyde and an alkoxy radical, or unimolecular decomposition C–C to isopropyl formate and a new radical that, by reaction with O_2, forms formaldehyde. The unimolecular C–O decomposition is considered to be a minor pathway (Aschmann et al., 2001, 2011; Stemmler et al., 1997). On the other hand, the peroxy radical could react with NO_2 forming a peroxynitrate or it could undergo unimolecular isomerization to form 2-isopropoxy-1, 2-ethanediol and isopropyl glycolate.

The alkyl radical formed in route II can form the 5-membered ring 2,2-dimethyl-1,1 dioxolane or can react with oxygen to form the peroxy radical. This radical evolves on the one hand by reaction with NO to form the alkoxy radical and subsequent unimolecular decomposition C–O or C–C (most favourable route). In the case of C–C decomposition, 2-hydroxyethyl acetate and formaldehyde will be formed. The alkoxy radical can also isomerize to form 2-hydropropoxyacetaldehyde or react with NO_2 to form an alkoxynitrate. Other possible reaction pathways of the peroxy radical are the formation of peroxynitrates and alkoxynitrates by reaction with NO_2 and NO respectively.

According to the proposed mechanism, we proceeded to the verification of the reaction products, also considering the differences among the oxidants. For that, as mentioned above, FTIR spectroscopy and Gas chromatography coupled to a mass spectrometer with a time-of-flight analyzer (GC-MSTOF) were used as detection techniques.

FTIR experiments. Fig. 2 shows an example of the residual spectra of the studied reactions after subtracting the 2iPE and the precursors in each case, and, in the case of NO_3·, also subtracting nitric acid.

The characteristic bands of carbonyl groups (C═O, around 1750 cm^{-1}), C–O bonds (between 1100 and 1300 cm^{-1}) and bands of C–H bonds (2700-3000 cm^{-1}) can be observed in all cases. In a previous study (Aschmann and Atkinson, 1999), the reaction products of 2-iPE with OH radicals were investigated, and isopropyl formate and 2-hydroxyethyl acetate were quantified using gas chromatography and in situ atmospheric pressure ionization tandem mass spectrometry. The detection of these products in the spectra of Fig. 2 has been attempted. Thus, comparing these spectra with the reference IR spectra of isopropyl formate (also shown in the figure), there are several spectral characteristics of this compound present in the collected spectra: 2986, 2937, 1726, 1377, 1191 and 1105 cm^{-1} and these increase during the reaction. Therefore, it is a reaction product and corresponds to the route I of the mechanism. The quantification could be carried out as it is a commercial compound. However, 2-hydroxyethyl acetate only has been identified (route II), its quantification was not possible due to experimental

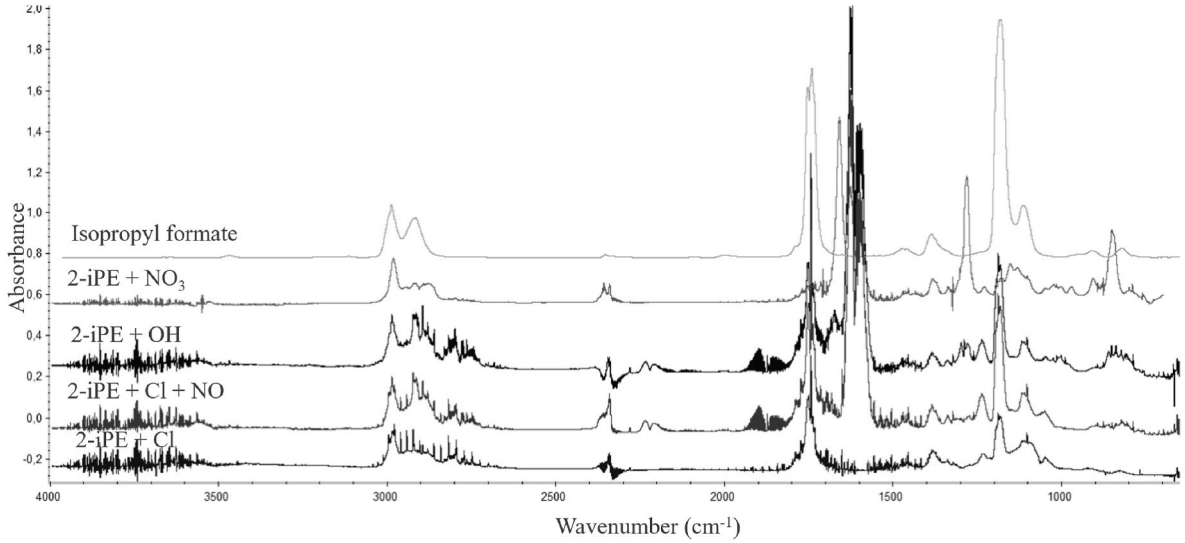


Fig. 2. FTIR spectra for the reactions of 2-iPE (25% conversion) with the atmospheric oxidants. The experimental reference spectrum of isopropyl formate is also shown in the figure.

difficulties. The available commercial product had a purity of only 60% and when recording the IR spectrum, the peaks of the compound and the impurity (diacetate) are overlapped. In addition, it is lost by reactions with the walls of the reactor.

Formaldehyde (co-product in route I, but also formed in the other routes) has also positively identified according to IR bands between 2600 and 3080 cm^{-1} and the intense IR peak at 1750 cm^{-1}. This compound has been quantified using reference IR spectra from the Eurochamp database (Doussin, 2017; Johnson, 2017).

In the case of the nitrate radical reactions, the bands attributed to alkoxy nitrated compounds ($RONO_2$ ~1663, 1284, 853 cm^{-1}) and to peroxynitrates ($ROONO_2$ ~1718, 1300 and 793 cm^{-1}) (Finlayson-Pitts and Pitts, 2000), are clearly observed. However, in the case of chlorine reactions in the presence of NO in which nitrate products (alkoxy- and peroxynitrates) are also formed, their peaks are not so evident as in previous works (Aranda et al., 2021; Colmenar et al., 2020a,b) and quantification has not been possible. Nitrated compounds could also be formed in the reactions with OH radicals, but these were not estimated due to the additional contribution of the precursor used. The quantification of nitrocompounds for NO_3· has been carried out considering the average integrated absorption coefficient of 1.2×10^{-17} cm $molecule^{-1}$ (range 1250–1330 cm^{-1}) determined for similar compounds (Tuazon and Atkinson, 1990).

Experimental time-concentration profiles of reactant and products for NO_3 radical reactions with 2-iPE obtained by FTIR are shown in Fig. 3. The observed trends indicate that these are primary products. Yields are obtained by plotting the variation of the concentration of the quantified products as a function of the reactant variation (Fig. S3). Similar plots for Cl and OH· reactions are shown in Figs. S4–S9. In the case of formaldehyde, at very long times it is observed how the yield of HCHO tends to decrease. For this reason, the yields have been recalculated using the formalism published by Tuazon et al. (1986) as explained in previous works (Colmenar et al., 2020a,b). This correction assumes that reaction products are subsequently consumed in secondary processes like photolysis, wall loss, and oxidation by Cl atoms in this case. Thus, their formation yields in the target reactions are underestimated when determined from plotting the formed product against the consumed compound of interest and the yields should increase when corrected. In the case of ethyl formate, corrected yields calculated are very similar to uncorrected ones for all the studied reactions, and no modification have been considered.

GC-MSTOF experiments. Fig. 4 shows an example of the chromatograms collected at different reaction times for the reactions of Cl atoms with 2-iPE in the presence of NO. Examples for the experiments carried out with the other oxidants are shown in Figs. S10–S12.

The peak at t_R (retention time) = 6.71 min corresponds to the reactant and decreases as the reaction proceeds. The product peaks perfectly observed from the first minutes of the reaction are that of t_R 8.7 min, 6.21 min and 2.63 min, also observed in the reactions of 2-iPE with the other oxidants (see Figs. S10–S12). Thus, the peak at $t_R = 2.63$ min has been assigned to isopropyl formate according to the library spectra and it has been confirmed experimentally with the commercial sample. The peak at $t_R = 8.7$ min is important and has been assigned to 2-hydroxyethyl acetate according to the mass spectrum of the library for this peak (96 % of similitude) and confirmed through the commercial compound available. The peak at t_R = 6.21 min, observed from the beginning of the reaction coming from the fiber, increases in the development of the reaction, so it also corresponds to a reaction product. The library establishes as the most probable 2-methylpropanoic acid,47% of similitude, a very low percentage to affirm that it is a reaction product, especially when it is not formed in any of the proposed routes. Fragmentations of the acid 2-methylpropanoic also corresponds to isopropyl glycolate, one of the expected products (route I) but it was not possible to verify experimentally since this compound is not commercial and its mass spectrum is not available. Other minor peaks are also observed to increase during the experiments. Only the unambiguous assignment (high similarity (88%)) has been possible of the product 2,2-dimethyl-1,3-dioxolane (t_R = 5.02 min), which could be generated by one of the pathways of the mechanism (route II). According to the mass spectrum of the peak at t_R = 7.32 min we proposed that it could be isopropoxyacetaldehyde, expected product of route III of the mechanism. Acetone, formaldehyde and glycolaldehyde, that are expected products, have retention times very short and they are hidden with the peak of the air. In the reaction of NO_3· with 2-iPE are also observed peaks at t_R 9.41 and 11.08 min that have been assigned to unidentified nitrated compounds. Mass spectra obtained for each compound detected, and the possible assignation are shown in Table S2. Some examples of the observed variation of the chromatographic peaks with time for the reactions of 2-iPE with the atmospheric oxidants are shown in Figs. S13–S15.

Table 2 summarizes the estimated yields (in %) for the quantified products in the studied reactions. It is known that the reaction of RO_2 + NO is more exothermic than the reaction RO_2+RO_2 favouring the decomposition route (Atkinson, 2007). Then in the presence of NO the formation of the alkoxy radical is favoured, which justifies the higher yields of isopropyl formate and HCHO observed compared to reactions with Cl without NO.

An appreciable difference between the yields measured using FTIR or

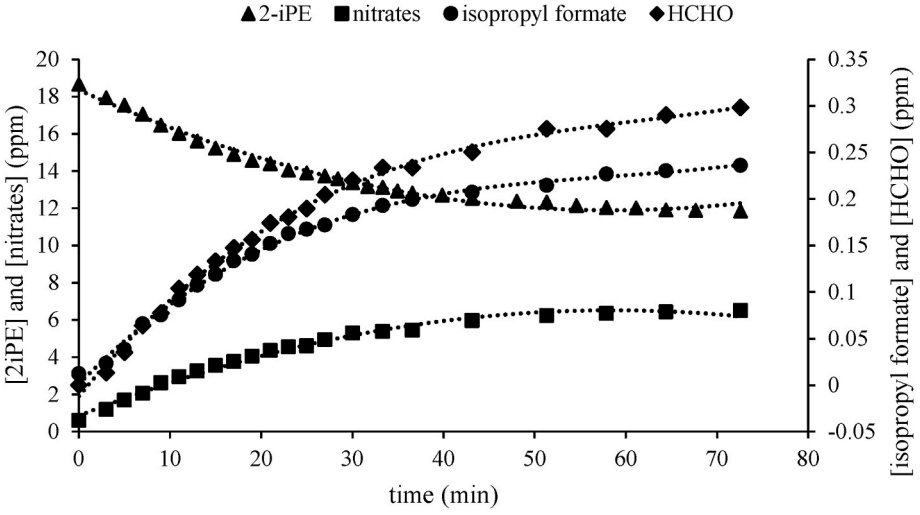


Fig. 3. Experimental time-concentration profiles of reactant and products for the reaction of 2-iPE with NO_3 radicals obtained by FTIR.

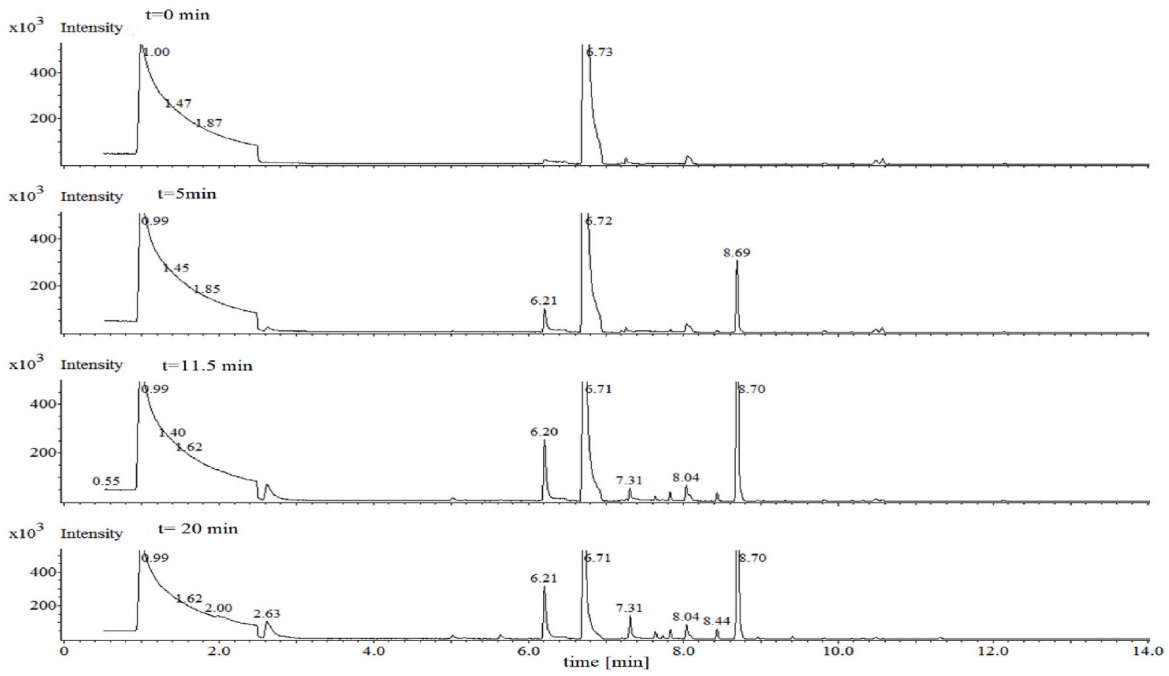


Fig. 4. Chromatograms collected for the reaction of Cl atoms with 2-iPE in the presence of NO.

GC-MS in the case of the reactions of Cl with 2-iPE in the absence of NO are observed. The detailed analysis of the chromatogram at that retention time seems to indicate that the automatically integrated area extends including a small peak very close, which may be another minor reaction product, and we think this is the cause of the yield obtained being higher than the real. This small peak is not observed in the other reactions studied and, in these cases, the calculated yields correspond only to isopropyl formate. Table S3 shows the proposed products generated according to the experiments developed using GC-MS.

According to the obtained yields and the estimation with SAR, route II has been proposed as the dominant process for the reactions with Cl atoms and OH radicals. For the reactions with nitrate radical, the formation of nitrated compounds is evident, but it has not been possible to identify which specific compounds are formed, and it is not possible to affirm which of the routes is the majority, although it is expected to be the one for which the radical attack is easier.

4. Atmospheric implications

To determine the atmospheric implications of the release of a compound into the atmosphere, several factors can be considered: the lifetime, the photolysis processes, its ozone generation potential, its influence on the global warming potential, its solubility and deposition processes and the effects derived from the products generated in atmospheric reactions. The determination of these parameters for 2-iPE are shown below along with their discussion.

Atmospheric lifetimes can be calculated relative to each degradation process according to the following expression: $\tau_R = 1/k_R[Ox]$, where k_R is the rate coefficient of the reaction and [Ox] is the typical atmospheric concentration of the oxidant. The values used for these concentrations have been: $[OH\cdot] = 1 \times 10^6$ radical cm^{-3} (12 h average) (Prinn et al., 2001), $[NO_3\cdot] = 5 \times 10^8$ radical cm^{-3} (Atkinson, 2000), $[Cl] = 1 \times 10^3$ atoms cm^{-3} (average global concentration) (Platt and Jansen, 1995), peak concentration of [Cl] (coastal and industrial areas) $= 1.3 \times 10^5$ atoms cm^{-3} (Spicer et al., 1998). From the kinetic data in Table S1, the atmospheric lifetimes of the series of hydroxyethers have been calculated and are presented in Table S4. As can be seen from the data of the table, reactions of hydroxyl radicals with hydroxyethers are expected to be the main oxidative degradation process of these compounds in the atmosphere (lifetimes of hours). For 2-iPE, the values obtained have been: 15 h, 7 days and 53 days for the reactions with OH·, $NO_3\cdot$ and Cl respectively. Only in coastal and industrial areas, the reaction with Chlorine could be competitive since in this case the lifetimes obtained are around 10 h.

Since ethers do not absorb in the tropospheric actinic region, photolysis is a negligible process in their transformation (Atkinson, 2003). It could also be postulated that wet deposition is a negligible loss process because of the low Henry's law constants for ethers (Johanson and Dynésius, 1988; Sander, 2023), but considering the presence of the alcohol group, it is expected that 2-iPE could be relatively soluble in water. From the Henry constant data (Johanson and Dynésius, 1988; Sander, 2023), a value of 486 M/atm for 2-iPE has been calculated, which allows to estimate the lifetime of this compound relative to the wet deposition process using the procedure given in Chen et al. (2003), obtaining a value of 50 days, which can be considered negligible relative to homogeneous oxidation processes in the gas phase.

Therefore, as this compound 2-iPE is eliminated in the atmosphere in a few hours, the products generated may also have environmental implications. Formaldehyde generated is one of the substances considered potentially carcinogenic to humans. (NTP, 2021). Aldehydes and organic nitrates are present in episodes of photochemical smog, one of the main current environmental problems. In addition, acetates and formates that have also been detected as products in the studied reactions are very soluble and will undergo wet deposition processes or acid formation. But also these multifunctional products with polar groups have low volatility and could contribute to the formation of Secondary Organic Aerosols (Calvert et al., 2011) (SOA).

Regarding the ozone generation potential, we must remember the negative effects that tropospheric ozone has on health (WHO, 2020). In this work, we have used as a control parameter for ozone generation, the Photochemical Ozone Creation Potential (POCP) index, which basically calculates the amount of O_3 formed when the emission of a compound is increased relative to that resulting from an identical increase in the emission (on a mass basis) of a reference VOC, which is ethene, using a photochemical trajectory model (Derwent et al., 1996; Jenkin et al., 2017). The estimated POCP values for 2-iPE that we have obtained have been of 45,0 and 40,9 for NW European conditions and USA urban conditions, respectively. If we compare with other hydroxyethers,

Table 2
Summary of the estimated yields (in %) for the quantified products in the reactions of 2-iPE with the three oxidants.

Reaction	Exp.	Isopropyl formate		HCHO[a]	Comp. Nitra.
		FTIR (%)	GC-MS (%)	FTIR(%)	FTIR (%)
2-iPE + Cl	1	13.20 ± 0.17		16–26	
	2	12.27 ± 0.16		16–26	
	3	12.32 ± 0.17		15–25	
	4	12.45 ± 0.15	44.67 ± 6.51	16–26	
	5	12.89 ± 0.34	38.53 ± 3.08	18–29	
	6	13.02 ± 0.34	33.69 ± 6.37	19–30	
	Average	**12.69 ± 0.79**	**38.96 ± 11.01**	**17–27**	
TC (%)[b]		**14.75**			
2-iPE + Cl + NO	1	27.68 ± 0.65		29–48	
	2	28.63 ± 0.26		29–49	
	3	27.49 ± 0.37		27–46	
	4	30.23 ± 0.28	28.46 ± 11.44	27–52	
	5	30.12 ± 0.29	32.97 ± 3.70	31–51	
	6	27.95 ± 0.49	27.04 ± 6.61	30–47	
	Average	**28.68 ± 2.44**	**29.49 ± 6.20**	**29–49**	
TC (%)[b]		**30.74**			
2-iPE + OH·	1	31.95 ± 0.44	24.83 ± 3.23		
	2	32.26 ± 0.42	22.74 ± 3.55		
	3	33.40 ± 0.44	25.14 ± 2.75		
	Average	**32.54 ± 1.52**	**24.23 ± 2.61**		
TC (%)[b]		**26.03**			
2-iPE + NO_3·	1	3.29 ± 0.09		4–4	87.22 ± 1.84
	2	4.02 ± 0.12		5–7	81.91 ± 2.78
	3	3.75 ± 0.09		5–7	78.02 ± 2.61
	4	4.56 ± 0.16		6–8	83.55 ± 3.20
	Average	**3.90 ± 1.06**		**5–7**	**82.67 ± 7.63**
TC (%)		**86.99**			

[a] Yields of formaldehyde estimated using two different reference IR spectra from the Eurochamp database (Doussin, 2017; Johnson, 2017), for this reason, a range is indicated. Yields.

[b] Total carbon $= \sum_1^i \left(\frac{\text{nº of carbon of product}_i}{\text{nº of carbon of 2-iPE}} \times \text{molar yield}_i \right)$ considering only the data obtained with FTIR.

values are in the expected range for these compounds (29–45) (Aranda et al., 2021; Barrera et al., 2019; Jenkin et al., 2017). Compared to other VOCs, values are higher than those of alkanes, in the same order than alcohols and ethers, and lower than unsaturated oxygenated and alkenes. Therefore, 2-iPE and other hydroxyethers are important in tropospheric ozone generation processes.

Regarding the calculation of GWP (global warming potential) parameter, the method of Hodnebrog et al. (2020) and the lifetimes calculated above have been used. A value of $1{,}3 \times 10^{-3}$ for a time horizon of 20 years has been calculated for 2-iPE. We can therefore consider that the direct contribution to radiative forcing of climate is negligible.

5. Conclusions

In this work, the rate coefficients of the reactions of 2-iPE with chlorine atoms and with the nitrate radical have been determined for the first time. In the case of reactions with the OH radical, the data available in the literature agrees perfectly with that obtained in this work. The results obtained also agree with the kinetic data of other hydroxy ethers confirming the observed increase of the reactivity when the chain length increases on both sides of the ether group. Thanks to the work carried out, we contribute to increase the database of this series of compounds, which is still scarce, especially regarding reactions with Cl and NO_3·.

The study of reaction products carried out using FTIR and CG-MSTOF has allowed the identification and quantification of isopropyl formate, formaldehyde and, in the case of NO_3· reactions, nitrated compounds. Other products identified but whose quantification has not been possible are: 2-hydroxyethyl acetate, 2,2-dimethyl-1,3-dioxolane, isopropyl glycolate and isopropoxyacetaldehyde. The proposed mechanism involves the first step of abstraction of a hydrogen atom from the radical, preferably the H attached to α-position carbons with respect to the alcohol or the ether group, and the subsequent reactions of the resulting radicals.

Regarding the atmospheric implications, it is concluded that the main loss process of 2-iPE is its daytime reaction with OH radicals. The estimated $POCP_E$ value indicates that this compound could be a potential contributor of tropospheric ozone. The direct contribution to radiative forcing of climate is negligible. Finally, some of the products generated may be harmful to health and the environment.

CRediT authorship contribution statement

Inmaculada Aranda: Formal analysis, Investigation, Methodology, Validation, Writing – original draft, Writing – review & editing. **Sagrario Salgado:** Conceptualization, Methodology, Supervision, Writing – original draft, Writing – review & editing. **Pilar Martín:** Conceptualization, Methodology, Supervision, Writing – original draft, Writing – review & editing. **Florentina Villanueva:** Methodology, Supervision. **María Teresa Pinés:** Formal analysis, Investigation, Methodology. **Beatriz Cabañas:** Conceptualization, Funding acquisition, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2024.120420.

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