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# Keto-ether and glycol-ethers in the troposphere: reactivity toward OH radicals and Cl atoms, global lifetimes, and atmospheric implications

Javier A. Barrera<sup>1</sup> · Pablo R. Dalmasso<sup>2</sup> · Raúl A. Taccone<sup>1</sup> · Silvia I. Lane<sup>1</sup>

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**Abstract** Rate coefficients for the gas-phase reactions of OH radicals and Cl atoms with 1-methoxy-2-propanone (1-M-2-PONE), 1-methoxy-2-propanol (1-M-2-POL), and 1-methoxy-2-butanol (1-M-2-BOL) were determined at room temperature and atmospheric pressure using a conventional relative-rate technique. The following absolute rate coefficients were derived:  $k_1(\text{OH} + 1\text{-M-2-PONE}) = (0.64 \pm 0.13) \times 10^{-11}$ ,  $k_2(\text{OH} + 1\text{-M-2-BOL}) = (2.19 \pm 0.23) \times 10^{-11}$ ,  $k_3(\text{Cl} + 1\text{-M-2-PONE}) = (1.07 \pm 0.24) \times 10^{-10}$ ,  $k_4(\text{Cl} + 1\text{-M-2-POL}) = (2.28 \pm 0.21) \times 10^{-10}$ , and  $k_5(\text{Cl} + 1\text{-M-2-BOL}) = (2.79 \pm 0.23) \times 10^{-10}$ , in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This is the first experimental determination of  $k_2$ - $k_5$ . These rate coefficients were used to discuss the influence of the structure on the reactivity of the studied polyfunctional organic compounds. The atmospheric implications for 1-M-2-PONE, 1-M-2-POL, and 1-M-2-BOL and their reactions were investigated estimating atmospheric parameters such as lifetimes, global warming potentials, and average photochemical ozone production. The approximate nature of these values was stressed

considering that the studied oxygenated volatile organic compounds are short-lived compounds for which the calculated parameters may vary depending on chemical composition, location, and season at the emission points.

**Keywords** Atmospheric chemistry · Keto- and glycol-ethers · OH radicals · Cl atoms · Relative rate coefficient · Gas-phase reactivity trends · Atmospheric acceptability

## Introduction

Oxygenated volatile organic compounds (OVOCs) are ubiquitous in the troposphere (Singh et al. 1995). They have both primary and secondary sources, being emitted directly into the atmosphere by biogenic and anthropogenic processes, as well as being formed from the gas-phase oxidation of parent hydrocarbons (Mellouki et al. 2015; Wyche et al. 2007). Natural OVOC emissions are predominant on a global scale. However, anthropogenic sources are the most important contributors to ambient concentrations near industrialized areas (Mellouki et al. 2015; Schade and Goldstein 2001). Among the anthropogenic OVOCs, the keto-ethers (KEs) and glycol-ethers (GEs) have received recurring attention. A variety of these compounds has been widely used mainly for industrial applications (Calvert et al. 2011). Glycol-ethers act as solvents, which are an essential part of everyday life. They are an invaluable solution for industries that range from pharmaceuticals and microelectronics to domestic cleaning, personal care, agricultural chemicals, and printing (Dow Chemical Company 2001; Whin and Johnson 1996). Whereas KEs are used for pesticide intermediates and polymer synthesis (Chemical Book 2016), and they are also formed in the tropospheric oxidation of some GEs (Aschmann and Atkinson 1998; Aschmann et al. 2011). Based on the use and

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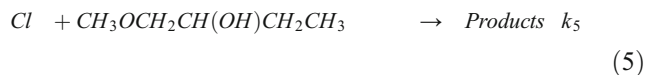
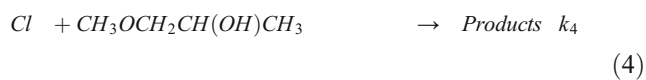
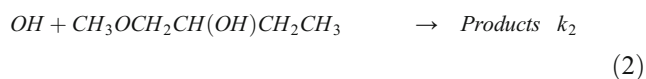
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applications of these organic compounds, their emission levels are expected to be considerable even when there are no emission inventories for these OVOCs.

Tropospheric removal processes for OVOCs are well established to be the chemical processes of photolysis and gas-phase reactions, and the physical loss processes of dry and wet deposition. While the major fate of OVOCs is expected to be via gas-phase reaction with OH radicals (Atkinson and Arey 2003; Finlayson-Pitts and Pitts 2000), in recent years, the Cl-initiated degradation has been postulated to be an important homogeneous loss process of OVOCs in marine and coastal environments, where high concentration of Cl atoms has been reported (Finlayson-Pitts and Hemminger 2000; Spicer et al. 1998). In addition, large amounts of reactive chlorine species were found over continental areas in the lowest part of the atmosphere (Thornton et al. 2010; von Glasow 2010). Thus, the chlorine chemistry in the atmosphere could play a significant role in the chemical oxidation of OVOCs.

The OVOCs degradation in the troposphere is complex and leads to the production of several secondary pollutants such as ozone, highly oxidized VOCs, and secondary organic aerosols. Hence, oxygenated compound emissions have an impact on the tropospheric oxidizing capacity both on a regional and global scale, and it is important to consider their possible effects on air quality (Mellouki et al. 2003, 2015). In addition, adverse effects on human health, vegetation (e.g., crops), and materials are known due to elevated levels of tropospheric ozone. Therefore, understanding the contribution of various OVOCs to ozone formation is of particular interest.

In this work, we report a relative kinetic study of the oxidation reactions of 1-methoxy-2-propanone (1-M-2-PONE) and 1-methoxy-2-butanol (1-M-2-BOL) initiated by OH radicals and Cl atoms, and 1-methoxy-2-propanol (1-M-2-POL) with Cl atoms, at room-temperature and atmospheric pressure:



To the best of our knowledge, this work constitutes the first experimental determination of the rate coefficients for the reactions of OH radicals ( $k_{\text{OH}}$ ) with 1-M-2-BOL, whereas for 1-

M-2-PONE, there is only one previous kinetic study performed by Dagaut et al. (1989) using the flash photolysis-resonance fluorescence technique at 298 K. Moreover, there are no prior kinetic determinations of the rate coefficients for the gas-phase reactions of Cl atoms ( $k_{\text{Cl}}$ ) with the three OVOCs here studied.

Additionally, this study aims to extend the existing scant database on the reactivity of KEs and GEs toward tropospheric oxidants as part of an ongoing program in our laboratory regarding the fate and impact of oxygenated species in atmospheric chemistry (Cometto et al. 2008; Dalmasso et al. 2010, 2012). Moreover, the kinetics results obtained provide an opportunity to examine the influence of the ether linkage (–O–) on the reactivity of these polyfunctional organic compounds. Finally, the atmospheric implications of the anthropogenic OVOCs studied were evaluated estimating their atmospheric lifetimes, radiative efficiencies (REs), global warming potentials (GWPs), and the average photochemical ozone production of each OVOC.

## Materials and methods

### Chemicals

1-M-2-PONE (Aldrich 95%), 1-M-2-POL (Aldrich 99%), 1-M-2-BOL (Aldrich 98%), cyclopentane (Merck, 99%), n-heptane (Merck, 99%), 1-pentene (Aldrich 98.5%), butyraldehyde (Aldrich 99%), n-pentane (Dorwill, 99.1%), and 2-chloro-ethyl-methyl-ether (Aldrich, 98%) were degassed by repeated freeze-pump-thaw cycling and purified by vacuum distillation until gas chromatographic analysis revealed no observable impurities.

A 70.5%  $\text{H}_2\text{O}_2$  solution was supplied by Atanor S.A., and it was concentrated by bubbling UHP  $\text{N}_2$  through this solution prior to use, to remove water.  $\text{Cl}_2$  was prepared via the reaction between HCl and  $\text{KMnO}_4$  and was purified by repeated trap to trap distillation until a sample of 99% purity was obtained, confirmed by IR and UV spectroscopy.

Synthetic air (purity 99.999%) and chromatographic gases were purchased from LINDE.

### Relative-rate measurements

Rate coefficients  $k_1$ – $k_5$  were determined using a relative-rate method at  $(298 \pm 2)$  K and atmospheric pressure of synthetic air. This method assumes that loss of the KE or GE and reference compound occurs only by reactions (6) and (7):



and it allows to obtain the relative-rate coefficient,  $k_{OVOC}/k_{Ref}$ , from the slope of a plot of  $\ln([OVOC]_0/[OVOC]_t)$  versus  $\ln([Ref]_0/[Ref]_t)$  given by

$$\ln\left(\frac{[OVOC]_0}{[OVOC]_t}\right) = \frac{k_{OVOC}}{k_{Ref}} \times \ln\left(\frac{[Ref]_0}{[Ref]_t}\right) \quad (8)$$

where  $[OVOC]_0$ ,  $[Ref]_0$ ,  $[OVOC]_t$ , and  $[Ref]_t$  are the concentrations of KE or GE and reference compound at times  $t = 0$  and  $t$ , respectively, and  $k_{OVOC}$  and  $k_{Ref}$  are the rate coefficients of reactions (6) and (7), respectively.

The experimental set-up used to measure  $k_1$ – $k_5$  was presented in a previous publication (Dalmaso et al. 2005), which consisted of a greaseless high vacuum system, a 200-L collapsible Teflon bag (reaction chamber), a photolysis box, and a gas chromatograph (GC-FID, Perkin Elmer Clarus 500) with flame-ionization detection.

Reaction mixtures consisting of a KE or GE, a reference organic compound, and the OH radical/Cl atom precursor, diluted in synthetic air, were prepared in the reaction chamber and left to mix, prior to photolysis, for at least 1 h. Synthetic air was used to simulate the concentration of  $O_2$  and  $N_2$  in the atmosphere.

The initial concentration ranges, in ppm, of 1-M-2-PONE, 1-M-2-POL, and 1-M-2-BOL, and reference compounds (cyclopentane, n-heptane, 1-pentene, butyraldehyde, n-pentane, and 2-chloroethylmethylether) used in the experiments are shown in Tables 1 and 2. OH radicals and Cl atoms were generated in situ in the collapsible Teflon bag by the UV photolysis of  $H_2O_2$  (germicide lamps,  $\lambda_{max} \sim 254$  nm) and molecular chlorine (black lamps,  $\lambda_{max} \sim 360$  nm), respectively. Typically four of these lamps were used, and the total time of photolysis varied from 1 to 7 min. The  $H_2O_2$  and  $Cl_2$  concentrations used were in the range 170–220 and 110–220 ppm, respectively (where 1 ppm =  $2.46 \times 10^{13}$  molecule  $cm^{-3}$  at 298 K and 760 Torr of total pressure).

After each photolysis, reaction mixtures were removed from the Teflon bag using calibrated gas syringes (Hamilton gas-tight). The organics were monitored by gas chromatography using an Elite-5 capillary column (Perkin Elmer, 30 m, 0.32 mm i.d., 0.25  $\mu m$  film thickness). The column temperature was maintained isothermally at 35 °C (1-M-2-PONE and 1-M-2-POL) or 45 °C (1-M-2-BOL), and the carrier gas flow was 0.9 mL of UHP He per min.

For each reaction mixture, typically 10 or more samples before photolysis were injected into the gas chromatograph to obtain the uncertainty associated with the sampling process. The relative standard deviations of these replicate injections were below 5% for both OVOC and reference compound.

### Infrared absorption spectra

To estimate the radiative efficiency, infrared spectra of the three OVOCs studied were recorded in the 800–1500  $cm^{-1}$  region at 298 K using a Nicolet FTIR spectrometer, with 1.0  $cm^{-1}$  resolution, varying the pressure of a pure compound between 0.5 and 4.0 Torr. The absorption cell used was a Pyrex cell sealed with NaCl windows and with an optical path length equal to  $(23.0 \pm 0.1)$  cm. Gas sample pressures were measured with a capacitance manometer (MKS Baratron, range 10 Torr). Background spectra were measured with the sample cell under vacuum.

### Results

Second-order rate coefficients  $k_1$ – $k_5$  were determined at  $(298 \pm 2)$  K and atmospheric pressure and obtained from the relative loss of the KE or GEs versus that of the reference compounds in the presence of OH radicals or Cl atoms.

**Table 1** Concentration of the reactants, rate coefficient ratios,  $k_{OVOC}/k_{Ref}$ , and the absolute rate coefficients,  $k_{OVOC}$ , for the reactions of OH radicals with 1-methoxy-2-propanone and 1-methoxy-2-butanol at 298 K and atmospheric pressure

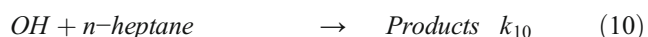
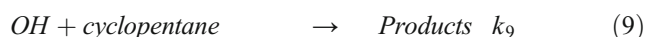
OVOC	$[OVOC]_0$ (ppm)	Reference compound	$[Ref]_0$ (ppm)	Number of runs	$k_{OVOC}/k_{Ref}$	$k_{OVOC}$ ( $cm^3$ molecule $^{-1}$ s $^{-1}$ )
<b>1-M-2-PONE</b>	39	Cyclopentane	46	1	$1.31 \pm 0.03$	$(0.64 \pm 0.08) \times 10^{-11}$
	52		45	2	$1.28 \pm 0.02$	$(0.62 \pm 0.07) \times 10^{-11}$
	46	n-Heptane	58	3	$1.33 \pm 0.03$	$(0.64 \pm 0.08) \times 10^{-11}$
	33		40	1	$0.96 \pm 0.03$	$(0.65 \pm 0.12) \times 10^{-11}$
	55		56	2	$0.95 \pm 0.04$	$(0.64 \pm 0.12) \times 10^{-11}$
					<b>Average</b>	<b><math>(0.64 \pm 0.13) \times 10^{-11}</math></b>
<b>1-M-2-BOL</b>	55	Butyraldehyde	60	1	$0.88 \pm 0.02$	$(2.10 \pm 0.14) \times 10^{-11}$
	49		55	2	$0.90 \pm 0.03$	$(2.15 \pm 0.16) \times 10^{-11}$
	40		45	3	$0.91 \pm 0.02$	$(2.17 \pm 0.15) \times 10^{-11}$
	40	1-Pentene	39	1	$0.71 \pm 0.04$	$(2.26 \pm 0.16) \times 10^{-11}$
	49		60	2	$0.70 \pm 0.03$	$(2.23 \pm 0.14) \times 10^{-11}$
					<b>Average</b>	<b><math>(2.19 \pm 0.23) \times 10^{-11}</math></b>

**Table 2** Concentration of the reactants, rate coefficient ratios,  $k_{OVOC}/k_{Ref}$ , and the absolute rate coefficients,  $k_{OVOC}$ , for the reactions of Cl atoms with three studied OVOCs at 298 K and atmospheric pressure

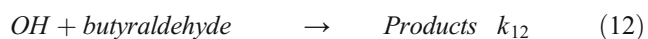
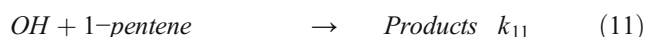
OVOC	[OVOC] <sub>0</sub> (ppm)	Reference compound	[Ref] <sub>0</sub> (ppm)	Number of runs	$k_{OVOC}/k_{Ref}$	$k_{OVOC}$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
<b>1-M-2-PONE</b>	50	n-Pentane	50	1	0.46 ± 0.04	(1.16 ± 0.11) × 10 <sup>-10</sup>
	52		58	2	0.45 ± 0.03	(1.13 ± 0.09) × 10 <sup>-10</sup>
	50		55	3	0.42 ± 0.02	(1.06 ± 0.07) × 10 <sup>-10</sup>
	55	CIEME <sup>a</sup>	56	1	0.90 ± 0.03	(1.01 ± 0.18) × 10 <sup>-10</sup>
	48		50	2	0.91 ± 0.02	(1.01 ± 0.18) × 10 <sup>-10</sup>
<b>Average</b>						<b>(1.07 ± 0.24) × 10<sup>-10</sup></b>
<b>1-M-2-POL</b>	40	n-Pentane	40	1	0.91 ± 0.05	(2.29 ± 0.16) × 10 <sup>-10</sup>
	49		44	2	0.87 ± 0.03	(2.19 ± 0.12) × 10 <sup>-10</sup>
	59		41	3	0.92 ± 0.02	(2.31 ± 0.12) × 10 <sup>-10</sup>
	40	Cyclopentane	39	1	0.72 ± 0.02	(2.34 ± 0.09) × 10 <sup>-10</sup>
	59		58	2	0.70 ± 0.03	(2.28 ± 0.12) × 10 <sup>-10</sup>
<b>Average</b>						<b>(2.28 ± 0.21) × 10<sup>-10</sup></b>
<b>1-M-2-BOL</b>	45	n-Pentane	43	1	1.12 ± 0.03	(2.82 ± 0.15) × 10 <sup>-10</sup>
	49		40	2	1.10 ± 0.04	(2.77 ± 0.17) × 10 <sup>-10</sup>
	39		61	3	1.11 ± 0.05	(2.79 ± 0.16) × 10 <sup>-10</sup>
	39	Cyclopentane	40	1	0.86 ± 0.05	(2.80 ± 0.19) × 10 <sup>-10</sup>
	55		48	2	0.85 ± 0.06	(2.77 ± 0.21) × 10 <sup>-10</sup>
<b>Average</b>						<b>(2.79 ± 0.23) × 10<sup>-10</sup></b>

<sup>a</sup> CIEME: 2-chloroethylmethylether

The following reactions were used as reference to determine the reaction rate coefficient of 1-M-2-PONE ( $k_1$ ):



where  $k_9 = (4.85 \pm 0.58) \times 10^{-12}$  (Gennaco et al. 2012) and  $k_{10} = (6.76 \pm 1.20) \times 10^{-12}$  (Atkinson 2003). For reaction (2) of 1-M-2-BOL, the reference reactions were:



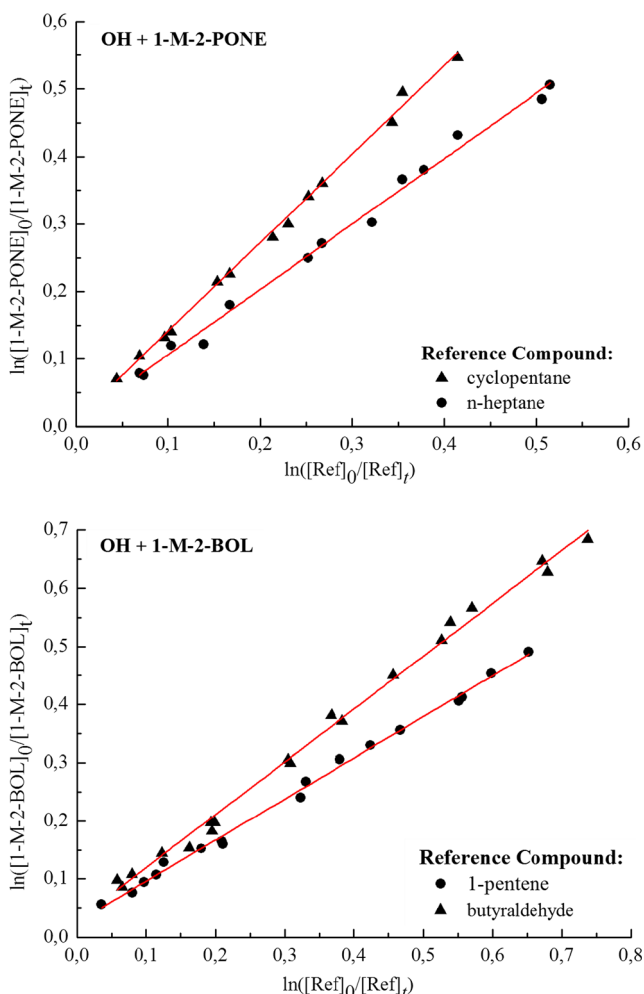
with  $k_{11} = (3.19 \pm 0.14) \times 10^{-11}$  (Atkinson 1986) and  $k_{12} = (2.39 \pm 0.16) \times 10^{-11}$  (D'Anna et al. 2001). All the  $k$  values are in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

For reaction (3) of 1-M-2-PONE with Cl atoms, n-pentane and 2-chloroethylmethylether were used as references, and n-pentane and cyclopentane for reactions (4) and (5) of 1-M-2-POL and 1-M-2-BOL with Cl atoms. The rate coefficients used were the following:  $k_{n\text{-pentane}} = (2.52 \pm 0.12) \times 10^{-10}$  (Atkinson and Aschmann 1985),  $k_{2\text{-chloroethylmethylether}} = (1.11 \pm 0.20) \times 10^{-10}$  (Dalmasso et al. 2005), and  $k_{\text{cyclopentane}} = (3.26 \pm 0.10) \times 10^{-10}$  (Wallington et al. 1989), all in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

The relative-rate technique relies on the assumption that both OVOC and reference compounds are removed

solely via reaction with OH radicals or Cl atoms. To verify this assumption, mixtures of H<sub>2</sub>O<sub>2</sub> or Cl<sub>2</sub> with both organic compounds were prepared and allowed to stand in the dark between 1 and 3 h. No loss of the organic species was observed over the typical time periods used in this work, which allowed to conclude that losses of both OVOC and reference compound due to dark reaction or by removal at the walls were of negligible importance. Furthermore, to test for possible photolysis of the reactants used, mixtures of both OVOC and reference compound in the absence of H<sub>2</sub>O<sub>2</sub> or Cl<sub>2</sub> were irradiated for 30 min using the output of all the lamps surrounding the chamber. No significant photolysis of any of the reactants was observed.

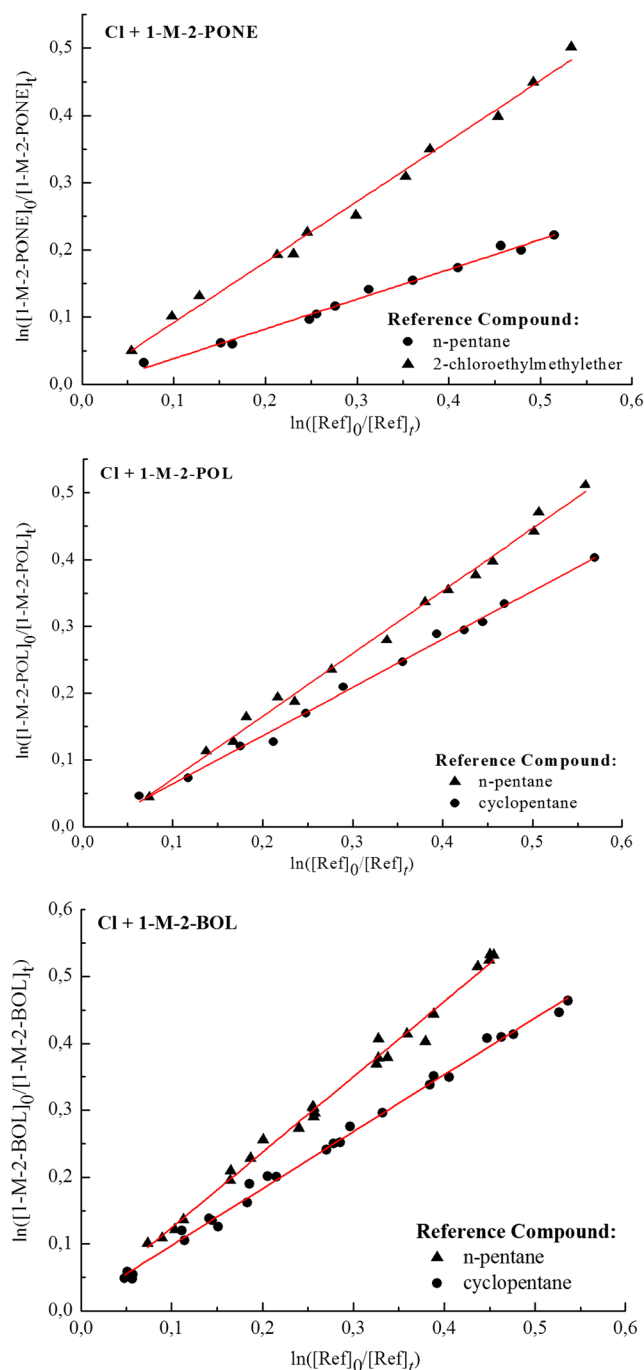
Figure 1 shows example plots of the relative-rate data obtained for the reactions of OH radicals with 1-M-2-PONE and 1-M-2-BOL using two different reference compounds. Similar plots for the reactions of Cl atoms with 1-M-2-PONE, 1-M-2-POL, and 1-M-2-BOL are shown in Fig. 2. For each OVOC studied, at least two runs were carried out to determine the rate coefficients and to test the internal consistency of the rate coefficient ratios. The results obtained using the different initial concentrations of the reactants were indistinguishable. Moreover, the linearity of the data points and the fact that the plots show practically zero intercepts, suggest that the contribution of secondary reactions with the products of the reactions studied could be considered negligible. Since, secondary reactions



**Fig. 1** Relative kinetic data for the OH radical reaction with 1-methoxy-2-propanone (1-M-2-PONE) and 1-methoxy-2-butanol (1-M-2-BOL) at room temperature and atmospheric pressure

involving the oxidation products could lead to an additional consumption of the organic compounds (OVOC, reference compound), which would result in curvature of the relative-rate plots (Wheeler et al. 2008). Thus, the ratios of the rate coefficients,  $k_{OVOC}/k_{Ref}$ , obtained from the slopes of the plots shown in Figs. 1 and 2, were reliable for determining the rate coefficients in absolute terms for reactions (1)–(5). The second-order rate coefficient values obtained were for the following OH radicals:  $k_1 = (0.64 \pm 0.13) \times 10^{-11}$  and  $k_2 = (2.19 \pm 0.23) \times 10^{-11}$ , and for Cl atoms:  $k_3 = (1.07 \pm 0.24) \times 10^{-10}$ ,  $k_4 = (2.28 \pm 0.21) \times 10^{-10}$ , and  $k_5 = (2.79 \pm 0.23) \times 10^{-10}$ , all in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

The estimated errors on the rate coefficients are propagated errors on the basis of the standard error of the slopes of the plots of  $\ln([OVOC]_t/[OVOC]_0)$  versus  $\ln([Ref]_t/[Ref]_0)$  and the error reported for the reference rate coefficients. In this approach, any systematic error due to sample handling and the chromatographic method is included in the dispersion of the experimental curves and therefore,



**Fig. 2** Relative kinetic data for the Cl atom reaction with 1-methoxy-2-propanone (1-M-2-PONE), 1-methoxy-2-propanol (1-M-2-POL), and 1-methoxy-2-butanol (1-M-2-BOL) at room temperature and atmospheric pressure

in the standard error of the slope. For each individual experiment, the error on the slopes was determined as twice the statistical deviation arising from the least-squares fit of the plots of  $\ln([OVOC]_t/[OVOC]_0)$  versus  $\ln([Ref]_t/[Ref]_0)$ , while the errors on the measured rate coefficients were determined using the error propagation method

according to the following expression (Ku 1966; Messaadia et al. 2013):

$$\Delta k_{OVOC} = k_{OVOC} \left[ \left( \frac{\Delta k_{Ref}}{k_{Ref}} \right)^2 + \left( \frac{\Delta \left( \frac{k_{OVOC}}{k_{Ref}} \right)}{\frac{k_{OVOC}}{k_{Ref}}} \right)^2 \right]^{1/2} \quad (13)$$

where  $(\Delta k_{Ref}/k_{Ref})$  and  $(\Delta(k_{OVOC}/k_{Ref})/k_{OVOC}/k_{Ref})$  are the relative errors on  $k_{Ref}$  and the slope  $(k_{OVOC}/k_{Ref})$ , respectively. The reported absolute rate coefficient for each OVOC is an average of the individual determinations with error limits that encompass the extremes of the determinations. Tables 1 and 2 show a summary of data on the relative-rate coefficients and the corresponding absolute rate coefficients for the reactions of OH radicals and Cl atoms with the KE and GEs here studied, respectively.

## Discussion

Kinetic data for reactions (1)–(5) in the gas phase at  $(298 \pm 2)$  K and atmospheric pressure were obtained in this work. To the best of our knowledge, there are no other prior reported values of the rate coefficients for reactions (2)–(5). Thus, the present work is the first kinetic study of these reactions and therefore no direct comparison with the literature can be made. The rate coefficient value for reaction (1) obtained in this work,  $k_1 = (6.4 \pm 1.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , is approximately 5% lower than the absolute one obtained by Dagaut et al. (1989), using the FP-RF technique at 298 K ( $k_1 = (6.8 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). Therefore, the two values are in very good agreement within the experimental error.

The available literature data indicate that the reactions of OH radicals and Cl atoms with ethers, alcohols, and ketones proceed mainly through H-atom abstraction from C-H bonds. Therefore, a similar mechanism is expected for polyfunctional organic compounds such as keto-ethers and glycol-ethers (Aschmann and Atkinson 1998; Mellouki et al. 2015; Tuazon et al. 1998). For comparison purposes of reactivity, Table 3 shows the OH/Cl reaction rate coefficients for the OVOCs studied in the present work together with those values reported previously for a series of compounds with similar structure. The experimental data indicate the presence of the carbonyl group decreases the rate coefficient of the butanone in comparison with the corresponding alkane, so that reaction of the electrophilic OH radicals with this ketone at the  $\alpha$ -position could be considerably less facile than the reaction with n-butane (Iwasaki et al. 2007; Mellouki et al. 2003). However, it is clear that if an ether linkage –O– is included in this ketone to obtain the keto-ether, an increase in molecular reactivity is observed ( $k_{OH + 1-M-2-PONE}/k_{OH + \text{butanone}} \approx 5.4$ ). This increase can be rationalized in terms of the known

activating effect of the ether linkage (–O–) exerted on the neighboring C–H bonds (Mellouki et al. 2003; Porter et al. 1997), which is related to a weakening of the adjacent C–H bonds due to the ability of oxygen atoms to transfer  $\pi$ -electron density from their filled lone pair to the carbon atom connected.

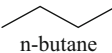

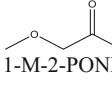

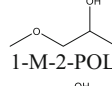
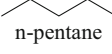

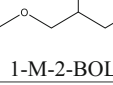
Unlike the ketone listed in Table 3, the enhanced reactivity for the reaction of OH radicals with 2-butanol and 3-pentanol compared to reaction with the corresponding alkanes can be explained in terms of the lowering of the  $\alpha$ -C–H bond strength, since it is accepted that, in general, the –OH group activates the neighboring C–H bonds (Mellouki et al. 2015). In addition, the available kinetic data for reactions of the OH radical with alcohols indicate that the functional group –OH has an activating effect which can reach a distance of up to three carbon atoms from the oxygen atom of the hydroxyl group (Nelson et al. 1990).

In particular, these reactions may involve H-abstraction from both the C–H and O–H bonds, although the former process is more favored on thermochemical grounds. Hence, the OH reactions with these alcohols appear to occur almost exclusively by H-atom abstraction from the C–H bonds (Calvert et al. 2011). Additionally, the presence of an ether group produces an increase in the reactivity of the alcohol even when the –O– linkage is at  $\beta$ -position across the –OH group (Mellouki et al. 2015; Nelson et al. 1990). This is corroborated by comparing the reactivity of glycol-ethers with that of homologous alcohols:  $k_{OH + 1-M-2-POL}/k_{OH + 2\text{-butanol}} \approx 2.5$  and  $k_{OH + 1-M-2-BOL}/k_{OH + 3\text{-pentanol}} \approx 2$ . The reactivity increase is mainly on the hydrocarbon groups positioned between the two functional groups. In conclusion, for the polyfunctional organic compounds studied in this work, the ether linkage (–O–) has demonstrated to play a key role in the reactivity of these compounds.

Finally, comparing the reaction rate coefficients of OH and Cl listed in Table 3, it is important to point out that the rate coefficients for the reactions with Cl atoms are always higher than with OH radicals, which can be explained by considering that the Cl atom is more reactive and less selective than OH radical, so that the H-atom abstraction from alkyl groups is much faster (Ballesteros et al. 2007; Calvert et al. 2011; Pilling and Seakins 1997; Thvénet et al. 2000). Then, the activating/deactivating role of the functional groups present in the organic compounds studied constitutes a factor of minor importance in the reactivity of KE and GEs with Cl atoms. Thus, the high reactivity toward Cl atoms indicates that reactions (3)–(5) seem to be limited by the collision frequency per se with the organic molecules, which also increases with the size of them, rather than by the collision frequency of a specific site of the molecule. However, further experiments and theoretical studies are needed to make any definite claims (Vijayakumar and Rajakumar 2017).



**Table 3** Rate coefficients for the reactions of OH radicals and Cl atoms with the three studied OVOCs, alkane, and homologous compounds at 298 K

Alkane	$k_{\text{OH}} \times 10^{-11\text{a}}$	$k_{\text{Cl}} \times 10^{-11\text{a}}$	Homologous compounds	$k_{\text{OH}} \times 10^{-11\text{a}}$	$k_{\text{Cl}} \times 10^{-11\text{a}}$	OVOC	$k_{\text{OH}} \times 10^{-11\text{a}}$	$k_{\text{Cl}} \times 10^{-11\text{a}}$
 n-butane	$0.24 \pm 0.04^{\text{b}}$	$20.5 \pm 2.9^{\text{c}}$	 Butanone	$0.12 \pm 0.05^{\text{c}}$	$3.3 \pm 0.2^{\text{e}}$ $4.0 \pm 0.4^{\text{f}}$	 1-M-2-PONE	$0.64 \pm 0.13^{\text{j}}$ $0.68 \pm 0.06^{\text{k}}$	$10.7 \pm 2.4^{\text{j}}$
			 2-butanol	$0.87 \pm 0.15^{\text{g}}$	$13.2 \pm 1.4^{\text{g}}$	 1-M-2-POL	$1.86 \pm 0.16^{\text{l}}$ $2.09 \pm 0.31^{\text{m}}$	$22.8 \pm 2.1^{\text{j}}$
 n-pentane	$0.39 \pm 0.02^{\text{b}}$	$25.2 \pm 1.2^{\text{d}}$	 3-pentanol	$1.32 \pm 0.15^{\text{h}}$ $1.1 \pm 0.1^{\text{i}}$	$20.3 \pm 2.3^{\text{h}}$ $22 \pm 1^{\text{i}}$	 1-M-2-BOL	$2.19 \pm 0.23^{\text{j}}$	$27.9 \pm 2.3^{\text{j}}$

<sup>a</sup> The units of  $k_{\text{OH}}$  and  $k_{\text{Cl}}$  are  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

<sup>b</sup> Calvert et al. 2008

<sup>c</sup> Atkinson et al. 2006

<sup>d</sup> Atkinson and Aschmann 1985

<sup>e</sup> Albadalejo et al. 2003

<sup>f</sup> Kaiser et al. 2009

<sup>g</sup> Calvert et al. 2011

<sup>h</sup> Hurley et al. 2008

<sup>i</sup> Lendar et al. 2013

<sup>j</sup> This work

<sup>k</sup> Dagaut et al. 1989

<sup>l</sup> Porter et al. 1997

<sup>m</sup> Aschmann and Atkinson 1998

#### Atmospheric implications

Global lifetime,  $\tau_{\text{global}}$ , is an important parameter of the environmental impact of an OVOC in the atmosphere, which can be obtained from the sum of the individual sink processes such as oxidation reactions initiated by OH and  $\text{NO}_3$  radicals, Cl atoms and  $\text{O}_3$  molecules, photolysis, and dry and wet deposition:

$$\tau_{\text{global}} = \left[ \frac{1}{\tau_{\text{OH}}} + \frac{H}{\tau_{\text{Cl}}} + \frac{1}{\tau_{\text{NO}_3}} + \frac{1}{\tau_{\text{O}_3}} + \frac{1}{\tau_{\text{photolysis}}} + \frac{1}{\tau_{\text{other processes}}} \right]^{-1} \quad (14)$$

An upper limit for the global atmospheric lifetime of the studied OVOCs can be estimated by oxidation reactions with

the tropospheric oxidants ( $\text{Ox} = \text{OH}, \text{NO}_3, \text{O}_3,$  and Cl), which are presented in Table 4. The lifetimes were calculated using the relationship  $\tau_{\text{Ox}} = 1/k_{\text{Ox}} [\text{Ox}]$ , considering the rate coefficients obtained in this work and by Aschmann and Atkinson (1998) and the following global concentrations for the oxidants: a 12-h average day-time concentration for OH of  $1 \times 10^6 \text{ radical cm}^{-3}$  (Prinn et al. 2001), a 12-h average night-time concentration for  $\text{NO}_3$  of  $5 \times 10^8 \text{ radical cm}^{-3}$  (Atkinson 2000), and a 24-h average concentration for  $\text{O}_3$  of  $7 \times 10^{11} \text{ molecule cm}^{-3}$  (Logan 1985). An average global concentration for Cl of  $1 \times 10^3 \text{ atom cm}^{-3}$  (Platt and Jansen 1995) or a peak concentration as high as  $1.3 \times 10^5 \text{ atom cm}^{-3}$  in the coastal marine boundary layer at dawn (Spicer et al. 1998) were also considered for calculations.

**Table 4** Estimated atmospheric lifetimes ( $\tau_x$ ) and global lifetimes of the studied OVOCs with OH and  $\text{NO}_3$  radicals,  $\text{O}_3$  molecules, and Cl atoms

OVOC	$\tau_{\text{OH}}$ (days)	$\tau_{\text{Cl}}^{\text{a}}$ (days)	$\tau_{\text{Cl}}^{\text{b}}$ (days)	$\tau_{\text{NO}_3}$ (days)	$\tau_{\text{O}_3}$ (days)	$\tau_{\text{global}}^{\text{a}}$ (days)	$\tau_{\text{global}}^{\text{b}}$ (days)
1-M-2-PONE	1.8	115.7	1.16	–	–	1.8	0.71
1-M-2-POL	$0.6^{\text{c}}$	50.3	0.5	$13.6^{\text{c}}$	$150.3^{\text{c}}$	0.6	0.26
1-M-2-BOL	0.5	41.3	0.41	–	–	0.5	0.22

<sup>a</sup>  $[\text{Cl}]_{\text{global}}$  of  $1 \times 10^3 \text{ atom cm}^{-3}$  from Platt and Jansen 1995

<sup>b</sup>  $[\text{Cl}]_{\text{coastal}}$  of  $1.3 \times 10^5 \text{ atom cm}^{-3}$  from Spicer et al. 1998

<sup>c</sup> Calculated using rate coefficients for the reactions of 1-M-2-POL with OH,  $\text{NO}_3$ , and  $\text{O}_3$  from Aschmann and Atkinson (1998)

Unfortunately, there are no data available for the reactions of 1-M-2-PONE and 1-M-2-BOL with  $O_3$  molecules or  $NO_3$  radicals. However, based on the values reported by Aschmann and Atkinson (1998), it is expected that the tropospheric removal rate with both oxidants to be very slow and then, it is reasonable to assume that their contributions will be negligible. Since, photodissociation quantum yields for alcohols and ethers are relatively low and the photolysis of ketones becomes important only at high atmospheric altitudes, tropospheric photolysis of the three studied OVOCs is a negligible loss mechanism (Mellouki et al. 2015).

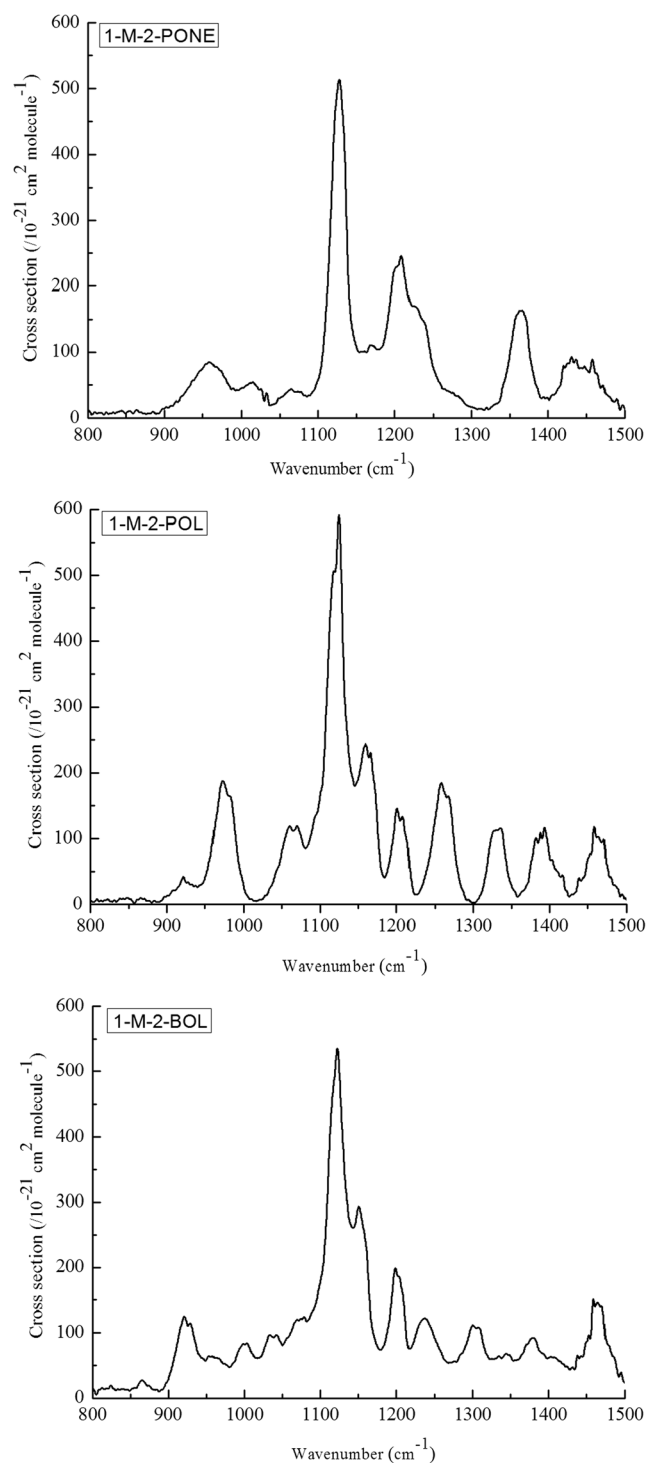
The term “other processes,” takes into account other loss processes in the atmosphere such as dry and wet deposition and heterogeneous reactions. The studied compounds are expected to be relatively soluble in water. The only tabulated value of the Henry's law coefficient is for 1-M-2-POL of  $4.8 \text{ mol m}^{-3} \text{ Pa}^{-1}$  (Sander 2015). Therefore, the  $\tau_w$  for 1-M-2-POL was estimated around 90 days, using the procedure given by Chen et al. (2003). If a similar value of  $\tau_w$  is considered for the other compounds (1-M-2-PONE and 1-M-2-BOL), it can be concluded that the wet deposition process for KE and GEs is negligible compared to the homogeneous degradation. Finally, the relative volatility of these compounds will render dry deposition an unlikely removal mechanism.

The estimated global atmospheric lifetimes in Table 4 indicate that the dominant atmospheric loss process for the studied compounds is the day-time reaction with OH radicals and that these OVOCs are rapidly removed in the gas phase on local and regional scales. These obtained global lifetimes are still a useful atmospheric parameter for these short-lived compounds, although the assumption of a uniform distribution of the compounds emitted into the troposphere is not ensured due to can vary depending of the emission location, season, and local atmospheric conditions. In addition, the reactions of these compounds with Cl atoms could play an important role in their tropospheric degradation in both coastal areas and boundary layer, where it is possible to record peaks of the Cl atoms as high as  $1 \times 10^5 \text{ atom cm}^{-3}$ . Under these conditions, the lifetimes of these OVOCs are on the order of 1 day.

Another atmospheric concern of the studied oxygenated compound emission is its contribution to the greenhouse warming as expected by the GWP. World Meteorological Organization (Law and Sturges 2007) have indicated that the GWP calculation for short-lived compounds (with lifetimes shorter than 0.5 years) cannot be considered as appropriate. However, GWPs for short-lived compounds have been estimated from their direct instantaneous cloudy-sky REs, which involve spectroscopic information of the studied OVOCs in the infrared atmospheric window (Aranguren Abrate et al. 2013; Baasandorj et al. 2010).

Radiative efficiency for the KE and GEs here studied was estimated from the corresponding IR spectra recorded in the

800–1500  $\text{cm}^{-1}$  region at 298 K using the Pinnock's method (Pinnock et al. 1995). Figure 3 shows the corresponding plots of the cross-section versus wavenumber ( $\text{cm}^{-1}$ ) obtained averaging four infrared spectra between 0.5 and 4.0 Torr of pure compound. The integrated IR absorption cross-section values



**Fig. 3** Infrared spectra of 1-methoxy-2-propanone (1-M-2-PONE), 1-methoxy-2-propanol (1-M-2-POL), and 1-methoxy-2-butanol (1-M-2-BOL) at room temperature

for 1-M-2-PONE, 1-M-2-POL, and 1-M-2-BOL were  $5.02 \times 10^{-17}$ ,  $5.78 \times 10^{-17}$ , and  $6.18 \times 10^{-17}$  in units of  $\text{cm}^2 \text{ molecule}^{-1}$ , respectively. A conservative uncertainty of  $\pm 6\%$  in the cross-section measurements is raised from the following sources: the sample concentration (1%), sample purity (2%), path length (1%), spectrum noise, and residual baseline offset after subtraction of background (1.5%). Unfortunately, it is not possible to compare the absorption cross-sections of the studied compounds, because there are no literature data for them.

However, for compounds that are not well-mixed in the atmosphere, a correction to the RE calculated using the Pinnock et al.'s method is needed. Hodnebrog et al. (2013) provide the correction factor  $f(\tau)$  to the RE based on the lifetime of the compound:

$$f(\tau) = \frac{a\tau^b}{1 + c\tau^d} \tag{15}$$

where  $a$ ,  $b$ ,  $c$ , and  $d$  are constants with values of 2.962, 0.9312, 2.994, and 0.9302, respectively. Using  $\tau_{\text{global}}$  listed in Table 5, the correction factors obtained were 0.02,  $7.24 \times 10^{-3}$ , and  $6.61 \times 10^{-3}$ , for 1-M-2-PONE, 1-M-2-POL, and 1-M-2-BOL, respectively. The RE and corrected RE\* for 1-M-2-PONE, 1-M-2-POL, and 1-M-2-BOL are shown in Table 5, together with the calculated values of GWP on a time horizon of 20 and 100 years.

GWP of the studied OVOCs relative to  $\text{CO}_2$  can be obtained considering the following expression (Hodnebrog et al. 2013):

$$\text{GWP}_{\text{OVOC}}(\text{TH}) = \frac{\text{AGWP}_{\text{OVOC}}(\text{TH})}{\text{AGWP}_{\text{CO}_2}(\text{TH})} \tag{16}$$

where the numerator and denominator are the absolute GWP (AGWP (TH)) over a given time horizon (TH) for the studied OVOC and  $\text{CO}_2$ , respectively. For each OVOC studied, the  $\text{AGWP}_{\text{OVOC}}(\text{TH})$  (in  $\text{W m}^{-2} \text{ year kg}^{-1}$ ) can be calculated as follows (Hodnebrog et al. 2013):

$$\text{AGWP}_{\text{OVOC}}(\text{TH}) = \text{RE}_{\text{OVOC}}\tau_{\text{OVOC}} \left( 1 - \exp\left(\frac{-\text{TH}}{\tau_{\text{OVOC}}}\right) \right) \tag{17}$$

where  $\text{RE}_{\text{OVOC}}$  (in  $\text{W m}^{-2} \text{ kg}^{-1}$ ) is the radiative efficiency due to a unit increase in atmospheric abundance of the OVOC, and  $\tau_{\text{OVOC}}$  (in years) is the atmospheric lifetime for OVOC. While, the used AGWPs values for  $\text{CO}_2$  were  $2.46 \times 10^{-14}$  and  $9.17 \times 10^{-14} \text{ W m}^{-2} \text{ year (kg CO}_2\text{)}^{-1}$  for time horizons of 20 and 100 years, respectively, which were reported by Hodnebrog et al. (2013). From Eq. 16, the 20-year time horizon GWPs for 1-M-2-PONE, 1-M-2-POL, and 1-M-2-BOL were estimated to be  $2.21 \times 10^{-2}$ ,  $2.95 \times 10^{-3}$ , and  $1.93 \times 10^{-3}$ , respectively, which were an order of magnitude higher than their corresponding GWPs (TH = 100 years) (Table 5). As a result of their global lifetimes and corrected lifetime radiative efficiencies, the OVOCs here studied have small GWPs, so their emission into the atmosphere will not contribute significantly to the global warming of the Earth.

Release of OVOCs into the troposphere may contribute to the photochemical formation of tropospheric ozone, which is a growing problem in the developing world and continues to be the most pervasive air pollution problem in industrialized countries. The effectiveness of ozone formation for the three studied OVOCs was assessed by examining the average ozone production during 99% reaction of them with OH radical, using the following equation indicated by Dash and Rajakumar (2013):

$$[\text{O}_3]_{\text{average}} = \frac{n' (k_{\text{OVOC}}[\text{OH}])^2}{4.6(2.7 \times 10^{-5} - k_{\text{OVOC}}[\text{OH}])} \times \left( \frac{1}{k_{\text{OVOC}}[\text{OH}]} - \frac{1 - \exp\left(\frac{-1.24 \times 10^{-4}}{k_{\text{OVOC}}[\text{OH}]}\right)}{2.7 \times 10^{-5}} \right) \tag{18}$$

where  $n'$  is the maximum possible ozone molecules that can be produced from one molecule of OVOC,  $k_{\text{OVOC}}$  is the rate coefficient of OH radical with OVOC, and  $[\text{OH}]$  is the global

average day-time concentration for OH of  $1 \times 10^6 \text{ radical cm}^{-3}$  (Prinn et al. 2001). The maximum number of ozone molecules ( $n\text{C} + n\text{H}$ ) that can be produced from 1-M-2-PONE, 1-M-2-

**Table 5** Global lifetimes ( $\tau_{\text{global}}$ ), radiative efficiency (RE), corrected lifetime radiative efficiency (RE\*), and Global Warming Potential (GWP) for the three studied OVOCs

OVOC	$\tau_{\text{global}}$ (years)	RE ( $\text{W m}^{-2} \text{ kg}^{-1}$ )	RE* ( $\text{W m}^{-2} \text{ kg}^{-1}$ )	GWP (TH = 20 years)	GWP (TH = 100 years)
1-M-2-PONE	$5.0 \times 10^{-3}$	$4.9 \times 10^{-12}$	$9.8 \times 10^{-14}$	$2.21 \times 10^{-2}$	$5.92 \times 10^{-3}$
1-M-2-POL	$1.6 \times 10^{-3}$	$5.7 \times 10^{-12}$	$4.1 \times 10^{-14}$	$2.95 \times 10^{-3}$	$8.03 \times 10^{-4}$
1-M-2-BOL	$1.4 \times 10^{-3}$	$5.1 \times 10^{-12}$	$3.4 \times 10^{-14}$	$1.93 \times 10^{-3}$	$5.41 \times 10^{-4}$

POL, and 1-M-2-BOL are 12, 14, and 17, respectively. The obtained values of average ozone concentration produced by the reaction of 1 ppm of OVOC were 0.62, 2.10, and 3.02 ppm for 1-M-2-PONE, 1-M-2-POL, and 1-M-2-BOL, respectively. Considering the Bufalini et al.'s scale (Bufalini et al. 1976), we could indicate that the degradation of the studied OVOCs would make a negligible contribution to ozone formation in the troposphere.

Based on mechanical studies of the oxidation of OVOCs in the gas phase (Aschmann et al. 2011; Calvert et al. 2011; Mellouki et al. 2015), the removal of the three organic compounds studied with OH/Cl, under tropospheric conditions in the presence of NO<sub>x</sub>, could proceed by initial H-atom abstraction from the –CH<sub>2</sub>– group located adjacent to the ether linkage. This pathway would lead to formation of carbonyl products such as methyl formate (CH<sub>3</sub>OC(O)H), acetaldehyde (CH<sub>3</sub>CHO), and propanal (CH<sub>3</sub>CH<sub>2</sub>CHO). In addition for the studied GEs, a significant amount of reaction should also occur at the –CH– group adjacent to the alcohol functionality, likely leading to 1-methoxy-2-propanone (CH<sub>3</sub>OCH<sub>2</sub>C(O)CH<sub>3</sub>) and 1-methoxy-2-butanone (CH<sub>3</sub>OCH<sub>2</sub>C(O)CH<sub>2</sub>CH<sub>3</sub>) for 1-M-2-POL and 1-M-2-BOL, respectively.

## Conclusions

In this work, we concerned a relative-rate study on the kinetics of the gas-phase reactions of OH radicals and Cl atoms with a keto-ether (1-M-2-PONE) and two glycol-ethers (1-M-2-POL and 1-M-2-BOL), which are emitted into the atmosphere as primary pollutants mainly from anthropogenic sources. The rate coefficients obtained for these OVOCs along with previous rate coefficients for a series of compounds with similar structure allow us to conclude that for the polyfunctional organic compounds studied in this work, the presence of an ether group plays a key role in the reactivity increased of these compounds. The atmospheric lifetimes calculated clearly indicate that 1-M-2-PONE, 1-M-2-POL, and 1-M-2-BOL will be removed from the troposphere in a few hours time and mainly by reaction with OH radicals. However, the reaction of Cl atoms with these OVOCs may contribute significantly to their tropospheric loss under certain atmospheric conditions. Particularly, their atmospheric removal in the marine boundary layer and the coastal areas could be important, because their major emission source will most likely be the large cities located in coastal areas. Then, the co-location of both, an emission source and regions with high concentrations of Cl-atoms, could enhance the removal rate of these OVOCs. REs and GWPs of the three studied OVOCs are low, and therefore, these compounds are expected to have a small climatic impact. In addition, the photochemical ozone production of these compounds is relatively low, so the tropospheric degradation

of these compounds would have a low impact on air quality. However, studies are needed to quantify the degradation of three studied OVOCs with OH radical and Cl atoms under atmospheric conditions to fully evaluate the impact of these compounds and their degradation products on climate and air quality.

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