Reactivity of hydrohaloethers with OH radicals and chlorine atoms: Correlation with molecular properties

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HIGHLIGHTS

- C–H bond energies and ionization potentials of hydrochloroethers are calculated.
- Reactivity of hydrohaloethers with OH radicals and Cl atoms is evaluated.
- Correlations between rate coefficients and molecular properties are established.
- Atmospheric implications of hydrohaloethers are briefly discussed.

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ABSTRACT

The reactivity of halogenated ethers, especially hydrochloroethers, with hydroxyl radicals and chlorine atoms was studied by correlating the room-temperature rate coefficients with both the C–H bond dissociation energies and the vertical ionization potentials of the parent molecules. These molecular properties were estimated at the composite G3B3 level of theory. The results suggest that Cl-substituted ethyl-methyl-ethers and ethyl-ethyl-ethers at the β-position tend to raise the activating effect of the ether linkage –O– and to enhance the possibility of the abstraction of H atoms bonded to α-carbon. Derived relationships between the rate coefficients (in $cm^3 \, molecule^{-1} \, s^{-1}$) and ionization potentials (in eV): $\log k_{OH} = -(1.248 \pm 0.065) \, IP + (1.06 \pm 0.73)$ and $\log k_{Cl} = -(1.46 \pm 0.12) \, IP + (4.5 \pm 1.3)$ allows, in average, to estimate rate coefficients within a factor of 2–3. The atmospheric implications of halogenated and hydrogenated ethers are briefly discussed on the basis of their estimated global lifetimes.

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1. Introduction

There is evidence for a large global source of oxygenated volatile organic compounds (OVOCs) in the atmosphere (Lewis et al., 2000; Singh et al., 2001). These compounds are emitted directly into the atmosphere from biogenic and anthropogenic sources and are also formed *in situ* from the oxidation of all atmospheric hydrocarbons (Atkinson and Arey, 2003; Mellouki et al., 2003). Oxygenated organic compounds are heavily involved in key atmospheric processes and play a central role in the chemical processes that determine the oxidizing capacity of the atmosphere (Atkinson and Arey, 2003; Lewis et al., 2000; Mellouki et al., 2003; Singh et al., 2001). The potential atmospheric significance of such pollutants is dependent on the transformations which they undergo in the troposphere, the nature of the products of these transformations and the atmospheric lifetimes of each species (Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 1998).

Among these oxygenated organic compounds of anthropogenic origin emitted into the atmosphere are the hydrochloroethers (HCEs), which are used in laboratories and as solvents for fats and oils, cleaners, varnishes and paints and in the manufacture of pesticides (Coe et al., 1997; McClay et al., 2007). Therefore, it is relevant to determine the reactivity of halogenated ethers and evaluate their potential atmospheric impact as acceptable

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candidates to replace harmful chlorofluorocarbons (CFCs) and their derivatives in industrial uses (Sekiya and Misaki, 2000).

While the reactivity of a large number of hydrofluoroethers (HFEs) toward tropospheric oxidants and their thermochemical properties have been widely studied in a number of experimental and theoretical investigations (NIST Chemical Kinetics Database, 2013), the experimental data for reactions of HCEs with tropospheric oxidants is scant. Therefore, the reaction kinetics of HCEs with OH radicals and Cl atoms will provide information on the tropospheric reactivity of HCEs and will aid in the elucidation of their degradation in the atmosphere.

It has been shown that the H-atom abstraction rate coefficients by OH radicals in a series of OVOCs at room temperature correlate with the molecular structure and with the C–H bond strengths of the OVOCs (Chandra et al., 2000; Chandra and Uchimaru, 2001; Chandra et al., 2003). Since it is expected that the reactivity toward the OH radical of a series of similar compounds will vary systematically, such relationships can be used to estimate the rate coefficients of reactions that have not yet been experimentally studied. Indeed, knowledge of the rate coefficients for the hydrogen abstraction reaction from HCEs, enables the estimation, for example, of their atmospheric lifetimes.

In this work, we have studied mainly the reactivity of several HCEs towards OH and Cl atoms as a function of their molecular structure by correlating the room-temperature rate coefficients with the calculated IP and D(C–H) values of the C–H bonds present in the ether. The influence of chlorine atoms as substituents on the reactivity of the H-abstraction reaction of the HCEs was also evaluated, providing an opportunity to examine halogen substituent effects as a function of extent and position around the –O– linkage of the HCEs. Also, the tropospheric lifetimes of HCEs, HFEs, and hydrogenated ethers (HEs) have been estimated.

2. Computational methods

The bond dissociation energies and ionization potentials of HEs and HCEs were calculated using the *ab initio* G3B3 model chemistry (Baboul et al., 1999), as implemented in the Gaussian 09 software package (Frisch et al., 2009). In this model the optimized molecular structure and harmonic vibrational frequencies (scaled by a factor of 0.96) are estimated at the B3LYP/6-31G(d) level of the density functional theory. Based on this geometry, the total electronic energy at 0 K is afterwards derived from a set of single-point energy calculations at the following post-Hartree–Fock levels: MP4/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p), QCISD(T)/6-31G(d) and MP2(full)/G3Large. Zero-point vibrational energy, thermal corrections, spin-orbit, and higher-level corrections are added *a posteriori* to approach quadratic configuration interaction QCISD(T, full)/G3Large level at 298.15 K, with a considerable reduction in the computational resources (Baboul et al., 1999).

The D(C–H) was assumed equal to the dissociation enthalpy change at 298.15 K for each of the different types of C–H bond in HEs and HCEs. The IPs were obtained by subtracting the total electronic energies of the ether to the corresponding singly ionized cation at the geometry of the parent molecule.

3. Results and discussion

Quantum-chemical methods provide an important tool to evaluate the dependence of the reactivity of HCEs on several factors such as the length of the carbon chain, the strength of the C–H bonds, the influence of the ether linkage (–O–), and the degree and position of chlorine substitution (Kambanis et al., 1998).

The calculated C–H bond dissociation energies and ionization potentials for HCEs and HEs, and the available room temperature rate coefficients for the reactions of these molecules with the OH radical and Cl atom are presented in Table 1. While there are some reported theoretical rate coefficients (Urata et al., 2003; Zavala-Oseguera et al., 2009; Mishra et al., 2013), Table 1 shows only experimental data. When necessary, average values of the rate coefficients were employed. Due to limited experimental information, computed D(C–H) and IPs values were used. The very good agreement between the calculated C–H bond dissociation energy in CH_3OCH_3, 403.3 kJ mol^{-1}, and the value derived from the recommended enthalpy of formation data, 405.9 kJ mol^{-1}, supports the present D(C–H) estimations (Sander et al., 2011). In this context, the assigned average absolute deviations for the enthalpies of formation and ionization potentials in the G3B3 model chemistry are, respectively, 3.9 kJ mol^{-1} and 0.05 eV (Baboul et al., 1999).

It can be seen in Table 1, that the lower D(C–H) for the chloro-methyl-methyl-ethers (CMMEs) corresponds to the H atom bonded to the same carbon atom as the chlorine substituent atoms. On the other hand, in the chloro-ethyl-methyl-ethers (CEMEs) and chloro-ethyl-ethyl-ether (CEEEs), the H atom bonded to the carbon atom next to the ether group (–O–) presents the lower C–H bond dissociation energy. In addition, it is possible to indicate, as a general trend, that the substitution of one of the H atoms in HCEs by one Cl atom produces a decrease in D(C–H), both for H atoms attached to the carbon where chlorine is a substituent and for those bonded to adjacent carbon atoms. Moreover, in agreement with the experimental data, the presence of the –O– linkage enhances the molecular reactivity of ethers compared to that of the corresponding alkanes, since the ether group would produce a decrease in the activation energy (a weakening of the C–H bond) of the H-atom abstraction reaction (Mellouki et al., 2003; Papadimitriou et al., 2004). For CEMEs and CEEEs, the chlorine substitutions at the β-position tend to raise the activating effect of the ether linkage and to enhance the possibility of the abstraction of H atoms bonded to α-carbon.

Due to the fact that the H-transfer reaction of HCEs occurs mainly *via* the H-abstraction from the weakest C–H bond, the lowest values in Table 1 were used to study the correlations between the rate coefficients and D(C–H). Figs. 1 and 2 show the results for the H-atom abstraction reactions of the haloethers (chloro- and fluoro-ethers) and HEs by Cl atoms and OH radicals, respectively. To better generalize the reactivity of these oxygenated compounds, experimental rate coefficients and calculated (at the B3P86/6-311G++(3df,2p) level) parameters of fluorine-substituted ethers studied by Papadimitriou et al. (2004) have been included in Figs. 1 and 2. Linear least-squares analysis gives the following expressions (where **k** is in units of cm^3 $molecule^{-1}$ s^{-1} and D(C–H) in kJ mol^{-1}) for the reactions of the hydrohaloethers with Cl and OH, respectively,

$$\log \boldsymbol{k}_{Cl} = -(0.087 \pm 0.014) \ D(C-H) + (23.7 \pm 5.6) \quad (1)$$

$$\log \boldsymbol{k}_{OH} = -(0.0794 \pm 0.0078) \ D(C-H) + (19.5 \pm 3.2), \quad (2)$$

where the errors are quoted at the 95% confidence level, and the correlation coefficients were 0.83 for Eq. (1) and 0.93 for Eq. (2). Eq. (1) is quite similar to the given by Papadimitriou et al. (2004) for the HFEs included in Fig. 1, log $\boldsymbol{k}_{Cl} = -(0.09 \pm 0.02)$ D(C–H) + (23.6 ± 7.4). However, to our knowledge, no similar correlation for OH + HCEs/HFEs/HEs reactions has been reported.

The observed effect of the degree and position of halogenation could be accounted for by the interplay between two electronic effects. On one hand, the strengthening of the C–H bonds due to the electronic withdrawing inductive effects of the halogen atom and/or O atom through σ-bonds, and, on the other hand, the weakening of the adjacent C–H bonds due to the ability of halogen

atoms and/or O atom to transfer π-electron density from their filled lone pair to the connected carbon atom.

It is interesting to explore the origin of the observed log k versus D(C–H) correlations. A simple way to do this is using the well-known relationship of Evans and Polanyi (1938). According to this model, further employed by Semenov (1958) for a series of closely related reactions of the type $X + RH \rightarrow XH + R$, the activation energies E_a and the corresponding reaction enthalpies ΔH_r are related through the simple expression $E_a = \alpha \Delta H_r + C$, where α and C are parameters specific of the series. For the present case, in which X = Cl or OH and R is varied, we have $E_a = \alpha$ (D(C–H)–(D(X–H)–C/α)) (Moore and Pearson, 1981). By replacing this expression in an Arrhenius equation, the following equation results:

$$\log k = -\alpha\ D(R-H)/(2.303RT) + \log A + \alpha(D(X-H) - C/\alpha)/(2.303RT) \tag{3}$$

Eq. (3) explains the reasonable correlation found between log k and D(R–H), and suggests that the observed scatter in Figs. 1 and 2, despite the inherent errors in k and D(R–H) values, is probably due to differences in the individual A, α, and C parameters along the reactions series. In fact, it is expected that the above relationships strictly hold for a family of entropically similar reactions. From the slopes of Eqs. (1)–(3), the values 0.50 and 0.45 are derived for α at 298 K for the H-abstraction by Cl and OH, respectively. Even though these values are about a factor of two larger than those found fifty years ago for a variety of simple exothermic atom-transfer reactions (Semenov, 1958), larger α values have been recently reported for a series of VOCs reactions of atmospheric interest (Kahn et al., 2009).

Similar correlations between log k and the calculated IPs for the H-atom abstraction reactions of HFEs, HCEs, and HEs by Cl atoms and OH radicals are depicted in Figs. 3 and 4, respectively. The

Table 1
Rate coefficients for the reactions of OH radicals and Cl atoms with HCEs and HEs at 298 K, bond dissociation energies (D(C*–H)) and ionization potentials (IP).

Ether[a]	k_{OH} (cm³ molecule⁻¹ s⁻¹)	k_{Cl} (cm³ molecule⁻¹ s⁻¹)	D(C*–H)[b] (kJ mol⁻¹)	IP[b] (eV)
C*H₃OCH₂Cl	–	$(2.9 \pm 0.2) \times 10^{-11}$[c]	411.7	10.38
CH₃OC*H₂Cl			410.5	
C*H₃OCHCl₂	–	$(1.05 \pm 0.11) \times 10^{-12}$[d]	416.7	10.63
CH₃OC*HCl₂			400.8	
C*H₃OCCl₃	–	–	420.1	10.90
C*H₃OCH₂CH₂Cl	$(5.2 \pm 1.2) \times 10^{-12}$[e]	$(1.14 \pm 0.10) \times 10^{-10}$[d]	401.7	10.00
CH₃OC*H₂CH₂Cl			384.9	
CH₃OCH₂C*H₂Cl			406.7	
CH₂ClOC*H₂CH₃	–	–	389.5	10.17
CH₂ClOCH₂C*H₃			430.5	
C*H₂ClOCH₂CH₃			397.1	
C*H₃OCHClCH₃	–	–	392.5	9.66
CH₃OC*HClCH₃			383.3	
CH₃OCHClC*H₃			413.8	
C*H₃CH₂OCH₂CH₂Cl	$(8.3 \pm 1.9) \times 10^{-12}$[e]	$(1.7 \pm 0.5) \times 10^{-10}$[f]	425.9	9.81
CH₃C*H₂OCH₂CH₂Cl			391.2	
CH₃CH₂OC*H₂CH₂Cl			384.5	
CH₃CH₂OCH₂C*H₂Cl			410.0	
ClCH₂CH₂OCH₂C*H₂Cl	$(7.6 \pm 1.9) \times 10^{-12}$[e]	$(1.0 \pm 0.3) \times 10^{-10}$[f]	409.2	10.07
ClCH₂CH₂OC*H₂CH₂Cl			386.6	
C*H₃OCH₃	2.78×10^{-12}[g] $(2.72 \pm 0.09) \times 10^{-12}$[h]	$(2.06 \pm 0.08) \times 10^{-10}$[i] $(1.51 \pm 0.07) \times 10^{-10}$[j] $(1.91 \pm 0.09) \times 10^{-10}$[c] $(1.73 \pm 0.22) \times 10^{-10}$[k]	403.3	10.01[l]
Average	2.75×10^{-12}	1.80×10^{-10}		
C*H₃OCH₂CH₃	$(6.6 \pm 3.3) \times 10^{-12}$[m]	$(3.49 \pm 0.67) \times 10^{-10}$[m]	405.4	9.80[n]
CH₃OC*H₂CH₃	5.06×10^{-12}[g]		398.3	
CH₃OCH₂C*H₃			428.9	
Average	5.83×10^{-12}			
C*H₃CH₂OCH₂CH₃	$(1.13 \pm 0.01) \times 10^{-11}$[j]	$(2.54 \pm 0.17) \times 10^{-10}$[j]	424.7	9.49[s]
CH₃C*H₂OCH₂CH₃	1.24×10^{-11}[o]	$(2.58 \pm 0.44) \times 10^{-10}$[q]	391.2	
	$(1.36 \pm 0.11) \times 10^{-11}$[p]	$(2.5 \pm 0.3) \times 10^{-10}$[r]		
Average	1.24×10^{-11}	2.54×10^{-10}		

[a] Asterisk indicates the site of the C–H bond considered in this work.
[b] Calculated using the G3B3 method.
[c] Jenkin et al. (1993).
[d] Dalmasso et al. (2008).
[e] Dalmasso et al. (2010).
[f] Dalmasso et al. (2012).
[g] Atkinson et al. (2001).
[h] Bonard et al. (2002).
[i] Wallington et al. (1988).
[j] Nelson et al. (1990).
[k] Giri and Roscoe (2010).
[l] IP$_{exp}$ = 10.025 eV (Butler et al., 1984). IP$_{calc}$ = 9.99 eV (Papadimitriou et al., 2004).
[m] Starkey et al. (1997).
[n] IP$_{exp}$ = (9.72 $\pm$ 0.07) eV (Bowen and Maccoll, 1984). IP$_{calc}$ = 9.77 eV (Papadimitriou et al., 2004).
[o] Semadeni et al. (1993).
[p] Mellouki et al. (1995).
[q] Mc Loughling et al. (1993).
[r] Notario et al. (2000).
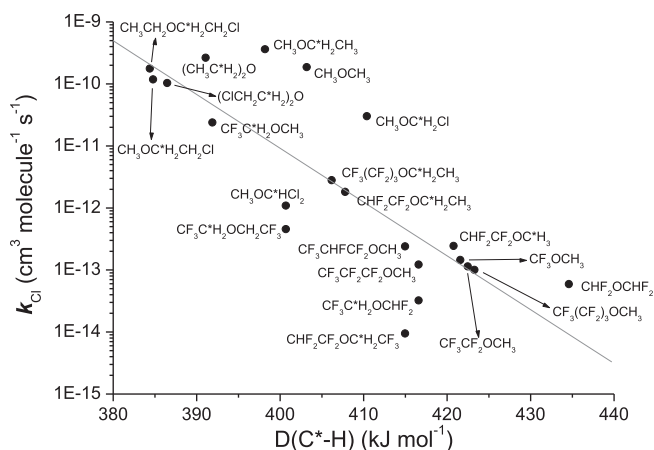[s] IP$_{exp}$ = (9.52 $\pm$ 0.07) eV (Bowen and Maccoll, 1984).

Fig. 1. Rate coefficients for the reactions of Cl atoms (k_{Cl}) at room temperature *versus* the bond dissociation energies (D(C*–H)) of the weakest C–H bond of the HCEs, HFEs and HEs considered in this work.

Fig. 3. Rate coefficients for the reactions of Cl atoms (k_{Cl}) at room temperature *versus* the ionization potential (IP) of the HCEs, HFEs and HEs considered in this work.

corresponding expressions (where k is in units of cm^3 molecule^{-1} s^{-1} and IP in eV) are:

$$\log k_{Cl} = -(1.46 \pm 0.12)IP + (4.5 \pm 1.3) \tag{4}$$

$$\log k_{OH} = -(1.248 \pm 0.065)IP + (1.06 \pm 0.73) \tag{5}$$

Improved correlation coefficients of 0.95 for Eq. (4) and 0.97 for Eq. (5) were found in this case. Eq. (4) compares very well with the reported by Papadimitriou et al. (2004) for the reactions of Cl atoms with HEs and HFEs molecules, $\log k_{Cl} = -(1.42 \pm 0.15)$ IP + (4.0 ± 1.7). No correlation for OH radicals + hydrohaloethers reactions has been reported.

Assuming as before that the dependence of the rate co-efficients with D(C–H) is mainly related to the correlation of this last property with the activation energy, it can be noted that for a series of H-abstraction of structurally similar reactions, in-terrelations of D(C–H) and E_a with IP have been proposed (Screttas, 1980; Screttas and Micha-Screttas, 1989). However, due to the fact that the log k values are better correlated with IP than with D(C–H), probably more complicated processes are certainly operative. In fact, as can be appreciated from Table 2, the rate coefficients values span over a large range of about four orders of magnitude, being most of the reactions clearly activated
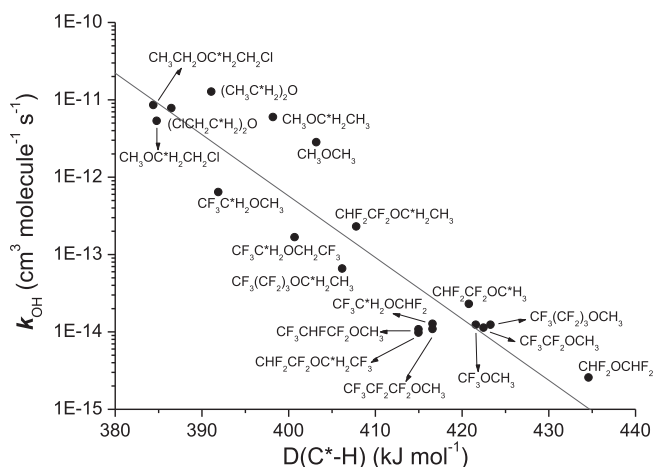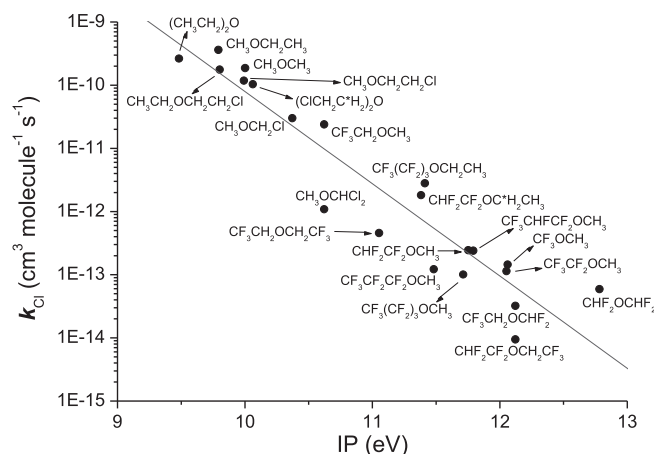
processes. However, the large k values exhibited for several of the analyzed reactions suggest the presence of very low electronic barriers. In this context, the ionic avoided curve-crossing model (Donahue et al., 1998; Donahue, 2003), which has been success-fully employed to explain barrier heights over the 0–41.8 kJ mol^{-1} range of a series of reactions of Cl atoms and OH radicals with alkanes, could be used to explain the present log k versus IP cor-relations. The development of this formulation was motivated by the observation that the height of the curve crossing is directly related to the ionic energy of the separated reactants. This last quantity amounts the energy gap between the ground state ([R•] [X–H]) and hypothetical ionic excited state ([R•$^-$][X$^+$•H]) of the reactants, given approximately by the IP of the hydrogen-atom donor minus the electronic affinity (EA) of the radical (Jing et al., 2008). Due to the fact that the EA of the chlorine atoms and OH radicals in this work are constant along the hydro-haloether reaction series, the decrease of the ionization energy of the ethers should stabilize the configuration of this hypothetical ionic excited state, with a concomitant increase in the reactivity of the H-atom abstraction reactions.

As mentioned before, for both set of studied reactions, the rate coefficients are better correlated with the IP than the D(C–H) values. This fact allows to predict rate coefficients for not measured structurally related reactions. To explore the accuracy of Eqs. (4)

Fig. 2. Rate coefficients for the reactions of OH radicals (k_{OH}) at room temperature *versus* the bond dissociation energies (D(C*–H)) of the weakest C–H bond of the HCEs, HFEs and HEs considered in this work.
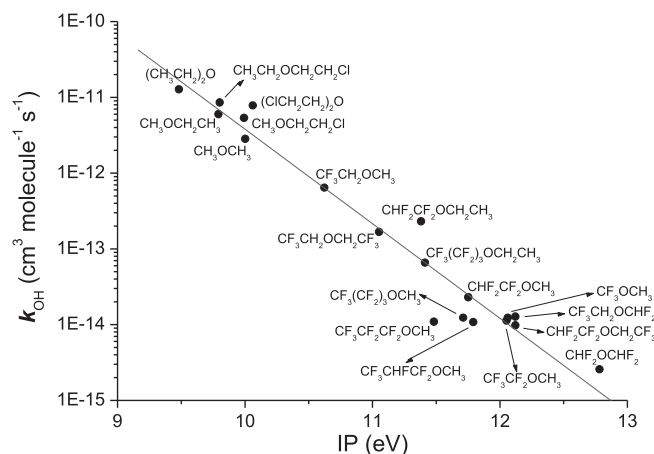

Fig. 4. Rate coefficients for the reactions of OH radicals (k_{OH}) at room temperature *versus* the ionization potential (IP) of the HCEs, HFEs and HFEs considered in this work.

Table 2
Room temperature rate coefficients of several ethers with OH radicals and Cl atoms and the corresponding atmospheric lifetimes.

Ether	$k_{OH}/10^{-14}$ cm^3 molecule^{-1} s^{-1}	$k_{Cl}/10^{-14}$ cm^3 molecule^{-1} s^{-1}	τ_{OH}[a] (days)	τ_{Cl}[a] (days)	τ_{global}[a] (days)
CF_3OCH_3	1.2	14	965	8267	864
CHF_2OCHF_2	0.25	5.7	4630	2.0×10^4	3770
$CF_3CH_2OCH_3$	62.4	231	19	501	18
$CHF_2CF_2OCH_3$	2.24	23.6	517	4904	467
$CF_3CH_2OCHF_2$	1.24	3.11	933	3.7×10^4	911
$CF_3CF_2OCH_3$	1.1	11.0	1052	1.1×10^4	957
$CHF_2CF_2OCH_2CH_3$	22.4	175	52	661	48
$CHF_2CF_2OCH_2CF_3$	0.95	0.911	1218	1.3×10^5	1207
$CF_3CH_2OCH_2CF_3$	16.3	44	71	2630	69
$CF_3CHFCF_2OCH_3$	1.05	23.1	1102	5010	904
$CF_3CF_2CF_2OCH_3$	1.06	11.8	1092	9809	983
$CF_3CF_2CF_2CF_2OCH_3$	1.2	9.7	965	1.2×10^4	892
$CF_3CF_2CF_2CF_2OCH_2CH_3$	6.4	270	181	429	127
CH_3OCH_2Cl	127[b]	2910	9.1	39.9	7.4
CH_3OCHCl_2	64.0[b]	105	18.1	1102.3	17.8
CH_3OCCl_3	28.6[b]	286[b]	40.5	404.7	36.8
$CH_2ClOCH_2CH_3$	233[b]	4485[b]	5.0	25.8	4.2
$CH_3OCHClCH_3$	1010[b]	24,912[b]	1.1	4.6	0.9
$CH_3OCH_2CH_2Cl$	520	11,400	2.3	10.2	1.8
$CH_3CH_2OCH_2CH_2Cl$	830	17,000	1.4	6.8	1.2
$CH_2ClCH_2OCH_2CH_2Cl$	760	10,000	1.5	11.6	1.3
CH_3OCH_3	275	18,000	4.2	6.4	2.5
$CH_3OCH_2CH_3$	583	34,900	2.0	3.3	1.2
$CH_3CH_2OCH_2CH_3$	1240	25,400	0.9	4.6	0.8

[a] τ_{OH} and τ_{Cl} are based on average diurnal concentrations of oxidants ([OH] = 1×10^6 radicals cm^{-3} [Cl] = 1×10^4 atoms cm^{-3}), and $\tau_{global} = [1/\tau_{OH} + 1/\tau_{Cl}]^{-1}$.
[b] Rate coefficients estimated from Eqs. (4) and (5).

and (5), a statistical analysis of the data was carried out. The results show that Eq. (4) allows for prediction of kinetic data for Cl + HCEs/ HFEs reactions with a mean deviation of about 130% (a factor of 2.9), while a better prediction capacity is expected for OH + HCEs/ HFEs reactions, where the estimated mean deviation is 56% (a factor of 1.7). Estimated k_{OH} and k_{Cl} for the reactions of OH radicals and Cl atoms with several HCEs are presented in Table 2.

In the absence of experimental information, the rate coefficients can be theoretically predicted utilizing different approaches of the transition state theory (Truhlar et al., 1985, 1996) combined with molecular information provided by high-level quantum chemical calculations. However, due to the small activation energies involved in the present reactions, the errors can be in some cases certainly large preventing a reliable estimation of k. Conversely, the correlations proposed in this work can achieve this with equal or less error, without major computational effort and can be applied to large size compounds.

The reactivity of halogenated ethers toward tropospheric oxidants is a relevant physicochemical property needed to evaluate global lifetimes, τ_{global}, and the atmospheric impact of these compounds (Sekiya and Misaki, 2000; Atkinson, 2007). The global atmospheric lifetimes for the HFEs, HCEs and HEs considered in this work were calculated assuming that they are determined only by chemical reactions with OH radicals and Cl atoms. It should be noted that the reaction rate of the OH radical with organic molecules often determines the upper lifetime limit and the persistence of these compounds in the troposphere.

The room temperature rate coefficients and the lifetimes calculated using the relationship $\tau_x = 1/k_x$ [X], with X = OH or Cl, are summarized in Table 2. The employed average diurnal global concentrations are [OH] = 1×10^6 radicals cm^{-3} (Kley, 1997) and [Cl] = 1×10^4 atoms cm^{-3} (Spicer et al., 1998). In this table, we present the rate coefficients predicted for a series of HCEs (CH_3OCH_2Cl, CH_3OCHCl_2, CH_3OCCl_3, $CH_2ClOCH_2CH_3$, and $CH_3OCHClCH_3$) together with their corresponding lifetimes, for which an uncertainty by a factor of 2–3 is estimated. Since the reactivity of HFEs towards both tropospheric oxidants is one to three orders of magnitude smaller than the reactivity of HCEs and

HEs, the τ_{global} for HCEs and HEs are on the order of days while for HFEs of years. In addition, it is interesting to note that the photo-oxidation by Cl atoms may be significant in those areas with higher concentration of this atom such as in marine and coastal environments (Riedel et al., 2012), where the atmospheric lifetimes for the haloethers and HEs with respect to the reaction with Cl atoms would be comparable to the lifetimes with respect to the reactions with OH radicals. Finally, the short global lifetimes for the HCEs studied will hinder the transport of these organic compounds into the stratosphere, making a negligible impact on stratospheric ozone by ClO$_x$ cycles, and their contribution to global warming is expected to be rather small.

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