

Measurement of kinetic parameters of gas-phase reactions relevant to atmospheric chemistry

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The kinetic parameters of the reactions of tropospheric oxidants with volatile organic compounds (VOCs), released into the atmosphere, are essential for assessing and comparing their environmental consequences. The most important tropospheric oxidant in the daytime is the OH radical, whereas Cl atom also becomes important in the conditions of marine boundary layer and polluted industrial locations. This article summarizes the recent measurements of the kinetic parameters for the reactions of OH and Cl, with two categories of VOCs – the less reactive ones with tropospheric lifetimes of more than 10 days, responsible for global problems, and the more reactive ones with tropospheric lifetimes of few hours, causing local effects. In addition to their atmospheric implications, the results are important for developing structure–activity relations and also reveal the complex chemistry involved in some of the reactions.

Keywords: Atmospheric chemistry, gas-phase reactions, kinetic parameters, volatile organic compounds.

Introduction

THE increased global awareness about the diverse effects of the chemicals released into the troposphere from anthropogenic and biogenic sources, has resulted in an increased interest to understand the complexities of the chemical processes occurring in the atmosphere. This has prompted a surge of activities, which include monitoring of chemical species in the atmosphere as well as laboratory measurements of relevant parameters and computer modelling. The recent success of the concerted effort of scientists worldwide in understanding, modelling and predicting the ozone depletion in stratosphere¹, has emphasized the importance of laboratory measurements.

The nature of impact of a chemical M on the atmosphere, whether local or global, depends on its tropospheric lifetime (τ), defined as $[M]/(d[M]/dt)$, where $[M]$ is its concentration and $d[M]/dt$ is the rate of its removal from the troposphere². The molecules having a long τ , such as chlorofluorocarbons (CFCs), methane, hydro-

fluorocarbons (HFCs), etc. are responsible for ozone depletion in the stratosphere or global warming, whereas reactive hydrocarbons with short τ cause local problems like photochemical smog. The value of τ depends on the rates of photodissociation of M , its reactions with atmospheric oxidants and its wet deposition (rain, snow) and intake by large water bodies, which are the major processes of removal of any molecule from the troposphere. The overall tropospheric lifetime, τ , can be expressed in terms of the process lifetimes corresponding to each of the above processes, $\tau_{\text{photolysis}}$, τ_{reaction} and τ_{ocean} respectively, and τ_{other} , if there are any other processes³.

$$\tau = \left[\frac{1}{\tau_{\text{photolysis}}} + \frac{1}{\tau_{\text{reaction}}} + \frac{1}{\tau_{\text{ocean}}} + \frac{1}{\tau_{\text{other}}} \right]^{-1} \quad (1)$$

The value of $\tau_{\text{photolysis}}$ is decided by the absorption cross-section of the molecule in the wavelength region of the solar spectrum available in the troposphere (> 350 nm) and the excited state properties of the molecule. τ_{ocean} , which includes wet deposition as well as ocean intake, depends on the Henry's law constants of the molecules. Since both these processes are negligible for many volatile organic compounds (VOCs), their major removal is by reactions with atmospheric oxidants. The most powerful tropospheric oxidant that initiates the reactions of these VOCs is the hydroxyl radical (OH), which has an ambient concentration of 2×10^6 molecule cm^{-3} during daytime⁴, whereas nitrate radical (NO_3) is the major oxidant during night-time. In addition, reactants like ozone (O_3), chlorine atoms (Cl), etc. also play an important role, depending on the nature of the molecule and the location of its release. Thus, τ_{reaction} is expressed as

$$\tau_{\text{reaction}} = \left(\sum_X (\tau_X)^{-1} \right)^{-1} = \left(\sum_X k_X [X] \right)^{-1}, \quad (2)$$

where $[X]$ is the average concentration of the oxidizing species X , which can be OH/ O_3 /Cl/ NO_3 in the atmosphere, k_X is the rate coefficient of the reaction of molecule M with X , and τ_X is the lifetime of the molecule considering only its reaction with X . For molecules with

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values of τ greater than 10 days, the rate coefficient at an average temperature of 272 K (k_X^{272K}) is to be used in the above equation, which takes care of the distribution of the molecule in troposphere and the varying tropospheric temperature³. If the molecule is very reactive, rate coefficient at room temperature, k_X^{298K} , gives a realistic estimation of τ_X .

The above discussion emphasizes the importance of the measurement of the rate coefficients (k_X) and activation energies (E_a/R) of the reactions of pollutant molecules with the oxidants for assessing their impact on the atmosphere. In the recent past, there have been many reports and reviews describing such measurements⁴⁻⁷. The measured kinetic parameters are mainly used in kinetic modelling, where reliability of the reported values is of utmost importance. Obtaining reliable parameters often necessitates multiple measurements by different methods for the same reaction, to avoid interference due to impurities and other intrinsic errors associated with the methods of measurement. In this context, measurement of kinetic parameters of gas-phase reactions of some VOCs, important in the atmosphere, has been initiated in the Radiation and Photochemistry Division, Bhabha Atomic Research Centre, Mumbai. The major focus has been on the relatively long-lived fluorocompounds, considered as new generation alternatives for CFCs and HFCs for various applications, and on short-lived cyclic molecules having unsaturation or heteroatoms, for which experimental measurements are limited. Another interest in these measurements is the generation of useful data for the development of structure–activity relationships (SARs) to enable prediction of the rate coefficients of the reactions of any new molecule, to assess its atmospheric impact.

Most of the HFCs, the presently used CFC alternatives, have τ of the order of a few years and hence contribute towards global warming due to their strong absorption in infrared region. Partially fluorinated ethers (HFES) and alcohols (HFAs) were recently identified as promising new-generation CFC/HFC alternatives⁸⁻¹⁰. These are expected to have higher chemical reactivity than HFCs due to the presence of the ether linkage and –OH group, and therefore shorter τ . Since these molecules do not absorb in the wavelength region available in the troposphere¹¹, their dominant loss processes are reactions with OH. Although the kinetic data available in the literature for some HFES and HFAs¹²⁻²⁰ are fairly consistent for some molecules, substantial variation is observed, especially in the E_a/R values for many molecules^{16,21}. Accurate determination is necessary for modelling the atmospheric fate of these molecules as well as for developing useful SARs. Hence, $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CF}_3$, $\text{CF}_3\text{CH}_2\text{OH}$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{OH}$, and $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OH}$, whose kinetic parameters were either not reported previously or the reported values had some discrepancies, were selected for our studies employing the laser photolysis–laser induced fluorescence (LP–LIF) method^{22,23}.

Compared to the fluorocompounds considered above, unsaturated hydrocarbons and heterocycles have much lower values of τ . However, their high reactivity with the atmospheric oxidants leads to the build-up of harmful products causing health hazard, as in the case of photochemical smog. Depending on the rates, reactions with certain oxidants may dominate in the tropospheric conditions. The relevant reaction pathways of these molecules for tropospheric degradation can be identified only by comparing the values of τ_X , as discussed earlier (eq. (2)). Thus, measurement of the values of k_X is essential for understanding and modelling of the tropospheric chemistry of these short-lived molecules. In the case of many cyclic alkenes (CAs), the required rate coefficients are available⁴⁻⁷, except for their reactions with Cl. Although the ambient concentration of Cl in the northern hemisphere is considered to be low²⁴, it is shown to be significant in the marine boundary layer (MBL) at mid-latitudes, reaching a peak concentration of about 1.3×10^5 atoms cm^{-3} (ref. 25). Recent field studies also indicate the concentration of Cl to be high in polluted industrial locations²⁶, including non-coastal urban areas²⁷. Considering this, it is necessary to examine the possibility of the reaction of CAs with Cl for complete understanding of their degradation under different conditions. In this context, we measured the rate coefficients of the reactions of Cl with CAs, namely cyclopentene, cyclohexene, cycloheptene, 1,4-cyclohexadiene and 1,5-cyclooctadiene. These molecules are released into the troposphere from automobile exhausts, gasoline vaporization, forest fire, rubber abrasion, etc.²⁸. In the class of heterocycles, values of relevant k_X are available for cyclic ethers, but there are no data for saturated nitrogen heterocycles. Morpholine, $\text{C}_4\text{H}_9\text{NO}$, a cyclic ether as well as nitrogen heterocycle, is a common industrial chemical used as a corrosion inhibitor in power plants²⁹, and for various other synthetic applications. This molecule was considered for kinetic measurements²³, so that the reactivity could also be compared to that reported for cyclic ethers. The results of these studies on different categories of VOCs are discussed below.

Reactions of OH with CFC alternatives and their tropospheric lifetimes

Details of the LP–LIF set-up, used for the study are described elsewhere^{22,23}. OH was generated *in situ*, by photolysis of H_2O_2 at 248 nm and monitored by exciting the $P_1(2)$ line in the (0, 0) band of the ($A^2\Sigma$, $v' = 0$) \leftarrow ($X^2\Pi$, $v'' = 0$) transition at 308 nm and collecting the resulting fluorescence. The number densities of H_2O_2 and OH generated inside the reaction cell were kept to be about 10^{14} and 10^{10} molecule cm^{-3} respectively, and a pseudo first-order condition was always maintained with [reactant] \gg [OH]. Although the rate coefficients at $T < 298$ K is important in tropospheric conditions, the studies were restricted to 298–363 K due to experimental limitations.

Table 1. The measured rate coefficients at room temperature and Arrhenius parameters for hydrofluoroethers and hydrofluoroalcohols (in bold) and literature data on the same or similar molecules obtained by different methods. The errors shown for our experimental results are 2σ , including systematic errors

Molecule	$k_{\text{OH}}^{298\text{K}} \times 10^{13}$ ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)	Temperature range	E_a/R (K)	$A \times 10^{12}$ ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)	Method
$\text{CF}_3\text{CH}_2\text{OCH}_2\text{CF}_3$	1.47 ± 0.15	298–363	1030 ± 120	4.5 ± 0.8	LP–LIF ²²
	1.63 ± 0.09		790 ± 47		FP–RF ¹²
	1.51 ± 0.24			$2.32^{+0.46}_{-0.41}$	RR ¹⁴
	1.3		962 ± 19	3.28	RR ¹⁶
$\text{CF}_3\text{CH}_2\text{OH}$	1.03 ± 0.11	298–363	760 ± 340	1.23 ± 1.03	LP–LIF ³⁰
	1.07 ± 0.05	250–430	890 ± 60	1.4	DF–LIF ¹⁷
	1.1		863	1.9	IUPAC ⁶
$\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$	1.0 ± 0.06	250–430	780 ± 60	1.4	LP–LIF ¹⁷
	1.02 ± 0.10	298			RR ²⁰
	1.16 ± 0.08	298–356	900 ± 70	2.27	RR ³⁴
$\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{OH}$	1.15 ± 0.12	298–363	765 ± 170	1.54 ± 0.80	LP–LIF ³⁰
	1.02 ± 0.10	298			RR ²⁰
	1.07 ± 0.05	288–368	1460 ± 120	14	DF ²¹
$\text{CF}_2\text{HCH}_2\text{OH}$	2.52 ± 0.44	298			LP–RF ¹⁸
	4.57 ± 0.38	298			RR ¹⁹
$\text{CFH}_2\text{CH}_2\text{OH}$	16.3 ± 0.9	238–355	330 ± 45	5.15	LP–LIF ³¹
	13.9 ± 0.5	298			RR ¹⁹
$\text{CF}_3\text{CHF}_2\text{CF}_2\text{CH}_2\text{OH}$	1.30 ± 0.08	250–430	880 ± 40	2.49	LP–LIF/RR ³⁴
$\text{CHF}_2\text{CF}_2\text{CH}_2\text{OH}$	1.67 ± 0.19	298–363	560 ± 80	1.12 ± 0.26	LP–LIF ³⁰

LP, Laser photolysis; LIF, Laser induced fluorescence; DF, Discharge flow; RF, Resonance fluorescence; RR, Relative rate; IUPAC, International Union of Pure and Applied Chemistry.

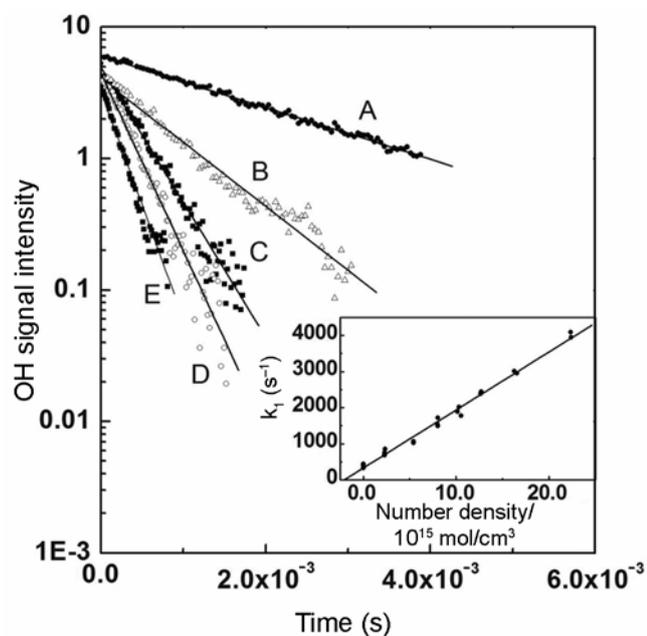


Figure 1. Typical decay profiles of OH at a particular temperature, with increasing concentration of $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CF}_3$ as follows: A, 0; B, 5.5×10^{15} ; C, 1.2×10^{16} ; D, 1.5×10^{16} and E, 2.3×10^{16} mol cm^{-3} . The curves fit into the first order kinetic equation, shown as solid line. (Inset) Variation of the pseudo first-order decay coefficients with the concentration at 308 K. Slope of the line gives the value of bimolecular rate coefficient.

Typical temporal profiles of OH at 298 K in the presence of varying concentration of the fluorocompound, and a typical plot of the pseudo first-order rate coefficient against concentrations of the reactant are given in Figure 1. The value of bimolecular rate coefficients, k_{OH}^T , at a particular temperature, T , is obtained from the slope. The Arrhenius plots, where $\log(k_{\text{OH}}^T)$ is plotted against the inverse of the respective temperature, are linear for all the molecules in the temperature range studied. The activation energy parameters (E_a/R), estimated from the slopes of these plots, are shown in Table 1 (shown in bold), along with the data from the literature for the same or similar molecules for comparison.

In the case of $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CF}_3$, the rate coefficient at room temperature is close to the average of the three previous measurements²². The value of E_a/R , 1030 K, is higher than those reported^{12,16}. The kinetic parameters determined for $\text{CF}_3\text{CH}_2\text{OH}$ (ref. 30) agree well with the IUPAC recommendation⁶. Although there is a good agreement in the measured values of $k_{\text{OH}}^{298\text{K}}$ for $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{OH}$ with the discharge flow measurement at 1 torr²¹, the E_a/R value from our study is considerably lower. There are no previous measurements of the rate coefficient for the reaction of $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OH}$ with OH. The results indicate that, not only $k_{\text{OH}}^{298\text{K}}$ (refs 17, 20), but the E_a/R values also remain the same in the series of

HFAs, $\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{OH}$, independent of the fluorinated chain length n . Interestingly, an increase in $k_{\text{OH}}^{298\text{K}}$ and a decrease in the E_a/R value are observed, when an additional H atom is present in the terminal carbon atom in $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OH}$.

Considering that the Arrhenius plot is linear up to 270 K, as observed for similar fluorocompounds^{17,31}, the rate coefficient at 272 K was estimated for these molecules, and the tropospheric lifetime with respect to reaction with OH, τ_{OH} was calculated (eq. (3)).

$$\tau_{\text{OH}} = \frac{1}{k_{\text{OH}}^{272\text{K}} [\text{OH}]} \quad (3)$$

Here [OH], the ambient 24 h average concentration of OH, which is present only in the daytime, is generally considered to be $\sim 1 \times 10^6$ molecules cm^{-3} , half of the daytime average concentration. Table 2 gives the tropospheric lifetimes estimated using these kinetic parameters, along with the values for HFC134a, a CFC alternative, currently in use, and HFE 7100, another HFC alternative molecule. The additional contribution from wet deposition³² for $\text{CF}_3\text{CH}_2\text{OH}$ and $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OH}$ is also included in the calculation. These lifetimes are required along with the absorption cross-section of the molecule in the IR region, to estimate their global warming potentials at different time horizons, normally 20, 100 and 500 years. Global warming potential (GWP) of a molecule, X , is defined as a ratio of the time-integrated radiative forcing from the instantaneous emission of 1 kg of X relative to that of 1 kg of a reference molecule³, either CO_2 or CFC-11 (CFCl_3). The GWP with respect to CO_2 , estimated for HFC 134a is 3200, 1090 and 337, and for HFE 7100 is 1180, 337 and 102, for time horizons of 20, 100 and 500 years respectively^{3,21}. From Table 2, it can be seen that the molecules in the present study have much lower tropospheric lifetimes compared to HFC 134a and HFE 7100, and hence are expected to have negligible contribution towards global warming.

Structure–activity relationships

As mentioned earlier, understanding the influence of the structural features of the molecules on the reactivity,

Table 2. Overall tropospheric lifetimes (τ) calculated for the molecules in this study, along with those of HFC134a and HFE7100 for comparison

Molecule	Tropospheric lifetime (τ)		
	τ_{OH}	τ_{ocean}	τ
$\text{CF}_3\text{CH}_2\text{OCH}_2\text{CF}_3$	113 days	> 10 years	109 days
$\text{CF}_3\text{CH}_2\text{OH}$	154 days	343 days ³²	106 days
$\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{OH}$	142 days	> 10 years	137 days
$\text{CHF}_2\text{CF}_2\text{CH}_2\text{OH}$	81 days	105 days ³²	46 days
$\text{CHF}_2\text{CHF}_2(\text{HFC134a})^3$	9.6 years		9.6 years
$\text{C}_4\text{F}_9\text{OCH}_3(\text{HFE7100})^3$	4.2 years		4.2 years

especially with OH, is also important. This will enable the selection of molecules with environmental compatibility from those found suitable for industrial applications. In this respect, though hydrofluoroethers are better suited than hydrofluorocarbons due to their higher reactivity with OH, the enhancement by the hydroxyl group in hydrofluoroalcohols is more than that of ether linkage. It can be seen from Table 1 that, in spite of the larger number of abstractable H atoms, the value of $k_{\text{OH}}^{298\text{K}}$ for $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CF}_3$ is only marginally higher than that for $\text{CF}_3\text{CH}_2\text{OH}$, and the activation energy parameter, E_a/R , is more than that for the fluoroalcohols.

In fluoroalcohols, our observation confirms that addition of more CF_2 groups does not affect the τ_{OH} of $\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{OH}$, since both $k_{\text{OH}}^{298\text{K}}$ and E_a/R values do not change (Table 1). Another feature that can be varied, for finding new molecules for suitable applications, is additional hydrogen atoms in HFAs of general formula, $\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{OH}$. This is observed to increase $k_{\text{OH}}^{298\text{K}}$ (refs 18, 19, 31), but the reports are not consistent with respect to its influence on the activation energy parameter. The presence of more abstractable hydrogen atoms is reported to decrease the E_a/R in hydrofluorocarbons³³ and similar trend is observed in $\text{CH}_2\text{FCH}_2\text{OH}$ (ref. 31). However, the E_a/R value reported for $\text{CF}_3\text{CHF}_2\text{CF}_2\text{CH}_2\text{OH}$ (ref. 34) is similar to that of $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{OH}$, though there is an increase in the value of $k_{\text{OH}}^{298\text{K}}$ (Table 1). A recent report on the reactions of OH with primary fluoroalcohols shows the E_a/R value for $\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ to be higher than that for $\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}$, though the former has more abstractable H atoms³⁵. However, our studies on $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OH}$ show an increase in the value of $k_{\text{OH}}^{298\text{K}}$ and a decrease in the activation energy with H-atom substitution in the terminal position of the HFAs. Such contradictions make the development of a reliable SAR, to predict the rate coefficients for fluorocompounds, difficult.

SAR applicable for a wide range of molecules other than fluorocompounds have been derived from the measured rate coefficients^{36,37}. Tokuhashi *et al.*¹⁷ have re-examined these methods to make them more suitable for fluorocompounds, based on the reported rate coefficients of hydrofluorocarbons. The similarity of the rate coefficients and activation energy parameters of $\text{CF}_3\text{CH}_2\text{OH}$ and $\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{OH}$ can be explained by SAR. However, the rate coefficients calculated by this method are different from those measured for $\text{CHF}_2\text{CH}_2\text{OH}$ and $\text{CH}_2\text{FCH}_2\text{OH}$ (refs 24, 31), probably due to the limitation of the SAR parameters derived from the small database available for fluorocompounds. This also emphasizes the necessity of determining the kinetic parameters of reactions of OH with more fluorocompounds, for the development of better SAR. Accurate calculations at higher levels of theory also would be useful to correlate and understand the trends in the observed kinetic parameters in the case of these molecules.

Reactions of molecules of short tropospheric lifetime (a few hours)

Reactions of Cl with cyclic alkenes

Relative rate method³⁸ was employed for the measurement of rate coefficients of the reactions of Cl with cyclic alkenes, using mainly *n*-hexane as the reference molecule for our study³⁹. Here, the concentrations of the sample molecule, for which rate coefficient is to be determined, and the reference molecule are followed using a gas chromatograph with appropriate columns and flame ionization detector. Assuming that the decrease in the concentration of both molecules is only due to reaction with Cl:

$$\ln\left(\frac{(S)_{t_0}}{(S)_t}\right) = \left(\frac{k_S}{k_R}\right) \ln\left(\frac{(R)_{t_0}}{(R)_t}\right), \quad (4)$$

where $[R]_{t_0}$ and $[S]_{t_0}$ are the concentrations of reference and sample respectively, at time t_0 , $[R]_t$ and $[S]_t$ are the corresponding concentrations at time t , and k_S and k_R are the rate coefficients of their reactions with chlorine atoms. Chlorine atoms were generated by photolysis of trichloroacetyl chloride (CCl_3COCl). The typical relative rate plots recorded for the reactions of Cl with 1,4-cyclohexadiene and 1,5-cyclooctadiene with *n*-hexane as reference are shown in Figure 2. The measured relative ratios, $k_{\text{OH}}^{298\text{K}}$, and the values of τ_{Cl} , are shown in Table 3. The errors quoted are 2σ of the measurements, and the errors in the calculated rate coefficients include those in the reference rate coefficient. The rate coefficients reported for their reactions with OH, NO_3 and O_3 as well as the values of τ_{OH} , τ_{NO_3} and τ_{O_3} are also listed in Table 3 for comparison. The typical ambient concentrations (in units of molecule cm^{-3}) used are 5×10^3 , 2×10^6 , 5×10^8 and 7×10^{11} respectively, for Cl (ref. 24), OH, NO_3 and O_3 (ref. 4). The concentrations of Cl and OH are 12 h daytime average and that of NO_3 is a 12 h night-time average. For MBL conditions, the concentration of Cl is considered to be 1.3×10^5 molecule cm^{-3} (ref. 25). In polluted urban areas, the local concentration of ozone and OH also may be higher than the ambient value considered above. From Table 3, it can be seen that these CAs are removed efficiently by OH and O_3 in the daytime and by NO_3 at night-time. However, in the conditions of MBL, the contribution from Cl reaction to the total reactions becomes $\sim 20\%$ for cyclohexene, cycloheptene and cyclohexadiene, and hence can not be neglected. It can be concluded that the reaction with Cl becomes a significant sink for cyclic alkenes, especially cyclohexene, cycloheptene and 1,4-cyclohexadiene, in regions such as MBL⁴⁰.

Correlation between the rate coefficients of reactions of Cl and OH: An approximate linear correlation, indicat-

ing similarity of the mechanisms of the reaction, has been observed in the logarithmic plot of k_{OH} and k_{Cl} , for many saturated molecules⁴¹. The rate coefficient of OH reaction increases by an order of magnitude with unsaturation, whereas a similar increase is not observed for the reaction of Cl. However, the logarithmic plot of the rate coefficients of reactions of OH and Cl with unsaturated molecules, including the CAs and biogenic molecules, some with rate coefficients greater than the diffusion controlled values, are also found to exhibit linearity⁴⁰ (Figure 3).

Effect of oxygen on the relative rate ratio and possibility of generation of OH: During these kinetic measurements, it was observed that the presence of oxygen increased the relative rate ratios of the reaction of Cl with respect to *n*-hexane. The effect is more pronounced in the case of 1,4-cyclohexadiene, where the ratio was found to increase with partial pressure of oxygen up to 20% and then remained constant⁴⁰. Such an increase in the presence of oxygen could be an indirect evidence of generation of OH during the Cl-initiated oxidation of these molecules, because OH has a higher reactivity for unsaturated molecules. The radicals formed by abstraction reaction by Cl being the same as that formed by OH reaction, any indication of generation of OH by the subsequent reactions of such radicals is of interest. There is a search for regeneration pathways of OH from the oxidation pathways of biogenic VOCs, to account for the large difference in the measured concentration of OH in the remote troposphere (Amazon and tropical rainforests) and that calculated using the existing model⁴². The studies on Cl-initiated oxidation of acetaldehyde indicated that reaction of acetyl peroxy radical (also formed as an intermediate in the isoprene oxidation) with HO_2 leads to OH

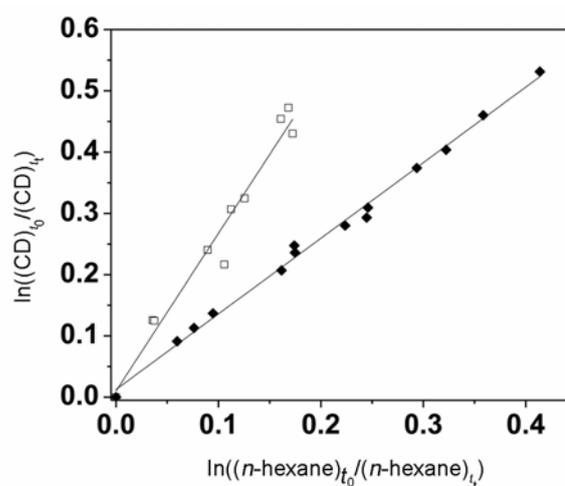


Figure 2. Typical relative rate plot where logarithmic ratio of the relative decrease in the concentration of 1,4-cyclohexadiene (\blacklozenge), and 1,5-cyclooctadiene (\square) due to reaction with Cl at 298 ± 2 K in N_2 is plotted against that of *n*-hexane, the reference molecule.

Table 3. Measured relative rate ratios and rate coefficients of the reaction of Cl with cycloalkenes, with *n*-hexane as reference molecule, and the tropospheric lifetimes (τ_x) calculated with respect to reactions with Cl, OH, NO₃ and O₃. τ_{Cl} and τ_{OH} are calculated only for daytime and τ_{NO_3} for only night-time. Unit of k is cm³ molecule⁻¹ s⁻¹

	Cyclopentene	Cyclohexene	Cycloheptene	1,4-Cyclohexadiene	1,5-Cyclooctadiene
Relative ratio	1.12 ± 0.38	1.31 ± 0.14	1.69 ± 0.18	1.29 ± 0.06	2.19 ± 0.32
k_{Cl}^{298K}	3.39 ± 10 ⁻¹⁰	3.97 × 10 ⁻¹⁰	5.12 × 10 ⁻¹⁰	4.06 × 10 ⁻¹⁰	6.9 × 10 ⁻¹⁰
τ_{Cl} (days)	13.7	11.7	9.0	11.4	6.7
τ_{Cl} (marine boundary layer) (h)	6.3	5.4	4.2	5.3	3.1
k_{OH}^{298K}	6.7 × 10 ⁻¹¹	6.77 × 10 ⁻¹¹	7.4 × 10 ⁻¹¹	9.9 × 10 ⁻¹¹	–
τ_{OH} (h)	2.1	2.1	1.9	1.4	–
$k_{NO_3}^{298K}$	4.2 × 10 ⁻¹³	5.1 × 10 ⁻¹³	5.1 × 10 ⁻¹³	6.6 × 10 ⁻¹³	–
τ_{NO_3}	1.3	1.1	1.1	0.9	–
$k_{O_3}^{298K}$	5.7 × 10 ⁻¹⁶	8.1 × 10 ⁻¹⁷	2.5 × 10 ⁻¹⁶	4.6 × 10 ⁻¹⁷	1.4 × 10 ⁻¹⁶
τ_{O_3} (h)	0.7	4.9	1.6	8.6	2.8

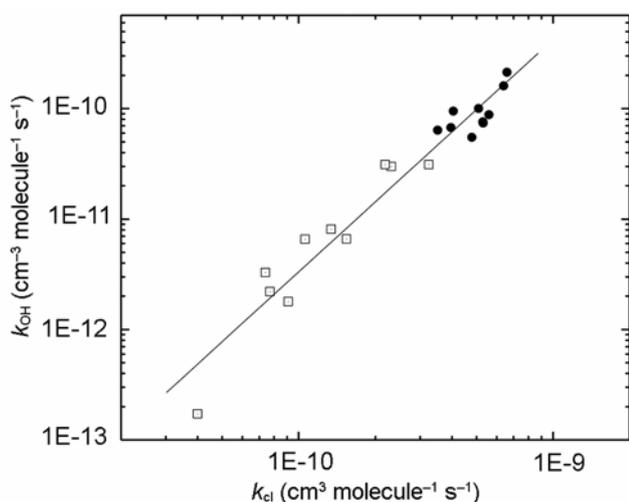


Figure 3. Correlation plots between the rate coefficients for the reactions of Cl and OH with unsaturated hydrocarbons at room temperature. □, C₂H₄, C₂H₃Cl, 1,1-C₂H₂Cl₂, *cis*-C₂H₂Cl₂, *trans*-C₂H₂Cl₂, C₂Cl₄, C₃H₆, 1-C₄H₈ and 1-C₅H₁₀ (ref. 41); ●, Cyclic alkenes (cyclopentene, cyclohexene, cycloheptene, 1,4-cyclohexadiene) and terpenes⁴⁸ (3-carene, α -pinene, β -pinene, limonene, isoprene and myrcene).

formation⁴³. In addition to isoprene, regeneration of OH during the tropospheric oxidation of terpenes, present in the forest environment, is a possibility being considered now⁴². Our product studies with 1,4-cyclohexadiene, structurally similar to the terpenes, indicate 30% formation of HO₂ during the Cl initiated oxidation by the following reactions⁴⁰:



But no direct evidence of OH generation by further reactions could be obtained. However, studies on the reactivity and pathways of Cl-initiated oxidation can be considered as a convenient way to experimentally follow the OH regeneration pathways.

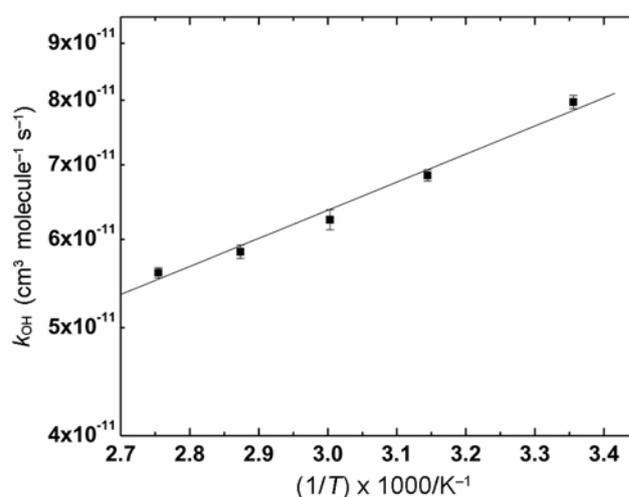


Figure 4. Arrhenius plot of the rate coefficients of reaction of OH with morpholine.

Reactions of morpholine with OH

Morpholine, the heterocycle that was studied²³, has both O and N atoms on the six-membered ring. Being moderately volatile, it is present in the troposphere either due to direct release from the industries or from volatilization from dry soil²⁹. Reaction with OH is expected to be the dominant degradation process. The high value of k_{OH}^{298K} , $(8.0 \pm 0.1) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, gives τ as 1.7 h. Although reactions with Cl, O₃ and NO₃ may also contribute to the tropospheric degradation, these could not be studied due to experimental limitations.

Interestingly, the Arrhenius plot based on the measurements at different temperatures shows an unusual behaviour of negative temperature dependence (Figure 4) fitting into an expression given by $k_{OH}^T = (1.1 \pm 0.1) \times 10^{-11} \exp[(590 \pm 20)/T]$ cm³ molecule⁻¹ s⁻¹. The apparent negative activation energy parameter can be attributed to a pre-reactive complex formation of the molecule with OH, involving hydrogen bond. This molecule has both an ether linkage and an amino group. Ground-state complex

formation with OH is known to increase the reactivity of ethers with OH, and negative temperature dependence is reported in some cases⁴⁴. However, the rate coefficient for the corresponding six-membered diether (1,4-dioxane), is only $1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The value of $k_{\text{OH}}^{298\text{K}}$ for secondary aliphatic amine is $6.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (refs 45, 46), close to that of morpholine, indicating the high reactivity of morpholine to be due to amino group rather than the ether linkage. Both studies on the reactivity of OH with amines report negative temperature dependence, but without any explanation^{45,46}. Our *ab initio* calculations²³ as well as those carried out for amino acid molecules⁴⁷ show the possibility of a strong pre-reactive complex formation with OH, involving the nitrogen atom.

Summary

Measurement of kinetic parameters of reactions of atmospheric oxidants with some important classes of molecules has been carried out. The focus has been on two types of molecules, namely fluorocompounds having long tropospheric lifetimes and highly reactive cyclic molecules with unsaturation or heteroatoms, having a tropospheric lifetime of a few hours. In the former, reactions of OH with hydrofluoroethers and hydrofluoroalcohols are studied so that their environmental suitability as potential CFC/HFC alternatives can be examined by estimating their tropospheric lifetimes. The molecules satisfy the criterion of lower tropospheric lifetimes, and hence lower GWP, as compared to HFCs. These measurements show that both $k_{\text{OH}}^{298\text{K}}$ and E_a/R , for the reaction of OH with fluoroalcohols of general formula, $\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{OH}$ are independent of fluorinated chain length, n . Further, an increase in $k_{\text{OH}}^{298\text{K}}$ and decrease in the E_a/R value are observed when an additional H atom is present in the terminal carbon atom in $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OH}$.

In the case of cyclic molecules, the present study on cyclic alkenes shows the reactions with Cl to be an important degradation pathway in the conditions of marine boundary layer, for cyclohexene, cycloheptene and cyclohexadiene, contributing to an extent of 20%. Very high value of $k_{\text{OH}}^{298\text{K}}$ is observed for morpholine, the heterocyclic molecule studied, and the tropospheric lifetime is estimated to be 1.7 h. The negative dependence of the rate coefficient of this reaction on temperature gives evidence for the formation of a hydrogen-bonded pre-reactive complex with OH, involving the nitrogen atom of the molecule.

In conclusion, it can be seen that the laboratory measurement of kinetic parameters gives useful data, essential for assessing and predicting the environmental impact of VOCs, released into the troposphere. These data are also helpful for developing SAR, so that selection of molecules with minimum environmental impact is possible for various applications. In addition, such measurements also

hint at subsequent reactions and often bring out interesting chemistry involving basic molecular interaction between the reactants.

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