# Rate Coefficients for the Gas-Phase Reactions of Chlorine Atoms with Cyclic Ethers at 298 K

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> ABSTRACT: Rate coefficients of reactions of Cl atoms with cyclic ethers, tetrahydropyran (THP), tetrahydrofuran (THF), and dihydrofurans (2,5-DHF and 2,3-DHF) have been measured at 298 K using a relative rate method. The relative rate ratios for THP and THF are  $0.80 \pm 0.05$  and  $0.80 \pm 0.08$ , respectively, with *n*-hexane as the reference molecule. The relative rate ratios for THF and 2,5-DHF with *n*-pentane as the reference molecule are 0.95  $\pm$  0.07 and 1.73  $\pm$  0.06, respectively, and for 2.5-DHF with 1-butene as reference is  $1.38 \pm 0.05$ . The average values of the rate coefficients are  $(2.52 \pm 0.36)$ ,  $(2.50 \pm 0.39)$ , and  $(4.48 \pm 0.59) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup>  $s^{-1}$  for THP, THF, and 2,5-DHF, respectively. The errors quoted here for relative rate ratios are  $2\sigma$  of the statistical variation in different sets of experiments. These errors, combined with the reported errors of the reference rate coefficients using the statistical error propagation equation, are the quoted errors for the rate coefficients. In the case of 2,3-DHF, after correcting for the dark reaction with CH<sub>3</sub>COCl and assuming no interference from other radical reactions. a relative rate ratio of  $0.85 \pm 0.16$  is obtained with respect to cycloheptene, corresponding to a rate coefficient of  $(4.52 \pm 0.99) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Unlike cyclic hydrocarbons, there is no increase with increasing number of CH<sub>2</sub> groups in these cyclic ethers whereas there is an increase in the rate coefficient with unsaturation in the ring. An attempt is also made to correlate the rate coefficients of cyclic hydrocarbons and ethers with the molecular size as well as HOMO energy. © 2013 Wiley Periodicals, Inc. Int J Chem Kinet 45: 295–305, 2013

#### INTRODUCTION

Most of the volatile organic compounds (VOCs) that are released into the troposphere react with hydroxyl radical (OH), the major tropospheric oxidant. Chlorine atoms (Cl), which react rapidly with VOCs, are also known to contribute significantly to the oxidative capacity of the troposphere. Although the global estimate of the Cl atom concentration in the northern hemisphere is only about  $10^3$  atoms cm<sup>-3</sup>, orders of magnitude lower than the ambient OH concentration ( $10^6$  atoms cm<sup>-3</sup>) [1], it is significantly higher in conditions of the marine boundary layer (MBL), coastal regions, and also in arctic region, reaching a peak concentration of about  $10^5$  atoms cm<sup>-3</sup>, especially during sunrise [2]. The generation of Cl atoms from inorganic

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chlorides via heterogeneous reactions is attributed to be responsible for this high concentration in these areas. A recent field study suggests that Cl atoms may be formed to a similar level, even in midcontinental regions, thousands of kilometers away from the coastal area, probably due to the presence of anthropogenic pollutants [3]. Cl atoms react with most of the organic molecules with rate coefficients that are higher, by an order of magnitude or more, as compared to the OH radical. Hence, despite the lower concentration, the reaction of Cl atoms contributes significantly to the tropospheric degradation of VOCs in the conditions prevalent in the MBL and highly polluted industrial and urban areas.

Recently, considerable effort has been put into the measurement of the rate coefficients of reactions of Cl atoms with different classes of VOCs. The reaction mechanism is expected to be similar to that of the OH radical, as suggested by a linear correlation of the rate coefficients for Cl atom reactions to those of the OH radical reaction [4,5]. The reactivity of OH with a large number of VOCs is very well correlated by structure activity relations (SARs) [6-9], whereas efforts to develop similar SARs for Cl reactivity are limited [10,11]. The reactivity of both OH and Cl toward unsaturated molecules is generally higher than that of the saturated ones, due to the higher rate coefficients of addition reactions [6,11]. However, our recent measurement of rate coefficients of reactions of Cl atoms with unsaturated cyclic hydrocarbons at room temperature [12,13] showed that their rate coefficients increase with the number of carbon atoms (from 5 to 8), but do not change significantly with unsaturation. Considering the importance of Cl atom reactions in the troposphere, it is desirable to understand these trends in their rate coefficients as compared to that of OH radicals, which requires measurement of rate coefficients of more molecules with different functional groups. In the present study, rate coefficients of the reaction of the Cl atom with cyclic ethers, including two unsaturated molecules, are measured and compared with cyclic hydrocarbons, to understand the effect of the O atom and unsaturation in the ring on the Cl reactivity. These measurements also contribute in estimating the role of Cl atom reactions toward their tropospheric degradation.

Cyclic ethers such as oxolane and oxane, commonly known as tetrahydrofuran (THF) and tetrahydro-2Hpyran (THP), are used widely in industry. A range of cyclic ethers have been detected and analyzed during the low-temperature oxidation of *n*-alkanes [14]. Substituted dihydrofurans are also reported to be important intermediates in the formation of aerosols from the atmospheric oxidation of hydrocarbons, through their reactions with OH radicals [15]. These cyclic ethers

are known to react very fast with OH radicals, their reactivity being higher than that of the corresponding hydrocarbons. The recent relative rate measurements of the rate coefficients of the reactions of Cl atoms with THP [16,17] and THF [17] show the reactivity of THP to be lower than that of THF in spite of the increased number of CH2 groups, and no clear trend is observed in the reactivity of Cl atoms with respect to the corresponding hydrocarbons. In the present study, the rate coefficients for the reaction of Cl atoms with THF and THP are measured at 298 K along with that of dihydrofurans, namely 2,5-dihydrofuran (2,5-DHF, also known as 3-oxolene) and 2,3-dihydrofuran (2,3-DHF or 2-oxolene), to see the effect of unsaturation. Reference molecules used are different from those used in the previous study.

# **EXPERIMENTAL**

Rate coefficients at room temperature (298 K) were determined using a relative rate method by comparing the rate of decrease in the concentration of the cyclic ethers (CE) due to their reaction with Cl atoms to that of a reference molecule (R) with the known rate coefficient:

$$CE + Cl \rightarrow products$$
 (1)

$$R + Cl \rightarrow products$$
 (2)

Assuming that the CE and the reference compounds react only with Cl atoms, the fractional loss of CE and R, is related by the standard expression

$$\ln\left[\frac{(\text{CE})_{t_0}}{(\text{CE})_t}\right] = \left[\frac{k_{\text{CE}}}{k_{\text{R}}}\right]\ln\left[\frac{(\text{R})_{t_0}}{(\text{R})_t}\right]$$
(3)

where  $[CE]_{t0}$ ,  $[CE]_t$  and  $[R]_{t0}$ ,  $[R]_t$  are the concentrations of the cyclic ethers and the reference compound at time 0 and *t*, respectively, and  $k_{CE}$  and  $k_R$  are the rate coefficients for reactions 1 and 2, respectively. Thus, the plots of logarithms of the ratios of fractional changes in the concentrations of both CE and R at specific time *t* give a straight line with zero intercept and the slope of  $k_{CE}/k_R$ . The rate coefficient  $k_{CE}$  is calculated using the known value of  $k_R$ .

All the experiments were performed at 298  $\pm$  2 K. The details of the experimental setup are given elsewhere [12,13]. The reaction mixture, consisting of CE (200–250 ppm), reference molecule (200–300 ppm), the source molecule for Cl generation (Cl<sub>2</sub>/CCl<sub>3</sub>COCl), and buffer gas (N<sub>2</sub>/air), was

prepared in a Pyrex/quartz reactor cell of volume 3 L, having a sealed port for taking out samples for concentration measurement. The total pressure was maintained at 800  $\pm$  3 Torr. Chlorine atoms were generated by the in situ photolysis of Cl<sub>2</sub> at 350 nm in the pyrex reactor, in the case of THF and THP. Since 2,5-DHF showed the dark reaction upon addition of molecular chlorine, Cl atoms were generated by photolysis of trichloroacetyl chloride (CCl<sub>3</sub>COCl) at 254 nm in a quartz reactor. Monochromatic UV lamps, either from Sankyo Denki or Rayonet, were used for photolysis at 254 and 350 nm. The mixture was photolyzed for a period of 4-5 min, in steps of 40-50 s, and depletion in the concentrations of the CEs, and the reference molecules was followed after each step. This is done by measuring the concentrations of CE and reference, before and after photolysis, using a gas chromatograph (Shimadzu GC-2014 with a flame ionization detector), by introducing sample aliquots of 500 µL manually for analysis, using a gas tight syringe (SGE-500F-GT). Either SE-30 (10%, 2 m × 3 mm) or Porapak-Q  $(1 \text{ m} \times 6 \text{ mm})$  stainless steel columns were employed for the separation with suitable temperature conditions. Before and after each photolysis, the prepared reaction mixture was allowed to reach equilibrium, which was confirmed by reproducibility of the concentration measured during consecutive gas chromatographic samples. Hexane, pentane, butane, and 1-butene were the different reference molecules used, except for 2,3-DHF, based on their comparable rate coefficients and the least interference during the gas chromatography (GC) analysis, either from the molecule or from the products of their reactions with Cl atoms.

Since 2.3-DHF was found to react rapidly with CCl<sub>3</sub>COCl even at low concentrations of about 50 ppm, a different procedure was adopted. The rate of reaction of 2,3-DHF with CH<sub>3</sub>COCl was found to be lower than that with CCl<sub>3</sub>COCl and hence photolysis of CH<sub>3</sub>COCl at 254 nm was used as the source molecule for the Cl atom. The utility of this molecule as the source of the Cl atom was tested with butane, 1-butene, and cycloheptene with *n*-hexane as the reference molecule, and the measured relative ratios and rate coefficients were found to match with the reported values [12,18,19]. 1-Butene and n-hexane could not be used as reference molecules for determining the rate coefficient of 2,3-DHF, since their depletion rate due to the reaction with the Cl atom was found to be slower than the rate of depletion of 2,3-DHF due to the dark reaction with CH<sub>3</sub>COCl. Hence cycloheptene was used as a reference molecule. The reaction mixture consisted of CH<sub>3</sub>COCl (100–120 ppm), 2,3-DHF (~100 ppm), cycloheptene ( $\sim$ 80 ppm), and N<sub>2</sub> (buffer gas, keeping the total pressure as 800 Torr). The mixture was subjected

to a single step of photolysis, with duration of photolysis varying in each experiment. Concentrations of DHF and cycloheptene were monitored by GC before and after photolysis. The total duration of experiment was kept the same. The blank experiments were carried out for the same duration to obtain the loss of 2,3-DHF due to the dark reaction.

Some of the major products were characterized by a gas chromatograph coupled with a mass spectrometer (GCMS QP2010, Shimadzu), using different columns, namely HT-8, BP-X-50, AB1-MS (30 m  $\times$  0.25 mm  $\times$  0.25 µm), for the separation.

Nitrogen gas of purity >99.9% (INOX Air Products, Mumbai, India) and ultrapure air (zero grade; Chemtron Science, Mumbai, India) were used as buffer gases. THF (spectrograde) was obtained from Thomas Baker (Mumbai, India) with >99.9% purity and 2,3-DHF from Sigma Aldrich (Steinheim, Germany) with 99% purity. All other reagents were obtained from Sigma Aldrich with purities >97%. Samples of the compounds were stored in evacuated glass vessels and subjected to freeze–pump–thaw cycles prior to use.

## RESULTS

Prior to the determination of rate coefficients, the stability of the reaction mixture with respect to wall losses and dark reactions was checked for about 7 h, which is more than the total duration of a relative rate measurement. The loss of the CEs through direct photolysis, in the absence of chlorine precursors, was also investigated, and no significant decrease was observed. In addition, reactions of the Cl atom with each CEs as well as reference molecules were carried out individually to ensure that the products of the reactions did not interfere with the GC measurement of the concentration of the CEs and the reference molecules. Based on this, *n*-pentane, *n*-hexane, and 1-butene, which have rate coefficients comparable to that of CEs, were chosen as the reference molecules. The rate coefficients for the reaction of *n*-hexane and *n*-pentane with Cl atoms were taken to be  $(3.15 \pm 0.40) \times 10^{-10}$  and  $(2.62 \pm 0.34) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. These values were obtained after modifying the values reported by Atkinson and Aschmann [18], using the best current IUPAC estimate,  $(2.05 \pm 0.25)$  $\times$  10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [19], as the rate coefficient of their reference reaction, namely Cl + nbutane. There is no IUPAC recommended value in the case of 1-butene, where the reported values are in the range of  $(2.89-3.38) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1}$ s<sup>-1</sup> [11,20–22]. Here,  $(3.21 \pm 0.41) \times 10^{-10} \text{ cm}^3$ molecule<sup>-1</sup> s<sup>-1</sup> is used as the rate coefficient for



**Figure 1** A typical plot of the relative decrease in the concentration of THP and *n*-hexane due to the reaction with the Cl atom at 298  $\pm$  2 K ( $\blacksquare$ ) in N<sub>2</sub> and ( $\bigcirc$ ) in air. (The *Y* axis for o is marginally shifted, shown at the right). The source of the Cl atom is Cl<sub>2</sub> gas.

the reaction of the Cl atom with 1-butene, calculated on the basis of the experimental relative rate ratio with respect to *n*-hexane [20],  $1.02 \pm 0.02$ , and the above rate coefficient for *n*-hexane. Trichloroacetyl chloride (CCl<sub>3</sub>COCl) was used as the Cl atom source in the case of 2,5-DHF instead of molecular chlorine, due to the latter's dark reaction with 2,5-DHF. To ensure that the change in a photolytic precursor does not affect the relative rate ratios, due to secondary reactions of the counterfragment, relative rate measurements with CCl<sub>3</sub>COCl as a photolytic precursor were also carried out for THF and the ratios were found to be the same as those with Cl<sub>2</sub> as a source of the Cl atom.

The typical plots of the logarithms of the fractional loss of CE versus that of the reference molecules, according to Eq. (1), are given in Figs. 1, 2, and 3 for THP, THF and 2,5-DHF, respectively. The plots are linear, with near zero intercept, in all experiments, suggesting the absence of any complications due to secondary reactions. The slopes of the linear least-square fits,  $k_{CE}/k_R$ , and the calculated rate coefficients for the three molecules ( $k_{CE}$ ) with different reference molecules, in either N<sub>2</sub> or air, are listed in Table I. The ratios given are average slopes from a number of measurements (indicated in parentheses), and the error is two times the standard deviation,  $2\sigma$ , calculated from the distribution in the slope values of independent runs, using the standard formula. The error in the slope,

from the linear regression analysis of the data in each experiment, arising from the scattering of the points due to random errors in sampling and concentration measurements, is found to be small (1-2%), in most of the cases, as compared to the variation in independent measurements. In a few cases, where it is more than 5%, both the errors are added quadratically. The error arising from continuous sampling from the reaction mixture is also very small, <1%, and hence not added to the total error. Since absolute concentrations are not measured and care was taken to passivate the syringe and use the same syringe throughout an experiment, systematic errors in these measurements are considered to be negligible. These errors in the relative rate ratios are combined with the errors reported for the respective reference rate coefficients, using the statistical error propagation equation and are quoted for  $k_{CE}$  in Table I. Except in the case of 2,5-DHF, with 1-butene as reference, the relative rate ratios are same in nitrogen and air. However, the average rate coefficients for each molecule, shown in bold in Table I, is the average from all data sets in N<sub>2</sub>. (The experiments in air were not considered.) The logarithms of fractional depletion of 2,3-DHF and cycloheptene, after correcting for the loss of 2,3-DHF due to the dark reaction, are plotted in Fig. 4. The treatment of the data is slightly different due to the presence of the dark reaction. The data plotted in Fig. 4 are obtained from 13 independent runs, each with single photolysis of varying duration, and



**Figure 2** Plot of the relative decrease in the concentration of THF due to the reaction with the Cl atom at  $298 \pm 2$  K; with *n*-pentane as the reference molecule in N<sub>2</sub> ( $\blacksquare$ ) and in air ( $\square$ ), The source of the Cl atom is Cl<sub>2</sub> gas. The linear fit shown is for ( $\blacksquare$ ). ( $\bigcirc$ ): with *n*-hexane as the reference molecule and CCl<sub>3</sub>COCl as the Cl atom source in N<sub>2</sub>. The *Y* axis for  $\bigcirc$  is marginally shifted, shown at the right.

all are corrected for the dark reaction, as mentioned in the Experimental section. The ratio of the rate coefficients and its error, given in Table I, corresponds to the slope and  $2\sigma$  from the linear regression analysis of these points, as shown in Fig. 4. The rate coefficient is estimated assuming no interference from other radical reactions. The rate coefficient of the reaction of the Cl atom with cycloheptene is  $(5.32 \pm 0.57) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [12].

Although the absence of heterogeneous chemistry cannot be completely ruled out in the present experimental conditions, the major products observed here match very well with those reported for THP in a 200 L Teflon bag [16], namely tetrahydro-4H-pyran-4-ol, tetrahydro-4H-pyran-4-one, tetrahydro-2Hpyran-2-one, 2-methyl tetrahydrofuran, tetrahydro-2-furanone, and ring-opened product 3-chloropropyl formate. Similar products, formed by H atom abstraction, are also observed in the case of Cl-initiated oxidation of THF. In the case of 2,5-DHF, Cl atom addition products, 3,4-dichlorotetrahydrofuran, 2,3-dichlorotetrahydrofuran, 4-chloro-3,6-dihydro-2-H-pyran, and 2,3-dichloro1-propanol were observed along with the products of H abstraction reactions, furan-2(5H)-one, 3-hydroxydihydro-2-(3H)-furanone, and furan.

#### DISCUSSION

The average values of the rate coefficients for the Cl atom reactions from the present work are listed in Table II, along with the previously reported average values for THP and THF. There is a good agreement, within experimental errors, among the values of THP and THF, though the present value is marginally higher in the case of THP [16,17]. The value reported for THP by Ballesteros et al. [16] is an average of the rate coefficients measured relative to ethene, propene, 1-butene, and 1,3-butadiene. Considering the IUPAC-recommended value [19] for 1-propene (2.7  $\times$  $10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) and the corrected value for 1-butene used in the present study  $(3.21 \times 10^{-10})$  $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup>), the rate coefficients reported by Ballesteros et al. [16] are modified to  $2.57 \times 10^{-10}$  and  $2.38 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively, closer to the present determination (Table II). The value reported by Giri and Roscoe for THP [17] is an average of the rate coefficients measured in the temperature range of 280-357 K with reference to THF and includes the error that they reported for THF. However, the rate coefficient that is reported for THF, with reference to isobutene, does not include the uncertainty in the value of the reference rate coefficient. Although



**Figure 3** Plot of the relative decrease in the concentration of 2,5-DHF due to the reaction with the Cl atom at  $298 \pm 2$  K; with *n*-pentane as the reference molecule in N<sub>2</sub> ( $\blacksquare$ ) and in air ( $\Box$ ); with 1-butene as the reference molecule in N<sub>2</sub> ( $\bullet$ ). The source of the Cl atom is CCl<sub>3</sub>COCl. The *Y* axis for  $\blacksquare$  and  $\bullet$  is marginally shifted, shown at the right.

their rate coefficients for THP and THF are the same within the combined error estimates, they observed the rate coefficient of THF to be consistently about 30% larger than that of THP, in spite of a lower number of hydrogen atoms. However, the present results indicate very similar rate coefficients for the reactions of THF and THP with Cl atoms. The rate coefficients for the reactions of DHFs with the Cl atom are almost 1.7–1.8 times higher than that of THF, indicating an increase due to the presence of unsaturation.

The products of the reactions of Cl atoms observed for THF and THP in our study are very similar to those reported by Ballesteros et al. [16] for THP. Even though the theoretical calculations of Ballesteros et al. [16] predict the predominance of abstraction of the  $\alpha$  H atom, they observed products arising due to H atom abstraction from all the possible positions in the ring. In the case of unsaturated molecule, 2,5-DHF, Cl-added products as well as those resulting from H abstraction are formed. These observations indicate that because Cl atoms are so highly reactive, there is less selectivity in their reactions.

Although the rate coefficients determined here are sums of rate coefficients of individual reaction channels, an attempt is made to compare the total reactivity of these cyclic ethers with that of cyclic hydrocarbons. The earlier study on cyclic molecules showed that the

rate coefficients of the reaction of Cl increases with increasing number of CH2 groups [12]. It was also observed that increasing unsaturation, i.e. the number of double bonds, does not influence the reactivity significantly in six-membered ring compounds, cyclohexane, cyclohexene, and cyclohexadiene [13]. For estimating the rate coefficients of Cl atom reactions with alkanes and alkenes, SARs have been developed earlier [7,10,11,24]. In general, these SARs consider the total rate coefficients as the summation of group rate coefficients, modified by substituent factors to take care of the neighboring group effects. Ezell et al. [11] have shown that these SARs are to be fairly in agreement with experimental values in the case of alkenes up to C5. However, these have not been applied in the case of cyclic alkanes and alkenes. The calculated values of rate coefficients in saturated molecules, cyclopentane, cyclohexane, (2.90 and  $3.51 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup>  $s^{-1}$ ), using these group additivity values [7,11], agree with the experimental values, 3.05 and 3.24  $\times$  $10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. However, there is considerable discrepancy between the calculated and experimental values in the case of cyclic alkenes such as cyclopentene (4.30 and 3.05  $\times$  10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>), cyclohexene (4.88 and  $3.97 \times 10^{-10}$  $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup>), and cyclohexadiene (6.70 and  $4.06 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). The trend shows

Cyclic Ether (Concentration $\times$ $10^{-15}$ molecules cm <sup>-3</sup>	Source of Cl (Concentration $\times 10^{-15}$ molecules cm <sup>-3</sup> )	Reference (Concentration $\times 10^{-15}$ molecules cm <sup>-3</sup> )	Buffer Gas	$k_{\rm CE}/k_{\rm R}$	$k_{298} \times 10^{10} (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$
THP					
6.0-7.2	Cl <sub>2</sub> (95–100)	<i>n</i> -Hexane (6.5–7.5)	N <sub>2</sub> (3)	$0.80 \pm 0.05$	$2.52\pm0.36$
6.0-6.5	Cl <sub>2</sub> (95–100)	<i>n</i> -Hexane (6.2–6.7)	Air (2)	$0.82\pm0.03$	$2.58\pm0.34$
	Avera			$2.52\pm0.36$	
THF					
4.6-6.0	Cl <sub>2</sub> (30–40)	<i>n</i> -Pentane (6.2–8.8)	N <sub>2</sub> (7)	$0.95\pm0.07$	$2.49\pm0.37$
5.7-6.5	Cl <sub>2</sub> (30–40)	<i>n</i> -Pentane (6.2–8.8)	Air (2)	$0.97\pm0.10$	$2.54\pm0.42$
6.0-6.5	Cl <sub>2</sub> (45–52)	<i>n</i> -Hexane (6.2–8.8)	N <sub>2</sub> (3)	$0.79\pm0.07$	$2.49\pm0.39$
5.2 - 5.4	CCl <sub>3</sub> COCl(20-22)	<i>n</i> -Hexane (6.2–8.8)	N <sub>2</sub> (2)	$0.81\pm0.11$	$2.55\pm0.47$
	Average in $N_2$				$2.50 \pm 0.39$
2,5-DHF					
2.9-3.1	CCl <sub>3</sub> COCl(13-16)	<i>n</i> -Pentane (6.2–8.8)	N <sub>2</sub> (3)	$1.73\pm0.06$	$4.53\pm0.59$
2.9-3.1	CCl <sub>3</sub> COCl(13-16)	<i>n</i> -Pentane (6.2–8.8)	Air (4)	$1.70\pm0.07$	$4.45\pm0.61$
2.9-3.1	CCl <sub>3</sub> COCl(13-16)	1-Butene (3.9–4.9)	N <sub>2</sub> (3)	$1.38\pm0.05$	$4.43\pm0.59$
3.1-3.4	CCl <sub>3</sub> COCl(13-16)	1-Butene (4.7–5.2)	Air (4)	$1.63\pm0.16$	$5.23\pm0.83$
Average in N <sub>2</sub>					$4.48 \pm 0.59$
2,3-DHF					
2.9–3.4	CH <sub>3</sub> COCl(3.0–4.7)	cycloheptene(1.6-2.3)	N <sub>2</sub> (13)	$0.85\pm0.16$	$4.52\pm0.99$

**Table I** Summary of the Measured Relative Rate Ratios and the Derived Rate Coefficients for the Reactions of the Cl Atom with Cyclic Ethers, at Different Experimental Conditions. T = 298 K, P = 800 Torr

The rate coefficients of reactions of reference molecules with the Cl atom at 298 K:  $k(Cl + n\text{-hexane}) = (3.15 \pm 0.40) \times 10^{-10}$ , and  $k(Cl + n\text{-pentane}) = (2.62 \pm 0.34) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (both from [18], corrected using the IUPAC recommended value for k(Cl + n-butane) [19]).  $k(Cl + 1\text{-butene}) = (3.21 \pm 0.41) \times 10^{-10}$  [20] and  $k(Cl + \text{cycloheptene}) = (5.32 \pm 0.57) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [12], both corrected, using the above value for k(Cl + n-hexane).

that the rate coefficient of Cl addition to the double bond is less in the case of cyclic alkenes as compared to straight chain alkenes, used to derive these values. The rate coefficient of addition, estimated based on the benzene yield in the case of cyclohexadiene (1.4  $\times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>), is only about half of the recommended rate coefficient of addition based on acyclic alkenes (2.98  $\times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) [13].

The neighboring group substituent effect for the ether functional group is estimated to be about 8 for OH reactions [6,7], leading to enhancement of rate coefficient of abstraction. This is assigned to be due to the formation of a hydrogen-bonded prereactive complex, as suggested by a negative temperature dependence of the rate coefficients [25]. Although Cl atom reactions with THP [17] and 1,4-dioxane [26] are also reported to have very small or no dependence on temperature, there is no increase in the rate coefficient of THP as compared to that of cyclopentane. It is also observed that the measured rate coefficient of THP is the same (present work) or marginally lower [17] as compared to that of THF. This contradicts with the SAR by Ezell et al. [11], which predicts an increase in the rate coefficient with more number of CH<sub>2</sub> groups. The reason for this difference is not clear, but a similar trend in rate coefficients is seen in the reactions of THP and THF with OH (25% larger for THF) and Br (70% larger for THF). Giri and Roscoe [17] have noted that in the case of the reactions of the Br atom, the higher rate coefficient of THF as compared to that of THP is attributed to the difference in the activation energies [17]. Being independent of temperature, the same reason is not applicable to rate coefficients of Cl atom reactions with THP and THF. It is possible that only the CH<sub>2</sub> group  $\alpha$  to the O atom contributes to the reactivity and the additional CH<sub>2</sub> groups do not have any effect. However, the product analysis shows that abstraction also takes place from  $CH_2$  groups other than those at  $\alpha$  position. Thus, it is difficult to give a clear explanation for the similarity of the rate coefficients of THP and THF. The higher rate coefficients of DHFs as compared to THF imply that the addition rate coefficient is higher than two times the rate coefficient for abstraction. A slightly enhanced rate coefficient for the abstraction from the allylic CH<sub>2</sub> group may also contribute to this increase.

The lack of activation barriers for the reactions, as suggested by the very small or negative dependence on temperature for the rate coefficients of the reaction of the Cl atom with alkanes and alkenes [7,21,23] as well as cyclic ethers [17,26], implies that these reaction rate



Figure 4 Plot of the relative decrease in the concentration of 2,3-DHF due to the reaction with the Cl atom at 298  $\pm$  2 K; with cycloheptene as the reference molecule in N<sub>2</sub>, after correction for the loss due to the dark reaction with CH<sub>3</sub>COCl.

coefficients are almost in the collision-controlled limits. The measured rate coefficient of reaction of Cl with cyclooctane also suggests the reactions to be approaching the collision-controlled limits for cyclohexane and cyclooctane, since the increase with the number of CH<sub>2</sub> groups is not as high as in the case of smaller cyclic alkanes [27]. The collision-controlled rate coefficient is proportional to the collision cross section, a function of molecular size and velocity, a function of mass and temperature. Hence, it is possible that the presence of unsaturation or other functional features in the molecule may not affect the rate coefficient significantly. In cyclic hydrocarbons, it was observed that unsaturation does not change the rate coefficients [13]. However, in the present study, the rate coefficient of the reaction of the Cl atom with DHFs is almost 1.8 times higher than that of THF, the corresponding saturated ether, though the molecular size remains the same.

The above discussion shows that different factors, such as size of the molecule and the presence of functional groups of different reactivities, may influence the overall rate coefficients in the case of reactions of Cl atoms that have high rate coefficients. This dependence

Cyclic Ether	$k_{298} \times 10^{10}$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	Reference	Comments Reference Molecule/Error in $k_{298}$
THP	$2.52\pm0.36$	Present work	n-hexane; includes error in $k_{\rm R}$ .
	$2.03 \pm 0.82$	Roscoe and Giri [17]	THF, from [17], includes error in $k_{\rm R}$ ; $k_{298}$ is average of the <i>k</i> in the temperature range 280–360 K.
	$2.21 \pm 0.32$	[16]	Ethene, propene, 1-butene, 1,3-butadiene; includes the errors in $k_{\rm R}$ .
THF	$2.50\pm0.39$	Present work	<i>n</i> -Hexane, <i>n</i> -pentane; includes the error in $k_{\rm R}$ .
	$2.71 \pm 0.34$	Roscoe and Giri [17]	$k_{298}$ is average of the k in the temperature range 280–360 K. Not inclusive of the error in $k_{\rm R}$ .
2,5-DHF	$4.48\pm0.59$	Present work	n-Pentane, 1-butene; includes the error in $k_{\rm R}$ .
2,3-DHF	$4.52\pm0.99$	Present work	Cycloheptene, includes the error in $k_{\rm R}$ .

**Table II**Summary of the Rate Coefficients of Reactions of Cl with Cyclic Ethers from the Present Work and from theLiterature



**Figure 5** Variation of rate coefficients of reactions of cyclic hydrocarbons/cyclic ethers with OH ( $\bullet$ ) and Cl ( $\Box$ ): (A) with size parameter and (B) with HOMO energy. The rate coefficients of reactions of Cl with cyclic hydrocarbons are marked by  $\blacksquare$ , to differentiate from those of cyclic ethers. The straight line fitting in (A) is for only cyclic hydrocarbons, whereas in (B) it is for all the molecules. Cyclic hydrocarbons considered are C<sub>5</sub>H<sub>10</sub>, C<sub>6</sub>H<sub>12</sub> [30,31], C<sub>8</sub>H<sub>16</sub> [27,30], C<sub>5</sub>H<sub>8</sub>, C<sub>6</sub>H<sub>10</sub>, C<sub>7</sub>H<sub>12</sub> [12,30], C<sub>6</sub>H<sub>8</sub>, and C<sub>8</sub>H<sub>12</sub> [13,30].

is further investigated and compared to that of OH radical reactivity. Fast reactions of radicals with organic molecules can be treated on the basis of the frontier orbital interactions. In the case of electrophiles such as OH and Cl, the important interaction is with the highest occupied molecular orbital (HOMO) of the molecule. The presence of more reactive functional groups raises the HOMO energy, and the values of HOMO energy are found to correlate very well with the rate coefficients of OH radical reactions with organic molecules [8] and also with the rate coefficients of Cl atoms with fluorocompounds such as fluoroalcohols [28]. Figure 5 shows the variation of rate coefficients with both size parameter and HOMO energy. The molecular size and HOMO energies are calculated using Gaussian 92 program [29]. The geometry optimization and energy calculations were carried out at the MP2/6-31G+ level. Size parameters were calculated as square of the sum of largest interatomic distance divided by  $\mu^{1/2}$  (reduced mass) to take care of the variation in the molecular velocity. The rate coefficients of OH radical reactions are from Moriarty et al. [25] for cyclic ethers and from Atkinson and Arey for cyclic hydrocarbons [30].

From Fig. 5A, it can be seen that the correlation of logarithmic value of the rate coefficients of all the cyclic hydrocarbons and ethers together with size parameter is quite poor for OH reactions, which have rate coefficients much lower than collision-controlled limits. In the case of rate coefficients of Cl atom reactions, in cyclic hydrocarbons alone, there is a good correlation with size parameter (a straight line fit is shown in the figure), if the value for cyclooctane, measured at low-pressure conditions (1 Torr) [27], is not considered. This correlation may be a consequence of the following facts: The increase in size corresponds to the increase in the number of CH<sub>2</sub> groups and hence the number of abstractable H atoms, leading to an increase in the rate coefficient. When there is unsaturation within the ring of same size or the number of carbon atoms, abstraction possibility from two CH<sub>2</sub> groups is replaced by the possibility of an addition reaction. If the rate coefficient of addition is equal to almost two times that of the abstraction rate coefficient per the CH<sub>2</sub> group, as observed in cyclohexadiene [13], the total rate coefficient may remain same as the saturated molecule. However, when cyclic ethers and hydrocarbons are considered together, the correlation is poor, showing that even though the rate coefficients are very high and reach collisioncontrolled limits, they are still dependent on the presence of different functional groups that can influence the reactivity. It is also possible that the poor dependence on size only reflects the deviation from the classical collision theory, as the molecules and radicals are not really hard spheres and are subjected to intermolecular interaction potential.

Figure 5B clearly shows that the rate coefficients of the reactions of these molecules with OH (in the logarithmic scale) have a good linear dependence on HOMO energy. This includes even the cyclic ethers, in which case the increased reactivity with OH is assigned to the prereactive complex formation, involving hydrogen bonding between the incoming OH group and the O atom in the ether. It can be seen from Fig. 5B that the rate coefficients of Cl atoms also correlate well with the HOMO energy. The correlation coefficient for the linear regression of the variation of rate coefficients of Cl with HOMO is not as good as that in the case of rate coefficients of OH reactions, even though the variations in the former are minor, all the values being in the  $10^{-10}$  range, as compared to that in latter, distributed in a wide range, from  $10^{-12}$  to  $10^{-10}$ . However, the rate coefficients of CEs and hydrocarbons, considered together, are correlated better when plotted against HOMO energy, as compared to the plot against size parameter.

The tropospheric lifetimes of THP and THF, with respect to their reactions with Cl and OH, have already been compared by Giri and Roscoe [17]. They have estimated the tropospheric lifetimes for the removal of THF and THP by Cl to be in the range of 10–16 h in the conditions of marine environment, which are comparable to the lifetimes for the removal by OH, 14 and 21 h for THF and THP, respectively. Lifetimes for the removal of THF and THP by Cl, estimated based on the present rate coefficients, are 11 h for both, almost same as that estimated earlier, indicating that the reactions of Cl and OH have similar importance for the removal of these molecules in the MBL. The concentration of Cl and OH, used for the above estimation, are the same as those considered by Giri and Roscoe [17], i.e., 10<sup>5</sup> and 10<sup>6</sup> molecules cm<sup>-3</sup>, respectively. In the case of unsaturated molecules, DHFs, the rate coefficient with Cl is only increased about 1.8 times as compared to that of THF, whereas the reactivity with OH is expected to be an order of magnitude higher than THF and an additional pathway of the reaction with O<sub>3</sub> is also possible, making them the most prominent pathway for the degradation of DHF, even under the conditions of the MBL.

#### CONCLUSION

The rate coefficients of reactions of Cl atom with cyclic ethers, THP, THF, and DHF, have been determined at 298  $\pm$  2 K, using the relative rate method and compared to those of cyclic hydrocarbons, to see the effect of the O atom and unsaturation on the ring. The rate coefficients determined for THF and THP are in agreement with the recent literature values, determined using different reference molecules. The results confirm that there is no increase in the rate coefficient of THP as compared to that of THF, whereas the rate coefficients increase with an increase in CH<sub>2</sub> groups in cyclic hydrocarbons. Unlike cyclic hydrocarbons, there is also an increase in the rate coefficient of the Cl atom reaction with unsaturation in cyclic ether, in DHF. A good correlation with molecular size parameter is observed for the rate coefficients of Cl atom reactions with cyclic hydrocarbons alone, but not when cyclic ethers and hydrocarbons are considered together. The logarithmic values of rate coefficients of the Cl atom reaction of CEs and hydrocarbons are found to be better correlated with HOMO energy of the molecule.

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