Rate Coefficients and Products for Gas-Phase Reactions of Chlorine Atoms with Cyclic Unsaturated Hydrocarbons at 298 K

A. SHARMA, K. K. PUSHPA, S. DHANYA, P. D. NAIK, P. N. BAJAJ

Radiation and Photochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

Received 15 July 2009; revised 23 September 2009; accepted 24 September 2009

DOI 10.1002/kin.20467 Published online in Wiley InterScience (www.interscience.wiley.com).

> ABSTRACT: Rate coefficients for the reaction of Cl atoms with cycloalkenes have been determined using the relative rate method, at 298 K and atmospheric pressure of N₂. Reference molecule was *n*-hexane, and the concentrations of the organics were followed by gas chromatographic analysis. Cl atoms were prepared by photolysis of trichloroacetyl chloride at 254 nm. The relative rates of reactions of Cl atoms with cycloalkenes, with respect to *n*-hexane, are measured as 1.12 ± 0.38 , 1.31 ± 0.14 , and 1.69 ± 0.18 for cyclopentene, cyclohexene, and cycloheptene, respectively. Considering the absolute value of the rate coefficient of the reaction of Cl atom with *n*-hexane as $3.03 \pm 0.06 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, the rate coefficient values for cyclopentene, cyclohexene, and cycloheptene are calculated to be $(3.39 \pm 1.08) \times 10^{-10}$, (3.97) \pm 0.43) \times 10⁻¹⁰, and (5.12 \pm 0.55) \times 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, respectively. The experiments for each molecule were repeated six to eight times, and the slopes and the rate coefficients given above are the average values of these measurements, and the quoted error includes 2σ as well as all other uncertainties in the measurement and calculations. The rate coefficient increases linearly with the number of carbon atoms, with an increment per additional CH₂ group being $(8.7 \pm 1.6) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. Chloroketones and chloroalcohols, along with unsaturated ketones and alcohols, were found to be the major products of Cl-atom-initiated oxidation of cycloalkenes in the presence of air. The atmospheric implications of these results are discussed, along with a comparison with the reported structure activity relationships. © 2009 Wiley Periodicals, Inc. Int J Chem Kinet 42: 98–105, 2010

INTRODUCTION

Alkenes, one of the major pollutants in the urban ambient air, are an important source of free radicals in the lower atmosphere. In the troposphere, source apportionment studies show that reactions of alkenes with ozone are responsible for jump-starting photochemistry after sunrise [1]. The oxidation reactions of alkenes are considered as important source of aerosols in the troposphere [2]. The atmospheric oxidation of these compounds involves reactions with OH radicals, O_3 , NO_2 , NO_3 , etc. The rate coefficients for the

Correspondence to: S. Dhanya; e-mail: sdhanya@barc.gov.in. © 2009 Wiley Periodicals, Inc.

gas-phase reactions of OH, NO2, NO3, O3, etc., with many alkenes have been determined recently [3-6]. Previous studies have suggested that, in addition to the above oxidants. Cl atoms are also important in the marine boundary layer at midlatitudes, especially at dawn. Although the upper limit for the chlorine atom concentration in the northern hemisphere is estimated to be less than 10^3 atoms cm⁻³ [7], the peak concentration during sunrise in the marine boundary layer is reported [8] to be 1.3×10^5 atoms cm⁻³. Reactions of Cl atoms with many volatile organic compounds (VOCs) proceed with high rate coefficients [9] and, therefore, may play an important role in the atmospheric chemistry of remote marine boundary layer [8] as well as the polluted urban areas, with significant anthropogenic emission of Cl₂ [10]. Hence, measurement of rate coefficients of reactions of Cl atoms with different VOCs has become important [4], and the same has been reported for a large number of saturated and unsaturated organic molecules with different substitutions [11–15]. In the case of alkenes, the rate coefficients of reactions of Cl atoms have been measured by different groups [11,16]. In addition to these straight chain alkenes, many cyclic alkenes have also been detected in the troposphere; the major source being automobile exhausts, gasoline vaporization, forest fire, rubber abrasion, etc. [17]. However, there are not many studies on the rate coefficients, or mechanism of reactions of Cl atoms with these cyclic alkenes, except for a measurement of Cl atom reactions with cyclopentene by Anderson et al [18]. In the present study, the rate coefficients of reactions of Cl atoms with three cyclic alkenes, cyclopentene, cyclohexene, and cycloheptene, are determined using the relative rate method, to assess the significance of these reactions in the troposphere. The major stable products of the Cl-atom-initiated oxidation of these molecules are also identified.

EXPERIMENTAL

All the reactions were carried out in a quartz reaction chamber of 3-L volume, fitted with vacuum stopcocks and a sealed port for taking out samples for GC analysis. Chlorine atoms were generated by photolysis of trichloroacetyl chloride (CCl₃COCl) at 254 nm, using a UV lamp (Rayonett). The reaction mixture, consisting of cycloalkene (CA), *n*-hexane as reference compound, and trichloroacetyl chloride, was prepared in the reaction chamber, using a vacuum manifold, and the total pressure was maintained at 800 ± 3 Torr, by adding 99.9% nitrogen (INOX Air Products Ltd., Mumbai, India). The pressure was measured, using a capacitance manometer (Pfeiffer Vacuum). Experi-

ments were also conducted in ultrapure air (zero grade; Chemtron Science Laboratories, Mumbai, India). The reactant mixture contained typically ~300 ppm of CCl₃COCl and 250–350 ppm of the sample and the reference molecules. The prepared reaction mixture was kept for 60-80 min for equilibration, before photolysis, which was confirmed by reproducibility of the gas chromatogram. Experiments were performed at room temperature (298 \pm 2K). Concentrations of the sample and the reference were monitored, prior to, and after photolysis, using gas chromatograph (Chemito GC 8610), with 10% SE 30 $(7' \times 1/8'')$ column, with temperature programming, in conjunction with flame ionization detector. The mixture was photolyzed for a period of 10 min, in steps of 1-2 min, and after each photolysis step, the decrease in the concentration of the two organics, cycloalkene and *n*-hexane, were followed. A sample of 500 µL was transferred from the reaction chamber to GC, using a gas-tight syringe. The decrease in the concentration of the sample and the reference was determined at each step.

The fractional loss of the CA molecules and the reference molecules, due to reaction with Cl atoms, is monitored to obtain the kinetic data. In the present study, *n*-hexane, for which the rate coefficient is well known [9], was the reference molecule (R), and cyclopentene, cyclohexene, and cycloheptene were the sample molecules (CA). The relative rate constants were then determined, using the following expression, assuming that both molecules react only with chlorine:

$$\ln\left(\frac{[CA]_{t_0}}{[CA]_t}\right) = \left(\left(\frac{k_{CA}}{k_R}\right)\ln\left(\frac{[R]_{t_0}}{[R]_t}\right)\right)$$
(I)

where $[R]_{t0}$ and $[CA]_{t0}$ are the concentrations of *n*-hexane and CA, respectively, at time t_0 , $[R]_t$ and $[CA]_t$ are the corresponding concentrations at time *t*, and k_{CA} and k_R are the rate coefficients of their reactions with chlorine atoms.

All the reagents were obtained from Sigma-Aldrich (Steinheim, Germany), with purities >95%. The reactants and *n*-hexane were subjected to freeze–pump–thaw cycles, before use.

The products of the reaction of the chlorine atoms with cyclic alkenes in the presence of air at atmospheric pressure were characterized by a gas chromatograph coupled with a mass spectrometer (Shimadzu), using BPX50 (30 m \times 0.25 mm \times 0.25 µm) and CP WAX 52CB (30 m \times 0.25 mm \times 0.25 µm) columns independently. The products were identified by matching the spectral features with the reported mass spectra.

RESULTS

Determination of Rate Coefficients

The relative rate method relies on the assumption that both the reactant and the reference compounds are removed solely by reaction with chlorine atoms. To verify this assumption, mixtures of CCl₃COCl, CA, *n*-hexane, and nitrogen/air were prepared and allowed to stand in the dark for about 6 h, and the concentration of the components were monitored by GC at regular time intervals. There was no significant decrease in the concentration of any of the molecules, indicating the absence of dark reactions as well as wall losses. To test for possible photolysis of the reactants, a mixture of CA, n-hexane, and nitrogen/air was photolyzed for 10 min in the absence of added chlorine source. There was no decrease in the concentration of the sample or the reference compound, which confirmed the absence of any significant loss due to direct photolysis.

The experimental data, the fractional loss of CA versus the fractional loss of the reference compound, are plotted, according to Eq. (I), in Fig. 1. In the presence of nitrogen (Fig. 1A) as well as air (Fig. 1B), a linear plot is obtained, with near zero intercept, for each CA, suggesting the absence of any complications due



Figure 1 Logarithmic plot of relative decrease in the concentration of cycloheptene (\blacksquare), cyclohexene (\bigcirc), and cyclopentene (\blacktriangle) with respect to *n*-hexane (reference compound), due to reaction with Cl atom at 298 ± 2 K. (A) in N₂ and (B) in air.

to secondary reactions. From the linear least-square fit, slopes of the lines are obtained, which are the ratios of the rate coefficients of the samples to that of the reference molecule. Considering k_1 , k_2 , k_3 , and k_R as the rate coefficients for the reactions of Cl atoms with cyclopentene, cyclohexene, cycloheptene, and *n*-hexane, respectively, the mean values of the slopes, obtained in N₂ are $k_1/k_R = 1.12 \pm 0.38$, $k_2/k_R = 1.31 \pm 0.14$, and $k_3/k_{\rm R} = 1.69 \pm 0.18$. From these slopes, using $k_{\rm R} =$ $3.03 \pm 0.06 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [9], the rate coefficients are calculated as $k_1 = 3.39 \pm 1.08 \times 10^{-10}$, $k_2 = 3.97 \pm 0.43 \times 10^{-10}$, and $k_3 = 5.12 \pm 0.55 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. The corresponding values of the slopes in air are 1.22 ± 0.40 , 1.58 ± 0.28 , and 1.76 ± 0.28 and the rate coefficients calculated from these values are $3.69 \pm 1.24 \times 10^{-10}$, $4.79 \pm 0.86 \times$ 10^{-10} , and $5.33 \pm 0.86 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, for cyclopentene, cyclohexene, and cycloheptene, respectively. The experiments for each molecule were repeated six to eight times, and the slopes and the rate coefficients given above are the average values of these measurements, with two standard deviation as quoted error, along with a 2% error added to take care of the error in the rate coefficient of the reference reaction.

Product Study of the Chlorine-Atom-Initiated Oxidation

The stable products formed during the chlorine-atominitiated oxidation of cyclic alkenes in atmospheric conditions were characterized. For this, a mixture of CA/CCl₃COCl/air was photolyzed at 254 nm, for a period ranging from 3 to 9 min. The main observed products were chloro-ketones, chloro-alcohols, enones, and enols for all CAs. The total ion chromatograms obtained for cyclopentene, cyclohexene, and cycloheptene are shown in Fig. 2. The products characterized by GC-MS, for each CA, are listed in Table I. The yield of the major products was found to increase with duration of the photolysis up to 9 min, as shown in the inset of Fig. 2.

DISCUSSION

Except for one rate coefficient measurement for the reaction with cyclopentene [18], there are no previous rate coefficient data, at least to our knowledge, for the reactions of chlorine atoms with cycloalkenes. Even in the case of cyclopentene, the reported value (Table II) is at least two times higher than the presently measured rate coefficient. The reason for this discrepancy is not clear. As mentioned earlier, we observed that the rate coefficient in the presence of air is marginally higher than that in the presence of nitrogen. A probable



Figure 2 Total ion chromatograms of the products of Clatom-initiated oxidation of A: cyclopentene, B: cyclohexene, and C: cycloheptene. The identities of the peaks, which could be characterized by GC-MS, are listed in Table I. Inset: Total ion chromatograms of the products after 3, 6, and 9 min of photolysis of the reaction mixture in the case of cycloheptene. The column temperature is lower than that in C.

reason is the formation of OH in the presence of air, as observed in the Cl-initiated oxidation of acetaldehyde, where reaction of acetyl peroxy radical with HO₂ [19,20] leads to OH formation. If OH is generated during the reaction, it will affect the determination of the rate coefficient of Cl atom reaction, because the ratio of the rate coefficients of the reactions of OH with CA and the reference molecule is not the same as the ratio of the rate coefficients of the reactions of Cl with CA and reference molecule. The former is expected to be much higher than the latter, based on the data for alkenes. This difference can lead to an overestimation of the rate coefficient of reaction of Cl atom with CA. Hence, the rate coefficient obtained in N₂ is considered as the true rate coefficient of the reaction of Cl atom with CA. However, it can be noted that the increase in the rate coefficient in the presence of air is not very pronounced, except in the case of cyclohexene, probably indicating a smaller extent of OH formation from these peroxy radicals as compared to that in the case of acetoxy peroxy radicals [19,20].

The rate coefficients of reactions of OH with these cyclic alkenes, reported by various groups [21,22], along with the present results for the reactions of Cl atoms, are listed in Table II, for comparison. The present results show that the rate coefficients of reactions of Cl atoms with cyclic unsaturated hydrocarbons are about five to seven times higher than those of OH reactions. The rate coefficients for the reactions of both OH [4] and Cl atom [23] with cyclic alkanes are also included in Table II. In all the cases, the rate coefficients are higher for the unsaturated cyclic hydrocarbons than those for the saturated ones. This indicates that the possibility of addition reaction of OH/Cl in unsaturated molecules makes them more reactive as compared to saturated molecules, where only abstraction reaction is possible.

Sr. No.	Cycloalkene	Products
1	Cyclopentene	2-Chlorocyclopentanone (1), 2-chlorocyclopentanol (2), 2-cyclopenten-1-one (3)
2	Cyclohexene	2-Chlorocyclohexanone (1), 2-chlorocyclohexanol (2), 2-cyclohexen-1-one (3), 3-cyclohexen-1-ol (4a), 3-chlorocyclohexene (5); peak 4 unidentified
3	Cycloheptene	2-Chlorocycloheptanone (1), cycloheptanol (2), 2-cycloheptene-1-one, (5), 4-cycloheptene-1-one (7), 1,4-dichlorocycloheptane or 1,3-dichlorocycloheptane (8); peaks 3, 4, and 6 unidentified

Table I Major Products of Atmospheric Oxidation, Characterized by GC-MS

The corresponding peak number in Fig. 2 is given in parenthesis.

Table II	Rate Coefficients of Reactions of	Cycloalkenes and	l Cycloalkanes v	with OH and Cl Atoms
----------	-----------------------------------	------------------	------------------	----------------------

Molecule	Rate Coefficient for Reaction with OH at 298 K (cm^3 molecule ⁻¹ s ⁻¹)	Rate Coefficient for Reaction with Cl Atom at 298 K (cm^3 molecule ⁻¹ s ⁻¹)
Cyclpentene	6.7×10^{-11} [22]	$3.39 \pm 1.08 \times 10^{-10} \text{ (present work)}^{a}$
	5.7×10^{-11} [21]	$7.32 \pm 0.88 \times 10^{-10}$ [18]
Cyclohexene	6.77×10^{-11} [22]	$3.97 \pm 0.43 \times 10^{-10} \text{ (present work)}^{a}$
-	6.1×10^{-11} [21]	-
Cycloheptene	7.4×10^{-11} [22]	$5.12 \pm 0.55 \times 10^{-10} \text{ (present work)}^{a}$
Cyclopentane	4.97×10^{-12} [4]	3.05×10^{-10} [23]
Cyclohexane	6.97×10^{-12} [4]	3.83×10^{-10} [23]

^{*a*}In the present work, the rate coefficients of CA with Cl atom are measured relative to *n*-hexane, considering $k_{n-hexane} = 3.03 \pm 0.06 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹.

Different predictive structure activity relationships, based on frontier molecular orbital calculations, have been developed for reactions of OH with many fluorosubstituted hydrocarbons [24]. In the case of alkenes, correlations with HOMO (highest occupied molecular orbital) energy have been developed for predicting rate coefficients of reactions of OH, O3, and NO3 [22]. Empirical correlations with position of substituents, double bonds, etc., have also been developed for reactions with OH [25]. These relations grossly predict the rate coefficient values of the different CAs to be very similar and do not reflect the marginal increase with increasing number of carbon atoms. In a recent study, Aschman and Atkinson [3] have shown that the rate coefficients for the reactions of OH with C_4 – C_{14} 1-alkenes increase linearly with the number of carbon atoms, and from the slope of the linear plot, the increase in the rate coefficient per CH2 group in noncyclic alkenes was derived as $(2.02 \pm 0.32) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This was found to be 1.4–1.5 times higher than that of *n*-alkane series, where only H abstraction takes place. Based on this, the increase in the rate coefficient with carbon number is assigned to H atom abstraction from the alkyl groups and to enhancement of addition at C=C bond with additional alkyl group upto C = 8 [26]. Although the number of CAs studied here is limited to three, a similar plot of the rate coefficient of Cl atom reaction with number of carbon atoms yields an approximate linear correlation (Fig. 3), with $(8.7 \pm 1.6) \times$ 10^{-11} cm³ molecule⁻¹ s⁻¹ as the increase in the rate coefficient of Cl atom reaction per CH₂ group. A similar plot of the rate coefficients for the reaction of OH rad-



Figure 3 Variation of rate coefficients of Cl atoms and OH radicals with the number of carbon atoms. Reactions of Cl atoms with cyclic alkenes from the present work (\blacktriangle); with straight chain alkenes from [16] (\bigtriangleup) and from [27] (\bullet); with *n*-alkanes from [13] (\Box); OH radicals with cyclic alkenes from [22] (\blacksquare).

ical with CAs with C > 4, obtained from the literature (Table II), yields the increase of the rate coefficient per CH₂ group as 3.5×10^{-12} cm³ molecule⁻¹ s⁻¹. This is smaller as compared to the increment for the reactions of Cl atom with cyclic alkenes, observed in the present work, but comparable to the increment for the reactions of OH with noncyclic alkenes [3]. For a similar comparison between the increment per CH₂ group in the case of Cl atom reactions of noncyclic and cyclic alkenes, the reported rate coefficients of the Cl atom reactions with noncyclic alkenes are also plotted in Fig. 3. In this case, there are two different sets of data reported at room temperature and atmospheric pressure [16,27], shown by different symbols in Fig. 3. Except for hexene, all other values are for molecules with terminal double bond, with no branching. There are no reports on 1-hexene and any other alkenes with higher carbon number. A linear variation with carbon number is observed up to C = 5, for both sets of data, with slopes of 0.9×10^{-10} and 1.34×10^{-10} cm³ molecule⁻¹ s⁻¹ for data from [16] and [27], respectively. In the case of Cl atom reaction with *n*-alkanes, the rate coefficients [13] increase with the carbon number and levels off at C = 7, as shown in Fig. 3, and the slope is less than that for straight chain alkenes and CAs. Similar data for C = 4 to C = 14 was used to separate and estimate the contribution of addition and abstraction reactions for OH reactions in alkenes [26]. However, due to lack of sufficient data, it is difficult to make similar estimations in the case of Cl atom reactions.

It can be noticed that in the case of reactions of OH with CAs, the rate coefficient increases by an order of magnitude with unsaturation (Table II). However, in the case of Cl atom reaction with CAs, the increase in the rate coefficient with unsaturation is only marginal, though the nature of the products (Table I) suggests the importance of addition, along with abstraction reaction. One reason for this could be that the rate coefficients of the reactions of saturated compounds are very close to diffusion-controlled limits, and thus there is not much scope for further increase due to unsaturation. However, we do find an increase in the rate coefficient with the increase in the number of carbon atoms. Another reason for not observing substantial increase with unsaturation could be that allylic hydrogen atoms react less rapidly with Cl atoms than the analogous alkyl hydrogens in alkanes, as observed earlier in a series of noncyclic alkenes [16].

An approximate linear correlation between the rate coefficients of reactions with OH and Cl atoms has been observed for many unsaturated [11] and saturated [28] hydrocarbons, including many halocarbons [15], with different slopes for saturated and unsaturated compounds. Such a linear correlation indicates similarity of the mechanisms of the reaction of these hydrocarbons with OH radical and Cl atom. Recently, during their study on the reactions of fluorochlorinated esters with OH radical and Cl, Blanco and Teruel [29] have also shown a linear correlation between the rate coefficients of reactions of OH and Cl atom with saturated VOCs. The least-square fitting of the data gives a relationship similar to that in [28]:

$$\log k_{\rm OH} = 0.485 \log k_{\rm Cl} - 7.00 \tag{II}$$

with the rate coefficients (k) in the units of cm³ molecule⁻¹ s⁻¹. The correlation is expected to be different for unsaturated compounds, because the reaction mechanism is different, involving both abstraction and addition reactions. The rate coefficient values for alkenes, given in [15], are plotted, along with the values reported here for CAs, in Fig. 4. The least-square fitting of the data yields the following relationship for alkenes:

$$\log k_{\rm OH} = 2.39 \log k_{\rm Cl} + 12.97 \tag{III}$$

The overall linearity appears to hold good within error limits, even after inclusion of the three CAs, shown as filled squares in Fig. 4. The linearity indicates the similarity of the reaction mechanism in the case of OH and Cl atom reactions.

In the present study, the most common products observed in all the three cycloalkenes are



Figure 4 Correlation plots between the rate coefficients for the reactions of Cl and OH radicals with unsaturated hydrocarbons at room temperature. —: for molecules and rate coefficients taken from [15] shown as \Box . --: after including the data for unsaturated cycloalkenes from the present work, shown as \blacksquare . The molecules from [15], included in fitting, are C₂H₄, C₂H₃Cl, 1,1-C₂H₂Cl₂, *cis*-C₂H₂Cl₂, *trans*-C₂H₂Cl₂, C₂Cl₄, C₃H₆, 1- C₄H₈, and 1- C₅H₁₀.

2-chloroketones, 2-chloroalcohols, and enones. The former two are the products of addition of Cl atom at the double bond, whereas the latter is due to the H abstraction reaction. In either case, the first step of addition or abstraction leads to a radical, which reacts with oxygen, leading to the formation of per-oxy radicals. Peroxy radicals are known to undergo reactions among themselves, leading to alcohol and ketone [30].

$$RO_2 + RO_2/R'O_2 \rightarrow alcohol + aldehyde/ketone + O_2$$
(IV)

Although the ketones have a weak absorption at 254 nm, the experimental results suggest that under the present conditions, there is not much degradation of ketone, as indicated by the increase in their concentration with duration of the photolysis. Very recently, enol formation and ring opening is reported during photolytic OH-initiated oxidation of cyclohexene, investigated by tunable synchrotron photoionization mass spectrometry [31]. We could not confirm the formation of such products in our studies on cyclohexene. It is quite likely that the yield of such products is very low. The number of products in the case of cyclohexene and cycloheptene is more than that in the case of cyclopentene, with keto or OH groups at different positions, indicating abstraction of H atom from different C atoms. The interference due to OH formation in the presence of air is probably responsible for the formation of cycloheptanol, an addition product of OH with cycloheptene. Equivalent products could not be identified in the case of cyclopentene and cyclohexene. There are a few unidentified peaks in GC-MS, suggesting the complexity and the variety of the products, especially in the case of cycloheptene. This could be probably due to the increased role of abstraction reactions, allowing ring opening as well as interference of OH or HO₂ reactions.

Atmospheric Lifetimes

Henry's law coefficients of these cyclic alkenes studied in the present work are not expected to be high, due to their low solubility in water. These molecules are not expected to undergo photodissociation in the troposphere, since they do not absorb at wavelengths above 320 nm, which is available in the troposphere. Hence, the main sink of the cyclic alkenes studied is the chemical reaction with oxidizing species available in the troposphere. Tropospheric lifetimes (τ) of these CAs with respect to removal by OH, Cl, O₃,

	Cyclopentene	Cyclohexene	Cycloheptene
$\overline{k_{\rm Cl} ({\rm cm}^3 {\rm molecule}^{-1} {\rm s}^{-1})}$ (present work)	3.39×10^{-10}	3.97×10^{-10}	5.12×10^{-10}
$\tau_{\rm Cl}$ (days)	13.7	11.7	9.0
$k_{\rm OH} ({\rm cm}^3 {\rm molecule}^{-1} {\rm s}^{-1}) [22]$	6.7×10^{-11}	6.77×10^{-11}	7.4×10^{-11}
τ_{OH} (h)	4.2	4.1	3.8
$k_{\rm NO_3} ({\rm cm}^3 {\rm molecule}^{-1} {\rm s}^{-1}) [4]$	4.2×10^{-13}	5.1×10^{-13}	5.1×10^{-13}
$\tau_{\rm NO_3}$ (h)	2.6	2.2	2.2
k_{O_3} (cm ³ molecule ⁻¹ s ⁻¹) [4]	5.7×10^{-16}	8.1×10^{-17}	2.5×10^{-16}
$ au_{O_3}$	41.8 min	4.9 h	1.6 h

Table III Tropospheric Lifetimes (τ) Calculated for the Cycloalkenes with Respect to Reactions with Different Species

The ambient concentrations used for Cl [31], OH, NO₃, and O₃ [32] are 2.5×10^3 , 1×10^6 , 2.5×10^8 , and 7×10^{11} molecules cm⁻³, respectively.

and NO₃ can be estimated from the rate coefficients, k_X , as

$$\tau = \frac{1}{k_{\rm X}[{\rm X}]} \tag{V}$$

where X is the ambient concentration of the abovementioned reactive species. The calculated values are shown in Table III. 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} for Cl [32], OH, NO₃, and O₃ [33], respectively. The concentrations of Cl and OH are 12-h daytime average concentrations and that of NO₃ is a 12-h night time average. Hence, these are corrected by a factor of 2, to get the average 24-h concentration, whereas the concentration of O_3 given above is 24-h average, and used directly. From Table III, it can be seen that in daytime, these CAs, especially cyclopentene and cycloheptene, are removed most efficiently by O₃, and in the nighttime, removal by NO₃ radical is also important. However, in the case of cyclohexene, daytime removal by OH is comparable with that by O₃, because the rate coefficient of reaction of ozone with this molecule is 10 times slower than that with cyclopentene and cycloheptene [34]. It can be concluded that the reaction with Cl atom becomes a minor but significant sink for CAs, in regions, such as marine boundary layer and urban industrial areas, where the local peak concentration of Cl atoms can be almost 50 times higher than the average concentration considered here. The atmospheric implications are higher in the case of the Cl-initiated oxidations of cyclohexene and cycloheptene.

The authors are thankful to Dr. S. K. Sarkar, Head, Radiation and Photochemistry Division, and Dr. T. Mukherjee, Director, Chemistry Group, for their keen interest and encouragement during the course of this work.

BIBLIOGRAPHY

- Calvert, J. G.; Atkinson, R.; Kerr, J. A.; Madronich, S.; Moortgat, G. K.; Wallington, T. J.; Yarwood, G. The Mechanisms of Atmospheric Oxidation of the Alkenes; Oxford University Press: New York, 2000.
- Hatakeyama, S.; Ohno, M.; Weng, J.; Takagi, H.; Akimoto, H. Environ Sci Technol 1987, 21, 52–57.
- Aschmann, S. M.; Atkinson, R. Phys Chem Chem Phys 2008, 10, 4159–4164.
- 4. Atkinson, R.; Arey, J. Chem Rev 2003, 103, 4605-4638.
- King, M. D.; Canosa-Mas, C. E.; Wayne, R. P. Phys Chem Chem Phys 2002, 4, 295–303.
- Pfrang, C.; Martin, R. S.; Nalty, A.; Waring, R.; Canosa-Mas, C. E.; Wayne, R. P. Phys Chem Chem Phys 2005, 7, 2506–2512.
- Rudolph, J.; Koppmann, R.; Plass-Dulmer, Ch.; Atmos Environ 1996, 30, 1887–1894.
- Spicer, C. W.; Chapman, E. G.; Finlayson-Pitts, B. J.; Plastridge, R. A.; Hubbe, J. M.;. Fast, J. D.; Berkowitz, C. M. Nature 1998, 394, 353–355.
- Atkinson, R.; Aschmann, S. M. Int J Chem Kinet 1985, 17, 33–41.
- Tanaka, P. L.; Oldfield, S.; Neece, J. D.; Mullins, C. B.; Allen, D. T. Environ Sci Technol 2000, 34, 4470–4473.
- Stutz, Z. J.; Ezell, M. J.; Ezell, A. A.; Filayson-Pitts, B. J. J Phys Chem A 1998, 102, 8510–8519.
- Kaiser, E. W.; Wallington, T. J. J Phys Chem A 2007, 111, 10667–10670.
- Manion, J. A.; Huie, R. E.; Levin, R. D.; Burgess, D. R., Jr.; Orkin, V. L.; Tsang, W.; McGivern, W. S.; Hudgens, J. W.; Knyazev, V. D.; Atkinson, D. B.; Chai, E.; Tereza, A. M.; Lin, C.-Y.; Allison, T. C.; Mallard, W. G.; Westley, F.; Herron, J. T.; Hampson, R. F.; Frizzell, D. H. NIST Chemical Kinetics Database, NIST Standard Reference Database 17, Version 7.0 (Web version), Release 1.4.3, Data version 2008.12, National Institute of Standards and Technology, Gaithersburg, MD. Web address: http://kinetics.nist.gov/
- Papadimitriou, V. C.; Papanastasiou, D. K.; Stefanopoulos, V. G.; Zaras, A. M.; Lazarou, Y. G.; Papagiannakopoulos, P. J. Phys Chem A 2007, 111, 11608– 11617.

- Garib, A.; Timerghazin, Q. K.; Ariya, P. A. Can J Chem 2006, 84, 1686–1695.
- Ezell, M. J.; Wang, W.; Ezell, A. A.; Soskin, G.; Finlayson-Pitts, B. J. Phys Chem Chem Phys 2002, 4, 5813–5820.
- 17. Graedel, T. E. Chemical Compounds in the Atmosphere; Academic Press: New York, 1978.
- Anderson, R. S.; Huang, L.; Iannon, R.; Rudolph, J. J Atmos Chem 2007, 56, 275–291.
- 19. Jenkin, M. E.; Hurley, M. D.; Wallington, T. J. Phys Chem Chem Phys 2007, 9, 3149–3162.
- 20. Hasson, A. S.; Tyndall, G. S.; Orlando, J. J. J Phys Chem A 2004, 108, 5979–5989.
- 21. Rogers, J. D. Environ Sci Technol 1989, 23, 177-181.
- 22. King, M. D.; Canosa-Mas, C. E.; Wayne, R. P. Phys Chem Chem Phys 1999, 1, 2231–2238.
- Anderson, R. S.; Huang, L.; Iannone, R.; Rudolph, J. J Phys Chem A 2007, 111, 495–504.
- 24. Dhanya, S.; Saini, R. D. Int J Chem Kinet 1997, 29, 187–194.
- 25. Peeters, J.; Boullart, W.; Pultau, V.; Vandenberk, S.; Vereecken, L. J Phys Chem A 2007, 111, 1618–1631.

- Nishino, N.; Arey, J.; Atkinson, R. J Phys Chem A 2009, 113, 852–857.
- 27. Coquet, S.; Ariya, P. A. Int J Chem Kinet 2000, 32, 478–484.
- Andersen, M. P. S.; Nielsen, O. J.; Wallington, T. J.; Hurley, M. D.; DeMore, W. B. J Phys Chem A 2005, 109, 3926–3934.
- 29. Blanco, M. B.; Teruel, M. A. Chem Phys Lett 2007, 441, 1–6.
- Lightfoot, P. D.; Cox, R. A.; Crowley, J. N.; Destriau, M.; Hayman, G. D.; Jenkin, M. E.; Moortgat, G. K.; Zabel, F. Atmos Environ A 1992, 26, 1805–1961.
- Melony, G.; Selby, T. M.; Osborn, D. L.; Taatjes, C. A. J Phys Chem A 2008, 112, 13444–13451.
- Pszenny, A. A. P.; Keene, W. C.; Jacob, D. J.; Fan, S.; Maben, J. R.; Zetwo, M. P.; Springer-Young, M.; Galloway, J. N. Geophys Res Lett 1993, 20, 699– 702.
- 33. Atkinson, R. Atmos Environ 2000, 34, 2063– 2101.
- 34. Cusick, R. D.; Atkinson, R. Int J Chem Kinet 2005, 37, 183–190.