J. Phys. Chem. A **1999,** *103,* 5321−5327

Study on the NO_3 Radical Reactivity: Reactions with Cyclic Alkenes

Ernesto Martínez,* Beatriz Cabañas, Alfonso Aranda, Pilar Martín, Alberto Notario, and Sagrario Salgado

*Facultad de Químicas, Universidad de Castilla-La Mancha, Campus Universitario s/n,
13071 Ciudad Real, Spain*

Received: December 10, 1998; In Final Form: May 4, 1999

The rate constants of the reactions of NO_3 with cyclopentene, cyclohexene, cycloheptene, 1-methylcyclohexene, and methylenecyclohexane have been measured as a function of temperature at low pressure in a fast flow system with LIF detection of NO_3. The measured room temperature (298 K) rate constants for these reactions are (cm^3 molecule^{-1} s^{-1}) $(0.70 \pm 0.20) \times 10^{-12}$, $(0.64 \pm 0.08) \times 10^{-12}$, $(0.57 \pm 0.10) \times 10^{-12}$, $(9.7 \pm 1.6) \times 10^{-12}$, and $(0.66 \pm 0.09) \times 10^{-12}$, respectively. The proposed Arrhenius expressions for the studied reactions are (in units of cm^3 molecule^{-1} s^{-1}) $k_1 = (52 \pm 49) \times 10^{-12} \exp[-(1329 \pm 330)/T]$, $k_2 = (7.3 \pm 1.9) \times 10^{-12} \exp[-(707 \pm 188)/T]$, $k_3 = (1.9 \pm 0.02) \times 10^{-12} \exp[-(368 \pm 16)/T]$, $k_4 = (1.0 \pm 0.3) \times 10^{-12} \exp[(675 \pm 96)/T]$, and $k_5 = (18.2 \pm 8.3) \times 10^{-12} \exp[-(1000 \pm 182)/T]$, respectively. The influence of substitution in the double bond and the ring size effect in unsubstituted cyclic monoalkenes has been investigated for the reactivity of the NO_3 radical reactions. The rate coefficients and the activation energies for the reaction of the nitrate radical with methylenecyclohexane and 1-methylcyclohexene have also been compared with the corresponding values of some selected terpenes with similar structure to these compounds.

Introduction

Much effort has been expended in studies of NO_3 radical chemistry. The emphasis has been placed on investigating reaction rates and products of various organic and inorganic compounds to understand the behavior of this reactive radical in the atmosphere. An impressive amount of kinetic data is available,[1−6] and it is also possible to predict, with some degree of certainty, the products from a specific reaction.[1,2,6]

In the last years the investigations about the NO_3 chemistry have been dedicated to the study of the reactivity of NO_3 with natural organic compounds. The impact of naturally emitted hydrocarbons in the atmosphere is not yet well-known and so it is not often considered in most urban air quality strategies, which tend to focus solely on the effects of anthropogenic hydrocarbons. However, since biogenic emissions are quantitatively important, they represent a significant source of reactive organic compounds due to their fast reactions with the tropospheric oxidants, O_3, OH, and NO_3 and, in this way, they probably contribute significantly to regional-scale air pollution.[7] Monoterpenes constitute about one-tenth of the total global amount of naturally emitted volatile nonmethane organic compounds (825−1150 TgCyr^{-1}).[8,9]

Since the NO_3 radical is found in the night-time troposphere in concentrations higher than 8×10^7 molecules cm^{-3} and its reactions with terpenes are fast, it seems that nitrate radical may dominate the chemistry of such volatile biogenic compounds under dark conditions.[1,2,5,6]

Despite the numerous kinetic and product studies of NO_3 radical gas-phase reactions with organic compounds and the importance of these reactions in the chemistry of the lower troposphere, to date the night-time reactions of NO_3 radical with monoterpenes has been the subject of only a few laboratory studies.[3,6,10−20] The majority of these studies have measured kinetic rate constants, and only a few works have investigated the reaction products and have proposed reaction mechanisms;[21−23] since the structure of terpenes is fairly complicated, they show a high reactivity and secondary chemistry involving aerosol formation takes place.

To facilitate the study of NO_3 reactions with compounds of unknown reactivity, Atkinson et al.[24] suggest that the rate constant of such reactions in the gas phase may be derived from the rate coefficients of the nitrate radical reaction with a smaller compound of a similar structure. In this sense, Ljungström et al.[25] have compared the reactivity of 1-methylcyclohexene with terpenes and Kind et al.[26] use simple model compounds containing the same reactive structural element as the terpenes.

In the same way, this study may contribute to the understanding of the reactivity of NO_3 with monoterpenes by comparing the reactivity of NO_3 and smaller model compounds, cyclic simple alkenes, which have a structural element in common with the terpenes. So, the 1-methyl-substituted hexene ring (that appears in compounds such as α-pinene, 2-carene, and limonene) and the methylene-substituted hexane ring (in compounds as β-pinene, camphene and sabinene) should be compared with 1-methylcyclohexene and methylenecyclohexane, respectively.

So, the aim of this work is to investigate the reaction of the nitrate radical with cyclic alkenes (cyclopentene, cyclohexene, cycloheptene, 1-methylcyclohexene, and methylenecyclohexane), some of them present in polluted atmospheres (cyclopentene, cyclohexene, from vehicles tailpipe exhaust) in order to find the room-temperature kinetic constants and to describe their behavior at different temperatures. The temperature dependence of NO_3 radical reactions with cyclopentene, cycloheptene, and methylenecyclohexane are reported for the first time. The temperature dependence of the reactions of NO_3 with cyclohexene and 1-methylenecyclohexane has been reinvestigated as only aproximate estimations were available.[25] So this work tries to contribute to a better understanding of the reactivity of NO_3 and alkenes.

---

* To whom correspondence should be addressed. E-mail: emartine@qifi-cr.uclm.es.

10.1021/jp9847181 CCC: $18.00

The studied reactions are as follows:

$$\text{cyclopentene} + NO_3 \rightarrow \text{products} \qquad (1)$$

$$\text{cyclohexene} + NO_3 \rightarrow \text{products} \qquad (2)$$

$$\text{cycloheptene} + NO_3 \rightarrow \text{products} \qquad (3)$$

$$\text{1-methylcyclohexene} + NO_3 \rightarrow \text{products} \qquad (4)$$

$$\text{methylenecyclohexane} + NO_3 \rightarrow \text{products} \qquad (5)$$

The experiments were carried out with an absolute technique in a fast flow tube reactor by detection of the nitrate radical by laser induced fluorescence, LIF, over a range of temperature from 298 to 435 K.

Experimental Section

All the kinetic measurements of absolute rate constants were carried out using a discharge-flow tube reactor with LIF detection for the nitrate radical. The experimental set up has been described elsewhere,[4,5] and only the relevant details are given here. All the experiments were carried out at a low pressure around 1 Torr. The flow tube was heated between room temperature and 435 K by an electronically regulated heating tape.

Nitrate radicals were generated by the reaction $F + HNO_3 \rightarrow NO_3 + HF$, and they were admitted to the flow tube through a fixed port. Fluorine atoms were obtained by passing F_2−He mixtures through a microwave discharge giving initial NO_3 concentrations in the range (0.6−10) × 10^{12} molecule cm^{-3}. The dissociation of F_2 into F atoms was close to 100%, and a massive excess of HNO_3 ($[HNO_3] > 50[F]$) was inmediately added to remove all the atomic fluorine. Under our experimental conditions, the reactor being coated with halocarbon wax, the wall loss of the nitrate radical was found negligible, with a $k_w < 0.1\ s^{-1}$.

Quantitative detection of NO_3 was carried out by monitoring the fluorescence emitted after exciting the (0−0) $2E' \leftarrow {}^2A'_2$ transition of NO_3 pumping with $\lambda = 662.0$ nm radiation from a dye laser (Scanmate 2C, Lambda Physik). Absolute concentrations of NO_3 were determined before or after each kinetic run by chemical titration with known amounts of tetramethylethene (TME);[27] the detection limit for the NO_3 concentration in our LIF detection system is around 10^{10} molecule cm^{-3}.

The coreactants were introduced through a sliding injector, whose position could be varied up to 70 cm from the center of the observation region. The concentrations of the studied cyclic alkenes, ranging from 1 to 50 × 10^{12} molecule cm^{-3}, were measured by the drop in pressure in relation with time on delivery from their calibrated volume storage bulbs. Contact times between NO_3 and the reactant were in the range 0−130 ms.

Materials

Helium was used as carrier gas, giving the physical properties of the mixture inside the reactor. Its purity (better than 99.999%, Carburos Metálicos C50) was improved by means of an Oxisorb (Messer Griesheim) trap and a molecular-sieve trap at room temperature.

The sources of the organic chemicals employed and their stated purities were as follows: cyclopentene (96%, Aldrich); cyclohexene (95%, Aldrich); cycloheptene (97%, Aldrich); 1-methylcyclohexexe (97%, Aldrich); methylenecyclohexane (98%, Aldrich).

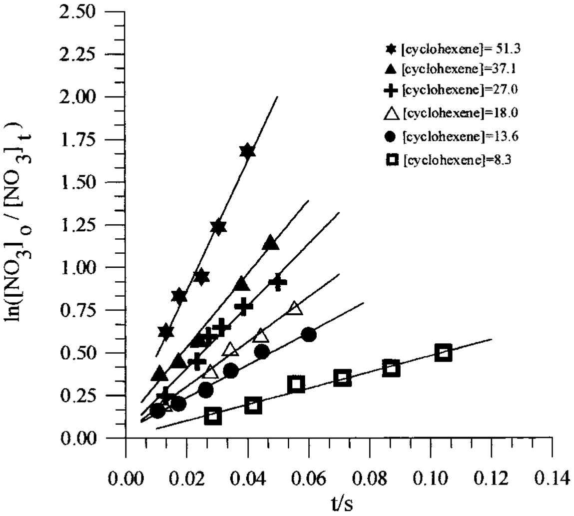


Figure 1. Example of pseudo-primer order plots for the reactions of NO_3 with cyclohexene at 298 K, using eq I.

All the cyclic alkenes were purified by successive trap-to-trap distillations. Nitric acid vapor was obtained by bubbling He through 2:1 concentrated sulfuric−nitric acid mixtures (P. A. quality, Panreac) at 252 K. Molecular fluorine was supplied by Union Carbide mixed with helium (5% F_2, 95% He).

Results

The experiments for cyclohexene, cyclopentene, and methylenecyclohexane were performed under pseudo-first-order conditions, with a large excess of reactant over NO_3. So for the analysis of the experimental results of the reactions of these compounds with NO_3, the integrated rate expression was[28]

$$\ln([NO_3]_o/[NO_3]_t) = k't \qquad \text{where} \qquad k' = k[\text{cyclic alkene}] \qquad (I)$$

Figure 1 shows the pseudo-first-order loss of NO_3 vs time, based on eq I, for the NO_3 radical−cyclohexene reaction at 298 K for different concentrations of cyclohexene. The slope of this plot yields the pseudo-first-order rate constant k', according to eq I. Figure 2 shows the values of k' vs [cyclic alkene] for the reaction of the NO_3 radical with cyclohexene; at room-temperature k, the second-order rate constants are obtained from the slope of such a straight line, according to the expression (I).

Due to the low vapor pressure of cycloheptene and to the high reactivity of 1-methylcyclohexene, the experiments on these compounds were carried out without a large excess of reactant over NO_3. The ratio [cyclic alkene]/[NO_3] was only varied between 1 and 4, so the data for the reaction of NO_3 with cycloheptene and 1-methylcyclohexene were analyzed using the second-order integrated rate expression, assuming a 1:1 stoicheiometry, eq II:[28]

$$\ln\frac{(M - X_a)}{(M(1 - X_a)} = (B_o - A_o)kT \qquad (II)$$

where $M = [\text{reactant}]_o/[NO_3]_o$, $B_o = [\text{reactant}]_o$, $A_o = [NO_3]_o$, and

$$X_a = \frac{[NO_3]_o - [NO_3]_t}{[NO_3]_o} \qquad (III)$$

Plots of $1/(B_0 - A_0)\ln[(M - X_a)/M(1 - X_a)]$ vs t, according to

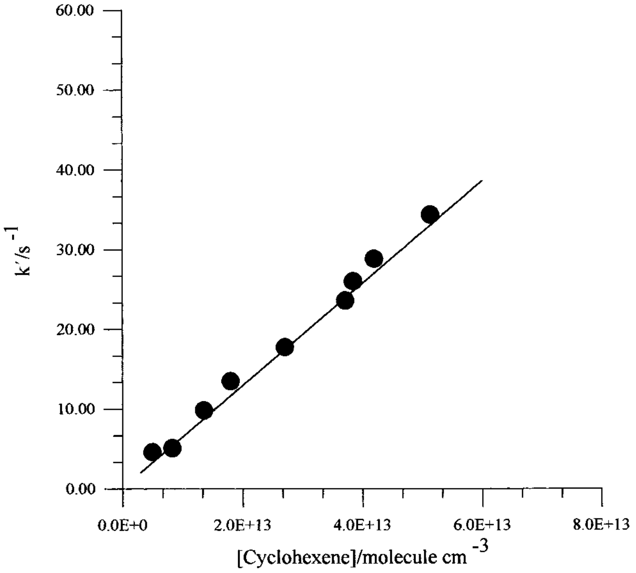


Figure 2. Second-order plot for the reaction of NO_3 with cyclohexene at room temperature. [cyclic alkene] in units of 10^{12} molecule cm^{-3}.

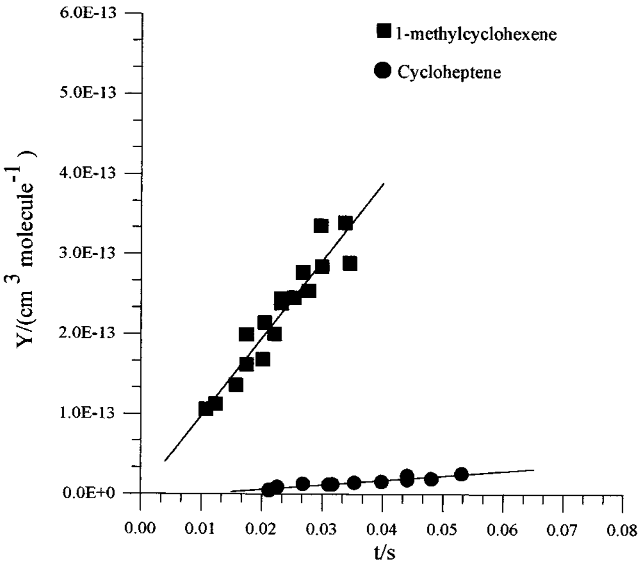


Figure 3. Plots of the data according to eq II for the reactions of NO_3 with 1-methylcyclohexene and cycloheptene at room temperature.

$$Y = \frac{1}{[[\text{cycloalkene}] - [NO_3]_0]} \ln\left[\frac{(M - X_a)}{(M(1 - X_a))}\right]$$

eq II yield the bimolecular rate constants k_3 and k_5 for the reactions 3 and 5, respectively. Figure 3 shows plots of $1/(B_0 - A_0)\ \ln[(M - X_a)/M(1 - X_a)]$ vs t for the reaction of the nitrate radical with 1-methylcyclohexene and cycloheptene at room temperature.

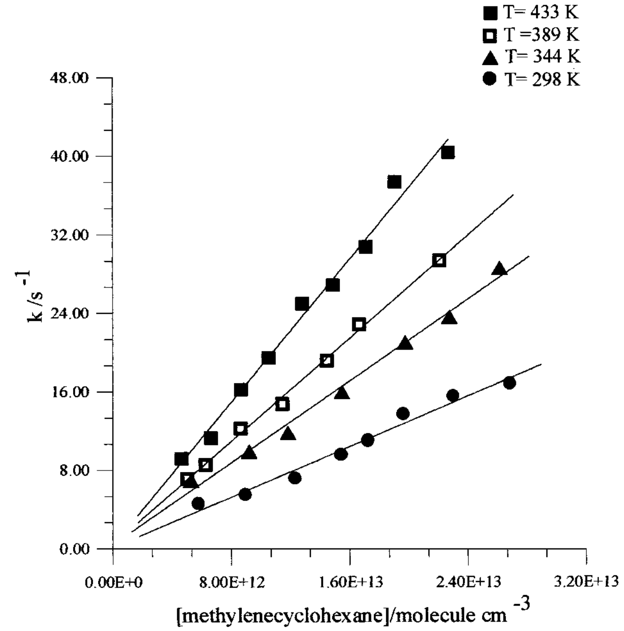


Figure 4. Second-order plots for the reactions of NO_3 with methylenecyclohexane at different temperatures.

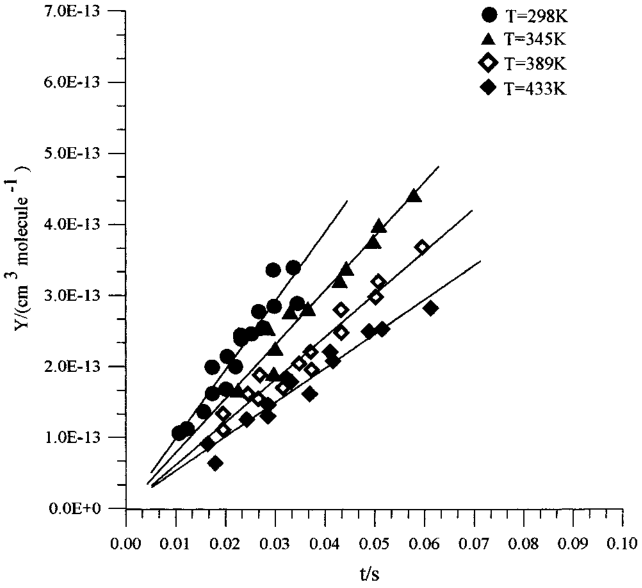


Figure 5. Evaluation of the rate coefficients from the experiments of NO_3 with 1-methylcyclohexene at different temperatures obtained using eq II.

$$Y = \frac{1}{[[\text{cycloalkene}] - [NO_3]_0]} \ln\left[\frac{(M - X_a)}{(M(1 - X_a))}\right]$$

For the experiments carried out at high temperature, direct measurements of the temperature inside the flow tube showed that it dropped rapidly at approximately 7 cm upstream from the detection cell. The temperature profiles as a function of distance from the cell were obtained as reported by Canosa-Mas et al.[29] and have been described previously.[4] The rate constants at elevated temperatures were calculated assuming that the entire flow tube was at the same elevated temperature and the cell was at room temperature. Thus the standard pseudo-first- (eq I) and second-order (eq II) equations have been applied separately to both regions at different temperatures. For the pseudo-first-order conditions, Figure 4 shows the plot of k' vs time for the reaction of NO_3 with methylenecyclohexane at different temperatures, and in Figure 5 the second-order plots of $1/(B_0 - A_0)\ \ln[(M - X_a)/M(1 - X_a)]$ vs t for the reactions of nitrate radical with 1-methylcyclohexene at different temperatures are shown. In both cases, t now means the contact time in the flow tube zone at high temperature. Airds et al.[30] have shown that this method leads to good results in systems with a similar temperature profile in the flow tube. Furthermore, in these reactions, as the variation of the kinetic rate constants with temperature is very small, the errors are minimized though the assumption of a sharp drop of temperature between the two zones is considered.

As will be shown in the Discussion, our results are in good agreement with those of other authors who reported data at room

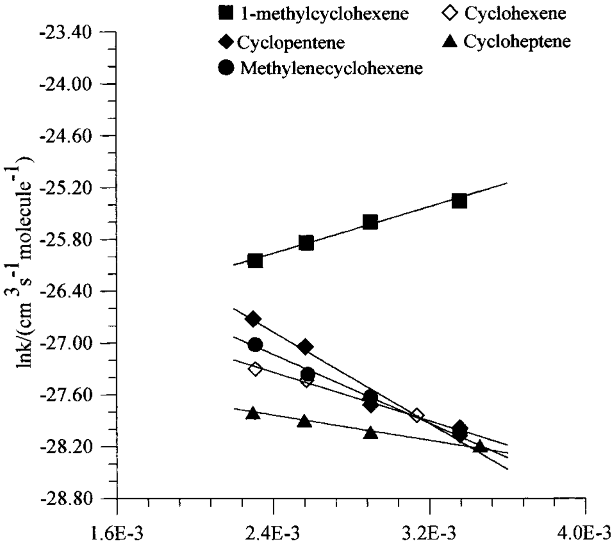


Figure 6. Arrhenius plots for the reactions of NO_3 with cyclic alkenes.

temperature obtained by the relative technique. This fact together with the absence of curvature in the plots of the data, Figures 1−5, including the data at large times, shows that secondary chemistry is not contributing to the measurement of primary rate constants. Nevertheleses some additional tests have been done. A kinetics model, FACSIMILE,[31] including NO_3 reactions with the product of the NO_3 addition to the cyclo alkenes, has been simulated with both constants as adjustable parameters. The best fits of the NO_3 experimental data were obtained when the weight of the second reaction was minimized, thus confirming a negligable effect of the secondary chemistry.

The data for reactions 1−5 are shown in Figure 6 in the form of Arrhenius plots, where ln k have been plotted vs $1/T$. A linear least-squares analysis of the data yields the activation energy and the preexponential factor. The rate constants at different temperatures for the reactions 1−5 with the corresponding activation energy and preexponential factor are summarized in Table 1.

According to these experimental results, the following expressions for the temperature dependence of the rate constants have been found:

$$k_1 = (51 \pm 49) \times 10^{-12} \exp[-(1329 \pm 330)/T] \quad (\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) \qquad \text{(IV)}$$

$$k_2 = (7.3 \pm 1.9) \times 10^{-12} \exp[-(707 \pm 188)/T] \quad (\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) \qquad \text{(V)}$$

$$k_3 = (1.9 \pm 0.1) \times 10^{-12} \exp[-(368 \pm 16)/T] \quad (\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) \qquad \text{(VI)}$$

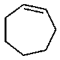
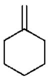
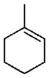
$$k_4 = (1.0 \pm 0.3) \times 10^{-12} \exp[(675 \pm 96)/T] \quad (\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) \qquad \text{(VII)}$$

$$k_5 = (18.2 \pm 8.3) \times 10^{-12} \exp[-(1000 \pm 182)/T] \quad (\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) \qquad \text{(VIII)}$$

Discussion

As can be seen in Table 1, the values of the rate coefficients for the studied reactions 1−5 are in the range of (0.5−10) × 10^{-12} $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. These values are in accordance with the rate constants found for the reactions of NO_3 with alkenes ($k = 2 \times 10^{-16}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$, for the reaction of this radical with ethene, to $k = 5.7 \times 10^{-11}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$, for its reaction with 2,3-dimethyl-2-butene, a substituted alkene).

TABLE 1: Arrhenius Parameters and Rate Constants k_2, for the Reactions of NO_3 with the Cycloalkenes at Different Temperatures[a]

T/K	$k_2/10^{-13}$ cm^3 molecule^{-1} s^{-1}	[reactant]/10^{12} molecule cm^{-3}	E_a/kJ mol^{-1}	$A/10^{-12}$ molecule^{-1} cm^3 s^{-1}	structure
		Cyclopentene			
298	7.0 ± 2	7−30			
345	9.2 ± 1.2	5−25	11.1 ± 2.7	52 ± 49	
390	18.0 ± 4.8	4−20			
435	24.9 ± 5.6	4−20			
		Cyclohexene			
298	6.4 ± 0.8	5−50			
319	8.1 ± 0.7	6.6−22			
344	9.8 ± 1.4	6.5−18	5.8 ± 1.5	7.3 ± 2.0	
389	12.2 ± 1.7	5−18			
433	14.0 ± 1.0	4−22			
		Cycloheptene			
298	5.7 ± 1.0	16−27			
345	6.7 ± 1.0	13−21	3.1 ± 0.1	2.0 ± 0.1	
391	7.6 ± 1.0	17−25			
435	8.4 ± 0.6	16−23			
		Methylenecyclohexane			
298	6.6 ± 0.9	4−28			
344	10.0 ± 1.2	4−28	8.3 ± 1.5	18.2 ± 8.3	
388	13.0 ± 0.8	5−24			
433	18.4 ± 1.0	4−24			
		1-Methylcyclohexene			
298	97 ± 16	1−8.5			
345	76 ± 10	3−8	−5.6 ± 0.8	1.0 ± 0.3	
388	60 ± 8	3−6.5			
433	48 ± 6	4−7.3			

[a] $[NO_3] = (0.6−10) \times 10^{12}$ molecule cm^{-3}, [cyclicalkene] = $(1−50) \times 10^{12}$ molecule cm^{-3}. Pt = 1−1.2 Torr, v = 4.7 m/s, t = 0.010 07 s. Error quoted = 2σ.

TABLE 2: Comparison of the Room Temperature Rate Constants for Reactions 1−5

cyclic alkene	k_{NO_3}/ 10^{-12} cm^3 molecule^{-1} s^{-1}	technique[a]	ref
cyclopentene	0.7	A-LIF	this work
	0.53	RR	Atkinson[3]
	0.59	A-AB	Ljungström et al.[25]
	0.38	RR	Kind et al.[26]
cyclohexene	0.64	A-LIF	this work
	0.59	RR	Atkinson[3]
	0.63	A-AB	Ljungström et al.[25]
	0.49	RR	Kind et al.[26]
cycloheptene	0.57	A-LIF	this work
	0.48	RR	Atkinson[3]
	0.54	RR	Kind et al.[26]
methylenecyclohexane	0.66	A-LIF	this work
	0.53	RR	Kind et al.[26]
1-methylcyclohexene	9.7	A-LIF	this work
	15	A-AB	Ljungström et al.[25]
	10.3	RR	Kind et al.[26]

[a] Key for technique: A = absolute rate, AB = absortion, LIF = laser−induced fluorescence, RR = relative rate.

The measured rate coefficients at room temperature for the reactions of NO_3 with cyclopentene, cyclohexene, cycloheptene, methylenecyclohexene, and 1-methylcyclohexane are shown in Table 2 and compared to those of other workers, measured by relative and absolute techniques. Generally, a good agreement between the data is found. Only in the study of Kind et al.[26] do the rate coefficients for the reactions of cyclopentene and cyclohexene show significant deviations. For these two cyclic alkenes the absolute rate coefficients measured in our work are slightly higher than those reported previously by Kind et al.,[26] obtained by relative methods, while our values for the reactions of the NO_3 radical with cyclopentene and cyclohexene are similar, within the experimental error, to the relative values proposed by Atkinson[24] and with the rate coefficients determined by Ljungström[25] by an absolute technique. However, the absolute rate constant reported in this work for the reaction of NO_3 radical with 1-methylcyclohexene is lower than the relative value obtained by Atkinson et al.[24]

The measured rate coefficients obtained in the present work for cyclopentene, cyclohexene, and cycloheptene are, as expected, quite similar, 7.0×10^{-13}, 6.4×10^{-13}, and 5.7×10^{-13} cm^3 $molecule^{-1}$ s^{-1} respectively, since the active structural element, a cis configurated double bond conected to the CH_2 groups, is the same in all of them because the virtually strain-free ring systems are almost invariant with ring size in these compounds.

The results for the methylenecyclohexane−NO_3 reaction give a rate coefficient of 6.4×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, at 298 K; this value is quite similar to that obtained for the reaction of the NO_3 radical with cyclohexene. The same is not observed for the reaction of NO_3 with methylenecyclopentane and methylenecycloheptane with respect to the reaction of the NO_3 radical with cyclopentene and cycloheptene, respectively.[26]

As has been discussed for the gas-phase reactions of alkenes and cycloalkenes with the OH[4,32] and NO_3 radicals,[1,4,5,19,25,26,33,34] the room-temperature rate constants for the alkenes and the unstrained cycloalkenes depend in a first approximation on the number and configuration of alkyl subtituents around the carbon−carbon double bond. Thus the rate constants for the reaction of NO_3 with 1-methylcyclohexene (9.70×10^{-12} cm^3 $molecule^{-1}$ s^{-1}), which has one substituent on the double bond, are higher than those compounds without a substituent around the double bond, e.g., cyclohexene 0.64×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, and as expected, the cyclic alkenes are more reactive toward NO_3 than the corresponding 1-alkenes.[1,3,33]

Not much data about the dependence of the rate constant with temperature have been reported for the reaction of NO_3 with cycloalkenes. Ljungström et al.[26] have studied the dependence with temperature in the reactions of NO_3 and cyclopentene and 1-methylcyclohexene, but they could only provide an approximation to the real value, given the high uncertainty of the reported data. However, no previous study has been made for the reaction of NO_3 with cyclopentene, cycloheptene, and methylenecyclohexane, and thus this study is the first work on the temperature dependence of reactions 1, 3, and 5. The activation energies obtained in this work for the reaction of NO_3 with cyclohexene and with 1-methylcyclohexene (5.8 ± 1.5 and -5.6 ± 0.8 kJ mol^{-1}) apparently show a significant deviation from those calculated by Ljungström et al.[25] (1 ± 4 and 0 ± 5 kJ mol^{-1}, respectively), but considering the high error limits in their work, the values could be considered to be in agreement.

Kinetic studies and product data for the reactions of NO_3 with alkenes show that the initial step proceeds predominantly via electrophilic addition of the NO_3 radical to the double bond. The values of the rate constant at room temperature for reactions 1−5, ranging from 0.57×10^{-12} to 9.7×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for cycloheptene and 1-methylcyclohexene, respectively, and the relatively low, or slightly negative activation energies found, agree with the values obtained for the reaction of NO_3 with alkenes[1−6,33,34,35] and are entirely consistent with a radical addition process.

Atkinson et al.[24] have proposed a method to predict the reactivity of a complex compound toward a radical, starting from the rate coefficient of the reaction of the radical with a simple compound that has structural similarities to the more complex one. Taking this idea into consideration and as the terpenes have similarities in their structure to cyclic alkenes, we could use the rate constants of the reactions of cyclic alkenes with the NO_3 radical to predict the reactivity of more complicated substances, the terpenes, toward such a radical. Thus the rate constants and the activation energies obtained in this work for the reaction of NO_3 radical with 1-methylcyclohexene and methylenecyclohexane have been compared with the corresponding rate coefficients and energies of some selected terpenes of similar structure.

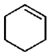
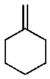
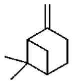
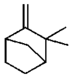
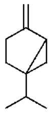
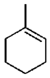
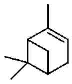
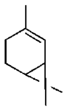
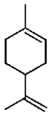
The 1-methyl-substituted hexene ring structure is found in, e.g., α-pinene, 2-carene, and limonene. Dlugokencky et al.[10] and Martinez et al.[12,13] have measured absolute rate coefficients for the reaction of NO_3 with α-pinene over the range 261−422 K. Both studies agree in the value of the rate constant and in the negative energy of activation found. Martinez et al.[13] have measured the absolute rate coefficients for the reaction of NO_3 with 2-carene and limonene over the temperature range 298−433 K, and negative activation energies were also found. In the present work the activation energy reported for the reaction of NO_3 with 1-methylcyclohexene is -5.6 ± 0.8 kJ mol^{-1}, which agrees with the results obtained for these terpenes.

The methylenecyclohexane may also be compared with methylene-substituted cyclohexane ring structures, β-pinene, camphene, or sabinene. Martinez et al.[13] measured the absolute rate coefficient for the reaction of NO_3 with these terpenes over the temperature range 298−433 K, and the calculated activation energies (10.7 ± 0.7, 4 ± 0.5, and 7.8 ± 1.6 kJ mol^{-1}) are in agreement with the value of activation energy obtained for methylenecyclohexane (8.3 ± 1.5 kJ mol^{-1}). Table 3 gives the rate coefficients at room temperature and the activation energies for the reaction of NO_3 with different cycloalkenes and terpenes. It can be seen that when the organic has a 1-methyl cycloalkene stucture, the activation energy is negative and when the structure is that of methylenecycloalkane the activation energy is positive.

In Table 3, we can also see that the rate coefficient for the reactions of the NO_3 radical with compounds with methylenecycloalkane structure (methylenecyclohexane, β-pinene, and camphene) are smaller than the rate constants for the reactions of NO_3 with methyl-substituted endocyclic double bond compounds (1-methylcyclohexene, α-pinene, and 2-carene) with the exception of sabinene. For sabinene an unexpectedly high value, at the same order as the rate constants for compounds with a methylenecycloalkane structure, has been found. However, it shows a positive activation energy, like the other compounds with methylcycloalkene structure. In the same sense, Kind et al.[26] reported a very high reactivity of methylenecyclopentane toward NO_3. The presence of a three-bond ring close to the double bond in the sabinene structure may induce a more rigid global system that could destabilize the double bond, making it more reactive. The same could be argued in the case of 2-carene also with a cyclopropane ring close to the double bonds and a higher reactivity than α-pinene or limonene.

In conclusion, all these experimental facts show a different reactivity for the reactions of NO_3 with cyclic compounds with an exocyclic double bond than for cycloalkenes 1-methyl substituted, which is probably due to the degree of substitution since the size of five, six, or seven member rings has no effect

TABLE 3: k_2 and E_a for the Reaction of NO_3 and Cyclic Alkenes and Some Monoterpenes

compound	structure	$k_2/10^{-12}$ cm^3 molecule^{-1} s^{-1}	E_a/kJ mol^{-1}
cyclohexene		0.64 ± 0.08^a	5.8 ± 1.5^a
methylenecyclohexane		0.66 ± 0.09^a	8.3 ± 1.5^a
β-pinene		2.10 ± 0.40^b	10.7 ± 0.3^b
camphene		0.62 ± 0.21^b	4.0 ± 0.5^a
sabinene		10.70 ± 1.60^b	7.8 ± 1.6^b
1-methylcyclohexene		9.70 ± 1.60^a	-5.6 ± 0.8^a
α-pinene		5.90 ± 0.80^b	-7.0 ± 1.2^b
2-carene		16.60 ± 1.80^b	-6.2 ± 1.5^b
limonene		9.40 ± 0.90^b	-3.9^b

[a] From this work. [b] From refs 4 and 5.

on the reactivity. As has been shown before, these results may be used in the prediction of the reactivity of compounds with similar structures.

It is known[4,5,36] that the reactivity of NO_3 toward alkenes, halogenoalkenes, and some monoterpenes depends on the ionization potential of the organic compound, E_i. According to Koopman's theorem E_i is equal in magnitude and opposite in sign to the HOMO (highest occupied molecular orbital) energy, E_{HOMO}. A good correlation has been found between the rate constant at room temperature and the ionization potential of the reactant, for the NO_3 reactions, and it is expressed by the following relationship:[4]

$$-\log(k/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = 3.27E_i/\text{eV} - 19.38 \qquad \text{(IX)}$$

In the present work the energies of ionization, E_i, have been obtained for cyclopentene (−9.53 eV), cyclohexene (−9.59 eV), cycloheptene (−9.61 eV), methylenecyclohexane (−9.82 eV), and 1-methylcyclohexene (−9.33 eV) by means of semiempirical calculations carried out with the AMPAC 5.0 packge[37] and PM3 parametrization.[38]

The measured kinetic rate constants at room temperature for the reactions of the nitrate radical with a series of compounds with an endocyclic double bond with or without substituents, 1-methylcyclohexene, cyclopentene, cyclohexene, and cycloheptene obtained in this work together with the values of α-pinene, 2-carene, and limonene calculated by Martinez et al.[12,13] fit quite well correlation (IX), as can be seen in Figure 7. However, the rate coefficients at room temperature for the reaction of NO_3 with compounds with methylenecycloalkane structure (the methylenecyclohexane data obtained in this work and the data of the reactions of NO_3 with β-pinene, camphene, and sabinene obtained by Martinez et al.[12,13]) deviates slightly from the previous correlation equation (IX).

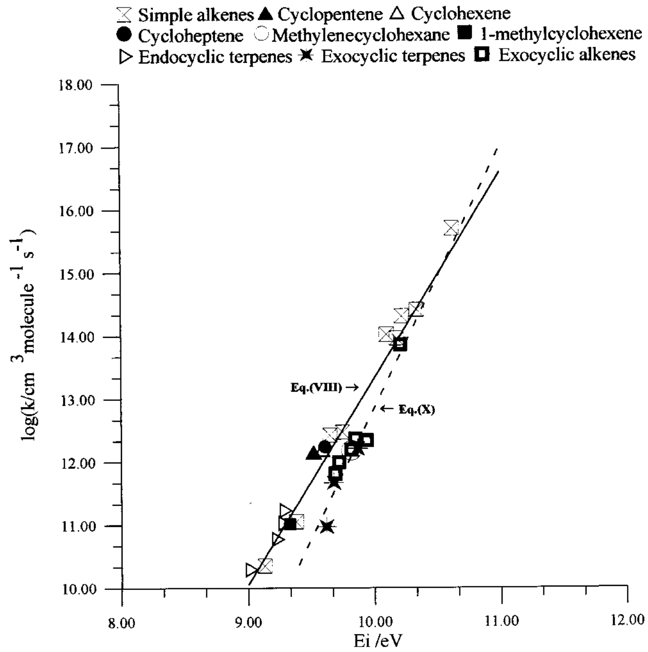


Figure 7. Logarithm of the room-temperature rate constant for the reactions of NO_3 with alkenes cycloalkenes and terpenes plotted as a function of the ionization potential of the organic reactant. See text.

In a recent study,[26] Kind et al. have obtained a different correlation applicable only to substances with an exocyclic double bond:

$$-\log(\text{k/cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = 3.905E_i/\text{eV} - 26.13 \qquad \text{(X)}$$

So, this is another fact showing that all the cyclic alkenes and monoterpenes with a subtituent in the carbon−carbon double bond present a different behavior than those cyclic alkenes and monoterpenes with methylenecycloalkane structure. Correlation (X) may be improved by including the data reported by Martinez et al.,[12,13] for β-pinene, camphene, and sabinene and the data reported here for methylcyclohexene. Use of the wider database results in a better correlation equation (XI), as may be seen also in Figure 7.

$$-\log(k/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = 4.14E_i/\text{eV} - 28.55 \qquad \text{(XI)}$$

The rate constants at room temperature for the gas-phase reactions of the cyclic alkenes studied here with NO_3 can be combined with the average tropospheric concentration of this radical species[39] to estimate the tropospheric lifetimes of these compounds.

The lifetimes for the disappearance of these cyclic alkenes with respect to the NO_3 reaction at night have been found to be around 2.5 h, with the exception of 1-methylcyclohexene, which is 0.2 h. These lifetimes are similar to those calculated[3] with respect to the O_3 reactions (using a 24-h average concentration for O_3), which are about 3 h and slightly larger than the daily lifetimes of about 1 h obtained taking into account the OH radical reactions (averaging its concentration during the daytime). Provided[39] that, at night, the OH and the O_3 concentrations are substantially lower than their corresponding averaged concentration used to calculate the corresponding lifetimes, it can be concluded that the night-time reaction with the NO_3

radical is an important loss process for these cycloalkenes in the atmosphere.

References and Notes

(1) Wayne, R. P.; Barnes, I.; Biggs, P.; Burrows, J. P.; Canosa-Mas, C. E.; Hjorth, J.; LeBras, G.; Moortgat, G. K.; Perner, D.; Poulet, G.; Restelli, G.; Sidebottom, H. *Atmos. Environ., Part A* **1991**, *25*, 1.

(2) Atkinson, R. J. *J. Phys. Chem. Ref. Data*. **1991**.

(3) Atkinson, R. *J. Phys. Chem. Ref. Data Monogr. 2* **1994**.

(4) Cabañas, B.; Marston, G.; Wayne, R. P. *J. Chem. Soc., Faraday Trans*. **1995**, *91*, 1185.

(5) Martinez, E.; Cabañas, B.; Aranda, A.; Wayne, R. P. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 53.

(6) Atkinson, R. *J. Phys. Chem. Ref. Data*. **1997**, *26*, 215.

(7) Calogirou, A.; Larsen, B.; Brussal, C.; Duane, M.; Kotzias, D. *Anal. Chem*. **1996**, *68*, 1499.

(8) Fehsenfeld, F.; Calvert, J.; Fall, R.; Goldan, P.; Guenter, A.; Hewitt, C.; Lamb, B.; Liu, S.; Trainer, M.; Webster, H.; Zimmerman, P. *Global Biochem. Cycles* **1992**, *6*, 389.

(9) Guenther, A.; Hewitt, N. C.; Fall, R.; Geron, C.; Graedel, T.; Harley, P.; Klinger, L.; Lerdan, M.; McKay, N. A.; Pierce, T.; Schoeles, B.; Steinbrecher, R.; Tallamraju, R.; Taylor, J.; Zimmerman, P. *J. Geophys Res*. **1995**, *100*, 8873.

(10) Dlugockenky, E. J.; Howard, C. J. *J. Phys. Chem*. **1989**, *93*, 1091.

(11) Barnes, I.; Bastian, V.; Becker, K. H.; Tong, Z. *J. Phys. Chem.* **1990**, *94*, 2413.

(12) Martinez, E.; Cabañas, B.; Aranda, A.; Martin, P. *Environ. Sci. Technol.* **1998**, *32*, 3730.

(13) Martinez, E.; Cabañas, B.; Aranda, A.; Martin, P.; Salgado, S. *J. Atmos. Chem.*, in press.

(14) Atkinson, R.; Aschmann, S. M.; Arey, J. *Atmos. Environ*. **1990**, *24*, 2647.

(15) Corchnoy, S. B.; Atkinson, R. *Environ. Sci. Technol*. **1990**, *24*, 1497.

(16) Wille, U.; Becker, K. H.; Schindler, R. N.; Lancar, I. T.; Poulet, G.; Le Bras, G. *Atmos. Chem*. **1991**, *13*, 183.

(17) Skov, H.; Hjorth, J.; Loshe, C.; Jensen, N. R.; Restelli, G. *Atmos. Environ*. **1992**, *26*, 2771.

(18) Atkinson, R.; Aschmann, S. M.; Winer A. M.; Pitts, J. N., Jr. *J. Phys. Chem*. **1988,** *92*, 3454.

(19) Atkinson, R.; Aschmann, S. M.; Winer, A. M.; Pitts, J. N., Jr. *J. Phys. Chem*. **1988**, *92*, 3454.

(20) Atkinson, R.; Aschmann, S. M.; Winer, A. M.; Pitts, J. N., Jr. *Environ. Sci. Technol.* **1984**, *18*, 370.

(21) Wängberg, I.; Barnes, I.; Becker, K. *Environ. Sci. Technol*. **1997**, *31*, 2130.

(22) Mattias, H.; Wängber, I.; Ljungström, E. *Environ. Sci. Technol*. **1997**, *31*, 3166.

(23) Skov, H.; Hjorth, J.; Loshe, C.; Jensen, N. R.; Restelli, G. *Atmos. Environ*. **1992**, *26*, 2771.

(24) Atkinson, R.; Aschmann, S. M.; Winer, A. M.; Long, W. D. *Int. J. Chem. Kinet.* **1985**, *17*, 957,

(25) Ljungström, E.; Wängberg, I.; Langer, S. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 16.

(26) Kind, I.; Berndt, T.; Böge, O. *Chem. Phys. Lett.* **1998**, *288*, 111.

(27) Sander, S. P. *J. Phys. Chem*. **1986**, *90*, 4135.

(28) Laidler, J. K. *Chemical Kinetics*, 3rd ed.; Harper Collins Publisher. Inc.: New York, 1987.

(29) Canosa-Mas, C. E.; Smith, S.; Waygood, S.; Wayne R. P. *J. Chem. Soc., Faraday Trans. 2* **1991**, *87*, 3473.

(30) Airds, S.; Canosa-Mas, C.; Cook, D.; Marston, G.; Monks, P.; Wayne, R.; Ljungström. E. *J. Chem. Soc., Faraday Trans*. **1992**, *88*, 1093.

(31) Chance, E. M.; Curtis, A. R.; Jones, I. P.; Kirdy C. R. FACSIMILE. A computer program for flow and chemistry simulation, and general initial values problems. UKAEA, Harwell Report, AERE-R8775; 1987.

(32) Atkinson, R. *J. Phys. Chem. Ref. Data Monogr*. *1* **1989**.

(33) Martinez, E.; Cabañas, B.; Aranda, A.; Albaladejo, J.; Wayne, R. P. *J. Chem. Soc., Faraday Trans*. **1997**, *93*, 2043.

(34) Martinez, E.; Cabañas, B.; Aranda, A.; Martin, P.; Wayne, R. P. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 22, 4385.

(35) Atkinson, R.; Darnell, K. R.; Lloyd, A. C.; Winer, A. M.; Pitts, J. N. *Adv. Photochem*. **1979**, *11*, 375.

(36) Marston, G.; Monks, P. S.; Canosa-Mas, C. E.; Wayne, R. P. *J. Chem. Soc., Faraday. Trans.* **1993**, *89*, 38, 3899.

(37) AMPAC 5.0. Semichem, 7128 Summit, Shawnee, k56621; 1994.

(38) Stewart, J. J. *J. Comput. Chem*. **1989**, *10*, 209.

(39) Platt, U.; Heitntz, F. *Isr. J. Chem*. **1994**, *34*, 289.