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Kinetics of the Reactions of NO_3 Radical with Selected Monoterpenes: A Temperature Dependence Study

E. MARTÍNEZ,* B. CABAÑAS,
A. ARANDA, AND P. MARTÍN

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

Terpenes from biogenic sources in the atmosphere are emitted in amounts comparable to those of non-methane organic compounds from antropogenic sources. The aim of this work is to study the reactivity of the terpenes α-pinene, β-pinene, and camphene toward the NO_3 radical in order to evaluate the importance of these reactions in the atmosphere and their atmospheric impact. The experiments have been carried out under second-order kinetic conditions over the temperature range 298−433 K using a discharge flow system and monitoring the NO_3 radical by Laser Induced Fluorescence (LIF). The measured room-temperature rate constants for reaction of NO_3 with α-pinene, β-pinene, and camphene are (cm^3 $molecule^{-1}$ s^{-1}) $(5.9 \pm 0.8) \times 10^{-12}$, $(2.1 \pm 0.4) \times 10^{-12}$, and $(0.62 \pm 0.21) \times 10^{-12}$, respectively. The proposed Arrhenius expressions, for the three studied reactions, are $k_1 = (3.5 \pm 1.4) \times 10^{-13}\exp[(841 \pm 144/T)]$ (cm^3 $molecule^{-1}$ s^{-1}), $k_2 = (1.6 \pm 1.5) \times 10^{-10}\exp[(-1248 \pm 36/T)]$ (cm^3 $molecule^{-1}$ s^{-1}), and $k_3 = (3.1 \pm 0.5) \times 10^{-12}\exp[(-481 \pm 55/T)]$ (cm^3 $molecule^{-1}$ s^{-1}). A negative activation energy of 7.0 ± 1.0 kJ mol^{-1} has been found from the temperature dependence of the rate constant for the reaction of α-pinene with NO_3, and positive values of 10.4 ± 0.3 and 4.0 ± 0.5 kJ mol^{-1} have been determined for β-pinene and camphene, respectively. Tropospheric half-lives for these terpenes have been calculated at night and during the day for typical NO_3 and OH concentrations and show that both radicals provide an effective tropospheric sink for these compounds, and the nighttime reaction with NO_3 radical can be an important, if not dominant, loss process for these organics.

Introduction

Vegetation emits a large number of volatile organic hydrocarbons (VOCs), especially isoprene, terpenes, and oxygenated terpenoids. From data derived from a limited number of field investigations and enclosure studies of the global biogenics, VOC emissions have been estimated at a magnitude of 1150 Tg/year (*1*). This quantity significantly exceeds the estimates of antropogenic nonmethane hydrocarbon (NMHC) emissions, which are of the order of 100 Tg/year (*2*). For some time, terpenes and terpenoids have been recognized as potential sources of aerosols and carbon monoxide and as important precursors in photochemical oxidant (ozone) formation in urban and rural areas (*3*−*6*). From this it can be inferred that biogenic NMHC emissions contribute significantly to regional-scale air pollution (*7*).

The most important biogenic hydrocarbons released from various types of plants and trees are isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$). They are emitted by vegetation at the surface and transported to and destroyed in the atmosphere. Their surface concentrations are typically low during daytime and maximize at night (*8*−*10*). As for other unsaturated compounds, they react in the atmosphere with OH radicals, O_3, NO_3 radicals, and $O(^3P)$ atoms with their relative importance depending on atmospheric conditions. During the day the most important removal processes for terpenes are their reactions with OH radicals and with O_3, while reaction with NO_3 radicals in addition to O_3 can be a major sink at night. The high rate constants for the reactions of some organics with NO_3, taken in conjunction with the atmospheric concentrations of NO_3 which have been observed in the nighttime troposphere as high as 350 pptv, have led to the suggestion that reaction with NO_3 may dominate the nighttime chemistry of volatile biogenic organic compounds (*11*−*13*).

Despite numerous kinetic and product studies of NO_3 radical gas-phase reactions with organic compounds and the importance of these reactions in the nighttime chemistry of the lower troposphere, to date the reactions of NO_3 radicals with monoterpenes have been the subject of only a few laboratory studies (*14*−*23*), and the available rate constant data have not been critically evaluated (*12*). The aim of the present study was to investigate the reactions of NO_3 with atmospherically important monoterpenes, in a fast flow system using LIF detection of the NO_3 radical. The rate constants at different temperatures have been measured, and the Arrhenius parameters calculated for the reactions of NO_3 radical with α-pinene, β-pinene, and camphene, which allows the calculation of their tropospheric lifetimes.

$$\alpha\text{-pinene} + NO_3 \rightarrow \text{products} \quad (1)$$

$$\beta\text{-pinene} + NO_3 \rightarrow \text{products} \quad (2)$$

$$\text{camphene} + NO_3 \rightarrow \text{products} \quad (3)$$

The values of the rate constants obtained have been compared with the available literature data. For α-pinene our experimental results are in good agreement with those of Dlugokencky et al. (*15*) and with the relative rate data of Barnes et al. (*16*) and Atkinson (*21, 23*). The other terpenes, camphene and β-pinene, had been investigated only at room temperature and using relative rate techniques (*17*, *21*, *22*). The experimental results from this work are in accord with these data.

Experimental Section

All measurements of the absolute rate constants were carried out using a discharge-flow tube reactor with laser-induced fluorescence (LIF) detection for the nitrate radical. The details of the apparatus and experimental procedure have been described previously, (*24*) and hence only the relevant details are given here.

Nitrate radicals were generated by the reaction

$$F + HNO_3 \rightarrow NO_3 + HF \quad (4)$$

and they were admitted to the flow tube through a fixed port

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* Corresponding author phone: (9) 26/29 53 00 ext 3422; fax: (9) 26/29 53 18; e-mail: emartine@qifi-cr.uclm.es.

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injector. Fluorine atoms were obtained by passing F_2−He mixtures through a microwave discharge. 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 by pumping with $\lambda = 662.0$ nm radiation from a dye laser. The initial NO_3 concentrations were in the range 3.2 to 6×10^{12} molecule cm^{-3}. Absolute concentrations of NO_3 were determined before or after each kinetic run by chemical titration with a known amount of tetramethylethene (TME) in an analogous manner as that described by Smith (*25*).

The reactants were introduced through a sliding injector, the position of which could be varied from 10 to 70 cm from the center of the observation region. The concentration of terpenes varied from 3 to 20×10^{12} molecule cm^{-3}. Contact times between NO_3 and the reactant were in the range of 10−120 ms.

All the experiments were carried out at a total pressure of ca. 1 Torr. The flow tube was heated between room temperature and 433 K by electronically regulated heating tape.

Helium (Carburos Metálicos, C50) was passed through an oxygen-removing column (Oxisorb, Messer Griesheim) and through a trap containing a molecular sieve. Molecular fluorine (5% in He) was supplied by Union Carbide. Anhydrous gaseous HNO_3 in He carrier was prepared by bubbling He through a mixture of H_2SO_4−HNO_3 (P. A. Panreac).

The organic reactants, α-pinene (Aldrich, 98%) β-pinene (Aldrich, 99%), and camphene (Merck 95%), were purified by successive trap-to-trap distillations.

Results

Due to the low vapor pressure of the monoterpenes, the reactants are not present in our experiments in a large excess over NO_3. The concentration of the reactant was between 1 and 3 times the concentration of the NO_3 radical, and hence the experimental data have to be analyzed using the second-order integrated rate expression (*26*), assuming a 1:1 stoicheiometry, as shown in eq I. The high values of the rate constant for the reaction of NO_3 with terpenes ($k \approx 10^{-10}$−10^{-13} cm^3 molecule^{-1} s^{-1}) and alkenes of similar structure and other kinetic evidence given by different authors (*11*−*14, 27, 28*) support the assumption of stoichiometry 1:1

$$\ln\frac{(M - X_a)}{(M \times (1 - X_a))} = (B_0 - A_0)kt \qquad \text{(I)}$$

where $M = [\text{reactant}]_0/[NO_3]_0$, $B_0 = [\text{reactant}]_0$, $A_0 = [NO_3]_0$, and

$$\text{Xa} = \frac{[NO_3]_0 - [NO_3]_t}{[NO_3]_0} \qquad \text{(II)}$$

The range of temperature studied was 298−423 K for the reaction of NO_3 with α-pinene, 298−393 K for the reaction with β-pinene, and 298−433 K for the reaction with camphene. Plots of $1/(B_0 - A_0) \ln [(M - X_a)/M(1 - X_a)]$ vs t, according to eq I, yield the bimolecular rate constants k_1, k_2, and k_3 for the reactions 1, 2, and 3, respectively. Figure 1 shows typical data plotted in the form of eq I for the reaction of NO_3 with α-pinene, β-pinene, and camphene at room temperature. In Figure 2 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 camphene at two different temperatures are shown. The rate constants at elevated temperatures were calculated assuming that the entire flow tube was at the same temperature, and the detection cell was at room temperature. Thus, the standard second-order equations were applied separately to both regions at different temperatures. Airds et al. (*29*) have shown that this method leads to good results in system with temperature profile in the flow tube. Furthermore, in these reactions, as the variation of the kinetic rate constants with temperature is small, the errors are minimized although the assumption of a sharp drop in temperature between the two zones is considered. Direct measurements of the temperature inside the flow tube showed that it dropped rapidly at approximately 7 cm upstream from the detection cell (*24*). The temperature profiles as a function of distance from the cell were obtained by the method reported by Canosa-Mas et al. (*30*).

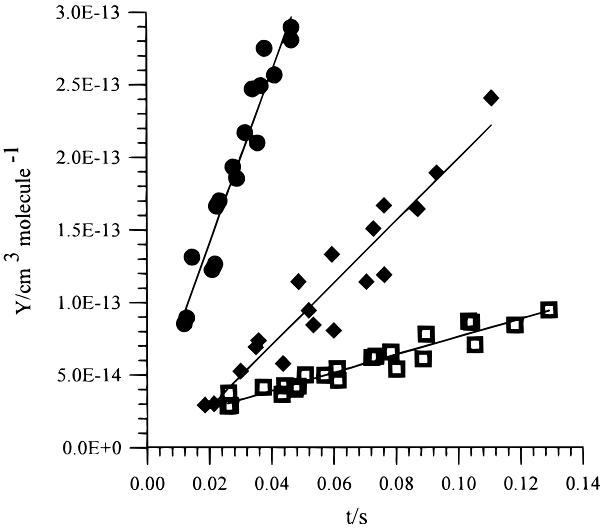


FIGURE 1. Plots of the data according to eq I for the reactions of NO_3 with ● α-pinene, ■ β-pinene, and □ camphene at room temperature. $Y = 1/(B_0 - A_0) \ln[(M - X_A)/M(1 - X_a)]$.

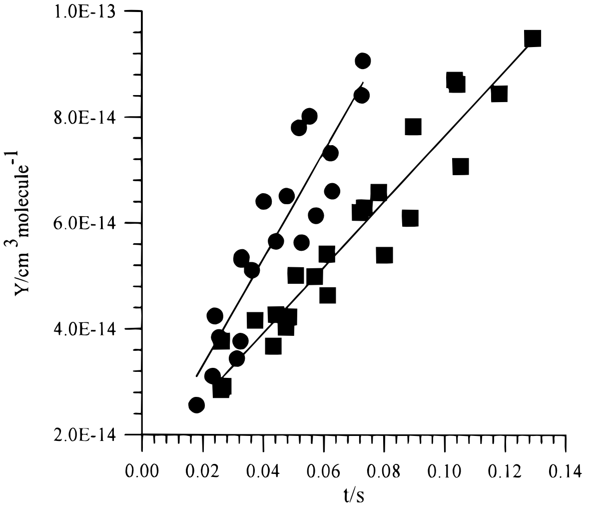


FIGURE 2. Plots of the data according to eq I for the reaction of NO_3 with camphene at different temperatures: ■ = 298 K, ● = 433 K. $Y = 1/(B_0 - A_0) \ln[(M - X_A)/M(1 - X_a)]$.

The data for reactions 1, 2, and 3 are shown plotted in Arrhenius form in Figure 3. A linear least-squares analysis of the data yields the activation energy and the preexponential factor. These results are also presented in Table 1.

According to these experimental results, we propose the expressions

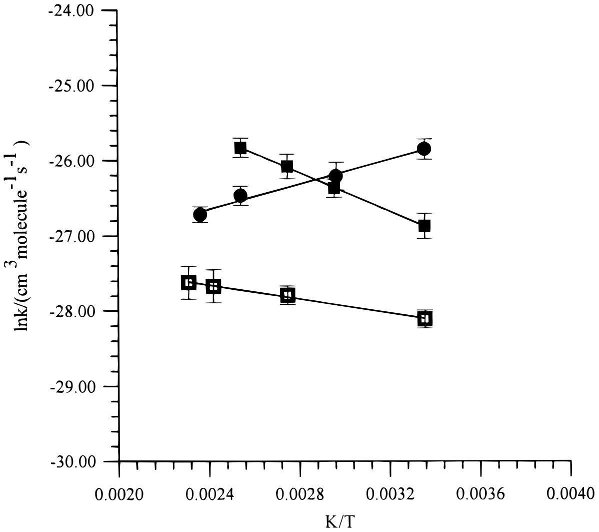


FIGURE 3. Arrhenius plots for the reactions of NO_3 with ● α-pinene, ■ β-pinene, and □ camphene.

TABLE 1. Summary of the Measured Rate Coefficients for the Reactions of NO_3 with Monoterpenes[a]

T/K	k/10^{-12} cm^3 molecule^{-1} s^{-1}	[reactant]/10^{12} molecule cm^{-3}	E_a/kJ mol^{-1}	A/10^{-10} molecule^{-1} cm^3 s^{-1}
		α-Pinene		
298	5.9 ± 0.8	4.1−9.4		
337	4.1 ± 0.7	6.9−10	−7.0 ± 1.0	(3.5 ± 1.4) × 10^{-3}
393	3.2 ± 0.4	4.0−9.3		
423	2.5 ± 0.7	4.4−12		
		β-Pinene		
298	2.1 ± 0.4	3.9−9.8		
339	3.5 ± 0.5	6.9−10		
364	4.7 ± 0.8	5.3−8.1	10.4 ± 0.3	1.6 ± 1.5
393	6.1 ± 0.8	3.8−11		
		Camphene		
298	0.62 ± 0.21	7.6−20		
364	0.85 ± 0.11	9.0−17	4.0 ± 0.5	(3.1 ± 0.5) × 10^{-2}
413	0.96 ± 0.21	5.7−16		
433	1.01 ± 0.22	7.1−16		

[a] $[NO_3] = (3.2{-}6.0) \times 10^{12}$ molecule cm^{-3}, $P_T = 0.9{-}1.1$ Torr, $t = 0.013{-}0.11$s, $v = 5{-}6$ m/s, quoted error, 2σ.

$$k_1 = (3.5 \pm 1.4) \times 10^{-13} \exp[(841 \pm 144/T)] \quad (\mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}) \quad \text{(III)}$$

$$k_2 = (1.6 \pm 1.5) \times 10^{-10} \exp[(-1248 \pm 36/T)] \quad (\mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}) \quad \text{(IV)}$$

$$k_3 = (3.1 \pm 0.5) \times 10^{-12} \exp[(-481 \pm 55/T)] \quad (\mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}) \quad \text{(V)}$$

to predict the rate constants of the reactions of α-pinene (298−423 K), β-pinene (298−393 K), and camphene (298−433 K) with NO_3, respectively.

Discussion

Rate constant data obtained in this work for the reactions of NO_3 radicals with α-pinene, β-pinene, and camphene at room temperature are compared to those of other workers in Table 2, where a good coincidence between the data is found. Table 1 summarizes the values obtained for the activation energies and preexponential factors of the studied reactions, and as can be readily seen, a negative energy of activation for the reaction of NO_3 with α-pinene is observed. This behavior is similar to that reported for α-pinene by Dlugokencky (*15*) over a slightly different temperature range (261−384 K). For the reaction of NO_3 with β-pinene and camphene no temperature dependence studies of the rate constants have been previously reported. In this work, we have found slightly positive activation barriers.

Kinetics 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. As the terpenes studied are structurally similar to simple or cyclic alkenes we can assume a similar mechanism for the reaction of nitrate radical with terpenes. The values of the rate constant at room temperature for reactions 1, 2, and 3 are ≈10^3 times larger than the rate constants for H-atom abstraction reactions by NO_3 radicals ($4{-}10 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}) and hence reinforce the proposed electrophilic addition mechanism. The relatively low activation or slightly negative (for α-pinene) energies also agree with the values obtained for the reaction of NO_3 with alkenes and are entirely consistent with a radical addition process. As previously discussed for the gas-phase reactions of alkenes and cycloalkenes with the OH radicals (*12, 31*) and the NO_3 radicals (*11−14, 32, 33*), the room-temperature rate constants for the alkenes and the unstrained cycloalkenes depend to a first approximation on the number and configuration of alkyl substituents around the carbon−carbon double bond. It seems that there is also no great effect of ring strain on the radicals reaction rate constants. Thus the rate constants for the reactions of NO_3 with terpenes would be expected to be of the same order of magnitude as those observed for alkenes with the same configuration and degree of substitution around the double bond. The rate coefficients for the reactions of alkenes with NO_3 span about 5 orders of magnitude from the reactions of the 1-alkenes ($k = 2 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} for ethene) to more substituted alkenes ($k = 5.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for 2,3-dimethyl-2-butene).

The double bonds in β-pinene and camphene are structurally similar to those of 2-methylpropene or methylene cyclohexane. In α-pinene the double bond is similar to the bond of 2-methyl-2-butene or methylcyclohexene. To allow a systematic analysis of structure-relativity correlations, the room-temperature rate constants for the gas-phase reactions of OH and NO_3 radicals with alkenes containing terminal ${=}CH_2$ group (2-methylpropene) and with trialkyl substitution in the $C{=}C$ bond (2-methyl-2-butene) are compared with those for the reactions of OH and NO_3 with the terpenes in Table 3. The room-temperature OH radical reaction rate constants span a range of ≈2, with no obvious trends for compounds containing different terminal groups. For the NO_3 radical reactions, the compounds that contain the $>C{=}CH-$ group have reasonably similar room-temperature rate constant $(5.9{-}9.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. However, the rate constants for compounds containing the $C{=}CH_2$ group cover the range from 0.31 to 2.36×10^{-12} cm^3 molecule^{-1} s^{-1}, β-pinene being significantly more reactive than the structurally analogous compound 2-methylpropene. Hence, NO_3 radical reactions seem to be more sensitive to changes in the double bond structure than OH reactions.

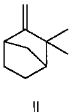
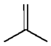
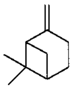
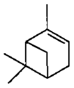
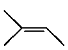
Addition of NO_3 to the double bond of an alkene results in the formation of a radical adduct. A negative temperature dependence is frequently associated with reactions proceeding via the formation of addition complexes; Atkinson (*12, 34, 35*) has explained the negative activation energies observed in the reactions of OH with alkenes, in terms of addition of the OH radical to the carbon−carbon double bond forming adducts which are either collisionally stabilized or decomposed to reform reactants. By analogy, it is possible to propose a similar mechanism for the reaction of α-pinene with the nitrate radical.

TABLE 2. Comparison of the Room Temperature Rate Constants (in Units of cm^3 molecule^{-1} s^{-1}) for Reactions 1−3

α-pinene (1)	β-pinene (2)	camphene (3)	technique[f]
$(5.9 \pm 0.8) \times 10^{-12\ a}$	$(2.1 \pm 0.4) \times 10^{-12\ a}$	$(0.62 \pm 0.21) \times 10^{-12\ a}$	LIF
$(6.18 \pm 0.74) \times 10^{-12\ b}$			FT-LIF
$(5.79 \pm 0.75) \times 10^{-12\ c}$	$(2.36 \pm 0.6) \times 10^{-12\ c}$		RR
$(6.5 \pm 1.0) \times 10^{-12\ d}$	$(2.8 \pm 0.5) \times 10^{-12\ d}$	$(0.654 \pm 0.016) \times 10^{-12\ e}$	RR

[a] Measured in this work. [b] From ref 14. [c] From ref 19. [d] From ref 13. [e] From ref 16. [f] Key to techniques: LIF, laser induced flourescence; FT, Fourier transform; RR, relative rate.

TABLE 3. Rate Constant for the Gas-Phase Reactions of Selected Alkenes with OH and NO_3 at Room Temperature

Alkene	structure	$k_{OH}/10^{-11}$ cm^3 molecule^{-1} s^{-1}	$k_{NO3}/10^{-12}$ cm^3 molecule^{-1} s^{-1}
camphene		5.33[a]	0.62[c]
2-methylpropene		5.14[b]	0.313[d]
β-pinene		7.89[b]	2.1[d]
α-pinene		5.37[b]	5.9[d]
2-methyl-2-butene		8.69[b]	9.33[d]

[a] From ref 16. [b] From ref 24. [c] This work. [d] References 12 and 13.

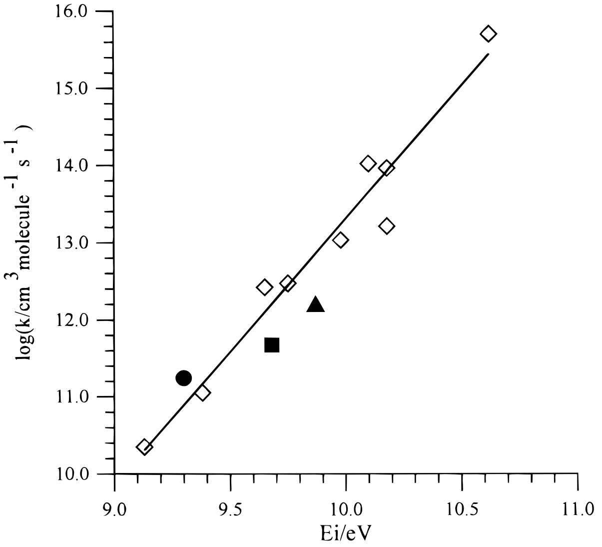


FIGURE 4. The logarithm of the room-temperature rate constant for the reactions of NO_3 with alkenes plotted as a function of the ionization potential (E_i, calculated using the AMPAC 5.0 package) □ simple alkenes, ● α-pinene, ■ β-pinene, and ▲ camphene.

TABLE 4. Calculated Tropospheric Lifetimes of Selected Monoterpenes[d]

compd	$k_{NO_3}/10^{-12}$ cm^3 molecule^{-1} s^{-1}	$k_{OH}/10^{-11}$ cm^3 molecule^{-1} s^{-1}	τ_{OH}/ daytime hours	τ_{NO_3}/ nighttime min
α-pinene	5.9[a]	5.9[b]	3.2	2.0
β-pinene	2.1[a]	7.76[b]	2.5	5.3
camphene	0.62[a]	5.33[c]	3.6	17.4

[a] Measured in this work. [b] From ref 24. [c] From ref 16. [d] $[NO_3] = 10^9$ molecule cm^{-3}, $[OH] = 10^6$ molecule cm^{-3}.

It has been shown (*24, 36−38*) that the reactivity of NO_3 toward alkenes and halogenoalkenes correlates with the ionization potential, E_i. A good correlation has been found between the rate constant at room temperature and the ionization potential expressed by the following relationship (*24*):

$$-\log(k_{296K}/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = 3.276E_i/\text{eV} - 19.38 \qquad \text{(VI)}$$

The energies, E_i, have been calculated for α-pinene (−9.29 eV), β-pinene (−9.699 eV), and (−9.87 eV) camphene using the semiempirical AMPAC 5.0 package (*39*) and PM3 parametrization (*40*). The measured rate constants at room temperature for the reactions of the nitrate radical with α-pinene, β-pinene and camphene fit quite well this correlation (VI) (see Figure 4). This provides further evidence that the reactions of NO_3 with the monoterpenes involve an addition mechanism.

There have been several attempts to study the products of the reaction of NO_3 with monoterpenes (*16, 41, 42*). However, since the reactions of NO_3 with terpenes give many products that have lower vapor pressures than the initial reactants, it is often difficult to isolate and identify all these compounds. Barnes et al. (*16*) reported the detection of nitrooxy-peroxynitrate-type compounds in the initial stages of the reactions of NO_3 with terpenes and the detection of carbonyl and nitrate-containing compounds, but no positive identification was given for the compounds. Jay and Stieglitz (*43*) have tentatively identified the main products of α-pinene−N_2O_5−air reaction systems as 1-methyl-2-nitrooxy-4-(2-propan-2-ol)-cyclohex-1-ene and 1-methyl-nitrate-4-(2-propan-2-ol)-cyclohex-1-ene. In these reaction systems the formation of other numerous aldehydic, nitrate, and keto-nitrate compounds was also observed. Recently, Wängberg et al. (*42*) have reported the study of the products of the reaction of NO_3 with α-pinene and Δ^3-carene; again product identification proved difficult.

Combination of the room-temperature rate constants for the gas-phase reaction of α-pinene, β-pinene, and camphene with OH and NO_3 radicals with the estimated ambient tropospheric concentrations of these reactive species provides tropospheric lifetimes of these biogenic compounds. The lifetime data allows an assessment of the absolute and relative importance of NO_3 radical removal for these naturally emitted organics (see Table 4). Clearly, the tropospheric lifetimes of these monoterpenes with respect to gas-phase reaction process are short, being of the order of minutes and in the range calculated for other terpenes. It can readily be seen from Table 4 that reaction with the NO_3 radical during nighttime is a very important loss process for these terpenes.

In conclusion, we have studied the kinetics of the reactions of NO_3 with α-pinene, β-pinene, and camphene as a function of temperature in the range of 298−433 K. The rate constants at room temperature determined for the reaction of NO_3 with these monoterpenes are in reasonable agreement with the literature data. The rate constant for the reactions of α-pinene with the nitrate radical shows a negative temperature dependence. While for the reaction with β-pinene and camphene a positive activation energies were obtained.

A good correlation has been found for the reaction of NO_3 with these monoterpenes between their rate constant at room temperature and the ionization potential. The available kinetic and product data strongly suggests that the reaction of the nitrate radical with the terpenes involvies electrophilic addition to the double bond system.

The calculated tropospheric lifetimes show that the reaction of monoterpenes with NO_3 may be the major atmospheric removal process for these compounds.

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