# Night-time Atmospheric Loss Process for Unsaturated Aldehydes: Reaction with $NO_3$ Radicals

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The rate constants for the gas-phase reactions of the $NO_3$ radical with a series of unsaturated aldehydes (acrolein, crotonaldehyde, *trans*-2-pentenal, *trans*-2-hexenal, *trans*-2-heptenal, and *cis*-4-heptenal) have been measured directly using a flow tube system coupled to a laser-induced fluorescence (LIF) detection system where the $NO_3$ radical was monitored. The kinetic study was conducted in the temperature range from 298 to 433 K to investigate the temperature dependence of these reactions. This work is the first temperature-dependence study for the reactions of the nitrate radical with the above-mentioned aldehydes. The measured room-temperature rate constants for the reaction of $NO_3$ with such unsaturated compounds (in units of $10^{-14}$ $cm^3$ molecule$^{-1}$ s$^{-1}$) are as follows: acrolein, 0.25 ± 0.04; crotonaldehyde, 1.61 ± 0.19; *trans*-2-pentenal, 2.88 ± 0.29; *trans*-2-hexenal, 5.49 ± 0.95; *trans*-2-heptenal, 9.59 ± 0.19; *cis*-4-heptenal, 26.40 ± 0.40. The proposed Arrhenius expressions for such reactions of $NO_3$ are, respectively, $k_1 = (1.7 \pm 3.2) \times 10^{-11} \exp[-(3232 \pm 355)/T]$ (cm$^3$ molecule$^{-1}$ s$^{-1}$), $k_2 = (5.52 \pm 0.82) \times 10^{-11} \exp[-(2418 \pm 57)/T]$ (cm$^3$ molecule$^{-1}$ s$^{-1}$), $k_3 = (5.4 \pm 0.3) \times 10^{-12} \exp[-(1540 \pm 200)/T]$ (cm$^3$ molecule$^{-1}$ s$^{-1}$), $k_4 = (1.20 \pm 0.3) \times 10^{-11} \exp[-(926 \pm 85)/T]$ (cm$^3$ molecule$^{-1}$ s$^{-1}$), $k_5 = (0.8 \pm 0.2) \times 10^{-12} \exp[-(632 \pm 47)/T]$ (cm$^3$ molecule$^{-1}$ s$^{-1}$), and $k_6 = (0.2 \pm 0.1) \times 10^{-11} \exp[-(657\pm 6.0)/T]$ (cm$^3$ molecule$^{-1}$ s$^{-1}$). Tropospheric lifetimes for these aldehydes have been calculated at night and during the daytime for typical $NO_3$ and OH concentrations showing that both radicals provide an effective tropospheric sink for these compounds and that the night-time reaction with $NO_3$ radical can be an important loss process for these emitted organics and for the $NO_3$ radicals. The present work aims to evaluate the importance of these reactions in the atmosphere and to contribute new data to the study of $NO_3$ reactivity.

## Introduction

Large quantities of organic compounds are emitted into the atmosphere from antropogenic and natural sources.[1−6] Aldehydes are emitted as primary pollutants from partial oxidation of hydrocarbon fuels, and they are the first stable products (secondary pollutants) from the atmospheric oxidation of hydrocarbons. Vegetation has also been a significant source of aldehydes, emitted from a variety of arboreous plants, shrubs, herbaceous plants, and mosses. In addition to the direct emission from vegetation, the atmospheric oxidation of naturally emitted volatile hydrocarbons constitutes a significant source of a various number of aldehydes. Of these, the $\alpha,\beta$-unsaturated aldehydes, the subject of this work, are formed from the reactions of conjugated dienes or terpenes as limonene or terpinolene. The principal representative of the $\alpha,\beta$-unsaturated aldehydes in the atmosphere is acrolein, which has been the subject of several studies.[7−17] The principal atmospheric source of acrolein is the oxidation of isoprene; other sources range from coffee manufacture to tobacco smoke and include forest fires and synthetic rubber manufacture. Other $\alpha,\beta$-unsaturated aldehydes have also been measured in ambient air in urban and rural areas; *trans*-2-hexanal and other larger aldehydes have been observed in the emission of mediterranean vegetation.

Aldehydes are removed from the troposphere by a photolytic process yielding radicals as primary products and by chemical reactions with the OH radical during the day time or with the $NO_3$ radical during the night. Although the $NO_3$-initiated degradation is not the prime loss process for $\alpha,\beta$-unsaturated aldehydes in the atmosphere, kinetic data for the $NO_3$ reaction with these aldehydes is needed to get a better understanding about the role of aldehydes in the atmosphere where the reactions of $NO_3$ radical with $\alpha,\beta$-unsaturated aldehydes could potentially lead to a night-time source of the OH radical[18] and to develop a reliable structure reactivity relationship for these compounds. The night-time reaction of $NO_3$ radical with $\alpha,\beta$-unsaturated aldehydes has been the subject of a few kinetic studies; several of these studies are on the $NO_3$ reactions with acrolein[11−17] and crotonaldehyde,[12] but less investigation has been directed to the reactions of $NO_3$ with other unsaturated aldehydes, with the kinetic and mechanistic data on the atmospheric behavior of larger $\alpha,\beta$-unsaturated aldehydes($>C_5$) being especially scarce. A great part of the obtained rate constants for the vapor-phase reaction of $NO_3$ with this series of aldehydes have been determined by relative technique.

In this article, we report the kinetic study of the reactions of $NO_3$ with some unsaturated aldehydes (acrolein, crotonaldehyde, *trans*-2-pentenal, *trans*-2-hexenal, *trans*-2-heptenal, and *cis*-4-heptenal) in a fast-flow system by using laser-induced fluorescence (LIF) detection of the $NO_3$ radical.

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$$\text{acrolein} + NO_3 \rightarrow \text{products} \tag{1}$$

$$\text{crotonaldehyde} + NO_3 \rightarrow \text{products} \tag{2}$$

$$\textit{trans}\text{-2-pentenal} + NO_3 \rightarrow \text{products} \tag{3}$$

$$\textit{trans}\text{-2-hexenal} + NO_3 \rightarrow \text{products} \tag{4}$$

$$\textit{trans}\text{-2-heptenal} + NO_3 \rightarrow \text{products} \tag{5}$$

$$\textit{cis}\text{-4-heptenal} + NO_3 \rightarrow \text{products} \tag{6}$$

The absolute rate constants at different temperatures have been measured and the Arrhenius parameters calculated for all the studied reactions. Although there are different kinetic studies for the reaction of the $NO_3$ radical with unsaturated aldehydes, in relation to the series of aldehydes presented in this work, only the reaction of $NO_3$ radical with acrolein,[11−17] crotonaldehyde,[12] and *trans*-2-hexenal[19] have been studied experimentally before and just at room temperature. Grosjean and Williams[20] have determined the value of the rate constant for the reactions of *trans*-2-pentenal and *trans*-2-hexenal with $NO_3$ radicals using a structure−reactivity relationship.

No temperature-dependence study of the rate constant for reactions 1−6 has been previously reported to allow us a comparison of our experimental data. Consequently, only the values of the absolute rate constants obtained at room temperature have been compared with the available reported data.

## Experimental Section

All the kinetic experiments were conducted in a fast-flow discharge system with LIF detection for the nitrate radical, excited at $\lambda = 662$ nm. The arrangement of the apparatus and experimental procedures were described in detail previously,[21,22] so only a brief description is given here.

Nitrate radicals were generated in a sidearm tube by the fast reaction between F atoms and $HNO_3$. A microwave discharge (2450 MHz) acting on $F_2$–He mixtures produced fluorine atoms efficiently. In all experiments the $HNO_3$ concentration was in a sufficiently large excess over the F atoms concentration to prevent the secondary reactions involving $F + NO_3 \rightarrow FO + NO_2$ from consuming $NO_3$. The radical was admitted to the flow tube at the upstream end through a fixed port. The initial $NO_3$ concentrations ranged from 4 to $12 \times 10^{12}$ molecules $cm^{-3}$. Absolute concentrations of $NO_3$ were determined before or after each kinetic run by chemical titration with a known amount of tetramethylethene (TME).[23] The flow tube was coated with halocarbon wax and, under the working conditions, the coefficient for the wall loss of the nitrate radical, $k_w$, was found to be $<0.1\ s^{-1}$.

The reactants were introduced to the flow through a sliding injector, the position of which varied from 3 to 70 cm from the center of the observation region. The time evolution of the reaction was archived by changing the distance between the injector and the detection cell. Contact times between the $NO_3$ radical and the reactant ranged from 6 to 130 ms. Concentration of aldehydes ranged from 0.06 to $5 \times 10^{14}$ molecules $cm^{-3}$.

Helium was used as a carrier gas, and the experiments were conducted at a total pressure of $1 \pm 0.1$ Torr. The flow tube was heated between room temperature, 298 K, and 433 K by an electronically regulated heating tape. Direct measurements of the temperature inside the flow tube showed that the temperature 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.[24]

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

The source of the organic reactants and their stated purity levels were as follows: acroleina (99.5%, Aldrich), crotolaldehyde (97%, Aldrich), *trans*-2-pentenal (99%, Acros Organic), *trans*-2-hexenal (97%, Acros Organic), *trans*-2-heptenal (99%, Acros Organic), *cis*-4-heptenal (95%, Acros Organic); all were purified by successive trap-to-trap distillations.

## Results

The kinetic experiments for acrolein and crotonaldehyde were performed under pseudo-first-order conditions, with both reactants present in a large excess over $NO_3$. The corresponding experimental data were analyzed using the pseudo-first-order integrated rate expression,[25] as it is shown in eq I.

$$\ln\frac{[NO_3]_0}{[NO_3]_t} = (k'[\text{reactant}])t = kt \tag{I}$$

Because the vapor pressure of the other unsaturated aldehydes is low, the experiments on these compounds were performed without a large excess of reactant over $NO_3$. The ratio [unsaturated aldehyde]/[$NO_3$] was only varied between 1 and 4, so the data for the reaction of $NO_3$ with *trans*-2-pentenal, *trans*-2-hexenal, *trans*-2-heptenal, and *trans*-4-heptenal were analyzed using the second-order integrated rate expression, assuming a 1:1 stoichiometry (eq II).[25]

$$\ln\frac{(M - X_a)}{[M(1 - X_a)]} = (B_o - A_o)kt \tag{II}$$

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

$$X_a = \frac{[NO_3]_o - [NO_3]_t}{[NO_3]_o} \tag{III}$$

The reactions were investigated in temperatures ranging from 298 to 433 K, and because of the existence of a temperature profile in the flow tube, the rate constants at elevated temperature were calculated assuming that the entire flow tube was at the same high temperature and the cell was at room temperature. Thus, the adequate standard kinetic equation is applied separately to both regions at the different temperatures. Airds et al.[26] and Martínez et al.[27] showed that this method leads to good results in a system with a similar temperature profile in the flow tube.

Plots of $\ln([NO_3]_0/[NO_3])_t$ vs time (first-order plot) were obtained in accordance with eq I for the reaction of the $NO_3$ radical with acrolein and crotonaldehyde, at all the studied temperatures, giving the corresponding pseudo-first-order rate constant $k$’. Figure 1 shows a typical first-order plot for the reaction of $NO_3$ with crotonaldehyde at 433 K. The obtained first-order rate constants $k$’ for each compound at a given temperature were plotted against the reactant concentration, and the second-order rate constants were obtained as the slope of least-squares fits of these data. Figure 2 shows plots of the pseudo-first-order rate coefficients $k$’ vs the reactant concentration for the reaction of $NO_3$ with crotonaldehyde at all the studied temperatures.

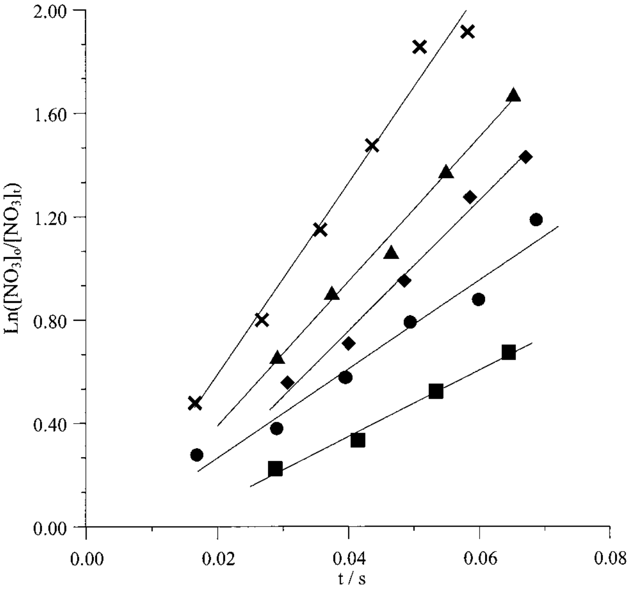

**Figure 1.** First-order plot for the reactions of $NO_3$ with crotonaldehyde at 433 K.

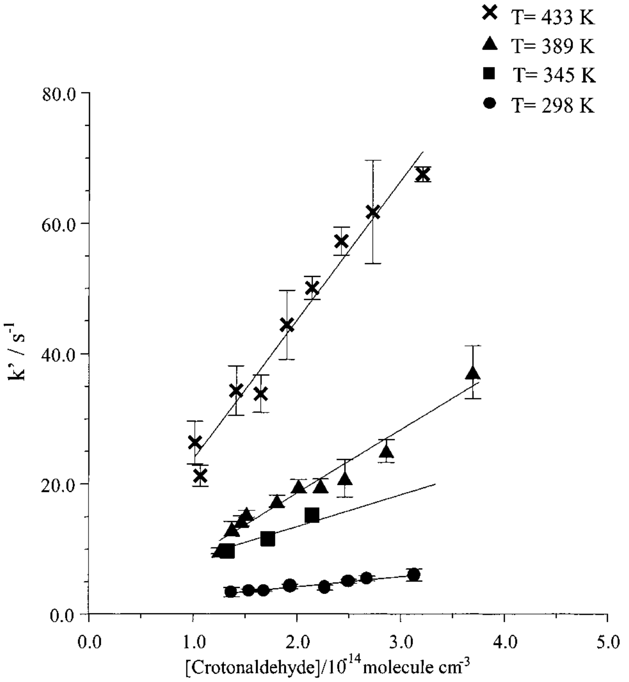

**Figure 2.** Plots of the pseudo-first-order rate coefficients *k*' vs the concentration of crotonaldehyde at different temperatures.

For the reactions 3−6, plots of $1/(B_0 - A_0)\ \ln[(M - X_a)/M(1 - X_a)]$ vs *t*, according to eq II yield the bimolecular rate constants. 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 *trans*-2-pentenal at different temperatures.

A summary of the absolute second-order rate coefficients obtained for all the studied reactions 1−6 is given in Table 1. The data for reactions 1−6 are shown in Figure 4 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 reactions 1−6 with the corresponding activation energy and preexponential factor are summarized in Table 1.

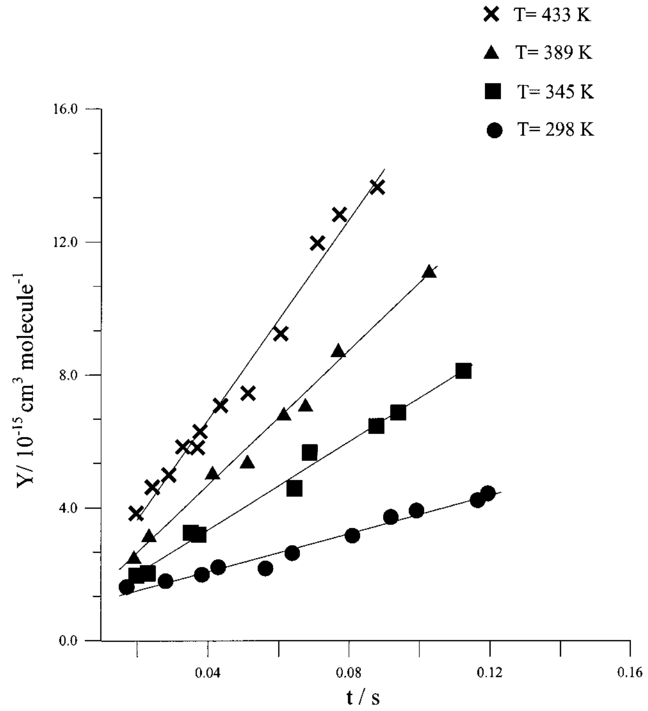

**Figure 3.** Plots of $1/(B_0 - A_0)\ \ln[(M - X_a)/M(1 - X_a)]$ vs *t*, for the reaction of the nitrate radical with *trans*-2-pentenal at different temperatures according to eq II.

**TABLE 1: Summary of the Measured Rate Coefficients for the Reactions of $NO_3$ with Aldehydes**

| *T* (K) | *k* ($10^{-14}$ $cm^3$ $molecule^{-1}$ $s^{-1}$) | [reactant] ($10^{14}$ molecule $cm^{-3}$) | $E_a$ (kJ $mol^{-1}$) | A ($10^{-11}$ $molecule^{-1}$ $cm^3$ $s^{-1}$) |
|---|---|---|---|---|
| | | acrolein | | |
| 298 | 0.25 ± 0.04 | 3−5 | 26.9 ± 3.2 | 1.7 ± 3.2 |
| 345 | 1.50 ± 0.32 | 1−2 | | |
| 389 | 4.85 ± 0.37 | 1−3 | | |
| 433 | 8.37 ± 0.66 | 1−3 | | |
| | | crotonaldehyde | | |
| 298 | 1.60 ± 0.19 | 1−4 | 20.1 ± 0.5 | 5.5 ± 0.8 |
| 345 | 5.10 ± 0.64 | 1−4 | | |
| 389 | 10.12 ± 2.49 | 1−4 | | |
| 433 | 20.87 ± 2.32 | 1−4 | | |
| | | *trans*-2-pentenal | | |
| 298 | 2.88 ± 0.29 | 0.4−1 | 12.8 ± 1.7 | 0.54 ± 0.30 |
| 345 | 6.60 ± 0.51 | 0.4−1 | | |
| 389 | 10.05 ± 0.75 | 0.4−1 | | |
| 433 | 15.04 ± 1.30 | 0.4−1 | | |
| | | *trans*-2-hexenal | | |
| 298 | 5.49 ± 0.95 | 0.1−0.4 | 7.7 ± 1.4 | 0.12 ± 0.03 |
| 345 | 8.56 ± 0.59 | 0.1−0.4 | | |
| 389 | 10.88 ± 0.97 | 0.1−0.4 | | |
| 433 | 15.22 ± 1.77 | 0.1−0.4 | | |
| | | *trans*-2-heptenal | | |
| 298 | 9.59 ± 0.19 | 0.06−0.4 | 5.2 ± 0.4 | 0.08 ± 0.02 |
| 345 | 11.8 ± 0.10 | 0.06−0.4 | | |
| 389 | 14.6 ± 0.20 | 0.06−0.4 | | |
| 433 | 18.0 ± 0.2 | 0.06−0.4 | | |
| | | *cis*-4-heptenal | | |
| 298 | 26.4 ± 0.4 | 0.06−0.02 | 5.5 ± 0.1 | 0.02 ± 0.01 |
| 345 | 35.6 ± 0.30 | 0.06−0.02 | | |
| 389 | 44.0 ± 0.5 | 0.06−0.02 | | |
| 433 | 52.9 ± 0.6 | 0.06−0.02 | | |

$[NO_3] = (4-12) \times 10^{12}$ molecule $cm^{-3}$; $P_T = 0.9-1.1$ Torr; $t = 0.006-0.130$ s; $v = 5-12$ m/s, quoted error, $2\sigma$.

To assess the possible influence of secondary reactions on the calculated rate coefficients, a set of simulation calculations for the reactions of these unsaturated aldehydes (1−6), considering the two possible processes, addition to the C═C double bond and the H-atom abstraction from the −CHO group was made, using the FACSIMILE code.[28] In the calculations for each primary reaction 1−6, a consecutive pathway including the possible reactions between the corresponding organic product radicals (RCO, RO and R) and the nitrate radical was proposed, and the reaction of nitrate radical with $NO_2$ was included. In this work, the best fits of the $NO_3$ experimental data were obtained when the weight of the secondary chemistry was minimized, thus confirming a negligible effect of the secondary reactions under the present experimental working condition. Indirect evidence of the absence of the secondary chemistry influence is provided by the reasonably good agreement between our results and those obtained by other authors, fundamentally by relative technique together with the absence of curvature in the plots of the data (Figures 1−3), including the data at large times.

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

$$k_1 = (1.7 \pm 3.2) \times 10^{-11} \exp[-(3232 \pm 355)/T] \quad (\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) \quad \mathrm{(IV)}$$

$$k_2 = (5.52 \pm 0.82) \times 10^{-11} \exp[-(2418 \pm 57)/T] \quad (\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) \quad \mathrm{(V)}$$

$$k_3 = (5.40 \pm 0.3) \times 10^{-12} \exp[-(1540 \pm 200)/T] \quad (\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) \quad \mathrm{(VI)}$$

$$k_4 = (1.2 \pm 0.3) \times 10^{-11} \exp[-(926 \pm 85)/T] \quad (\mathrm{cm^3\ molecule{-}^{1}\ s^{-1}}) \quad \mathrm{(VII)}$$

$$k_5 = (0.08 \pm 0.02) \times 10^{-11} \exp[-(632 \pm 47)/T] \quad (\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) \quad \mathrm{(VIII)}$$

$$k_6 = (0.2 \pm 0.1) \times 10^{-11} \exp[-(657 \pm 6)/T] \quad (\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) \quad \mathrm{(IX)}$$

These expressions can predict the rate constants of the reactions of acrolein, crotonaldehyde, *trans*-2-pentenal, *trans*-2-hexenal, *trans*-2-heptenal, and *cis*-4-heptenal, respectively, with $NO_3$ in the range of temperatures cited above.

## Discussion

The rate coefficients for the gas-phase reactions of the $NO_3$ radical with organic molecules span several orders of magnitude.[28−30] The published rate constants for the reaction of $NO_3$ with oxygen-containing organic compounds (aldehydes, ketones, alcohols, ethers) range from $10^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for ketones to $10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the reactions with aldehydes.[17,28−33] The absolute rate constants measured in this work at room temperature (shown in Table 1) have been found in the range (0.2−27) × $10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$; this range of values is, in part, in accordance with the above-mentioned range for the reaction of $NO_3$ with oxygen-containing compounds, but the obtained rate constants are also in the range of the rate constant for the reaction of $NO_3$ with alkenes[7,17,28−31,34−37] (between $10^{-16}$ and $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$). From the analysis of the data given in Table 1, it can be observed that the rate constant increases with the length of the organic chain, the biggest increase being for the rate constant of the reaction of $NO_3$ with crotonaldehyde, which is about 6 times bigger than the rate coefficient for the $NO_3$ reaction with acrolein. It can also be observed that for each aldehyde the rate constant increases with temperature. The values of the rate constants at room temperature obtained for the reactions studied in the present work are compared with available reported data in Table 2.

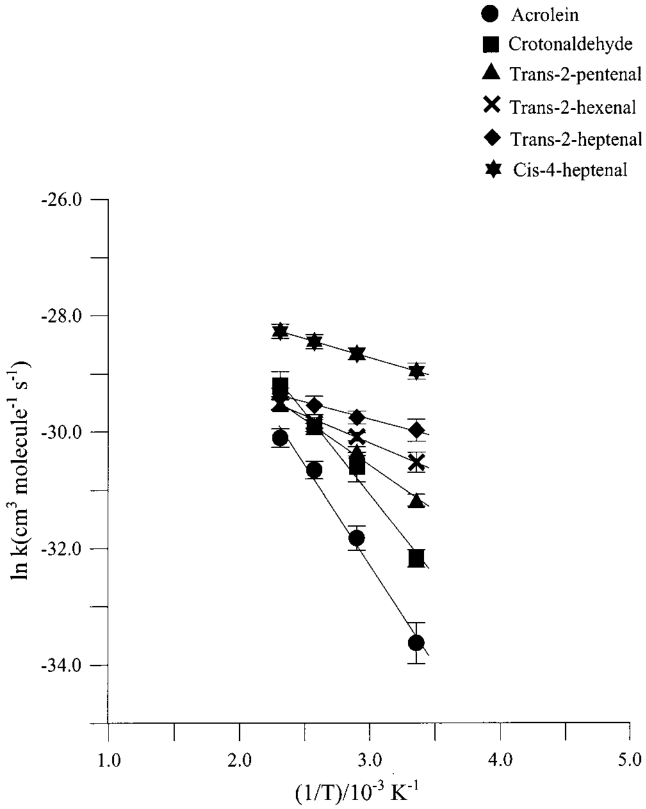

**Figure 4.** Arrhenius plots for the reactions of $NO_3$ with all the studied aldehydes.

**TABLE 2: Comparison of the Room Temperature Rate Constants (in units of cm$^3$ Molecule−$^1$ s$^{-1}$) for Reactions 1−6**

| compound | $k_{NO_3}$ ($10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) (this work) | $k_{NO_3}$ ($10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) | technique[a] |
|---|---|---|---|
| acrolein | 0.25 ± 0.04 | 0.89 ± 2.8[b] | A |
| | | 0.11 ± 0.04[b] | RR |
| | | 0.11 ± 0.17[c] | RR |
| crotonaldehyde | 1.61 ± 0.19 | 0.50 ± 0.10[c] | RR |
| *trans*-2-pentenal | 2.88 ± 0.29 | | |
| *trans*-2-hexenal | 5.49 ± 0.95 | 1.21[d] | RR |
| *trans*-2-heptenal | 9.59 ± 0.19 | | |
| *cis*-4-heptenal | 26.40 ± 0.40 | | |

[a] Key to techniques: A, Absolute; RR, Relative Rate. [b] From ref 17. [c] From ref 12. [d] From ref 19.

The reaction of the nitrate radical with acrolein is the most studied; different experimental values for its rate constant, obtained by absolute and relative technique, are presented. It can be seen that our absolute experimental value of rate constant is only slightly higher than the relative values given by Atkinson[19] and Canosa et al.,[15] and quite lower than the absolute value obtained for Canosa et al.[15] The comparative values for the other studied reactions are scarce, for the reaction of crotonaldehyde and *trans*-2-hexenal the rate constant obtained in the present work are much higher than the relative values presented by Atkinson.[12,19] No experimental values of the rate constant have been found for the reactions of *trans*-2-pentenal, *trans*-2-heptenal, and *cis*-4-heptenal.

No data about the dependence of the rate constant for the reactions of $NO_3$ with unsaturated aldehydes with temperature have been reported.

Therefore, this is the first study on temperature dependence for the reactions of $NO_3$ with acrolein, crotonaldehyde, *trans*-2-pentenal, *trans*-2-hexenal, *trans*-2-heptenal, and *cis*-4-heptenal. Table 1 shows a positive energy of activation for all the reactions of $NO_3$ with compounds such as acrolein (26.9 ± 3.2 kJ/mol), crotonaldehyde (20.1 ± 0.5 kJ/mol), *trans*-2-pentenal (12.8± 1.7 kJ/mol), *trans*-2-hexenal (7.7 ± 1.4 kJ/mol), *trans*-2-heptenal (5.2 ± 0.4 kJ/mol), and *cis*-4-heptenal (5.5 ± 0.1 kJ/mol). These positive values of activation energy can be compared with the values obtained for other reactions of the $NO_3$ radical. The calculated values for the reactions studied in this work for acrolein and crotonaldehyde (about 20 kJ/mol) are of the same order as the activation energies for the $NO_3$ abstraction process with alkanes,[7,17,28−30] and similar to those obtained for the reaction of $NO_3$ with aliphatic aldehydes.[32] These values of activation energies could lead to suppose a process of abstraction of the aldehydic H. However, the obtained activation energies of the reactions of the other aldehydes with $NO_3$, are lower, between 12 and 5 kJ/mol values similar to those obtained for the reactions of the $NO_3$ radical with alkenes, haloalkenes, or terpenes which have been reported as of a few kilojoules per mole or show negative values.[7,28−31,33−36]

Although temperature-dependence studies have not been performed previously for the $NO_3$ reactions with unsaturated aldehydes, Atkinson[37] has reported studies of the temperature dependence for the reactions of aldehydes with the OH radical. The reaction of aldehydes with OH are faster (rate constants of about $10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$) than the reaction with the $NO_3$ radical, and a decrease of the rate constant has been observed with the increase of the temperature and a negative activation energy of a few kilojoules per mole for all the studied aldehydes. These results for the reaction of OH with acrolein[37] have been explained through a mechanism of H-atom abstraction from the $-CHO$ group with the OH-radical addition pathway being of minor importance at 298 K. For the reaction of OH with crotonaldehyde, a mechanism has been proposed that proceeds by H-atom abstraction from the $-CHO$ group and the OH-radical addition to the $C=C$ bond at room temperature and only the H-atom abstraction process at high temperature. It is known from kinetics and mechanistic studies that the reactivity of the $NO_3$ and OH radicals shows a similar behavior toward the same kind of compound. The reactions of OH and $NO_3$ radicals with alkenes, haloalkenes, dienes, and terpenes proceed predominantly via the electrophilic addition of $NO_3$ or OH radical to the double bond or the reactions of these radicals with alkanes are consistent with a mechanism in which a H atom is abstracted from the $C-H$ bonds. In this sense, the similarity between the reactions of different kinds of substances with the $NO_3$ and OH radicals leads us to think of a similar mechanism for the reactions of both radicals with $\alpha,\beta$-unsaturated aldehydes. For the reactions with unsaturated aldehydes the $NO_3$ radical (electrophilic species) will add to the carbon−carbon double bond but may also abstract the aldehydic hydrogen. From the obtained values of the room-temperature rate constant and activation energy for the reactions of $NO_3$ with unsaturated aldehydes, it can be observed that the reaction of $NO_3$ with acrolein presents the smaller rate constant of this series of unsaturated aldehydes and it is also smaller than the rate constant for the reaction of $NO_3$ with propanal (aldehyde saturated with the same number of carbon atom, $k = 0.60 \pm 0.06 \times 10^{-14}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, Cabañas et al.[32]). For the reaction of crotonaldehyde with the nitrate radical the rate constant increases with respect to those of acrolein and it is also slighter higher than the rate coefficient for the reaction of $NO_3$ with butanal, the corresponding saturated aldehyde ($k = 1.46 \pm 0.06 \times 10^{-14}$ $cm^3$ $molecule{-}^{1}$ $s{-}^{1}$, Cabañas et al.[32]). The same effect, an increase of the rate constant when the length of the chain increases and a rate constant higher than the corresponding saturated aldehyde, is observed for the reactions of $NO_3$ with the rest of the unsaturated aldehydes studied in the present work. These facts can be explained, because the presence of a conjugated double bond with a carbonilic group reduces the reactivity of both groups, but the presence of $-CH_3$ group donates electron density to the double bond increasing the reactivity and then the reactivity increases with the length of the hydrocarbon chain. Because these compounds have two reactive groups ($-C=C-$ and $-CHO$), and the addition process is faster than the abstraction, the increase in reactivity involves a major proportion of the addition process. The unexpected increase in the rate constant of the reaction of $NO_3$ with *cis*-4-heptenal could be because, in this compound, the carbon−carbon double bond is not conjugated with the carbonilic group and, because the addition is faster than the abstraction process, the first occurs in a large proportion and this compound behaves principally as alkene.

All these kinetic results, together with those of other authors,[7,17,28−30] suggested that for the reactions of the $NO_3$ radical with acrolein, and probably with crotonaldehyde, the abstraction pathway is the dominant process. However, when the hydrocarbon chain increases, the addition process could take precedence, and the principal process could be the addition for *trans*-2-pentenal, *trans*-2-hexenal, *trans*-2-heptenal, and *cis*-4-heptenal; but at the moment, it is difficult to accurately define the contribution of each process in the global mechanism.

In conclusion, in the present kinetic study of the reaction of the $NO_3$ radical with a group of unsaturated aldehydes at different temperatures, values of rate constants agreeing in part with the reported values of $NO_3$-radical aldehydes and with the range given for the reactions of $NO_3$ with alkenes have been obtained. All the studied reactions show a positive activation energy but, meanwhile, the reactions of $NO_3$ with acrolein and crotonaldeyde have a higher activation energy value, in accordance with the values obtained for the reactions of $NO_3$ with alkanes and aldehydes; the values obtained for the other unsaturated aldehydes are in greater accordance with those obtained for the reaction of $NO_3$ with alkenes. That fact could be explained by the presence or not of a conjugated double bond with the carbonilic group that may have influence in the contribution of both processes, addition to the $C-C$ double bond and H-atom abstraction, to the whole mechanism.

To date all these ideas have to be considered with caution because of the lack of data about these reactions; therefore, more kinetics and, in particular, product information about the reactions of the $NO_3$ radical with these types of aldehydes ought to be obtained. In this way we continue with the systematic investigation of the $NO_3$ radical with other aldehydes to obtain more information to elucidate the reaction mechanism.

## Atmospheric Implications

The atmospheric lifetimes of the unsaturated aldehydes studied in this article have been calculated with respect to the $NO_3$ and OH radical reactions using the rate constants at room

**TABLE 3: Calculated Tropospheric Lifetimes of the Selected Aldehydes with Respect to $NO_3$ and OH**

| compound | $k_{NO_3}$ ($10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$)$^a$ | $k_{OH}$ ($10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$)$^b$ | $\tau_{OH}$ (day-time hours) | $\tau_{NO_3}$ (night-time hours) |
|---|---|---|---|---|
| acrolein | 0.25 | 1.99 | 8 | 221 |
| crotonaldehyde | 1.61 | 3.6 | 5 | 34 |
| *trans*-2-pentenal | 2.88 | 2.53 | 4.7 | 19 |
| *trans*-2-hexenal | 5.49 | 2.80 | 4.3 | 10 |
| *trans*-2-heptenal | 9.59 | – | – | 6 |
| *cis*-4-heptenal | 26.4 | – | – | 3 |

[a] $[NO_3] = 5 \times 10^8$ molecule cm$^{-3}$ (12 h average), from ref 39; $[OH] = 1.6 \times 10^6$ molecule cm$^{-3}$ (12 h average), from ref 40. [a]Measured in this work. [b]From ref 37.

temperature for the gas-phase reaction of such series of aldehydes with both radicals, $k_R$, in combination with estimated ambient tropospheric concentrations of these reactive species [R], according to the equation:

$$\tau_R = 1/k_R[R] \qquad (X)$$

The rate constant measured in the present work have been used as $k_R$ for the reactions of these unsaturated aldehydes with $NO_3$ and the rate constant corresponding to the OH-reaction have been obtained from bibliographic references (Table 3). The calculated lifetimes are also shown in Table 3 and allows an assessment of the absolute and relative importance of $NO_3$ radical removal for these emitted organics. It is clear that the calculated tropospheric lifetimes of these unsaturated aldehydes with respect to the daily OH reaction, being of the order of few hours, are shorter than the estimated lifetimes respect to the $NO_3$ reaction which have been found to be on the order of days. It was only possible, according to the bibliographic sources, to estimate the daily lifetimes for acrolein and crotonaldehyde. These daily lifetimes are quite similar (8 h for acrolein and 5 h for crotonaldeyde); however, a larger variation for the night lifetimes from 221 h for acrolein to 3 h for *cis*-4-heptanal can be appreciated, with the corresponding night lifetimes for acrolein and crotonaldehyde being quite different. Although the lifetimes for the disappearance of these aldehydes with respect to the $NO_3$ reaction at night are larger than those corresponding to the daily process with respect to the OH radical, during the night time, the reaction with the $NO_3$ radical could be considered as an important loss process for these kinds of compounds in the atmosphere, and the degradation products from these reactions must also be considered. The peroxyacyl nitrate radicals, the degradation products of the chain of reaction of $NO_3$ radical with $\alpha,\beta$-unsaturated aldehydes, can provide a mechanism for the transport of $NO_2$ species from the polluted regions to the clear areas[38] of the globe, and these peroxyacyl radicals also yield $HO_2$, which can participate in chemical cycles, then in night time, in the presence of the $NO_3$ radical, produce OH radicals in the troposphere.[18]

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