Kinetics and Products of the Reactions of Ethyl and Propyl Nitrates with OH Radicals

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ABSTRACT. The kinetics of the reactions of ethyl (1) and propyl (2) nitrates with OH radicals has been studied using a low pressure flow tube reactor combined with a quadrupole mass spectrometer. The rate constants of the title reactions were determined under pseudo-first order conditions from kinetics of OH consumption in high excess of nitrates. The overall rate coefficients, $k_1 = 1.14 \times 10^{-13} (T/298)^{2.45} \exp(193/T)$ and $k_2 = 3.00 \times 10^{-13} (T/298)^{2.50} \exp(205/T)$ cm^{3}molecule^{-1}s^{-1} (with conservative 15% uncertainty), were determined at a total pressure of 1 Torr of helium over the temperature range (248–500) and (263-500) K, respectively. The yields of the carbonyl compounds, acetaldehyde and propanal, resulting from the abstraction by OH of an α-hydrogen atom in ethyl and propyl nitrates, followed by α-substituted alkyl radical decomposition, were determined at T = 300K to be 0.77 ± 0.12 and 0.22 ± 0.04, respectively.

Keywords: Kinetics, hydroxyl radical, alkyl nitrates, α-hydrogen, abstraction, rate coefficient.

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INTRODUCTION

Organic nitrates are the intermediates of the atmospheric oxidation of volatile organic compounds in the presence of nitrogen oxides. They are formed in the minor (addition) channel of the reaction of peroxy radicals with NO and also in the NO_3-initiated oxidation of unsaturated organic compounds [1]. Organic nitrates are temporary reservoirs of NO_x with a tropospheric lifetime from a few days to a few weeks, depending on their reactivity toward OH radicals and photolysis rate [2-5].

In the present work, we report the results of the experimental investigation of the reactions of ethyl (ENT) and propyl (PNT) nitrates with OH radicals:

$$OH + C_2H_5ONO_2 \rightarrow products \tag{1}$$

$$OH + C_3H_7ONO_2 \rightarrow products \tag{2}$$

Previously, the rate constant of reaction (1) was measured in several absolute [3, 6-7] and relative rate studies [6, 8-9]. Currently there is significant disagreement between the reported data concerning both room temperature value of k_1 (roughly a factor of three spread) and its temperature dependence. For example, Nielsen et al. [6] and Shallcross et al. [7] have reported negative (E/R = -716 K) and positive (E/R = 699 K) temperature dependence of k_1, respectively, in the temperature range 298-373K. One absolute [6] and three relative rate measurements [6, 8-10] are available for the rate constant of OH + PNT reaction, however temperature dependence of the rate constant has been investigated in only one study and in a rather narrow temperature range T = 298-368 K [6].

Abstraction of an α-hydrogen atoms in organic nitrates by OH radicals leads to the formation of an α-substituted alkyl radicals:

$$OH + CH_3CH_2ONO_2 \rightarrow CH_3C^{\bullet}HONO_2 + H_2O \tag{1a}$$

$$OH + CH_3CH_2CH_2ONO_2 \rightarrow CH_3CH_2C^{\bullet}HONO_2 + H_2O \tag{2a}$$

These radicals are known to be unstable, dissociating spontaneously without an energetic barrier to form a carbonyl compound and NO_2 [11]:

$$CH_3C^\bullet HONO_2 \rightarrow CH_3CHO + NO_2$$

$$CH_3CH_2C^\bullet HONO_2 \rightarrow CH_3CH_2CHO + NO_2$$
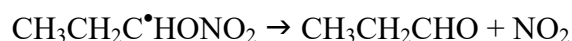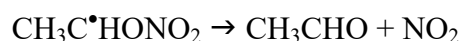
In this respect, the measurements of the yield of corresponding carbonyl compound provide the information on the extent of H-atom abstraction from α carbon. In the present paper we report the measurements of the temperature dependence of k_1 and k_2 in an extended temperature range (248-500) K and the yields of the carbonyl compounds (at T = 300K), acetaldehyde and propanal, resulting from α-hydrogen atoms abstraction by OH in ENT and PNT, respectively.

EXPERIMENTAL

The gas-phase reactions of OH radicals with alkyl nitrates were studied at 1 Torr total pressure of helium over the temperature range 248−500 K. Experiments were carried out in a discharge flow tube under laminar flow conditions. Modulated molecular beam mass spectrometer (MS) was used to monitor the reactants and reaction products in the gas phase. Depending on the temperature range, we have used two different flow reactors. The first one, thermostated Pyrex tube (45 cm length and 2.4 cm i.d.) covered with halocarbon wax [12-14], was employed at low temperatures (248 – 355K). The second reactor (Fig. 1S, Supporting Information), which was recently developed for high temperature kinetic studies (up to T = 1000 K), consisted of a Quartz tube with an electrical heater and water-cooled extremities [15]. Temperature in the reactor was measured with a K-type thermocouple positioned in the middle of the reactor in contact with its outer surface. Temperature gradients along the flow tube measured with a thermocouple inserted in the reactor through the movable injector was found to be less than 1% [15].

OH radicals were generated in the fast reaction of hydrogen atoms with NO_2, H atoms being produced in a microwave discharge of H_2/He mixture:

$$H + NO_2 \rightarrow OH + NO \tag{3}$$

NO_2 was always used in excess over H atoms. OH radicals were detected as $HOBr^+$ (m/z = 96/98) after scavenging by an excess of Br_2 ($[Br_2] \approx 5\times10^{13}$ molecule cm^{-3}, added at the end of the reactor, 5 cm upstream of the sampling cone) via reaction:

$$OH + Br_2 \rightarrow HOBr + Br \tag{4}$$

This method for OH detection was preferred to the direct detection of these radicals at m/z = 17 (OH^+) due to significant background signal at this mass. Similarly, the chemical conversion of OH to HOBr was used for the measurements of the absolute concentrations of the radicals: $[OH] = [HOBr] = \Delta[Br_2]$, i.e. concentrations of OH were determined from the consumed fraction of $[Br_2]$. $[Br_2]$ was determined from the measured flow rate of known Br_2/He mixtures. The possible influence of secondary chemistry on this method of HOBr detection and their absolute calibration procedure was discussed in details in previous papers from this group [12-13].

ETN and PNT were introduced into the flow reactor from a 10L flask containing nitrate-He mixture or by passing helium through a thermostated glass bubbler containing liquid nitrate and were detected by mass spectrometry at their fragment peaks at m/z = 76 ($CH_2ONO_2^+$), which were much more intensive than the parent ones (m/z = 91 and 105, respectively). All other species were detected at their parent peaks: m/z= 44 (acetaldehyde, CH_3CHO^+), 58 (propanal, $C_2H_5CHO^+$), 160 (Br_2^+), 96/98 ($HOBr^+$), 46 (NO_2^+). The absolute concentrations of the nitrates as well as of other stable species in the reactor were calculated from their flow rates obtained from the measurements of the pressure drop of mixtures of the species with helium in calibrated volume flasks.

The nitrates were synthesized in the laboratory via slow mixing of 5 ml of the corresponding alcohol with 20 ml mixture of H_2SO_4:HNO_3 (1:1) kept at temperature < 5°C [16]. After neutralization of the final solution with water the supernatant layer was separated and mixed with anhydrous magnesium sulfate in order to remove remaining water. Finally, the solution was filtered to retrieve the liquid nitrate. The synthesized nitrates were degassed before use. Gas chromatographic analysis of the nitrates has shown that impurities were less than 0.1%. The purities and origin of other gases used were as follows: He >99.9995% (Alphagaz), was passed through liquid nitrogen traps; H_2 > 99.998% (Alphagaz); Br_2 >99.99% (Aldrich); NO_2 > 99% (Alphagaz); acetaldehyde > 99.5% (Sigma-Aldrich); propanal > 97.0% (Sigma-Aldrich).

RESULTS AND DISCUSSION

Rate constants of reactions (1) and (2)

The measurements of the rate constants were carried out under pseudo-first order conditions in high excess of nitrates over OH radicals. The initial concentration of OH radicals was nearly 5×10^{11} molecule cm^{-3}. The ranges of the concentrations of nitrates are shown in Tables I and II. The flow velocity in the reactor was in the range (660-1660) cm s^{-1}. Examples of the exponential decays of OH in reaction (2) are shown in Fig. 1. Figures 2 and 3 show examples of the dependencies of the pseudo-first order rate constants, $k_1' = k_1[ENT] + k_w$ and $k_2' = k_2[PNT] + k_w$, on concentration of the corresponding nitrate. k_w represents the rate of OH decay in the absence of nitrate in the reactor and was measured in separate experiments. All the measured values of k_1' and k_2' were corrected for axial and radial diffusion of OH.[17] The diffusion coefficient of OH in He was calculated using the following expression: $D_0 = 640 \times (T/298)^{1.85}$ Torr cm^2 s^{-1} [18-19]. Corrections were generally less than 10%, however, in a few kinetic runs they were somewhat higher (up to 19%).
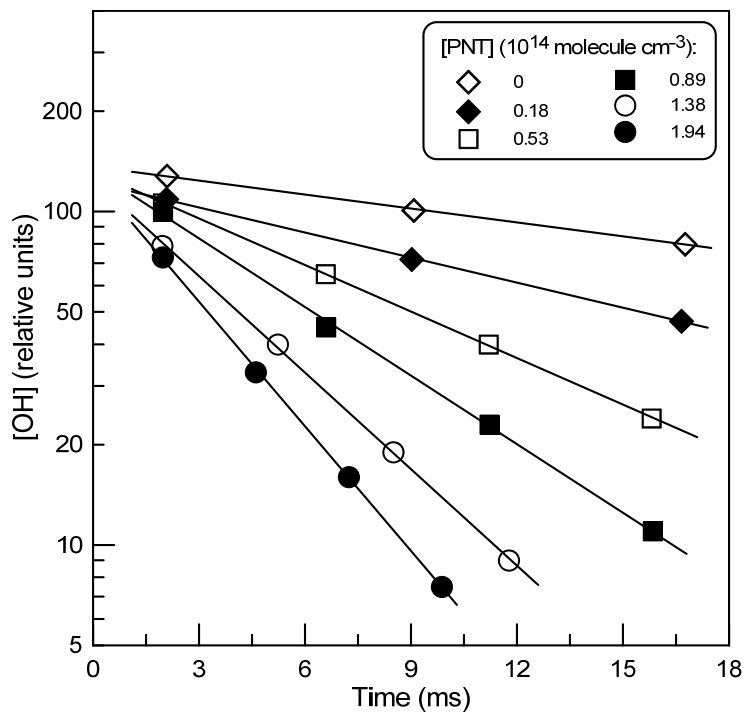
Figure 1 Examples of the exponential decays of OH in reaction with PNT: T = 500 K.
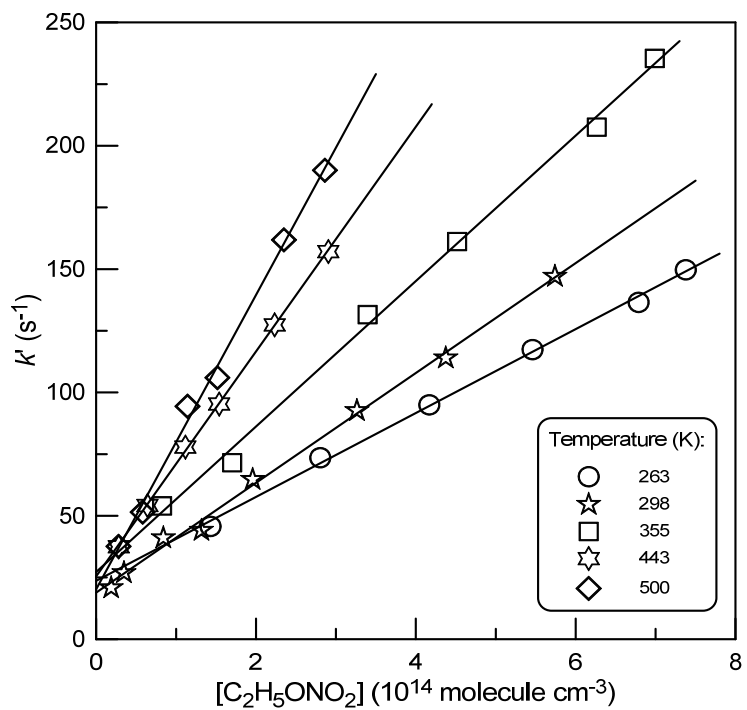

Figure 2 Example of pseudo-first order plots obtained from OH decay kinetics in excess of ethyl nitrate.
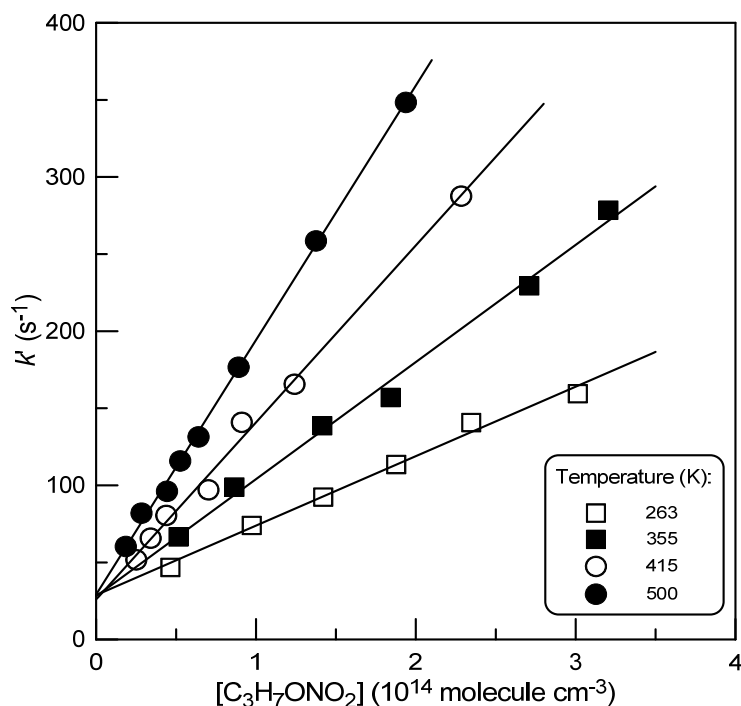
Figure 3 Example of pseudo-first order plots obtained from OH decay kinetics in excess of propyl nitrate.

The slopes of the straight lines in Fig. 2 and 3 provide the values of k_1 and k_2 at respective temperatures. The intercepts were generally somewhat higher (however in agreement in the range of the experimental uncertainty) than the corresponding OH loss rate measured in the absence of nitrates in the reactor. All the results obtained for k_1 and k_2 at different temperatures are shown in Tables I and II, respectively. The lowest temperature in the rate constant measurements was limited by impact of the heterogeneous chemistry which was manifested in an anomalous increase of the measured rate constant with decreasing temperature. Highest temperature of the study (500 K) was limited by thermal decomposition of the nitrates.

The possible impact on the measurements of the rate constants of secondary chemistry was explored in separate series of experiments, where reaction rate was measured as a function of initial concentration of OH. Fig. 2S (Supporting Information) shows the results of the measurements of k_2' at fixed concentration of PNT (1.0×10^{14} molecule cm^{-3}) and OH

varied in the range $(0.4 - 4.4) \times 10^{12}$ molecule cm^{-3}. Independence of k_2' of the initial concentration of OH for $[OH]_0 < 10^{12}$ molecule cm^{-3} indicates the negligible contribution of the secondary chemistry to the OH loss under experimental conditions of the study ($[OH]_0 \approx 5 \times 10^{11}$ molecule cm^{-3}). Similar picture was also observed in the case of OH reaction with ETN.

Temperature dependences of k_1 and k_2 are shown in Fig. 4 and 5, respectively. The combined uncertainty on the measurements of the rate constants was estimated to be nearly 15%, including statistical error (within a few percent) and those on the measurements of the flows (5%), pressure (2%), temperature (1%) and the absolute concentrations of the nitrates (~ 10%).
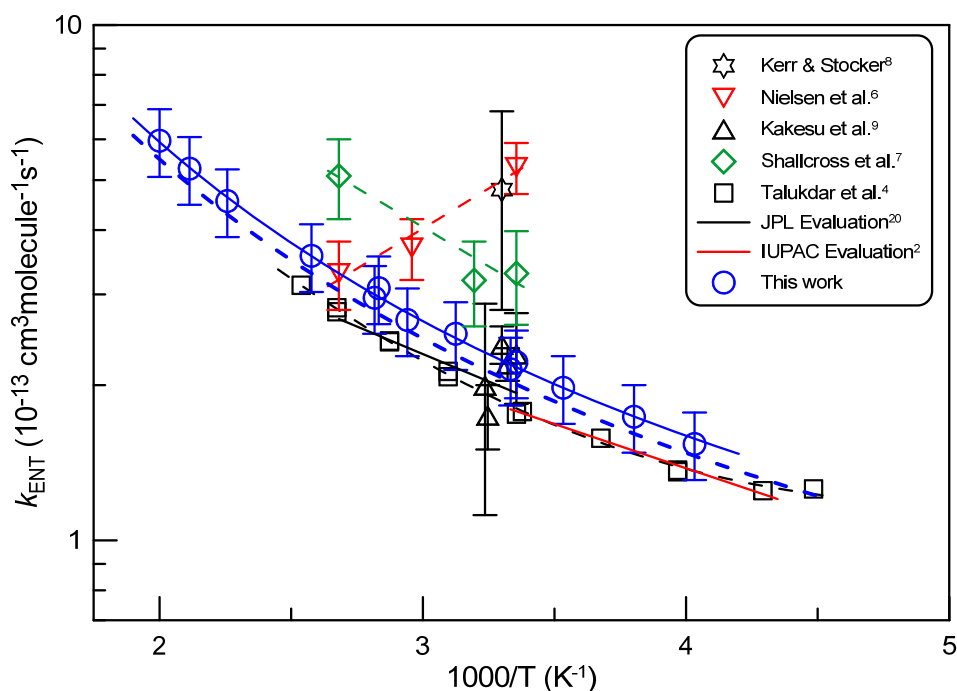

Figure 4 Summary of the measurements of the rate constant of the reaction OH + ethyl nitrate.

Both rate constants increase with temperature, however deviate from a simple Arrhenius behavior. The experimental data were fitted with three-parameter expression, leading to the following results for k_1 and k_2:

$$k_1 = 1.14 \times 10^{-13} \, (T/298)^{2.45} \exp(193/T) \, \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \, (T = 248\text{-}500\text{K}),$$

$$k_2 = 3.00 \times 10^{-13} \, (T/298)^{2.50} \exp(205/T) \, \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \, (T = 263\text{-}500\text{K})$$

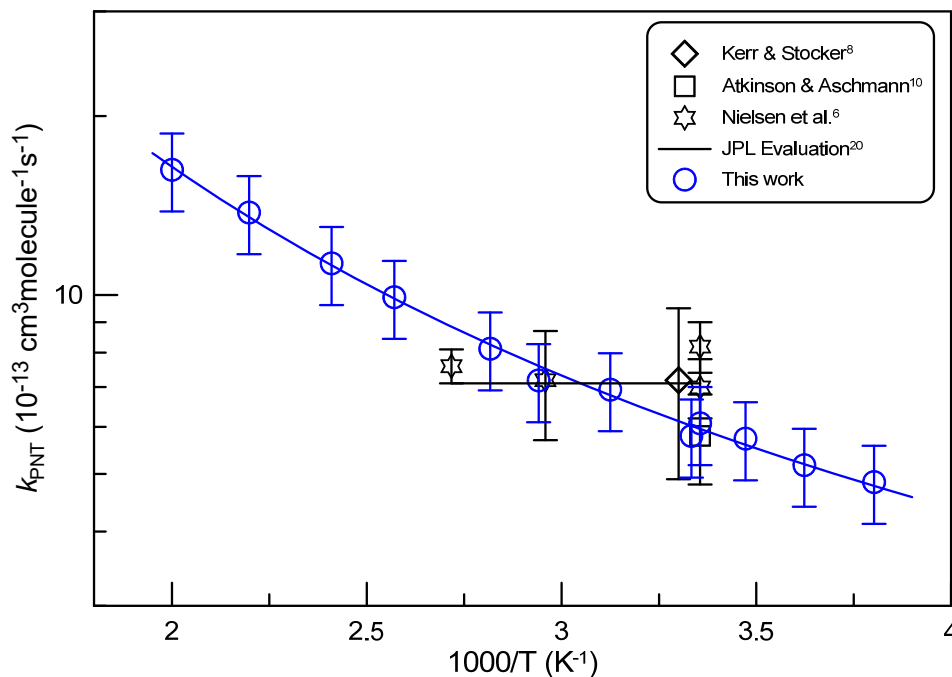with conservative 15% uncertainty.

Figure 5 Summary of the measurements of the rate constant of the reaction OH + propyl nitrate.

Reaction products

In this study, we have determined at T = 300 K the yield of the carbonyl compounds, acetaldehyde and propanal, resulting from the abstraction by OH of an α-hydrogen atom in ethyl and propyl nitrates, followed by α-substituted alkyl radical decomposition. Examples of the kinetics of the product formation along with the kinetics of OH consumption are shown in Fig. 6 and 3S (Supporting Information). Solid and dashed lines in the Figures represent the simulation of the experimental profiles of OH (exponential function) and reaction product, respectively. Temporal profiles of products are fitted with the following equation:

$$[\text{product}] = \alpha \times (k' - k_w')/k' \times [\text{OH}]_0 \times (1 - \exp(-k't)),$$

where α is the product yield, k' and k_w' are the first order rate constants of OH consumption in the presence and in the absence (heterogeneous loss) of nitrate in the reactor, respectively. α was the only fitting parameter. The values of α obtained from the best fit to the acetaldehyde profile in Fig. 6 and propanal profile in Fig. 3S (Supporting Information) were 0.76 and 0.23, respectively.
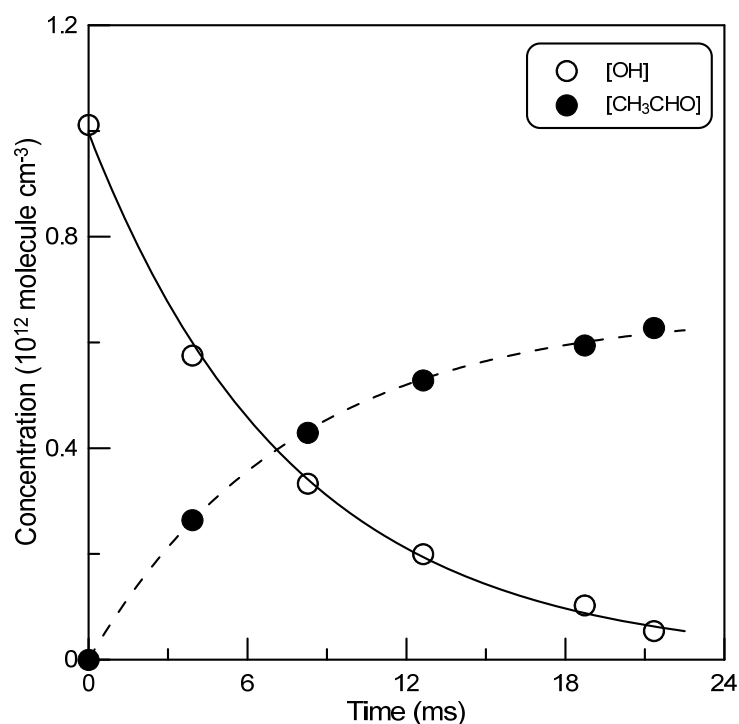

Figure 6 Example of kinetics of OH consumption and acetaldehyde formation in reaction of OH radicals with ethyl nitrate: T = 300K; [ENT] = 5.0×10^{14} molecule cm^{-3}.

The bulk of the experiments on the determination of the yields of acetaldehyde and propanal in reactions (1) and (2) consisted in the monitoring of the consumed [OH] and [CH$_3$CHO] (or [C$_2$H$_5$CHO]) formed at a fixed reaction time of $\approx$ 10 ms. Initial concentrations of the reactants were largely varied: [OH] = $(0.3\text{-}2.7) \times 10^{12}$, [ENT] = $(1.8 - 10.1) \times 10^{14}$ and [PNT] = $(0.6 - 5.4) \times 10^{14}$ molecule cm^{-3}. The experimental data are shown in Fig. 7 and 8. The slopes of the straight lines in Fig. 7 and 8 provide the yields of acetaldehyde and propanal in reactions (1) and (2) at T = 300K: 0.77 $\pm$ 0.12 and 0.22 $\pm$ 0.04, respectively. The estimated nearly 15%

uncertainty on the measurements arises mainly from the combined errors on the measurements of the absolute concentrations of OH and corresponding reaction product.
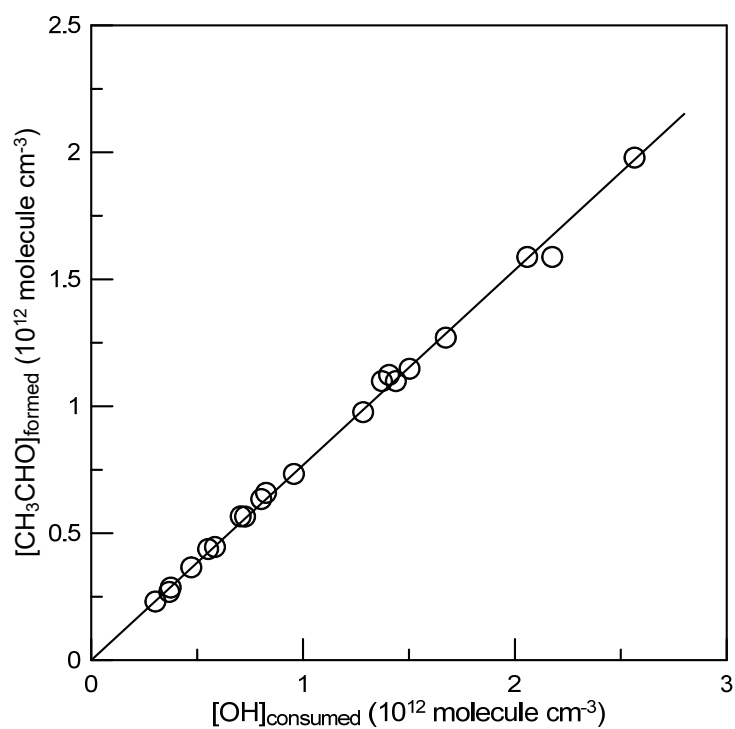

Figure 7 Concentration of acetaldehyde formed in reaction (1) as a function of the consumed concentration of OH.
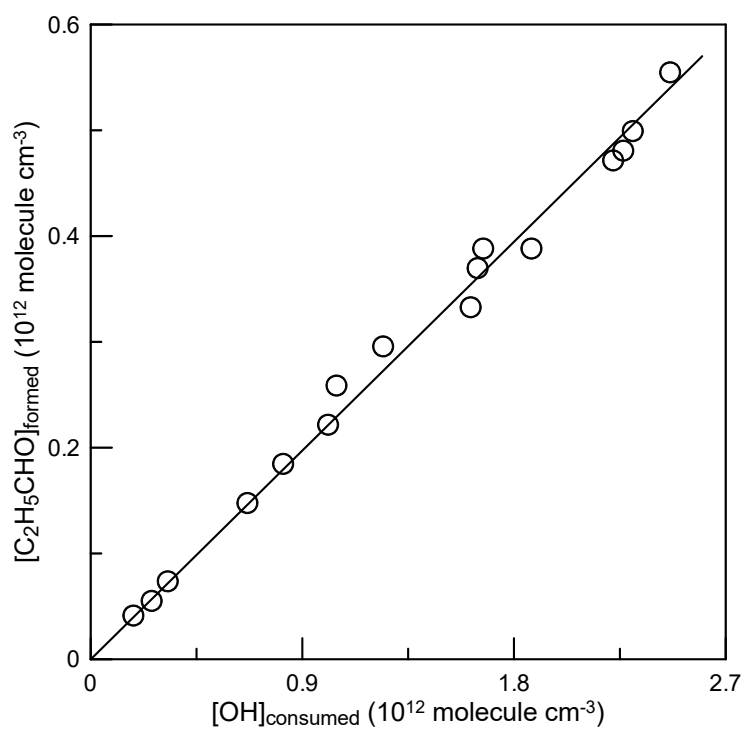

Figure 8 Concentration of propanal formed in reaction (2) as a function of the consumed concentration of OH.

Comparison with previous studies

Previously the rate constant of reaction (1) was measured in two room temperature[8-9] and three temperature dependence studies [3, 6-7]. All these data are shown in Fig. 4 together with those from the present work. Current recommendations for k_1 [2, 20] are based on the experimental data from the most extensive study of reaction (1) by Talukdar et al. [3] who also observed the curvature of the Arrhenius plot and fitted the rate constant data to a sum of two exponentials:

$$k_1 = 3.68 \times 10^{-13} \exp(-1077/T) + 5.32 \times 10^{-14} \exp(126/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperatrure range 223-394K. One can note that the experimental data of Talukdar et al. [3] and those from the present study (fitted to a three-parameter expression) exhibit identical temperature dependence (Fig. 4), the absolute values of k_1 from the present study being systematically higher by 10-15%. In this respect, the expression for k_1 obtained in the present work with somewhat reduced A-factor seems to be a good compromise between the results of two studies (dashed blue line in Fig. 4) and can be recommended for use over the temperature range 220-500K:

$$k_1 = 1.05 \times 10^{-13} (T/298)^{2.45} \exp(193/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}.$$

It can be noted that the experiments of Talukdar et al. [3] were carried out at total pressure of 50-300 Torr with different buffer gases (He, N_2, SF_6), while the data from the present study were obtained at nearly 1 Torr pressure of helium. Good agreement between the results of two studies supports the conclusion of Talukdar et al. [3] that addition of OH to the alkyl nitrate is unlikely, reaction is a bimolecular one and proceeds via abstraction of an H atom from the alkyl group.

For reaction OH + PNT, three relative [6, 8, 10] and one absolute rate [6] measurements are available in the literature (Fig. 5). Temperature dependence of k_2 was explored in only one study: the Arrhenius expression $k_2 = 5.3 \times 10^{-13} \exp(140 \pm 144/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ was reported

in the temperature range T = 298-368K [6]. On the absolute basis, all the previous data are in a reasonable agreement with those from the present work obtained in an extended temperature range. The similarity of the results obtained in previous studies in one atmosphere of air and present data at 1 Torr total pressure of He seems to indicate that rate constant of reaction (2) is pressure independent.

In this study, we have determined at T = 300 K the yields of acetaldehyde and propanal resulting from the decomposition of α-substituted alkyl radicals formed upon initial abstraction by OH of an α-hydrogen atom in ethyl and propyl nitrates, respectively. The measured product yields can be considered as the branching ratios for an α-hydrogen atom abstraction pathway of the respective reactions:

$k_{1a}/k_1 = 0.77 \pm 0.12$,

$k_{2a}/k_2 = 0.22 \pm 0.04$

It can be noted that these values are in good agreement with those estimated within Structure-Activity Relationship (SAR) [21], 0.77 and 0.24 (calculated with substituent factor $F(-O-NO_2)$ = 0.1) [22], for the extent of H-atom abstraction from α carbon in ethyl and propyl nitrate, respectively. However, the total rate constants of the reactions of OH with ENT and PNT calculated within SAR are lower than the experimental values by a factor of 1.8 and 1.3 respectively. Currently, we continue the experimental studies of the kinetics and products of the OH reactions with other alkyl nitrates and hope that the gathered kinetic information will allow to refine the substituent factors for the $-ONO_2$ containing groups used in the calculations of the rate constants.

The tropospheric lifetimes of ENT and PNT, with respect to their loss in reaction with OH only, calculated using the measured rate constants (at T = 298 K) and a 24h average concentration of the OH radical of 10^6 molecules cm^{-3} are 52.6 and 19.2 days, respectively. The tropospheric lifetimes of these nitrates with respect to their photodissociation reported by

Clemitshaw et al. [5] for summer conditions are between 3 and 17 days depending on altitude (0 – 10 km) and latitude (0 – 60°N). Comparison of these data indicates that although photolysis is the dominant atmospheric sink of the nitrates, relative contribution of OH reactions is appreciable even for small less reactive nitrates.

CONCLUSIONS

In this work, we investigated the kinetics and products of the reaction of OH radicals with ethyl and propyl nitrates. The reaction rate constants were measured at T = (248-500) K and, for both reactions, the Arrhenius plots were found to exhibit substantial curvature. Acetaldehyde and propanal were directly detected as products of the OH reactions with ENT and PNT for a first time. Their yields measured at T = 300K, 0.77 $\pm$ 0.12 and 0.22 $\pm$ 0.04, respectively, correspond to the branching ratios for the α-hydrogen atom abstraction pathway of the reactions of OH with ENT and PNT and are in good quantitative agreement with SAR predictions.

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Tables

Table I Summary of the measurements of the rate constant of the reaction OH + ethyl nitrate

T (K)	Reactor surface[a]	Number of kinetics	$[C_2H_5ONO_2]$ (10^{14} molecule cm^{-3})	k_1[b] (10^{-13} cm^3molecule^{-1}s^{-1})
248	HW	7	1.1-9.1	1.54
263	HW	7	0.4-7.4	1.74
283	HW	6	0.9-8.4	1.98
298	HW	9	0.2-5.7	2.22
300	HW	6	0.8-8.1	2.15
320	HW	6	1.6-9.2	2.52
340	HW	7	1.3-8.7	2.68
353	Q	6	0.2-2.7	3.09
355	HW	6	0.8-7.0	2.96
388	Q	6	0.4-3.0	3.57
443	Q	6	0.3-2.9	4.56
473	Q	7	0.2-2.3	5.27
500	Q	6	0.3-2.9	5.97

[a] HW: halocarbon wax, Q: quartz
[b] Estimated uncertainty on k_1 is nearly 15%.

Table II Summary of the measurements of the rate constant of the reaction OH + propyl nitrate

T (K)	Reactor surface[a]	Number of kinetics	$[C_3H_7ONO_2]$ (10^{14} molecule cm^{-3})	k_2[b] (10^{-13} cm^3molecule^{-1}s^{-1})
263	HW	6	0.4-3.0	4.85
276	HW	6	0.6-4.0	5.18
288	HW	6	0.5-3.0	5.74
298	HW	7	0.2-2.3	6.09
300	HW	6	0.3-2.4	5.80
320	HW	6	0.4-2.7	6.94
340	HW	6	0.5-3.2	7.19
355	HW	6	0.5-3.2	8.13
389	Q	7	0.2-1.2	9.93
415	Q	7	0.2-2.3	11.32
455	Q	9	0.2-1.5	13.78
500	Q	8	0.2-1.9	16.26

[a] HW: halocarbon wax, Q: quartz
[b] Estimated uncertainty on k_2 is nearly 15%.