

Experimental Study of the Reaction of Isopropyl Nitrate with OH Radicals: Kinetics and Products.

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ABSTRACT: The kinetics of the reaction of isopropyl nitrate (IPN) with OH radicals has been studied using a low pressure flow tube reactor coupled with a quadrupole mass spectrometer: $\text{OH} + (\text{CH}_3)_2\text{CHONO}_2 \rightarrow \text{products}$ (2). The rate constant of the title reaction was determined using both absolute method, monitoring the kinetics of OH radicals consumption in excess of IPN, and the relative rate method using the reaction of OH with Br_2 as reference one and following HOBr formation. As a result of the absolute and relative measurements, the overall rate coefficients, $k_2 = (6.6 \pm 1.2) \times 10^{-13} \exp(-(233 \pm 56)/T)$ was determined at a pressure of 1 Torr of helium over the temperature range 268 – 355 K. Acetone, resulting from H-atom abstraction from the tertiary C-H bond of IPN followed by 2-nitroso-2-propyl radical decomposition, was found to be a major reaction product with the yield of 0.82 ± 0.13 , independent of temperature in the range 277 – 355 K.

Keywords: Hydroxyl radical, alkyl nitrates, rate coefficient, reaction products, acetone.

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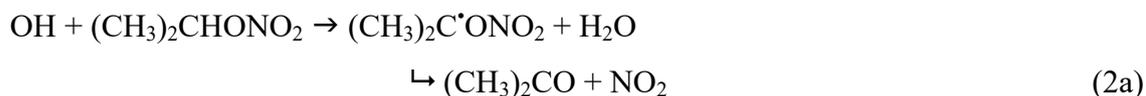
INTRODUCTION

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 channel (1b) of the reaction of peroxy radicals with NO:



and also in the NO₃-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 the reactivity of nitrates toward OH radicals and their photolysis rate [2-5]. Photolysis of organic nitrates is known to produce NO₂ and alkoxy radicals. The products of OH radical initiated degradation of nitrates are not so well characterized, in particular, with regard to the release of NO₂. The understanding of the complex multistep mechanism of the atmospheric oxidation of nitrates requires first of all the information on kinetics and primary products of their initial reaction with OH.

In the present work, we report the results of the experimental investigation of the reaction of isopropyl nitrate with OH radicals. This reaction is of special kinetic and mechanistic interest, since it is expected to proceed to a great extent via tertiary H-atom abstraction [6], followed by rapid decomposition of 2-nitroxy-2-propyl radical formed [7], leading to recycling of NO₂ (reaction 2a):



Previously, the reaction rate constant was measured in two relative rate kinetic studies, at room temperature and 760 Torr total pressure [8,9], and with an absolute rate method in the temperature range 233 - 395 K [3]. There is roughly a factor of two spread in the values of the rate coefficient reported in the three studies at room temperature. The existing uncertainty on the rate constant is reflected also by a difference of factor 1.4 in the recommendations of JPL [10] and IUPAC [2] evaluations. In the present paper we report complementary results on reaction (2), including temperature dependence of k_2 , and branching ratio for the acetone forming channel (2a) as a function of temperature.

EXPERIMENTAL

Experiments were carried out in a discharge flow reactor using a modulated molecular beam mass spectrometer as the detection method [11-15]. The main reactor, shown in Fig. 1 along with the movable injector of the reactants, consisted of a Pyrex tube (45 cm length and 2.4 cm i.d.) with a jacket for the thermostated liquid circulation (water or ethanol). The walls of the reactor as well as of the injector were coated with halocarbon wax in order to minimize the heterogeneous loss of active species.

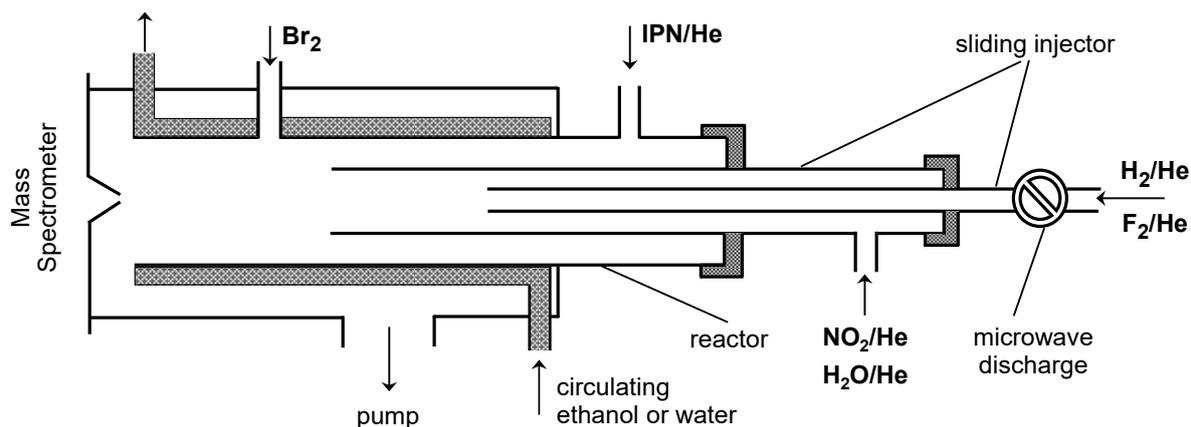


Figure 1 Diagram of the flow reactor.

Two different methods were used for the generation of OH radicals. In the first one, the fast reaction of hydrogen atoms with NO_2 was used, H atoms being produced in a microwave discharge of H_2/He mixture:



NO_2 was always used in excess over H atoms. In the second method, OH radicals were produced in the reaction of F atoms with an excess of H_2O , with F atoms formed in the microwave discharge of F_2/He mixtures



To reduce F atom reactions with glass surface inside the microwave cavity, a ceramic (Al_2O_3) tube was inserted in this part of the injector. OH radicals were detected as HOBr^+ ($m/z = 96/98$) after scavenging by an excess of Br_2 ($[\text{Br}_2] = (5-10) \times 10^{13} \text{ molecule cm}^{-3}$, added at the end of the reactor, 5 cm upstream of the sampling cone) via reaction:



This method for OH detection was preferred to the direct detection of these radicals at $m/z = 17$ (OH^+) due to significant contributions of water vapor (traces or precursor of OH) at this mass. Similarly, the chemical conversion of OH to HOBr was used for the measurements of the absolute concentrations of the radicals: $[\text{OH}] = [\text{HOBr}] = \Delta[\text{Br}_2]$, i.e. concentrations of OH were determined from the consumed fraction of $[\text{Br}_2]$. $[\text{Br}_2]$ 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 [11,12].

Isopropyl nitrate was introduced into the flow reactor by passing Helium through a thermostated glass bubbler containing liquid IPN and was detected by mass spectrometry at its fragment peak at $m/z = 90$ ($\text{CH}_3\text{CHONO}_2^+$), which was much more intensive than the parent one ($m/z = 105$). All other species were detected at their parent peaks: $m/z = 58$ (acetone, $\text{C}_3\text{H}_6\text{O}^+$), 160 (Br_2^+), 96/98 (HOBr^+), 46 (NO_2^+), 30 (NO^+), 18 (H_2O^+). The absolute concentrations of IPN 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 purities of the 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); F_2 , 5% in helium (Alphagaz); NO_2 > 99% (Alphagaz). Isopropyl nitrate > 99.0% (Sigma-Aldrich), was degassed before use; acetone > 99.8 (Sigma-Aldrich).

RESULTS AND DISCUSSION

Rate constant of reaction (2)

Absolute measurements. The measurements of the rate constant of reaction (2) were carried out under pseudo-first order conditions in high excess of isopropyl nitrate over OH radicals. The initial concentration of OH radicals was $(0.3\text{-}0.8) \times 10^{12}$ molecule cm^{-3} , and the initial concentration of IPN was varied in the range $(0.2\text{-}22.4) \times 10^{14}$ molecule cm^{-3} . The flow velocity in the reactor was $(900\text{-}1400)$ cm s^{-1} . The concentrations of OH radical and isopropyl nitrate were simultaneously measured as a function of reaction time. A consumption of IPN was negligible as a result of the sufficient excess of IPN over OH radicals. Examples of the exponential decay kinetics of OH in reaction (2) are shown in Fig. 2.

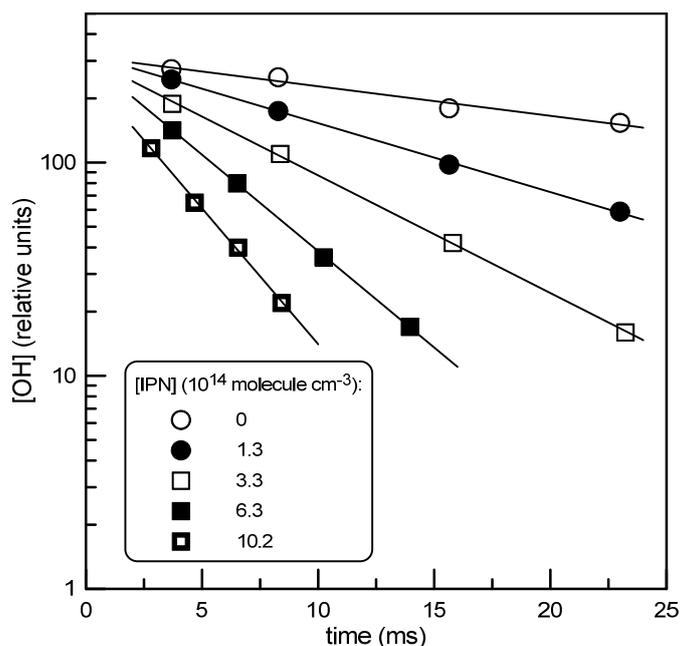


Figure 2 Examples of the exponential decay kinetics of OH in reaction (2): $T = 293$ K; OH source, reaction $H + NO_2$.

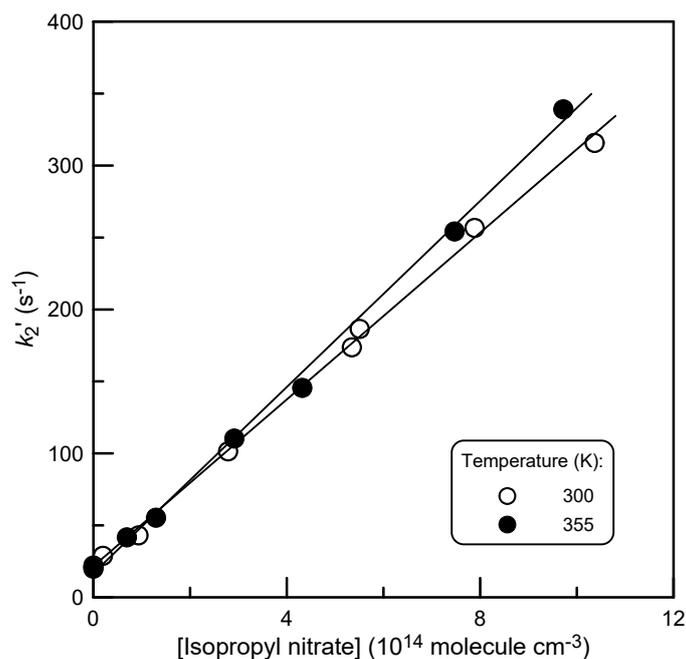


Figure 3 Example of pseudo-first order plots obtained from OH decay kinetics in excess of isopropyl nitrate ($T = 300$ and 355 K).

Fig. 3 shows the pseudo-first order rate constant, $k_2' = k_2[\text{IPN}] + k_w$, as a function of the concentration of isopropyl nitrate. k_w represents the rate of OH decay in the absence of IPN in the reactor and was measured in separate experiments. All the measured values of k_2' were corrected for axial and radial diffusion [16] of OH. The diffusion coefficient of OH in He was calculated using the following expression: $D_0 = 640 \times (T/298)^{1.85} \text{ Torr cm}^2 \text{ s}^{-1}$ [17-19].

Corrections were generally less than 10%, however, for a few kinetic runs they reached up to 25%. The slopes of the straight lines in Fig. 3 give the values of k_2 at respective temperatures. The intercepts are in good agreement with the corresponding OH loss rate measured in the absence of isopropyl nitrate in the reactor. All the results obtained for k_2 within the described approach and at different temperatures are shown in Table 1. At negative temperatures in the reactor, we have observed an abnormal increase of the reaction rate constant, which was attributed to the heterogeneous reaction of OH with surface-adsorbed nitrate. For this reason the measurements of the rate constant were limited to relatively high temperatures (Table 1).

The possible impact on the measurements of k_2 of the secondary reactions of OH radicals with primary products of reaction (2) was explored in separate series of experiments at $T = 300$ K, where the rate of reaction (2) was measured for fixed concentration of IPN (5.5×10^{14} molecule cm^{-3}) with four different $[\text{OH}]_0$ varied in the range $(0.3 - 2.5) \times 10^{12}$ molecule cm^{-3} . The measured reaction rate $k_2' = (180 \pm 17) \text{ s}^{-1}$ was found to be independent (within 10%) of the initial concentration of OH, indicating the negligible contribution of the secondary chemistry to the OH loss.

Relative rate measurements. The rate constant of reactions (2) was measured using reference reaction of OH with Br_2 . The experiments consisted in a fast titration of the initial concentration of OH radicals, $[\text{OH}]_0$, by a mixture of excess IPN and Br_2 and the measurements of HOBr yield as a function of the $[\text{IPN}]/[\text{Br}_2]$ ratio. The concentration of HOBr formed was defined by the fraction of $[\text{OH}]_0$ reacting with Br_2 :

$$[\text{HOBr}] = \frac{k_5[\text{Br}_2]}{k_5[\text{Br}_2] + k_2[\text{IPN}]} \times [\text{OH}]_0$$

Considering the derived expression,

$$\frac{[\text{OH}]_0}{[\text{HOBr}]} - 1 = \frac{k_2[\text{IPN}]}{k_5[\text{Br}_2]} \quad (\text{I})$$

k_2/k_5 , and hence k_2 , could be obtained by plotting $([\text{OH}]_0/[\text{HOBr}] - 1)$ as a function of the $[\text{IPN}]/[\text{Br}_2]$ ratio. It can be noted that this method did not need absolute calibration of the mass-spectrometric signals for OH radicals and HOBr because the initial concentration of OH could be expressed as HOBr signal in the absence of isopropyl nitrate, when OH is titrated with an excess of Br_2 . Thus, in the experiments, only the HOBr signal was detected, first in the IPN-free system, corresponding to $[\text{OH}]_0$, and then in the Br_2 and IPN-containing system, corresponding to the fraction of $[\text{OH}]_0$ reacted with Br_2 . The initial concentration of OH radicals in these experiments was nearly 2×10^{12} molecule cm^{-3} . The concentration ranges of

isopropyl nitrate and Br₂ used in these experiments are shown in Table 2. The reaction time was typically ≈ 20 ms.

Fig. 4 shows experimental data observed at T = 277 and 347 K. According to expression I, the slopes of the linear dependences in Fig. 4 give the k_2/k_5 ratios. All the results obtained in this way for k_2/k_5 as well as the final results obtained for k_2 are presented in Tables 2.

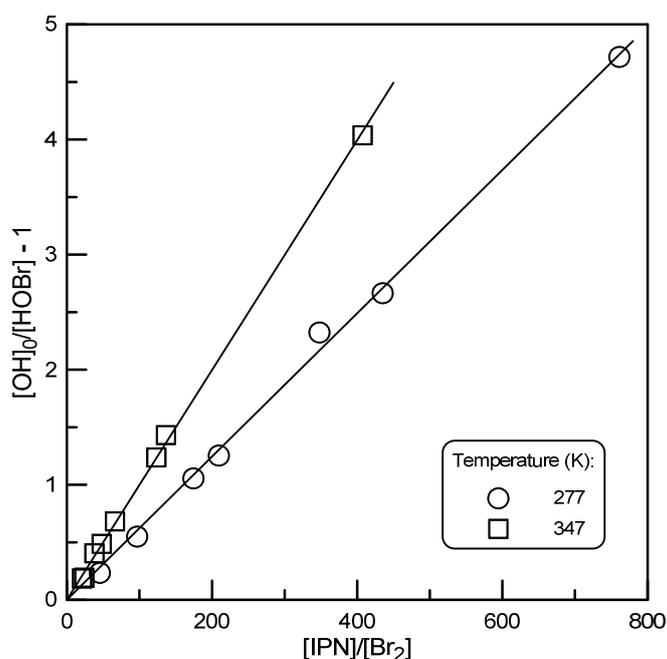


Figure 4 HOBr yield from OH titration with Br₂ + isopropyl nitrate mixtures at different temperatures (see equation (I) in the text).

The values of k_5 used in the calculations of k_2 were determined from the Arrhenius expression $k_5 = 1.9 \times 10^{-11} \exp(235/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This last expression is based on two previous studies of reaction (5) [12,20], where similar values were measured for the activation factor, $E/R = 235$ [12] and 238 K [20], and the difference between the reported preexponential factors was around 10%.

Temperature dependence of k_2 . All the results obtained for k_2 in the present study are shown in Table 1 and Fig. 5 (open symbols). The combined uncertainty on the measurements of the rate constants was estimated to be in the range 15-20%, including statistical error and those on the measurements of the flows, pressure, temperature and the absolute concentrations of the relevant species. The unweighted exponential fit to the present data for k_2 yields the following Arrhenius expression:

$$k_2 = (6.6 \pm 1.2) \times 10^{-13} \exp(-233 \pm 56/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

where the cited uncertainties are 1σ statistical ones.

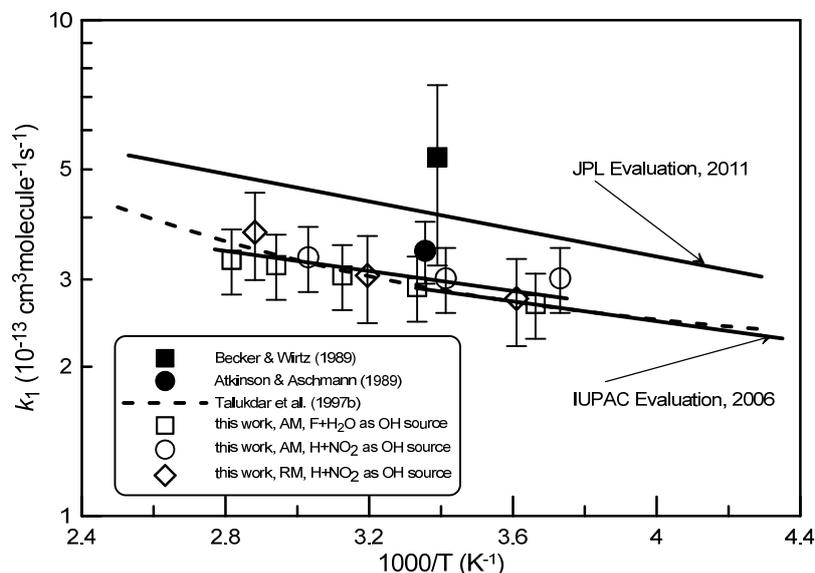


Figure 5 Summary of the measurements of the rate constant of the reaction OH + isopropyl nitrate. For the data from this study: AM, absolute measurements; RM, relative rate method.

Reaction products.

The formation of the reaction product was clearly observed at $m/z = 58$ (and attributed to acetone) despite the relatively high background signal at this mass due to fragmentation of the isopropyl nitrate in the ion source of the mass spectrometer. Example of the kinetics of the product formation along with the kinetics of OH decay is shown in Fig. 6. Solid lines in Fig. 6 represent the results of simulation of the experimental data. Temporal profile of acetone was fitted with the following equation:

$$[\text{acetone}] = \alpha \times (k_2' - k_w') / k_2' \times [\text{OH}]_0 \times (1 - \exp(-k_2't)),$$

where α is the acetone yield in reaction (2), k_2' and k_w' are the first order rate constants of OH consumption in the presence and in the absence (heterogeneous loss) of IPN in the reactor, respectively. α was the only fitting parameter; $k_2' = 55 \text{ s}^{-1}$ and $k_w' = 19 \text{ s}^{-1}$ (for the data in Fig. 6) were determined from the exponential fit of the OH decays in reaction with IPN (Fig. 6, open symbols) and on the wall of the reactor (not shown), respectively. The value of α obtained from the best fit to the acetone profile in Fig. 6 is 0.76.

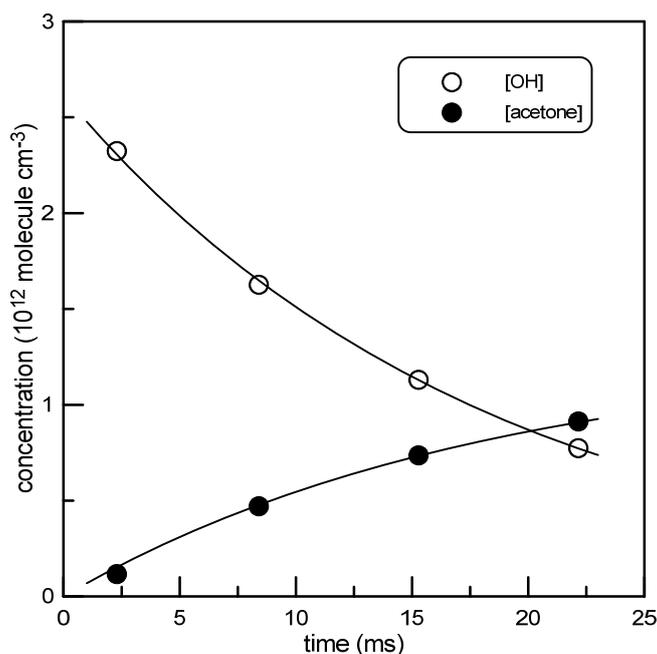


Figure 6 Example of kinetics of OH consumption and acetone formation in reaction of OH radicals with isopropyl nitrate: $T = 300\text{K}$; $[\text{IPN}] = 1.3 \times 10^{14} \text{ molecule cm}^{-3}$; OH source, reaction $\text{F} + \text{H}_2\text{O}$.

The branching ratio for acetone forming reaction pathway (2a) was measured at different temperatures in the reactor. Experiments consisted in the monitoring of the OH consumption and acetone formation in the reaction of OH with isopropyl nitrate. Initial concentrations of the reactants were largely varied: $[\text{OH}] = 2.8 \times 10^{11} - 2.5 \times 10^{12}$, $[\text{IPN}] = 2.0 \times 10^{13} - 3.7 \times 10^{14} \text{ molecule cm}^{-3}$. Typical reaction time was $\approx 20 \text{ ms}$. The formation of acetone at $m/z = 58$ was monitored by switching on and off the OH source (microwave discharge). It can be noted that the background signal at $m/z = 58$ (from IPN fragmentation) was not changed upon switch on and off of the microwave discharge, since no consumption of IPN was observed in these experiments. The fraction of [OH] consumed in reaction with isopropyl nitrate (and not on the wall of the reactor) was determined from the reduction of the OH concentration upon addition of IPN in the reactor. Example of the experimental data observed at $T = 300 \text{ K}$ is shown in Fig. 7. One can note good agreement between the results obtained with different methods of the generation of OH radical, indicating that the possible reactions of the radical precursors, NO_2 and H_2O , with $(\text{CH}_3)_2\text{C}'\text{ONO}_2$ formed in the first step of the reaction (2a) are not competitive with its decomposition. The slope of the straight line in Fig. 7 provides the branching ratio for the acetone forming channel of reaction (1): 0.77 at $T = 300\text{K}$. All the results obtained in this way for k_{2a}/k_2 at different temperatures are shown in Table 3.

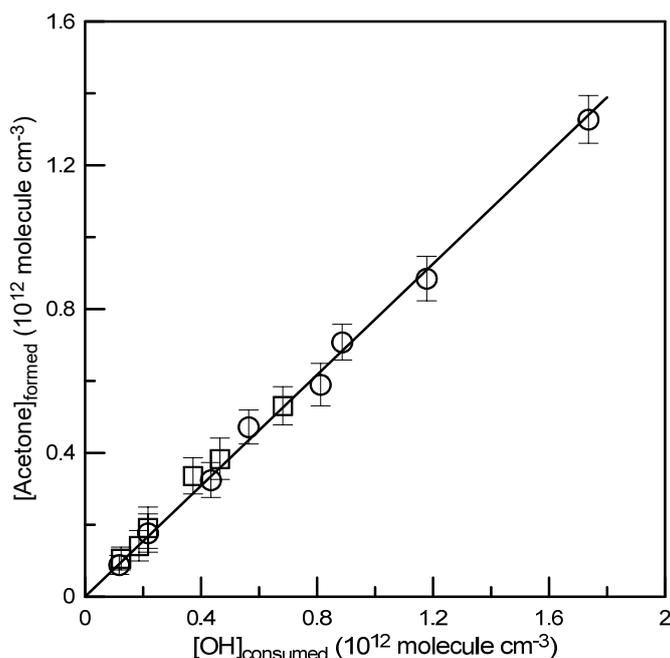


Figure 7 Concentration of acetone formed in reaction (2) as a function of the consumed concentration of OH: T = 300 K. Source of OH radicals: circles, reaction H + NO₂; squares, reaction F + H₂O.

The k_{2a}/k_2 ratio can be considered as independent of temperature between 277 and 355 K, and a mean value

$$k_{2a}/k_2 = 0.82 \pm 0.13$$

can be recommended from this study, with estimated uncertainty of nearly 15%.

An attempt was undertaken to detect the co-product of acetone, NO₂. Direct detection of NO₂ by mass spectrometry on its parent peak $m/z = 46$ (NO₂⁺) was impossible, because of the very strong contribution of the isopropyl nitrate fragment on this mass. We have tried to monitor the fragment peak of NO₂ on $m/z = 30$ (NO⁺), where the contribution of IPN was much lower. Indeed, increase of the signal at $m/z = 30$ was clearly observed upon reaction of OH with isopropyl nitrate. If this signal is entirely attributed to the production of NO₂, then the calculated yield of NO₂ is 1.7 ± 0.3 , independent of temperature in the temperature range 277-355 K. This abnormal yield of NO₂ indicates that, besides NO₂, other species - products of reaction (2), contribute to the signal at $m/z = 30$, preventing correct measurement of the NO₂ yield.

Comparison with previous data.

Previously, the rate constant of reaction (2) was measured in two relative rate kinetic studies, at room temperature and 760 Torr total pressure, $k_2 = (5.3 \pm 2.1) \times 10^{-13}$ [8] and $(3.83 \pm 0.49) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [9], and with an absolute rate method in the temperature range 233 - 395 K: $k_2 = 4.3 \times 10^{-12} \exp(-1250/T) + 2.5 \times 10^{-13} \exp(-32/T)$ [3]. All these results are shown in Fig. 5 together with the data from the present study. Also shown are the current recommendations from the JPL [10], $k_2 = 1.2 \times 10^{-12} \exp(-320/T)$ and IUPAC [2], $6.2 \times 10^{-13} \exp(-230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230 – 300 K, evaluations, the first one being based on the mean of the room temperature values from the three previous studies and temperature dependence from Talukdar et al [3] and the second one, essentially, on the data of Talukdar et al [3]. The values of k_2 measured in the present study are in excellent agreement with the data of Talukdar et al [3] and support the current recommendation of IUPAC [2]. It should 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, O₂, SF₆), while the data from the present study were obtained at nearly 1 Torr pressure of helium. The 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. Product data from the present study also point in favor of this mechanism.

In a previous study of Aschmann et al [21], the products of the OH-initiated degradation of isopropyl nitrate were investigated in a smog chamber, at room temperature and 740 Torr total pressure of air, and in presence of NO in the reactive system. Acetone was the only reported quantified product with a yield of 58±18%. This value is in a satisfactory agreement with that from the present study, 82±13%, considering the reported uncertainties. In a theoretical study of Vereecken [7], α -nitroxy-substituted alkyl radicals were shown to be unstable, dissociating spontaneously without an energetic barrier to form a carbonyl compound and NO₂. In this respect, the measured acetone yield is in good agreement with the value of 78% which can be predicted using the estimation method [6] for the extent of H-atom abstraction from the tertiary C-H bond followed by 2-nitroxy-2-propyl radical, (CH₃)₂C•ONO₂, decomposition [7] to acetone and NO₂. It should be noted that the study of Aschmann et al [21] was carried out at 1 atm total pressure of air, while the data from the present work were obtained at nearly 1 Torr pressure of helium. The good agreement between the results from the two studies indicates that the rate of the prompt (CH₃)₂C•ONO₂ radical

decomposition under atmospheric conditions is much higher than the rate of its possible stabilization and/or reaction with O₂ in agreement with the conclusion of Vereecken [7] that the radical decomposition occurs on timescales that are too short for any chemical process to compete.

CONCLUSION

In this work, we investigated the kinetics and products of the reaction of OH radicals with isopropyl nitrate (IPN) in the temperature range between 277 and 355 K. The temperature dependence of the reaction rate constant, measured using both absolute and relative rate methods, is in excellent agreement with the data from the sole previous study. Acetone was directly detected as a primary product of the OH reaction with IPN for a first time. The measured relatively high yield of acetone, 0.82 ± 0.13 , indicates that the main channel of the IPN reaction with OH leads to NO₂ (co-product of acetone) recycling from the nitrate. In addition, the measured acetone yield is in good quantitative agreement with the theoretical predictions for the extent of H-atom abstraction from the tertiary C-H bond followed by 2-nitroso-2-propyl radical, (CH₃)₂C[•]ONO₂, decomposition to acetone and NO₂.

This study was supported by ANR from an ONCEM grant.

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TABLES

Table 1 Summary of the measurements of the rate constant of the reaction OH + isopropyl nitrate.

T, K	^a k_2 , 10^{-13} cm ³ molecule ⁻¹ s ⁻¹	^b Method
268	3.02	AM/H+NO ₂
273	2.68	AM/F + H ₂ O
277	2.75	RM
293	3.02	AM/H+NO ₂
300	2.90	AM/F + H ₂ O
313	3.06	RM
320	3.06	AM/F + H ₂ O
330	3.33	AM/H+NO ₂
340	3.21	AM/F + H ₂ O
347	3.74	RM
355	3.29	AM/F + H ₂ O

^a Typical uncertainty on k_2 is nearly 15%.

^b AM/H+NO₂ and AM/F+H₂O: absolute rate measurements with H + NO₂ and F + H₂O reactions as OH source, respectively; RM: relative rate method with OH + Br₂ as reference reaction.

Table 2 Experimental conditions and results of the relative measurements of k_2 using OH + Br₂ (k_5) as reference reaction.

^a No./exp.	T, K	^b [IPN]	^c [Br ₂]	[IPN]/[Br ₂]	k_2/k_5	^d k_2
7	277	3.9-4.6	0.6-9.4	45-761	0.0062	2.75
7	313	3.8-5.3	0.5-42.0	9-1045	0.0076	3.06
8	347	4.6-4.8	1.1-22.0	21-407	0.0100	3.74

^a Number of data points; ^b units of 10^{14} molecule cm⁻³; ^c units of 10^{12} molecule cm⁻³; ^d units of 10^{-13} cm³ molecule⁻¹ s⁻¹, estimated uncertainty on k_2 is nearly 20%.

Table 3 Acetone yield in the reaction of OH with isopropyl nitrate as a function of temperature.

^a No./exp.	T (K)	^b k_{2a}/k_2
6	277	0.82
6	288	0.87
14	300	0.77
5	320	0.78
5	340	0.79
5	355	0.89
		mean: 0.82±0.05

^a Number of experimental runs.

^b Typical uncertainty on k_{2a}/k_2 is nearly 15%.