



Thermal decomposition of *n*-propyl and *n*-butyl nitrates: Kinetics and products



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ABSTRACT

Thermal decomposition of *n*-propyl ($C_3H_7ONO_2$, PPN) and *n*-butyl ($C_4H_9ONO_2$, BTN) nitrates has been studied in a low pressure flow reactor combined with a quadrupole mass spectrometer. The rate constants of the nitrates decomposition were measured as a function of pressure (0.95–12.8 Torr of helium) and temperature in the range 473–659 K using two different approaches: from kinetics of nitrate loss and those of the formation of the reaction products. The fit of the observed falloff curves with two parameter

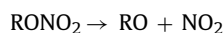
expression $k = \frac{k_0 k_\infty [M]}{k_0 [M] + k_\infty} \times 0.6^{(1 + (\log(\frac{k_0 [M]}{k_\infty}))^2)^{-1}}$ provided the following low and high pressure limits for the rate constants of the nitrates decomposition: $k_0(\text{PPN}) = 0.68 \times 10^{-4} \exp(-15002/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_\infty(\text{PPN}) = 7.34 \times 10^{15} \exp(-19676/T) \text{ s}^{-1}$, $k_0(\text{BTN}) = 2.80 \times 10^{-4} \exp(-15382/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_\infty(\text{BTN}) = 7.49 \times 10^{15} \exp(-19602/T) \text{ s}^{-1}$, which allow to reproduce (via above expression and with 20% uncertainty) all the experimental data obtained for the rate constants of PPN and BTN decomposition in the temperature and pressure range of the study. It was observed that the initial step of the thermal decomposition of the nitrates is O–NO₂ bond cleavage leading to formation of NO₂ and alkoxy radical, which rapidly decomposes or isomerizes to form C₂H₅ and formaldehyde and C₃H₇, CH₂O and hydroxybutyl radical as final products of PPN and BTN decomposition, respectively. In addition, the kinetic data were used to determine the O–NO₂ bond dissociation energy of 38.0 ± 1.2 and $37.8 \pm 1.0 \text{ kcal mol}^{-1}$ in PPN and BTN, respectively.

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1. Introduction

Organic nitrates are important species in atmospheric and combustion chemistry. In the atmosphere, they are formed in a minor addition channel of the reaction of peroxy radicals with NO and also in the NO₃-initiated oxidation of unsaturated organic compounds [1]. Organic nitrates are considered as stable species with atmospheric lifetimes of several days or weeks (depending on their photolysis rate and reactivity toward OH radicals [2]), and play a key role in the distribution of reactive nitrogen by undergoing long-range transport in the free troposphere. In combustion processes, nitrates, used as fuel additives, are known to promote the ignition of diesel fuel. Production of chain-initiating radicals and, possibly, the heat released during nitrate decomposition in the pre-ignition phase are thought to decrease the ignition-delay time [3–5].

Thermal decomposition of acyclic nitrates is supposed to proceed through a radical mechanism with initial dissociation of the O–NO₂ bond leading to formation of NO₂ and alkoxy radical (RO):



The alkoxy radicals can undergo a number of competing reaction pathways, including unimolecular decomposition, which usually occurs through C–C bond fission to produce a carbonyl compound, and a unimolecular isomerization, which generates a hydroxy-substituted alkyl radical [6].

Although thermal decomposition of nitrates has been studied previously for several times [7–15], available quantitative information on the rate constants and products of these reactions is very scarce. To our knowledge, no experimental data are available for thermal decomposition of *n*-butyl nitrate and those for *n*-propyl nitrate pyrolysis were reported in two studies only [13,16]. In our recent paper [17], we have reported the results of the experimental study of the kinetics and products of the thermal decomposition of isopropyl nitrate. In the present work, we applied a similar experimental approach to study thermal decomposition of *n*-propyl (PPN) and *n*-butyl (BTN) nitrates, including the measurements of the rate

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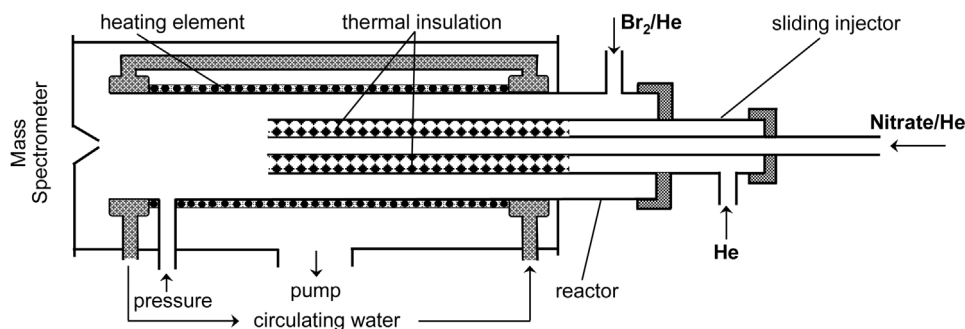
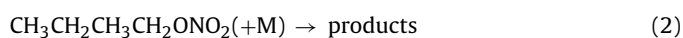
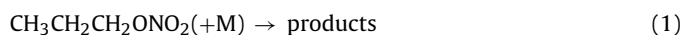


Fig. 1. Diagram of the flow reactor.

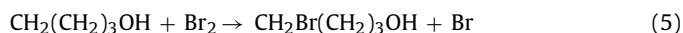
constants as a function of pressure and temperature and identification and quantification of the reaction products:



2. Materials and methods

Thermal decomposition of the nitrates was studied at a total pressure of helium between 0.95 and 12.8 Torr and in the temperature range (473–659) K. Experiments were carried out in a flow reactor using a modulated molecular beam electron impact ionization (with ion source operating at 25–30 eV) mass spectrometer as the detection method [17,18]. The flow reactor (Fig. 1) consisted of a Quartz tube (45 cm length and 2.5 cm i.d.) with an electrical heater and water-cooled extremities [18]. 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 gradient along the flow tube measured with a thermocouple inserted in the reactor through the movable injector was less than 1% [18].

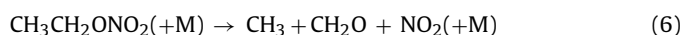
The nitrates were introduced into the flow reactor through the movable injector (that allowed to vary their residence time in the reactor) from a 10L flasks containing nitrate-He mixture or (when high concentrations of the nitrates were needed) by passing helium through a thermostated glass bubbler containing liquid nitrate. The inner tube of the injector, through which nitrates were supplied, was thermally insulated in order to minimize their possible decomposition prior introduction into the main reactor (Fig. 1). Both nitrates was detected by mass spectrometry at their fragment peak at $m/z=76$ ($\text{CH}_2\text{ONO}_2^+$), which is much more intensive than the parent ones (at $m/z=105$ and 119, for PPN and BTN, respectively). C_2H_5 , C_3H_7 and hydroxybutyl ($\text{C}^*\text{H}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$) radicals were detected as bromoethane, 1-bromopropane and 4-bromo-1-butanol at $m/z=108/110$ ($\text{C}_2\text{H}_5\text{Br}^+$), 122/124 ($\text{C}_3\text{H}_7\text{Br}^+$) and fragment peak 134/136 ($\text{CH}_2\text{Br}(\text{CH}_2)_2\text{CH}^+$), respectively, after being scavenged by an excess of Br_2 ($[\text{Br}_2] \sim 5 \times 10^{13} \text{ molecule cm}^{-3}$) via reactions [19]:



All other species were detected at their parent peaks: $m/z=30$ (formaldehyde, CH_2O^+), 160 (Br_2^+), 46 (NO_2^+).

The absolute calibration of mass spectrometer for formaldehyde was realized by injecting known amounts (0.2–0.8 μL) of the 36.5% wt solution of CH_2O in water inside the flow tube, and recording the parent mass peak intensity of CH_2O at $m/z=30$. The integrated area of the mass spectrometric signals corresponding to known total number of CH_2O molecules injected into the reactor allowed the determination of the calibration factor. Similar procedure was

applied for the measurements of the absolute concentrations of 4-bromo-1-butanol. Another alternative method used for absolute calibrations of CH_2O consisted in thermal decomposition of ethyl nitrate (at $T \geq 600 \text{ K}$) in the presence of Br_2 in the reactor:



(products of this reaction were studied in an unpublished work from our group). Experimentally, total consumption of the nitrate and appearance of the decomposition products, NO_2 and CH_2O , was observed and absolute concentrations of the species could be determined in accordance with: $[\text{CH}_2\text{O}] = [\text{NO}_2] = [\text{C}_2\text{H}_5\text{ONO}_2]_0$. The results of this calibration method were in good agreement (within 10–15%) with that by injection of CH_2O and measurements of $[\text{NO}_2]$ from their calibrated mixtures. The absolute calibration of mass spectrometer for other stable species (Br_2 , $\text{C}_2\text{H}_5\text{Br}$, $\text{C}_3\text{H}_7\text{Br}$, $\text{C}_2\text{H}_5\text{ONO}_2$, $\text{C}_3\text{H}_7\text{ONO}_2$, $\text{C}_4\text{H}_7\text{ONO}_2$) was realized through calculation of their absolute concentrations in the reactor from their flow rates obtained from the measurements of the pressure drop of their mixtures in He stored in calibrated volume flasks.

Ethyl and *n*-propyl nitrates were synthesized in the laboratory via slow mixing of the corresponding alcohol with $\text{H}_2\text{SO}_4:\text{HNO}_3$ (1:1) mixture at temperature $< 5^\circ\text{C}$ [20,21]. The synthesized nitrate was degassed before use. The purities and origin of other gases used were as follows: He > 99.9995% (Alphagaz); Br_2 > 99.99% (Aldrich); NO_2 > 99% (Alphagaz); 36.5% wt solution of formaldehyde in water (Sigma-Aldrich); *n*-butyl nitrate > 99% (Chemos); bromoethane ($\geq 99\%$, Sigma-Aldrich); 1-bromopropane ($\geq 99\%$, Sigma-Aldrich); 4-bromo-1-butanol ($\geq 85\%$, Aldrich).

3. Results and discussion

We employed two different methods for the measurements of the rate of nitrate decomposition [17]. The first one, used at higher temperatures ($T=563\text{--}659 \text{ K}$), consisted in a direct monitoring of the kinetics of nitrate loss. In the second approach, used at lower temperatures ($T=473\text{--}577 \text{ K}$), where consumption of nitrate was too low to be measured accurately, the rate constant was determined from the kinetics of the reaction product formation.

3.1. Kinetics of *n*-propyl and *n*-butyl nitrate decomposition

In this series of experiments the rate constant of Reactions (1) and (2) was determined from the kinetics of nitrate loss due to its decomposition. It was observed that at a given total pressure consumption of nitrate follows first order kinetics: $d[\text{Nitrate}]/dt = -k \times [\text{Nitrate}]$. Example of the exponential decays of *n*-propyl nitrate observed at different pressures in the reactor at $T=627 \text{ K}$ is shown in Fig. 2.

The values of k_1 and k_2 (in s^{-1}) determined from the loss kinetics of PPN and BTN (like those shown in Fig. 2) at different temperatures in the reactor are plotted in Figs. 3 and 4 as a function of total

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