

# Reactions of OH Radicals with Ethyl and Propyl Nitrates: Kinetics and Products

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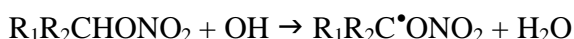
Organic nitrates are the intermediates of the atmospheric oxidation of volatile organic compounds in the presence of nitrogen oxides. They are formed in the minor channel (1b) of the reaction of peroxy radicals with NO:



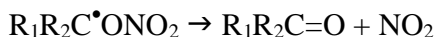
and also in the NO<sub>3</sub>-initiated oxidation of unsaturated organic compounds. Organic nitrates are temporary reservoirs of NO<sub>x</sub> with a tropospheric lifetime from a few days to a few weeks, depending on the reactivity of nitrates toward OH radicals and their photolysis rate. Photolysis of organic nitrates is known to produce NO<sub>2</sub> 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 NO<sub>2</sub>. In the present work, we report the results of the kinetic and mechanistic experimental study of the reactions of ethyl (ETN) and propyl nitrates (PN) with OH radicals.

The title reactions were studied at 1 Torr total pressure of helium over the temperature range 238–500 K. Highest temperature of the study was limited by thermal decomposition of the nitrates. Experiments were carried out in a discharge flow tube combined with modulated molecular beam mass spectrometer used for monitoring the reactants and reaction products. The measurements of the rate constants were carried out under pseudo-first order conditions in high excess of nitrates over OH radicals. For both reactions, the rate constants were found to increase with temperature showing non-Arrhenius behavior:  $k(\text{ETN}) = 1.55 \times 10^{-21} \times T^{3.035} \exp(436/T)$  and  $k(\text{PN}) = 4.87 \times 10^{-19} \times T^{2.363} \exp(165/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Abstraction of an  $\alpha$ -hydrogen atom in organic nitrates by OH radicals leads to the formation of an  $\alpha$ -substituted alkyl radical:



These radicals are known to be unstable, dissociating spontaneously without an energetic barrier to form a carbonyl compound and NO<sub>2</sub>:



In this respect, the measurements of the yield of corresponding carbonyl compound provide the information on the extent of H-atom abstraction from  $\alpha$  carbon. We have determined the yield of the carbonyl compounds formed in reactions of OH with ETN (acetaldehyde, CH<sub>3</sub>CHO) and PN (propanal, CH<sub>3</sub>CH<sub>2</sub>CHO) at T = 298K:  $0.77 \pm 0.12$  and  $0.22 \pm 0.03$ , respectively.

The kinetic and mechanistic data from the present study are in good agreement with previous experimental results and those calculated within structure-activity relationship.