Gas Phase Reaction of the Hydroxyl Radical with the Unsaturated Peroxyacyl Nitrate $CH_2 = C(CH_3)C(O)OONO_2$

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Abstract

The gas phase reaction of the hydroxyl radical with the unsaturated peroxyacyl nitrate $CH_2 = C(CH_3)C(O)OONO_2$ (MPAN) has been studied at 298 ± 2 K and atmospheric pressure. The OH-MPAN reaction rate constant relative to that of OH + *n*-butyl nitrate is 2.08 ± 0.25. This ratio, together with a literature rate constant of 1.74×10^{-12} cm^3 molecule^{-1} s^{-1} for the OH + *n*-butyl nitrate reaction at 298 K, yields a rate constant of $(3.6 \pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for the OH-MPAN reaction at 298 ± 2 K. Hydroxyacetone and formaldehyde are the major carbonyl products. The yield of hydroxyacetone, 0.59 ± 0.12, is consistent with preferential addition of OH at the unsubstituted carbon atom. Atmospheric persistence and removal processes for MPAN are briefly discussed. © 1993 John Wiley & Sons, Inc.

Introduction

Biogenic hydrocarbons including isoprene and terpenes play an important role in the formation of ozone and other photochemical oxidants in the atmosphere [1]. Isoprene is one of the most abundant biogenic hydrocarbons [2]. The atmospheric oxidation of isoprene leads to two peroxyacyl nitrates, peroxyacetyl nitrate (PAN, $CH_3C(O)OONO_2$) and the unsaturated compound MPAN ($CH_2 = C(CH_3)C(O)OONO_2$, Chemical Abstracts Service index name 2-methyl-2-propenoyl nitro peroxide, common nomenclature name for PAN homologues peroxymethacryloyl nitrate). MPAN is also produced by oxidation of methacrolein, $CH_2 = C(CH_3)CHO$, which is a major product of the isoprene-hydroxyl radical (OH) and isoprene-ozone reactions [3–5]. MPAN/PAN concentration ratios of 0.65 from isoprene and 2.3 from methacrolein have been reported [3]. Peroxyacyl nitrates are phytotoxic and mutagenic [6–9] and are major components of the odd reactive nitrogen in the troposphere [10–14]. MPAN has been recently identified in ambient air at southern California mountain forest locations [15] as well as in Atlanta, Georgia [16], where biogenic hydrocarbon emissions may play an important role in photochemical oxidant formation [1]. Thus, information regarding formation and removal processes for MPAN is of obvious importance with regard to the atmospheric chemistry of biogenic hydrocarbons, their impact on ecosystems and the corresponding regulatory implications.

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While the atmospheric persistence of saturated peroxyacyl nitrates including PAN and peroxypropionyl nitrate (PPN, $C_2H_5C(O)OONO_2$ [17,18]), is controlled by their thermal decomposition [19], the unsaturated compound MPAN may also be removed by reactions with electrophiles including ozone, the hydroxyl radical, and the nitrate radical [19]. Thus, there is a need to obtain kinetic and product data for these reactions in order to assess the persistence and fate of MPAN in the atmosphere. Using a relative rate method, we have measured the rate of reaction of OH with MPAN at 298 ± 2 K and atmospheric pressure. The corresponding carbonyl reaction products have been identified, and the OH-MPAN reaction mechanism has been outlined. The results are briefly discussed with regard to removal pathways for MPAN in the atmosphere.

Experimental Methods

Kinetic and Product Studies

The reaction of OH with MPAN has been studied using 3.5–3.9 m^3 chambers constructed from 200A FEP Teflon film [3,20]. The use of Teflon film minimizes reactants and products loss to the chamber walls [21]. The photolysis of ethyl nitrite (Aldrich, 15% in ethanol) in sunlight was used as the source of OH radicals, see relevant reactions in Results and Discussion. Purified air was obtained by passing ambient air through large cartridge containing activated carbon, silica gel, molecular sieves, and permanganate-coated alumina. The particle-free, purified air thus obtained contained less than 0.1–1 ppb of impurities including reactive organics, oxides of nitrogen, carbonyls, ethyl nitrite, and MPAN [3,20]. A typical experiment involved sunlight irradiation of mixtures of ethyl nitrite, (130 or 1000 ppb), MPAN (25–40 ppb) and of the reference compound *n*-butyl nitrate (15 ppb). Initial concentrations and other conditions are summarized in Table I. *N*-butyl nitrate was selected as the reference compound since it can be readily measured

TABLE I. Summary of experimental conditions and linear regression parameters.

Experiment	1	2	3	4
Initial concentrations, ppb:				
MPAN	25	32	27	41
n-butyl nitrate	15	16	15	15
ethyl nitrite	130	130	130	1010
T, *K*	299 ± 1	297 ± 1	297 ± 1	299 ± 1
duration, *h*	2.5	2.5	2.7	4.2
statistical parameters for eq. (8)				
slope (a)	2.02 ± 0.12	2.35 ± 0.27	1.76 ± 0.14	2.19 ± 0.21
$10^3 \times$ intercept (a)	27 ± 17	23 ± 6	17 ± 4	20 ± 15
R	0.982	0.983	0.971	0.981
n	12	12	12	14

(a) ± one std deviation

at ppb levels by electron capture gas chromatography under the same conditions as those employed to measure ppb levels of MPAN, see details later in this section.

Control experiments involved sunlight irradiation of purified air, sunlight irradiation of ethyl nitrite alone in purified air, and measurements of the loss of MPAN to the walls of the Teflon chamber. Sunlight irradiation of purified air alone resulted in the formation of less than 5 ppb of ozone, thus indicating that only low levels of oxidant precursors (oxides of nitrogen and reactive organics) were present in the matrix air and/or desorbed from the walls of the Teflon chambers. Sunlight irradiations of ethyl nitrite in purified air were carried out to verify the absence of reaction products that may interfere with EC-GC measurements of MPAN and *n*-butyl nitrate (see below). PAN was formed in these experiments as expected [22]. Loss of MPAN to the chamber walls was measured in the dark and was $(6.5 \pm 0.6) \times 10^{-6}\ s^{-1}$ in one Teflon chamber (mean ±1 std deviation, 3 experiments) and $(2.0 \pm 0.2) \times 10^{-6}\ s^{-1}$ (2 experiments) in the other Teflon chamber. These values are consistent with those measured for other peroxyacyl nitrates in Teflon chambers similar to the ones employed in this study [3,21].

Analytical Methods

Ozone was measured by ultraviolet photometry using a calibrated Dasibi Model 1108 continuous ozone analyzer. Oxides of nitrogen were measured by chemiluminescence using a Monitor Labs Model 8840 continuous analyzer calibrated using the diluted output of a certified cylinder of NO in nitrogen and of a certified NO_2 permeation tube. MPAN and *n*-butyl nitrate were measured by electron capture gas chromatography (EC-GC) as is described below. Carbonyl products were isolated as their 2,4-dinitrophenylhydrazones by sampling the reaction mixture through small C_{18} cartridges coated with 2,4-dinitrophenylhydrazine [23]. Following collection, the cartridges were eluted with HPLC-grade acetonitrile and the corresponding aliquots were analyzed by reverse phase liquid chromatography with uv detection [23,24]. The DNPH derivatives were separated on a Whatman Partisphere C_{18} column, 110 × 4.7 mm, with 55:45 by volume $CH_3CN—H_2O$ eluent at a flow rate of 1 mL/min. The liquid chromatograph components included a solvent delivery system equipped with 0.2 μm pore size Teflon filters, a SSI 300 pump, a 20 μL injection loop, a Whatman Partisphere C_{18} guard cartridge, and a Perkin Elmer LC75 uv-visible detector. The detection wavelength was 360 nm. Quantitative analysis involved the use of external hydrazone standards, from which calibration curves, i.e., absorbance (peak height) vs. concentration, were constructed. Calibration curves were constructed in the concentration range that bracketed those found in the DNPH cartridge samples collected in the MPAN-OH experiments. More details regarding the sampling and analytical protocols have been given elsewhere including collection efficiency, cartridge elution recovery, precision, accuracy, and interlaboratory comparison studies [23,24].

MPAN Synthesis and Measurements

MPAN was synthesized in the liquid phase using a method first described for PAN [25] and subsequently extended to higher molecular weight peroxyacyl nitrates [17,18] including MPAN [3,26]. For MPAN, the method involves oxidation of methacrylic anhydride (Aldrich, purity ≥97%) to peroxymethacrylic acid, followed by nitration of the peroxy acid with nitric acid:

(1)
$$(RCO)_2O + 2H_2O_2 \xrightarrow{H+} RC(O)OOH + H_2O \quad (R = CH_2 = C(CH_3)-)$$

(2)
$$RC(O)OOH + HONO_2 \xrightarrow{H+} RC(O)OONO_2 + H_2O$$

Batches of MPAN thus prepared also contain small and variable amounts of PAN as a by-product [3]. They were stored at −5°C as solutions in *n*-dodecane (Aldrich, purity >99%). Upon storage of the solution at room temperature, MPAN decomposes rapidly to $CO_2 + CH_2 = C(CH_3)ONO_2$ (2-propenyl nitrate), which is measurable by EC-GC [3], thus providing a test to verify the presence of MPAN. Other MPAN characterization tests include its decomposition in the gas phase (at ppb levels in air) through a tube heated at 180°C [3] and its preparation by a second method, in situ sunlight irradiation of isoprene-NO or methacrolein-NO mixtures in purified air [3].

MPAN was measured by EC-GC using SRI 8610 gas chromatographs and Valco 140 BN detectors [3,17]. The columns used were 70 × 0.3 cm Teflon-lined stainless steel column packed with 10% Carbowax 400 on Chromosorb P 60/80 mesh, acid washed and DMCS-treated. The column and detector temperatures were 36 and 60°C, respectively. The carrier gas was ultra-high purity nitrogen. The column flow rate was 58 mL/min. Air was continuously pumped through a short section of 6 mm diameter Teflon tubing connected to a 6.7 mL stainless steel sampling loop housed in the GC oven and was injected every 20 min using a timer-activated 10-port sampling valve. Two EC-GC instruments were operated in all experiments.

To calibrate the EC-GC instruments, ppb levels of MPAN in the gas phase were obtained by dilution, with purified air, of the output of a diffusion vial containing a small aliquot of a solution of MPAN in *n*-dodecane and maintained at 2°C. A silica gel trap was inserted upstream of the diffusion vial to minimize water condensation. Calibration involved side-by-side readings with one or more EC-GC instruments and with the Monitor Labs 8840 chemiluminescent NO_x analyzer, which uses a molybdenum surface converter to convert oxides of nitrogen to NO and responds quantitatively to organic nitrates and peroxyacyl nitrates [27]. Additional details regarding the calibration protocol have been given previously [3,17]. *N*-butyl nitrate was measured by EC-GC using conditions identical to those described above for MPAN [18]. Baseline resolution of PAN, *n*-butyl nitrate, and MPAN is achieved under these conditions, with retention times relative to that of PAN of 1.38 ± 0.02 for *n*-butyl nitrate and 1.69 ± 0.02 for MPAN.

Results and Discussion

Kinetic Measurements

Under the conditions employed, hydroxyl radicals are formed upon sunlight irradiation of ethyl nitrite and react with MPAN and with *n*-butyl nitrate as follows:

(3) $C_2H_5ONO + h\nu \longrightarrow C_2H_5O + NO$

(4) $C_2H_5O + O_2 \longrightarrow CH_3CHO + HO_2$

(5) $HO_2 + NO \longrightarrow NO_2 + OH$

(6) $OH + MPAN \longrightarrow \text{products}$

(7) $OH + n - C_4H_9ONO_2 \longrightarrow \text{products}$

The OH-MPAN reaction rate constant k_6 relative to that of the OH-*n*-butyl nitrate reaction rate constant k_7 is given by:

(8) $k_6/k_7 = \ln([\text{MPAN}]_o/[\text{MPAN}]_t)/(\ln[n\text{BN}]_o/[n\text{BN}]_t)$

where $[\text{MPAN}]_t$ and $[n\text{BN}]_t$ are the concentrations of MPAN and *n*-butyl nitrate, respectively, at time *t* and $[\text{MPAN}]_o$ and $[n\text{BN}]_o$ are the corresponding initial concentrations.

As is shown in Figure 1, plots of $\ln[\text{MPAN}]_o/[\text{MPAN}]_t$ vs. $\ln[n\text{BN}]_o/[n\text{BN}]_t$ yielded straight lines with near-zero intercepts and correlation coefficients ≥ 0.97. The corresponding least-squares linear regression parameters are listed in Table I. The relative standard deviations (RSDs) on the slopes given in Table I are a measure of experimental precision and averaged 8.7% ($n = 4$, range 6–11%). Linear regressions of data for each EC-GC instrument yielded similar RSDs which averaged 9.3% ($n = 8$, range 5–12%). The agreement between the two EC-GC instruments used in each experiment, another measure of precision, was on the average 6.5% (9.1, 8.0, 2.8, and 5.9% in Experiments 1, 2, 3, and 4, respectively). Thus, the precision of the measurements carried out in this study and used as input to calculate the k_6/k_7 ratio was consistent, in our experience, with that obtained in earlier studies involving measurements by EC-GC of ppb levels of peroxyacyl nitrates and alkyl nitrates including MPAN and *n*-butyl nitrate [3,15–18].

The mean value of the k_6/k_7, ratios listed in Table I is 2.08 ± 0.25 (one standard deviation). Using this mean value for k_6/k_7 together with the literature value of $k_7 = (1.74 \pm 0.19) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for the OH-*n*-butyl nitrate reaction rate constant at 298 K [28], we derive a rate constant $k_6 = (3.6 \pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for the reaction of MPAN with OH at $T = 298 \pm 2$ K and atmospheric pressure. The stated uncertainty is that measured for the ratio k_6/k_7 and does not include the uncertainty in the reference measurement, i.e., k_7, for which the two literature values at 298 K, both derived from relative rate measurements, are in excellent agreement [19,28].

The rate constant ratio k_6/k_7 reported here is predicated on the assumption that both MPAN and *n*-butyl nitrate are consumed by reaction with

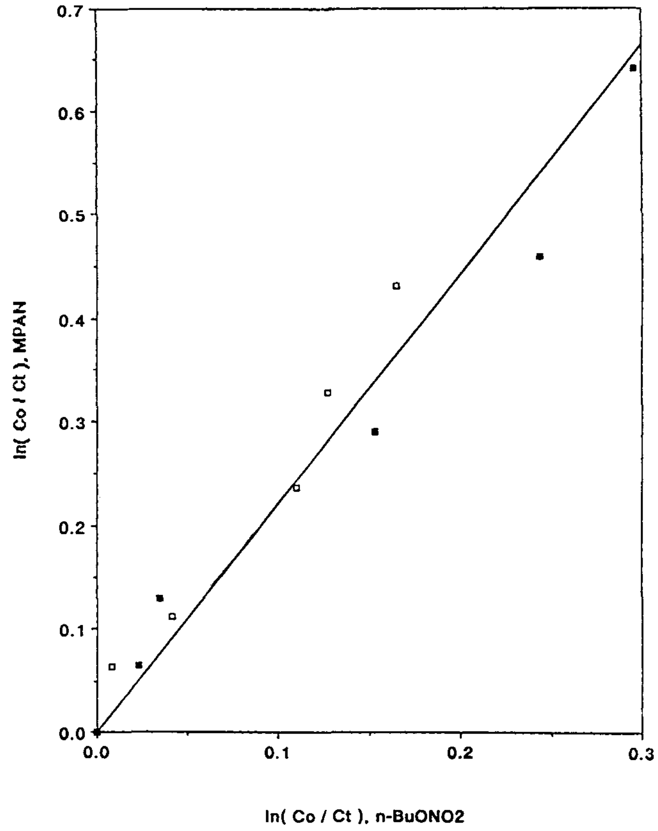

Figure 1. Scatter plot of eq. (8) for Experiment 4. Empty and filled symbols indicate data derived from measurements made with two electron capture gas chromatographs. See Table I for experimental conditions and linear regression parameters.

OH. Literature data [19] indicate that, under our experimental conditions, photolysis is a negligible loss process for *n*-butyl nitrate and for peroxyacyl nitrates (this was verified experimentally for MPAN). Reaction with atomic oxygen (due mostly to the low reactant concentrations employed) and reaction with the nitrate radical (owing to the rapid photolysis of NO_3 in sunlight) are also deemed negligible. Reaction with ozone could remove MPAN (but not *n*-butyl nitrate) at longer reaction times, i.e., when ozone accumulates in our reaction mixture. Reaction of MPAN with ozone would result in pronounced curvature in plots of eq. (8); this was not observed. While thermal decomposition of MPAN may contribute to its removal along with reaction with OH, decomposition is unlikely to be a significant factor considering the high levels of NO_2 (and high NO_2/NO ratios) in the reaction mixture. Measurements of PAN, whose thermal decomposition rate is comparable to that of MPAN and whose reaction with OH is negligibly slow [19], indicated no loss of PAN due to thermal decomposition. Finally, plots of the experimental data in the form of $\ln[\mathrm{MPAN}]_o/[\mathrm{MPAN}]_t$ vs. time and $\ln[n\mathrm{BN}]_o/[n\mathrm{BN}]_t$ vs. time yielded pseudo-first order removal rates of $2-7 \times 10^{-5}\ \mathrm{s}^{-1}$, with near-zero intercepts and high correlation coefficients, $R = 0.96-0.99$. These rates are one order of magnitude higher than those given in the Experimental Section for loss of MPAN and *n*-butyl nitrate to the chamber walls, thus indicating that wall loss was a negligible component of MPAN and *n*-butyl nitrate removal under the conditions of this study.

The magnitude of the OH-MPAN reaction rate constant is consistent with considerations regarding substituent affects for electrophilic addition at the unsaturated carbon—carbon bond and is also consistent with estimates derived from structure-reactivity and linear free-energy relationships [29,30] for structural homologues of MPAN bearing electron-withdrawing substituents. The 298 K rate constant for OH + propene is 26.3×10^{-12} cm^3 molecule^{-1} s^{-1} [19]. Rate constants for 1, 1-disubstituted olefins are, in units of 10^{-12} cm^3 molecule^{-1} s^{-1}, 51.4 for isobutene, 61 for 2-methyl-1-butene, 62 for 2-methyl-1-pentene, and 79 for β-pinene [19]. Thus, replacing H in propene by an alkyl group results in a 2-3 fold increase in reactivity, as expected for electron-donating substituents. Replacing H in propene by the electron-withdrawing substituent —C(O)CH_3 group results in a decrease in reactivity, from 26.3×10^{-12} in propene to 18.8×10^{-12} cm^3 molecule^{-1} s^{-1} in methylvinyl ketone [19]. Replacing H in propene by the strong electron-withdrawing substituent —C(O)$OONO_2$ results in a 7-fold decrease in reactivity towards OH.

The major carbonyls identified as reaction products were formaldehyde, acetaldehyde, and hydroxyacetone. Unidentified carbonyl products were present in small amounts. Their retention times and abundances relative to those of formaldehyde were 2.4 (0.7%), 4.1 (2.0%), 4.3 (4.5%), and 4.8 (1.8%). These retention times did not match those of some 35 carbonyl-DNPH standards synthesized in our laboratory [23,24]. Of the three major carbonyl products, acetaldehyde is formed from ethyl nitrite, reaction [4] above; formaldehyde is formed from ethyl nitrite, in the OH-MPAN reaction (see below), and probably by OH-initiated oxidation of *n*-butyl nitrate.

Production of formaldehyde and hydroxyacetone from MPAN is consistent with OH addition on the unsaturated carbon—carbon bond (H-atom abstraction from the MPAN methyl group is deemed negligible):

$$\text{(9a)} \qquad \text{MPAN} + \text{OH} \longrightarrow \text{CH}_2\text{OHC(CH}_3\text{)C(O)OONO}_2$$

$$\text{(9b)} \qquad \longrightarrow \text{CH}_2\text{C(OH)(CH}_3\text{)C(O)OONO}_2$$

The two β-hydroxyalkyl radicals formed in [9] are expected to react with oxygen ($R + O_2 \rightarrow RO_2$) followed by reaction of the peroxy radicals with NO ($RO_2 + NO \rightarrow RO + NO_2$) to yield the corresponding β-hydroxyalkoxy radicals. Unimolecular decomposition of these β-hydroxy alkoxy radicals is expected to predominate over their reaction with oxygen [31]:

(10a)

$$\text{OCH}_2\text{C(OH)(CH}_3\text{)C(O)OONO}_2 \longrightarrow \text{HCHO} + \text{CH}_3\text{C(OH)C(O)OONO}_2$$

(10b)

$$\text{CH}_2\text{OHC(O)(CH}_3\text{)C(O)OONO}_2 \longrightarrow \text{CH}_2\text{OHC(O)CH}_3 + \text{CO}_3\text{NO}_2$$

$$\text{(10c)} \qquad \longrightarrow \text{CH}_2\text{OH} + \text{CH}_3\text{C(O)C(O)OONO}_2$$

with the two α-hydroxy alkyl radicals produced in (10a) and (10c) reacting rapidly with oxygen by H-atom abstraction to yield $HO_2 + CH_3C(O)C(O)OONO_2$ and HO_2 + formaldehyde, respectively. The PAN-like carbonyl product postulated to form in (10c) and/or by reaction of O_2 with the alkyl radical formed in (10a) was not observed by EC-GC or by HPLC. The yield of hydroxyacetone, 0.59 ± 0.12 (measured in 3 experiments), suggests that (10b) is a major decomposition pathway and implies that OH adds preferentially to MPAN at the unsubstituted carbon atom. This has been reported previously for methacrolein, which is a structural homologue of MPAN [3,5].

Known in situ formation processes for MPAN include the photooxidation of isoprene and of methacrolein [3–5]. Methacrolein is a product of isoprene; its possible formation from other unsaturated biogenic hydrocarbons is undocumented, as are possible direct emissions from vegetation. Since MPAN reacts with OH at a much slower rate than do isoprene and methacrolein (for example, the half-life of MPAN against removal by OH is about 2 days for $[OH] = 1.0 \times 10^6$ molecules cm^{-3}), photooxidation of these biogenic hydrocarbons will result in a net formation of MPAN, as has been observed in laboratory experiments [3–5]. However, MPAN in turn reacts with OH about 35–50 times faster than PAN does [19], thus resulting in selective removal of MPAN as compared to PAN under typical tropospheric conditions and therefore reducing the importance of MPAN relative to that of PAN as a reservoir for long-range transport of reactive nitrogen.

Other removal processes for MPAN include its thermal decomposition, which proceeds at a rate comparable to that of PAN [32] and is therefore a major process for removal of MPAN in the lower troposphere. Reaction with ozone and reaction with the nitrate radical provide additional removal pathways for MPAN. Thus, unless MPAN (and/or its precursor methacrolein) are produced in situ by yet to be identified biogenic hydrocarbons that are not precursors of PAN, ambient MPAN/PAN concentration ratios downwind of biogenic sources are expected to decrease rapidly to values much lower than that of 0.65 obtained in laboratory studies of the oxidation of isoprene [3]. Hydroxyacetone, a major product of the MPAN-OH reaction, may in turn produce PAN via pathways involving its reaction with the OH radical [3], which proceeds at a rate comparable to that of the MPAN-OH reaction.

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