# Formation and Thermal Decomposition of Butyl-Substituted Peroxyacyl Nitrates: $n-C_4H_9C(0)OONO_2$ and $i-C_4H_9C(0)OONO_2$

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The butyl-substituted peroxyacyl nitrates  $n-C_4H_9C(0)$ - $OONO_2$  and  $i-C_4H_9C(O)OONO_2$  have been synthesized in the liquid phase, prepared in-situ in the gas phase by sunlight irradiation of aldehyde-NO mixtures, measured by electron capture gas chromatography, and characterized in a number of gas-phase and liquid-phase tests. Gasphase yields as a fraction of initial NO were 0.39 for the n-butyl isomer and 0.20 for the isobutyl isomer. The corresponding gas-phase aldehyde oxidation mechanisms are outlined. Thermal decomposition in the presence of excess NO yielded n-butanal and isobutanal as the major carbonyl products. Thermal decomposition rates at ambient temperature and atmospheric pressure are comparable to that of PAN [CH<sub>3</sub>C(O)OONO<sub>2</sub>], with  $k_{298} = 1.8$  $\times 10^{-4} \text{ s}^{-1}$  for  $n \cdot C_4 \text{H}_9 \text{C}(0) \text{OONO}_2$  and  $2.4 \times 10^{-4} \text{ s}^{-1}$  for  $i-C_4H_9C(0)OONO_2$ . Emission data for precursor hydrocarbons indicate C<sub>4</sub>H<sub>9</sub>C(0)OONO<sub>2</sub>/PAN ambient concentration ratios of <0.19 in urban air. Atmospheric implications for the formation and removal of C<sub>4</sub>H<sub>9</sub>C-(0)OONO<sub>2</sub> are briefly discussed.

#### Introduction

Peroxyacyl nitrates,  $RC(0)OONO_2$ , play an important role in the chemistry of the atmosphere where they are formed in-situ by oxidation of organic compounds in the presence of oxides of nitrogen (1). Peroxyacyl nitrates are phytotoxic, mutagenic, eye irritants (1-4). For these reasons, they have received attention for their adverse impact on human health and on ecosystems. Peroxyacyl nitrates have also been studied for their role as reservoirs for the long-range transport of reactive nitrogen (5, 6) and for their importance as input parameters to computer kinetic models that describe oxidant formation in the atmosphere (7).

The simplest peroxyacyl nitrate, peroxyacetyl nitrate  $(PAN, R = CH_3)$ , is the most abundant in ambient air (1, 8). Three higher molecular weight peroxyacyl nitrates have been identified in ambient air (9-12): the alkylsubstituted compounds peroxypropionyl nitrate (PPN, R =  $C_2H_5$ ) and peroxy-*n*-butyryl nitrate (PnBN, R = n- $C_3H_7$ ) and the unsaturated compound peroxymethacryloyl nitrate [MPAN,  $R = CH_2 = C(CH_3)$ -]. MPAN is a product of the oxidation of the biogenic hydrocarbon isoprene (13-15). These recent measurements of  $C_2$ - and  $C_3$ -substituted compounds in ambient air (9-12) prompted us to initiate a search for higher molecular weight peroxyacyl nitrates including the  $C_4$ -substituted compounds. To our knowledge, the butyl-substituted peroxyacyl nitrates, C<sub>4</sub>H<sub>9</sub>C- $(O)OONO_2$ , have not been described. Yet, examination of hydrocarbon emission inventories together with reactivity considerations (see Discussion) suggests that these compounds may form in photochemically polluted air.

The atmospheric persistence of peroxyacyl nitrates is limited by their thermal decomposition, which increases rapidly with increasing temperature and, at a given temperature, with the NO/NO<sub>2</sub> ratio (16-20). The thermal decomposition of PAN has been extensively studied (16-21). More limited thermal decomposition data are also available for several C<sub>2</sub>-substituted and C<sub>3</sub>-substituted compounds (20-25). One C<sub>5</sub>-substituted compound, R =*n*-pentyl, has been studied in solution but not in the gas phase (26). The C<sub>6</sub>-substituted aromatic compound PBzN,  $R = C_6H_5$ -, has also been studied (27, 28). To our knowledge, no data are available for the C<sub>4</sub>-substituted peroxyacyl nitrates. Yet, this information is needed to assess the importance of these peroxyacyl nitrates in the atmosphere and to describe their formation and removal processes.

We describe here two  $C_4$ -substituted peroxyacyl nitrates, namely, the *n*-butyl and isobutyl isomers. These compounds have been synthesized in the liquid phase and prepared in-situ in the gas phase from the appropriate aldehyde precursors. The relevant chemical reactions are outlined. Characterization tests have been carried out, and thermal decomposition rates have been measured for both compounds. The results are compared to literature data for PAN and for other lower molecular weight peroxyacyl nitrates. Atmospheric implications are briefly discussed.

# Experimental Methods

**Preparation in Liquid Phase.** The butyl-substituted peroxyacyl nitrates were synthesized in the liquid phase using a method described earlier for PAN (29) and subsequently extended to the synthesis of  $C_{2^-}$  and  $C_{3^-}$  substituted peroxyacyl nitrates (9–11, 24, 25). This method involves oxidation of the commercially available anhydride (Aldrich, purity 97–99%) to the corresponding peroxycarboxylic acid:

$$(\text{RCO})_2\text{O} + 2\text{H}_2\text{O}_2 \xrightarrow{\text{H}^+} \text{H}_2\text{O} + 2\text{RC}(\text{O})\text{OOH}$$
  
(R = n-butyl or isobutyl) (1a)

followed by nitration of the peroxycarboxylic acid with nitric acid:

$$\mathrm{RC}(0)\mathrm{OOH} + \mathrm{HNO}_3 \xrightarrow{\mathrm{H}^+} \mathrm{H}_2\mathrm{O} + \mathrm{RC}(0)\mathrm{OONO}_2 \quad (1\mathrm{b})$$

Solutions of n-C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub> and i-C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub> in *n*-dodecane (Aldrich, purity >99%) were stored at -5 °C in the dark.

**Preparation in Gas Phase.** The two  $C_4H_9C(0)OONO_2$ isomers were prepared in-situ by sunlight irradiation, in 3.7-m<sup>3</sup> collapsible chambers constructed from 200A FEP Teflon film, of 0.4 ppm nitric oxide and 1.5-2.0 ppm of the appropriate aldehyde precursor in purified air. The *n*-butyl isomer was prepared from *n*-pentanal and the isobutyl isomer from 3-methylbutanal. These aldehydes were obtained from Aldrich (stated purity 97-99%) and were used without further purification.

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The Teflon chamber facility has been described previously (15). The matrix air was purified by passing ambient air through large cartridges containing activated carbon, silica gel, molecular sieves, and permanganate-coated alumina. A glass fiber filter was inserted downstream of the sorbent cartridges to remove particulate matter from the purified air stream, which contained less than 1 ppb of reactive hydrocarbons, ozone, and oxides of nitrogen; less than 0.1-0.5 ppb of aldehydes; and no detectable amounts (less than 0.05-0.1 ppb) of peroxyacyl nitrates.

Electron Capture Gas Chromatography Analysis. The two  $C_4H_9C(O)OONO_2$  isomers were measured by electron capture gas chromatography (EC-GC) using SRI 8610 gas chromatographs equipped with Valco 140 BN detectors (9–12). The columns used were 70 × 0.3 cm Teflon-lined stainless steel columns 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 ultrahigh-purity nitrogen. The column flow rate was 60 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.

To calibrate the gas chromatographs, ppb levels of the n-butyl and isobutyl isomers in the gas phase were obtained by passing purified air through small impingers containing aliquots of a solution of  $n-C_4H_9C(0)OONO_2$  or  $i-C_4H_9C$ - $(0)OONO_2$  in *n*-dodecane. Calibration involved simultaneous measurements with two gas chromatographs and with a chemiluminescent  $NO_x$  analyzer (Monitor Labs 8840), which employs a surface converter to convert oxides of nitrogen to NO and therefore responds quantitatively to peroxyacyl nitrates (9-12). The chemiluminescent NO<sub>x</sub> analyzer was calibrated using the diluted outputs of a certified cylinder of NO in  $N_2$  and of a certified  $NO_2$ permeation tube maintained at  $30.0 \pm 0.1$  °C. Details of the calibration procedure have been given previously (9-12). The well-studied compound PAN was included for comparison in these calibrations. PAN was also included for consistency in the characterization tests described below.

Heated Tube Test. A short section of Teflon tubing heated to about 170 °C was inserted in the sampling line that connects the Teflon chamber to the gas chromatograph. The temperature was selected on the basis of previous work with lower molecular weight peroxyacyl nitrates, which decompose at 170 °C while alkyl nitrates do not (15). The same heated tube was also inserted in the sampling line that connects the Teflon chamber to the chemiluminescence  $NO_x$  analyzer. In this way, the analyzer's converter efficiency for  $NO_2$  could be compared to that for the peroxyacyl nitrate tested.

Alkaline Decomposition Test. A small alumina cartridge coated with an alkaline solution (30) was inserted in the sampling line that connects the Teflon chamber to the gas chromatograph. Alkaline decomposition of the peroxyacyl nitrate was recorded by comparing the compound's peak height before and after insertion of the alkaline cartridge (30).

Test of Decomposition to Alkyl Nitrate in the Liquid Phase. Solutions of the peroxyacyl nitrates in *n*-dodecane were stored in the dark at room temperature in closed containers for 1–7 days. Aliquots of the solutions thus stored were injected in the Teflon chamber as described above. The remaining peroxyacyl nitrate, if any, and the corresponding alkyl nitrate formed, i.e., *n*-butyl nitrate from n-C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub> and isobutyl nitrate from i-C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub>, were measured by EC-GC as described above. Retention times of the butyl nitrates have been established in previous work using authentic standards (15).

**Thermal Decomposition Experiments.** The thermal decomposition of the butyl-substituted peroxyacyl nitrates was studied by adding nitric oxide (1.3-6.2 ppm) to ppb levels of peroxyacyl nitrate in purified air. The experiments were carried out in the dark using  $3.5\text{-m}^3$  and  $3.7\text{-m}^3$  collapsible chambers constructed from FEP Teflon film and covered with opaque plastic film (15). All experiments were carried out at ambient temperature and 1 atm of air. The duration of the experiments was 2-4 h. Concentrations of the peroxyacyl nitrates were measured by EC-GC before and after the addition of nitric oxide. Several of the experiments involved measurements made simultaneously with two gas chromatographs. The concentrations of NO and NO<sub>2</sub> were monitored using a continuous chemiluminescent analyzer.

Chamber wall loss rates were measured in control experiments with ppb levels of peroxyacyl nitrates in purified air (no NO present) and were, in units of  $10^{-6}$  s<sup>-1</sup>, 4.0 for n-C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub>; 10.1 ± 1.0 (n = 2) for i-C<sub>4</sub>H<sub>9</sub>C-(O)OONO<sub>2</sub>; and 3.7 ± 1.0 (n = 2) for PAN in the same experiments. These loss rates are consistent with those measured previously for PAN and for C<sub>2</sub>- and C<sub>3</sub>-substituted peroxyacyl nitrates in similar Teflon chambers (15, 21, 24, 25).

Carbonyl Measurements. Carbonyl products were isolated as their 2,4-dinitrophenylhydrazones by sampling the reaction mixture through small C<sub>18</sub> cartridges coated with twice-recrystallized 2,4-dinitrophenylhydrazine (DNPH) as described previously (31). The cartridge sampling flow rate was 0.9 L/min. Following collection, the cartridges were eluted with HPLC-grade acetonitrile. Aliquots of the acetonitrile extracts were analyzed by liquid chromatography with ultraviolet detection (31). The DNPH derivatives were separated on a Whatman Partisphere C<sub>18</sub> column,  $110 \times 4.7$  mm, with 55:45 by volume  $CH_3CN \cdot H_2O$  eluent at a flow rate of 1 mL/min. The liquid chromatograph components included a solvent delivery system equipped with 0.2- $\mu$ m pore-size Teflon filters, a SSI 300 pump, a  $20-\mu L$  injection loop, a Whatman Partisphere C<sub>18</sub> guard cartridge, and a Perkin Elmer LC75 UV-visible detector. The detection wavelength was 360 nm. Retention times of carbonyl-DNPH standards relative to that of formaldehyde-DNPH were 4.35 for npentanal, 3.95 for 3-methylbutanal (isopentanal), 3.0 for n-butanal, and 2.9 for 2-methylpropanal (isobutanal). Quantitative analysis involved the use of external hydrazone standards. Calibration curves, i.e., absorbance (peak height) vs hydrazone concentration, were constructed as described previously (31).

# Results and Discussion

Characterization Tests. Experimental results are summarized in Table 1 and are described below for each category of test carried out. These tests have useful diagnostic value. Three of the tests, i.e., liquid-phase

# Table 1. Summary of Diagnostic Tests

	$n-C_4H_9C(0)OONO_2$	$i-C_4H_9C(O)OONO_2$
measurement by EC-GC: retention time relative to that of PAN <sup>a</sup>		
EC-GC no. 1	$3.23 \pm 0.52$ (3)	$2.08 \pm 0.36$ (29)
no. 2	$3.58 \pm 0.10$ (63)	$2.14 \pm 0.03$ (33)
no. 3	$3.80 \pm 0.05 (105)$	$2.31 \pm 0.04$ (60)
measurement by chemiluminescence: converter efficiency relative to that for $NO_2$	$1.0 \pm 0.1$	$1.1 \pm 0.1$
alkaline decomposition, fraction decomposed	1.0	1.0
thermal decomposition (heated tube test), fraction decomposed	0.93	0.96
thermal decomposition (with excess NO): major carbonyl products <sup><math>b</math></sup>	<i>n</i> -butanal	2-methylpropanal
liquid-phase decomposition to RONO <sub>2</sub> : alkyl nitrate formed	n-butyl	isobutyl
retention time of RONO <sub>2</sub> relative to that of PAN <sup>a</sup>	-	
EC-GC no. 1	$1.36 \pm 0.04$ (89)	$0.80 \pm 0.02$ (42)
no. 2	$1.37 \pm 0.02 (149)$	$0.83 \pm 0.03$ (33)
no. 3	$1.42 \pm 0.02 (141)$	$0.84 \pm 0.02$ (70)
<sup>a</sup> Number of measurements in parentheses. <sup>b</sup> Verified by comparison with carbonyl-l	ONPH reference standards	s ( <i>31</i> ).

decomposition to alkyl nitrate, alkaline decomposition to carboxylic acid, and identification of the carbonyl product(s) of the gas-phase decomposition in the presence of NO, are compound-specific. These tests represent a simple, cost-effective alternative to structure elucidation using conventional methods such as infrared spectroscopy and mass spectrometry, which are suitable for the identification of peroxyacyl nitrates as a group but have limited applicability to structure confirmation for individual compounds (1, 14, 32, 33).

Liquid-Phase Synthesis. The *n*-dodecane solutions of the *n*-butyl and isobutyl isomers also contained small amounts of the alkyl nitrates that are their liquid phase decomposition products, i.e., *n*-butyl nitrate from  $n-C_4H_9C$ -(O)OONO<sub>2</sub> and isobutyl nitrate from  $i-C_4H_9C$ (O)OONO<sub>2</sub>:

$$C_4H_9C(0)OONO_2 \rightarrow CO_2 + C_4H_9ONO_2$$
(2)

Some of the batches prepared also contained small amounts of PAN and of its liquid-phase decomposition product methyl nitrate. PAN may originate from acetic anhydride, which may be present as an impurity in the butyl anhydride used as the starting material. PAN may also form as a byproduct in reactions that accompany reactions 1a and 1b. As is shown in Table 1, the peroxyacyl nitrates and alkyl nitrates of interest are well-resolved under our EC-GC conditions.

**Decomposition in Liquid Phase.** Upon standing at room temperature, both isomers decomposed to the corresponding alkyl nitrates according to reaction 2. No other products were observed by EC-GC. The isobutyl isomer decomposed faster than the n-butyl isomer.

Heated Tube and Alkaline Decomposition Tests. The two peroxyacyl nitrates decomposed at 170 °C; the corresponding butyl nitrates did not, in agreement with previous work with lower molecular weight homologues including PAN, PPN, and PnBN (9–11, 15). Alkaline decomposition was observed for both C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub> isomers. This test can be used to identify the peroxyacyl nitrate by liquid chromatography analysis of the corresponding carboxylic acid (30), i.e., acetic, *n*-valeric, and isovaleric acids from PAN, n-C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub>, and *i*-C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub>, respectively.

**Response of Chemiluminescence NO<sub>x</sub> Analyzer.** The chemiluminescence  $NO_x$  analyzer gave a positive response when sampling ppb levels of n-C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub> and i-C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub> in purified air. The response remained the same when inserting a heated tube (to thermally decompose the peroxyacyl nitrate to RCO<sub>3</sub> + NO<sub>2</sub>) upstream of the analyzer. This indicated that the analyzer's converter efficiency for n-C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub> and for *i*-C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub> was the same as that for NO<sub>2</sub>.

Thermal Decomposition in the Presence of NO. The two isomers decomposed in the presence of excess NO, converting NO to NO<sub>2</sub> and leading to carbonyl products. The major carbonyl products, identified by liquid chromatography using carbonyl-DNPH reference standards (31), were *n*-butanal from n-C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub> and 2-methylpropanal from i-C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub>. The relevant reactions are (16-21)

$$RC(0)OONO_2 \rightleftharpoons RC(0)OO + NO_2 \qquad (3, -3)$$

$$RC(0)OO + NO \rightarrow NO_2 + RCO_2$$
(4)

$$\mathrm{RCO}_2 \to \mathrm{R} + \mathrm{CO}_2 \tag{5}$$

followed by

$$\mathbf{R} + \mathbf{O}_2 \to \mathbf{R}\mathbf{O}_2 \tag{6}$$

$$\mathrm{RO}_2 + \mathrm{NO} \rightarrow \mathrm{RO} + \mathrm{NO}_2$$
 (7a)

$$\rightarrow \text{RONO}_{2}$$
 (7b)

$$RO + NO_2 \rightarrow RONO_2$$
 (8a)

 $\rightarrow$   $\rightarrow$  carbonyls and other products (8b)

where reaction 8b represents all reactions of the alkoxy radical including unimolecular decomposition, reaction with oxygen, and isomerization (34). Thus, *n*-butanal and 2-methylpropanal are formed from  $n-C_4H_9C(O)OONO_2$  and  $i-C_4H_9C(O)OONO_2$ , respectively, by reactions 3-7a followed by reaction of the *n*-butoxy and isobutoxy radicals with oxygen:

$$CH_{3}CH_{2}CH_{2}CH_{2}O + O_{2} \rightarrow HO_{2} + CH_{3}CH_{2}CH_{2}CH_{0}$$
(8c)

$$(CH_3)_2 CHCH_2 O + O_2 \rightarrow HO_2 + (CH_3)_2 CHCHO$$
 (8d)

In-Situ Formation in Gas Phase from Aldehyde-NO Mixtures. Sunlight irradiation of *n*-pentanal-NO and 3-methylbutanal-NO mixtures in purified air resulted in the rapid conversion of NO to NO<sub>2</sub> and in the formation of ozone and of  $C_4H_9C(0)OONO_2$  (Table 2). Concentration-time profiles for these products are shown in Figures 1 and 2. Also formed in smaller amounts were the peroxyacyl nitrates PAN (from both aldehydes) and

 Table 2.
 Summary of Data for Sunlight Irradiation of

 Aldehyde-NO Mixtures
 Instant Sunday

	<i>n</i> -pentanal	3-methylbutanal
initial concentrations		
aldehyde, ppm	1.5	2.0
NO, ppb	390	380
maximum concns, ppb		
$NO_2$	326	344
ozone	255	330
$C_4H_9C(O)OONO_2^a$	153	77
minor products, ppb:		
PAN	8	4
$n-C_3H_7C(O)OONO_2$	8	b
$C_4H_9ONO_2^a$	7	6
$C_2H_5ONO_2$	≤1	5
$n-C_3H_7ONO_2$	≤1	b

 $^a$  n-Butyl from n-pentanal; is obutyl from 3-methyl butanal.  $^b$  None detected.



**Figure 1.** Concentration-time profiles for NO, NO<sub>2</sub>, and ozone (top) and for  $CH_3(CH_2)_3C(O)OONO_2$  (bottom, squares) and PAN (bottom, triangles, concentration multiplied by 10 for clarity) during sunlight irradiation of *n*-pentanal and nitric oxide in purified air.

 $n-C_3H_7C(0)OONO_2$  (from *n*-pentanal) and the alkyl nitrates *n*-butyl nitrate (from *n*-pentanal) and isobutyl nitrate (from 3-methylbutanal).

Under the conditions of this study, the two  $C_4H_9C(O)$ -OONO<sub>2</sub> isomers are formed in a sequence initiated by reaction of the aldehyde with OH and involving H-atom abstraction from the carbonyl carbon (1):

$$RCHO + OH \rightarrow H_2O + RCO (R = n-butyl or isobutyl)$$
(9)

$$RCO + O_2 \rightarrow RCO_3$$
 (10)



**Figure 2.** Concentration-time profiles for NO, NO<sub>2</sub>, and ozone (top) and for  $(CH_3)_2CHCH_2C(O)OONO_2$  (bottom, squares) and PAN (bottom, diamonds, concentration multiplied by 10 for clarity) during sunlight irradiation of 3-methylbutanal and nitric oxide in purified air.

$$\mathrm{RCO}_3 + \mathrm{NO}_2 \rightleftharpoons \mathrm{RC}(0)\mathrm{OONO}_2 \tag{3, -3}$$

The fraction of initial NO that was converted to  $C_4H_9C(O)OONO_2$  was 0.39 for the *n*-butyl isomer and 0.20 for the isobutyl isomer (ppb basis), thus indicating that reaction 9 was a major aldehyde loss process. Competing with reaction 9 are reactions that do not lead to  $C_4H_9C(O)OONO_2$ , including aldehyde photolysis and aldehyde reaction with OH by H-atom abstraction at C-H bonds, e.g., for 3-methyl butanal:

$$(CH_3)_2 CHCH_2 CHO \rightarrow (CH_3)_2 CHCH_2 + HCO$$
(11a)

$$\rightarrow$$
 other products (11b)

$$(CH_3)_2CHCH_2CHO + OH \rightarrow (CH_3)_2CCH_2CHO + H_2O$$
(12a)

followed by reactions of the alkyl radicals (analogous to reactions 3–10) to form products including lower molecular weight carbonyls, alkyl nitrates, and peroxyacyl nitrates. These compounds, some of which were indeed observed as minor products (Table 2), may also form from  $C_4H_9C$ -(O)OONO<sub>2</sub> before the NO–NO<sub>2</sub> crossover, see reactions 4–8, and also possibly from small amounts of lower molecular weight carbonyl impurities initially present along with *n*-pentanal or 3-methylbutanal.

Thermal Decomposition Rates. The thermal decomposition rates of  $n-C_4H_9C(0)OONO_2$  and  $i-C_4H_9C(0)OONO_2$  were measured in the presence of excess NO

Table 3. Summary of Experimental Conditions and Thermal Decomposition Rates for  $n-C_4H_9C(O)OONO_2$  and  $i-C_4H_9C(O)OONO_2$ 

initial concentrations				
$\overline{C_4H_9CO_3NO_2}$ , ppb	PAN, ppb	NO, ppm	<i>Т</i> , К	$10^5  imes k_4,  { m s}^{-1}$ a
	n-H	Butyl		
200	7	4.3	291.3	$82 \pm 0.9^{b}$
100	4	5.0	292.3	$9.0 \pm 0.9^{b}$
300	0	2.3	293.0	$9.5 \pm 0.1$
75	4	8.0	293.6	$12.1 \pm 1.0^{b}$
230	20	3.0	294.1	$10.3 \pm 1.3$
96	5	4.5	295.9	$14.7 \pm 0.6^{b}$
	Iso	butyl		
11	40	3.2	288.0	$4.0 \pm 0.5^{b}$
7	<b>24</b>	6.0	289.5	$4.3 \pm 0.2^{b}$
41	2	7.6	293.4	$8.1 \pm 0.6^{b}$
130	19	2.0	293.6	$13.1 \pm 2.1^{b}$

 $^a$  From least-squares linear regression according to eq 16, unit-weighed, not forced through the origin.  $^b$  Average of data from two EC-GC instruments.

in experiments carried out at ambient temperature (288–296 K) and at 1 atm of air. From reactions 3–8 above, the peroxyacyl nitrate concentration  $[C_4H_9CO_3NO_2]$  is given by:

$$-d[C_4H_9CO_3NO_2]/dt = k_3k_4([C_4H_9CO_3NO_2][NO])/(k_4[NO] + k_{-3}[NO_2]) (13)$$

$$-d(\ln [C_4H_9CO_3NO_2])/dt = (k_3k_4[NO])/(k_4[NO] + k_{-3}[NO_2]) (14)$$

Under our conditions of excess NO, i.e.,  $(k_4 \text{ [NO]} \gg k_{-3} \text{ [NO_2]})$ , eq 14 simplifies to:

$$-d(\ln [C_4 H_9 CO_3 NO_2])/dt = k_4$$
(15)

$$\ln \left( \left[ C_4 H_9 C O_3 N O_2 \right]_0 / \left[ C_4 H_9 C O_3 N O_2 \right]_t \right) = k_4 t \quad (16)$$

where  $[C_4H_9CO_3NO_2]_0$  is the initial peroxyacyl nitrate concentration.

While the hydroxyl radical is formed in our system in reactions 8c or 8d followed by  $HO_2 + NO \rightarrow NO_2 + OH$ , removal of  $C_4H_9C(O)OONO_2$  by reaction with OH is not important since OH reacts rapidly with NO, which is present in large excess.

Plots of eq 16 yielded straight lines for both compounds, with near-zero intercepts and correlation coefficients of  $R^2 > 0.98$ . The slopes of the corresponding linear regressions, i.e.,  $k_4$ , are listed in Table 3.

Although the range of ambient temperatures covered in this study is quite narrow (about 5 K), it is of interest to examine the data in the form of the Arrhenius relation:

$$k_4 = A \exp(-E_a/RT) \tag{17}$$

Plots of the experimental data as a function of temperature according to eq 17 are shown in Figure 3. The corresponding Arrhenius parameters, calculated from linear regression of the data shown in Figure 3, are listed in Table 4. Thermal decomposition rate constants at 298 K, calculated from the data in Table 4 are (in units of  $10^{-4}$  s<sup>-1</sup>) 1.8 for n-C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub> and 2.4 for i-C<sub>4</sub>H<sub>9</sub>C(O)-OONO<sub>2</sub>. These rate constants are comparable to and lower than that of  $3.0 \times 10^{-4}$  s<sup>-1</sup> calculated for PAN using eq 17 from data obtained under identical conditions (including



Figure 3. Scatter plots of eq 17 for the thermal decomposition rate of n-C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub> (top) and i-C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub> (bottom).

Table 4.	Summary	of	Arrhenius	Parameters	for
$C_4H_9C(O)$	OONO <sub>2</sub>				

	n-C4H9C- (0)00NO2	<i>i</i> -C <sub>4</sub> H <sub>9</sub> C- (O)OONO <sub>2</sub>	PAN (ref 21)
<i>T</i> , K	291.3-295.9	288.0-293.6	288-298
$\log_{10} A$ , s <sup>-1</sup> a	$12.1 \pm 3.1$	$19.4 \pm 6.4$	$16.2 \pm 1.6$
$E_{\rm a}, \rm kcal/mol^a$	$21.6 \pm 4.1$	$31.4 \pm 8.5$	$26.9 \pm 2.1$
R	0.935	0.933	0.933
n	6	4	26
$10^4  imes k_{298}$ , s <sup>-1</sup>	1.8	2.4	$3.0^{b}$

<sup>a</sup> Unit weighted linear least-squares regression,  $\pm 1$  SD. <sup>b</sup> Compares to previous literature data of  $(3.1-5.3) \times 10^{-4}$  s<sup>-1</sup> (16-20).

a narrow range of ambient temperatures, 288–298 K) and using the same measurement protocol (21). While the data we obtained for PAN (21) are entirely consistent with previous literature data (16–20), we stress that the temperature range covered in this study may be too narrow to warrant presentation of the data for  $n-C_4H_9C(O)OONO_2$ and for  $i-C_4H_9C(O)OONO_2$  in Arrhenius form.

Formation of Butyl-Substituted Peroxyacyl Nitrates. Formation rates for  $C_4H_9C(O)OONO_2$  are proportional to the emission rates and chemical reactivity of their precursor hydrocarbons. Even if reliable hydrocarbon emission inventories were available (35), precise calculations of formation rates for butyl-substituted peroxyacyl nitrates would require, for each hydrocarbon, a detailed knowledge of oxidation mechanisms, of the relative importance of the corresponding pathways, and of the peroxyacyl nitrate yield. While this information is not available for most hydrocarbons, estimates can be made by simply taking the product of the hydrocarbon emission

#### Table 5. Hydrocarbon Precursors to C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub>

$C_4H_9C(O)OONO_2$ isomer	hydrocarbon precursor	$A =  ext{emission rate,} t/ ext{day}$	$B = 10^{11} \times \text{OH}$ reaction rate constant, cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$A \times B$	forming potential relative to that of PAN
<i>n</i> -butyl	1-hexene	0.5	3.7	1.9	
·	<i>n</i> -butylbenzene	0.5	0.6	0.3	
	n-hexane	19.6	0.56	11.0	
	<i>n</i> -heptane	9.9	0.71	7.0	
	· · · · · · · · · · · · · · · · · · ·			total <i>n</i> -butvl 20.2	0.026
isobutvl				0	0
s-butyl	s-butylbenzene	0.5	0.6	0.3	-
č	3-methyl-1-pentene	34.6	3.1	107.3	
				total s-butvl 107.6	0.139
t-butyl	t-butvlbenzene	1.9	0.6	1.2	
	2.4.4-trimethyl-1-pentene	4	3.5	14.0	
	2.2.4-trimethylpentane	4.3	0.37	1.6	
	_,_, <b></b>			total t-butyl 16.8	0.022
sum of all four isomers				144.6	0.186

rate and of some measure of the hydrocarbon reactivity, for example, the hydrocarbon-hydroxyl radical reaction rate constant since all hydrocarbons react with OH. Such estimates are listed in Table 5 for the four butyl-substituted isomers, using available kinetic data (36) and, as an example, the hydrocarbon emission rates for the California South Coast Air Basin (37).

The formation potential for butyl-substituted peroxyacyl nitrates thus estimated is an upper limit for olefins [which also react with ozone to yield products other than  $RC(0)OONO_2$ , for aromatics [for which reaction with OH leads in part to ring-retaining products that do not form  $RC(0)OONO_2$  and for paraffins [whose reaction with OH generally involves several H-atom abstraction pathways, not all of which lead to  $RC(0)OONO_2$ ]. With these simplifying assumptions, the estimates given in Table 5 suggest that  $s-C_4H_9C(O)OONO_2$  could be the most abundant butyl-substituted peroxyacyl nitrate in urban air, and this is as a result of the high emission rate of its olefin precursor 3-methyl-1-pentene. This alkene ranks among the three most abundant olefins emitted in urban air (37). Formation potentials for the *n*-butyl and *t*-butyl isomers are about 5-6 times lower than that for the s-butyl isomer; no precursors of the isobutyl isomer are listed in current emission inventories (37).

Comparison of the estimates given in Table 5 to those presented earlier for PAN using a similar method (10) suggests a  $C_4H_9C(0)OONO_2/PAN$ -forming potential ratio of about 0.19 for the sum of the four isomers. Thus, ambient levels of  $C_4H_9C(0)OONO_2$  in urban air may be at least 5–7 times lower than that of PAN. This estimate may serve as a guide for future work aimed at measuring ambient levels of  $C_4H_9C(0)OONO_2$ .

Atmospheric Implications. Possible removal processes for  $C_4H_9C(O)OONO_2$  in the atmosphere include their thermal decomposition and their reaction with the hydroxyl radical. Our results indicate that the thermal decomposition rates of n- $C_4H_9C(O)OONO_2$  and i- $C_4H_9C(O)OONO_2$  are comparable in magnitude to that of PAN. Therefore, as is the case for PAN (16–20), thermal decomposition may be an important atmospheric removal process for  $C_4H_9C(O)OONO_2$  with, for example, a lifetime of 1–2 h at 298 K when NO  $\gg$  NO<sub>2</sub>.

Under the opposite conditions, i.e.,  $NO_2 \gg NO$ , thermal decomposition becomes negligibly slow, and removal by reaction with OH may become the dominant loss process. Unlike PAN, which reacts very slowly with OH (36),

C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub> may react with OH by H-atom abstraction from the secondary C–H bonds and, for the isobutyl isomer, from the tertiary C–H bond. While no kinetic data are available for the OH–C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub> reaction, data for structural homologues, e.g., esters and alkyl nitrates (*36*), suggest ambient temperature reaction rate constants of (1–2) × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the *n*-butyl and isobutyl isomers, leading to half-lives of 4–8 days against removal by OH when OH =  $1.0 \times 10^6$  molecule cm<sup>-3</sup>.

Therefore, reaction with OH will further reduce the atmospheric persistence of C<sub>4</sub>-substituted peroxyacyl nitrates as compared to that of PAN and, correspondingly, reduce their importance relative to that of PAN as reservoirs for long-range transport of reactive nitrogen in the atmosphere. Owing to reaction with OH, ambient levels of C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub> relative to that of PAN downwind of urban areas may be lower than those estimated above for the urban situation unless yet to be identified biogenic sources exist for hydrocarbons that are precursors to C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub> but not to PAN.

Finally, the carbonyl products of  $C_4H_9C(0)OONO_2$ thermal decomposition, e.g., *n*-butanal and isobutanal, are precursors to free radicals, thereby contributing to ozone formation and other atmospheric oxidation processes (7). Among these, lower molecular weight peroxyacyl nitrates may form in a "cascade effect", e.g., *n*- $C_4H_9C(0)OONO_2$ yields butanal, which is a precursor to PnBN (11) which decomposes to propanal (11), leading to PPN (9, 10) and subsequently to PAN.

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