# **Peroxyisobutyryl Nitrate**

#### Daniel Grosjean, Eric Grosjean, and Edwin L. Williams II

DGA, Inc., 4526 Telephone Road, Suite 205, Ventura, California 93003

Peroxvisobutyryl nitrate, (CH<sub>3</sub>)<sub>2</sub>CHC(0)OONO<sub>2</sub>(PiBN), has been synthesized in the liquid phase, measured by electron capture gas chromatography (EC-GC), characterized in a number of decomposition tests, and prepared in-situ in the gas phase by sunlight irradiation of isobutyl nitrite, of isobutanal with NO, and of 3-methyl-1-butene with NO in air. The corresponding reaction mechanisms are outlined. In the liquid phase, PiBN decomposes to isopropyl nitrate. In the gas phase, thermal decomposition in the presence of NO yields acetone  $(91 \pm 7\%)$ . Isobutanal reacts with OH predominantly ( $\geq 98\%$ ) by H abstraction from the carbonyl carbon, and 3-methyl-1-butene reacts with OH predominantly ( $\geq$ 98%) by addition on the C=C bond. Reaction with oxygen predominates ( $\geq 96\%$ ) over unimolecular decomposition for the alkoxy radicals  $(CH_3)_2$ - $CH(\dot{O})$  and  $(CH_3)_2CHCH_2(\dot{O})$ . Emission inventory data for hydrocarbons that are precursors to PiBN indicate that the PiBN-forming potential relative to that of PAN is  $\leq 0.10$ . This ratio also represents an upper limit for the positive bias due to PiBN when measuring ambient PAN by EC-GC with packed columns, on which PiBN and PAN co-elute.

# Introduction

Peroxyacyl nitrates, RC(0)OONO<sub>2</sub>, have been studied for their adverse effects on human health and ecosystems (1-7) and for their role in the long-range transport of reactive nitrogen in the atmosphere (8-11). Peroxyacetyl nitrate (PAN,  $R = CH_3$ ) is the most abundant peroxyacyl nitrate in the atmosphere; ambient levels of PAN have been measured many times (1, 12). Less information is available regarding higher molecular weight peroxyacyl nitrates. Yet this information is of importance since higher molecular weight peroxyacyl nitrates may be even more phytotoxic than PAN (5). They may also account for some of the "missing" organic nitrogen, i.e., the reactive odd nitrogen that is not accounted for by NO<sub>2</sub>, nitric acid, PAN, and organic nitrates (6-9, 13). Peroxyacyl nitrates other than PAN have been recently measured in ambient air at several southern California locations (14-17): peroxypropionyl nitrate ( $R = C_2H_5$ , PPN), peroxy-nbutyryl nitrate ( $R = n - C_3 H_7$ , PnBN), and peroxymethacryloyl nitrate [ $R = CH_2 = C(CH_3)$ -, MPAN]. PPN and MPAN have also been measured along with PAN in downtown Atlanta, GA (18).

The simplest branched-chain peroxyacyl nitrate, peroxyisobutyryl nitrate  $[(CH_3)_2CHC(O)OONO_2$ , hereafter PiBN], has seldom been studied. Stephens briefly mentioned having prepared PiBN and indicated that PiBN had not been purified or studied in any detail (1). To our knowledge, no other information is available regarding PiBN, its characterization, or the chemical reactions involved in its formation and persistence in the atmosphere. We have prepared PiBN using several methods, measured PiBN at ppb levels by electron capture gas chromatography, and carried out several tests to characterize PiBN in the gas phase and in the liquid phase. PiBN formation mechanisms are outlined, and the corresponding atmospheric implications are briefly discussed.

# Experimental Methods

Liquid-Phase Synthesis. PiBN was prepared in the liquid phase using a method first described for the preparation of PAN (19) and subsequently applied to the synthesis of PPN and PnBN (14-16). Peroxyisobutyric acid was prepared by oxidation of 2-methylpropionic anhydride (Aldrich, purity 97%):

$$(\text{RCO})_2\text{O} + 2\text{H}_2\text{O}_2 \xrightarrow{\text{H}^+} \text{H}_2\text{O} + 2\text{RC}(\text{O})\text{OOH}$$
$$[\text{R} = (\text{CH}_3)_2\text{CH}-] (1)$$

and was subsequently esterified by acid-catalyzed nitration to yield PiBN:

$$RC(0)OOH + HNO_3 \xrightarrow{H^+} H_2O + RC(0)OONO_2$$
(PiBN) (2)

Solutions of PiBN in *n*-dodecane (Aldrich, purity  $\geq 99\%$ ) were stored in the dark at -5 °C. Parts per billion (ppb) levels of PiBN in purified air were obtained by passing pure air through small impingers containing 2-5-mL aliquots of a solution of PiBN in *n*-dodecane and by directing the air stream to a 3.5-m<sup>3</sup> Teflon chamber.

In-Situ Formation in Gas Phase. PiBN was prepared in-situ by sunlight irradiation, in a 3.5-m<sup>3</sup> collapsible chamber constructed from 200A FEP Teflon film (20); of isobutyl nitrite (Aldrich, purity 95%) in purified air (one experiment); of mixtures of nitric oxide and isobutanal (2-methylpropanal, Aldrich, purity  $\geq 99\%$ ) in purified air (two experiments); of mixtures of isobutanal with ethyl nitrite in purified air (one experiment); and of mixtures of NO and 3-methyl- 1-butene (Aldrich, purity 95%) in purified air (two experiments). Initial concentrations were 1-5 ppm for the organic compounds and 0.14-1.0 ppm for nitric oxide. Purified air was obtained by passing ambient air through large sorbent cartridges containing silica gel, molecular sieves 13×, activated carbon, and permanganatecoated alumina. The purified air contained less than 1 ppb of oxides of nitrogen, ozone, reactive hydrocarbons, formaldehyde, and peroxyacyl nitrates (20).

Electron Capture Gas Chromatography. PiBN was measured by electron capture gas chromatography (EC-GC) using SRI Model 8610 gas chromatographs and Valco Model 140 BN electron capture detectors as described previously for the other peroxyacyl nitrates PAN, PPN, PnBN, and MPAN (14-18). The columns used were 70 cm  $\times$  3 mm Teflon-lined stainless steel columns packed with 10% Carbowax 400 on Chromosorb P, acid-washed, and treated with dimethyldichlorosilane. The column and detector temperatures were 36 and 60 °C, respectively. The carrier gas was ultrahigh-purity nitrogen. The column flow rate was 58 mL/min. Air from the Teflon chamber was continuously pumped through a 6-mm diameter Teflon

<sup>\*</sup> Corresponding author.

sampling line and a 6.7-mL stainless steel loop housed in the GC oven. The residence time in the sampling line was about 5 s. Air was injected every 20 min with a timeractivated 10-port sampling valve.

To calibrate the EC-GC instruments, ppb levels of PiBN were introduced in the Teflon chamber, and side-by-side readings of the PiBN concentration were carried out with the EC-GC instruments and with a chemiluminescent NO<sub>r</sub> analyzer (Monitor Labs Model 8840) which uses a surface converter (molybdenum, T = 325 - 350 °C) to convert oxides of nitrogen to NO and therefore responds quantitatively to organic nitrates and peroxyacyl nitrates (14-18). The chemiluminescence NO<sub>x</sub> analyzer was calibrated with the diluted outputs of a certified cylinder of NO in nitrogen and of a certified  $NO_2$  permeation tube maintained at  $30.0 \pm 0.1$  °C. The efficiency of the converter to convert NO<sub>2</sub> to NO was measured according to the manufacturer's prescribed procedure. Plots of PiBN peak height vs chemiluminescence analyzer response ( $NO_x$ -NO, ppb) were constructed for several concentrations of PiBN. By use of a Teflon tube heated to 170 °C and inserted upstream of the chemiluminescent  $NO_x$  analyzer, we verified that the efficiency of the molybdenum converter for PiBN was the same as that for  $NO_2$ .

Heated Tube Test. A short section of Teflon tubing heated to about 170 °C was inserted in the sampling line connecting the Teflon chamber to the EC-GC instrument. The temperature was selected on the basis of previous work with other peroxyacyl nitrates, which decompose at 170 °C while alkyl nitrates do not (14-18).

Test of Decomposition to Isopropyl Nitrate in Liquid Phase. Solutions of PiBN in *n*-dodecane were stored in the dark at room temperature in closed containers for periods of 1–7 days. Aliquots of the solutions thus stored were injected in the Teflon chamber as described above. The remaining PiBN and the isopropyl nitrate formed were measured by EC-GC. The retention time of isopropyl nitrate was compared to that of an authentic standard.

Alkaline Decomposition Test. A small alumina cartridge coated with an alkaline solution was inserted in the sampling line connecting the Teflon chamber to the EC-GC instrument. Alkaline decomposition of PiBN was recorded by comparing EC-GC peak heights before and after insertion of the alkaline-coated cartridge (14-18).

Thermal Decomposition in Presence of NO. With the Teflon chamber covered with opaque plastic, ppb levels of PiBN were allowed to decompose, at ambient temperature and atmospheric pressure, in the presence of 2–5 ppm NO in the dark. Concentration vs time data were recorded by EC-GC as described above. Carbonyl products of the thermal decomposition of PiBN were identified as described below.

**Carbonyl Measurements.** Carbonyl products were isolated as their 2,4-dinitrophenylhydrazones by sampling the reaction mixture through small  $C_{18}$  cartridges coated with twice-recrystallized 2,4-dinitrophenylhydrazine as described previously (21, 22). The sampling flow rate was 0.52 L/min, and the sampling duration was typically 30– 60 min. Following collection, the cartridges were eluted with HPLC-grade acetonitrile, and aliquots of the acetonitrile extracts were analyzed by liquid chromatography with ultraviolet detection (21, 22). The carbonyl 2,4dinitrophenylhydrazones were separated on a Whatman Partisphere  $C_{18}$  column, 110 × 4.7 mm, with 55:45 by volume CH<sub>3</sub>CN·H<sub>2</sub>O eluent (both HPLC-grade) 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, an 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.

Confirmation of the presence of carbonyl or dicarbonyl derivatives was obtained by measuring their 430/360-nm absorbance ratios. The 2,4-dinitrophenylhydrazones of dicarbonyls absorb with a maximum at 430 nm as compared to a maxima of about 360 nm for derivatives of aliphatic compounds containing only one carbonyl group (21, 22). In this way, positive identification could be made by matching retention times and 430/460-nm absorbance ratios of sample peaks to those of reference standards that had been synthesized in our laboratory and for which structure confirmation had been obtained independently by chemical ionization mass spectrometry (23).

Quantitative analysis involved the use of external hydrazone standards, for 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 samples collected in the experiments. The slopes of these calibration curves, i.e., response factors, were used to calculate the concentrations of the carbonyl products (21, 22).

## Results and Discussion

Summary of Characterization Tests. Results of the characterization tests, several of which are described in more detail below, can be summarized as follows:

(1) PiBN could be detected and measured by EC-GC, with a retention time essentially equal to that of PAN on three EC-GC instruments.

(2) PiBN could be detected and measured by chemiluminescence using a  $NO_x$  analyzer with a molybdenum converter.

(3) PiBN decomposed in the heated tube tests ( $\geq 85\%$  at 170 °C) and in the alkaline cartridge tests ( $\geq 95\%$  at room temperature). Isopropyl nitrate did not decompose at 170 °C. Decomposition of PiBN through a heated tube did not affect the response of the chemiluminescent analyzer, i.e., the instrument's converter efficiency for PiBN is the same as that for NO<sub>2</sub>.

(4) In the liquid phase, PiBN decomposed to isopropyl nitrate upon standing for 1-7 days at room temperature.

(5) In the gas phase, PiBN decomposed at room temperature in the presence of excess NO and yielded acetone as the major carbonyl product.

EG-GC Retention Times. Retention times relative to that of PAN were measured on three EC-GC instruments (with slightly different columns and operating conditions) and were  $0.37 \pm 0.01$  (n = 128),  $0.37 \pm 0.02$  (n = 436), and  $0.38 \pm 0.01$  (n = 402) for methyl nitrate;  $0.48 \pm 0.01$  (n = 10),  $0.50 \pm 0.01$  (n = 120), and  $0.51 \pm 0.01$  (n = 117) for isopropyl nitrate; and  $1.00 \pm 0.1$  (n = 10),  $1.00 \pm 0.01$  (n= 93), and  $1.00 \pm 0.01$  (*n* = 98) for PiBN. Thus, PiBN and PAN, if present together, would not be resolved under our EC-GC conditions. This was verified in an experiment involving sunlight irradiation of isobutanal (a precursor to PiBN, see below) and of ethyl nitrite (used as a source of OH radicals and as a precursor to PAN, see below). Both PiBN and PAN were formed and co-eluted. Thermal decomposition in the presence of excess NO, discussed in more detail below, yielded acetone from PiBN and



Figure 1. Scatter plot of acetone formed (ppb) vs reacted PiBN (ppb) in two experiments involving the thermal decomposition of PiBN in the presence of excess NO.

formaldehyde from PAN. These two carbonyls are wellresolved by liquid chromatography (21, 22).

**Decomposition of PiBN in Liquid Phase.** In the liquid phase, peroxyacyl nitrates decompose to carbon dioxide and to the corresponding alkyl nitrate (1, 24):

$$RC(0)OONO_2 \rightarrow CO_2 + RONO_2$$
(3)

Thus, PAN yields CO<sub>2</sub> and methyl nitrate, as we have verified many times (14-18) when reanalyzing batches of PAN stored as solutions in *n*-dodecane in the dark and at -5 °C for periods of several months. We have also observed the decomposition, under the same conditions, of PPN to ethyl nitrate (15) and of PnBN to *n*-propyl nitrate (16). In the same way, reanalysis of aliquots of PiBN in *n*-dodecane allowed to stand at room temperature in closed containers in the dark for 1-7 days indicated that essentially all ( $\geq 99\%$ ) of the PiBN had decomposed to isopropyl nitrate:

$$(CH_3)_2 CHC(0)OONO_2 \rightarrow CO_2 + (CH_3)_2 CHONO_2 \qquad (4)$$

Some of the batches of PiBN we have prepared also contained PAN as a byproduct. We have also observed PAN to be a byproduct in the liquid-phase synthesis of MPAN (25) and, to a lesser extent, of PnBN (16). Although the starting materials are of high-stated purity, the presence of PAN precursors, e.g., acetic anhydride as an impurity in 2-methylpropionic anhydride, cannot be ruled out. PAN and/or its precursors may also form in side reactions that accompany eqs 1 and 2. Since PAN and PiBN coelute, but their liquid-phase decomposition products methyl nitrate and isopropyl nitrate do not, the decomposition test described above represents a convenient test to distinguish between PAN and PiBN. This test is quantitative since the EC-GC can be calibrated for its responses to methyl nitrate (25, 26), and to isopropyl nitrate (25).

Thermal Decomposition of PiBN: Carbonyl Products. The decomposition of PiBN in the presence of NO yielded acetone as the major carbonyl product (Figure 1) with a yield of  $0.91 \pm 0.07$  (R = 0.975, n = 11). By analogy with its simpler structural homologue PAN (27, 28), PiBN is expected to undergo thermal decomposition in the presence of excess NO according to:

$$PiBN \rightleftharpoons NO_2 + (CH_3)_2 CHC(O)OO \qquad (5, -5)$$

$$(CH_3)_2 CHC(0)OO + NO \rightarrow NO_2 + (CH_3)_2 CHCO_2$$
 (6)



**Figure 2.** Concentration-time profiles for NO (open squares),  $NO_2$  (solid squares), ozone (triangles), and PIBN (diamonds, concentration multiplied by 10 for clarity) in an experiment involving sunlight irradiation of 2.0 ppm isobutanal and 0.4 ppm NO in purified air.

$$(CH_3)_2 CHCO_2 \rightarrow CO_2 + (CH_3)_2 CH \tag{7}$$

The isopropyl radical formed in eq 7 reacts with oxygen, followed by reactions of the corresponding peroxy radical with NO:

$$(CH_3)_2CH + O_2 \rightarrow (CH_3)_2CHO_2 \tag{8}$$

$$(CH_3)_2CHO_2 + NO \rightarrow (CH_3)_2CHONO_2$$
 (9a)

 $\rightarrow$  (CH<sub>3</sub>)<sub>2</sub>C(O)H + NO<sub>2</sub> (9b)

with isopropyl nitrate formation, pathway 9a, accounting for only 4% of the overall RO<sub>2</sub> + NO reaction (29). The alkoxy radical formed in pathway 9b may decompose or may react with oxygen (30):

$$(CH_3)_2C(O)H \rightarrow CH_3CHO + CH_3$$
 (10a)

$$CH_3 + O_2 \rightarrow HO_2 + HCHO$$
 (10b)

$$(CH_3)_2 C(O)H + O_2 \rightarrow CH_3 COCH_3 + HO_2$$
(11)

The observation of acetone as the major carbonyl product is consistent with pathway 11 being predominant: measured concentrations of acetone (Figure 1), acetaldehyde, and formaldehyde (not shown) were consistent with  $k_{11}/(k_{10}+k_{11}) \ge 0.96$ . This ratio is most likely a lower limit for the actual ratio since formaldehyde and acetaldehyde, in addition to being possibly formed in reaction 10, may also be present in small amounts as impurities in isobutanal.

**PiBN Formation from Isobutanal.** The formation of PiBN from isobutanal–NO, isobutanal–ethyl nitrite, isobutyl nitrite, and 3-methyl-1-butene–NO involves in all four systems a common sequence of reactions initiated by the reaction of isobutanal with the hydroxyl radical:

$$OH + (CH_3)_2 CHCHO \rightarrow (CH_3)_2 CHCO + H_2 O \quad (12)$$

$$(CH_3)_2 CHCO + O_2 \rightarrow (CH_3)_2 CHCO_3$$
(13)

$$(CH_3)_2CHCO_3 + NO_2 \rightleftharpoons (CH_3)_2CHC(0)OONO_2$$
  
(PiBN) (5, -5)

Shown in Figure 2 is a concentration-time profile for one of the isobutanal-NO experiments. Before the NO/ NO<sub>2</sub> cross-over, i.e., under conditions of excess NO, PiBN does not accumulate in the system since the peroxyacyl radical  $(CH_3)_2CHCO_3$  formed in reaction 13 reacts predominantly with NO to yield acetone, reactions 6-11.

Competing with PiBN formation in the isobutanal-NO system are two sets of reactions, one initiated by isobutanal photolysis and the other initiated by the reaction of isobutanal with OH and involving H-atom abstraction from the weak tertiary C-H bond. Photolysis leads to acetone:

$$(CH_3)_2 CHCHO + h\nu \rightarrow (CH_3)_2 CH + HCO$$
 (12)

via reactions 8-11. Reaction with OH:

$$(CH_3)_2CHCHO + OH \rightarrow (CH_3)_2CCHO + H_2O$$
 (15)

may lead to acetone and/or to formaldehyde + methylglyoxal according to reactions analogous to eqs 8-11. The room temperature rate constant for the OH-isobutanal reaction is  $2.6 \times 10^{-11}$  cm<sup>-3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (31). The rate constant  $k_{15}$ , using that for the OH-isobutane reaction as a guide (31), is probably  $2.3 \times 10^{-12}$  cm<sup>-3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, thus suggesting that pathway 15 may account for  $\leq 9\%$  of the overall OH-isobutanal reaction. We did not observe formaldehyde and methylglyoxal as reaction products, thus suggesting that pathway 15 is indeed a minor pathway. The measured acetone/formaldehyde concentration ratio was  $\geq 0.98$ , thus indicating that pathway 15 accounted for only  $\leq 2\%$  of the overall OH-isobutanal reaction.

PiBN formation in the isobutanal-ethyl nitrite system is analogous to that described above for the isobutanal-NO system. The photolysis of ethyl nitrite leads to OH radicals (1):

$$CH_3CH_2ONO + h\nu \rightarrow NO + CH_3CH_2O$$
 (16)

$$CH_3CH_2O + O_2 \rightarrow CH_3CHO + HO_2$$
(17)

$$HO_2 + NO \rightarrow NO_2 + OH$$
 (18)

followed by reactions 12 and 13 and by equilibrium 5, -5. PAN is also formed in this system by the reaction of OH with acetaldehyde produced in eq 17 followed by reactions identical to eqs 12, 13, 5, and -5 (1). As indicated earlier, this system was studied to produce PAN and PiBN together in-situ, to verify that they co-elute under our EC-GC conditions, and to resolve them as their respective thermal decomposition carbonyl products, i.e., formaldehyde from PAN and acetone from PiBN

PiBN Formation from Isobutyl Nitrite. The in-situ preparation of peroxyacyl nitrates by photolysis of alkyl nitrites in oxygen or in air, first described by Stephens for PAN (1), has been extended in this study to the preparation of PiBN from isobutyl nitrite. By analogy with methyl nitrite and ethyl nitrite (1, 32):

$$(CH_3)_2CHCH_2ONO + h\nu \rightarrow NO + (CH_3)_2CHCH_2O$$
 (19)

$$(CH_3)_2 CHCH_2 O + O_2 \rightarrow HO_2 + (CH_3)_2 CHCHO$$
(20)

followed by reaction 18 and the subsequent reaction of isobutanal with OH as discussed above. Competing with reactions 18-20 are pathways that do not form PiBN, i.e., unimolecular decomposition of the alkoxy radical formed in reaction 19:

$$(CH_3)_2CHCH_2O \rightarrow HCHO + (CH_3)_2CH$$
 (21)

followed by reactions 8-11 that lead to acetone. On the basis of the data presented above for the  $(CH_3)_2C(O)H$ alkoxy radical, the structurally similar  $(CH_3)_2CHCH_2(O)$ alkoxy radical is expected to react predominantly with oxygen, i.e.,  $k_{20} \gg k_{21}$ . Indeed, the measured formaldehyde/(formaldehyde + isobutanal + PiBN) concentration ratio was 0.04, consistent with  $k_{20}/(k_{20} + k_{21}) \ge 0.96$ .



Figure 3. Concentration-time profiles for NO, NO2, ozone, and PIBN (same symbols as in Figure 2) in an experiment involving sunlight irradiation of 5.0 ppm 3-methyl-1-butene and 0.43 ppm NO in purified air.

PiBN Formation from 3-Methyl-1-butene. Concentration-time profiles for one of the 3-methyl-1-butene-NO experiments are shown in Figure 3. The oxidation of 3-methyl-1-butene is initiated by its reaction with the OH radical (reaction with ozone becomes important after the NO/NO<sub>2</sub> cross-over, see below) and involves OH addition as the major pathway:

$$(CH_3)_2CHCH = CH_2 + OH \rightarrow (CH_3)_2CHCHCH_2OH \quad (22a)$$

 $\rightarrow$  (CH<sub>3</sub>)<sub>2</sub>CHCHOHCH<sub>2</sub> (22b)

Reaction with OH may also involve H-atom abstraction from the weak C-H bond as a minor pathway:

$$(CH_3)_2CHCH=CH_2 + OH \rightarrow (CH_3)_2CCH=$$
  
CH<sub>2</sub> + H<sub>2</sub>O (23)

leading to formaldehyde and to methyl vinyl ketone and/ or acetone. The alkyl radicals formed in eq 22 lead to the corresponding alkoxy radicals (via  $R + O_2 \rightarrow RO_2$ ,  $RO_2 + O_2 \rightarrow RO_2$ )  $NO \rightarrow RO + NO_2$ ). These  $\beta$ -hydroxy alkoxy radicals are expected to evolve mostly by unimolecular decomposition (30), thus yielding formaldehyde and isobutanal:

$$(CH_3)_2CHCH(O)CH_2OH \rightarrow$$
  
 $(CH_3)_2CHCHO + CH_2OH$  (24a)  
 $CH_2OH + O_2 \rightarrow HCHO + HO_2$  (24b)

$$CH_2OH + O_2 \rightarrow HCHO + HO_2$$
 (24b)

\* 
$$(CH_3)_2CHCHOH CH_2O \rightarrow$$

HCHO +  $(CH_3)_2$  CHCHOH (24c)

$$(CH_3)_2$$
CHCHOH +  $O_2 \rightarrow$   
H $O_2$  +  $(CH_3)_2$ CHCHO (24d)

followed by reactions of isobutanal and production of PiBN. Concentrations of isobutanal, methyl vinyl ketone (none was detected), and acetone in carbonyl samples collected before the NO/NO<sub>2</sub> cross-over indicated that  $k_{22}$ /  $k_{23} \ge 0.98$ , i.e., that most of the OH-3-methyl-1-butene reaction proceeds by addition of OH on the C=C bond. Later in the experiment ozone is formed and reacts with 3-methyl-1-butene to yield formaldehyde and isobutanal (therefore leading to more PiBN) as the major products (33).

Estimates of Relative Abundance of PiBN and PAN in Urban Air. Since PiBN and PAN co-elute on the type

Table 1.	<b>PiBN-Forming</b>	Potential of	Hydrocarbon	Precursors Usi	ng Los A	Angeles 1	Emission	Inventory
----------	---------------------	--------------	-------------	----------------	----------	-----------	----------	-----------

precursor hydrocarbon	$\begin{array}{l} A = \text{emission rate} \\ (t/day) \end{array}$	$B = 10^{11} \times OH$ reaction rate constant (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	AB	$C = correction \ factor^a$	ABC
olefins					
3-methyl-1-butene	8.6	3.2	27.5	0.54	14.9
2,3-dimethyl-1-butene	5.2	5.5	28.6	0.65	18.6
aromatics					
isopropyl benzene	0.2	~0.6	0.12	0.5	0.06
diisopropyl benzene (isomers)	unknown	-	-	0.5	
carbonyls					
isobutanal	0	2.63	0		0
paraffins					
2.3-dimethylbutane	5	0.63	3.15		3.15
2.4-dimethylpentane	2.6	0.51	1.3		1.3
1.2.4-trimethylpentane	20	$\sim 0.5$	10		10
total PiBN			70.6		48.0
total PAN <sup>b</sup>			776		430
ratio PiBN/PAN			0.09		0.11

of packed columns that have been used in virtually all previous measurements of ambient PAN made by EC-GC, it is of interest to estimate the possible contribution of PiBN (i.e., positive bias) to reported PAN concentrations in urban air.

Since PiBN and PAN have comparable thermal decomposition rates (34), the ratio of their ambient concentrations in urban air should to a large extent reflect the ratio of their rates of formation. These formation rates are proportional to the emission rates and chemical reactivity of the hydrocarbons that are precursors to PAN and PiBN. Even if reliable hydrocarbon emission inventories were available (35, 36), precise calculations of PiBN and PAN formation rates would require, for each hydrocarbon, a detailed knowledge of photooxidation pathways, of the relative importance of these pathways, and of the corresponding PiBN and PAN yields. This information is not available for most hydrocarbons. However, estimates of the relative production rates of PiBN and PAN can be made by simply taking the product, for each hydrocarbon, of its emission rate and of some measure of its chemical reactivity. Such estimates are presented in Table 1 for hydrocarbons that are precursors to PiBN.

The emission rates given in Table 1 are those for the California South Coast Air Basin updated and modified by Grosjean and Seinfeld (36). Since all hydrocarbons react with the OH radical, we take the OH-hydrocarbon reaction rate constant as a measure of the hydrocarbon reactivity. The PiBN-forming potential thus estimated is an upper limit for olefins, which also react with ozone to form products other than PiBN. It is also an upper limit for aromatics, since ring-opening products (which lead to PiBN) typically account for only 40-50% of the overall OH-aromatic reaction (15, 16). For paraffins, our estimates are limited to those 16 alkanes that are among the 25 most abundant hydrocarbons in Los Angeles ambient air (15, 16). No correction factor has been applied to take into account the several possible sites of H-atom abstraction involved in the OH-alkane reaction, some of which lead to products other than PiBN.

With these symplifying assumptions, the PiBN-forming potentials listed in Table 1 are dominated by two olefins (3-methyl-1-butene and 2,3-dimethyl-1-butene, which together account for about 80% of the total) followed by several alkanes (combined contribution = 20%). As discussed in detail elsewhere (15, 16), the total PANforming potential has been estimated for the same set of urban (Los Angeles) hydrocarbon emissions using the same assumptions. While the PiBN and PAN-forming potentials thus calculated will require revisions as more reliable emission inventories become available (35), their ratio should remain about the same irrespective of changes in total hydrocarbon emission rates. The ratio of the two forming potentials (PiBN/PAN) is about 0.10, i.e., 0.09 and 0.11 with and without using the correction factors discussed above. This ratio, by virtue of the assumptions made as explained above, is most likely to represent an upper limit for actual PiBN/PAN concentration ratios in urban air. For example, with the same assumptions, we have previously calculated a forming potential ratio of 0.16 for peroxy-n-butyryl nitrate (PnBN) relative to that of PAN. Measured PnBN/PAN concentration ratios in ambient air averaged 0.08 (16), i.e., only half of the calculated ratio. Thus, the actual PiBN positive bias to ambient (urban) PAN measurements is probably less than the value of 10% calculated from forming potential vs HC precursors considerations. This bias is small and is comparable in magnitude to the precision of PAN measurements at ppb levels in urban air (1, 14-18).

Conversely, the results of this study indicate that attempts to measure ambient PiBN must involve GC columns other than those traditionally used to measure PAN (and suitable to measure PPN, PnBN, etc.) in ambient air (1, 14-18). In rural areas, caution should be exercised since localized sources of PiBN precursors, e.g., biogenic emissions, could result in a positive bias from PiBN to the PAN concentrations measured by electron capture gas chromatography using packed columns.

#### Acknowledgments

This work has been supported by a contract with the Southern California Edison Co., Rosemead, CA, and by internal research and development funds, DGA, Inc., Ventura, CA. Denise Velez prepared the draft and final versions of the manuscript.

### Literature Cited

- Stephens, E. R. Adv. Environ. Sci. Technol. 1969, 1, 119– 146.
- (2) Peak, M. J.; Belser, W. L. Atmos. Environ. 1969, 3, 385-397.
- (3) Kleindienst, T. E.; Shepson, P. B.; Edney, E. O.; Claxton, L. D. Mutat. Res. 1985, 157, 123-128.

- (4) Kleindienst, T. E.; Shepson, P. B.; Smith, D. F.; Hudgens, E. E.; Nero, C. M.; Cupitt, L. T.; Bufalini, J. J.; Claxton, L. D. Environ. Mol. Mutagen. 1990, 16, 70-80.
- (5) Taylor, O. C. J. Air Pollut. Control Assoc. 1969, 19, 347– 351.
- (6) Taylor, O. C.; MacLean, D. C. Nitrogen oxides and the peroxyacyl nitrates. In *Recognition of Air Pollution Injury* to Vegetation: A Pictorial Atlas; Jacobson, J. S., Hill, A. C., Eds.; Air Pollution Control Association: Pittsburgh, PA, 1970; pp E1-E14.
- (7) Mudd, J. B. Peroxyacyl nitrates. In Responses of Plants to Air Pollution; Mudd, J. B., Kozlowski, T. T., Eds.; Academic Press: New York, 1975; pp 97-119.
- (8) Singh, H. B.; Hanst, P. L. Geophys. Res. Lett. 1981, 8, 941– 944.
- (9) Singh, H. B.; Salas, L. J.; Ridley, B. A.; Shetter, J. D.; Donohue, N. M.; Fehsenfeld, F. C.; Fahey, D. W.; Parrish, D. D.; Williams, E. J.; Liu, S. C.; Huebler, G.; Murphy, P. C. Nature 1985, 318, 347-349.
- (10) Kasting, J. F.; Singh, H. B. J. Geophys. Res. 1986, 91, 13239– 13256.
- (11) Singh, H. B. Environ. Sci. Technol. 1987, 21, 320-327.
- (12) Williams, E. L., II; Grosjean, D. Atmos. Environ. 1990, 24A, 2369–2377.
- (13) Fahey, D. W.; Hübler, G.; Parrish, D. D.; Williams, E. J.; Norton, R. B.; Ridley, B. A.; Singh, H. B.; Liu, S. C.; Fehsenfeld, F. C. J. Geophys. Res. 1986, 91, 9781–9793.
- (14) Williams, E. L., II; Grosjean, D. Environ. Sci. Technol. 1991, 25, 653–659.
- (15) Grosjean, D.; Williams, E. L., II; Grosjean, E. Environ. Sci. Technol. 1993, 27, 110-121.
- (16) Grosjean, D.; Williams, E. L., II; Grosjean, E. Environ. Sci. Technol. 1993, 27, 326-331.
- (17) Grosjean, D.; Williams, E. L., II J. Air Waste Manage. Assoc. 1992, 42, 805–809.
- (18) Williams, E. L., II; Grosjean, E.; Grosjean, D. J. Air Waste Manage Assoc. 1993, 43, 873-879.
- (19) Gaffney, J. S.; Fajer, R.; Senum, G. I. Atmos. Environ. 1984, 18, 215-218.

- (20) Grosjean, D.; Williams, E. L., II; Seinfeld, J. H. Environ. Sci. Technol. 1992, 26, 1526-1533.
- (21) Druzik, C. M.; Grosjean, D.; Van Neste, A.; Parmar, S. S. Int. J. Environ. Anal. Chem. 1990, 38, 495-512.
- (22) Grosjean, D. Environ. Sci. Technol. 1991, 25, 710-715.
- (23) Grosjean, D. Anal. Chem. 1983, 55, 2436-2439.
- (24) Senum, G. I.; Fajer, R.; Gaffney, J. S. J. Phys. Chem. 1986, 90, 152–156.
- (25) Grosjean, D.; Williams, E. L., II; Grosjean, E. Environ. Sci. Technol. 1993, 27, 830–840.
- (26) Grosjean, D.; Parmar, S. S.; Williams, E. L. Atmos. Environ. 1990, 24A, 1207–1210.
- (27) Cox, R. A.; Roffey, M. J. Environ. Sci. Technol. 1977, 11, 900–906.
- (28) Tuazon, E. C.; Carter, W. P. L.; Atkinson, R. J. Phys. Chem. 1991, 95, 2434–2437.
- (29) Carter, W. P. L.; Atkinson, R. J. Atmos. Chem. 1989, 83, 165–173.
- (30) Atkinson, R.; Carter, W. P. L. J. Atmos. Chem. 1991, 13, 195-210.
- (31) Atkinson, R. Atmos. Environ. 1990, 24A, 1-41.
- (32) Atkinson, R.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. J. Air Pollut. Control Assoc. 1981, 31, 1090-1092.
- (33) Grosjean, D.; Williams, E. L., II; Grosjean, E. Environ. Sci. Technol. 1994, 28, 186–196.
- (34) Grosjean, D.; Grosjean, E.; Williams, E. L., II Res. Chem. Intermed., in press.
- (35) Fujita, E.; Croes, B. E.; Bennett, C. E.; Lawson, D. R.; Lurmann, F. W.; Main, H. H. J. Air Waste Manage. Assoc. 1992, 42, 264–276.
- (36) Grosjean, D.; Seinfeld, J. H. Atmos. Environ. 1989, 23, 1733– 1747.

Received for review July 2, 1993. Revised manuscript received September 30, 1993. Accepted October 4, 1993.\*

• Abstract published in Advance ACS Abstracts, November 15, 1993.