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Alkyl Nitrate Formation from the NO_x–Air Photooxidations of C_2–C_8 *n*-Alkanes

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The yields of alkyl nitrates formed in the NO_x–air photooxidations of the homologous series of *n*-alkanes from ethane through *n*-octane have been determined at 299 ± 2 K and 735 torr total pressure for two different chemical systems. Alkyl peroxy radicals were generated by reaction of the *n*-alkanes with OH radicals (generated from the photolysis of methyl nitrite in air) or Cl atoms (from photolysis of Cl_2 in air). The alkyl nitrate yields obtained from the two systems, corrected for secondary reactions, were in agreement within the experimental errors and increased monotonically with the carbon number of the *n*-alkane, from $\leq 1\%$ for ethane to $\sim 33\%$ for *n*-octane, with the yields apparently approaching a limit of $\sim 35\%$ for large *n*-alkanes. The relative yields of the various secondary alkyl nitrate isomers in the *n*-pentane through *n*-octane systems were in good agreement with those expected from OH radical or Cl atom reaction with the corresponding secondary C–H bonds. However, the relative yields of the primary alkyl nitrates in the propane and butane systems were a factor of ~2 lower than expected. The data are consistent with the alkyl nitrates being formed almost entirely from the reaction of peroxy radicals with NO, and the ratios of the corrected alkyl nitrate yields thus reflect the fraction of RO_2 radicals which react with NO to form alkyl nitrates. These nitrate yields from the reaction of RO_2 radicals with NO are important inputs into chemical computer models of the atmospheric NO_x–air photooxidations of the large *n*-alkanes.

Introduction

Radical species and oxides of nitrogen (NO_x) are both essential to the formation of photochemical air pollution,[1-7] and thus an accurate knowledge of their major sinks is critical to our understanding of this process. The formation of alkyl nitrates ($RONO_2$), which can occur in the atmosphere either via the reactions of alkoxy radicals with NO_2[2]

$$RO + NO_2 \xrightarrow{M} RONO_2 \qquad (1)$$

or via the reactions of alkylperoxy radicals with NO[2,5,8]

$$RO_2 + NO \xrightarrow{M} [RO_2NO] \rightarrow RONO_2 \qquad (2)$$

(where RO and RO_2 are formed as intermediates in the atmospheric oxidation of most reactive organics[2]) represent a sink for both radicals and NO_x. Thus the amount of alkyl nitrate formation occurring during the photooxidation of a given reactive organic must be known if the impact of the emission of that organic on photochemical smog formation is to be accurately assessed.

Since most alkoxy radicals react rapidly under atmospheric conditions with O_2,[2,9-16] and most large ($\geq C_4$) alkoxy radicals also rapidly decompose[2,10-12,17] or isomerize,[2,10,18-21] alkyl nitrate formation from reaction 1 is relatively unimportant for most organics under atmospheric conditions. However, Darnall et al.[8] observed relatively high yields of alkyl nitrates in environmental chamber studies of the NO_x–air photooxidations of *n*-butane, *n*-pentane, and *n*-hexane, with yields which increased with the size of the molecule and which could only be attributed to their formation via reaction 2.

In this work, alkyl nitrate yields have been determined for the NO_x–air photooxidations of the C_2 through C_8 *n*-alkane series, and the importance of reaction 2, relative to the competing radical chain-propagating and NO_x-conserving reaction of alkyl peroxy radicals with NO

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (3)$$

has been quantitatively determined, allowing its dependence on alkane chain length to be better understood.

Experimental Section

Two chemical systems were used to form RO_2 radicals in the presence of NO. The first consisted of photolysis at ≥290 nm of methyl nitrite–NO–*n*-alkane mixtures in ultra-zero air, with typical initial reactant concentrations

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being CH_3ONO, ~0.7–1.7 ppm; NO, ~0.5–1.7 ppm; and *n*-alkane, ~1.0 ppm (where 1 ppm = 2.37×10^{13} molecule cm^{-3} at 299 K and 735 torr total pressure). One irradiation of this system was also carried out with ~1 ppm of NO_2 included in the reaction mixture. The other chemical system used consisted of the photolysis of Cl_2–NO–*n*-alkane mixtures in ultra-zero air, with typical initial reactant concentrations being Cl_2, ~1.0 ppm; NO, ~0.6 ppm; and *n*-alkane, ~1.0 ppm.

The irradiations were carried out in ~75 L FEP Teflon cylindrical reaction chambers surrounded by 24 GE F15T8-BL 15-W blacklights. For the irradiations carried out in this study, 1/3 of the maximum light intensity was employed corresponding to photolysis half-lives of ~30 min for methyl nitrite and ~20 min for Cl_2. All irradiations were carried out at 299 ± 2 K and ~735 torr total pressure.

NO, total NO_x, and the *n*-alkane reactants and the alkyl nitrate products were quantitatively monitored prior to and during the irradiations. NO and NO_x were monitored with a Columbia Industries, Inc., Model 1600 chemiluminescence analyzer and the organics were analyzed by gas chromatography with flame ionization detection (GC-FID). The alkanes *n*-butane through *n*-octane were analyzed with a 20 ft × $^1/_8$ in. stainless steel (SS) column with 5% DC703/C20M on 100/120 mesh AW, DMCS Chromosorb G, operated at 333 K, while propane was analyzed with a 36 ft × $^1/_8$ in. SS column of 10% 2,4-dimethylsulfolane (DMS) on C-22 firebrick (60/80 mesh) operated at 273 K. No sample preconcentration was required for the analyses of these *n*-alkanes. The alkyl nitrates were analyzed with a 10 ft × $^1/_8$ in. SS column of 10% Carbowax 600 on C-22 firebrick (100/110 mesh), operated at 348 K, for the propyl, butyl, and pentyl nitrates, and a 5 ft × $^1/_8$ in. SS column of 5% Carbowax 600 on C-22 firebrick (100/110 mesh), operated at 348 K, for the hexyl, heptyl, and octyl nitrates. For these analyses 100 cm^3 of gas sample was preconcentrated in a ~1-cm^3 SS loop at liquid argon temperature prior to injection onto the column.

Gas chromatographic (GC) calibrations and retention times were determined for all of the individual *n*-alkanes studied and for 1-propyl, 2-propyl, 1-butyl, 2-butyl, 2-pentyl, 3-pentyl, 2-hexyl, 3-hexyl, 3-heptyl, and 3-octyl nitrates. For the 2-heptyl, 4-heptyl, 2-octyl, and 4-octyl nitrates, the retention times were determined from the GC positions of peaks due to minor levels of these isomers in the authentic 3-heptyl and 3-octyl nitrate samples. The GC calibration factors were derived for these isomers by assuming that the GC-FID response was constant for all the heptyl nitrates, and similarly for the octyl nitrates. 2-Propyl nitrate was obtained from Eastman Kodak; 1-butyl nitrate was obtained from Matheson Coleman and Bell; and the 2-butyl, 2-pentyl, 2-hexyl, 3-heptyl, and 3-octyl nitrates were obtained from Fluorochem, Inc. The 2-pentyl and 2-hexyl nitrates had significant levels (~15–30%) of the 3 isomers.[22] Methyl nitrite was prepared and purified as described elsewhere.[22,23] For the other reactants, commercial samples (>98% stated purity level) were used without further purification.

For the experiments involving methyl nitrite photolysis, the irradiations were of ~30–60-min duration. For experiments involving Cl_2, which were of a more confirmatory nature (see below), because of the higher photolysis rate of Cl_2, yielding two Cl atoms per Cl_2 photolyzed (and hence of production of alkyl peroxy radicals) several 1-, 2-, or 5-min irradiations of the same mixture were carried out during each experiment, with GC analyses being conducted at the end of each irradiation period.

Results

The initial reactant concentrations and the observed amounts of *n*-alkane consumed and alkyl nitrate formed, as measured at various times during the irradiations, are given in Tables I–VI for the CH_3ONO–NO–alkane–air irradiations and in Table VII for the Cl_2–NO–alkane–air runs. (Tables I–VII are available as supplementary material to this manuscript, see paragraph at end of text regarding supplementary material.) It can be seen from these tables that alkyl nitrate formation was observed without any apparent induction period and that it increased linearly with the amount of *n*-alkane consumed. One CH_3ONO–NO–*n*-butane–*n*-octane–air irradiation was carried out with 1 ppm of NO_2 also initially present, and the presence of NO_2 had no significant effect on the alkyl nitrate yields or isomeric ratios (see Tables II and VI, run 9–10).

The isomeric distribution of the 2- and 3-alkyl nitrates formed in the Cl_2–NO–*n*-alkane–air photolysis system were not significantly different from those in the methyl nitrite photolysis system for the *n*-pentane and *n*-hexane systems, but for propane and *n*-butane the observed ratios of [1-alkyl nitrate]/[2-alkyl nitrate] were significantly higher than those observed in the methyl nitrite system. These results are discussed in more detail in the following section.

Discussion

Methyl Nitrite Photolysis System. The major reactions occurring in the CH_3ONO–NO–*n*-alkane–air photolysis system can be represented as follows:[2]

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \qquad (4)$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \qquad (5)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (6)$$

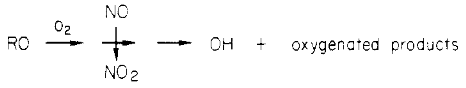
$$OH + RH \rightarrow R + H_2O \qquad (7)$$

$$R + O_2 \xrightarrow{M} RO_2 \qquad (8)$$

$$RO_2 + NO \xrightarrow{M} RONO_2 \qquad (2)$$

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (3)$$

$$RO + NO_2 \xrightarrow{M} RONO_2 \qquad (1)$$



$$RO \xrightarrow{O_2} \overset{NO}{\underset{NO_2}{+}} \longrightarrow OH + \text{oxygenated products} \qquad (9)$$

$$RONO_2 + OH \rightarrow \text{products} \qquad (10)$$

In this system, the *n*-alkane and the alkyl nitrates are consumed essentially solely by reaction with OH radicals (reactions 7 and 10). Reaction with NO, forming either the corresponding alkyl nitrate (reaction 2) or the alkoxy radical (reaction 3), is the only significant sink for the alkyl peroxy radicals formed from the reaction of OH radicals with the *n*-alkanes, since the reactions of alkyl peroxy radicals with NO_2 forming alkyl peroxynitrates

$$RO_2 + NO_2 \rightleftarrows RO_2NO_2 \qquad (11, -11)$$

are insignificant due to the rapid back-decomposition of the alkyl peroxynitrates.[5,24,25]

In this system the formation of alkyl nitrates can occur either from the reaction of alkyl peroxy radicals with NO (reaction 2) or from the reaction of alkoxy radicals with NO_2 (reaction 1). However, since alkoxy radicals can also

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react with O$_2$,[2,9–16] decompose,[2,10–12,17] or isomerize[2,10,18–21] to ultimately give rise to products other than alkyl nitrates (shown overall as reaction 9), a number of other reactions compete with alkyl nitrate formation from alkoxy radicals.

Upper limits for the contribution of reaction 1 to the observed alkyl nitrate yields for these experiments can be estimated from the rate constants for the reactions of alkoxy radicals with NO$_2$ and O$_2$, and the NO$_2$ and O$_2$ concentrations. Alkoxy radicals react with NO$_2$ with a rate constant of $k_1 \simeq 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at room temperature and atmospheric pressure.[2] The reactions of alkoxy radicals with O$_2$ have received little direct attention, but recently Gutman et al.[16] have determined a rate constant of 8×10^{-15} cm^3 molecule^{-1} s^{-1} at 296 K for the reaction

$$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$$

Furthermore, from thermochemical considerations, Gutman et al.[16] have derived rate constants at room temperature for the reaction of 1-alkoxy radicals with O$_2$ of $\sim 7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, with the 2-propoxy and 2-butoxy radicals reacting ~5 times faster. Hence, assuming a maximum of 2 ppm of NO$_2$ in these experiments (based on the total initial concentrations of nitrogen-containing species, e.g., NO and CH$_3$ONO, which can yield NO$_2$), and considering only the reactions of RO radicals with O$_2$ and NO$_2$, then a maximum yield of alkyl nitrate formation from the reaction of RO radicals with NO$_2$ of 2.0% can be calculated for 1-alkyl nitrates, with yet lower maximum yields for the secondary alkyl nitrates. Since (a) all the initial nitrogenous species are not converted to NO$_2$ during NO$_x$–organic–air irradiations,[1–7] (b) larger ($\geq$C$_4$) alkoxy radicals undergo significant decomposition and isomerization reactions,[2,10–12,17–21] and (c) the secondary alkoxy radicals undergo faster reaction with O$_2$,[16] it may be concluded that less than 1% of the observed alkyl nitrate yields are due to the reaction of alkoxy radicals with NO$_2$ in the CH$_3$ONO–NO–*n*-alkane (propane through *n*-octane)–air irradiations carried out in this study. This is negligible for these *n*-alkanes.

The conclusion that alkyl nitrate yields from the RO + NO$_2$ reactions are minor is supported by the results of the experiment in which 1 ppm of NO$_2$ was also added to the initial CH$_3$ONO–NO–alkane–air mixture. The alkyl nitrate yields in this experiment were observed to be indistinguishable from those without added NO$_2$ (Tables II and VI). For the Cl atom initiated systems (discussed in the following section), where NO$_2$ formation from CH$_3$ONO photolysis did not occur, alkyl nitrate formation from the RO + NO$_2$ reaction would be less significant still, and even for the ethane system would be $\leq$0.7%.

Thus it is clear that the major source of alkyl nitrates observed in the present experiments is from reaction 2, and that the observed alkyl nitrate yields should reflect the rate constant ratio $k_2/(k_2 + k_3) = \alpha$, since alkoxy radical formation (reaction 3) is the only significant process competing with reaction 2 in the alkane photooxidation chain. However, so that α can be derived from the observed alkyl nitrate product yields, a correction must be made for the secondary reactions of the alkyl nitrates. This was carried out as indicated below.

Recent work in these laboratories[22,23] has shown that reaction with OH radicals is the major loss process for the alkyl nitrates and the alkanes under the conditions of these experiments. Therefore, the alkane and alkyl nitrate concentrations are governed by

$$d[RH]/dt = -k_7[OH][RH] \qquad (I)$$

$$d[RONO_2]/dt = \alpha k_7[OH][RH] - k_{10}[OH][RONO_2] \qquad (II)$$

where k_7 and k_{10} are the rate constants for the reactions of OH radicals with the alkanes and the alkyl nitrates, respectively. Under conditions where the OH radical concentration is constant, these equations can be integrated to obtain

$$[RH]_t = [RH]_0 e^{-k_7[OH]t} \qquad (III)$$

$$[RONO]_t = [RH]_0 \frac{\alpha k_7}{(k_7 - k_{10})}\left[e^{-k_{10}[OH]t} - e^{-k_7[OH]t}\right] \qquad (IV)$$

where $[RH]_0$ is the initial *n*-alkane concentration, [OH] is the constant hydroxyl radical concentration, and $[RH]_t$ and $[RONO_2]_t$ are the alkane and alkyl nitrate concentrations, respectively, at time *t*. Equations III and IV can be combined to obtain

$$\alpha = F\{[RONO_2]_t/\Delta[RH]_t\} \qquad (V)$$

where

$$F = \left(\frac{k_7 - k_{10}}{k_7}\right)\left\{\frac{1 - ([RH]_t/[RH]_0)}{([RH]_t/[RH]_0)^{k_{10}/k_7} - ([RH]_t/[RH]_0)}\right\} \qquad (VI)$$

and $\Delta[RH]_t = ([RH]_0 - [RH]_t)$. Note that the correction factor *F* does not have any dependence on the OH radical concentration, and thus eq VI might be expected to be valid even under conditions where [OH] is not constant throughout the experiment, as was the case for the irradiations carried out in this work. Computer simulations indeed showed that the use of these equations introduced a totally negligible error in accounting for the OH radical reactions with the alkyl nitrates.

Equations V and VI were used to correct each of the data points for each alkyl nitrate isomer given in Tables I–VI. *F* was calculated from the experimentally observed amounts of *n*-alkanes consumed and the values of k_7 and k_{10} obtained from recent kinetic studies from these laboratories.[22,23] The largest correction corresponded to a value of *F* of 1.18 for the 2-octyl nitrate yield at 35% *n*-octane reacted (run 9-2A, Table VI), and in most cases these corrections were relatively minor.

Plots of the total corrected alkyl nitrate yields against the amount of *n*-alkane reacted are shown in Figures 1 and 2 for the methyl nitrite photolysis runs. It can be seen that, consistent with our assumption that the alkyl nitrates are a primary product in the *n*-alkane photooxidations, in all cases straight line plots with zero intercepts (within one least-squares standard deviation) were obtained. Table VIII lists the least-squares slopes obtained from those plots, which can be identified with the fraction, α, of the *n*-alkane reacted yielding the observed alkyl nitrates.

Chlorine Photolysis System. The major reactions occurring in the Cl$_2$–NO–alkane–air irradiations can be represented as follows:

$$Cl_2 + h\nu \rightarrow 2Cl \qquad (12)$$

$$Cl + NO_2 \rightarrow ClNO_2 \qquad (13)$$

$$Cl + NO \underset{h\nu}{\rightleftharpoons} ClNO \qquad (14)$$

$$Cl + RH \rightarrow HCl + R \qquad (15)$$

$$OH + RH \rightarrow H_2O + R \qquad (7)$$

$$R \xrightarrow{O_2,\ NO_x} \alpha'\ RONO_2 + (\text{oxygenated products}) + (1 - \alpha')\ OH \qquad (16)$$

$$RONO_2 + Cl \rightarrow \text{products} \qquad (17)$$

$$RONO_2 + OH \rightarrow \text{products} \qquad (10)$$

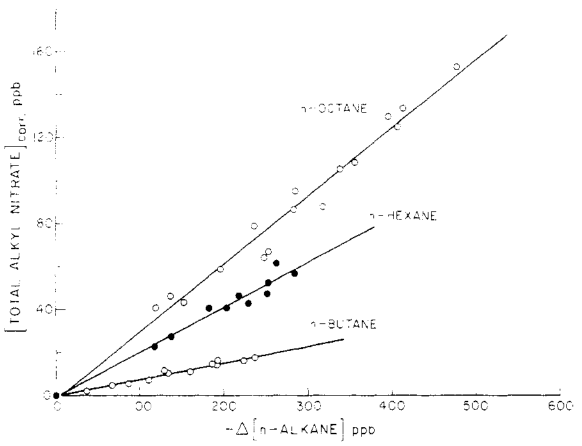

Figure 1. Plots of total alkyl nitrate yields observed in CH_3ONO-NO-*n*-alkane-air irradiations, corrected for reaction with OH radicals (see text), against the amount of *n*-alkane consumed for *n*-butane, *n*-hexane, and *n*-octane.

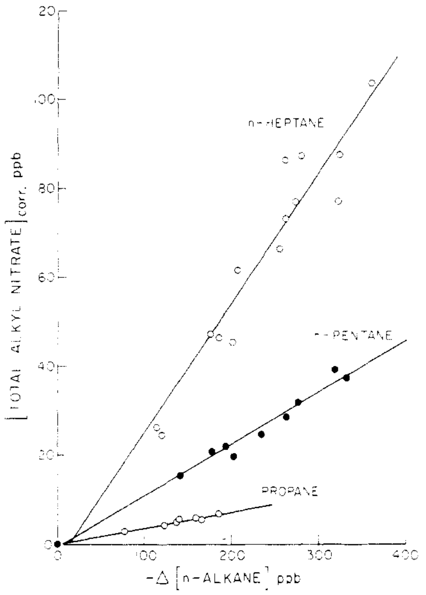

Figure 2. Plots of total alkyl nitrate yields observed in CH_3ONO-NO-*n*-alkane-air irradiations, corrected for reaction with OH radicals (for *n*-pentane and *n*-heptane, see text), against the amount of *n*-alkane consumed for propane, *n*-pentane, and *n*-heptane.

TABLE VIII: Yields of Alkyl Nitrates, Relative to the *n*-Alkane Consumed, in CH_3ONO-NO-*n*-Alkane-Air Irradiations

n-alkane	[total alkyl nitrate]^a/$-\Delta$[*n*-alkane]
propane	0.036 ± 0.005
n-butane	0.077 ± 0.009
n-pentane	0.117 ± 0.013, 0.129 ± 0.019^b
n-hexane	0.208 ± 0.027, 0.223 ± 0.035^b
n-heptane	0.293 ± 0.042, 0.309 ± 0.050^b
n-octane	0.318 ± 0.027, 0.332 ± 0.034^b

[a] Obtained by least-squares analyses of the data given in Tables I-VI and shown in Figures 1 and 2. For *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane, no gas chromatographic retention times were available for the 1-alkyl nitrates, hence the data for these *n*-alkanes are the sum of the yields of the 2-, 3-, and, for *n*-heptane and *n*-octane, the 4-alkyl nitrates. The indicated error limits are two least-squares standard deviations. Corrected for alkyl nitrate loss reaction with OH radicals (see text). [b] Calculated to take into account 1-alkyl nitrate formation, based on the OH + *n*-alkane kinetic data of ref 23. Error limits have been increased corresponding to a 50% uncertainty in these unobserved yields of 1-alkyl nitrate.

TABLE IX: Yields of Alkyl Nitrates, Relative to the *n*-Alkane Consumed, in Cl_2-NO-*n*-Alkane-Air Irradiations

	[total alkyl nitrate]/$-\Delta$[*n*-alkane]	
n-alkane	obsd^a	corr^b
ethane	0.010 ± 0.002	0.012 ± 0.002
propane	0.024 ± 0.005	0.029 ± 0.003
n-butane	0.075 ± 0.005	0.085 ± 0.009
n-pentane	0.120 ± 0.005^c	0.133 ± 0.004^c
n-hexane	0.171 ± 0.032^c	0.193 ± 0.036^c

[a] Based on observed yields. [b] Ratio assuming that the alkyl nitrates are consumed as fast as are the *n*-alkanes in the experimental system employed. [c] 2- and 3-alkyl nitrates; due to no retention times for 1-alkyl nitrates, no data for these isomers were obtained.

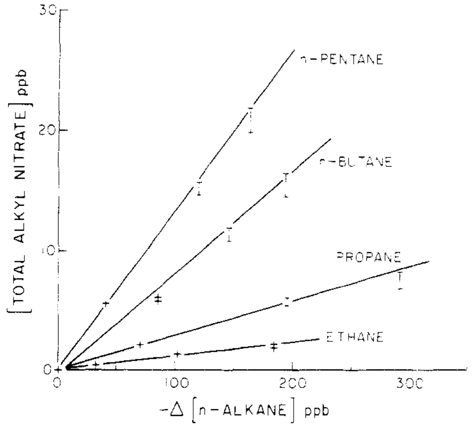

Figure 3. Plots of total alkyl nitrate observed in Cl_2-NO-*n*-alkane-air irradiations against the amount of *n*-alkane consumed for ethane, propane, *n*-butane, and *n*-pentane. The bottom horizontal bar of the data points is the observed yield, the top bar is that assuming that the alkyl nitrates are removed by reactions with rate constants equal to those for removal of the parent *n*-alkanes (see text). The lines drawn are from the least-squares analyses of the data assuming that the alkyl nitrates react with Cl atoms as fast as do the parent *n*-alkanes.

Note that OH radicals are generated in the NO_x-air photooxidation of the alkyl radicals formed by the reaction of Cl atoms with the alkanes, so the alkane is consumed by reaction with OH radicals as well as with Cl atoms. In reaction 16 α' represents the fractional alkyl nitrate yield in the Cl_2 photolysis system. Since in general a somewhat different ratio of the isomeric alkyl radicals is expected to be formed in reaction 15 than in reaction 7 (see following section), and it is possible that the different RO_2 isomers may have slightly different alkyl nitrate formation efficiencies, α' may not necessarily be the same as α, the fractional yield obtained when all of the alkane reacts with OH radicals.

Since the rate constants for the reaction of Cl atoms with alkyl nitrates are not known, and since the fraction of alkane or alkyl nitrate reaction with OH radicals vs. Cl atoms is also not known, accurate values of the correction factor to account for reactive loss processes of the alkyl nitrates cannot be calculated. However, an upper limit to this factor can be obtained by assuming that Cl atoms react with the alkyl nitrates no faster than they react with the parent alkanes. This assumption is likely, since the Cl atom reaction rates for the alkanes at room temperature

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TABLE X: Ratios of Alkyl Nitrate Isomers Formed during CH_3ONO-NO-*n*-Alkane-Air Irradiations, Compared with Ratios Calculated from Kinetic Data[a,b]

	[1-alkyl nitrate]/ [2-alkyl nitrate]		[3-alkyl nitrate]/ [2-alkyl nitrate]		[4-alkyl nitrate]/ [2-alkyl nitrate]	
n-alkane	obsd[a]	calcd[b]	obsd[a]	calcd[b]	obsd[a]	calcd[b]
propane	0.22 ± 0.10	0.45				
n-butane	0.07 ± 0.21	0.17				
n-pentane	*c*	0.17	0.67 ± 0.09	0.71		
n-hexane	*c*	0.17	1.34 ± 0.11	1.43		
n-heptane	*c*	0.17	1.35 ± 0.15	1.43	0.62 ± 0.10	0.71
n-octane	*c*	0.17	1.41 ± 0.14	1.43	1.32 ± 0.18	1.43

[a] Observed alkyl nitrate yields corrected for reaction of alkyl nitrates with OH radicals (see text). Indicated error limits are two standard deviations. [b] Calculated ratios from the kinetic study of ref 23. [c] Not observed, no retention times available.

are in the range ~5 × 10^{-11} to ~2 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} for the C_2 through C_4 alkanes.[26] With this assumption, and assuming no involvement of OH radicals, then the correction factor would be 1.055 for 10% alkane reaction and 1.118 for 20% alkane reaction.

The total observed and corrected alkyl nitrate yields in the Cl_2–NO–*n*-alkane–air irradiations are listed for each data point in Table VII and plotted against the amount of *n*-alkane consumed in Figure 3. The fractional alkyl nitrate yields from these systems, α', obtained from least-squares slopes of the lines plotted in Figure 3, are given in Table IX. The corrected yield ratios for the observed alkyl nitrates in the Cl_2 photolysis experiments agreed with those in the CH_3ONO photolysis experiments to within ±15% for *n*-butane through *n*-hexane, and within ±20% for propane. The Cl atom initiation system also enabled an upper limt to the alkyl nitrate yield to be obtained for the ethane system; this was not practical using CH_3ONO initiation since OH radicals react with ethane too slowly to yield an appreciable degree of reaction.

Isomeric Yield Ratios. Table X gives the ratios of the isomeric yields of the alkyl nitrates observed in the CH_3ONO–NO–alkane–air irradiations, together with the expected ratios as calculated from the recent kinetic data of Atkinson et al.,[23] assuming the efficiency of alkyl nitrate formation is the same for each isomer formed from a given alkane. Atkinson et al.[23] showed that the total OH radical rate constant for the *n*-alkanes propane through *n*-decane (at 299 ± 2 K) can be given by the sum of group rate constants (i.e., rate constants for each CH_3 group; for each CH_2 bonded to two CH_3 groups; for each CH_2 bonded to one CH_3 and one CH_2, etc.), and the calculated ratios shown in Table X are based on the reasonable assumption that these group rate constants actually reflect the rate of OH radical attack on the corresponding group.

The observed isomeric alkyl nitrate ratios for the secondary alkyl nitrates in the CH_3ONO photolysis-initiated system are seen (Table X) to be in excellent agreement with those predicted from RO_2 formation yields from this previous kinetic study,[23] i.e., the alkyl nitrate ratios for the 2-, 3-, and 4-alkyl nitrate isomers are in excellent agreement with the ratios of the 2-, 3-, and 4-alkyl radical formation rates based on kinetic evidence. For propane and *n*-butane, however, the amounts of primary alkyl nitrate observed were approximately a factor of 2 lower than expected from kinetic results (though within the error limits for the butane system). This may reflect either a lower fraction of nitrate formation from RO_2 radicals for 1-alkyl peroxy radicals, as compared to 2-, 3-, or 4-alkyl peroxy radicals, or a lower reactivity of primary C–H bonds toward OH radicals than presumed.[23]

TABLE XI: Ratios of Alkyl Nitrate Isomers Formed during Cl_2-NO-*n*-Alkane-Air Irradiations, Compared with Ratios Calculated from Kinetic Data

	[1-alkyl nitrate]/ [2-alkyl nitrate]		[3-alkyl nitrate]/ [2-alkyl nitrate]
n-alkane	obsd[a]	calcd[b]	obsd[a]
propane	0.36 ± 0.06	0.82	
n-butane	0.14 ± 0.13	0.40	
n-pentane	*c*	*d*	0.62 ± 0.02
n-hexane	*c*	*d*	1.12 ± 0.12

[a] Indicated errors are two standard deviations. [b] From ref 27. [c] Not observed. [d] Not available.

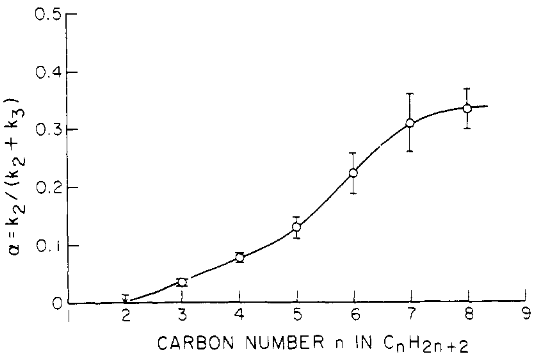

Figure 4. Plot of $k_2/(k_2 + k_3)$ against the *n*-alkane carbon number. $k_2/(k_2 + k_3)$ is set to be the fractional yield of alkyl nitrate observed under the present atmospheric conditions and hence is an average for the isomeric alkyl nitrates observed (see text). The datum for ethane is from the Cl_2–NO–ethane–air irradiation and is an upper limit. The other data are from CH_3ONO–NO–*n*-alkane–air irradiations.

The data obtained in the Cl atom-initiation system were not so extensive and were designed mainly for confirmation purposes. The alkyl nitrate isomeric ratios observed in this system are given in Table XI. The [3-alkyl nitrate]/[2-alkyl nitrate] ratios observed for *n*-pentane and *n*-hexane are similar, though somewhat lower, than those in the CH_3ONO photolysis systems, and are more nearly statistical. This is consistent with the fact that Cl atoms react much more rapidly with *n*-alkanes than do OH radicals and are thus less selective. These data, together with the corresponding isomeric ratios from the CH_3ONO system, indicate that for a given *n*-alkane all secondary alkyl peroxy radicals form the same fraction of secondary alkyl nitrates.

On the other hand, the 1-alkyl nitrate yields in the Cl_2 photolysis system are similar to those in the CH_3ONO system in that they are approximately a factor of 2 lower than expected on the basis of the relative amounts of alkyl, and hence alkyl peroxy, radicals initially formed.[27] Al-

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TABLE XII: Fractions of n-Alkanes Reacting to Form Alkyl Nitrates via Reaction 2, i.e., the Rate Constant Ratio $k_2/(k_2 + k_3)$, under Atmospheric Conditions, together with Previous Literature Data

	$\alpha = k_2/(k_2 + k_3)$	
n-alkane	this work	lit.
ethane	$\leqslant 0.014^a$	$\leqslant 0.20$[29]
propane	0.036 ± 0.005^b	0.04[5]
n-butane	0.077 ± 0.009^b	0.083 ± 0.02;[8] 0.086[5]
n-pentane	0.129 ± 0.019^b	0.14 ± 0.05;[8] 0.11[28]
n-hexane	0.223 ± 0.035^b	0.37 ± 0.08;[8] 0.15 ± 0.03[28]
n-heptane	0.309 ± 0.050^b	
n-octane	0.332 ± 0.034^b	

[a] From the Cl_2-NO-ethane-air irradiation. [b] From CH_3ONO-NO-n-alkane-air irradiations. 1-Alkyl nitrate yields either monitored or calculated (see Table VIII). The rate constant ratios $k_2/(k_2 + k_3)$ for the 1-alkyl nitrates from 1-alkyl peroxy radicals are probably approximately a factor of two lower than these values. (1-alkyl peroxy radicals formed account for 17% of all peroxy radicals for n-butane decreasing to 5% for n-octane, but account for 30% of the peroxy radicals from propane).

though this could be due, at least in part, to a contribution to alkyl radical formation by OH radical reaction with the n-alkanes, these data further suggest that the fraction of 1-alkyl nitrates formed from primary alkyl peroxy radicals is indeed lower than the corresponding fraction of secondary alkyl nitrates from secondary alkyl peroxy radicals. Obviously, further work is necessary to confirm and elucidate this observation.

Dependence of Alkyl Nitrate Yield on Carbon Number. The fraction of the n-alkanes which react to form alkyl nitrates under atmospheric conditions are given in Table XII and are plotted against carbon number in Figure 4. These data were obtained for propane through n-octane from the CH_3ONO–NO–n-alkane–air irradiations together with the data for the Cl_2–NO–ethane–air irradiation. The experimental data for n-pentane through n-octane, which are for the secondary alkyl nitrates only, have been increased based on the kinetic data of ref 23 to allow for 1-alkyl nitrate formation (this correction is minor in all cases, decreasing from 10% for n-pentane to 4% for n-octane (Table XII)). The datum for ethane is rigorously an upper limit since alkoxy radical combination with NO_2 could contribute a significant amount of the ethyl nitrate yields observed; this contribution is, as discussed above, minor for the other alkanes. These fractions α in Table XII and Figure 4 are equated to the rate constant ratios $k_2/(k_2 + k_3)$.

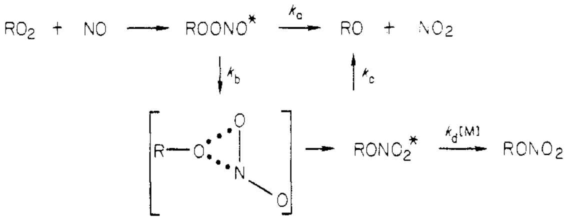
It can be seen from Figure 4 that the amount of reaction 2 proceeding via alkyl nitrate formation increases rapidly from ≤1% for ethane to ~30–33% for n-heptane and n-octane. The present data for propane through n-hexane are also compared with previous literature estimates in Table XII, and can be seen to be, at least for propane and n-butane, in excellent agreement. Since these previous data[5,8,28] were obtained from product studies carried out in an ~5800-L environmental chamber, vs. the 75-L chamber used here, surface or heterogeneous effects are unlikely to be involved in the observed alkyl nitrate formation.

Of further interest is the present observation of ≤1% $C_2H_5ONO_2$ formation from the reaction of ethoxy radicals with NO, indicating that the pathway

$$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$$

accounts for ≥99% of the overall reaction. This is in accord with the recent data of Plumb et al.[29] which show that ≥80% of the reaction of $C_2H_5O_2$ radicals with NO produces NO_2.

The reaction pathway leading to alkyl nitrate formation, which is exothermic by ~57 kcal mol^{-1} overall,[30] probably involves a three-member transition state. The available data are consistent with the following detailed mechanism:



where the asterisk denotes vibrational excitation, k_a, k_b, and k_c are overall rate constants for unimolecular decompositions or isomerizations of the vibrationally excited intermediates, and $k_d[M]$ is the overall rate of collisional stabilization of $RONO_2{}^*$. Thus the overall efficiency of alkyl nitrate production, α, is given by

$$\alpha = \left(\frac{k_b}{k_a + k_b} \right) \frac{k_d[M]}{(k_c + k_d[M])} \qquad \text{(VII)}$$

From the theory of unimolecular reactions,[31] at a given total pressure decomposition of the vibrationally excited species is expected to become slower relative to collisional stabilization as the size of the molecule increases. Thus, from eq VII, α is predicted to increase with the size of the molecule, consistent with the present experimental data. In addition, for sufficiently large molecules (or at sufficiently high pressures) where $k_d[M] >> k_c$, eq VII yields

$$\alpha \rightarrow \alpha_\infty = k_b/(k_a + k_b)$$

and our data indicate that $\alpha_\infty \simeq 0.35$ based on the apparent limiting alkyl nitrate yield at high carbon number (Figure 4). Although this mechanism is reasonable and consistent with the present data, further work regarding the effects of pressure and temperature on the alkyl nitrate yields is clearly required. Such experimental data are presently being obtained in these laboratories.

As indicated in the Introduction, the formation of alkyl nitrates in hydrocarbon–NO_x–air irradiations is a sink for both oxides of nitrogen and radicals. Thus the observed increase of the alkyl nitrate yields with the size of the n-alkane means that the potential for contributing to photochemical air pollution (or at least some aspects of it) may be less for the larger (≥C_6) n-alkanes than for the smaller ones. Since the larger n-alkanes are important constituents of gasoline, diesel, and aircraft fuels,[32] this must be taken into account in modeling the role of these species in polluted atmospheres.

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Supplementary Material Available: Tables I-VII, listing experimental data for the CH_3ONO–NO–alkane–air and Cl_2–NO–alkane–air irradiations (7 pages). Ordering information is available in any current masthead page.

Kinetics and Product Channels of the Reactions of HO_2 with O and H Atoms at 296 K

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Rate constants for the reactions $HO_2 + O$ (1) and $HO_2 + H$ (2) were measured in a discharge-flow apparatus fitted with back-to-back laser-induced fluorescence and vacuum UV resonance fluorescence detectors. The decays of [O] and [H] were monitored under conditions of large excess HO_2, generated by $F + H_2O_2$ and detected as OH after conversion with added excess NO. k_1 and k_2 were found to be $(5.4 \pm 0.9) \times 10^{-11}$ and $(7.4 \pm 1.2) \times 10^{-11}$ $cm^3\ s^{-1}$, respectively. The branching ratios of (2), whose three sets of products are OH + OH (2a), H_2O + O (2b), and $H_2 + O_2$ (2c) were determined by reacting small, known concentrations of HO_2 with large excess of H and measuring the [OH] and [O] formed. They were found to be 0.87 ± 0.04, 0.04 ± 0.02, and 0.09 ± 0.045, respectively. These results are compared with published data and discussed in terms of the likely course of the molecular interactions.

Introduction

The chemistry of the HO_2 radical is of extraordinary importance in atmospheric processes as well as in combustion. HO_2 plays a major role in all phases of homogeneous chain reactions: in initiation steps where it is formed via H abstraction by O_2; in propagation or chain transfer steps, as, for example, in $HO_2 + O_3 \rightarrow OH + O_2 + O_2$, $OH + O_3 \rightarrow HO_2 + O_2$, or $HO_2 + NO \rightarrow OH + NO_2$; and in termination steps such as $OH + HO_2 \rightarrow H_2O + O_2$ or $H + HO_2 \rightarrow H_2 + O_2$. The two reactions investigated here

$$O + HO_2 \rightarrow OH + O_2 \qquad \Delta H^\circ_{298} = -52.7 \pm 1.0\ \text{kcal mol}^{-1} \quad (1)$$

$$H + HO_2 \rightarrow OH + OH \qquad \Delta H^\circ_{298} = -36.0 \pm 1.0\ \text{kcal mol}^{-1} \quad (2a)$$

$$\rightarrow H_2O + O \qquad \Delta H^\circ_{298} = -52.9 \pm 1.0\ \text{kcal mol}^{-1} \quad (2b)$$

$$\rightarrow H_2 + O_2 \qquad \Delta H^\circ_{298} = -54.6 \pm 1.0\ \text{kcal mol}^{-1} \quad (2c)$$

take part in many atmospheric processes. Their roles may be classified as odd oxygen removal, (1); HO_x radical propagation, (1) and (2a); partial chain termination, (1) and (2b); and full termination, (2c). These steps are important in the upper stratosphere and mesosphere, because fast atom–radical reactions are increasingly able to compete with three-body recombination at higher altitudes. They are also important in the detailed understanding and modeling of H_2–O_2 flame chemistry.

The reactions of HO_2 with reactive species display surprising variety and unpredictability in their rate parameters. For example, reaction 3 is uncommonly fast,[1-3]

$$OH + HO_2 \rightarrow H_2O + O_2 \qquad \Delta H^\circ_{298} = -69.6 \pm 1.0\ \text{kcal mol}^{-1} \quad (3)$$

$k \sim (6\text{-}7) \times 10^{-11}$ $cm^3\ s^{-1}$, and apparently exhibits a small pressure dependence,[4] strange as this may seem. The symmetrical reaction 4, on the other hand, is much slower,

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad \Delta H^\circ_{298} = -37.6 \pm 1.5\ \text{kcal mol}^{-1} \quad (4)$$

and, in spite of much recent experimental work,[5] its basic mechanism is still in doubt. The reactions of HO_2 with atomic species are necessarily simpler in terms of their intermediates, but major uncertainties persist regarding both their rate constants and product channels, the latter particularly for (2). For (1), only one set of products, $OH + O_2$, is possible, but even there, one may visualize two different routes, H-atom transfer or O-atom transfer. This question may be resolved by oxygen isotope labeling but is unanswered now. Its rate constant, k_1, has been measured only recently,[6-9] the reported values ranging from

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