J. Phys. Chem. A **2006,** *110,* 6617−6622

Pressure Dependence of Pentyl Nitrate Formation from the OH Radical-Initiated Reaction of *n*-Pentane in the Presence of NO[†]

Sara M. Aschmann, William D. Long, and Roger Atkinson*,[‡]

Air Pollution Research Center, University of California, Riverside, California 92521

Received: August 17, 2005; In Final Form: October 8, 2005

The formation yields of 2- and 3-pentyl nitrate from the reactions of 2- and 3-pentyl peroxy radicals with NO have been measured at room temperature over the pressure range 51−744 Torr of $N_2 + O_2$, using the OH radical-initiated reaction of *n*-pentane to generate the pentyl peroxy radicals. The influence of 2- and 3-pentyl nitrate formation from the reaction of 2- and 3-pentoxy radicals with NO_2 was investigated by conducting experiments with the initial CH_3ONO (the OH radical precursor) and NO concentrations being varied by a factor of 5−10. From experiments carried out with low initial CH_3ONO and NO concentrations, the measured yields of 2-pentyl nitrate and 3-pentyl nitrate, defined as ([pentyl nitrate] formed)/([*n*-pentane] reacted), each increase with increasing total pressure, from 1.10 ± 0.09% and 1.11 ± 0.10%, respectively, at 51 ± 1 Torr of O_2 to 5.48 ± 0.51% and 4.07 ± 0.31%, respectively, at 737 ± 4 Torr of $N_2 + O_2$.

Introduction

The reaction of organic peroxy ($RO_2^\bullet$) radicals with NO, a key reaction in the atmospheric degradation of volatile organic compounds, proceeds by two pathways.[1]

$$RO_2^\bullet + NO \rightarrow RO^\bullet + NO_2 \qquad (1a)$$

$$RO_2^\bullet + NO\ (+ M) \rightarrow RONO_2\ (+ M) \qquad (1b)$$

Reaction 1a leads to the formation of the corresponding alkoxy radical plus NO_2, with photolysis of NO_2 in the troposphere leading to O_3 formation. In contrast, reaction 1b forming the organic nitrate is a sink for NO_x and radicals, leading to a decrease in O_3 formation.[2] An accurate knowledge of organic nitrate formation from reaction 1 (i.e., of k_{1b}/k_1) is therefore needed for modeling ozone formation in the atmosphere.[2,3] While there have been a number of studies of organic nitrate formation from the reactions of organic peroxy radicals with NO,[4−24] the majority of these have been carried out at room temperature and atmospheric pressure.[4−6,8,9,12−17,20,21] Furthermore, while several studies of alkyl nitrate formation from alkyl peroxy radical reactions with NO have been carried out at temperatures and pressures other than room temperature and atmospheric pressure,[7,10,11,18,19,22−24] the only pressure-dependent organic nitrate yield data reported to date are those of Atkinson et al.[7,10] for the formation of alkyl nitrates from the OH radical-initiated reactions of *n*-pentane,[7] *n*-heptane,[7] 2,2-dimethylpropane,[10] 2-methylbutane,[10] and 3-methylpentane[10] over the temperature and pressure ranges ∼280−340 K and ∼55−740 Torr. Percival and co-workers[23,24] have also investigated the reactions of $CH_3O_2^\bullet$ and $C_2H_5O_2^\bullet$ radicals with NO over the respective temperature ranges 193−300 and 203−298 K at 100−200 Torr total pressure, but only upper limits to the rate constant ratios k_{1b}/k_1 of $k_{1b}/k_1 < 0.10$ for the $CH_3O_2^\bullet$ radical reaction[23] and $k_{1b}/k_1 < 0.05$ for the $C_2H_5O_2^\bullet$ radical reaction[24] were obtained for these temperature and pressure conditions.

Reaction 1 is believed to occur as shown in Scheme 1,[6,25,26] and theoretical calculations of organic nitrate formation from reaction 1 have been carried out recently by Barker and coworkers[25,26] and Zhang et al.[27] Barker et al.[26] could only reproduce the experimental data of Atkinson et al.[7] for the formation of 2-pentyl nitrate from the 2-pentyl peroxy + NO reaction using unrealistically low amounts of energy transferred per collision (∼25 cm^{-1}).[26] Zhang et al.[27] propose that the intermediate ROONO* species occurs in two noninterconverting conformers, only one of which can isomerize to form the nitrate $RONO_2$. Zhang et al.[27] then predict that nitrate formation yields do not extrapolate to zero with decreasing pressure but rather asymptotically approach nonzero values. Considering that the only experimental data concerning the pressure dependence of organic nitrate yields from reaction 1 over a pressure range representative of the troposphere are from studies conducted ∼20 years ago,[7,10] additional experimental studies are clearly needed.[26,27] In this work, we have reinvestigated the formation of 2- and 3-pentyl nitrate from the reactions of 2- and 3-pentyl peroxy radicals with NO at 297 ± 1 K and 51−744 Torr total pressure of $N_2 + O_2$. The OH radical-initiated reaction of *n*-pentane was used to generate the pentyl peroxy radicals (RH = *n*-pentane)

$$OH + RH \rightarrow H_2O + R^\bullet \qquad (2)$$

$$R^\bullet + O_2\ (+ M) \rightarrow RO_2^\bullet\ (+ M) \qquad (3)$$

Experimental Methods

The majority of experiments were carried out in a 5870 L Teflon-coated, thermostatted evacuable chamber at 297 ± 1 K and 51−744 Torr total pressure of $N_2 + O_2$, with irradiation provided by a 24 kW xenon arc lamp filtered through a 6 mm thick Pyrex pane to remove wavelengths <300 nm. Additional

---

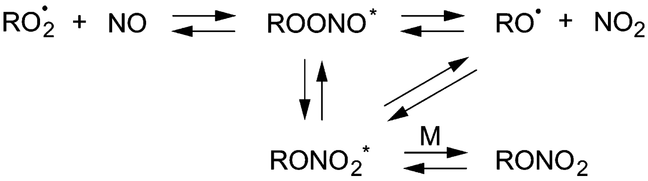
[†] Part of the special issue "David M. Golden Festschrift".

* To whom correspondence should be addressed. E-mail: ratkins@mail.ucr.edu. Tel: (951) 827-4191.

[‡] Also Department of Environmental Sciences and Department of Chemistry.

10.1021/jp054643i CCC: $33.50

SCHEME 1



experiments were carried out in a ~7000 L volume Teflon chamber, equipped with two parallel banks of black lamps for irradiation, at 297 ± 1 K and 735 Torr total pressure of purified air at ~5% relative humidity. Both chambers contained Teflon-coated fans to ensure rapid mixing of reactants during their introduction into the chamber. Hydroxyl radicals were generated by the photolysis of methyl nitrite (CH_3ONO) in the presence of O_2 at wavelengths >300 nm,[6−8,10,13,14,20,21] and NO was included in the reactant mixtures to suppress the formation of O_3 and hence of NO_3 radicals.

Two series of experiments were carried out, with the initial *n*-pentane concentration being in the range $(2.23-2.59) \times 10^{13}$ molecule cm^{-3} for both series of experiments but with the initial CH_3ONO and NO concentrations (which were equal in each experiment) being $\sim 2.4 \times 10^{14}$ molecule cm^{-3} each in the "high-NO_x" experiments and $(1.2-4.8) \times 10^{13}$ molecule cm^{-3} each in the "low-NO_x" experiments. The reactant mixtures were irradiated for 10−60 min at 20% of the maximum light intensity in the ~7000 L Teflon chamber, resulting in up to 30% reaction of the initial *n*-pentane, and for 10−120 min in the 5870 L evacuable chamber, resulting in maximum reaction of the initial *n*-pentane ranging from 25 to 27% at 740−744 Torr to 41−48% at 51−102 Torr total pressure. The concentrations of *n*-pentane and 2- and 3-pentyl nitrate were measured during the experiments by gas chromatography with flame ionization detection (GC-FID). For the analysis of *n*-pentane, gas samples were collected from the chamber into a 100 cm^3 volume gastight, all-glass syringe and transferred via a 1 cm^3 gas sampling valve onto a 30 m DB-5 megabore column, initially held at −25 °C and then temperature programmed to 200 °C at 8 °C min^{-1}. For the analysis of 2- and 3-pentyl nitrate, gas samples of 100 cm^3 volume were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption (with the heating block at ~250 °C) onto a 30 m DB-1701 megabore column, initially held at −40 °C and then temperature programmed to 200 °C at 8 °C min^{-1}.

Experiments in the 5870 L evacuable chamber were carried out with the diluent gas being N_2-O_2 mixtures with an O_2 partial pressure of 150 ± 5 Torr, except for experiments at 51 ± 1 and 100 ± 2 Torr, where the diluent gas was all O_2, and for the "high-NO_x" experiments at 202 ± 2 Torr, where the O_2 partial pressures were 102 ± 1 Torr. The concentrations of *n*-pentane and 2- and 3-pentyl nitrate in the evacuable chamber were measured during the experiments by GC-FID as described above. Gas samples were collected from the chamber into an attached evacuated 5 L Pyrex bulb which was then pressurized to 740−745 Torr with N_2 (obviously, pressurization was not necessary for experiments conducted at ~740 Torr total pressure). The samples for GC-FID analyses were then obtained from this 5 L bulb at atmospheric pressure.

Control experiments were carried out with measured amounts of *n*-pentane and 2- and 3-pentyl nitrate (corresponding to *n*-pentane and 2- + 3-pentyl nitrate concentrations in the chamber of $(2.4-2.5) \times 10^{13}$ and $(1.2-2.2) \times 10^{13}$ molecule cm^{-3}, respectively) being introduced into the chamber at 100 or 300 Torr total pressure and analyzed using this procedure. The chamber was then pressurized with N_2 to ~745 Torr and the analyses repeated, collecting samples for analysis from the 5-L bulb (as described above) as well as directly out of the chamber. The measured concentrations of *n*-pentane agreed to within 2% and those of 2- and 3-pentyl nitrate agreed to within 4%, showing that the sample collection procedure from the evacuable chamber at subambient pressures was valid. Calibrations of the GC-FID response factors for *n*-pentane and 2- and 3-pentyl nitrate were carried out as described previously,[28] with estimated overall uncertainties in the GC-FID response factors for *n*-pentane and the pentyl nitrates of ±5% each. Three independent calibrations were conducted over a two month period during each of the two series of experiments, and during each series of experiments, the GC-FID response factors for the pentyl nitrates vs that for *n*-pentane (the important calibration parameter for the yield measurements) agreed to within 3.3%. The standard of 2-pentyl nitrate contained ~30% of the isomeric 3-pentyl nitrate, and we therefore assumed, consistent with predictions using the effective carbon number concept,[29] that 2-pentyl nitrate and 3-pentyl nitrate have identical GC-FID response factors.

The chemicals used, and their stated purities, were *n*-pentane (99+%), Aldrich Chemical Co.; 2- and 3-pentyl nitrate, Fluorochem., Inc.; and NO (99.0%), Matheson Gas Company. Methyl nitrite was prepared as described by Taylor et al.[30] and stored at 77 K under vacuum.

Results and Discussion

A series of $CH_3ONO-NO-n\text{-pentane}-N_2-O_2$ irradiations were carried out in a ~7000 L volume Teflon chamber at 735 Torr total pressure and in a 5870 L evacuable chamber at 51−744 Torr total pressure, with three or four experiments being conducted at each pressure apart from 51 ± 1 Torr where two experiments were carried out with triplicate GC-FID analyses after a single irradiation period. Because 2- and 3-pentyl nitrate also react with OH radicals, the measured 2- and 3-pentyl nitrate concentrations were corrected for secondary reactions with OH radicals,[6] with this correction increasing with the extent of reaction.[6] The room-temperature rate constants used in the calculation of these corrections were (in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) *n*-pentane, 3.80;[31] 2-pentyl nitrate, 1.72;[32] and 3-pentyl nitrate, 1.02,[32] with the rate constants of Atkinson et al.[32] for 2- and 3-pentyl nitrate measured relative to that for cyclohexane being reevaluated using the most recent recommendation for the cyclohexane reaction rate constant.[31] The maximum corrections were 18% for 2-pentyl nitrate and 11% for 3-pentyl nitrate.

The formation of 2- and 3-pentyl nitrate can also occur from the reactions of 2- and 3-pentoxy radicals with NO_2 (reaction 4).[6]

$$RO^{\bullet} + NO_2\,(+\,M) \rightarrow RONO_2\,(+\,M) \tag{4}$$

Reaction 4 must therefore be considered as an additional pathway to reaction 1b for 2- and 3-pentyl nitrate formation. 2- and 3-Pentoxy radicals react with NO_2 (reaction 4) and with NO, to form 2- and 3-pentyl nitrite, and also react with O_2,

$$RO^{\bullet} + NO\,(+\,M) \rightarrow RONO\,(+\,M) \tag{5}$$

unimolecularly decompose and unimolecularly isomerize (through a six-member transition state),[1] as shown for the 2-pentoxy radical.

$$CH_3CH(O^\bullet)CH_2CH_2CH_3 + O_2 \rightarrow CH_3C(O)CH_2CH_2CH_3 + HO_2 \quad (6)$$

$$CH_3CH(O^\bullet)CH_2CH_2CH_3 \rightarrow CH_3CHO + CH_3CH_2C^\bullet H_2 \quad (7)$$

$$CH_3CH(O^\bullet)CH_2CH_2CH_3 \rightarrow CH_3CH(OH)CH_2CH_2C^\bullet H_2 \quad (8)$$

The isomerization reaction is not feasible for the 3-pentoxy radical. On the basis of literature data[1,13,33] and the theoretical falloff calculations of Somnitz and Zellner[34] for the decomposition and isomerization reactions of pentoxy radicals, at 297 K the respective rates of the O_2 reaction, decomposition, and isomerization (in s^{-1}) for the 2-pentoxy radical are 4.5×10^4, $\sim 3 \times 10^4$, and 2.5×10^5 at 740 Torr of air and 1.5×10^4, $\sim 2.5 \times 10^3$, and $\sim 9.3 \times 10^4$ at 50 Torr of O_2. The rates of the O_2 reaction and decomposition (in s^{-1}) for the 3-pentoxy radical at 297 K are, respectively, 4.5×10^4 and 3.3×10^4 at 740 Torr of air and 1.5×10^4 and $\sim 1.4 \times 10^4$ at 50 Torr of O_2. The 2-pentoxy radical is therefore removed via reactions 6−8 significantly more rapidly than is the 3-pentoxy radical (via reactions analogous to 6 and 7), by a factor of ∼4 at both 50 Torr of O_2 and 740 Torr of air.

The reactions of 2- and 3-pentoxy radicals with NO_2 (reaction 4) are probably at the high-pressure limit at 50 Torr of O_2,[35,36] and at a given NO_2 concentration, the contribution of reaction 4 to the formation of both 2 and 3-pentyl nitrate will therefore increase with decreasing pressure. This is expected both in an absolute sense as well as relative to pentyl nitrate formation via reaction 1b, which decreases with decreasing pressure. However, for any given set of experimental conditions, the formation of 2-pentyl nitrate from the reaction of the 2-pentoxy radical with NO_2 (reaction 4) is significantly less important than the formation of 3-pentyl nitrate from the reaction of the 3-pentoxy radical with NO_2. Hence, the 2-pentyl nitrate data are expected to be less affected by the occurrence of reaction 4 than are the 3-pentyl nitrate data. For example, with a constant NO_2 concentration of 2.4×10^{13} molecule cm^{-3} throughout an experiment, a room-temperature rate constant for reaction 4 of 3.8×10^{-11} cm^3 $molecule^{-1}$ s^{-1},[37] and estimated fractions of H-atom abstraction from the 2- and 3-positions in *n*-pentane by OH radicals (see below),[38] reaction 4 is calculated to result in 2- and 3-pentyl nitrate yields from *n*-pentane, ([pentyl nitrate] formed/[*n*-pentane] reacted), of 0.2% and 0.4%, respectively, at 740 Torr total pressure of air, and 0.5% and 1.1%, respectively, at 50 Torr total pressure of O_2.

Our measured 2- and 3-pentyl nitrate formation yields in the experiments at total pressures of 102−744 Torr using initial CH_3ONO and NO concentrations of $\sim 2.4 \times 10^{14}$ molecule cm^{-3} ("high-NO_x" experiments) were consistently higher than the yields from the experiments with a factor of 5−10 lower initial CH_3ONO and NO concentrations ("low-NO_x" experiments). However, at all pressures studied in the "low-NO_x" experiments, the 2- and 3-pentyl nitrate yields were unaffected by a factor of 2 variation in the initial CH_3ONO and NO concentrations. The ratios of the 2-pentyl nitrate yields from the "high-NO_x" experiments relative to those from the "low-NO_x" experiments were 1.41 ± 0.41 at 100−102 Torr, 1.27 ± 0.25 at 201−202 Torr, 1.35 ± 0.38 at 300 Torr, 1.12 ± 0.22 at 498−499 Torr, and 1.05 ± 0.49 at 737−744 Torr, and the corresponding ratios of the 3-pentyl nitrate yields were 1.39 ± 0.25 at 100−102 Torr, 1.41 ± 0.20 at 201−202 Torr, 1.35 ± 0.19 at 300 Torr, 1.24 ± 0.17 at 498−499 Torr, and 1.11 ± 0.17 at 737−744 Torr, where the indicated errors are two least-squares standard deviations. Although the error limits are large, there may be a trend with the effect of higher initial CH_3ONO and NO concentrations being more pronounced at lower total pressures. Our 2- and 3-pentyl nitrate formation yields from the experiments carried out with the lower initial CH_3ONO and NO concentrations are therefore expected to be less affected by pentyl nitrate formation from reaction 4.

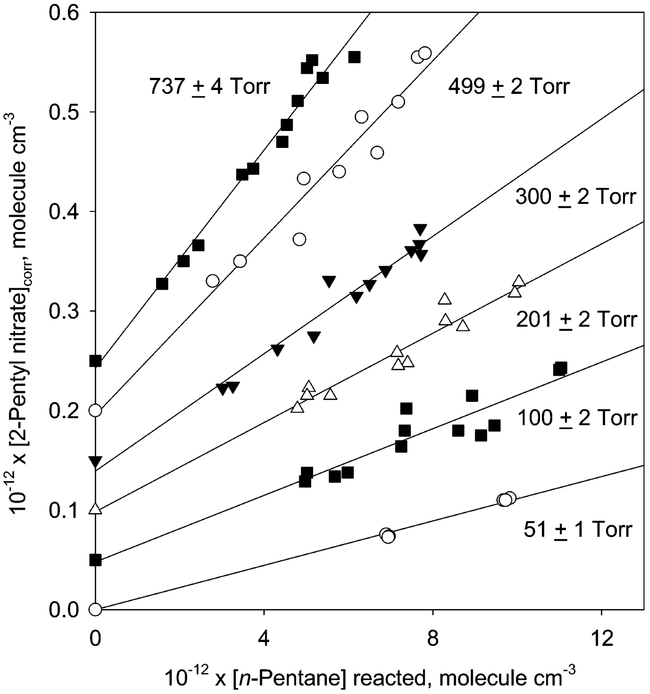


Figure 1. Plot of the amounts of 2-pentyl nitrate formed in the "low-NO_x" experiments, corrected for reaction with OH radicals (see text), against the amounts of *n*-pentane reacted with OH radicals at 297 ± 1 K and at the various total pressures (Torr) noted on the figure. The 2-pentyl nitrate data at 100 ± 2, 201 ± 2, 300 ± 2, 499 ± 2, and 737 ± 4 Torr have been displaced vertically by 5×10^{10}, 1.0×10^{11}, 1.5×10^{11}, 2.0×10^{11}, and 2.5×10^{11} molecule cm^{-3}, respectively, for clarity.

Figure 1 shows plots of the amounts of 2-pentyl nitrate formed in the "low-NO_x" experiments, corrected for reaction with OH radicals, against the amounts of *n*-pentane reacted with the OH radical at the various total pressures studied, including those at atmospheric pressure in the Teflon chamber. The formation yields of 2- and 3-pentyl nitrate (defined as [pentyl nitrate formed]/[*n*-pentane reacted]) and the combined yields of 2- + 3-pentyl nitrate obtained by least-squares analyses of the data are listed in Table 1, together with corresponding data from our previous studies.[6,7,13] Figures 2 and 3 show plots of the 2-pentyl nitrate and 3-pentyl nitrate formation yields from *n*-pentane as a function of pressure at room temperature (298 ± 4 K) from the present and previous[6,7,13] studies.

As evident from Table 1 and Figures 2 and 3, our present 2- and 3-pentyl nitrate formation yields are consistently lower than our previous data,[6,7] by up to ∼35% for 2-pentyl nitrate at ∼50 Torr total pressure. There is closer agreement between the present and previous[6,7] yields for 3-pentyl nitrate than for 2-pentyl nitrate, and this may be due, at least in part, to the presence of small interfering GC peaks in the analyses of 2-pentyl nitrate in both this and our previous[6,7] work. It should be noted that our previous pressure-dependent data[7] were from a single experiment carried out at each pressure (and temperature) studied. The present 2- and 3-pentyl nitrate yields at atmospheric pressure of air are in good agreement with those from our 1995 study.[13]

Our present 2- and 3-pentyl nitrate formation yields from the OH radical-initiated reaction of *n*-pentane at 297 ± 1 K are

TABLE 1: Pentyl Nitrate Formation from the OH Radical-Initiated Reaction of *n*-Pentane at 298 ± 4 K, from the Present and Previous[6,7,13] Works

		10^{-13} × initial concentration (molecule cm^{-3})		nitrate molar formation yield (%)[a]				
P (Torr)[b]	*T* (K)	CH_3ONO	NO	2-pentyl	3-pentyl	2- + 3-pentyl	3-/2-pentyl nitrate ratio[c]	reference
735	299 ± 2	2.40−2.64	1.56−3.62	7.08 ± 0.86	4.63 ± 0.55	11.7 ± 1.3	0.66 ± 0.08	6
740	300 ± 2	1.56	2.39	7.36 ± 0.12	5.17 ± 0.32	12.5 ± 0.3	0.69 ± 0.06	7
505	300 ± 2	1.42	2.36	5.45 ± 0.59	3.78 ± 0.46	9.23 ± 0.99	0.70 ± 0.06	7
352	300 ± 2	1.42	2.42	5.25 ± 0.90	3.65 ± 0.42	8.90 ± 1.29	0.70 ± 0.06	7
155[d]	300 ± 2	1.36	2.36	3.32 ± 0.09	2.11 ± 0.22	5.42 ± 0.27	0.63 ± 0.06	7
153	300 ± 2	0.61	2.36	2.95 ± 0.42	2.09 ± 0.29	5.03 ± 0.57	0.70 ± 0.12	7
57[d]	300 ± 2	0.28	2.39	1.92 ± 0.36	1.33 ± 0.45	3.24 ± 0.70	0.73 ± 0.21	7
56[d]	300 ± 2	0.36	2.36	1.76 ± 0.35	1.20 ± 0.17	2.96 ± 0.49	0.69 ± 0.08	7
740	296 ± 2	21	16−19	6.12 ± 1.06	4.66 ± 0.49	10.8 ± 1.5	0.72 ± 0.09	13
740[e]	296 ± 2	21	16−19	6.36 ± 0.68	4.29 ± 0.21	10.6 ± 0.8	0.68 ± 0.07	13
737 ± 4[f]	297 ± 1	2.4−4.8	2.4−4.8	5.48 ± 0.51	4.07 ± 0.31	9.55 ± 0.73	0.74 ± 0.06	this work
499 ± 2[f]	297 ± 1	2.4−4.8	2.4−4.8	4.45 ± 0.58	3.18 ± 0.34	7.63 ± 0.86	0.74 ± 0.07	this work
300 ± 2[f]	297 ± 1	2.4−4.8	2.4−4.8	2.95 ± 0.32	2.26 ± 0.20	5.21 ± 0.51	0.81 ± 0.06	this work
201 ± 2[f]	297 ± 1	2.4−4.8	2.4−4.8	2.24 ± 0.26	1.76 ± 0.15	3.98 ± 0.40	0.82 ± 0.07	this work
100 ± 2[d]	297 ± 1	2.4−4.8	2.4−4.8	1.67 ± 0.31	1.50 ± 0.22	3.18 ± 0.47	0.89 ± 0.12	this work
51 ± 1[d]	297 ± 1	1.2−2.4	1.2−2.4	1.10 ± 0.09	1.11 ± 0.10	2.21 ± 0.18	1.01 ± 0.04	this work

[a] Indicated errors are two least-squares standard deviations. Additional combined uncertainties in the GC-FID response factors for *n*-pentane and the pentyl nitrates are estimated to be ±7%. [b] Diluent gas was air unless noted otherwise. [c] Obtained from least-squares analysis of the 3-pentyl nitrate concentrations against the 2-pentyl nitrate concentrations (both corrected for reaction with OH radicals), constrained to pass through the origin. Indicated errors are two standard deviations. [d] Diluent gas was O_2. [e] Diluent gas was $N_2 + O_2$, with 590 ± 40 Torr O_2. [f] Diluent gas was $N_2 + O_2$, with 150 ± 5 Torr O_2.

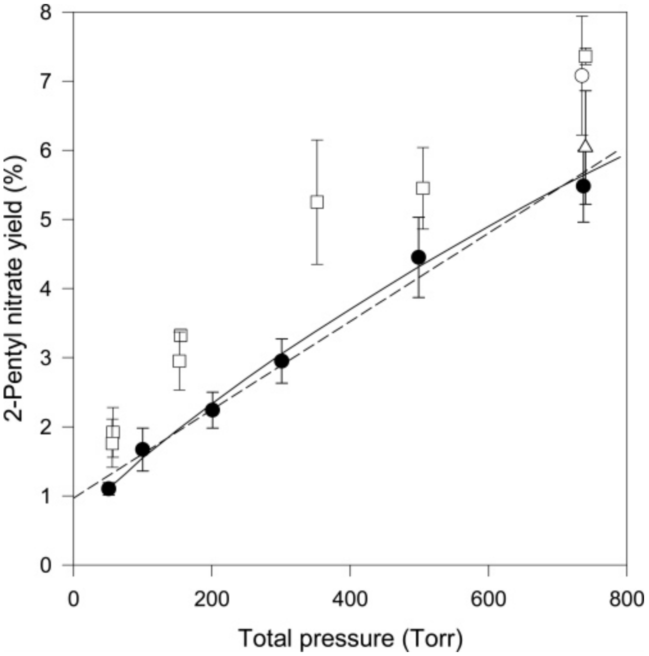


Figure 2. Plot of the 2-pentyl nitrate formation yield from the OH radical-initiated reaction of *n*-pentane as a function of pressure at 298 ± 4 K. ○, Atkinson et al.;[6] □, Atkinson et al.;[7] △, Atkinson et al.;[13] ●, this work. The dashed straight line and the solid curve are for illustrative purposes only.

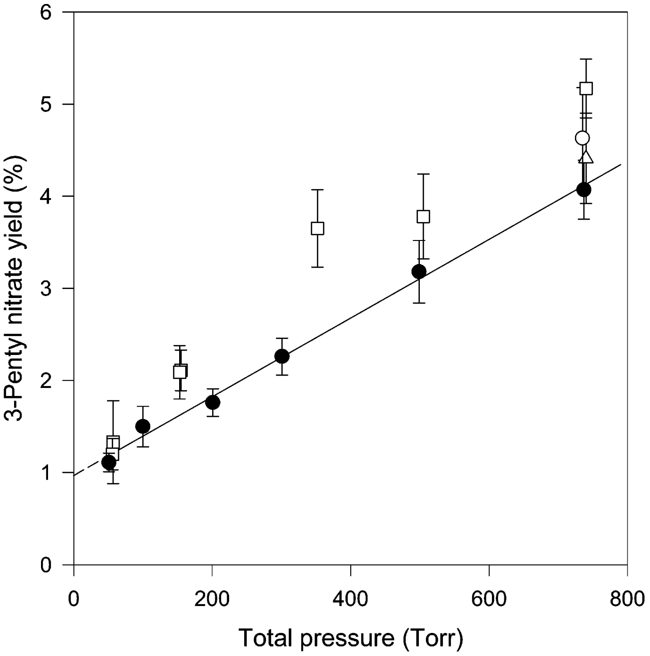


Figure 3. Plot of the 3-pentyl nitrate formation yield from the OH radical-initiated reaction of *n*-pentane as a function of pressure at 298 ± 4 K. ○, Atkinson et al.;[6] □, Atkinson et al.;[7] △, Atkinson et al.;[13] ●, this work. The solid and dashed straight line is for illustrative purposes only.

well represented by the empirical expressions shown as the solid curve in Figure 2 and the solid straight line in Figure 3; the dashed straight line in Figure 2 for 2-pentyl nitrate also gives a good representation of the data at ≥100 Torr pressure. For both 2- and 3-pentyl nitrate, our yield data show no evidence for leveling off at low pressure, although nonzero intercepts are not ruled out, especially for 3-pentyl nitrate where the yield can be linearly extrapolated to a value of ~1.0% at zero pressure (linear least-squares analyses lead to extrapolated zero-pressure intercepts of 0.96 ± 0.28% for 2-pentyl nitrate and 0.97 ± 0.12% for 3-pentyl nitrate, where the indicated errors are two least-squares standard deviations). As discussed above, the 3-pentyl nitrate data are more susceptible to artifact formation via reaction 4, especially at lower total pressures, and it is possible that our measured 3-pentyl nitrate yields at the lower pressures were affected to some extent by formation from reaction 4, even in the "low-NO_x" experiments (and similarly for 2-pentyl nitrate, but to a lesser extent). This is suggested by the increasing formation yield ratio of (3-pentyl nitrate/2-pentyl nitrate) with decreasing total pressure (Table 1).

Our measured pentyl nitrate yields at the two lowest pressures studied here can be corrected for the formation of pentyl nitrates via reaction 4, assuming that the (3-pentyl nitrate/2-pentyl nitrate) yield ratio from the reaction of the pentyl peroxy radicals

TABLE 2: Rate Constant Ratios, $k_{1b}/(k_{1a} + k_{1b})$, for the Reactions of 2- and 3-Pentyl Peroxy Radicals with NO at 297 ± 1 K Obtained from the Present Work

	$k_{1b}/(k_{1a} + k_{1b})$[a]	
pressure (Torr)[b]	2-pentyl peroxy	3-pentyl peroxy
737 ± 4	0.096 ± 0.009	0.116 ± 0.009
499 ± 2	0.078 ± 0.011	0.091 ± 0.010
300 ± 2	0.052 ± 0.006	0.065 ± 0.006
201 ± 2	0.039 ± 0.005	0.050 ± 0.005
100 ± 2	0.029 ± 0.006	0.043 ± 0.007
51 ± 1	0.019 ± 0.002	0.032 ± 0.003

[a] Calculated from the measured 2- and 3-pentyl nitrate yields from this work listed in Table 1, using the estimated[38] fractions of H-atom abstraction from the 2- and 3-position CH_2 groups in *n*-pentane of 57% and 35%, respectively. The indicated errors are two least-squares standard deviations and do not include uncertainties in the fractions of H-atom abstraction from the 2- and 3-position CH_2 groups in *n*-pentane. [b] $N_2 + O_2$ or O_2 (see Table 1 for details).

with NO (reaction 1) in the *n*-pentane reaction is 0.74, independent of pressure (from our data in Table 1 at ≥499 Torr) and that formation of pentyl nitrate from the pentoxy radical reactions with NO_2 is a factor of 4 more important for the 3-pentoxy radical than for the 2-pentoxy radical (see above). Hence, {measured 2-pentyl nitrate yield} = {2-pentyl nitrate yield from reaction 1} + {2-pentyl nitrate yield from reaction 4} and {measured 3-pentyl nitrate yield} = 0.74 × {2-pentyl nitrate yield from reaction 1} + 0.74 × 4 × {2-pentyl nitrate yield from reaction 4}. Solving these two equations results in the 2-pentyl nitrate formation yield via reaction 1 from *n*-pentane decreasing from the measured value of 1.10% to ∼0.93% at 51 ± 1 Torr and from the measured value of 1.67% to ∼1.51% at 100 ± 2 Torr, with correspondingly larger decreases of the 3-pentyl nitrate yields from the measured value of 1.11% to ∼0.69% at 51 ± 1 Torr and from the measured value of 1.50% to ∼1.12% at 100 ± 2 Torr. Additional yield data at lower total pressures are clearly needed to determine the pressure dependence of the 2- and/or 3-pentyl nitrate yields from reaction 1 below ∼50 Torr total pressure.

The yield data presented in Table 1 and in Figures 2 and 3 (and discussed above) can be converted into yields of the pentyl nitrate from reaction of its precursor pentyl peroxy radical with NO, $k_{1b}/(k_{1a} + k_{1b})$, if the fractions of the reaction of OH radicals proceeding by H-atom abstraction from the 2- and 3-position CH_2 groups in *n*-pentane are known. The empirical estimation method of Kwok and Atkinson[38] leads to formation yields of the 2- and 3-pentyl radicals (and hence in the atmosphere of the 2- and 3-pentyl peroxy radicals) of 57% and 35%, respectively, at 298 K. The product data obtained by Atkinson et al.[13] at two O_2 partial pressures (155 Torr and 590 ± 40 Torr) at 296 ± 2 K resulted in formation yields of the 2- and 3-pentyl peroxy radicals from the reaction of OH radicals with *n*-pentane of 46% each[13] but with uncertainties which encompass the estimated[38] values. The rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ obtained from our data in Table 1, using the 2- and 3-pentyl radical formation yields from *n*-pentane calculated using the Kwok and Atkinson estimation method (57% and 35%, respectively),[38] are given in Table 2. While the rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ for the reactions of 2- and 3-pentyl peroxy radicals are similar at higher pressures (≥499 Torr), differences become apparent at lower pressures and this presumably reflects the additional formation of 3-pentyl nitrate from the reaction of 3-pentoxy radicals with NO_2. The similarity in the rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ for the 2- and 3-pentyl peroxy radicals at the higher pressures, where the impact of the $RO^\bullet + NO_2$ reaction is least, suggests that the Kwok and Atkinson estimation method[38] gives reasonably reliable partial rate constants for the reaction of OH radicals with *n*-pentane.

Our present data provide a more comprehensive data set than previously available for the formation of 2- and 3-pentyl nitrate from the corresponding pentyl peroxy radical + NO reactions as a function of pressure at room temperature. In particular, the 2-pentyl nitrate yields obtained in this work and presented in Table 1 and Figure 2, and the corresponding rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ given in Table 2, are expected to have only a minor contribution from the potentially confounding reaction of 2-pentoxy radicals with NO_2, and these data should be useful for testing theoretical models of the reactions of $RO_2^\bullet$ radicals with NO.

Acknowledgment. The authors gratefully thank the National Science Foundation (Grant No. ATM-0234586) for supporting this research. While this research has been supported by this agency, it has not been reviewed by the agency and no official endorsement should be inferred.

References and Notes

(1) Atkinson, R.; Arey, J. *Chem. Rev.* **2003**, *103*, 4605.
(2) Carter, W. P. L.; Atkinson, R. *Environ. Sci. Technol.* **1989**, *23*, 864.
(3) Carter, W. P. L. *J. Air Waste Manage. Assoc.* **1994**, *44*, 881.
(4) Darnall, K. R.; Carter, W. P. L.; Winer, A. M.; Lloyd, A. C.; Pitts, J. N., Jr. *J. Phys. Chem.* **1976**, *80*, 1948.
(5) Takagi, H.; Washida, N.; Bandow, H.; Akimoto, H.; Okuda, M. *J. Phys. Chem.* **1981**, *85*, 2701.
(6) Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. *J. Phys. Chem.* **1982**, *86*, 4563.
(7) Atkinson, R.; Carter, W. P. L.; Winer, A. M. *J. Phys. Chem.* **1983**, *87*, 2012.
(8) Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. *Int. J. Chem. Kinet.* **1984**, *16*, 1085.
(9) Shepson, P. B.; Edney, E. O.; Kleindienst, T. E.; Pittman, J. H.; Namie, G. R.; Cupitt, L. T. *Environ. Sci. Technol.* **1985**, *19*, 849.
(10) Atkinson, R.; Aschmann, S. M.; Winer, A. M. *J. Atmos. Chem.* **1987**, *5*, 91.
(11) Harris, S. J.; Kerr, J. A. *Int. J. Chem. Kinet.* **1989**, *21*, 207.
(12) Muthuramu, K.; Shepson, P. B.; O'Brien, J. M. *Environ. Sci. Technol.* **1993**, *27*, 1117.
(13) Atkinson, R.; Kwok, E. S. C.; Arey, J.; Aschmann, S. M. *Faraday Discuss.* **1995**, *100*, 23.
(14) Aschmann, S. M.; Chew, A. A.; Arey, J.; Atkinson, R. *J. Phys. Chem. A* **1997**, *101*, 8042.
(15) O'Brien, J. M.; Czuba, E.; Hastie, D. R.; Francisco, J. S.; Shepson, P. B. *J. Phys. Chem. A* **1998**, *102*, 8903.
(16) Chen, X.; Hulbert, D.; Shepson, P. B. *J. Geophys. Res.* **1998**, *103*, 25563.
(17) Platz, J.; Sehested, J.; Nielsen, O. J.; Wallington, T. J. *J. Phys. Chem. A* **1999**, *103*, 2688.
(18) Orlando, J. J.; Iraci, L. T.; Tyndall, G. S. *J. Phys. Chem. A* **2000**, *104*, 5072.
(19) Ranschaert, D. L.; Schneider, N. J.; Elrod, M. J. *J. Phys. Chem. A* **2000**, *104*, 5758.
(20) Arey, J.; Aschmann, S. M.; Kwok, E. S. C.; Atkinson, R. *J. Phys. Chem. A* **2001**, *105*, 1020.
(21) Aschmann, S. M.; Arey, J.; Atkinson, R. *J. Phys. Chem. A* **2001**, *105*, 7598.
(22) Chow, J. M.; Miller, A. M.; Elrod, M. J. *J. Phys. Chem. A* **2003**, *107*, 3040.
(23) Bacak, A.; Bardwell, M. W.; Raventos, M. T.; Percival, C. J.; Sanchez-Reyna, G.; Shallcross, D. E. *J. Phys. Chem. A* **2004**, *108*, 10681.
(24) Bardwell, M. W.; Bacak, A.; Raventós, M. T.; Percival, C. J.; Sanchez-Reyna, G.; Shallcross, D. E. *Int. J. Chem. Kinet.* **2005**, *37*, 253.
(25) Lohr, L. L.; Barker, J. R.; Shroll, R. M. *J. Phys. Chem. A* **2003**, *107*, 7429.
(26) Barker, J. R.; Lohr, L. L.; Shroll, R. M.; Reading, S. *J. Phys. Chem. A* **2003**, *107*, 7434.
(27) Zhang, J.; Dransfield, T.; Donahue, N. M. *J. Phys. Chem. A* **2004**, *108*, 9082.
(28) Atkinson, R.; Tuazon, E. C.; Aschmann, S. M. *Environ. Sci. Technol.* **1995**, *29*, 1674.
(29) Scanlon, J. T.; Willis, D. E. *J. Chromatogr. Sci.* **1985**, *23*, 333.
(30) Taylor, W. D.; Allston, T. D.; Moscato, M. J.; Fazekas, G. B.; Kozlowski, R.; Takacs, G. A. *Int. J. Chem. Kinet.* **1980**, *12*, 231.

(31) Atkinson, R. *Atmos. Chem. Phys*. **2003**, *3*, 2233.

(32) Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Winer, A. M. *Int. J. Chem. Kinet*. **1982**, *14*, 919.

(33) Meunier, N.; Doussin, J. F.; Chevallier, E.; Durand-Jolibois, R.; Picquet-Varrault, B.; Carlier, P. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4834.

(34) Somnitz, H.; Zellner, R. *Phys. Chem. Chem. Phys*. **2000**, *2*, 1907.

(35) Balla, R. J.; Nelson, H. H.; McDonald, J. R. *Chem. Phys.* **1985**, *99*, 323.

(36) Mund, Ch.; Fockenberg, Ch.; Zellner, R. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 709.

(37) Atkinson, R. *J. Phys. Chem. Ref. Data* **1997**, *26*, 215.

(38) Kwok, E. S. C.; Atkinson, R. *Atmos. Environ*. **1995**, *29*, 1685.