

Alkyl Nitrate Formation from the Reaction of a Series of Branched RO₂ Radicals with NO as a Function of Temperature and Pressure

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Abstract. Alkyl nitrate yields from the NO_x photooxidations of neopentane, 2-methylbutane and 3-methylpentane have been determined over the temperature and pressure ranges 281–323 K and 54–740 torr, respectively. The formation of the alkyl nitrates is attributed to the reaction pathway



and rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ are estimated, where (1a) is the reaction pathway

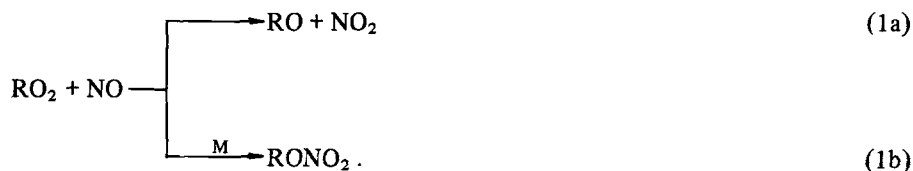


A method for estimating this rate constant ratio for primary, secondary and tertiary alkyl peroxy radicals is presented.

Key words. Alkane, alkyl nitrate, tropospheric chemistry, nitrogen oxides, alkyl peroxy radical.

1. Introduction

The reactions of alkyl peroxy (RO₂) radicals with NO are an important intermediate step in the atmospheric degradation of alkanes (Atkinson and Lloyd, 1984; Carter and Atkinson, 1985). These reactions have been shown to proceed via two pathways; formation of the alkoxy radical and NO₂ [reaction (1a)] and combination to yield the alkyl nitrate (RONO₂) [reaction (1b)] (Darnall *et al.*, 1976; Atkinson *et al.*, 1982a, 1983, 1984)



Secondary alkyl peroxy radicals have been the most studied RO₂ radicals to date and, consistent with expectations for a radical combination reaction, the rate constant ratio $k_{1b}/(k_{1a} + k_{1b})$ increases with the complexity of the RO₂ radical (Atkinson *et al.*, 1982a, 1984; Carter and Atkinson, 1985), and increases with increasing pressure and with

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decreasing temperature (Atkinson *et al.*, 1983; Carter and Atkinson, 1985). The available data also show that the rate constant ratio $k_{1b}/(k_{1a} + k_{1b})$ at room temperature and ~ 740 torr total pressure of air depends on whether the alkyl peroxy radical is primary, secondary or tertiary (Atkinson *et al.*, 1984; Carter and Atkinson, 1985), with this rate constant ratio increasing along the series tertiary $RO_2 \lesssim$ primary $RO_2 <$ secondary RO_2 .

However, to date no pressure or temperature dependence studies have been carried out for primary or tertiary alkyl peroxy radicals. Thus, in this work we have extended our previous room temperature study of the formation of alkyl nitrates from the reaction of branched alkyl peroxy radicals (Atkinson *et al.*, 1984) to obtain rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ as a function of both temperature (281–323 K) and total pressure (54–740 torr) for primary, secondary and tertiary RO_2 radicals. The data obtained allow the amount of alkyl nitrate formed from the reaction of primary, secondary, and tertiary alkyl peroxy radicals with NO to be estimated for the temperature and pressure conditions encountered in the lower troposphere.

2. Experimental

The experimental techniques employed have been described in detail previously (Atkinson *et al.*, 1982a, 1983, 1984) and, hence, only the relevant details are given here. Alkyl peroxy radicals were formed in the presence of NO by photolysis of CH_3ONO -NO-alkane-air (or O_2) mixtures at >300 nm, with typical initial reactant concentrations of: CH_3ONO , $\sim 3 \times 10^{13}$ molecule cm^{-3} ; NO, $\sim 2.4 \times 10^{13}$ molecule cm^{-3} ; and alkane, $\sim 2.4 \times 10^{13}$ molecule cm^{-3} . Irradiations were carried out in a 5800 L evacuable, Teflon-coated, thermostatted environmental chamber with a 25 kW xenon arc solar simulator (Winer *et al.*, 1980). The alkanes and alkyl nitrates were quantitatively analyzed prior to and during the irradiations by gas chromatography with flame ionization detection (GC-FID), as described previously (Atkinson *et al.*, 1984).

GC-FID calibrations and retention times for neopentyl nitrate, 2-methyl-3-nitratobutane and 3-methyl-2-nitratopentane were determined using authentic samples obtained from Fluorochem, Inc. (the 3-methyl-2-nitratopentane was present as the two diastereomers, which were only partially resolved by GC). For 2-methyl-2-nitratobutane, which was a tentative identification (Atkinson *et al.*, 1984), the GC-FID calibration factor, on an area basis, was taken to be equal to that for the 2-methyl-3-nitratobutane isomer. Methyl nitrite was prepared and stored as described previously (Atkinson *et al.*, 1982b), and the alkanes and NO were obtained from commercial sources and used as received.

3. Results and Discussion

Irradiations of CH_3ONO -NO-alkane mixtures were carried out in dry pure air or, for total pressures $\lesssim 160$ torr, O_2 over the temperature and total pressure ranges 281–323 K and 54–740 torr, respectively. As described previously (Atkinson *et al.*, 1984), the observed alkyl nitrate yields were corrected for their consumption by reaction with the OH radical using the measured (Atkinson, 1986a) or (for 2-methyl-2-nitratobutane)

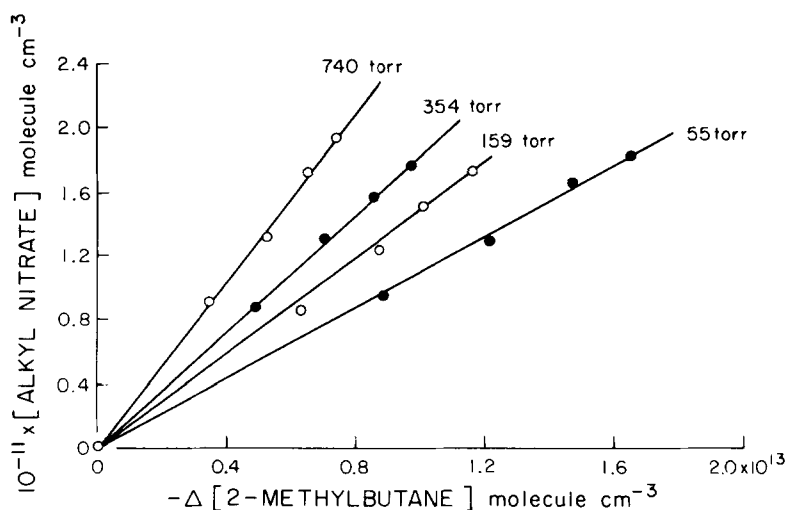


Fig. 1. Plots of the yields of 2-methyl-3-nitratobutane, corrected for reaction with the OH radical (see text), against the amount of 2-methylbutane consumed at 323 ± 2 K as a function of the total pressure.

estimated (Atkinson, 1986a, b) OH radical reaction rate constants. These correction factors were always ≤ 1.34 , and were typically ≤ 1.2 . Examples of plots of the corrected alkyl nitrate concentrations against the amounts of alkane consumed are shown in Figure 1, and the yields of the alkyl nitrates, obtained by least-squares analyses of the slopes of such plots, are given in Tables I–III for the various temperatures and pressures studied.

Table I. Alkyl nitrate yields and rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ from the irradiation of $\text{CH}_3\text{ONO-NO-neopentane-air}$ (or O_2) mixtures

Temperature (K)	Total pressure (torr)	Neopentyl nitrate yield = $k_{1b}/(k_{1a} + k_{1b})^a, ^b$
282 ± 2	54	0.0169 ± 0.0009
	153	0.0223 ± 0.0017
	352	0.0338 ± 0.0086
	733	0.0755 ± 0.0062
300 ± 1	56	0.0128 ± 0.0016
	155	0.0187 ± 0.0028
	351	0.0242 ± 0.0046
	741	0.0507 ± 0.0056
323 ± 2	54	0.0125 ± 0.0011
	159	0.0143 ± 0.0034
	357	0.0215 ± 0.0012
	741	0.0326 ± 0.0034

^a Corrected for reaction of neopentyl nitrate with OH radicals (see text).

^b Indicated error limits are two least-squares standard deviations.

Table II. Alkyl nitrate yields and rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ from the irradiation of $\text{CH}_3\text{ONO-NO-2-methylbutane-air}$ (or O_2) mixtures

Temperature (K)	Total pressure (torr)	2-methyl-2-nitratobutane		2-methyl-3-nitratobutane	
		Yield ^{a, b}	$k_{1b}/(k_{1a} + k_{1b})^b$	Yield ^{a, b}	$k_{1b}/(k_{1a} + k_{1b})^b$
282 ± 2	56	0.0175 ± 0.0020	0.0283 ± 0.0032	0.0139 ± 0.0014	0.0535 ± 0.0054
	158	0.0210 ± 0.0006	0.0339 ± 0.0010	0.0196 ± 0.0007	0.0754 ± 0.0027
	349	0.0317 ± 0.0014	0.0512 ± 0.0023	0.0350 ± 0.0015	0.135 ± 0.006
	740	0.0415 ± 0.0035	0.0670 ± 0.0057	0.0509 ± 0.0020	0.196 ± 0.008
300 ± 1	55	0.0127 ± 0.0011	0.0217 ± 0.0019	0.0121 ± 0.0008	0.0445 ± 0.0029
	158	0.0151 ± 0.0010	0.0258 ± 0.0017	0.0164 ± 0.0010	0.0603 ± 0.0037
	365	0.0216 ± 0.0015	0.0369 ± 0.0026	0.0263 ± 0.0017	0.0967 ± 0.0063
	740	0.0328 ± 0.0010	0.0560 ± 0.0017	0.0408 ± 0.0011	0.150 ± 0.004
323 ± 2	55	0.0104 ± 0.0006	0.0190 ± 0.0011	0.0110 ± 0.0006	0.0386 ± 0.0021
	159	0.0132 ± 0.0010	0.0241 ± 0.0019	0.0149 ± 0.0010	0.0523 ± 0.0035
	354	0.0150 ± 0.0005	0.0274 ± 0.0009	0.0181 ± 0.0006	0.0635 ± 0.0021
	740	0.0199 ± 0.0013	0.0364 ± 0.0024	0.0260 ± 0.0013	0.0912 ± 0.0042

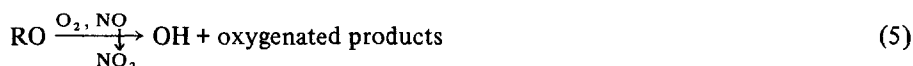
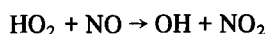
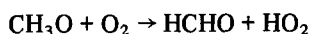
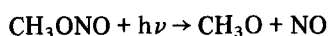
^a Corrected for reaction of the methyl nitratobutanes with OH radicals (see text).^b Indicated error limits are two least-square standard deviations, and do not take into account uncertainties associated with the fractions of H-atom abstraction occurring from the differing C-H bonds in 2-methylbutane.Table III. Alkyl nitrate yields and rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ from the irradiation of $\text{CH}_3\text{ONO-NO-3-methylpentane-air}$ (or O_2) mixtures

Temperature (K)	Total pressure (torr)	3-methyl-2-nitratopentane	
		Yield ^{a, b}	$k_{1b}/(k_{1a} + k_{1b})^b$
281 ± 2	58	0.0227 ± 0.0005	0.0636 ± 0.0014
	157	0.0354 ± 0.0051	0.0992 ± 0.0143
	348	0.0566 ± 0.0036	0.159 ± 0.010
	740	0.0804 ± 0.0055	0.225 ± 0.016
300 ± 1	59	0.0188 ± 0.0013	0.0497 ± 0.0034
	159	0.0272 ± 0.0026	0.0720 ± 0.0069
	358	0.0427 ± 0.0052	0.113 ± 0.014
	735	0.0614 ± 0.0032	0.162 ± 0.009
323 ± 2	56	0.0135 ± 0.0014	0.0339 ± 0.0035
	159	0.0203 ± 0.0020	0.0510 ± 0.0050
	357	0.0324 ± 0.0012	0.0814 ± 0.0030
	740	0.0434 ± 0.0030	0.109 ± 0.008

^a Corrected for reaction of 3-methyl-2-nitratopentane with OH radicals (see text).^b Indicated error limits are two least-squares standard deviations, and do not take into account uncertainties associated with the fractions of H-atom abstraction occurring from the differing C-H bonds in 3-methylpentane.

At 298–300 K and 735–740 torr total pressure the present alkyl nitrate yields of neopentyl nitrate (0.0507 ± 0.0056), 2-methyl-2-nitratobutane (0.0328 ± 0.0010), 2-methyl-3-nitratobutane (0.0408 ± 0.0011), and 3-methyl-2-nitratopentane (0.0614 ± 0.0032) are in reasonable agreement with our previously measured yields of 0.0513 ± 0.0053 , 0.0277 ± 0.0011 , 0.0381 ± 0.0009 , and 0.0671 ± 0.0064 , respectively. (The indicated errors are two least-squares standard deviations of the slopes of plots such as those shown in Figure 1, and do not include any systematic errors due to the alkane and alkyl nitrate GC-FID calibration factors.) This agreement is gratifying since these two sets of measurements involved totally independent GC-FID calibrations, which have estimated overall errors of $<5\%$ for the alkanes and possibly up to $\sim 10\%$ for the alkyl nitrates.

As discussed previously (Atkinson *et al.*, 1982a, 1983, 1984) the major reactions occurring in irradiated $\text{CH}_3\text{ONO-NO-alkane-air}$ (or O_2) mixtures are as follows:



In these systems the alkanes and the alkyl nitrates are consumed essentially solely by reaction with the OH radical [reactions (2) and (6), respectively]. The only significant sink for the alkyl peroxy radicals formed from reactions (2) and (3) is reaction with NO, forming either the corresponding alkyl nitrate [reaction (1b)] or the alkoxy radical [reaction (1a)], since the reactions of RO_2 radicals with NO_2 to form alkyl peroxy-nitrates (RO_2NO_2) are of negligible importance due to the rapid back-decomposition of the alkyl peroxy-nitrates (Atkinson and Lloyd, 1984).

The formation of alkyl nitrates can occur either from the reaction of alkyl peroxy radicals with NO [reaction (1b)] or from the reaction of alkoxy radicals with NO_2 [reaction (4)]. Under the experimental conditions employed here, alkoxy radicals also react with O_2 , decompose or isomerize (Atkinson and Lloyd, 1984; Carter and Atkinson, 1985). Based upon a recent review of the reactions involved in the atmospheric degradation of the alkanes (Carter and Atkinson, 1985), it can be calculated that at 282 K and 55 torr of O_2 [the most favorable conditions for alkyl nitrate formation via reaction (4)] the removal rates of the alkoxy radicals involved in the present study are (in

units of 10^4 s^{-1}): $(\text{CH}_3)_3\text{CCH}_2\dot{\text{O}}$, 1.3 (reaction with O_2); $(\text{CH}_3)_2\text{C}(\dot{\text{O}})\text{CH}_2\text{CH}_3$, 2.3 (decomposition); $(\text{CH}_3)_2\text{CHCH}(\dot{\text{O}})\text{CH}_3$, 2.0 (mainly reaction with O_2); and $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\dot{\text{O}})\text{CH}_3$, 7.7 (mainly isomerization and reaction with O_2). At 323 K and 55 torr of O_2 , the overall removal rates for these alkoxy radicals are calculated to increase to (in units of 10^4 s^{-1}): 1.4, 50, 8.2, and 45, respectively.

Making the worst-case assumption that all of the initially present NO and CH_3ONO is converted to NO_2 by the end of the irradiations, then for a rate constant of $k_4 = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Lloyd, 1984) the rate of reaction (4) is calculated to be $\sim 720 \text{ s}^{-1}$. Under this worst-case scenario, the highest fractional yield of alkyl nitrate from reaction (4) would occur for the neopentane system, with neopentyl nitrate yields at 55 torr total pressure of O_2 being up to $\sim 0.05\text{--}0.06$ at 282, 300 and 323 K.

However, the observations of neopentyl nitrate yields as low as 0.017 at 282 K and 0.013 at 323 K (Table I) show that reaction (4) must be much less important than the above calculations predict for the worse-case conditions. Furthermore, if reaction (4) was a significant contributor to the observed yields of alkyl nitrates in these irradiated $\text{CH}_3\text{ONO-NO-alkane-air}$ systems, then the formation of NO_2 during the irradiations would lead to curvature in the plots of the type shown in Figure 1. However (as shown, for example, in Figure 1), plots of the corrected alkyl nitrate yields against the amount of alkane reacted at all of the temperatures and total pressures studied were good straight lines within the experimental scatter, and no curvature was evident.

Thus, while a small contribution to the observed alkyl nitrate yields from the reaction of the alkoxy radicals with NO_2 [reaction (4)] at the lowest temperatures and O_2 pressures employed cannot be ruled out (≤ 0.01 of the fractional alkyl nitrate yields from the precursor radicals), the alkyl nitrates observed are formed mainly from the reaction of the precursor alkyl peroxy radicals with NO via reaction (1b). The alkyl nitrate yields given in Tables I–III, after correction for their reaction with the OH radical, then reflect the amount of the particular RONO_2 formed for each alkane molecule removed.

In order to derive the rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ for the individual alkyl peroxy radicals from the observed overall yields, it is necessary to determine the fraction of the overall OH radical reaction with the parent alkane which gave rise to the individual alkyl peroxy radicals. Recent schemes for the estimation of OH radical reaction rate constants with the alkanes (Atkinson, 1986a, b) allow the apparently accurate assessment of the fraction of alkyl and alkyl peroxy radicals formed from these OH radical reactions. The most recent temperature dependent estimation technique of Atkinson (1986b) has been used to derive the rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ for the individual alkyl peroxy radicals for which the corresponding alkyl nitrates were monitored. The rate constant ratios derived are given in Tables I–III and, analogous to those for the alkyl peroxy radicals from n-pentane and n-heptane (Atkinson, *et al.*, 1983), they increase with increasing total pressure and with decreasing temperature.

We have previously shown (Atkinson *et al.*, 1983; Carter and Atkinson, 1985) that the available rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ for a series of secondary alkyl peroxy radicals are fit by the general fall-off equation

$$\left[\frac{k_{1b}}{(k_{1a} + k_{1b})} \right]_{\text{sec}} = \left(\frac{Y_0^{300} [M] (T/300)^{-m_0}}{1 + \frac{Y_0^{300} [M] (T/300)^{-m_0}}{Y_\infty^{300} (T/300)^{-m_\infty}}} \right)^F F^Z \quad (\text{I})$$

where

$$Z = \left\{ 1 + \left[\log \left(\frac{Y_0^{300} [M] (T/300)^{-m_0}}{Y_\infty^{300} (T/300)^{-m_\infty}} \right) \right]^2 \right\}^{-1} \quad (\text{II})$$

[M] is the concentration of air in molecule cm^{-3} , and $Y_0^{300} = \alpha e^{\beta n}$, where n is the number of carbons in the alkyl peroxy radical and α and β are constants, with (Carter and Atkinson, 1985; Atkinson, 1986a)

$$Y_\infty^{300} = 0.435$$

$$\alpha = 1.95 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1}$$

$$\beta = 0.947$$

$$m_0 = 2.99$$

$$m_\infty = 4.69$$

and

$$F = 0.556$$

The experimental data for the 2-methyl-3-butyl- and 3-methyl-2-pentyl peroxy radicals are plotted in Figure 2 as a function of temperature and pressure, together with the fall-off curves calculated from Equations (I) and (II) with the parameters given above. Analogous plots are given in Figure 3 for the 2- and 3-pentyl peroxy and the 2-, 3- and 4-heptyl peroxy radicals previously studied (Atkinson *et al.*, 1983), using the most recent estimation techniques (Atkinson, 1986a, b) to recalculate the rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$.

A comparison of the experimental and calculated rate constant ratios obtained at 298–300 K and 735–740 torr total pressure of air for the secondary alkyl peroxy radicals studied to date is given in Table IV. It can be seen from Table IV and Figures 2 and 3 that the calculated rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ are consistent, to within ~25%, with the experimental data. Considering the likely uncertainties of approximately 10–15% in the GC-FID calibrations and those in the derivations of the rate constant ratios from the experimental alkyl nitrate yields, this level of agreement must be considered to be good.

For the rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ for the primary and tertiary alkyl peroxy radicals, we have carried out least-squares fits of the available data to the equations

$$[k_{1b}/(k_{1a} + k_{1b})]_{\text{prim}} = f_{\text{prim}} [k_{1b}/(k_{1a} + k_{1b})]_{\text{sec}}$$

and

$$[k_{1b}/(k_{1a} + k_{1b})]_{\text{tert}} = f_{\text{tert}}[k_{1b}/(k_{1a} + k_{1b})]_{\text{sec}}$$

where f_{prim} and f_{tert} are constants, and obtain

$$f_{\text{prim}} = 0.37 \quad \text{and} \quad f_{\text{tert}} = 0.41$$

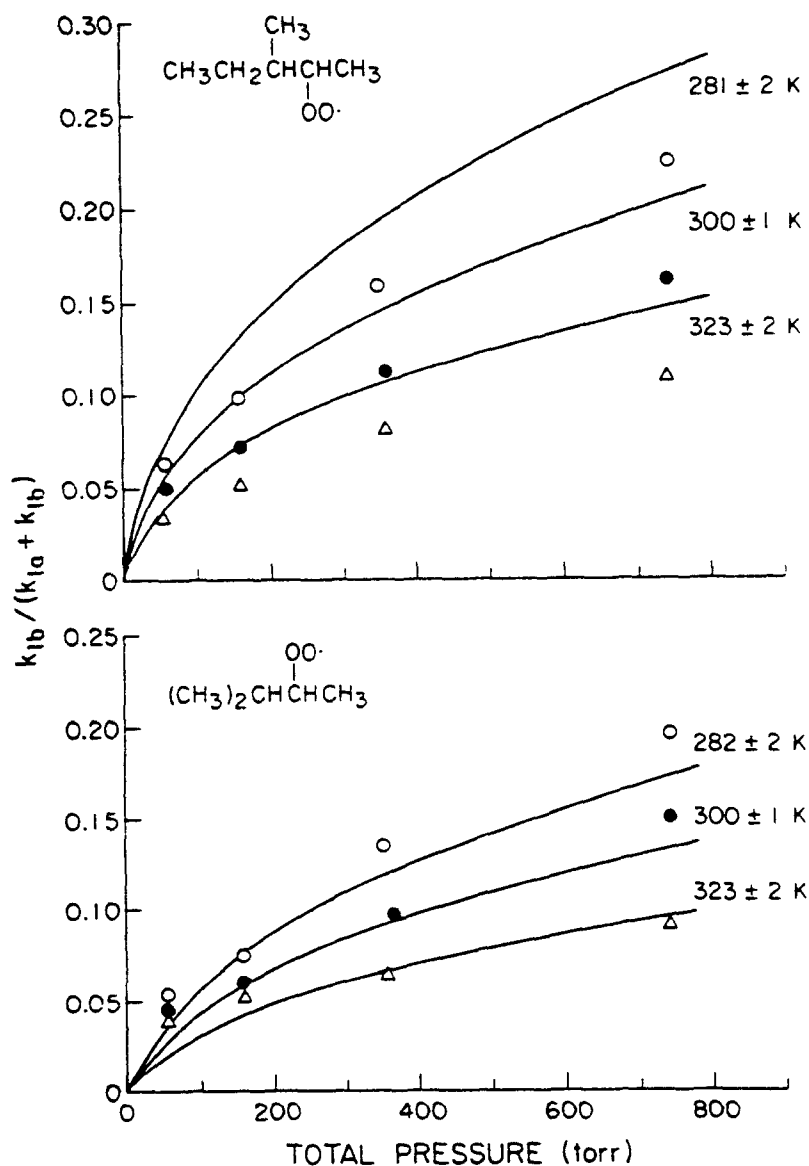


Fig. 2. Comparison of the experimentally derived rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ for 2-methyl-3-butyl peroxy and 3-methyl-2-pentyl peroxy radicals with the calculated values as a function of temperature and pressure. (\circ , 281 ± 2 or $282 \pm 2 \text{ K}$; \bullet , $300 \pm 1 \text{ K}$; \triangle , $323 \pm 2 \text{ K}$).

Plots of the present experimental data for 2,2-dimethyl-1-propyl peroxy and 2-methyl-2-butyl peroxy radicals as a function of temperature and pressure, together with the calculated fall-off curves, are shown in Figure 4. It is clear from this figure that while the calculated fall-off curves reproduce the general features of the experimental data, the

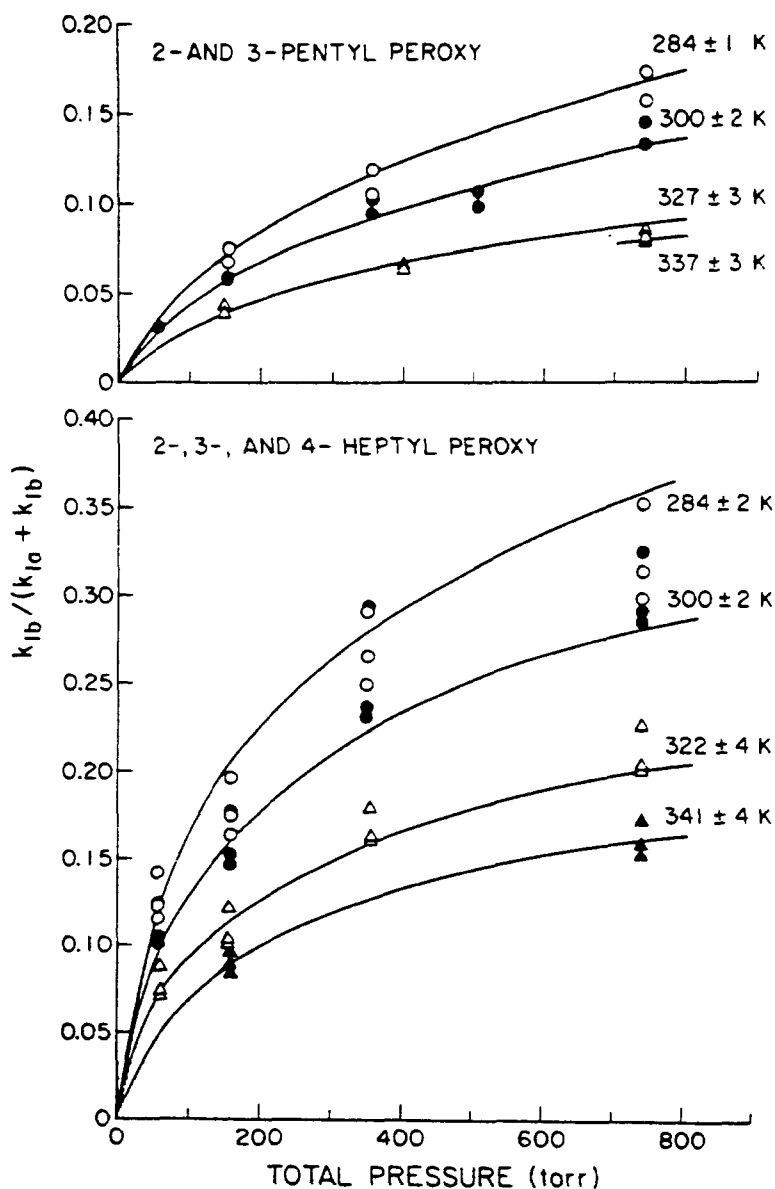


Fig. 3. Comparison of the experimentally derived rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ for 2- and 3-pentyl peroxy and 2-, 3- and 4-heptyl peroxy radicals [recalculated from the data of Atkinson *et al.* (1983)] with the calculated values as a function of temperature and pressure. (\circ , 284 K; \bullet , 300 \pm 2 K; Δ , 322 \pm 4 or 327 \pm 3 K; \blacktriangle , 337 \pm 3 or 341 \pm 4 K).

Table IV. Comparison of experimental and calculated rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ for secondary alkyl peroxy radicals at ~ 299 K and 740 torr total pressure of air

Carbon number n	$k_{1b}/(k_{1a} + k_{1b})$		Peroxy radical
	Calculated ^a	Experimental ^b	
3	0.046	0.042 ± 0.003	2-propyl
4	0.083	0.090 ± 0.008	2-butyl
5	0.135	0.129 ± 0.016 , 0.134 ± 0.002	2-pentyl
		0.131 ± 0.016 , 0.146 ± 0.009	3-pentyl
		0.141 ± 0.003 , 0.150 ± 0.004	2-methyl-3-butyl
6	0.208	0.209 ± 0.032	2-hexyl
		0.230 ± 0.031	3-hexyl
		0.160 ± 0.015	cyclohexyl
		0.190 ± 0.018	2-methyl-4-pentyl
			+ 2-methyl-4-pentyl
7	0.284	0.162 ± 0.009 , 0.178 ± 0.017	3-methyl-2-pentyl
		0.291 ± 0.022 , 0.301 ± 0.049	2-heptyl
		0.323 ± 0.048 , 0.325 ± 0.014	3-heptyl
		0.285 ± 0.015 , 0.301 ± 0.045	4-heptyl
8	0.340	0.323 ± 0.024	2-octyl
		0.348 ± 0.032	3-octyl
		0.329 ± 0.032	4-octyl

^a At 299 K and 735 torr total pressure.

^b At 298–300 K and 735–740 torr total pressure [from Atkinson *et al.* (1982a, 1984) and the present work]. The indicated error limits are two least-squares standard deviations, but do not take into account errors due to GC-FID calibrations of the alkanes and alkyl nitrates, nor of the estimation procedure used to derive the rate constant ratios from the observed alkyl nitrate yields.

experimental rate constant ratios for the neopentane system exhibit a significant degree of scatter, and are consistently higher than the calculated values at the lowest total pressures studied. The agreement for the 2-methyl-2-butyl peroxy radical is better, but discrepancies are again evident for the data obtained at ~ 55 torr total pressure of O_2 . These discrepancies may be at least partially due to the low alkyl nitrate yields observed and to a contribution from reaction (4) at the lowest pressure and temperature studied.

It is clear, however, from the data presented in Table IV and Figures 2–4 that the use of Equations (I) and (II) with the values of the parameters given here allows the prediction of the rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ to within acceptable limits for the temperature and pressure conditions appropriate to the lower troposphere. Hence Equations (I) and (II), the factors f_{prim} and f_{tert} , and the parameters α , β , m_0 , m_∞ , Y_∞^{300} and F presented here can be used as inputs into computer modeling studies of the atmospheric reactions of the alkanes. However, it should be noted that these estimations are applicable only for the alkyl peroxy radicals, since the limited data reported (Carter and Atkinson, 1985) suggest that the corresponding rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ for substituted peroxy radicals may be very different from those for the non-substituted alkyl peroxy radicals studied to date.

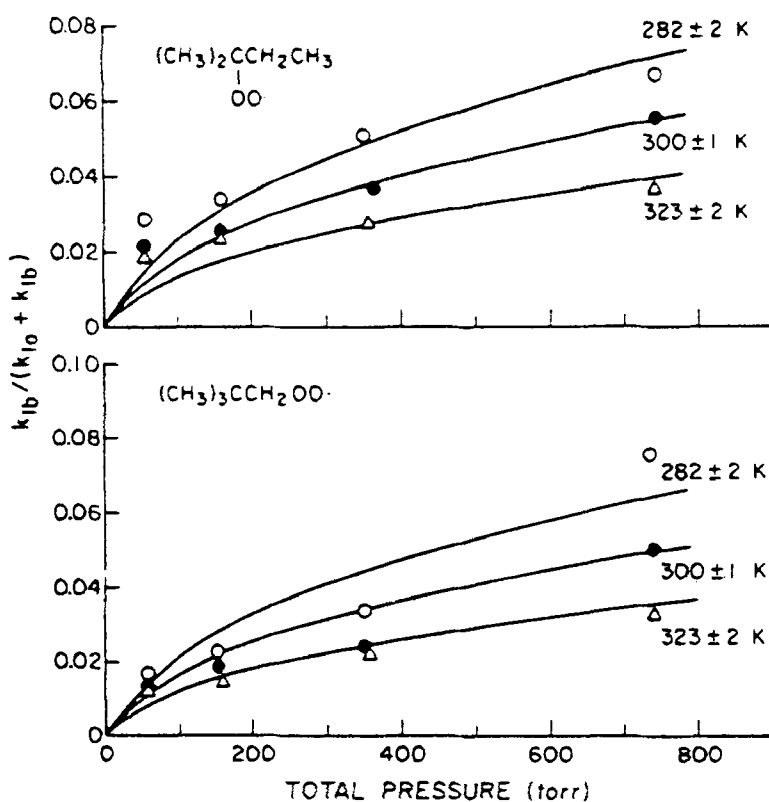


Fig. 4. Comparison of the experimentally derived rate constant ratios $k_{1b}/(k_{1a} + k_{1b})$ for the 2,2-dimethyl-1-propyl peroxy and 2-methyl-2-butyl peroxy radicals with the calculated values as a function of temperature and pressure. (o, 282 ± 2 K; •, 300 ± 1 K; △, 323 ± 2 K).

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References

- Atkinson, R., 1986a, Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions, *Chem. Rev.* **86**, 69–201.
- Atkinson, R., 1986b, Estimations of OH radical rate constants for H-atom abstraction from C–H and O–H bonds over the temperature range 250–1000 K, *Int. J. Chem. Kinet.* **18**, 555–568.
- Atkinson, R. and Lloyd, A. C., 1984, Evaluation of kinetic and mechanistic data for modeling of photochemical smog, *J. Phys. Chem. Ref. Data* **13**, 315–444.
- Atkinson, R., Aschmann, S. M., Carter, W. P. L., Winer, A. M., and Pitts, J. N., Jr., 1982a, Alkyl

- nitrate formation from the NO_x -air photooxidations of C_2 – C_8 *n*-alkanes, *J. Phys. Chem.* **86**, 4563–4569.
- Atkinson, R., Aschmann, S. M., Winer, A. M., and Pitts, J. N., Jr., 1982b, Rate constants for the reaction of OH radicals with a series of alkanes and alkenes at 299 ± 2 K, *Int. J. Chem. Kinet.* **14**, 507–516.
- Atkinson, R., Carter, W. P. L., and Winer, A. M., 1983, Effects of temperature and pressure on alkyl nitrate yields in the NO_x photooxidations of *n*-pentane and *n*-heptane, *J. Phys. Chem.* **87**, 2012–2018.
- Atkinson, R., Aschmann, S. M., Carter, W. P. L., Winer, A. M., and Pitts, J. N., Jr., 1984, Formation of alkyl nitrates from the reaction of branched and cyclic alkyl peroxy radicals with NO, *Int. J. Chem. Kinet.* **16**, 1085–1101.
- Carter, W. P. L. and Atkinson, R., 1985, Atmospheric chemistry of alkanes, *J. Atmos. Chem.* **3**, 377–405.
- Darnall, K. R., Carter, W. P. L., Winer, A. M., Lloyd, A. C., and Pitts, J. N., Jr., 1976, Importance of $\text{RO}_2 + \text{NO}$ in alkyl nitrate formation from C_4 – C_6 alkane photooxidations under simulated atmospheric conditions, *J. Phys. Chem.* **80**, 1948–1950.
- Winer, A. M., Graham, R. A., Doyle, G. J., Bekowies, P. J., McAfee, J. M., and Pitts, J. N., Jr., 1980, An evacuable environmental chamber and solar simulator facility for the study of atmospheric photochemistry, *Adv. Environ. Sci. Technol.* **10**, 461–511.