

# Chemical Reactions and Transport of Alkanes and Their Products in the Troposphere

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**Abstract.** The product distributions have been calculated for more abundant alkanes contributing most of the carbon atoms in the alkane fraction of an ambient air hydrocarbon mixture reasonably representative of U.S. emissions. The effects of ambient temperatures on product yields has been calculated for a range of temperatures from 250 to 330 K. The sensitivity of product yields to uncertainties in alkoxy radical process rate constants has been examined with emphasis on uncertainties in decomposition reactions. Chemical lifetimes are estimated at 300 K under summertime conditions for hydrocarbons and for products of alkane photooxidation in the atmosphere. The atmospheric distribution of alkanes and products is evaluated in terms of the extent to which reaction processes are likely to occur in the planetary boundary layer compared to the free troposphere.

The calculations predict a substantial effect of temperature on product yields. A large decrease in alkyl nitrate yields and a smaller decrease in ketone yields occur with increasing temperature. The yields of the short-lived, more reactive aldehydes undergo substantial increases with increasing temperature. Lower yields of ketones and higher yields of aldehydes are associated with the use of higher compared to lower decomposition process rate constants. For the type of U.S. hydrocarbon mixture available from measurements, 16 oxygenated products account for more than 60% of the total alkane carbon atoms converted to products, with most of these carbon atoms accounted for by four products. The effects of increased temperature on product reactivity and radical production may also influence  $O_3$  production.

**Key words:** Alkanes, lifetimes, tropospheric processes, product yields.

## 1. Introduction

Alkanes are an important component of atmospheric gas mixtures on all scales from urban and regional to global. Procedures have been developed for (1) estimating the OH radical rates of reaction with alkanes and their products, (2) for the reactions of peroxyalkyl radicals, and (3) the processes involving alkoxy radicals (Atkinson and Lloyd, 1984; Carter and Atkinson, 1985; Atkinson, 1985, 1990; Carter *et al.*, 1986). This work emphasizes the procedures and processes needed to develop a detailed chemical kinetic module for atmospheric photochemical modeling. The chemical kinetic mechanisms developed have been tested with experiments carried out in several environmental chambers (Carter *et al.*, 1986). Similar procedures have been applied to predict product distributions in an atmospheric hydrocarbon mixture under  $NO_x$ -rich and zero  $NO_x$  conditions based on analyses of hydrocarbon composition in Los Angeles (Calvert and Madronich, 1987).

In the present work the procedures developed were applied to the alkane fraction of a hydrocarbon mixture based on analyses of hydrocarbon composition in 39 U.S. cities (Seila and Lonneman, 1988). This hydrocarbon mixture has a much smaller loading of total carbon and of higher molecular weight alkanes than the Los Angeles mixture of hydrocarbons (Calvert and Madronich, 1987). The emphasis in the present work is on calculating the detailed product distributions for each of a number of more abundant alkanes as the yields vary over an ambient temperature range from 250 to 330 K. The effects of uncertainties in rate constants for alkoxy processes were investigated and emphasis was placed on the decomposition reactions of alkoxy radicals. The yields and chemical lifetimes were combined with transport characteristics of these alkanes and their products to estimate their distributions in the planetary boundary layer and the free troposphere.

## 2. Concentrations, Composition, and Lifetimes of Atmospheric Hydrocarbons

Before becoming involved in the details of chemical reactions of alkanes, it is useful to develop a brief overview of the concentrations, composition, and lifetimes of atmospheric hydrocarbons. A number of these hydrocarbons are likely to be involved in photochemical atmospheric reactions not only over urban and polluted regions but also over less populated land areas, and oceans and above the planetary boundary in the free troposphere.

A recent investigation of the concentrations and composition of hydrocarbons over urban areas provides averaged results from 39 U.S. cities covering much of the contiguous United States (Seila and Lonneman, 1988; Seila *et al.*, 1989). Although only a few cities in the far western United States are included, most other areas are adequately represented. The selection of locations resulted in some over representation to cities in Texas and Louisiana with petrochemical industrial activities. Therefore, the hydrocarbon concentrations do not provide a weighted average representation of hydrocarbon emissions throughout the United States.

In individual 6 to 9 a.m. samples, from 50 to more than 200 peaks were identified as hydrocarbons (Seila and Lonneman, 1988; Seila *et al.*, 1989). However, statistical results are tabulated for the abundant hydrocarbons, excluding methane. These fully identified hydrocarbons consisted of 25 alkanes, 13 aromatic hydrocarbons, 8 alkenes, and acetylene. The alkanes contributed 61% of the median carbon atom concentration, while the aromatic hydrocarbons, alkenes, and acetylene contributed 25, 11, and 3%, respectively (Table I).

The median alkane concentration was 266 ppbC and one half of the carbon atoms were associated with straight-chain alkanes. About 40% of the carbon atoms were associated with monosubstituted methyl alkanes, and the remaining alkanes consisted of other branched-chain alkanes and of cycloalkanes. Six of the two-carbon through five-carbon alkanes contributed 64% of the alkanes on a ppbC basis.

The rate constants with OH radicals at 298 K are listed in Table I for 48 hydro-

carbons. The lifetimes of the alkanes, aromatic hydrocarbons, and acetylene are determined by their rates of reaction with OH radicals (Atkinson, 1985). The rates of the reactions with OH predominate over those with O<sub>3</sub> (Atkinson and Lloyd, 1984; Atkinson, 1985). The rates of reaction with NO<sub>3</sub> radicals are not significant for the hydrocarbons listed (Atkinson and Lloyd, 1984; Atkinson, 1985).

The lifetimes of these hydrocarbons can be estimated if OH concentrations are available. Considerable uncertainties exist in the literature for the seasonally averaged OH concentrations by latitude zone (Altshuler, 1989). For purposes of calculating lifetimes in this work, the average daylight OH concentrations near ground level at midlatitudes in the Northern Hemisphere were assumed to have the following values: July,  $2 (\pm 1) \times 10^6$  molecule cm<sup>-3</sup>; April and October,  $0.8 (\pm 0.4) \times 10^6$  molecule cm<sup>-3</sup>; and January,  $0.2 (\pm 0.1) \times 10^6$  molecule cm<sup>-3</sup>. The OH ranges are meant only to indicate that substantial uncertainties are involved in these values. These average daylight OH concentration values are substantially lower than mid-day OH concentrations because of the low rates of O(<sup>1</sup>D) formation from O<sub>3</sub> during the first several hours after sunrise and before sunset.

These OH concentration values are not necessarily representative of the OH concentrations within urban areas. Model predictions of OH concentrations have been made over a wide range of NO<sub>x</sub> concentrations (Liu and Trainer, 1988). A rapid increase in OH concentrations is predicted, especially above about 0.5 ppb of NO<sub>x</sub>. A threefold to fourfold increase in OH concentration is predicted between the 10 to 100 ppt NO<sub>x</sub> range and the 5 to 10 ppb NO<sub>x</sub> range. The highest OH concentrations predicted for 5 to 10 ppb of NO<sub>x</sub> equal  $4$  to  $5 \times 10^6$  molecule cm<sup>-3</sup>, and these values agree within a factor of 2 with the highest OH concentrations reported experimentally within the 0800 to 1600 h period (Perner *et al.*, 1987; Platt *et al.*, 1988). These investigators also measured NO and NO<sub>2</sub> concurrently. The experimental relationship between OH and NO<sub>x</sub> concentrations does not appear to show the consistent increase of OH concentration with NO<sub>x</sub> predicted by others (Liu and Trainer, 1988). Other recent experimental OH measurements in a suburban area (Shirinzadeh *et al.*, 1987) average about  $0.6 \times 10^6$  molecule cm<sup>-3</sup> during daylight hours, which is appreciably below the model predictions. However, under actual ambient air conditions the various species and the fluxes are not necessarily maintaining the relationships assumed in modeling.

The summer OH lifetimes are listed in Table I for the more abundant atmospheric hydrocarbons. These lifetimes are several months for ethane; about a week for propane, acetylene, and benzene; and as short as a few hours for most alkenes. There is appreciable overlap in lifetimes between various types of hydrocarbons. The lifetimes of the internally double-bonded alkenes are shorter because of their higher reaction rates with O<sub>3</sub> than with OH, so the lifetimes listed are upper limits.

Especially for ethane, propane, acetylene, and benzene, estimation of lifetimes should take into consideration the vertical transport of varying fractions of these hydrocarbons into the free troposphere. The effect is relatively small except for ethane. For ethane the OH lifetime actually is substantially longer than indicated

Table I. Concentrations, rate constants with OH radicals and OH lifetimes for the more abundant hydrocarbons measured in U.S. cities

Hydrocarbon	Median concn. <sup>a</sup> (in ppbc)	$k \times 10^{12}$ (298 K) <sup>b</sup> ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	Summer daylight lifetimes (h) <sup>c</sup>
ethane	23.3	0.268	460
propane	23.5	1.15	120
<i>n</i> -butane	40.3	2.54	54
2-methylpropane	14.8	2.34	59
<i>n</i> -pentane	22.0	3.94	35
2-methylbutane	45.3	3.9	36
cyclopentane	2.1	5.16	27
<i>n</i> -hexane	(11.0) <sup>d</sup>	5.61	25
2-methylpentane	14.9	5.6	25
3-methylpentane	10.7	5.7	24
2,3-dimethylbutane	3.8	6.3	22
cyclohexane	2.2	7.49	19
methylcyclopentane	6.4	7.1	20
<i>n</i> -heptane	4.7	7.15	19
2-methylhexane	7.3	6.8 <sup>e</sup>	20
3-methylhexane	5.9	7.2 <sup>e</sup>	19
2,4-dimethylpentane	2.2	5.1	27
methylcyclohexane	3.4	10.4	13
<i>n</i> -octane	2.6	8.68	16
2-methylheptane	2.5	8.2 <sup>e</sup>	17
3-methylheptane	2.2	8.6 <sup>e</sup>	16
2,2,4-trimethylpentane	6.8	3.68	16
2,3,4-trimethylpentane	2.5	7.0	20
<i>n</i> -nonane	2.2	10.2	14
<i>n</i> -decane	3.3	11.6	12
benzene	12.6	1.23	115
toluene	33.8	5.96	23
ethylbenzene	5.9	7.1	20
<i>o</i> -xylene	7.2	13.7	10
<i>p</i> -xylene	18.1	14.3	10
<i>m</i> -xylene		23.6	5.9
<i>o</i> -ethyltoluene	2.9	12.3	11
<i>p</i> -ethyltoluene	2.8	12.1	11
<i>m</i> -ethyltoluene	5.3	19.2	7.2
1,2,3-trimethylbenzene	3.4	32.7	4.2
1,2,4-trimethylbenzene	10.6	32.5	4.3
1,4-diethylbenzene	2.4	12.0 <sup>f</sup>	11
1,2-dimethyl-3-ethylbenzene	2.5	33.0 <sup>f</sup>	4
ethene	21.4	8.52	16
propene	7.7	26.3	5.3
1-butene	5.9	31.4	4.4
2-methylpropene		51.4	2.7
<i>trans</i> -2-butene	2.5	64.0	2.29 <sup>b</sup>
2-methyl-1-butene	2.6	61.0	2.3
<i>trans</i> -2-pentene	2.9	67.0	2.19 <sup>b</sup>
<i>cis</i> -2-pentene	3.6	65.0	2.29 <sup>b</sup>
acetylene	12.9	0.90	155

Table I. (continued)

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- <sup>a</sup> From Seila and Lonneman (1988).  
<sup>b</sup> From Atkinson (1990).  
<sup>c</sup> Assuming a summertime average daylight OH radical concentration of  $2 \times 10^6$  molecules<sup>-1</sup> cm<sup>-3</sup>.  
<sup>d</sup> Hexane plus 2-ethyl-1-butene concentrations, but assuming that the unresolved peak consists predominantly of *n*-hexane.  
<sup>e</sup> Computed values from structure activity relationships, Atkinson (1987).  
<sup>f</sup> The *k* values assumed essentially the same as *p*-ethyltoluene and 1,2,3-trimethylbenzene, respectively.  
<sup>g</sup> An upper limit lifetime estimate only since the lifetime of this alkene is primarily determined by its rate of reaction with O<sub>3</sub>.

because the OH concentration should be adjusted downward by a factor of 2 for midtropospheric conditions (Logan *et al.*, 1981; Kasting and Singh, 1986; Golombek and Prinn, 1986; Isaksen and Hov, 1987; Henderson *et al.*, 1989).

To a first approximation, the OH concentration values assumed above for spring and fall will increase the lifetimes of all of these hydrocarbons by a factor of 2.5 and for winter by a factor of 10. The lifetimes in air parcels moving through the planetary boundary layer should be appreciably increased during these seasons of the year which will increase the potential for transport into the free troposphere. However, this tendency will be partially offset during these seasons by decreased vertical diffusion (Liu *et al.*, 1984). An additional consideration is the change in OH rate constants with seasonal temperatures. For the alkanes, the rate constants with OH decrease moderately with decreasing temperature. The rate constants for aromatic hydrocarbons show very small changes with temperature. For the alkenes, the rate constants with OH increase with decreasing temperature. Usually these shifts in rate constants with temperature are much smaller than the uncertainties in the OH concentration values.

### 3. Procedures for Calculating Product Yields from the Reaction of Alkanes

The procedures used to calculate the yields of the products of atmospheric photooxidation reactions of alkanes with NO<sub>x</sub> are based on those developed in recent years (Atkinson and Lloyd, 1984; Atkinson, 1985; Carter *et al.*, 1986; Atkinson, 1987, 1990). These procedures, although reasonable and consistent, can only provide estimates of product yields. There is relatively little experimental work available to validate a number of the reaction processes involved. Examples of how certain experimental results indicate a range of possible yields are given in this section.

The initial attack on alkanes involves hydrogen abstraction by hydroxyl radicals to form alkyl radicals. The first step in the overall procedure for calculating yields involves applying group rate constants and substituent factors for alkyl groups to

calculation of the ratios of reaction rates of OH with alkyl groups. A relatively substantial set of kinetic measurements provides reaction rate constants over a range of temperatures for a large number of alkanes (Atkinson, 1985; 1990).

The group rate constants are in this order:  $k_{\text{prim}}^{\circ} < k_{\text{sec}}^{\circ} < k_{\text{tert}}^{\circ}$ . This order is maintained throughout the ambient temperature range. The substituent factors represent the influence of adjacent groups on the rates of abstraction of hydrogen by OH from any particular alkyl group. The effective rate constants,  $k$ , are products of the  $k^{\circ}$  values multiplied by the appropriate substituent factors for all adjacent groups. The recommended range of temperatures for the use of these parameters is from 250 to 1000 K (Atkinson, 1987). A summary of  $k^{\circ}$  and  $F$  values over the temperature range from 250 to 330 K are tabulated in Table II.

Because of the effect of temperature on  $k^{\circ}$  and  $F$ , the relative amounts of hydrogen abstraction by OH radicals from the types of alkyl groups varies substantially over this temperature range. These variations in ratios of partial rate to total rates for alkyl groups are tabulated for a number of alkanes in Table III.

After the initial abstraction of a hydrogen atom by an OH radical, the alkyl radical very rapidly reacts with oxygen to form an alkyl peroxy radical.



Considerable experimental work has been done on the subsequent reactions of alkyl peroxy radicals. Within the planetary boundary layer over populated regions of continents, sufficient nitric oxide is emitted so that its reaction with the alkyl peroxy radical is the predominant pathway for the conversion of the radical to products. In remote regions of the planetary boundary layer such as over the Pacific Ocean or in the free troposphere  $\text{NO}_x$  concentration are very low (Fehsenfeld *et al.*, 1988). In such regions of the atmosphere reactions of  $\text{RO}_2$  with  $\text{HO}_2$  and  $\text{RO}_2$

Table II. Group rate constants and substituent factors for primary, secondary and tertiary groups in alkanes over the temperature range from 250 to 330 K

Rate constant expression <sup>a</sup> ( $k$ )	Rate constants, $\times 10^{12}$ , in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$					
	250 K	270 K	285 K	300 K	315 K	330 K
$k_p^{\circ} = 4.47 \times 10^{-18} T^2 e^{303/T}$	0.083	0.106	0.125	0.147	0.170	0.194
$k_s^{\circ} = 4.32 \times 10^{-18} T^2 e^{233/T}$	0.686	0.746	0.795	0.845	0.898	0.953
$k_t^{\circ} = 1.89 \times 10^{-18} T^2 e^{711/T}$	2.03	1.92	1.86	1.82	1.79	1.78
Substituent factor expression						
$F(-\text{CH}_2-) = F(>\text{CH}-) = F(>\text{C}<) =^{76/T}$	1.355	1.325	1.306	1.288	1.273	1.259
$F(-\text{CH}_3)^b$	1.000	1.000	1.000	1.000	1.000	1.000

<sup>a</sup> From Atkinson (1987).

<sup>b</sup> By definition.

Table III. Ratios of partial rates for OH abstraction from primary, secondary and tertiary groups to the total rates for OH abstraction of hydrogen atoms from alkanes over the temperature range 250 to 330 K

Alkane	Partial rate ratios	250 K	270 K	285 K	300 K	315 K	330 K
propane	$\frac{2k_p^o F(-\text{CH}_2-)}{2k_p^o F(\text{CH}_2-) + k_s^o}$	0.247	0.274	0.291	0.308	0.325	0.339
	$\frac{k_p^o}{2k_p^o F(-\text{CH}_2-) + k_s^o}$	0.753	0.726	0.709	0.692	0.675	0.661
<i>n</i> -butane	$\frac{k_p^o}{k_p^o + k_s^o}$	0.108	0.124	0.136	0.148	0.159	0.169
	$\frac{k_s^o}{k_p^o + k_s^o}$	0.892	0.876	0.864	0.852	0.841	0.831
2-methyl- propane	$\frac{3k_p^o F(>\text{CH}-)}{3k_p^o F(>\text{CH}-) + k_t^o}$	0.142	0.180	0.209	0.238	0.266	0.292
	$\frac{k_t^o}{3k_p^o F(>\text{CH}-) + k_t^o}$	0.858	0.820	0.791	0.762	0.734	0.708
<i>n</i> -pentane	$\frac{2k_p^o}{2k_p^o + k_s^o[2 + F(-\text{CH}_2)]}$	0.067	0.079	0.087	0.096	0.104	0.111
	$\frac{2k_s^o}{2k_p^o + k_s^o[2 + F(-\text{CH}_2)]}$	0.556	0.554	0.552	0.550	0.548	0.546
	$\frac{k_s^o F(-\text{CH}_2-)}{2k_p^o + k_s^o[2 + F(-\text{CH}_2)]}$	0.377	0.367	0.361	0.354	0.349	0.343

Table III. (continued)

Alkane	Partial rate ratios	250 K	270 K	285 K	300 K	315 K	330 K
2-methyl- butane	$\frac{3k_p^o}{3k_p^o + k_s^o + k_t^o}$	0.084	0.107	0.124	0.142	0.159	0.176
	$\frac{k_s^o}{3k_p^o + k_s^o + k_t^o}$	0.231	0.250	0.262	0.272	0.280	0.287
	$\frac{k_t^o}{3k_p^o + k_s^o + k_t^o}$	0.685	0.643	0.614	0.586	0.560	0.537
<i>n</i> -hexane	$\frac{k_p^o}{k_p^o + k_s^o[1 + F(-CH_2-)]}$	0.049	0.058	0.064	0.071	0.077	0.083
	$\frac{k_s^o}{k_p^o + k_s^o[1 + F(-CH_2-)]}$	0.404	0.405	0.406	0.406	0.406	0.406
	$\frac{k_t^o F(-CH_2-)}{k_p^o + k_s^o[1 + F(-CH_2-)]}$	0.547	0.537	0.530	0.523	0.517	0.511
2-methyl- pentane	$\frac{3k_p^o}{3k_p^o + k_s^o[1 + F(-CH_2-)]} + k_t^o$	0.064	0.080	0.092	0.105	0.118	0.129



	$\frac{k_s}{3k_p^o + k_s[1 + F(-CH_2-)] + k_i^o}$	0.176	0.188	0.196	0.202	0.207	0.211
	$\frac{k_i^o F(-CH_2-)}{3k_p^o + k_s[1 + F(-CH_2-)] + k_i^o}$	0.239	0.249	0.255	0.259	0.263	0.266
	$\frac{k_i^o}{3k_p^o + k_s[1 + F(-CH_2-)] + k_i^o}$	0.521	0.483	0.457	0.434	0.412	0.394
3-methyl- pentane	$\frac{k_p^o}{3k_p^o + 2k_s^o + k_i^o F(-CH_2-)}$	0.019	0.024	0.028	0.033	0.037	0.041
	$\frac{2k_p^o}{3k_p^o + 2k_s^o + k_i^o F(-CH_2-)}$	0.038	0.049	0.057	0.066	0.074	0.082
	$\frac{2k_s^o}{3k_p^o + 2k_s^o + k_i^o F(-CH_2-)}$	0.314	0.343	0.362	0.377	0.392	0.403
	$\frac{k_i^o F(-CH_2-)}{3k_p^o + 2k_s^o + k_i^o F(-CH_2-)}$	0.629	0.584	0.554	0.524	0.497	0.474
2,3-dimethyl- butane	$\frac{2k_p^o}{2k_p^o + k_i^o}$	0.076	0.099	0.118	0.139	0.160	0.179
	$\frac{k_i^o}{2k_p^o + k_i^o}$	0.924	0.901	0.882	0.861	0.840	0.821

can become the dominant reactions. In such regions the alkyl nitrate yields discussed below can drop drastically.

The reaction of alkyl peroxy radicals with NO proceed by two competitive pathways



A number of investigations provide yields of alkyl nitrates from the photooxidations of alkanes with  $\text{NO}_x$  in air (Atkinson *et al.*, 1982a, b; Atkinson *et al.*, 1983; Atkinson *et al.*, 1984, 1987; Harris and Kerr, 1989). Most of the measurements have been of the yields of secondary alkyl nitrates with more limited measurements of the yields of primary and tertiary alkyl nitrates usually at temperatures near 300 K and total pressures near surface pressures. The exception are studies of the photooxidation of *n*-pentane, 2,2-dimethylpropane, 2-methylbutane, and *n*-heptane and 3-methylpentane with  $\text{NO}_x$  at the temperatures within the 281 to 342 K range and with total pressures in the 56 to 740 torr range (Atkinson *et al.*, 1983; 1987). The yields of alkyl nitrates from these studies have been used to develop empirical expressions relating alkyl nitrate yields to carbon number, temperature, and pressure.

The various studies indicate that alkyl nitrate yields are low from the smaller alkyl peroxy radicals. These radicals predominantly react with NO to form alkoxy radicals. The alkyl nitrate yields increase steadily with carbon number and the secondary alkyl nitrate yields approach an upper limit yield near 0.35 at 298 K for *n*-octane and higher molecular weight alkanes. Alkyl nitrate yields increase with decreasing temperature and increasing pressure.

The empirical expression fits the experimental results for alkyl nitrate yields produced from the alkyl peroxy radicals from *n*-pentane, 2,2-dimethyl propane, 2-methylbutane, 3-methylpentane and *n*-heptane in air reasonably well, ~25% over the range of temperatures and pressures used (Atkinson *et al.*, 1983, 1987). The expression also provides good agreement with the experimentally derived yields of alkyl nitrates for the  $\text{C}_4$  to  $\text{C}_8$  straight-chain alkane photooxidations at 299 K and 735 torr. (Atkinson *et al.*, 1983).

To obtain the yields for the primary and tertiary alkyl nitrate, the yields for secondary alkyl nitrates predicted by the empirical expression are multiplied by factors of 0.4 and 0.25, respectively (Carter and Atkinson, 1985). In order to calculate the alkyl nitrate yields from these types of alkanes with temperature and pressure, the empirical expression developed from the results for straight-chain alkanes is used. It also should be noted that, although the empirical expression has been verified only at 285 K and above (Atkinson, *et al.*, 1983, 1987) in this work, the expression has been used in this work to estimate alkyl nitrate yields down to 250 K. These calculated values for alkyl nitrate yields for heptanes and higher alkanes appear to be overestimated in the 250 to 285 K range by at least 10% (Atkinson *et al.*, 1983; Carter and Atkinson, 1989).

Alkyl nitrate formation reduces the reactivity of the photooxidative atmospheric systems because alkyl peroxy radicals and nitric oxide are removed from the reacting system. This effect is especially significant to O<sub>3</sub> formation from the higher molecular weight alkanes. As is discussed in more detail later in this work, a number of the alkyl nitrates are long-lived because they photolyze slowly in the atmosphere and react slowly with OH radicals. Therefore, although the alkyl nitrates do react slowly to contribute reactive species to the troposphere, they contribute very little to reactive species within the region of the planetary boundary layer where they originate.

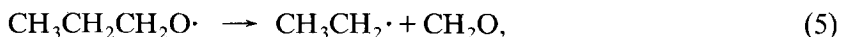
As mentioned above, alkyl nitrate yields increase with decreasing temperature. Within the planetary boundary layer, the effect will be to substantially increase yields of alkyl nitrates at lower ambient temperatures. For longer lived alkanes which can be transported up into the free troposphere, the reductions in alkyl nitrate yields associated with lower atmospheric pressures will tend to offset the effect of the lower temperatures in the free troposphere on alkyl nitrate yields.

There is a potential for dinitrate products to form in subsequent reactions of alkyl peroxy radicals formed from primary products. However, some experimental evidence indicates that dinitrates probably do not form in significant yields. This evidence relates to the better fit of model predictions to the experimental concentration-time profiles for O<sub>3</sub>, NO, and NO<sub>2</sub> in the photooxidation of *n*-heptane and *n*-octane systems if dinitrate formation is assumed not to occur (Carter and Atkinson, 1985; Carter *et al.*, 1986). If dinitrate formation is assumed to occur, the reactivity of the systems will be consistently and significantly underpredicted (Carter *et al.*, 1986).

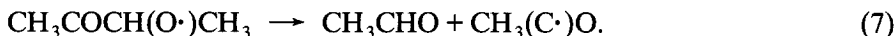
The preceding considerations are important not only because of the importance of alkyl nitrate formation but also as alkyl nitrate formation relates to alkoxy radical yields. The relative partial yields of the alkoxy radical reaction processes are obtained after subtracting the alkyl nitrate yield from the total alkyl peroxy yield at each alkyl position on an alkane molecule.

The alkoxy radicals formed in reaction (4) can undergo several subsequent types of reaction processes: (a) oxygen abstraction of a hydrogen atom attached to the alkoxy carbon position, (b) decomposition of the alkoxy radical into smaller alkoxy radicals and alkyl radicals, (c) 1,*n*-hydrogen isomerization shifts of a hydrogen atom from the *n*-position to the electron-deficient alkoxy position to form a hydroxyl group at that position. (Carter and Atkinson, 1985).

The O<sub>2</sub> abstraction of hydrogen atoms can occur only for methoxy and other primary and secondary alkoxy radicals because tertiary radicals lack hydrogen atoms to abstract. Decomposition reactions can occur for any alkoxy radical. However, the rates of decomposition are very low to O<sub>2</sub> abstraction of such decompositions, as in the following examples.



On the other hand, there is experimental evidence (Cox *et al.*, 1981) that the decomposition of  $\alpha$ -carbonyl alkoxy radicals will dominate over the  $O_2$  abstraction reaction.



In considering 1,*n*-H shift isomerizations, many *n*-membered ring transition states are possible. However, the strain energies for 1,2- 1,3- and for 1,6-H and larger ring H shifts are so high as to result in very low rates of isomerization (Carter and Atkinson, 1985). The 1,4-H shift can occur, but the rates for 1,4-H shifts for the various types of hydrogen abstraction from alkyl groups are all more than a factor of 1000 lower than are the 1,5-H shift isomerizations (Carter and Atkinson, 1985). The rates of the 1,5-H shift isomerizations, although fast, are still somewhat uncertain, as will be illustrated later in this work.

Diverse products are formed from the alkyl peroxy radical and alkoxy radical reactions discussed above. These various products have a wide range of atmospheric lifetimes because of their wide range of rates of reaction with OH radicals and photolytic rates in the atmosphere. These lifetimes also will vary substantially both with season of the year and according to the region of the troposphere into which they can be transported.

Rate expressions and rate constants at 250, 270, 285, 300, 315, and 330 K are tabulated (a) for the abstraction of hydrogen atoms by oxygen from alkoxy radicals in Table IV, (b) for the 1,5-H isomerizations of alkoxy radicals in Table V and (c) for the decomposition of alkoxy radicals in Table VI. Although rate expressions for abstractions by  $O_2$  only discriminate between primary and secondary alkoxy radicals (Table IV) the rate expressions for decomposition of alkoxy radicals vary with

Table IV. Rate expressions and rate constants for the reactions of alkoxy radicals with oxygen over the temperature range from 250 to 330 K

Reaction	Rate expression <sup>a</sup> ( $k, s^{-1}$ )	$T(K)$	Rate constant ( $s^{-1}, \times 10^{-4}$ )
$RCH_2O\cdot + O_2$	$5.69 \times 10^7 T^{-1} e^{-493/T}$	250	3.3
		270	3.5
		285	3.65
		300	3.8
		315	3.9
		330	4.0
$R'CH(O\cdot)R'' + O_2$	$2.77 \times 10^7 T^{-1} e^{-196/T}$	250	5.1
		270	5.0
		285	4.9
		300	4.8
		315	4.7
		330	4.6

<sup>a</sup> At 1 atm pressure from Carter *et al.* (1986).

Table V. Rate expressions and rate constants for the 1,5-H shift. Isomerizations of alkoxy radicals over the temperature. Range from 250 to 330 K

Type of H abstracted	Rate expression <sup>a</sup> ( <i>k</i> )	<i>T</i> (K)	Rate constant (s <sup>-1</sup> )
—CH <sub>3</sub>	$1.3 \times 10^{11} e^{-4127/T}$	250	$8.8 \times 10^3$
		270	$3.0 \times 10^4$
		285	$6.7 \times 10^4$
		300	$1.4 \times 10^5$
		315	$2.7 \times 10^5$
		330	$4.8 \times 10^5$
—CH <sub>2</sub> —	$8.4 \times 10^{10} e^{-2567/T}$	250	$2.9 \times 10^6$
		270	$6.2 \times 10^6$
		285	$1.0 \times 10^7$
		300	$1.6 \times 10^7$
		315	$2.4 \times 10^7$
		330	$3.5 \times 10^7$
>CH—	$4.2 \times 10^{10} e^{-2567/T}$	250	$1.4 \times 10^6$
		270	$3.1 \times 10^6$
		285	$5.0 \times 10^6$
		300	$8.0 \times 10^6$
		315	$1.2 \times 10^7$
		330	$1.8 \times 10^7$
—CH <sub>2</sub> OH	$8.4 \times 10^{10} e^{-3523/T}$	250	$6.4 \times 10^4$
		270	$1.8 \times 10^5$
		285	$3.6 \times 10^5$
		300	$6.7 \times 10^5$
		315	$1.2 \times 10^6$
		330	$1.9 \times 10^6$
—CH(OH)—	$4.2 \times 10^{10} e^{-1963/T}$	250	$1.6 \times 10^7$
		270	$2.9 \times 10^7$
		285	$4.3 \times 10^7$
		300	$6.0 \times 10^7$
		315	$8.3 \times 10^7$
		330	$1.1 \times 10^8$

<sup>a</sup> From Carter and Atkinson (1985).

details of structure and fragmentation. The rate constants in Table VI for decomposition are for single reaction paths. That is, when the same decomposition products occur by more than one path, as in  $\text{CH}_3\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_2\text{CH}_3$ , the rate constant given in Table VI should be multiplied by 2.

As a result of the types of rate expressions involved, the rate constants for the reactions of alkoxy radicals with  $\text{O}_2$  vary over a narrow range. Over the range from 250 to 330 K, the rate constants for abstraction of hydrogen atoms by  $\text{O}_2$  from primary alkoxy radicals increase by only 20%, whereas the rate constants for abstraction of hydrogen atoms by  $\text{O}_2$  from secondary alkoxy radicals decrease by only 10%. In contrast, over this temperature range, the rate constants for the 1,5-H shift isomerizations of various types of alkoxy radicals vary by factors of 7 to 55.

Table VI. Rate expressions and rate constants for the decomposition of alkoxy radicals over the temperature range between 250 and 330 K

Expressions and reaction	R·	T(K)	Rate expression and rate	
			Rate const. (s <sup>-1</sup> ) <sup>a</sup>	Rate const. (s <sup>-1</sup> ) <sup>b</sup>
RC(O·)H <sub>2</sub> → R· + HCHO	—CH <sub>2</sub> ·		$k = 8 \times 10^{14} e^{-18400/RT}$	$k = 8 \times 10^{14} e^{-17400/RT}$
		250	$6.6 \times 10^{-2}$	$4.9 \times 10^{-1}$
		270	$1.0 \times 10^0$	$6.6 \times 10^0$
		285	$6.2 \times 10^0$	$3.6 \times 10^1$
		300	$3.1 \times 10^1$	$1.7 \times 10^2$
		315	$1.4 \times 10^2$	$6.8 \times 10^2$
		330	$5.2 \times 10^2$	$2.4 \times 10^3$
RC(O·)H <sub>2</sub> → R· + HCHO	>CH·		$k = 8 \times 10^{14} e^{-18000/RT}$	$k = 8 \times 10^{14} e^{-17000/RT}$
		250	$1.5 \times 10^{-1}$	$1.1 \times 10^0$
		270	$2.1 \times 10^0$	$1.4 \times 10^1$
		285	$1.3 \times 10^1$	$7.3 \times 10^1$
		300	$6.1 \times 10^1$	$3.3 \times 10^2$
		315	$2.6 \times 10^2$	$1.3 \times 10^3$
		330	$9.6 \times 10^2$	$4.4 \times 10^3$
$\begin{array}{c} \text{RC(O·)R}' \\   \\ \text{H} \end{array} \rightarrow \text{R·} + \text{R}'\text{CHO}$	CH <sub>3</sub> ·		$k = 8 \times 10^{14} e^{-18300/RT}$	$k = 8 \times 10^{14} e^{-17300/RT}$
		250	$8.0 \times 10^{-2}$	$6.0 \times 10^{-1}$
		270	$1.2 \times 10^0$	$7.9 \times 10^0$
		285	$7.4 \times 10^0$	$4.3 \times 10^1$
		300	$3.7 \times 10^1$	$2.0 \times 10^2$
		315	$1.6 \times 10^2$	$7.9 \times 10^2$
		330	$6.1 \times 10^2$	$2.8 \times 10^3$
RC(O·)R' → R· + R'CHO	—CH <sub>2</sub> ·		$k = 8 \times 10^{14} e^{-15300/RT}$	$k = 8 \times 10^{14} e^{-14300/RT}$ H
		250	$3.4 \times 10^1$	$2.5 \times 10^2$
		270	$3.3 \times 10^2$	$2.1 \times 10^3$
		285	$1.5 \times 10^3$	$8.6 \times 10^3$
		300	$5.7 \times 10^3$	$3.0 \times 10^4$
		315	$1.9 \times 10^4$	$9.5 \times 10^4$
		330	$5.9 \times 10^4$	$2.7 \times 10^5$
RC(O·)R' → R· + R'CHO	>CH·		$k = 8 \times 10^{14} e^{-14900/RT}$	$k = 8 \times 10^{14} e^{-13900/RT}$ H
		250	$7.7 \times 10^1$	$5.6 \times 10^2$
		270	$6.9 \times 10^2$	$4.5 \times 10^3$
		285	$3.0 \times 10^3$	$1.75 \times 10^4$
		300	$1.1 \times 10^4$	$6.0 \times 10^4$
		315	$3.65 \times 10^4$	$1.8 \times 10^5$
		330	$1.1 \times 10^5$	$5.0 \times 10^5$
$\begin{array}{c} \text{RC(O·)R}' \\   \\ \text{H} \end{array} \rightarrow \text{R·} + \text{R}'\text{CHO}$	→C·		$k = 8 \times 10^{14} e^{-13800/RT}$	$k = 8 \times 10^{14} e^{-12800/RT}$
		250	$6.9 \times 10^2$	$5.2 \times 10^3$
		270	$5.4 \times 10^3$	$3.5 \times 10^4$
		285	$2.1 \times 10^4$	$1.2 \times 10^5$
		300	$7.1 \times 10^4$	$3.8 \times 10^5$
		315	$2.1 \times 10^5$	$1.05 \times 10^6$
		330	$5.8 \times 10^5$	$2.7 \times 10^6$

Table VI. (continued)

Expressions and reaction	R·	T(K)	Rate expression and rate	
			Rate consts. (s <sup>-1</sup> ) <sup>a</sup>	Rate consts. (s <sup>-1</sup> ) <sup>b</sup>
$\begin{array}{c} \text{RC(O}\cdot\text{)R}' \rightarrow \text{R}\cdot + \text{R}'\text{COR}'' \\   \\ \text{R}'' \end{array}$	CH <sub>3</sub> ·		$k = 8 \times 10^{14} e^{-16600/RT}$	$k = 8 \times 10^{14} e^{-15600/RT}$
		250	$2.5 \times 10^0$	$1.8 \times 10^1$
		270	$2.9 \times 10^1$	$1.9 \times 10^2$
		285	$1.5 \times 10^2$	$8.7 \times 10^2$
		300	$6.4 \times 10^2$	$3.4 \times 10^3$
		315	$2.4 \times 10^3$	$1.2 \times 10^4$
$\begin{array}{c} \text{RC(O}\cdot\text{)R}' \rightarrow \text{R}\cdot + \text{R}'\text{COR}'' \\   \\ \text{R}'' \end{array}$	—CH <sub>2</sub> ·		$k = 8 \times 10^{14} e^{-13600/RT}$	$k = 8 \times 10^{14} e^{-12600/RT}$
		250	$1.0 \times 10^3$	$7.7 \times 10^3$
		270	$7.8 \times 10^3$	$5.05 \times 10^4$
		285	$3.0 \times 10^4$	$1.7 \times 10^5$
		300	$9.9 \times 10^4$	$5.3 \times 10^5$
		315	$2.9 \times 10^5$	$1.45 \times 10^6$
$\begin{array}{c} \text{RC(O}\cdot\text{)R}' \rightarrow \text{R}\cdot + \text{R}'\text{COR}'' \\   \\ \text{R}'' \end{array}$	>CH·		$k = 8 \times 10^{14} e^{-13300/RT}$	$k = 8 \times 10^{14} e^{-12300/RT}$
		250	$1.9 \times 10^3$	$1.4 \times 10^4$
		270	$1.4 \times 10^4$	$8.9 \times 10^4$
		285	$5.0 \times 10^4$	$3.0 \times 10^5$
		300	$1.6 \times 10^5$	$8.8 \times 10^5$
		315	$4.7 \times 10^5$	$2.3 \times 10^6$
$\begin{array}{c} \text{RC(O}\cdot\text{)R}' \rightarrow \text{R}\cdot + \text{R}'\text{COR}'' \\   \\ \text{R}'' \end{array}$	→C·		$k = 8 \times 10^{14} e^{-12100/RT}$	$k = 8 \times 10^{14} e^{-11100/RT}$
		250	$2.1 \times 10^4$	$1.6 \times 10^5$
		270	$1.3 \times 10^5$	$8.3 \times 10^5$
		285	$4.2 \times 10^5$	$2.5 \times 10^6$
		300	$1.2 \times 10^6$	$6.6 \times 10^6$
		315	$3.2 \times 10^6$	$1.6 \times 10^7$
330	$7.7 \times 10^6$	$3.6 \times 10^7$		

<sup>a</sup> Based on Carter and Atkinson (1985).

<sup>b</sup> Assuming  $E_a$  value is 1 kcal mole<sup>-1</sup> lower than assumed by Carter and Atkinson (1985).

The decomposition reactions of alkoxy radicals are even more sensitive to temperature, with variations in rate constants by factors of 200 to almost 8000 over this temperature range.

Rate constants for decomposition reactions change substantially with relatively small changes in the large activation energies associated with these reactions. Uncertainties in estimating these activation energies can amount to at least 1 kcal mole<sup>-1</sup> (Carter and Atkinson, 1985). Kinetic measurements on alkoxy radicals and on alkane-NO<sub>x</sub>-air systems suggest that the activation energies recommended (Carter and Atkinson, 1985) are likely to be too high. Kinetic measurements on the 2-butoxy radical (Cox *et al.*, 1981) are consistent with a rate constant for decomposition near 300 K corresponding to the higher decomposition rate in Table VI.

Similarly, kinetic measurements on the 2-pentoxy radical (Dóbe *et al.*, 1986) are consistent with a rate constant for decomposition that is a factor of 10 higher than the lower decomposition rate in Table VI. The 2-propanone yields from the photooxidations of the isopentane-NO<sub>x</sub>-air and 2,4,4-trimethylpentane-NO<sub>x</sub>-air systems are consistent with rate constants for decomposition reactions which are factors of 2 and 6 higher than (Carter *et al.*, 1986). Based on these results of kinetic measurements, two rate expressions for decomposition reactions are used. One set of rate expressions comprises those recommended (Carter and Atkinson, 1985); the other set of rate expressions uses activation energies one kcal mole<sup>-1</sup> lower. This reduction of 1 kcal mole<sup>-1</sup> in the activation energies results in rate constants which are higher by factors of about 7.5 at 250 K, 5.5 at 300 K and 4.5 at 330 K.

Many types of alkoxy radicals undergo reactions by two or more processes, including decomposition processes, with these processes being comparable in rates. When decomposition process rates are involved, they usually become comparable to other processes at 285 K and higher temperatures. Under these circumstances, the uncertainties in alkoxy radical rates can substantially influence the calculated product yields. Other alkoxy radicals are insensitive or relative insensitive to uncertainties in the decomposition rates of the radical. These latter alkoxy radicals meet the following criteria (1) small alkoxy radicals, methoxy, ethoxy and propoxy, for which O<sub>2</sub> abstractions are the predominate process throughout the 250 K to 330 K range (2) lower molecular weight tertiary alkoxy radicals for which decomposition reactions are the predominate processes throughout the 250 to 330 K range (3) alkoxy radicals for which 1,5-H shift isomerizations such as those involving shifts from —CH<sub>2</sub> or >CH groups are the predominate processes throughout the 250 to 330 K range.

#### 4. Calculation of the Product Yields from the Photooxidations of Alkanes in Air

The procedures discussed in the previous section have been applied to the calculation of the product yields of 10 alkanes in the C<sub>2</sub> to C<sub>6</sub> range. These alkanes are ethane, propane, *n*-butane, isobutane, *n*-pentane, isopentane, *n*-hexane, 2-methylpentane and 3-methylpentane, and 2,3-dimethylbutane. The 10 C<sub>2</sub> to C<sub>6</sub> alkanes contribute 210 ppbC, or 79%, of the carbon atoms constituting the 25 abundant alkanes included in Table I. The calculations are made only for the yields of the first, or 'primary', stable, nonradical products formed after OH reactions and the subsequent reactions of peroxy alkyl radicals and alkoxy radicals, as discussed in the previous section. Detailed calculations of the product yields are made and presented in a set of tables for nine C<sub>3</sub> to C<sub>6</sub> alkanes at each of six temperatures: 250, 270, 285, 300, 315 and 330 K. This set of temperatures spans those ambient temperatures experienced in the planetary boundary layer, excepting winter conditions at high latitudes and extremely hot desert conditions. This temperature range also includes the temperatures occurring in the free troposphere up to about 6 km in

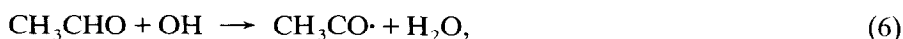


summer and 4 km in winter again except at very high latitudes (Sissenwine, 1969). In addition, when alkoxy radical decompositions are significant, competitive processes in determining product yields, the lower and higher decomposition rates discussed above are applied at each temperature.

The OH lifetimes or photolytic lifetimes, expressed by  $\tau_{\text{OH}} = 1/k_{\text{OH}}[\text{OH}]$  or  $\tau_{h\nu} = 1/k_{h\nu}$ , are calculated and listed in the product yield tables. These lifetimes involve use of either the experimentally determined rate constants of those obtained by use of structure-activity estimation techniques (Atkinson, 1987). Based on lifetimes and estimates of vertical transport times, the distributions of individual alkanes and products between the planetary boundary layer and the free troposphere are considered.

#### 4.1. Ethane

The reaction of NO with the peroxy ethyl radical formed from the reaction of OH radicals with ethane results predominantly in formation of ethoxy radicals 99% and about a 1% yield of ethyl nitrate (Atkinson *et al.*, 1982a). In the polluted planetary boundary layer, the conversion of peroxy ethyl radicals to ethoxy radicals is followed by O<sub>2</sub> abstraction of hydrogen atoms to produce ethanal. The ethoxy radicals also can undergo decomposition to form methyl radicals and formaldehyde. However, the rate constant for the decomposition reaction is very small compared to that for O<sub>2</sub> abstraction, so decomposition is a negligible pathway (Carter and Atkinson, 1985). The rate constants for reaction of OH with ethanal and its photolysis rates are well known, with OH reaction predominating over photolysis in the lower troposphere (Carter *et al.*, 1986; Gery *et al.*, 1988; Atkinson, 1990).



The CHO· radical reacts with O<sub>2</sub> to form CO, and the methyl radical reacts to form HCHO.

#### 4.2. Propane

The 2-propanone accounts for between 60 and 70% of the propane consumed by reaction of OH radicals throughout the temperature range from 250 to 330 K (Table VII). The 2-propanone is formed by O<sub>2</sub> abstraction of hydrogen atoms from the 2-propoxy radicals. Oxygen abstraction of hydrogen atoms from the 1-propoxy radicals accounts for the yield of propanal, the other major product. Formaldehyde and ethanal are minor products formed from the decomposition of the 2-propoxy radicals. Although yields are listed down to 0.001 in order to include minor products the yields in Table VII and subsequent tables are much more uncertain as discussed above.

Table VII. Effects of temperature and alkoxy radical decomposition rates on the yields of primary products formed following OH reactions with propane in air

Product	Product yields, carbon atom basis								
	300 K	250 K	270 K	285 K	300 K	315 K		330 K	
	$(\tau_{OH}, h)^a$					LDR <sup>b</sup>	HDR <sup>c</sup>	LDR <sup>b</sup>	HDR <sup>c</sup>
1-propyl nitrate	225	0.009	0.007	0.006	0.005	0.004	0.004	0.003	0.003
2-propyl nitrate	195 <sup>d</sup>	0.069	0.047	0.035	0.028	0.021	0.021	0.017	0.017
sum nitrates		0.078	0.054	0.041	0.033	0.025	0.025	0.020	0.020
formaldehyde + ethanal	8 <sup>e</sup> 9	0.000	0.000	0.000	0.003	0.002	0.016	0.011	0.056
propanal	7	0.238	0.267	0.285	0.303	0.321	0.316	0.332	0.317
sum aldehydes		0.238	0.267	0.285	0.306	0.323	0.332	0.343	0.373
2-propanone	600	0.684	0.679	0.674	0.661	0.652	0.643	0.637	0.607

<sup>a</sup> Average daylight lifetimes, in hours, assuming average OH value for summer daylight hours, 14–15 h, of  $2 \times 10^6$  molecule  $\text{cm}^{-3}$

<sup>b</sup> Lower decomposition rate. <sup>c</sup> Higher decomposition rate.

<sup>d</sup> Average daylight lifetime  $\tau_p$  based on photolysis rate for 2-propylnitrate (Dimerjian *et al.*, 1980; Roberts and Fajer, 1989; Roberts, 1990).

<sup>e</sup> Average daylight lifetime  $\tau_p$  based on photolysis rate of formaldehyde (Gery *et al.*, 1988).

The summer OH lifetimes of the products also are given in Table VII. The exceptions are formaldehyde and 2-propyl nitrate, for which the photolysis rates are higher than its rate of reaction with OH; thus, photolysis determines their lifetimes. The lifetimes of 2-propanone and the propyl nitrates range 20 to 100 times than the lifetimes of the aldehyde products.

The estimated summer OH lifetime of propane within the planetary boundary layer is about 8 days and the spring and fall lifetimes are estimated at about 20 days within the planetary boundary layer. An appreciably larger fraction of propane compared to ethane will be converted to products within the planetary boundary layer. Based on vertical eddy coefficients calculated from averaged summer vertical profiles of  $^{222}\text{Rn}$ , it has been estimated that about 70% of a gas with a 10-day lifetime should be transported above 2 km into the free troposphere (Liu *et al.*, 1984). The vertical mixing ratio is far from uniform and decreases by a factor of 5 between the surface and 5 km. Other 1-D eddy diffusion calculations for the vertical profiles of propane at midlatitudes are consistent with this result (Henderson *et al.*, 1989). Therefore, most of a gas with about a 10 day lifetime should be present in the lower half of the troposphere. The mass-weighted average tropospheric temperature if it is assumed the air parcels are distributed in the lower remote free troposphere, is 284 K. The rate constant for the reaction of OH with propane at 284 K is  $1.03 \times 10^{-12}$   $\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>, so the average tropospheric lifetime would be 1.12 times longer than at the 298 K temperature assumed in the planetary boundary layer, or about 135 h (Table I). This calculation ignores any change in OH con-

centration between the planetary boundary layer and the average value over the lower free troposphere at midlatitudes in summer. The estimates available from tropospheric photochemical models vary sufficiently to limit quantitation of an average OH value (Logan *et al.*, 1981; Crutzen and Gidel, 1983; Kasting and Singh, 1986; Golombek and Prinn, 1986; Isaksen and Hov, 1987). The estimates usually predict a moderate decrease from the surface OH concentration to an average lower tropospheric OH concentration value; the prediction is applicable to a gas distributed as estimated for propane.

The OH or the photolytic lifetimes of 2-propanone and the propyl nitrates are substantially longer than for propane and equal or exceed the lifetime for ethane. Therefore, these slowly reacting products should be uniformly distributed throughout the troposphere in a midlatitude zone.

The sources and sinks of 2-propanone in the troposphere have been evaluated (Chatfield *et al.*, 1987). Measured 2-propanone concentrations vary from 0.5 ppb at surface rural locations down to 0.12 ppm in the upper troposphere (Henderson *et al.*, 1989). It is estimated that the OH lifetime of 2-propanone will be shorter than the photolytic lifetime near the surface, but the photolytic lifetime of 2-propanone will become shorter than the OH lifetime above 5 km. This calculation was done for a tropical atmosphere but should approximate the summer atmosphere at midlatitudes. On the basis of the work of Chatfield *et al.* (1987), as well as on modeling by Henderson *et al.* (1989), it is likely that 2-propanone has a relatively constant vertical profile from the surface to the tropopause.

Measurements of the rate constants of OH radicals with many alkyl nitrates near 300 K have been compiled (Atkinson, 1990; Roberts, 1990). Absorption cross sections also have been measured for one through five carbon alkyl nitrates (Roberts and Fajer, 1989; Roberts, 1990). In addition direct photolytic rates have been obtained for several alkyl nitrates (Luke, *et al.*, 1989; Luke and Dickerson, 1988). As a result it is possible to estimate the OH lifetimes and the photolytic lifetimes of 1-propyl nitrate and 2-propyl nitrate.

The available rate constant with OH radicals of 1-propyl nitrate is  $0.62 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson, 1990) and for 2-propyl nitrate are  $0.42 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson, 1990) or  $0.59 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Becker and Wirtz, 1989). Used along with a OH radical concentration of  $2 \times 10^6 \text{ molecule}^{-1} \text{ cm}^{-3}$ , the OH daylight lifetime for 1-propyl nitrate is 225 h and the lifetime of 2-propyl nitrate is between 235 and 340 h. The photolytic lifetimes can be calculated from the absorption cross sections, actinic fluxes (Dimerjian *et al.*, 1980) and quantum yield. A quantum yield in the range of 0.5 to 1.0 is reported in several studies (Roberts, 1990). Use of the absorption spectra and the photolytic rate measurements indicate quantum yields near 1.0. Based on the absorption cross sections, actinic fluxes and quantum yield of 1.0, the daytime photolytic lifetimes for 1-propyl nitrate is 405 h while the lifetime for 2-propyl nitrate is 195 h. The OH radical reaction is the dominate process in estimating the lifetime of 1-propyl nitrate while the photolytic process probably is the dominate process in estimating

the lifetime of 2-propyl nitrate. It should be noted that there are substantial uncertainties in the values for the rate constants of these alkyl nitrates and the quantum yield may not be equal to one.

The  $\text{NO}_x$  concentrations in the lower free troposphere can limit the yields of these alkyl nitrates. In the lower free troposphere, the nitric oxide and nitrogen dioxide concentration levels measured are several orders of magnitude lower than in the planetary boundary layer. (Fehsenfeld *et al.*, 1988; Ridley *et al.*, 1989). Concentrations of 10 pptv and below of NO have been measured in aircraft flights in the lower free troposphere (Fehsenfeld *et al.*, 1988; Ridley *et al.*, 1989). From flights in the midtroposphere over the United States average NO and  $\text{NO}_2$  values of 18 pptv and 29 pptv, respectively, have been measured (Ridley *et al.*, 1989). At these low concentrations, reactions of  $\text{HO}_2$ ,  $\text{RO}_2$ , and  $\text{RCO}_3$  radicals with  $\text{RO}_2$  become competitive with the corresponding reactions with NO or  $\text{NO}_2$ .

The rate constants for the  $k(\text{RO}_2 + \text{NO})$  reactions can be estimated at 260 K as about  $1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and the rate constants for  $k(\text{RO}_2 + \text{HO}_2) = k(\text{RCO}_3 + \text{HO}_2)$  reactions also have been estimated at about  $8 \times 10^{-12}$  and  $1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson and Lloyd, 1984; Atkinson, 1990). The  $\text{RO}_2$  rate constant with  $\text{RO}_2$  radicals are in the  $10^{-13}$  to  $10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  range. The NO and  $\text{HO}_2$  concentrations are likely to be similar in the free troposphere (Logan *et al.*, 1981). Therefore, within the uncertainties in concentration and in rate constants that the  $\text{HO}_2$  rates of reaction with  $\text{RO}_2$  radicals are strongly competitive with those involving NO in the free troposphere. As a consequence, the yields estimated for alkyl nitrates from laboratory simulations of polluted atmospheres will substantially overestimate the yields of these products in the free troposphere as well as at remote locations in the planetary boundary layer with low  $\text{NO}_x$  concentrations (Roberts, 1990). Formation of alkyl hydroperoxides also should occur to an appreciable extent in the free troposphere relative to formation of carbonyl compounds.

#### 4.3. *n*-Butane

The major product formed subsequent to the OH radical reaction with *n*-butane is 2-butanone except at high ambient temperatures (Table VIII). The 2-butanone is formed by  $\text{O}_2$  abstraction of hydrogen from the 2-butoxy radical. With increasing temperature, the decomposition of the 2-butoxy radical produces an increasing yield of ethanal. This shift in products is especially significant if the higher rates of decomposition of 2-butoxy radical based on the experimental work by Cox and coworkers (1981) are used rather than the decomposition rates recommended by Carter and Atkinson (1985). The 4-hydroxybutanal and butanal are formed from the 1,5-H shift isomerization and the  $\text{O}_2$  abstraction of the 1-butoxy radical. Because of the rapidly increasing rates of 1,5-H shift isomerization with increasing temperature the 4-hydroxybutanal becomes the major product from the 1-butoxy radical at higher ambient temperatures.

Table VIII. Effects of temperature and alkoxy radical decomposition rates on the yields of primary products following OH reactions with *n*-butane in air

Product	Product yields, carbon atom basis							
	300 K ( $\tau_{OH}, h$ ) <sup>a</sup>	250 K	270 K	285 K	300 K	315 K	330 K	
			LDR <sup>b</sup>	HDR <sup>c</sup>	LDR <sup>b</sup>	HDR <sup>c</sup>	LDR <sup>b</sup>	HDR <sup>c</sup>
1-butyl nitrate	80	0.007	0.006	0.006	0.005	0.005	0.004	0.004
2-butyl nitrate	150	0.146	0.100	0.100	0.077	0.077	0.060	0.060
sum nitrates		0.153	0.106	0.106	0.082	0.082	0.064	0.064
ethanal	9	0.004	0.005	0.031	0.023	0.118	0.084	0.305
4-hydroxybutanal	5 <sup>d</sup>	0.021	0.054	0.054	0.085	0.085	0.113	0.113
<i>n</i> -butanal	6	0.080	0.064	0.064	0.046	0.046	0.031	0.031
sum aldehydes		0.105	0.123	0.149	0.154	0.249	0.228	0.449
2-butanone	120	0.742	0.771	0.745	0.764	0.669	0.708	0.487
							0.565	0.263
							0.446	0.531
							0.153	0.135
							0.013	0.020
							0.612	0.686
							0.348	0.116

<sup>a</sup> Average daylight lifetimes, in hours, assuming average OH value for summer daylight hours, 14–15 h, of  $2 \times 10^6$  molecule  $\text{cm}^{-3}$ .<sup>b</sup> Lower decomposition rate. <sup>c</sup> Higher decomposition rate. <sup>d</sup> Based on calculated value for  $k_{OH}$ .

The OH lifetimes of the three aldehyde products are consistently much shorter than the lifetimes of 2-butanone or the butyl nitrates. Because *n*-butane has an estimated OH lifetime of less than four days in summer (Table I) and about 10 days in spring or fall within the planetary boundary layer, the conversion of *n*-butane to products would be expected to occur to a substantial extent within the polluted planetary boundary layer. On the basis of vertical eddy coefficients obtained from vertical profiles for  $^{222}\text{Rn}$ , it has been estimated that 40% of a gas with a three-day summer lifetime would be transported out of the planetary boundary layer into the free troposphere (Liu *et al.*, 1984). As a consequence, a substantial fraction of the butyl peroxy and butoxy radicals should be formed after OH reaction with *n*-butane in the free troposphere at lower temperatures and in the presence of much lower concentrations of nitrogen oxides (Fehsenfeld *et al.*, 1988; Ridley *et al.*, 1989).

It is difficult at present to delineate the variations in OH radical concentrations with which a molecule with a lifetime such as that of *n*-butane would react along air parcels. A significant part of the lifetime could involve travel within moderately polluted areas in the planetary boundary layer, but later the air parcel could be in much cleaner areas of the planetary boundary layer and free troposphere. Several-fold decreases in OH concentrations have been predicted between areas with nitric oxide concentrations in the 1 to 10 ppbv range to areas with nitric oxide concentrations less than 0.1 ppbv (Liu and Trainer, 1988). Clean tropospheric models predict somewhat different vertical profiles. The OH radical concentrations between clean surface conditions and the middle troposphere in summer near 45° N are predicted to decrease by factors of 2 by several models (Crutzen and Gidel, 1983; Kasting and Singh, 1986; Golombek and Prinn, 1986; Isaksen and Hov, 1987). Another earlier model predicts a maximum OH concentration near 2 km with a slower decrease in OH concentration from 2 km up to the middle troposphere (Logan *et al.*, 1981).

The effect of temperature on the rate of reaction of OH with *n*-butane is about 20% when comparison is made of the rate of reaction between a surface temperature of 300 K and a middle troposphere temperature of 260 K. Therefore, changes in the lifetime of *n*-butane will depend predominantly on the assumed changes in OH concentration values. For aldehydes with very short lifetimes in the summer within the planetary boundary layer, their lifetimes will remain relatively short at lower temperatures and with several-fold decreases in OH concentration. Product distributions of aldehydes will change with altitude.

For alkyl nitrates formed the considerations discussed under propane with respect to the effects of altitude apply to a lesser extent with respect to competition between NO and HO<sub>2</sub> reactions in the free troposphere.

Because products such as the alkyl nitrates and 2-butanone have several-fold longer lifetimes than the *n*-butane in the planetary boundary layer, a substantially greater fraction of these products will be transported into the free troposphere compared to *n*-butane. The combined effects of formation of these products in the

free troposphere from the fraction of *n*-butane transported there plus their own transport into the free troposphere indicates that much of the yield of these slow reacting products may be present in the lower free troposphere.

#### 4.4. 2-Methylpropane

The 2-propanone and formaldehyde are the major products formed from the decomposition of the tertiary alkoxy radical (Table IX). This tertiary alkoxy radical neither can undergo O<sub>2</sub> abstraction for isomerization. The 2-methylpropanal is the major product formed from the primary alkoxy radical as a result of O<sub>2</sub> abstraction. With use of the higher decomposition rate (Table VI) 2-propanone and formaldehyde also become minor products of the decomposition of the primary alkoxy radical at higher temperatures. The yields of the aldehyde products from 2-methylpropane as from *n*-butane, increase with increasing temperature.

There is an especially large spread in OH lifetimes between the aldehyde products and the other longer lived products, the 2-propanone and the butyl nitrates formed. The discussion in the section on *n*-butane as to the vertical and horizontal transport of alkane and products similarly applies to isobutane and its products.

#### 4.5. *n*-Pentane

The relative yields of products formed from *n*-pentane are very sensitive to temperature (Table X). The 2-pentanone and 3-pentanone which are formed by O<sub>2</sub> abstractions at secondary positions contribute more than half of the total yield of products at 270 K and below. However, the yields of these two ketones decrease rapidly with increasing temperature. The yields of ethanal and of propanal increase rapidly with temperature as the rates of decomposition for the secondary alkoxy radicals increase with temperature (Table VI). Similarly, the yields of the 4-hydroxypentanal and especially the 5-hydroxy-2-pentanone increase with temperature because of the increase in the rates of 1,5-H shift isomerization with temperature (Table V). The effect of using the higher decomposition rate (Table VI) results in much higher yields of ethanal and propanal at 285 K and higher temperatures (Table X).

The yields of products in Table X also depend strongly on the use of the rate constants for 1,5-H shift isomerizations of alkoxy radicals (Atkinson and Lloyd, 1984; Carter and Atkinson, 1985). These investigators emphasize that their estimates of rate constants are highly uncertain. Such uncertainties are substantiated by an experimental study of the decomposition and 1,5-H shift isomerization reactions of the 2-pentoxy radical (Dóbé *et al.*, 1986). On the basis of the product yields measured, these investigators conclude that alkoxy 1,5-H shift isomerizations do not dominate over O<sub>2</sub> abstraction and decomposition reactions for the 2-pentoxy radical at 298 K.

Dóbé and coworkers obtain a ratio for the rate of 1,5-H shift isomerization to

Table IX. Effects of temperature and alkoxy radical decomposition rates on the yields of primary products following OH reactions with 2-methylpropane

Product	Product yields, carbon atom basis								
	300 K ( $\tau_{OH}$ , h) <sup>a</sup>	250 K	270 K	285 K	300 K	315 K	330 K		
					LDR <sup>b</sup>	HDR <sup>c</sup>	LDR <sup>b</sup>	HDR <sup>c</sup>	
2-methyl-1-propyl nitrate	160 <sup>d</sup>	0.009	0.008	0.007	0.007	0.007	0.006	0.006	0.005
1,1-dimethyl-1-ethylnitrate	80 <sup>e</sup>	0.035	0.023	0.018	0.013	0.013	0.010	0.010	0.008
sum nitrates		0.044	0.031	0.025	0.020	0.020	0.016	0.016	0.013
formaldehyde	8 <sup>f</sup>	0.206	0.199	0.193	0.188	0.188	0.181	0.183	0.176
2-methylpropanal	5	0.133	0.172	0.202	0.231	0.229	0.259	0.252	0.258
sum aldehydes		0.339	0.371	0.395	0.419	0.417	0.440	0.435	0.458
2-propanone	600	0.617	0.598	0.580	0.563	0.565	0.544	0.549	0.547

<sup>a</sup> Average daylight lifetimes, in hours, assuming average OH value for summer daylight hours, 14–15 h, of  $2 \times 10^6$  molecule  $\text{cm}^{-3}$ .

<sup>b</sup> Lower decomposition rate.

<sup>c</sup> Higher decomposition rate.

<sup>d</sup> Based on calculated  $k_{OH}$  value at 300 K.

<sup>e</sup> Average daylight lifetime  $\tau_p$  based on photolysis rate for 1,1-dimethyl-1-ethyl nitrate (Dimerjian *et al.*, 1980; Roberts and Fajer, 1989; Roberts, 1990).

<sup>f</sup> Average daylight lifetime  $\tau_p$  based on photolytic rate of formaldehyde (Gery *et al.*, 1988).



Table X. Effects of temperature and alkoxy radical decomposition rates on the yield of primary products following OH reactions with *n*-pentane in air

Product	300 K		250 K		270 K		285 K		300 K		315 K		330 K	
	( $\tau_{\text{OH}}$ , h) <sup>a</sup>		LDR <sup>b</sup>	HDR <sup>c</sup>	LDR <sup>b</sup>	HDR <sup>c</sup>	LDR <sup>b</sup>	HDR <sup>c</sup>	LDR <sup>b</sup>	HDR <sup>c</sup>	LDR <sup>b</sup>	HDR <sup>c</sup>	LDR <sup>b</sup>	HDR <sup>c</sup>
1-pentyl nitrate	45 <sup>d</sup>	0.008	0.008	0.006	0.006	0.005	0.005	0.005	0.005	0.005	0.004	0.004	0.003	0.003
2-pentyl nitrate	75	0.156	0.156	0.109	0.109	0.084	0.084	0.067	0.067	0.067	0.053	0.053	0.043	0.043
3-pentyl nitrate	125	0.106	0.106	0.072	0.072	0.055	0.055	0.043	0.043	0.043	0.034	0.034	0.027	0.027
sum nitrates		0.270	0.270	0.187	0.187	0.144	0.144	0.115	0.115	0.115	0.091	0.091	0.073	0.073
4-hydroxypentanal	4 <sup>d</sup>	0.059	0.059	0.073	0.073	0.082	0.082	0.091	0.091	0.091	0.100	0.100	0.108	0.108
ethanal +	9	0.000	0.005	0.006	0.034	0.024	0.112	0.075	0.186	0.075	0.169	0.367	0.278	0.463
propanal	7													
sum aldehydes		0.059	0.064	0.079	0.107	0.106	0.194	0.166	0.277	0.166	0.269	0.467	0.386	0.571
3-pentanone	70	0.271	0.268	0.291	0.272	0.288	0.226	0.251	0.191	0.251	0.174	0.062	0.089	0.024
2-pentanone	30	0.341	0.340	0.277	0.271	0.195	0.184	0.120	0.106	0.120	0.069	0.056	0.040	0.029
5-hydroxy-2-pentanone	15 <sup>d</sup>	0.059	0.059	0.166	0.163	0.267	0.252	0.349	0.310	0.349	0.398	0.324	0.413	0.303
sum ketones		0.671	0.667	0.734	0.706	0.750	0.662	0.720	0.607	0.720	0.641	0.442	0.542	0.356

<sup>a</sup> Average daylight lifetimes, in hours, assuming average OH value for summer daylight hours, 14–15 h, of  $2 \times 10^6$  molecule  $\text{cm}^{-3}$ .<sup>b</sup> Lower decomposition rate. <sup>c</sup> Higher decomposition rate. <sup>d</sup> Based on calculated  $k_{\text{OH}}$  at 300 K.

O<sub>2</sub> abstraction of 0.56, in contrast to the ratio of 2.9 obtained from the values given at 300 K in Tables IV and V. These investigators obtain a ratio for the rate of 1,5-H shift isomerization to decomposition of 1.2, in contrast to the ratios of 4.7 or 25 obtained from the values given at 300 K in Tables V and VI. These differences in rates result in yields for 5-hydroxy-2-pentanone, 2-pentanone, and ethanal plus propanal of 0.13, 0.24 and 0.11, respectively, at 298 K. The yields for the two ketones are much different from those given in Table X. The yields in Table X for ethanal and propanal from the 2-pentoxy radical are only 0.015 or 0.066. Even the higher yield is factor of 2 less than that obtained from the results of Dóbé and coworkers (1986).

Dóbé and coworkers also tabulate the various estimates for rate constants at 298 K for the 1,5-H shift isomerizations from —CH<sub>3</sub> given in the literature. These values range from  $5.7 \times 10^5 \text{ s}^{-1}$  obtained from a thermochemical-kinetic estimate down to the value of  $1.4 \times 10^4 \text{ s}^{-1}$  given by Dóbé and coworkers. The values obtained directly from kinetic measurements are consistently lower than those involving thermochemical estimates also. Although the value used in Table V falls roughly in midrange, it is clear that the range in these estimated rate constants is very large.

The 1,5-H shift isomerizations with the shifts from —CH<sub>3</sub> groups are important pathways in determining products for many alkanes. In view of the uncertainties in rate constants for this pathway relative to O<sub>2</sub> abstraction and decomposition, calculated yields are subject to significant revision as additional experimental measurements on the reactions of alkoxy radicals become available.

The summer daytime OH lifetime for *n*-pentane is estimated at 35 hours (Table I). The products from *n*-pentane as for the smaller alkanes discussed above fall into two groups, the short-lived aldehydes and the longer lived ketones and pentyl nitrates. However, with increase in the size of alkane groups in these ketones and nitrates, their lifetimes are decreasing. According to the vertical diffusion coefficients obtained by Liu and coworkers (1984) and the lifetime of *n*-pentane, approximately 30% of the *n*-pentane can be transported above the summer planetary boundary layer. Because of decreasing vertical transport of the parent alkane and decreasing lifetimes of products a larger fraction of the reactions of products of *n*-pentane will be confined to the planetary boundary layer than for the products of the smaller alkanes discussed above.

#### 4.6. 2-Methylbutane

A large number of products are formed because of the several different types of carbon atom positions in 2-methylbutane, as well as the competitive processes of reaction (Table XI). The 2-propanone and ethanal are major products throughout the entire temperature range used, and 3-methyl-2-butanone also is a major product except at the highest temperatures. As for the other alkanes discussed above, aldehyde yields tend to increase with increasing temperature, with much of

Table XI. Effects of temperature and alkoxy radical decomposition rates on the yields of primary products following OH reactions with 2-methylbutane in air

Product	Product yields, carbon atom basis											
	300 K ( $\tau_{\text{OH}}, \text{h}$ ) <sup>a</sup>	250 K	270 K	285 K	300 K	315 K	330 K	LDR <sup>b</sup>	HDR <sup>c</sup>	HDR <sup>c</sup>		
2-methyl-1-butyl nitrate & 3-methyl-1-butyl nitrate	70 <sup>4,5d</sup>	0.010	0.009	0.008	0.008	0.007	0.006	0.006	0.006	0.006	0.006	0.006
2-methyl-2-butyl nitrate	70 <sup>e</sup>	0.048	0.032	0.023	0.023	0.018	0.014	0.014	0.014	0.014	0.010	0.010
2-methyl-3-butyl nitrate	80 <sup>d</sup>	0.065	0.049	0.040	0.040	0.033	0.027	0.027	0.027	0.027	0.023	0.023
sum of nitrate		0.123	0.090	0.071	0.071	0.058	0.047	0.047	0.047	0.047	0.038	0.038
formaldehyde	8 <sup>f</sup>	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.002
ethanal	9	0.254	0.248	0.239	0.257	0.242	0.278	0.259	0.295	0.295	0.282	0.304
3-methylbutanal	5	0.016	0.012	0.008	0.008	0.005	0.005	0.003	0.003	0.003	0.002	0.002
4-hydroxy-3-methylbutanal	3,9 <sup>d</sup>	0.009	0.021	0.030	0.030	0.040	0.040	0.048	0.048	0.048	0.054	0.054
2-methylbutanal	5 <sup>d</sup>	0.039	0.035	0.027	0.027	0.019	0.013	0.013	0.013	0.013	0.009	0.009
4-hydroxy-2-methylbutanal	4,4 <sup>d</sup>	0.011	0.030	0.051	0.051	0.071	0.089	0.089	0.089	0.089	0.104	0.103
sum of aldehydes <sup>f</sup>		0.330	0.347	0.356	0.374	0.378	0.414	0.414	0.450	0.450	0.453	0.474
2-propanone	600	0.381	0.374	0.359	0.385	0.363	0.416	0.388	0.443	0.443	0.422	0.455
2-butanone	120	0.002	0.004	0.005	0.005	0.006	0.006	0.007	0.007	0.007	0.008	0.010
3-methyl-2-butanone	50 <sup>d</sup>	0.165	0.184	0.209	0.165	0.195	0.106	0.143	0.052	0.052	0.078	0.022
sum of ketones		0.548	0.562	0.573	0.555	0.564	0.528	0.538	0.502	0.502	0.508	0.487

<sup>a</sup> Average daylight lifetimes, in hours, assuming average OH value for summer daylight hours, 14–15 h, of  $2 \times 10^6$  molecule  $\text{cm}^{-3}$ .

<sup>b</sup> Lower decomposition rate. <sup>c</sup> Higher decomposition rate. <sup>d</sup> Based on calculated value for  $k_{\text{OH}}$ .

<sup>e</sup> Average daylight lifetime based on estimated photolysis rate for 2-methyl-2-butyl nitrate (Dimerjian *et al.*, 1980; Roberts and Fajer, 1989; Roberts, 1990).

<sup>f</sup> Average daylight lifetime based on photolytic rate  $\tau_p$  for formaldehyde (Gery *et al.*, 1988).

the aldehyde present as ethanal. The use of the higher rate constants for decomposition increase ethanal and 2-propanone yields moderately except 270 K and below. The increases in the yields of these two products at the higher decomposition rate is associated with the effect of their yields from the secondary but not the tertiary alkoxy radical. The yields of 3-methyl-2-butanone formed by  $O_2$  abstraction decrease as decomposition reactions become dominant at higher temperatures. As discussed above for *n*-pentane, uncertainties in the 1,5-H shift isomerization rates from  $-CH_3$  may be resulting in overestimates for the hydroxypentanal yields (Table XI).

The 2-methylbutane has an estimated summer lifetime of about 36 h periods (Table I). As for the other alkanes discussed above, the aldehyde products all have much shorter lifetimes than the parent alkane while the ketones and nitrates have much longer lifetimes than the parent alkane.

#### 4.7. *n*-Hexane

The 5-hydroxy-2-hexanone which is formed by the 1,5-H shift isomerization of the 2-hexoxy radical constitutes a major product throughout the entire temperature range (Table XII). The 3-hexanone formed by  $O_2$  abstraction from the 3-hexoxy radical is a major product at lower temperatures, but its yield decreases rapidly with increasing temperature as formation of the 6-hydroxy-3-hexanone by 1,5-H shift isomerization becomes increasingly dominant. To a lesser extent the increase in decomposition rates with increasing temperature results in higher yields of ethanal, propanal, and butanal from the 3-hexoxy radical. The yields of the secondary hexyl nitrates also are substantial at lower temperatures. As occurred for other alkanes, the yields of the more reactive aldehydes increase substantially at higher temperatures, but the yields of the less reactive hexyl nitrates and ketones decrease with increasing temperatures.

The average summer daylight OH lifetime for *n*-hexane is 25 h (Table I). All of the products except for the hexyl nitrates have OH lifetimes shorter than that of the *n*-hexane. Even the hexyl nitrates have lifetimes only moderately longer than the parent alkane. Therefore, the reactions of *n*-hexane and its products should tend to occur to a large extent within the planetary boundary layer.

#### 4.8. 2-Methylpentane

A wide range of products is formed from the atmospheric photooxidation of 2-methylpentane (Table XIII). At lower temperatures the most important individual product is 4-hydroxy-4-methylpentanal, formed by 1,5-H shift isomerization. Decomposition rates of the alkoxy radical increase more rapidly than the rates for 1,5-H shift isomerization, so the yields of the decomposition products 2-propanone and propanal become increasingly important with increasing temperature. The 2-methyl-3-pentanone is a significant product at lower temperatures where  $O_2$

Table XII. Effects of temperature and alkoxy radical decomposition rates on the yields of primary products following OH reactions with *n*-hexane

Product	Product yields, carbon atom basis												
	300 K ( $\tau_{OH}, h$ ) <sup>a</sup>	250 K	270 K	285 K	300 K	315 K	330 K	LDR <sup>b</sup>	HDR <sup>c</sup>	LDR <sup>b</sup>	HDR <sup>c</sup>	LDR <sup>b</sup>	HDR <sup>c</sup>
1-hexyl nitrate	30 <sup>d</sup>	0.009	0.007	0.007	0.006	0.006	0.006	0.006	0.006	0.005	0.005	0.004	0.004
2-hexyl nitrate	45	0.180	0.128	0.128	0.100	0.080	0.080	0.080	0.080	0.064	0.064	0.052	0.052
3-hexyl nitrate	50	0.243	0.169	0.169	0.131	0.103	0.103	0.103	0.103	0.082	0.082	0.065	0.065
sum of nitrates <sup>e</sup>		0.432	0.304	0.304	0.237	0.189	0.189	0.189	0.189	0.151	0.151	0.121	0.121
ethanal	9	0.000	0.0005	0.003	0.0015	0.009	0.004	0.004	0.017	0.008	0.028	0.015	0.039
propanal	7	0.001	0.0015	0.009	0.005	0.026	0.012	0.051	0.023	0.082	0.082	0.041	0.113
butanal	6	0.001	0.001	0.006	0.0035	0.017	0.009	0.035	0.016	0.055	0.055	0.029	0.077
4-hydroxyhexanal	4 <sup>d</sup>	0.040	0.051	0.051	0.058	0.058	0.065	0.065	0.072	0.072	0.072	0.079	0.079
sum of aldehydes <sup>f</sup>		0.042	0.054	0.069	0.068	0.110	0.090	0.168	0.119	0.236	0.236	0.164	0.308
3-hexanone	20	0.257	0.228	0.219	0.164	0.147	0.101	0.081	0.058	0.040	0.040	0.032	0.019
2-hexanone	15	0.004	0.002	0.002	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.000	0.000
6-hydroxy-3-hexanone	15 <sup>d</sup>	0.044	0.137	0.131	0.225	0.200	0.295	0.237	0.331	0.232	0.232	0.332	0.201
5-hydroxy-2-hexanone	10 <sup>d</sup>	0.220	0.275	0.275	0.304	0.304	0.324	0.324	0.340	0.340	0.340	0.351	0.351
sum of ketones		0.525	0.642	0.627	0.695	0.653	0.721	0.643	0.730	0.616	0.616	0.715	0.571

<sup>a</sup> Average daylight lifetimes, in hours, assuming average OH value for summer daylight hours, 14–15 h, of  $2 \times 10^6$  molecule  $\text{cm}^{-3}$ .<sup>b</sup> Lower decomposition rate.<sup>c</sup> Higher decomposition rate.<sup>d</sup> Based on calculated  $k_{OH}$  value at 300 K.<sup>e</sup> Traces of ethyl nitrate and propyl nitrate also formed.<sup>f</sup> Trace of hexanal formed.

Table XIII. Effects of temperature and alkoxy radical decomposition rates on the yields of primary products following OH reactions with 2-methylpentane in air

Product	Product yields, carbon atom basis													
	300 K ( $\tau_{OH}, h$ ) <sup>a</sup>	250 K	270 K	285 K	300 K	315 K	330 K	LDR <sup>b</sup>	HDR <sup>c</sup>	LDR <sup>b</sup>	HDR <sup>c</sup>	LDR <sup>b</sup>	HDR <sup>c</sup>	
2-methylpentyl nitrate	40 <sup>d</sup>	0.008	0.008	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.004
4-methylpentyl nitrate	30 <sup>d</sup>	0.004	0.004	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.002
4-methyl-2-pentyl nitrate	45 <sup>d</sup>	0.078	0.078	0.059	0.059	0.048	0.048	0.040	0.040	0.033	0.033	0.027	0.027	0.027
2-methyl-3-pentyl nitrate	100 <sup>d</sup>	0.106	0.106	0.078	0.078	0.063	0.063	0.051	0.051	0.042	0.042	0.034	0.034	0.034
2-methyl-2-pentyl nitrate	80 <sup>d</sup>	0.058	0.058	0.038	0.038	0.028	0.028	0.021	0.021	0.016	0.016	0.013	0.013	0.013
sum of nitrates		0.254	0.254	0.184	0.184	0.148	0.148	0.121	0.121	0.100	0.100	0.080	0.080	0.080
formaldehyde	8 <sup>f</sup>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001	0.001	0.001
ethanal	9	0.000	0.000	0.000	0.003	0.002	0.011	0.007	0.022	0.019	0.035	0.027	0.046	0.046
propanal	7	0.024	0.108	0.047	0.146	0.072	0.175	0.103	0.208	0.141	0.226	0.177	0.236	0.236

2-methylpropanal	5	0.000	0.001	0.001	0.006	0.005	0.021	0.016	0.045	0.034	0.070	0.054	0.093
4-hydroxy-2-methylpentanal	3.8 <sup>d</sup>	0.034	0.034	0.048	0.048	0.056	0.056	0.064	0.064	0.072	0.072	0.082	0.082
4-hydroxy-4-methylpentanal	5 <sup>d</sup>	0.433	0.264	0.371	0.185	0.312	0.143	0.251	0.109	0.191	0.087	0.138	0.072
3,4-dihydroxy-4-methylpentanal	2.4 <sup>d</sup>	0.001	0.001	0.005	0.003	0.012	0.005	0.022	0.008	0.035	0.011	0.046	0.014
sum of aldehydes		0.492	0.408	0.472	0.391	0.459	0.412	0.463	0.457	0.491	0.502	0.525	0.544
2-propanone	600	0.023	0.109	0.047	0.146	0.071	0.175	0.103	0.206	0.141	0.226	0.176	0.236
2-pentanone	28	0.000	0.000	0.000	0.002	0.001	0.003	0.002	0.003	0.003	0.005	0.004	0.006
4-methyl-2-pentanone	10	0.084	0.084	0.081	0.079	0.062	0.058	0.040	0.036	0.024	0.020	0.014	0.011
2-methyl-3-pentanone	40 <sup>d</sup>	0.133	0.131	0.168	0.151	0.176	0.125	0.154	0.072	0.101	0.032	0.050	0.013
5-hydroxy-4-methyl-2-pentanone	95 <sup>d</sup>	0.014	0.014	0.048	0.047	0.084	0.080	0.117	0.104	0.140	0.114	0.151	0.111
sum of ketones		0.254	0.338	0.344	0.425	0.394	0.441	0.416	0.421	0.409	0.397	0.395	0.377

<sup>a</sup> Average daylight lifetimes, in hours, assuming average OH value for summer daylight hours, 14–15 h, of  $2 \times 10^6$  molecule  $\text{cm}^{-3}$ .

<sup>b</sup> Lower decomposition rate.

<sup>c</sup> Higher decomposition rate. <sup>d</sup> Based on calculated  $k_{\text{OH}}$  value at 300 K.

<sup>e</sup> Average daylight lifetime  $\tau_p$  based on estimated photolytic rate for 2-methyl-2-pentyl nitrate (Dimerjian *et al.*, 1980; Roberts and Fajer, 1989; Roberts, 1990).

<sup>f</sup> Average daylight lifetime based  $\tau_p$  on photolytic rate for formaldehyde (Gery *et al.*, 1988).

abstraction is dominant and alkyl nitrate yields are decreasing rapidly with increasing temperature. At higher temperatures the rates of decomposition of the alkoxy radical become larger than those for  $O_2$  abstraction so the yields of the decomposition products 2-propanone, ethanal, propanal and 2-methylpropanal become substantial.

The average summer daytime lifetime for 2-methylpentane is 25 hours. (Table I). The lifetimes of products vary widely, with aldehyde lifetimes ranging from 2.4 to 9 h, ketone lifetimes from 10 to 600 h, and alkyl nitrate lifetimes from 30 to 100 h (Table XIII). The 2-methylpentane, its aldehyde products and several of the ketones and alkyl nitrate products should be consumed to a large extent within the planetary boundary layer. On the other hand, such products as 2-methyl-3-pentyl nitrate, 2-methyl-2-pentyl nitrate, 5-hydroxy-4-methyl-2-pentanone, and especially 2-propanone have long enough lifetimes after their formation from 2-methylpentane to be transported up into the free troposphere.

#### 4.9. *3-Methylpentane*

The major products formed from the atmospheric photooxidation of 3-methylpentane include 2-butanone, 3-methyl-2-pentanone, 5-hydroxy-3-methyl-2-pentanone, ethanal and the secondary 3-methyl-3-pentyl nitrate (Table XIV). Because the tertiary alkoxy radical reacts predominantly by decomposition, 2-butanone and ethanal are major products throughout the 250 to 330 K range of temperatures. The secondary alkoxy radicals react largely by  $O_2$  decomposition at lower temperatures to form the 3-methyl-2-pentanone, but these alkoxy radicals at higher temperatures react by 1,5-H shift isomerization to form 5-hydroxy-3-methyl-2-pentanone. As a result, the ratio of yields of these two products varies from 5.7 at 250 K down to 0.09 at 330 K. In addition to the formation of 2-butanone and ethanal from the decomposition of the tertiary alkoxy radical, the decomposition of the secondary alkoxy radical also contributes a significant yield of these two products at higher temperatures. A number of minor products formed in trace concentrations are noted in footnotes to Table XIII.

The average summer daylight lifetime for 3-methylpentane is 24 h (Table I). Because of their relatively short lifetimes, the 3-methylpentane and more than half of its products should react to a large extent within the planetary boundary layer on a regional scale.

#### 4.10. *2,3-Dimethylbutane*

Most of the 2,3-dimethylbutane is converted to 2-propanone following decomposition of the tertiary alkoxy radical (Table XV). The other products individually make only minor contributions to the overall product yield with the exception of 2,3-dimethyl-2-butyl nitrate at lower temperatures.

The average summer daylight lifetime for 2,3-dimethylbutane is 22 h (Table I).



Table XIV. Effects of temperature and alkoxy radical decomposition rates on the yields of primary products following OH reactions with 3-methylpentane in air

Product	Product yields, carbon atom basis							
	300 K ( $\tau_{OH}, h$ ) <sup>a</sup>	250 K	270 K	285 K	300 K	315 K	330 K	
	LDR <sup>b</sup>	HDR <sup>c</sup>	LDR <sup>b</sup>	HDR <sup>c</sup>	LDR <sup>b</sup>	HDR <sup>c</sup>	LDR <sup>b</sup>	HDR <sup>c</sup>
2-ethyl-1-butyl nitrate	40 <sup>d</sup>	0.003	0.003	0.003	0.003	0.003	0.002	0.002
3-methyl-1-pentyl nitrate	30 <sup>d</sup>	0.007	0.006	0.006	0.006	0.005	0.005	0.004
3-methyl-2-pentyl nitrate	40 <sup>d</sup>	0.140	0.108	0.089	0.089	0.074	0.062	0.052
3-methyl-3-pentyl nitrate	70	0.070	0.046	0.034	0.034	0.026	0.020	0.015
sum of nitrates <sup>f</sup>		0.220	0.163	0.132	0.132	0.108	0.089	0.073
ethanal	9	0.186	0.184	0.175	0.185	0.172	0.170	0.173
2-methylbutanal	4.5 <sup>d</sup>	0.010	0.009	0.005	0.005	0.004	0.002	0.002
4-hydroxy-2-methylbutanal	4 <sup>d</sup>	0.006	0.013	0.020	0.020	0.026	0.033	0.037
4-hydroxy-3-methylpentanal	3.5 <sup>d</sup>	0.031	0.043	0.051	0.051	0.061	0.069	0.078
sum of aldehydes <sup>g</sup>		0.233	0.244	0.249	0.251	0.263	0.274	0.290
2-butanone	120	0.373	0.360	0.367	0.351	0.343	0.341	0.347
3-methyl-2-pentanone	20 <sup>d</sup>	0.149	0.146	0.139	0.112	0.100	0.044	0.025
5-hydroxy-3-methyl-2-pentanone	0.13 <sup>d</sup>	0.026	0.087	0.083	0.154	0.137	0.252	0.179
sum of ketones <sup>h</sup>		0.548	0.593	0.589	0.617	0.607	0.637	0.608

<sup>a</sup> Average daylight lifetimes, in hours, assuming average OH value for summer daylight hours, 14–15 h, of  $2 \times 10^6$  molecule  $\text{cm}^{-3}$ .

<sup>b</sup> Lower decomposition rate. <sup>c</sup> Higher decomposition rate. <sup>d</sup> Based on calculated  $k_{OH}$  value at 300 K.

<sup>e</sup> Average daytime lifetime  $\tau_p$  based on photolysis rate of 3-methyl-3-pentyl nitrate (Dimerjian *et al.*, 1980; Roberts and Fajer, 1989; Roberts, 1990).

<sup>f</sup> Other trace products include ethyl nitrate and 2-butyl nitrate.

<sup>g</sup> Other trace products include formaldehyde and  $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{CHO})\text{CH}_2\text{CH}_3$ . <sup>h</sup> Other trace product include diethyl ketone.

Table XV. Effects of temperature on the yields of primary products formed following OH reactions with 2,3-dimethylbutane in air

Product	Product yields, carbon atom basis						
	300 K ( $\tau_{\text{OH}}$ , h) <sup>a</sup>	250 K	270 K	285 K	300 K	315 K	330 K
2-propyl nitrate	195	0.038	0.027	0.021	0.016	0.012	0.010
2,3-dimethyl-2-butyl nitrate	70 <sup>b</sup>	0.103	0.071	0.054	0.042	0.033	0.026
2,3-dimethyl-1-butyl nitrate	40 <sup>c</sup>	0.014	0.012	0.012	0.011	0.010	0.009
sum of nitrates		0.155	0.110	0.087	0.069	0.055	0.045
formaldehyde	8 <sup>d</sup>	0.000	0.000	0.001	0.001	0.001	0.002
2,3-dimethylbutanal	4 <sup>c</sup>	0.049	0.047	0.037	0.027	0.019	0.013
4-hydroxy-2,3-dimethyl butanal	3.5 <sup>c</sup>	0.013	0.040	0.069	0.101	0.131	0.157
sum of aldehydes		0.062	0.087	0.107	0.129	0.151	0.172
2-propanone	600	0.781	0.800	0.802	0.797	0.787	0.775
3-methyl-2-butanone	55 <sup>c</sup>	0.002	0.003	0.004	0.005	0.007	0.008
sum of ketones		0.783	0.803	0.806	0.812	0.794	0.783

<sup>a</sup> Average daylight lifetimes, in hours, assuming average OH value for summer daylight hours, 14–15 h, of  $2 \times 10^6$  molecule  $\text{cm}^{-3}$ .

<sup>b</sup> Average daylight lifetime  $\tau_p$  based on estimated photolysis rate of 2,3-dimethyl-2-butyl nitrate (Dimerjian *et al.*, 1980; Roberts and Fajer, 1989; Roberts, 1990).

<sup>c</sup> Based on calculated  $k_{\text{OH}}$  value at 300 K.

<sup>d</sup> Average daylight lifetime based on photolysis rate of formaldehyde (Gery *et al.*, 1988).

Most of the product yield from the atmospheric photooxidation of 2,3-dimethylbutane is associated with products with much longer lifetimes than the parent alkane. As a result, these products although largely formed from 2,3-dimethylbutane within the planetary boundary layer should be transported well up into the free troposphere.

#### 4.11. Higher Molecular Weight Alkanes and Cycloalkanes

The 15 alkanes listed in Table I but not discussed in the previous sections contribute a total of 56 ppbC or 21% of the carbon atoms of the total group of 25 alkanes listed. In addition, a number of less abundant structurally identified alkanes contribute a total of 10 ppbC. For many of the heptanes and higher molecular weight alkanes, the major products will be the secondary alkyl nitrates, hydroxy aldehydes, and hydroxy ketones. This will be so for the straight-chain alkanes and some of the methyl alkanes. For these alkanes, 1,5-H shift isomerizations from  $-\text{CH}_2-$  or  $>\text{CH}$  groups can occur for most or all of the alkoxy radicals formed. The rate constants for these types of 1,5-H shift isomerizations are so fast,  $1 \times 10^6$  to  $3 \times 10^7$  (Table V), that the isomerizations will predominate throughout the temperature range from 250 to 330 K over  $\text{O}_2$  abstractions and decomposition reactions.

For several of the abundant branched-chained heptanes and octanes measured in the atmosphere (Table I), including 2-methylhexane, 3-methylhexane, 2,4-dimethylpentane, 2,3,4-trimethylpentane, decomposition reactions are important and can contribute substantially to the yield of products at temperatures above 285 K for lower decomposition rates and down to 250 K at higher decomposition rates. These branched-chained alkanes through decomposition reactions of their alkoxy radicals form a wide range of  $C_1$  to  $C_5$  aldehydes and  $C_3$  to  $C_5$  ketones. Many of these same products are formed by  $O_2$  abstraction or decomposition of the lower molecular weight alkanes discussed in prior sections.

The mechanisms for cycloalkane photooxidation reactions are uncertain but are believed to involve ring opening followed by isomerization (Carter and Atkinson, 1985). Large yields of hydroxy carbonyl products are to be expected as major products.

A very large number of products are formed from the larger alkanes. The nine abundant heptanes and octanes listed in Table I should form about 100 unique product molecules, of which almost half should be alkyl nitrates. In addition, they would form through decomposition reactions a number of the same lower molecular weight aldehydes and ketones as noted above. Because of the large number of products formed, the individual yields usually are very small. The exceptions are several of the lower molecular weight aldehydes and ketones. Yields from decomposition reactions of alkoxy radicals have been calculated from all of the appropriate branched-chain alkanes with temperature and decomposition rate.

## 5. General Discussion

The product yields calculated in the previous section have been combined with the median ambient air concentration values from United States cities for the appropriate alkanes (Table I). The resulting total yields of alkyl nitrates, aldehydes and ketones from the  $C_2$  through  $C_6$  alkanes are given in Table XVI. These overall yields are based on the individual yields of more than 60 primary products.

Table XVI. Summed yields of products from photooxidation in air of ambient air two to six carbon alkanes

Product	Decomp. rate	250 K	270 K	285 K	300 K	315 K	330 K
alkyl nitrates		0.153	0.109	0.085	0.068	0.055	0.044
aldehydes	LDR <sup>a</sup>	0.306	0.322	0.388	0.370	0.427	0.501
	HDR <sup>b</sup>	0.302	0.326	0.369	0.459	0.521	0.590
ketones	LDR <sup>a</sup>	0.541	0.569	0.577	0.562	0.518	0.455
	HDR <sup>b</sup>	0.545	0.565	0.546	0.473	0.424	0.366

<sup>a</sup> Lower decomposition rate.

<sup>b</sup> Higher decomposition rate.

The predicted yields of ambient air alkyl nitrates are substantial at lower temperatures, but their yields decrease rapidly with increasing temperature. The aldehyde yields increase with increasing temperature, whereas the yields of ketones decrease at higher temperatures. The higher decomposition rates result in predictions of higher yields of aldehydes at or above 270 K, but lower yields of ketones.

A small number of the products account for most of the carbon atoms from the photooxidation of these alkanes. The overall yields for ethanal, propanal, 2-propanone, and 2-butanone produced from the alkanes are listed in Table XVII. The sums of the carbon atoms associated with these four products account for from 45% to 57% of the carbon atoms of all of the structurally identified C<sub>2</sub> through C<sub>10</sub> alkanes. The yields of both of the aldehydes increase substantially with increasing temperature, and their yields also are appreciably higher at the higher decomposition rates. The 2-propanone yields tend to be insensitive to temperature changes, but rise slightly at the higher decomposition rates. This result contrasts with that for the total ketones because most of the 2-propanone formed, unlike most of the other ketones, is produced by decomposition reactions rather than by O<sub>2</sub> abstraction reactions. The 2-propanone is produced by decomposition of alkoxy radicals from several different C<sub>4</sub> to C<sub>8</sub> alkanes, which account for from 65% to 71% of the total yield of 2-propanone. The yields of 2-butanone decrease with increasing temperature, and its yields are lower at higher decomposition rates. Most of the yield of 2-butanone is associated with the O<sub>2</sub> abstraction reaction involving the 2-butoxy radical. This reaction process is less significant with increasing temperature and higher decomposition rates.

The yields for 12 additional products with moderate yields, reaching 1 to 4% with the temperature range considered, also are listed in Table XVII. These products are members of each of the classes of products formed from alkanes. The total yields for these latter 12 compounds are much smaller than for the four major products, especially at higher temperatures. The 16 compounds correspond to about 10% of all of the products estimated to be produced. Their total yields account for 71 to 75% of the carbon atoms of the more abundant two through ten carbon alkanes (Table I).

Most of the other products of the photooxidation of alkanes occur at low yields because they are unique products of a reaction process involving a single peroxy alkyl or alkoxy radical. Such products include most alkyl nitrates, hydroxy-aldehydes and hydroxyketones. Several of the smaller alkyl nitrates can be formed from the small alkyl radicals formed in the decomposition reactions of larger alkoxy radicals but only at very low yields.

It should be emphasized that only a small number of the products predicted from the atmospheric photooxidation of alkanes ever have been measured in the ambient air. The limited number of measurements also have been involved in specific types of geographical locations (Grosjean, 1982; Atlas, 1988). It also should be noted that most of the carbonyl products measured are not unique photooxida-

tion products of alkanes but also are the products of the atmospheric photooxidation of alkenes.

The ethanal, propanal, butanal and 2-methylpropanal yields in Table XVII show significant sensitivities to uncertainties in decomposition rates. For ethanal this effect can be emphasized by subtracting the ethanal yield from the  $O_2$  abstraction of the ethoxy radical from ethane. At 300 K the ethanal yield associated with assuming the lower decomposition rates for the other contributing alkoxy radicals is 17.4 ppbc, while the ethanal yield associated with assuming the higher decomposition rates for the other contributing alkoxy radicals is 29.7 ppbc. For propanal this effect can be emphasized by subtracting the propanal yield from the  $O_2$  abstraction from the primary propoxy radical of propane. At 300 K the propanal yield associated with assuming the lower decomposition rates for the other contributing alkoxy radicals is 3.0 ppbc, while the propanal yield associated with assuming the higher decomposition rates for the other contributing alkoxy radicals is 6.8 ppbc. The total 2-propanone yield also is moderately sensitive to the uncertainties in decomposition rates. Yields of the 4-hydroxy-4-methyl pentanal decrease markedly at the higher compared to the lower decomposition rate because of the much greater contribution of decomposition products to the total yield of the tertiary alkoxy radical products. Therefore, a better estimation of decomposition rates relative to other processes is quite important for improving such yield calculations as presented in this work.

Ethanal and propanal will be formed immediately after emission of precursor hydrocarbons as the alkenes and more rapidly reacting alkanes react with OH radicals and  $O_3$  in air parcels during transport in the hours following emission. The uncertainties in the decomposition rates of the alkoxy radicals from the more reactive alkanes can cause a significant range of uncertainty in the yields of ethanal and propanal generated on an urban and a regional scales. Because of their short lifetimes the ethanal and propanal produced on urban or regional scales will be rapidly converted to secondary products. Ethanal and propanal will continue to be produced from the slowly reacting ethane and propane many days later as air parcels move far downwind of emission sources. As a result a substantial fraction of the ethanal and propanal will be formed within the free troposphere or at remote areas within the planetary boundary layer.

The 2-propanone can be formed from several alkenes as well as from propane and a number of faster reacting alkanes. Production of 2-propanone can occur on an urban or regional scale, but 2-propanone also can be formed from propane in the free troposphere and in remote areas within the planetary boundary layer. Irrespective of the area where 2-propanone is formed because of its long lifetime 2-propanone will subsequently be distributed zonally throughout the free troposphere.

The alkyl nitrates are produced from alkanes with a wide range of lifetimes. Once formed in the atmosphere the various alkyl nitrates also have lifetimes

Table XVII. Yields of more abundant primary products from photooxidations of the two through 10 carbon alkanes in the atmosphere

Product	Product yields, carbon atom basis												
	250 K		270 K		285 K		300 K		315 K		300 K		
	LDR <sup>a</sup>	HDR <sup>b</sup>	LDR <sup>a</sup>	HDR <sup>b</sup>	LDR <sup>a</sup>	HDR <sup>b</sup>	LDR <sup>a</sup>	HDR <sup>b</sup>	LDR <sup>a</sup>	HDR <sup>b</sup>	LDR <sup>a</sup>	HDR <sup>b</sup>	
ethanal	ppbC decimal <sup>c</sup>	36.2 0.131	36.7 0.133	36.2 0.13	38.2 0.138	37.0 0.134	43.2 0.157	40.2 0.146	52.8 0.191	48.0 0.174	65.1 0.236	62.8 0.228	73.8 0.267
propanal	ppbC decimal <sup>c</sup>	6.1 0.022	7.7 0.028	7.3 0.026	9.5 0.034	8.4 0.030	11.6 0.042	10.1 0.037	13.9 0.050	12.5 0.045	17.4 0.063	15.1 0.055	19.3 0.070
2-propanone	ppbC decimal <sup>c</sup>	46.8 0.174	48.6 0.186	46.0 0.173	49.2 0.185	46.2 0.173	50.3 0.188	46.9 0.175	51.9 0.194	48.3 0.181	53.0 0.199	50.2 0.188	53.0 0.198
2-butanone	ppbC decimal <sup>c</sup>	34.3 0.129	34.8 0.132	35.4 0.133	34.7 0.130	35.1 0.132	31.9 0.120	32.9 0.124	24.7 0.093	27.3 0.102	16.1 0.060	18.7 0.070	10.6 0.039
subtotal	ppbC decimal <sup>c</sup>	123.4 0.447	127.9 0.463	124.9 0.453	131.6 0.477	126.7 0.459	137.0 0.496	130.1 0.471	143.3 0.519	136.1 0.493	151.6 0.549	146.8 0.532	156.7 0.568
formaldehyde	ppbC decimal <sup>c</sup>	3.1 0.011	3.1 0.011	3.0 0.011	3.0 0.011	2.9 0.011	2.9 0.011	2.8 0.010	2.8 0.010	2.8 0.010	2.9 0.011	2.8 0.010	3.2 0.012
butanal	ppbC decimal <sup>c</sup>	3.2 0.012	3.2 0.012	2.6 0.090	2.7 0.010	1.9 0.007	2.2 0.008	1.4 0.005	1.9 0.007	1.1 0.004	1.8 0.007	1.0 0.004	1.9 0.007
2-methyl propanal	ppbC decimal <sup>c</sup>	2.1 0.008	2.4 0.009	2.8 0.010	3.4 0.012	3.5 0.013	4.4 0.016	4.5 0.016	5.5 0.020	5.5 0.020	6.4 0.023	6.4 0.023	7.0 0.025

3-pentanone	ppbC	6.0	5.9	6.4	6.0	6.3	5.0	5.5	4.2	3.8	1.4	2.0	0.5
	decimal <sup>c</sup>	0.022	0.021	0.023	0.022	0.023	0.018	0.020	0.015	0.014	0.005	0.007	0.002
2-pentanone	ppbC	7.7	8.1	6.4	6.7	4.7	4.8	3.1	3.1	2.1	2.0	1.6	1.4
	decimal <sup>c</sup>	0.028	0.029	0.022	0.024	0.017	0.017	0.011	0.011	0.008	0.007	0.006	0.005
3-methyl-2-butanone	ppbC	8.2	8.4	9.7	9.4	10.3	8.6	9.8	6.0	7.5	3.6	4.6	2.2
	decimal <sup>c</sup>	0.030	0.030	0.035	0.034	0.037	0.031	0.036	0.022	0.027	0.013	0.017	0.008
4-hydroxyl-4-methyl pentanal	ppbC	6.5	3.9	5.5	2.8	4.6	2.1	3.7	1.6	2.8	1.3	2.1	1.1
	decimal <sup>c</sup>	0.024	0.014	0.020	0.010	0.017	0.008	0.013	0.006	0.010	0.005	0.008	0.004
5-hydroxy-3- methyl-2-pentanone	ppbC	0.3	0.9	0.9	1.6	1.5	2.8	2.3	1.8	2.7	1.9	2.8	1.8
	decimal <sup>c</sup>	0.001	0.003	0.003	0.006	0.006	0.010	0.008	0.007	0.010	0.007	0.010	0.007
2-butyl nitrate	ppbC	5.9	5.9	4.0	4.0	3.1	3.1	2.4	2.4	1.9	1.9	1.5	1.5
	decimal <sup>c</sup>	0.021	0.021	0.014	0.014	0.011	0.011	0.009	0.009	0.007	0.007	0.006	0.006
2-pentyl nitrate	ppbC	3.4	3.4	2.4	2.4	1.9	1.9	1.5	1.5	1.2	1.2	1.0	1.0
	decimal <sup>c</sup>	0.012	0.012	0.009	0.009	0.007	0.007	0.006	0.006	0.004	0.004	0.004	0.004
2-methyl-2-butyl nitrate	ppbC	2.2	2.2	1.4	1.4	1.0	1.0	0.8	0.8	0.6	0.6	0.4	0.4
	decimal <sup>c</sup>	0.008	0.008	0.005	0.005	0.004	0.004	0.003	0.003	0.002	0.002	0.001	0.001
3-methyl-2-butyl nitrate	ppbC	2.9	2.9	2.1	2.1	1.8	1.8	1.5	1.5	1.2	1.2	1.0	1.0
	decimal <sup>c</sup>	0.011	0.011	0.008	0.008	0.007	0.007	0.006	0.006	0.004	0.004	0.004	0.004
subtotal	ppbC	51.5	50.3	47.2	45.5	43.6	40.5	39.2	33.0	33.1	26.1	27.0	22.9
	decimal <sup>c</sup>	0.187	0.182	0.177	0.171	0.164	0.152	0.147	0.124	0.124	0.098	0.101	0.086
total	ppbC	174.9	178.2	172.1	177.1	170.3	177.5	169.3	176.3	169.2	177.7	173.8	179.6
	decimal <sup>c</sup>	0.634	0.646	0.624	0.642	0.617	0.643	0.613	0.639	0.613	0.644	0.630	0.651

<sup>a</sup> Low decomposition rate. <sup>b</sup> High decomposition rate.

<sup>c</sup> Concentration in ppbC divided by total alkane concentration of 276 ppbC including all structurally identified C<sub>2</sub> to C<sub>10</sub> alkane isomers.

ranging over a factor of about 10. As the  $\text{NO}_x$  concentrations decrease substantially in air parcels transport into the free troposphere or to remote areas the production of alkyl nitrates will decrease drastically (Roberts, 1990). Therefore the geographical origins of the alkyl nitrates measured in the free troposphere or remote areas are likely to be substantially different than for the aldehydes or ketones.

The effect of both increasing temperature and higher decomposition rates on primary product formation also increase the generation of  $\text{HO}_2$  and  $\text{RO}_2$  radicals thereby influencing other subsequent atmospheric processes including ozone formation in the troposphere. These effects on radical formation are significant in terms of both episodic and seasonal and other products of environmental concern.

## 6. Conclusions

- (1) Alkanes constituted 61% of the median carbon atom concentrations based on the basis of measurements of hydrocarbons in 39 U.S. cities. The  $\text{C}_2$  through  $\text{C}_6$  alkanes constituted 79% of the alkanes and 47% of the total for the more abundant hydrocarbons in these cities.
- (2) The product yields of many of the products are predicted to be sensitive to ambient temperature conditions during formation and transport. Yields of alkyl nitrates and of most ketones decrease with increasing temperature whereas the yields of the most of the aldehydes increase with increasing temperature.
- (3) Product yields also are predicted to be sensitive to the decomposition rates of alkoxy radicals and higher yields ethanal, propanal and 2-propanone are associated with higher rates of alkoxy radical decomposition.
- (4) A large fraction of the consumption of alkanes is accounted for by a relatively small number of their products. Four products, ethanal, propanal, 2-propanone, and 2-butanone, account for from 45 to 57% of the carbon atoms converted from the  $\text{C}_2$  to  $\text{C}_{10}$  alkanes to products the amount depending on ambient temperatures and on decomposition rates of alkoxy radicals.
- (5) The summer daytime chemical lifetimes of products of alkanes are estimated to range from a few hours to several months. The daylight lifetimes of the four most abundant products range from 7 h for propanal to 600 h for 2-propanone under summertime conditions.
- (6) The lifetimes of the alkanes and their products determine the extent to which they undergo reactions in the polluted planetary boundary layer compared to the 'clean' free troposphere. A number of the lower molecular weight alkanes, along with many of the alkyl nitrates and ketones, to an appreciable extent should undergo vertical transport into the lower free troposphere. Ethane and 2-propanone have long enough chemical lifetimes to be well distributed throughout the troposphere within a latitude zone.



- (7) Because of the widely varying lifetimes of precursor hydrocarbons some of the compounds which are products from the reactions of a number of these hydrocarbons should continue to be formed over periods of many days to many weeks. These production times should exceed the estimated chemical lifetimes for a number of these products.
- (8) The effects of temperature on product yields also should influence reactivity of the overall photochemical system, including radical formation and the rates and amounts of ozone and other products of environmental concern in the troposphere.

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