# Rate Constants for the Gas-Phase Reactions of a Series of $C_3-C_6$ Aldehydes with OH and $NO_3$ Radicals

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ABSTRACT: By using relative rate methods, rate constants for the gas-phase reactions of OH and $NO_3$ radicals with propanal, butanal, pentanal, and hexanal have been measured at 296 ± 2 K and atmospheric pressure of air. By using methyl vinyl ketone as the reference compound, the rate constants obtained for the OH radical reactions (in units of $10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) were propanal, 20.2 ± 1.4; butanal, 24.7 ± 1.5; pentanal, 29.9 ± 1.9; and hexanal, 31.7 ± 1.5. By using methacrolein and 1-butene as the reference compounds, the rate constants obtained for the $NO_3$ radical reactions (in units of $10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) were propanal, 7.1 ± 0.4; butanal, 11.2 ± 1.5; pentanal, 14.1 ± 1.6; and hexanal, 14.9 ± 1.3. The dominant tropospheric loss process for the aldehydes studied here is calculated to be by reaction with the OH radical, with calculated lifetimes of a few hours during daytime.  Int J Chem Kinet 32: 79–84, 2000

## INTRODUCTION

Carbonyl compounds are directly emitted into the troposphere from biogenic and anthropogenic sources [1–7] and are also formed in situ in the troposphere from the atmospheric reactions of volatile organic compounds, including other carbonyl compounds [8,9]. In the troposphere, carbonyl compounds can undergo photolysis and reactions with OH radicals, $NO_3$ radicals, and $O_3$ [8,9]. The available literature data indicate that aldehydes, RCHO, are generally more reactive than are ketones (due to the weak C—H bond in the —CHO group) toward reaction with OH and $NO_3$ radicals [8,9], and in the troposphere a $C_n$–aldehyde reacts to form mainly the $C_{n-1}$–aldehyde [8,9].

Rate constants for the gas-phase reactions of the OH radical with formaldehyde [8,10]; acetaldehyde [8,10]; and the $\geq C_3$ aliphatic aldehydes propanal, butanal, 2-methylpropanal, pentanal, 3-methylbutanal, and 2,2-dimethylpropanal [11–16] have been measured at around room temperature. For the reactions of the $NO_3$ radical with aliphatic aldehydes, rate constants have been measured for formaldehyde [8,10], acetaldehyde [8,10], and a number of $C_3$– to $C_6$–aldehydes [17,18]. However, for each of the $\geq C_3$ aldehydes studied to date, rate constants for the $NO_3$ radical reaction are available from only a single study [17,18], and they increase with increasing carbon number more rapidly than expected if the reaction involves almost exclusively H-atom abstraction from the —CHO group [17,19]. In this work, we have measured rate constants for the reactions of OH and $NO_3$

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radicals with propanal, butanal, pentanal, and hexanal at room temperature; no rate constant has been reported to date for the reaction of the OH radical with hexanal.

## EXPERIMENTAL

The experimental methods were similar to those used previously [20,21]. Experiments were carried out in a 6500-liter all-Teflon chamber at 296 ± 2 K and 740 Torr total pressure of purified air at ~5% relative humidity. The chamber is equipped with two parallel banks of black lamps for irradiation and a Teflon-coated fan to ensure rapid mixing of reactants during their introduction into the chamber. Rate constants for the OH radical and $NO_3$ radical reactions were measured using relative rate methods in which the relative disappearance rates of the aldehydes and a reference compound, whose OH or $NO_3$ radical reaction rate constant is reliably known, were measured in the presence of OH radicals or $NO_3$ radicals [20,21]. Providing that the aldehydes and the reference compound reacted only with OH radicals or $NO_3$ radicals, then [20,21]

$$\ln\left(\frac{[\text{aldehyde}]_{t_0}}{[\text{aldehyde}]_t}\right) - D_t = \frac{k_1}{k_2}\ln\left[\left(\frac{[\text{reference compound}]_{t_0}}{[\text{reference compound}]_t}\right) - D_t\right] \quad \text{(i)}$$

where $[\text{aldehyde}]_{t_0}$ and $[\text{reference organic}]_{t_0}$ are the concentrations of the aldehyde and the reference compound, respectively, at time $t_0$; $[\text{aldehyde}]_t$ and $[\text{reference organic}]_t$ are the corresponding concentrations at time $t$; $D_t$ is a factor to account for dilution due to any additions to the chamber during the reactions; and $k_1$ and $k_2$ are the rate constants for reactions (1) and (2), respectively.

$$\left.\begin{matrix}\text{OH}\\ \text{NO}_3\end{matrix}\right\} + \text{aldehyde} \longrightarrow \text{products} \quad (1)$$

$$\left.\begin{matrix}\text{OH}\\ \text{NO}_3\end{matrix}\right\} + \text{reference organic} \longrightarrow \text{products} \quad (2)$$

Therefore, plots of $\{\ln([\text{aldehyde}]_{t0}/[\text{aldehyde}]_t) - D_t\}$ against $\{\ln([\text{reference organic}]_{t0}/[\text{reference organic}]_t) - D_t\}$ should be straight lines with slope $k_1/k_2$ and zero intercept.

OH radicals were generated by the photolysis of methyl nitrite ($CH_3ONO$) in air at wavelengths > 300 nm [22], and NO was added to the reactant mixtures to suppress the formation of $O_3$ and hence of $NO_3$ radicals [22]. The initial reactant concentrations (in molecule $cm^{-3}$ units) were $CH_3ONO$, $\sim 2.4\times10^{14}$; NO, $\sim 2.4\times10^{14}$; and aldehydes and reference compound, $\sim 2.4\times10^{13}$ each. Methyl vinyl ketone was used as the reference compound because its OH radical reaction rate constant [23–25] is similar to those of the $\geq C_3$ aldehydes measured to date [8] and it could be analyzed by gas chromatography using the same sampling procedure and gas chromatographic column as the aldehydes studied. Irradiations were carried out at 20% of maximum light intensity for 2–40 min, resulting in up to 57–76% reaction of the initially present aldehydes or methyl vinyl ketone. Because no additions were made to the chamber during the OH radical reactions, $D_t = 0$ for these experiments.

In addition, irradiations of aldehyde ($\sim 2.4 \times 10^{13}$ molecule $cm^{-3}$) –cyclohexane ($8.6 \times 10^{15}$ molecule $cm^{-3}$) or *n*-nonane ($5.2 \times 10^{15}$ molecule $cm^{-3}$)–air mixtures were carried out to assess the importance of photolysis of the aldehydes during the OH radical reaction rate constant determinations. Cyclohexane or *n*-nonane were present to scavenge any OH radicals formed during these irradiations, carried out at 20% of the maximum light intensity for up to 60 min.

$NO_3$ radicals were generated in the dark by the thermal decomposition of $N_2O_5$ [26], and methacrolein or 1-butene was used as the reference compound because their $NO_3$ radical reaction rate constants [20,24] are of a similar magnitude to those for the $\geq C_3$ aldehydes [17,18]. The initial aldehyde and reference compound concentrations were $\sim 2.4 \times 10^{13}$ molecule $cm^{-3}$ each, and $(4.8–9.6) \times 10^{13}$ molecule $cm^{-3}$ of $NO_2$ was also included in the reactant mixture [27]. Three additions of $N_2O_5$ were made to the chamber during an experiment, with each addition corresponding to an initial concentration of $(1.21–11.0) \times 10^{13}$ molecule $cm^{-3}$ of $N_2O_5$ in the chamber. For these experiments, the value of $D_t$ was 0.0028 per $N_2O_5$ addition to the chamber.

The concentrations of the aldehydes and the reference compounds were measured using gas chromatography with flame ionization detection (GC-FID). For the analysis of propanal, butanal, pentanal, hexanal, methyl vinyl ketone, and methacrolein, 100-$cm^3$ gas samples were collected from the chamber onto Tenax-TA solid adsorbent with subsequent thermal desorption at ~225°C onto a 30-m DB-1701 megabore column held at −40°C and then temperature programmed to 240°C at 8°C $min^{-1}$. For the analysis of 1-butene, gas samples were collected from the chamber in 100 $cm^3$ all-glass, gas-tight syringes, and transferred via a 1-$cm^3$ stainless steel loop and gas sampling valve onto a 30m DB-5 megabore column held at −25°C and then temperature programmed to 200°C at 8°C $min^{-1}$. Based on replicate analyses in the dark, the GC-FID

measurement uncertainties for the aldehydes and reference compounds were ≤5% (and generally in the range 1–3%). The NO and initial $NO_2$ concentrations were measured using a Thermo Environmental Instruments Model 42 chemiluminescence NO–$NO_2$–$NO_x$ analyzer.

The chemicals used, and their stated purities, were propanal (99%), butanal (99%), pentanal (99%), hexanal (99%), methyl vinyl ketone (99%), and methacrolein (95%), Adrich Chemical Co.; NO (≥99%) and 1-butene (≥99.0%), Matheson Gas Products; *n*-nonane, (99.9%), Burdick and Jackson; and cyclohexane (HPLC grade), Fisher Scientific. Methyl nitrite and $N_2O_5$ were prepared and stored as described previously [22,26]. $NO_2$ was prepared as needed by reacting NO with an excess of $O_2$.

## RESULTS

### OH Radical Rate Constants

Photolysis of propanal–butanal–pentanal–*n*-nonane (in excess)–air and hexanal–cyclohexane (in excess)–air mixtures showed <3% losses of any of the aldehydes over 60-min irradiation periods (at the same light intensity as used in the OH radical reaction rate constant determination experiments). Hence photolysis of the aldehydes during the ≤40-min irradiations employed in the OH radical reaction rate constant determinations was of negligible importance.

A series of $CH_3ONO$–NO–aldehyde–methyl vinyl ketone–air irradiations were carried out, and the experimental data obtained are plotted in accordance with Eq. (i) in Figure 1. Good straight line plots are observed, and the rate constant ratios $k_1/k_2$ obtained by least-squares analyses of the data are given in Table I. These rate constant ratios $k_1/k_2$ are placed on an absolute basis by use of a rate constant $k_2$ for the reaction of the OH radical with methyl vinyl ketone of $k_2 = 2.06 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (with an estimated overall uncertainty of ±10−15%) at 296 K [23,25]. The resulting rate constants $k_1$ are also given in Table I.

### $NO_3$ Radical Rate Constants

A series of $NO_3$–$N_2O_5$–$NO_2$–aldehyde–methacrolein–air and $NO_3$–$N_2O_5$–$NO_2$–hexanal–1-butene–air reactions were carried out. 1-Butene was used as an additional reference compound for hexanal to have a reference compound of similar reactivity as hexanal (as shown in Table II, hexanal is a factor of ~5 more reactive than methacrolein toward the $NO_3$ radical).

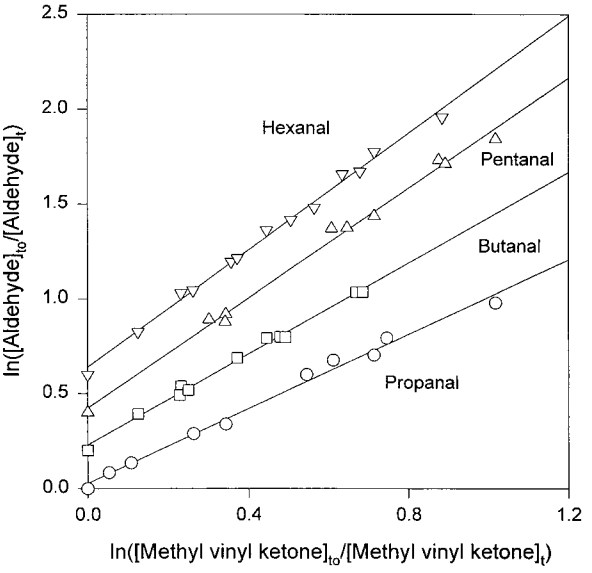


**Figure 1** Plots of Eq. (i) for the gas-phase reactions of the OH radical with propanal, butanal, pentanal, and hexanal, with methyl vinyl ketone as the reference compound. The data for butanal, pentanal, and hexanal have been displaced vertically by 0.2, 0.4, and 0.6 units, respectively, for clarity.

The data obtained from reacting $NO_3$–$N_2O_5$–$NO_2$–aldehyde–methacrolein–air mixtures are plotted in accordance with Eq. (i) in Figure 2. Good straight line plots are observed, and the rate constant ratios $k_1/k_2$ obtained by least-squares analyses of our experimental data are given in Table II. These rate constant ratios $k_1/k_2$ are placed on an absolute basis by use of rate constants $k_2$ for the reactions of the $NO_3$ radical with methacrolein and 1-butene at 296 K of (3.3 ± 1.0) × $10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ [20] and 1.32 × $10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (±30%) [24], respectively. The resulting rate constants $k_1$ are given in Table II.

## DISCUSSION

### OH Radical Reactions

As evident from Table I, our rate constants for the reactions of the OH radical with propanal, butanal, and pentanal are in agreement with the data of Niki et al. [12], Kerr and Sheppard [13], and Semmes et al. [15], although the absolute rate constants measured by Semmes et al. [15] are consistently 10–17% lower than our present values. As discussed previously [8,28], the rate constants obtained by Audley et al. [14] show significant discrepancies with those of Kerr and Sheppard [13] and Semmes et al. [15] for several of the aldehydes studied (2-methyl-1-propanal, pentanal,

**Table I** Rate Constant Ratios $k_1/k_2$ and Rate Constants $k_1$ for the Gas-Phase Reactions of the OH Radical with Propanal, Butanal, Pentanal, and Hexanal at 296 ± 2 K and Atmospheric Pressure of Air

| | | $10^{12} \times k$ ($cm^3$ $molecule^{-1}$ $s^{-1}$) | | |
|---|---|---|---|---|
| Aldehyde | $k_1/k_2$[a] | This Work[b] | Literature | Ref. |
| Propanal | 0.982 ± 0.065 | 20.2 ± 1.4 | 30.6 | Morris and Niki [11] |
| | | | 22.2 ± 0.9[c] | Niki et al. [12] |
| | | | 19.4 ± 1.5[c] | Kerr and Sheppard [13] |
| | | | 18.0 ± 2.1[d] | Audley et al. [14] |
| | | | 17.1 ± 2.4 | Semmes et al. [15] |
| | | | 22.0 | Estimated, Kwok and Atkinson [29] |
| Butanal | 1.20 ± 0.07 | 24.7 ± 1.5 | 25.2 ± 0.6[c] | Kerr and Sheppard [13] |
| | | | 25.6 ± 3.2[d] | Audley et al. [14] |
| | | | 20.6 ± 3.0 | Semmes et al. [15] |
| | | | 25.4 | Estimated, Kwok and Atkinson [29] |
| Pentanal | 1.45 ± 0.09 | 29.9 ± 1.9 | 27.6 ± 4.2[c] | Kerr and Sheppard [13] |
| | | | 13.9 ± 1.8[d] | Audley et al. [14] |
| | | | 26.9 ± 3.9 | Semmes et al. [15] |
| | | | 27.4 | Estimated, Kwok and Atkinson [29] |
| Hexanal | 1.54 ± 0.07 | 31.7 ± 1.5 | 28.8 | Estimated, Kwok and Atkinson [29] |

[a] Indicated errors are two least-squares standard deviations.

[b] Placed on an absolute basis using a rate constant for the reaction of the OH radical with methyl vinyl ketone of $k_2 = 2.06 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 296 K [23,25]. The indicated errors are two least-squares standard deviations and do not take into account uncertainties in the rate constant $k_2$ (estimated to be ±10–15%).

[c] Relative to the rate constant for the reaction of the OH radical with ethene of $8.52 \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 298 K [24].

[d] Relative to the rate constant for the reaction of the OH radical with acetaldehyde of $1.58 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 298 K [8].

3-methyl-1-butanal, and 2,2-dimethylpropanal [28]), and hence are not considered reliable [8,28]. To date, no rate constant for the reaction of the OH radical with hexanal has been reported.

As shown in Table I, the 298 K rate constants calculated using the estimation method of Kwok and Atkinson [29] are in agreement (to within 10%) with our measured rate constants. The reactions of the OH radical with aldehydes proceed by H-atom abstraction from the various C-H bonds, with H-atom abstraction from the -CHO group being estimated to dominate for the $C_3$–$C_6$ straight-chain aldehydes studied here and

**Table II** Rate Constant Ratios $k_1/k_2$ and Rate Constants $k_1$ for the Gas-Phase Reactions of the $NO_3$ Radical with Propanal, Butanal, Pentanal, and Hexanal at 296 ± 2 K and Atmospheric Pressure of Air

| | | | $10^{15} \times k$ ($cm^3$ $molecule^{-1}$ $s^{-1}$) | | |
|---|---|---|---|---|---|
| Aldehyde | $k_1/k_2$[a] | Reference Compound | This Work | Literature | Ref. |
| Propanal | 2.14 ± 0.12 | Methacrolein | 7.1 ± 0.4[b] | 5.7 ± 0.4[c,d] | D'Anna and Nielsen [17] |
| | | | | 4.0 | Estimated, Atkinson [19] |
| Butanal | 3.38 ± 0.15 | Methacrolein | 11.2 ± 0.5[b] | 10.9 ± 0.8[d] | D'Anna and Neilsen [17] |
| | | | | 4.2 | Estimated, Atkinson [19] |
| Pentanal | 4.26 ± 0.48 | Methacrolein | 14.1 ± 1.6[b] | 14.6 ± 0.9[d] | D'Anna and Nielsen [17] |
| | | | | 4.3 | Estimated, Atkinson [19] |
| Hexanal | 4.75 ± 0.62 | Methacrolein | 15.7 ± 2.1[b] | 17.3 ± 1.8[d] | D'Anna and Neilsen [17] |
| | 1.07 ± 0.12 | 1-Butene | 14.1 ± 1.6[e] | 4.3 | Estimated, Atkinson [19] |

[a] Indicated errors are two least-squares standard deviations.

[b] Placed on an absolute basis using a rate constant for the reaction of the $NO_3$ radical with methacrolein of $k_2 = 3.3 \times 10^{-15}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 296 K [20]. The indicated errors are two least-squares standard deviations and do not take into account the uncertainties in the rate constant $k_2$, of ±33% [20].

[c] Relative to the rate constant for the reaction of the $NO_3$ radical with propene of $9.45 \times 10^{-15}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 298 K [8,24].

[d] Relative to the rate constant for the reaction of the $NO_3$ radical with 1-butene of $1.35 \times 10^{-14}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 298 K [24].

[e] Placed on an absolute basis using a rate constant for the reaction of the $NO_3$ radical with 1-butene of $k_2 = 1.32 \times 10^{-14}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 296 K [24]. The indicated errors are two least-squares standard deviations and do not take into account the uncertainties in the rate constant $k_2$, of ±30% [24].

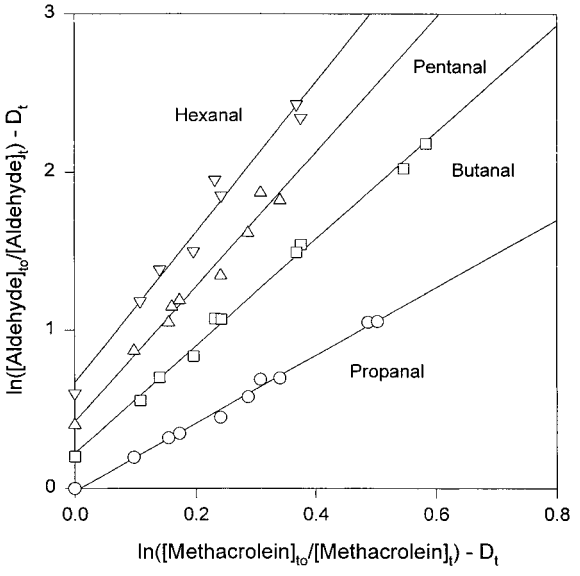


**Figure 2** Plots of Eq. (i) for the gas-phase reactions of the $NO_3$ radical with propanal, butanal, pentanal, and hexanal, with methacrolein as the reference compound. The data for butanal, pentanal, and hexanal have been displaced vertically by 0.2, 0.4, and 0.6 units, respectively, for clarity.

with the $CH_2$ group *i* $\beta$ to the -CHO group being significantly activated [29]. This predicted activation of the $CH_2$ group $\beta$ to the -CHO group results in the rapid increase in calculated rate constant in going from propanal to butanal, with the increase in rate constant from pentanal to hexanal being similar to those predicted (and observed) in the *n*-alkane series [28,29].

## $NO_3$ Radical Reactions

The rate constants measured for the reaction of the $NO_3$ radical with hexanal using methacrolein and 1-butene as the reference compounds are in good agreement (Table II). Furthermore, our rate constants for propanal, butanal, pentanal, and hexanal are in generally good agreement with the only other published data of D'Anna and Nielsen [17]. As in this work, D'Anna and Nielsen [17] used a relative rate method, with propene and/or 1-butene as the reference compounds. Their experiments [17] were carried out in a 250-liter reaction chamber at higher initial reactant concentrations (by a factor of 2–10 for the aldehydes). The rate constants for the $C_2$—$C_6$ straight-chain aldehydes (this work and references 17 and 19) show that the room temperature rate constants for reaction with the $NO_3$ radical increase rapidly with carbon number, from $2.8 \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for acetaldehyde [8,19] to $(1.4–1.7) \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for hexanal (Table II).

As discussed by D'Anna and Nielsen [17], this increase of $NO_3$ radical reaction rate constant with increasing carbon number in the aldehydes is much more rapid than expected from a structure–reactivity estimation method [19] based on that for the corresponding OH radical reactions [29] (Table II). The observed increase in $NO_3$ radical reaction rate constant from propanal to hexanal (Table II) implies that (i) the $CH_2$ groups several carbon atoms away from the —CHO group are activated, (ii) the reaction is not a simple H-atom abstraction [17], or (iii) the estimation method for calculating $NO_3$ radical reaction rate constants [19] is not accurate.

## Tropospheric Lifetimes

Our measured room temperature rate constants for the reactions with OH radicals and $NO_3$ radicals can be combined with estimated ambient concentrations of OH radicals and $NO_3$ radicals to derive the tropospheric lifetimes of the aldehydes studied. Using a global tropospheric 12-h daytime average OH radical concentration of $2.0 \times 10^6$ molecule cm$^{-3}$ [30,31] leads to calculated lifetimes ranging from 4 h for hexanal to 7 h for propanal. With a 12-h average nighttime $NO_3$ radical concentration of $5 \times 10^8$ molecule cm$^{-3}$ [19], the calculated lifetimes due to $NO_3$ radical reaction range from 3 days for hexanal to 7 days for propanal. Therefore, the daytime OH radical reactions are calculated to be the dominant tropospheric loss process for the aldehydes studied here.

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