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Rate constants of long, branched, and unsaturated aldehydes with OH at elevated temperatures

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Abstract

The overall rate constants for the H-abstraction reactions of a series of aldehydes, namely isobutyraldehyde ($i\text{-C}_3\text{H}_7\text{CHO}$), n -valeraldehyde ($n\text{-C}_4\text{H}_9\text{CHO}$), isovaleraldehyde ($i\text{-C}_4\text{H}_9\text{CHO}$), *trans*-2-pentenal ($\text{C}_2\text{H}_5\text{CH}=\text{CHCHO}$), trimethylacetaldehyde ($((\text{CH}_3)_3\text{CCHO})$ and benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$), by hydroxyl radicals (OH), were studied behind reflected shock waves at temperatures of 976 – 1346 K and pressures around 0.6 atm. The OH radicals, produced pyrolytically from tert-butyl hydroperoxide (TBHP), were quantitatively measured by UV absorption using a narrow-linewidth laser near 306.69 nm, targeting the well-characterized $R_1(5)$ rovibronic transition of OH in the A-X (0, 0) band. The high sensitivity of this OH diagnostic allowed for very dilute reactant concentrations, which simplified the reaction systems to pseudo-first-order kinetics. For each aldehyde + OH, its overall rate constant was inferred by fitting simulated OH profiles to the measured OH time histories when a detailed reaction mechanism for this aldehyde was available, or directly from exponential fits to the measured OH time-histories (after correcting for a small effect of different TBHP/aldehyde ratios). Both approaches yielded similar results. The resulting reaction rate constants, measured for the first time at temperatures above 1000 K, can be expressed in Arrhenius equations in units of $\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$ as follows: $k_{i\text{C}_3\text{H}_7\text{CHO}+\text{OH}} = 7.70 \times 10^{13} \exp(-1700\text{K}/T) \pm 7\%$, valid over 976 – 1346 K; $k_{n\text{C}_4\text{H}_9\text{CHO}+\text{OH}} = 1.03 \times 10^{14} \exp(-1730\text{K}/T) \pm 7\%$, valid over 986 – 1313 K; $k_{i\text{C}_4\text{H}_9\text{CHO}+\text{OH}} = 1.02 \times 10^{14} \exp(-1750\text{K}/T) \pm 10\%$, valid over 976 – 1322 K; $k_{(\text{CH}_3)_3\text{CCHO}+\text{OH}} = 7.20 \times 10^{13} \exp(-1670\text{K}/T) \pm 8\%$, valid over 979 – 1243 K; $k_{\text{C}_2\text{H}_5\text{CHCHCHO}+\text{OH}} = 6.93 \times 10^{13} \exp(-1340\text{K}/T) \pm 8\%$, valid over 993 – 1285 K; $k_{\text{C}_6\text{H}_5\text{CHO}+\text{OH}} = 3.10 \times 10^{13} \exp(-1380\text{K}/T) \pm 8\%$, valid over 983 – 1333 K.

Keywords: Aldehydes; OH; Rate constant; High temperature; Shock tube

Introduction

Aldehydes are receiving increased attention in combustion research. They are recognized not only for their key roles in the low-temperature oxidation of hydrocarbons [e.g. 1-7], but also as primary intermediate products derived either from radicals or from molecular dehydrogenation reactions in the combustion of bio-alcohols [e.g. 8-12], the study of which has attracted growing interest in the face of the global energy challenge. Despite their abundance in fuel combustion processes, however, aldehydes are usually unwanted in the final products. They are known as toxic emissions in the exhaust gas of spark-ignition or compression-ignition engines [13, 14], and a high level of aldehydes in the engine exhaust can be a sign of abnormal reaction quenching [15]. As critical steps in the reaction pathway toward complete fuel combustion, aldehyde removal reactions, either through unimolecular decomposition [16] or via dehydrogenation/H-abstraction by radicals [17], are worth special attention in combustion studies.

Of particular interest are the H-abstraction reactions of aldehydes by hydroxyl radicals (OH). Except for formaldehyde (CH_2O), both theoretical and experimental studies on these reactions have mostly been concentrated near atmospheric temperature [e.g. 18-22], whereas studies at elevated temperatures relevant to combustion research are sparse. Mendes et al. [17] performed a series of quantum chemical calculations for the rate constants of OH + formaldehyde (CH_2O), acetaldehyde (CH_3CHO), propionaldehyde ($\text{C}_2\text{H}_5\text{CHO}$) and isobutyraldehyde ($\text{i-C}_3\text{H}_7\text{CHO}$). Taylor et al. [23] measured the rate constant of acetaldehyde + OH by pulsed laser photolysis and LIF over 297–860 K, and Veloo et al. [24, 25] studied the oxidation of propionaldehyde, n-butyraldehyde ($\text{n-C}_3\text{H}_7\text{CHO}$) and isobutyraldehyde in a jet reactor and flames. So far, the only direct experimental measurement for the rate constants of longer (C_2 and above) aldehydes + OH at $T > 1000$ K has been the recent shock tube study from our laboratory [26], where we investigated a series of straight-chain small (C_1 - C_4) aldehydes and observed a clear trend with the progression of the carbon chain length. Here we extend our previous measurement to include long, branched and unsaturated aldehydes, namely isobutyraldehyde, n-valeraldehyde ($\text{n-C}_4\text{H}_9\text{CHO}$), isovaleraldehyde ($\text{i-C}_4\text{H}_9\text{CHO}$), *trans*-2-pentenal ($\text{C}_2\text{H}_5\text{CH=CHCHO}$), trimethylacetaldehyde ($((\text{CH}_3)_3\text{CCHO})$) and benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) (their molecular structures is shown in Fig. 1), in hopes that the new data obtained from our study would not only enrich fundamental combustion kinetic databases, but also provide insights into site-specific reactivity of these H-abstraction reactions, or create unique targets for testing/calibrating state-of-the-art transition-state-theory calculations.

Figure 1. Molecular structures of the aldehydes investigated in the current study

Experimental Setup

Experiments were carried out in a 14.13-cm diameter high-purity shock tube at Stanford. After shock-heating mixtures of aldehydes and an OH precursor behind reflected shock waves, the current study measured the OH concentration time-histories using a narrow-linewidth dye laser tuned to the OH $R_1(5)$ rovibronic transition in the A-X (0, 0) band at 306.69 nm, from which the aldehyde + OH rate constants were inferred. Details about the Stanford shock tube facility and laser absorption diagnostic for OH have been documented in our previous work [26] and not repeated here.

In this study we used tert-butyl hydroperoxide (TBHP, $(\text{CH}_3)_3\text{COOH}$) as the pyrolytic precursor for OH; when heated by reflected shock waves at temperatures above 1000 K, it decomposed almost instantaneously into OH, CH_3 and acetone (CH_3COCH_3). Gas-phase TBHP was vaporized from a TBHP/water solution of 70% TBHP by weight (supplied by Sigma-Aldrich), mixed with aldehyde that was vaporized from high-purity liquid (isobutyraldehyde, > 99.5% purity; n-valeraldehyde, > 97% purity; isovaleraldehyde, > 97% purity; trimethylacetaldehyde, > 96% purity; trans-2-pentenal, > 95% purity; benzaldehyde, > 99.5% purity; all supplied by Sigma-Aldrich), and diluted in argon (> 99.999% purity, supplied by Praxair). The small amount of impurities (< 5%) in the aldehydes were expected to be either low-volatile hydrocarbons that were not vaporized into the test gas mixtures, or dissolved air that had been removed through a freeze–pump–thaw procedure before the mixture preparation. Even in the extreme case that a maximum impurity level in the mixtures was assumed, a conservative estimate would suggest an uncertainty of at most $\pm 5\%$ in the current rate constant measurement from contributions of impurities. The test gas mixtures were prepared manometrically in a 14-L stainless steel mixing tank, which was equipped with a magnetic stirrer that ensured mixture homogeneity and accelerated mixing, and constantly heated to 50 C to prevent wall condensation. A double-dilution technique, as elaborated in previous studies [26–28], was exercised to control the mixture composition more precisely. For each set of experiments, several batches of mixture were prepared allowing for a consistency check of the mixture composition, and the uncertainty in aldehyde concentration was estimated to

be less than $\pm 5\%$. To prevent contamination of the test mixture from any residual impurity inside the shock tube, the shock tube and mixing assembly were routinely evacuated between experiments with a turbo-molecular pump to $\sim 6 \mu\text{torr}$, and the subsequent leak-plus-outgassing rate was measured to be less than $5 \mu\text{torr}/\text{min}$.

Previous studies [16, 24, 25] suggest that aldehydes, especially the long and branched ones, undergo unimolecular decomposition at high temperatures, producing CO as a by-product. This aldehyde unimolecular decomposition is strongly temperature dependent and limited the temperature range of our measurements. To quantify its effect on our current measurement, we also exploited a sensitive CO absorption diagnostic, implemented with the same setup as in [27], to monitor the decomposition of aldehydes (see Fig. 2 for an example). The upper temperature limit of our measurements was chosen to ensure that less than 5% aldehydes decomposed within the $1/e$ decay time of OH.

Figure 2. Example data trace of the aldehydes + TBHP experiment

Rate Constant Determination

Reaction rate constants of OH + aldehydes were determined from OH concentration time-histories, which were calculated from logarithmic transition, or absorbance, of the laser intensity using the Beer-Lambert relation: $\text{absorbance} = -\ln(I/I_0) = k_{\text{OH}}X_{\text{OH}}PL$, where I and I_0 were the transmitted and incident laser intensities, respectively, k_{OH} the OH absorption constant, P the total gas pressure, L the diameter of the shock tube (14.13 cm), and X_{OH} the OH mole fraction of interest. The concentration of OH near $t = 0$ was also used to determine the initial TBHP concentration in the mixture. As shown in Fig. 2, the OH diagnostic recovered a TBHP concentration of about 6.6ppm and a balancing H_2O concentration of about 43ppm, which agreed well with the ideal gas-phase TBHP/ H_2O ratio calculated from Raoult's law (roughly 1:7 at the mixing tank temperature of about 50 C).

In our experiment design of having aldehydes in excess of the TBHP (at an aldehyde/TBHP ratio of 10 and higher), the time-history of OH concentration simplified to pseudo-first order kinetics, yet care was still needed to account for secondary reactions. For some aldehydes, a detailed reaction mechanism was available and could be used to aid inference of the + OH reaction rate, as illustrated by a representative example of isobutyraldehyde + OH in Fig. 3. In this example, a base mechanism for n-butyraldehyde and isobutyraldehyde from Veloo et al. [25], supplemented with an additional TBHP sub-mechanism comprising the following reactions, was used for the analysis.

The rate constants of reactions 1, 3 and 4 were obtained from Pang et al. [29], reaction 2 from Choo and Benson [30] (see Table 1 for details), and the thermodynamic parameters of TBHP and tert-butoxy radical ($(\text{CH}_3)_3\text{CO}$) were obtained from Goos et al. [31]. The rate constants of the following reactions were updated to incorporate results from the most recent experimental measurements:

with their values obtained from Hong et al. [32], Wooldridge et al. [33], Lam et al. [34], and Pang et al. [29], respectively.

Figure 3. Example OH time-history of isobutyraldehyde + OH

Table 1

Rate constants^a updated in the Veloo et al. [25] mechanism

for modeling the TBHP / i-C₃H₇CHO reaction system

Rxn. #	A	m	E	Ref.
(1)	2.15×10^{37}	0.00	149.4	[29]
(2)	7.59×10^{37}	0.00	60.0	[30]
(3)	2.30×10^{13}	0.00	21.8	[29]
(4)	2.49×10^{13}	0.00	22.0	[29]
(5)	1.04×10^{14}	0.00	126.8	[32]
(6)	3.57×10^4	2.40	-8.8	[33]
(7)	2.95×10^{13}	0.00	19.2	[34]
(8)	1.65×10^{13}	0.00	0.00	[29]

a: $k = AT^m \exp(-E/RT)$; units: kJ, cm³, mol, s and K.

As shown in Fig. 3, the updated Veloo et al. [25] mechanism underpredicts (by about 25%) the decay rate of OH. A formal sensitivity analysis (Fig. 4) shows that under the current pseudo-first-order condition, the OH decay is dominated by the aldehyde + OH reaction, and thus we can infer its rate constant by fitting the model prediction to the measured OH time-history. For example, from the case in Fig. 3, a nominal value of $k = 1.83 \times 10^{13}$ cm³/mol-s is obtained for the rate constant of isobutyraldehyde + OH at T = 1160 K. And according to a detailed uncertainty analysis as shown in Fig. 5, its 2 σ uncertainty limits are as low as +/-7%, with a majority of the uncertainty derived from experimental sources such as the mixture composition, but very little contributed from secondary chemistry such as the CH₃ + OH = CH₂(s) + H₂O reaction.

Figure 4. OH sensitivity of the example isobutyraldehyde + TBHP experiment

Figure 5. Uncertainty analysis for the measured rate constant of isobutyraldehyde + OH at 1160 K

Unfortunately, not every aldehyde in this study had a corresponding reaction mechanism available, which has motivated us to try a mechanism-independent approach to determine the target rate constants. Under our pseudo-first-order setup, the measured OH concentration decayed exponentially in time. Thus we could calculate an “apparent” OH + aldehyde rate constant, k' , from a least-square fit of $\ln[\text{OH}]$ vs. time, as illustrated in Fig. 6. The resulting value, $k' = 1.91 \times 10^{13} \text{ cm}^3/\text{mol}\cdot\text{s}$ at $T = 1160 \text{ K}$, was slightly (about 4%) larger than the value of k determined from the mechanism-assisted approach, due to contributions from secondary reactions, such as 1) $\text{OH} + \text{CH}_3$, 2) $\text{OH} + \text{CH}_3\text{COCH}_3$, and 3) $\text{OH} + \text{aldehyde fragments}$ generated from H-abstraction. Note that the contributions of these secondary reactions to the OH depletion rate were all proportional to the initial TBHP concentration, while the target reaction was proportional to the initial aldehyde concentration. This leads to a simple relation between k' and k , i.e. $k' = k + [\text{TBHP}]_0/[\text{Aldehyde}]_0 \cdot k^*$, where k^* is a correction constant accounting for the overall effects of the secondary reactions. The correction term, $[\text{TBHP}]_0/[\text{Aldehyde}]_0 \cdot k^*$, was usually small under our typically experimental conditions ($< 5\%$ of k at $[\text{TBHP}]_0/[\text{Aldehyde}]_0$ around $1/50$), and we could obtain the value of k^* (that may be different for each aldehyde) and hence recover the target rate constant k by varying the initial TBHP/aldehyde ratio in our measurement, as illustrated in Fig. 7. The rate constant k obtained from this method, shown in Fig. 8, was consistent with the mechanism-assisted approach; its 2σ uncertainty, estimated from the RMS scatter of individual data points in combination with possible contributions from the impurities in the aldehydes, was calculated to be $\pm 7\%$, also consistent with the mechanism-assisted approach. After the success on isobutyraldehyde + OH, we readily applied this mechanism-independent approach to the rate constant measurements for other aldehydes + OH.

Figure 6. Apparent rate constant obtained from exponential fit to the measured OH time-history

Figure 7. Apparent rate constant measured at different initial TBHP/aldehyde ratios

Figure 8. The isobutyraldehyde + OH rate constant measured with the mechanism-independent approach

Results and Discussion

A total number of 158 reflected shock waves experiments, including 32 for isobutyraldehyde, 31 for valeraldehyde, 28 for isovalaldehyde, 25 for trimethylacetaldehyde, 20 for trans-2-pentenal, and 22 for benzaldehyde, were performed to determine the rate constants of these aldehydes reacting with OH. These experiments were carried out over the temperature range of 976 – 1346 K, at pressures near 0.6 atm, and at different initial TBHP/aldehyde ratios. Measurement was also conducted at higher pressures (~ 2.2 atm), and no pressure dependence was observed, which suggested that the overall OH + aldehydes rates measured under the current conditions were dominated by H-abstraction. A complete list of data from these experiments can be found in the attached supplementary material.

The resulting reaction rate constants can be expressed in Arrhenius equations, in units of $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$, as below:

$$k_{\text{C}_3\text{H}_7\text{CHO}+\text{OH}} = 7.70 \times 10^{13} \exp(-1700\text{K}/T) \pm 7\%;$$

$$k_{\text{nC}_4\text{H}_9\text{CHO}+\text{OH}} = 1.03 \times 10^{14} \exp(-1730\text{K}/T) \pm 7\%;$$

$$k_{\text{iC}_4\text{H}_9\text{CHO}+\text{OH}} = 1.02 \times 10^{14} \exp(-1750\text{K}/T) \pm 10\%;$$

$$k_{(\text{CH}_3)_3\text{CCHO}+\text{OH}} = 7.20 \times 10^{13} \exp(-1670\text{K}/T) \pm 8\%;$$

$$k_{\text{C}_2\text{H}_5\text{CHCHCHO}+\text{OH}} = 6.93 \times 10^{13} \exp(-1340\text{K}/T) \pm 8\%;$$

$$k_{\text{C}_6\text{H}_5\text{CHO}+\text{OH}} = 3.10 \times 10^{13} \exp(-1380\text{K}/T) \pm 8\%.$$

And the temperature ranges of these expressions are 976 – 1346 K, 986 – 1313 K, 976 - 1322 K, 979 - 1243 K, 993 - 1285 K, and 983 - 1333 K, respectively.

Figure 9. Cross-comparison between the rate constants of 10 different aldehydes + OH

Fig. 9 summarizes the high-temperature H-abstraction rate constants of 10 different aldehydes by OH, including the C₁-C₄ straight-chain aldehydes from our earlier study [26]. As shown by Fig. 9, the overall rate constant of a saturated aldehyde reacting with OH is seen to increase with its carbon chain length (in this comparison, the rate constant of formaldehyde + OH has been divided by 2), primarily a result of the increased number of H-abstraction sites in the aldehyde. In a saturated aldehyde, there are two types of H-abstraction sites, namely the aldehydic H atoms (also known as the alpha sites) as in R-(C=O)-H, and the alkylic H atoms (beta, gamma, delta sites and so on, which are one, two, three and more carbons away from the formyl group -CHO) as in R-CH₃ or R-CH₂-R'. The aldehydic H-abstraction sites are generally more reactive than their alkylic counterparts, but there is only one such site in each aldehyde molecule; the only exception being formaldehyde, which has two aldehydic sites, making it more reactive with OH even than propionaldehyde. The alkylic sites, on the other hand, accumulate as the aldehyde carbon chain length progresses. Their contribution to the overall rate constant appears to be roughly proportional to the number of sites, but can also be affected by the aldehyde molecular structure. This is evident in the case of trimethylacetaldehyde ((CH₃)₃CCHO), whose rate constant of reaction with OH is substantially lower than that of its isomers n-valeraldehyde and isovaleraldehyde, though less difference is seen between the latter two. This observation is also supported by the typical dissociation energies of different C-H bonds in these aldehydes, which have been reported in the works of Pelucchi et al. [16] and da Silva and Bozzelli [41]. Both studies have suggested that the C-H bonds at the alpha and beta sites are the weakest and second weakest, respectively, which explains why the alpha and beta sites have the most contribution per site to the overall H-abstraction rate constants. As for the unsaturated aldehydes reacting with OH, trans-2-pentenal has a rate constant slightly lower than that of its saturated counterpart, valeraldehyde, but the difference diminishes at temperatures close to 1000 K; benzaldehyde, the least reactive aldehyde in the current study, has a rate constant only slightly higher than half of the formaldehyde + OH value.

Figure 10. Comparison between the current measurement and the SAR model

Fig. 10 compares our measurement rate constants of C₁-C₅ straight-chain aldehydes with the estimated values using the structure-activity relationship (SAR) developed by Atkinson and co-workers [35-37]. This SAR model estimates the rate constants for the reactions of OH with organic compounds by summing the contributions of primary (−CH₃), secondary (−CH₂−), and tertiary (−CH<) groups, whose rate constants can be affected by the identity of the substituents attached to them according to their corresponding substituent factors. This SAR model has successfully predicted the high-temperature rate constant of alkanes + OH in the studies of Pang et al. [29] and Badra et al. [38], and recovers the ketones + OH rate constants in the study of Lam et al. [34] under a scaling factor of 0.75. In this study we extend the comparison to aldehydes + OH. As shown in Fig. 10, the SAR model accurately recovers the rate constants of formaldehyde and acetaldehyde + OH, but significantly overpredicts the values of C₃-C₅ aldehydes, possibly due to errors in the high-temperature values of the substituent factors, or due to unaccounted effects from the next-nearest neighbors [39, 40]. Further improvements to structural estimation models such as the SAR are still needed to fully resolve this discrepancy.

Figure 11. Comparison between the Veloo et al. rate constants and the current measurement

Also compared with our current measurement are two theoretical and modeling studies. Fig. 11 shows the rate constants of propionaldehyde, normal- and iso-butyraldehyde + OH from the Veloo et al. model [24, 25]. Compared to the current study, the Veloo et al. model is seen to underpredict all these rate constants by about 30%. The transition-state-theory (TST) calculation from Mendes et al. [17] (see Fig. 12), on the other hand, overpredicts the rate constants of formaldehyde, acetaldehyde, propionaldehyde and isobutyraldehyde + OH by factors of about 2.3, 4.6, 5.5 and 4.9, respectively. The discrepancies between the model estimates, the TST calculations and the experiment results are possibly due to large uncertainties in the vibrational partition functions, particularly of the torsion and other low-frequency modes, or due to uncertainties in the barrier height, as evident in the study of Mendes et al. [17] (uncertainty of 1 kcal/mol or higher, which translates to a factor of about 1.6 difference in the rate constant at 1000 K). This may suggest a need for future refinement to the H-abstraction reaction rate constants of aldehydes in combustion models, where the current data can be useful.

Figure 12. Comparison between the Mendes et al. TST calculation and the current measurement

Conclusions

In this study we report the first direct measurements for the H-abstraction rate constants of six long, branched and unsaturated aldehydes by OH at temperatures above 1000 K. The use of pseudo-first order reaction systems with dilute reactant mixtures, in combination with our sensitive OH absorption diagnostic, yielded high-precision data with tight uncertainty bounds ($< \pm 10\%$). A cross-comparison of these data and the data from our previous study [26], performed between 10 different aldehydes, revealed effects of both the carbon chain length and the molecular structure of the aldehyde on its rate constant for reaction with OH. The results from this study should prove very useful for validating/calibrating future structural estimation models and transition-state-theory calculations.

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