

# The Reaction of OH with Acetaldehyde and Deuterated Acetaldehyde: Further Insight into the Reaction Mechanism at both Low and Elevated Temperatures

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ABSTRACT: The pulsed laser photolysis/laser-induced fluorescence technique has been used to conduct additional measurements of the gas-phase  $\text{CH}_3\text{CHO} + \text{OH}$  reaction. These measurements were conducted to verify the complex temperature dependence previously observed by the authors and to acquire mechanistic information about the reaction mechanism in the form of primary kinetic isotope effects. Primary kinetic isotope effect measurements at temperatures of 297, 383, 600, and 860 K indicate that H abstraction from the acetyl group dominates that of the methyl group at low to modest temperatures ( $\leq 600$  K) and H abstraction from the methyl group dominates that from the acetyl group at higher temperatures (860 K). A bi-exponential

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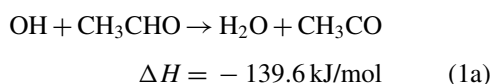
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fit to all experimental measurements of the  $\text{CH}_3\text{CHO} + \text{OH}$  reaction published since 1990, excluding our prior results (Taylor et al., *Symp (Int) Combust (Proc)* 1996, 26, 497) that were approximately 20–30% lower than the present results, resulted in the following expression (in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ):  $k(202\text{--}860 \text{ K}) = 8.36 \times 10^{-11} * \exp(-2410.3/T) + 4.34 \times 10^{-12} * \exp(368.9/T)$ . © 2006 Wiley Periodicals, Inc. *Int J Chem Kinet* 38: 489–495, 2006

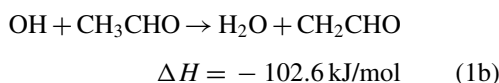
## INTRODUCTION

Acetaldehyde ( $\text{CH}_3\text{CHO}$ ) and its degradation products are intermediates in combustion of hydrocarbon-based fuels. Acetaldehyde is a byproduct of the combustion of ethanol [2]. The vinoxy radical ( $\text{CH}_2\text{CHO}$ ) is a likely product of the OH radical-initiated oxidation of acetaldehyde at elevated temperatures [1]. Vinoxy is also an intermediate in the high-temperature oxidation of ethylene (via reaction with O atoms) [3] and acetylene (via reaction with OH) [4]. Acetaldehyde is also an air pollutant. In the troposphere,  $\text{CH}_3\text{CHO}$  reacts to produce peroxyacetyl nitrate (PAN), which exhibits mutagenic activity and is a strong eye irritant [5]. The formation of PAN is believed to be initiated by the reaction of acetaldehyde with OH [6]. The kinetics and products of reaction of OH with  $\text{CH}_3\text{CHO}$  are thus of considerable interest under both combustion and atmospheric conditions.

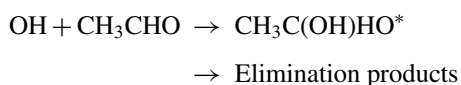
At room temperature, the bimolecular rate coefficient for the reaction of OH with  $\text{CH}_3\text{CHO}$  is well established [7]. However, serious uncertainties exist concerning the reaction mechanism. Until recently, it was assumed that the reaction occurred by abstraction of the weakly bound aldehydic hydrogen atom



although abstraction of a methyl hydrogen

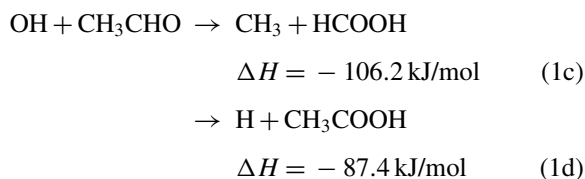


is not ruled out. However, it is well known that the reaction exhibits a negative temperature dependence that is similar to that displayed by many addition reactions involving OH. For this reason, it has been suggested that the reaction occurs via an alkoxy intermediate as an addition–elimination reaction



Energetically favored channels in addition to (1a) and

(1b) include



where heats of reaction are derived from a recent compilation [7].

Michael et al. [8] were the first to examine in some detail the mechanism of the  $\text{OH} + \text{CH}_3\text{CHO}$  reaction. These authors favored an abstraction mechanism. The most compelling argument cited in support of this mechanism was that the addition of  $\text{O}_2$  to the reaction significantly decreased the rate at which OH was consumed. They interpreted this observation as indicating that OH is reformed in a reaction between  $\text{CH}_3\text{CO}$  and  $\text{O}_2$ . They were unable to propose a specific mechanism for reformation of H, but nonetheless concluded that acetyl radicals were the most probable products of the reaction of OH with  $\text{CH}_3\text{CHO}$ .

Taylor et al. [1] measured absolute rate coefficients for the reactions of OH with  $\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{CDO}$ , and  $\text{CD}_3\text{CDO}$  over a temperature range of 295–900 K and proposed a more complex mechanism based on quantum RRK calculations for the addition channels ((1c) and (1d)). At low temperatures, they proposed that the dominant mechanism involved addition of OH to form a covalently bound intermediate, which subsequently dissociated by  $\text{CH}_3$  or H elimination to form carboxylic acids (channels (1c) and (1d)). In that work, Taylor et al. did not locate a barrier to addition via ab initio calculations, and assumed (incorrectly) that it had a rate similar to the addition of OH to isoelectronic ethylene. This implied rapid reaction, and they estimated that, at 295 K, H-atom abstraction was only a minor channel, accounting for ca. 10% of the total rate. At temperatures above 600 K, the authors observed a switch in temperature dependence of the rate from negative to positive. They attributed this change in temperature dependence to a change in reaction mechanism from OH addition to H-atom abstraction. Transition state theory calculations indicated H-atom abstraction from both the aldehydic-H and the  $\text{CH}_3$ -H contributed to the observed

rate at elevated temperatures, with the contribution from the CH<sub>3</sub> group increasing with increasing temperature. Kinetic isotope measurements supported their proposed mechanism.

Several subsequent experimental studies have focused on the products of reaction (1), at room temperature and below. Tyndall et al. used FTIR analysis to set an upper limit of 10% for carboxylic acid formation [9]. Cameron et al. used time-resolved UV spectroscopy to monitor CH<sub>3</sub>CO, CH<sub>3</sub>, and H directly, and they set upper limits of 3% and 2% for channels (1c) and (1d), respectively [10]. They assigned a dominant role, 93 ± 18%, for channel (1a). Wang et al. used IR laser spectroscopy to deduce that the yield of H<sub>2</sub>O is high (ca. 100%), CH<sub>3</sub> formation was below 5%, and H formation was 5 ± 5% [11]. Vandenberk and Peeters employed molecular beam/mass spectrometer sampling in a flow reactor to deduce an H<sub>2</sub>O yield of 89 ± 6% with an upper limit of 3% to formic acid production [12]. Most recently, Butkovskaya et al. applied chemical ionization/mass spectrometry in a flow reactor to determine an H<sub>2</sub>O yield of about 98 ± 5% and, via direct detection of CH<sub>2</sub>CHO, a contribution of channel (1b) of about 5 ± 2% [13]. Two computational studies by Alvarez-Idaboy et al. [14] and D'Anna et al. [15] via ab initio calculations showed there is a significant barrier to the initial addition step to form an alkoxy intermediate, so that channels (1c) and (1d) would be negligibly slow. They further proposed that the reaction mainly occurs via the formation of a prereactive complex in which the H atom of OH is hydrogen bonded to the O atom of acetaldehyde.

This manuscript presents kinetic measurements of the gas-phase reaction between hydroxyl (OH) radicals and CH<sub>3</sub>CHO, CH<sub>3</sub>CDO, and CD<sub>3</sub>CHO at selected temperatures (297, 383, 600, and 860 K) at 740 ± 10 Torr in a helium bath gas. The purpose of these measurements was to re-examine primary kinetic isotope effects of these reactions in light of the controversy regarding the dominant reaction mechanism under both atmospheric and high temperature combustion conditions, and in particular to provide the first mechanistic information above room temperature.

## EXPERIMENTAL APPROACH

The apparatus and experimental procedures are well established [16–18]. In brief, OH was generated in the presence of a large excess of CH<sub>3</sub>CHO by excimer laser photolysis of a precursor, and monitored by off-resonance laser-induced fluorescence excited at 282 nm. HONO and N<sub>2</sub>O/H<sub>2</sub>O mixtures were used as OH radical precursors. HONO was used at low tem-

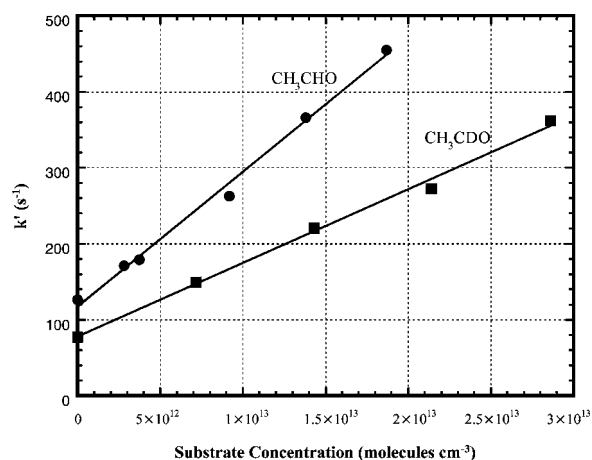
peratures (≤600 K); N<sub>2</sub>O/H<sub>2</sub>O mixtures were used primarily at elevated temperatures (≥ 600 K). An excimer laser (Lambda Physik Compex model 102) operating with XeF (351 nm) or ArF (193 nm) was used as the photodissociation source for the HONO and N<sub>2</sub>O/H<sub>2</sub>O mixtures, respectively. Initial OH concentrations for the HONO and N<sub>2</sub>O/H<sub>2</sub>O experiments were ca. 3 × 10<sup>11</sup> molecules cm<sup>-3</sup> and 1 × 10<sup>11</sup> molecules cm<sup>-3</sup>, respectively.

Acetaldehyde samples were prepared daily in 2 L glass bulbs, where the substrate pressure was measured with an absolute pressure transducer (MKS type 622) before dilution. The prepared acetaldehyde sample was introduced into the experimental system using a syringe pump (KDS100, KD Scientific). Acetaldehyde concentrations in the reactor were determined from the measured mass flow rate (Porter Instruments, model VCD 1000) of the diluted acetaldehyde, the total gas flow and the reactor pressure, measured with an absolute pressure transducer (MKS Type 626). The absence of adsorption on the injector probe (coated with boric acid) and reactor walls was verified using GC/MS analysis. All experiments were conducted at a total pressure of 740 ± 10 Torr with helium as the bath gas. High purity samples (>99.9%) of CH<sub>3</sub>CHO, CH<sub>3</sub>CDO, and CD<sub>3</sub>CDO were obtained from Aldrich, Inc., and used as received. GC/MS analyses indicated the absence of any reactive impurities that would impact the rate measurements. Analysis of the reactor gas stream showed that HONO generation did not produce detectable concentrations of potentially interfering NO, NO<sub>2</sub>, or HCl (<1.2 × 10<sup>12</sup> molecule cm<sup>-3</sup>).

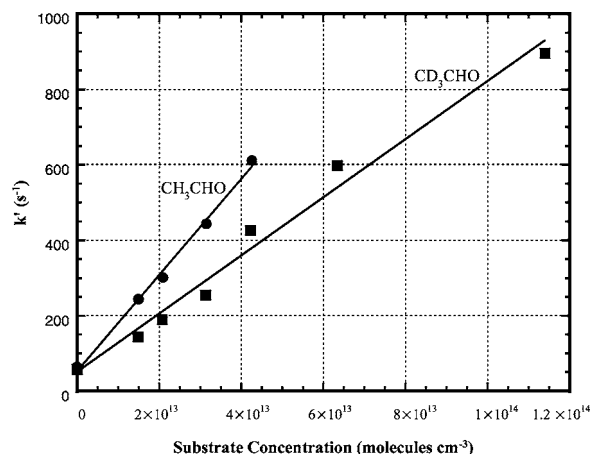
All experiments were performed under pseudo-first-order conditions, [CH<sub>3</sub>CHO] ≫ [OH]. OH decays were obtained over 2–3 lifetimes (0.5–30 ms). For all conditions, the OH decays exhibited exponential behavior and were fit by the following nonlinear expression:

$$[\text{OH}] = [\text{OH}]_0 \exp(-k't) + c$$

where  $k' = k[\text{CH}_3\text{CHO}] + k_d$  and  $c$  are an additional term accounting for background light levels. This expression was fitted by using the Levenberg-Marquardt method [19], an iterative  $\chi^2$  minimizing technique (least squares). The bimolecular rate coefficient  $k$  was separated from the diffusive rate coefficient,  $k_d$ , by fitting a weighted least-squares line ( $\omega_k = 1/\sigma_k^2$ ) through the ( $[\text{CH}_3\text{CHO}]$ ,  $k'$ ) data points. Plots of  $k'$  vs.  $[\text{CH}_3\text{CHO}]$  and  $[\text{CH}_3\text{CDO}]$  at 297 K are shown in Fig. 1. Plots of  $k'$  vs.  $[\text{CH}_3\text{CHO}]$  and  $[\text{CD}_3\text{CHO}]$  at 860 K are shown in Fig. 2. Typical uncertainties in  $k'$  at the 2 $\sigma$  level ranged from 5–10%. Typical uncertainties in the gas-phase substrate concentration were 3–5%.



**Figure 1** Plot of pseudo-first-order rate coefficient vs.  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{CDO}$  concentration at a temperature of 297 K.



**Figure 2** Plot of pseudo-first-order rate coefficient vs.  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{CDO}$  concentration at a temperature of 860 K.

## RESULTS AND DISCUSSION

Table I presents the rate measurements and associated experimental conditions. Error limits,  $\pm 2\sigma$ , based on a statistical error analysis, ranged from 3.5% to 17.8%. A 5% systematic error, largely due to uncertainties in substrate concentration in the reactor, is not included in this error limit. Measurements were possible up with this apparatus up to ca. 900 K. Thermal decomposition of the substrate under these experimental conditions is not a source of measurable ( $>5\%$ ) systematic error at temperatures below 1000 K [20].

Figure 3 presents an Arrhenius plot of the  $\text{CH}_3\text{CHO} + \text{OH}$  measurements (this work), the recommended three-parameter expression (298–528 K) for data published prior to 1990 [21], and more

recent experimental measurements at low temperatures [10,11,22–26]. The measurements at 297 K, ca. 20–30% higher than our previous results [1], are in good agreement with the recommendation of Atkinson [21] and the most recent measurements of Crowley et al. [10,26] and Wang et al. [11]. The higher temperature measurements, also ca. 20–30% higher than our previous results, verify the previously reported complex temperature dependence of the overall reaction [1]. The systematic error in our prior measurements is likely due to sample polymerization during storage in 2 L glass bulbs [1]. Each measurement presented here was derived from a freshly prepared sample, minimizing this source of error.

Figure 3 also presents a biexponential fit to experimental measurements published since 1990 including the present study. The results of Taylor et al. [1], approximately 20–30% lower than the present results, were excluded from the fit. A nonlinear least squares minimization algorithm resulted in the following expression (in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ):

$$k(202\text{--}860 \text{ K}) = 8.36 \times 10^{-11} * \exp(-2410.3/T) \\ + 4.34 \times 10^{-12} * \exp(368.9/T)$$

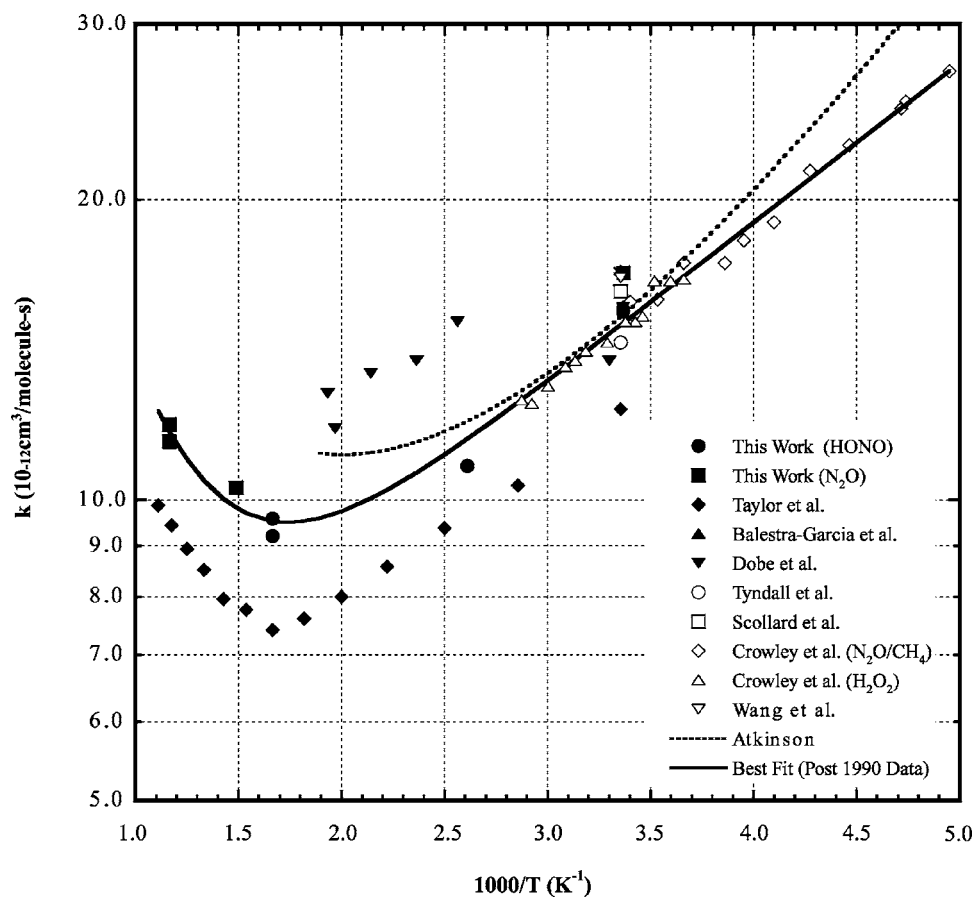
with deviations from the mean of experimental measurements of  $<1\%$  at 202 K,  $<7\%$  at 298 K,  $<1\%$  at 600 K, and  $<3\%$  at 860 K. This expression predicts a rate coefficient at 1500 K of  $2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

The purpose of these measurements was two-fold: (1) to verify the previously observed complex temperature dependence between 295 and 900 K; and (2) to acquire mechanistic information about the reaction mechanism in the form of primary kinetic isotope effects. As illustrated in Table II, a primary kinetic isotope effect (KIE) was observed for  $\text{CH}_3\text{CDO}$  at low temperature (297, 383, and 600 K) indicating H abstraction from the acetyl group dominates that from the methyl group at low temperature. A primary KIE for  $\text{CD}_3\text{CHO}$  was observed only at high temperature (860 K) indicating H abstraction from the methyl group dominates that from the acetyl group at high temperature.

There are two prior reports of KIE values for  $\text{CH}_3\text{CHO}/\text{CH}_3\text{CDO}$ . Taylor et al. [1] previously reported values at 298, 400, 600, and 750 K. The temperature-dependent trend in the previous results, a decreasing KIE with increasing temperature with values approaching unity above 750 K, is consistent with the present measurements. D'Anna et al. [15] have recently published KIE values for this reaction at 298 K. Their measurements are consistent with our present and prior observations, and lend further

**Table I** Rate Coefficients and Experimental Conditions for the Reactions of OH Radicals with Acetaldehyde and Deuterated Acetaldehyde

Temperature (K)	Substrate	OH Precursor	Substrate Concentration ( $\times 10^{12}$ molecules/cm <sup>3</sup> )	$10^{12}k$ cm <sup>3</sup> /molecules/s
297	CH <sub>3</sub> CHO	HONO	7.2–36	$15.46 \pm 2.22^a$
297	CH <sub>3</sub> CHO	N <sub>2</sub> O/H <sub>2</sub> O	2.8–19	$16.90 \pm 1.54$
297	CH <sub>3</sub> CDO	HONO	7.2–29	$9.65 \pm 0.68$
297	CD <sub>3</sub> CHO	N <sub>2</sub> O/H <sub>2</sub> O	3.1–21	$18.32 \pm 1.20$
298	CH <sub>3</sub> CDO	HONO	7.2–29	$9.15 \pm 1.28$
383	CH <sub>3</sub> CHO	HONO	5.5–33	$10.83 \pm 1.30$
383	CH <sub>3</sub> CDO	HONO	5.5–22	$6.70 \pm 0.74$
383	CH <sub>3</sub> CDO	HONO	11–33	$6.77 \pm 0.82$
600	CH <sub>3</sub> CHO	HONO	4.7–23	$9.58 \pm 1.42$
600	CH <sub>3</sub> CHO	HONO	22–86	$9.20 \pm 0.96$
600	CH <sub>3</sub> CDO	HONO	4.7–23	$6.76 \pm 1.20$
602	CD <sub>3</sub> CHO	N <sub>2</sub> O/H <sub>2</sub> O	5.0–33	$10.11 \pm 0.98$
672	CH <sub>3</sub> CHO	N <sub>2</sub> O/H <sub>2</sub> O	5.2–34	$10.30 \pm 0.98$
859	CH <sub>3</sub> CHO	N <sub>2</sub> O/H <sub>2</sub> O	15–43	$11.91 \pm 0.56$
860	CH <sub>3</sub> CHO	N <sub>2</sub> O/H <sub>2</sub> O	5.2–39	$11.45 \pm 0.40$
860	CH <sub>3</sub> CDO	N <sub>2</sub> O/H <sub>2</sub> O	2.9–14	$10.64 \pm 1.86$
861	CD <sub>3</sub> CHO	N <sub>2</sub> O/H <sub>2</sub> O	1.5–110	$7.14 \pm 0.94$

<sup>a</sup> Error limits represent  $\pm 2\sigma$  statistical uncertainties.**Figure 3** Arrhenius plot of kinetic data for the  $\text{CH}_3\text{CHO} + \text{OH}$  reaction. Also shown are recent experimental measurements (post-1990) [1,10, 22–26], Atkinson's temperature-dependent recommendation [21] based on pre-1990 measurements, and the biexponential fit of post-1990 measurements, excluding the data of Taylor et al. [1].

**Table II** Experimental Kinetic Isotope Effects for the Reactions of OH Radicals with Acetaldehyde

Temperature (K)	CH <sub>3</sub> CHO/ CH <sub>3</sub> CDO	CH <sub>3</sub> CHO/ CD <sub>3</sub> CHO
297	1.68 <sup>a</sup>	0.88 <sup>a</sup>
298	1.77 <sup>a</sup> 1.31 <sup>b</sup> 1.42 <sup>c</sup>	
383	1.61 <sup>a</sup>	
400	1.05 <sup>b</sup>	
600	1.39 <sup>a</sup> 1.01 <sup>b</sup>	
602		1.10 <sup>a</sup>
750	0.98 <sup>b</sup>	
860	1.10 <sup>a</sup>	
861		1.64 <sup>a</sup>

<sup>a</sup> This study.<sup>b</sup> From Taylor et al. [1].<sup>c</sup> From D'Anna et al. [15].

support for the proposed H abstraction mechanism at low temperatures.

The positive activation energy observed above about 700 K is consistent with simple H abstraction, cf. OH + ethane [7], but the negative activation energy at lower temperatures, also attributed to a C–H abstraction channel, deserves closer attention. The C–H bond in acetyl is unusually weak, as may be seen from the relative exothermicities of channels (1a) and (1b). In our prior study [1], we noted that while low levels of ab initio theory (HF and MP2) yielded saddle points for abstraction from the CHO group, when more rigorous calculations were applied at points along the reaction path, negligible barriers were derived. Here we evaluated the energy at the MP2 = full/6-31G(d) saddle point relative to reactants using Gaussian 03 theory (with the minor modifications that MP2 frequencies scaled by 0.95 were employed instead of scaled HF frequencies and the energy of OH was corrected for spin orbit splitting) [27,28]. The results are relative 0 K enthalpies of –10.1 and –7.4 kJ mol<sup>-1</sup> for direct OH attack on CH<sub>3</sub>CHO and CH<sub>3</sub>CDO, respectively. Application of simple transition state theory yields, over 200–400 K, approximate Arrhenius parameters of  $A \sim 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , with  $E_a \sim -8.6$  and  $-4.9 \text{ kJ mol}^{-1}$ , respectively. The computed  $k_{1a}$  is about  $5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for CH<sub>3</sub>CHO, about a factor of 3 too high at room temperature, while for CH<sub>3</sub>CDO the rate constant is too high by 20%. Thus the KIE and the temperature dependence of the rate constant are qualitatively reproduced, although  $k_{1a}$  for H abstraction is too large. The dominant flaw in this initial analysis is neglect of variational effects: the true

reaction bottleneck probably lies at a greater separation than indicated by MP2 theory, where the resulting rate constants will be smaller and will have a less negative  $E_a$ . A more detailed theoretical analysis of the entire potential energy surface and the corresponding kinetics is the topic of a forthcoming study.

## CONCLUSIONS

The complex temperature dependence of the CH<sub>3</sub>CHO + OH reaction has been verified. Primary kinetic isotope effect measurements at temperatures of 297, 383, 600, and 860 K indicate that H abstraction from the acetyl group dominates that of the methyl group at low to modest temperature ( $\leq 600 \text{ K}$ ), and H abstraction from the methyl group dominates that from the acetyl group at higher temperatures (860 K). A biexponential fit to all experimental measurements of the CH<sub>3</sub>CHO + OH reaction published since 1990, excluding our prior results [1] that were approximately 20–30% lower than the present results, resulted in the following expression (in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ):

$$k(202\text{--}860 \text{ K}) = 8.36 \times 10^{-11} * \exp(-2410.3/T) \\ + 4.34 \times 10^{-12} * \exp(368.9/T)$$

This expression is recommended for incorporation in both low temperature and high temperature models describing the transformation and fate of oxygenated pollutants.

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