The reaction of OH with acetone and acetone-d₆ from 298 to 832 K: Rate coefficients and mechanism

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The pulsed laser photolysis/pulsed laser-induced fluorescence technique has been applied to obtain rate coefficients for $\text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}_3$ and $\text{CD}_3\text{C}(\text{O})\text{CD}_3$ of $k_{\text{H}}(298\text{--}832\text{ K}) = (3.99 \pm 0.40) \times 10^{-24} T^{4.00} \exp(453 \pm 44)/T$ and $k_{\text{D}}(298\text{--}710\text{ K}) = (1.94 \pm 0.31) \times 10^{-21} T^{3.17} \exp(-529 \pm 68)/T \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. Three pathways were characterized via the CBS-QB3 *ab initio* method to obtain complete basis set limits for coupled-cluster theory. Addition to form $\text{CH}_3\text{C}(\text{O})(\text{OH})\text{CH}_3$, followed by dissociation to $\text{CH}_3 + \text{CH}_3\text{C}(\text{O})\text{OH}$, is negligibly slow. Variational transition state theory reveals that the dominant products are $\text{CH}_3\text{C}(\text{O})\text{CH}_2 + \text{H}_2\text{O}$ formed by direct abstraction at higher temperatures and via a hydrogen-bonded complex below about 450 K. Inclusion of tunneling gives good accord with the observed kinetic isotope effect down to about 250 K. © 2003 American Institute of Physics. [DOI: 10.1063/1.1619950]

I. INTRODUCTION

The hydroxyl radical plays a central role in both atmospheric and combustion chemistry. Oxygenated species such as alcohols, aldehydes, ketones, and ethers have important roles in combustion, and the kinetics of OH attack on acetone at elevated temperatures is the subject of this investigation. The atmospheric lifetime of acetone is controlled by photolysis and OH attack. Its degradation products may be a source of HO_x in the troposphere,¹ and therefore mechanistic information is important. This motivates our study of deuterated acetone, especially as there are several contradictions in the recent literature, as noted below.

Previous measurements of the $\text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}_3$ rate coefficient k are plotted in Fig. 1,^{2–9} and it may be seen that while different experiments have yielded different activation energies, overall there is good agreement between the magnitude of the k values. There is an unusual temperature dependence, with k increasing with T above room temperature, and decreasing much more slowly, or perhaps even increasing slightly, at lower temperatures. Different explanations have been offered.

Wollenhaupt *et al.*⁵ speculated that $\text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}_3$ exhibits a change in mechanism, with addition dominating at lower temperatures. They later determined yields of CH_3 , a likely product of an addition/elimination channel also producing acetic acid, to be 50% and 30% at 298 and 200 K, respectively,¹⁰ consistent with *less* addition at lower temperatures. Vasvári *et al.* measured a 50% yield of acetylonyl, the H-abstraction product, at 298 K.⁶ By contrast, Vandenberg *et al.*¹¹ and Tyndall *et al.*¹ found no evidence for acetic acid formation (upper limits of 3% and 10%, respectively) at

room temperature. Talukdar *et al.* very recently published an even lower limit for acetic acid formation, below 1%, and reported a $96\% \pm 11\%$ yield of acetylonyl.¹²

Previous computational studies are also contradictory. Vasvári *et al.* argued for OH abstraction from C–H bonds via a transition state (TS) in the plane of the carbon atoms, or addition to the central carbon atom normal to this plane, with weakly bound adducts at the entrances of both paths.⁶ They commented that the high barrier they found for formation of a covalently bound adduct was inconsistent with their observations, and that a new unidentified mechanism might operate at low temperatures. Vandenberg *et al.* presented a qualitatively different potential energy surface, with channels for addition, direct abstraction and abstraction via a hydrogen-bonded intermediate.¹¹ They commented that if the energy of the tight exit TS from this intermediate was lower or comparable to the energy of the loose TS for entering the intermediate, then a negative activation energy may be expected. Vandenberg *et al.* in fact calculated a higher energy exit TS, but suggested their results might be an overestimate. In an initial presentation we argued for a similar set of three channels.¹³ Very recently, Henon *et al.*¹⁴ have expanded their original potential energy diagram⁶ to include two hydrogen abstraction pathways leading to water plus acetylonyl formation, both with entrance adducts. Henon *et al.* concluded with several open issues, including: can the measured low-temperature activation energy which is close to zero be reconciled with the significant barriers computed for H-abstraction? Can hydrogen-bonded complexes be stabilized by collision, and are they exit channels for the reaction of OH with acetone?

In the present work we address these issues, and present new, direct measurements of the reactions

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FIG. 1. Arrhenius plot of rate coefficients for $\text{OH} + \text{CD}_3\text{C}(\text{O})\text{CD}_3$, ■, this work, and $\text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}_3$; ●, LP-LIF with HONO precursor, this work; +, LP-LIF with $\text{N}_2\text{O}/\text{H}_2\text{O}$ precursor, this work; lines, best fits to this work; △, Vasvari *et al.* (Ref. 6); ▼, Wollenhaupt *et al.* (Ref. 5); ○, Le Calvé *et al.* (Ref. 4); □, Wallington and Kurylo (Ref. 3); ◇, Bott and Cohen (Ref. 7); ▲, Tranter and Walker (Ref. 8); ◻, Gierczak *et al.* (Ref. 9); ▲, $\text{OH} + \text{CD}_3\text{C}(\text{O})\text{CD}_3$, Gierczak *et al.* (Ref. 18); and ×, Atkinson *et al.* (Ref. 2).

from ambient conditions up to temperatures of 832 K, obtained by the pulsed laser photolysis–laser induced fluorescence (PLP/LIF) technique. This range bridges the gap between data from low-temperature^{4,5} and high-temperature techniques.^{7,8} Possible reaction paths have been investigated with high-level *ab initio* methods, and the experimental results are interpreted quantitatively via variational transition state theory.¹⁵ An overall mechanism and rationalization of the unusual temperature dependence of k is proposed.

II. EXPERIMENTAL APPROACH AND DATA REDUCTION

The apparatus and experimental procedures are well established.^{16–18} In brief, OH was generated in the presence of a large excess of acetone by excimer laser photolysis of a precursor, and monitored by off-resonance laser-induced fluorescence excited at 282 nm. Most experiments were conducted with HONO as the OH source, photolyzed at 351 nm to minimize acetone photolysis between 200 and 340 nm. H-atom production is negligible.⁵ Parts per million concentrations of pure HONO (>99%) were generated as described by Febo *et al.*¹⁹ and Brust *et al.*²⁰ Initial $[\text{OH}]_0$ ranged from $\sim 3\text{--}9 \times 10^{10}$ molecules cm^{-3} , determined from the measured laser fluence (9–18 mJ cm^{-2}); the absorption cross

section for HONO, 1.54×10^{-19} cm^2 molecule⁻¹ at 351 nm;²⁰ a quantum yield of unity;²¹ and measured values of $[\text{NO}_2^-]$ taken to represent $[\text{HONO}]$ determined using ion chromatography ($\sim 1\text{--}3 \times 10^{13}$ molecule cm^{-3}). Above about 725 K, HONO dissociates and OH signals decrease unacceptably (S/N ratio <10). Two measurements were subsequently made using 193 nm photolysis (ca. 1 mJ cm^{-2}) of $\text{N}_2\text{O}/\text{H}_2\text{O}$ mixtures as the OH source to show internal consistency between the two OH precursors (685 K) and to extend the measurements to slightly higher temperatures (832 K).

Acetone stock samples were prepared in 2 L glass bulbs, where the acetone pressure was measured with an absolute pressure transducer (MKS Type 622) before dilution. The prepared acetone sample was introduced into the experimental system using a syringe pump (KDS100, KD Scientific). Acetone concentrations in the reactor of $\sim (1\text{--}8) \times 10^{15}$ molecule cm^{-3} were determined from the measured mass flow rate (Porter Instruments, model VCD 1000) of the diluted acetone, the total gas flow and the overall 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 735 ± 10 torr with helium as the bath gas. High purity samples (>99.9%) of acetone and acetone- d_6 were obtained from Aldrich, Inc. and used as received, and 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_2 or HCl ($< 1.2 \times 10^{12}$ molecule cm^{-3}).

Decay constants k' for exponential decays of OH LIF signals under our pseudo-first-order conditions, $[\text{CH}_3\text{C}(\text{O})\text{CH}_3] \gg [\text{OH}]$, were obtained over 2–3 lifetimes (0.5–30 ms). The bimolecular rate coefficient k was found as the slope of a linear plot of k' versus $[\text{CH}_3\text{C}(\text{O})\text{CH}_3]$.^{16–18} The intercept is k_d was measured before and after a rate determination and observed to be constant within experimental uncertainties, indicating that the HONO source was stable. Typical values of k_d decreased with increasing temperature, from ~ 350 s^{-1} to ~ 50 s^{-1} , suggesting a decrease in the rate of OH with its precursor HONO or a reduction in the background concentration of reactive carrier gas impurities.

III. EXPERIMENTAL RESULTS

Data were obtained from 298 to 832 K and are given in Tables I and II. Random error limits ($\pm 2\sigma$) were typically <15% for k_{H} and typically <20% for k_{D} . These values are derived from the statistical uncertainties of the slopes of the plots of k' versus reactant concentration. The uncertainty for the total flow rate was estimated to be 2%. The uncertainty in the syringe pump injection rate is <1% and the uncertainty in pressure is <0.15% based on the manufacturer's specifications. These combine to give an uncertainty in the acetone concentration of approximately 2.2%, which is relatively small compared to the statistical error. Our new measurements and previous rate measurements for k_{H} and k_{D} are

TABLE I. Absolute rate coefficients for OH+acetone.

Temperature K	Substrate conc. 10^{15} molecule cm^{-3}	$k_H \pm \sigma_{kH}$ 10^{-13} cm^3 molecule $^{-1}$ s $^{-1}$
298	1.5–7.7	1.56 ± 0.08
310	1.5–7.6	1.58 ± 0.07
324	1.2–7.8	1.82 ± 0.18
339	1.1–6.7	1.97 ± 0.06
355	1.2–7.8	2.13 ± 0.12
373	1.1–6.8	2.21 ± 0.26
390	1.3–7.6	2.85 ± 0.18
414	1.1–6.8	3.69 ± 0.13
439	1.1–4.3	4.55 ± 0.27
467	0.8–4.8	4.76 ± 0.34
498	0.7–3.7	6.05 ± 0.62
534	0.8–3.9	8.22 ± 0.17
575	0.7–3.5	9.49 ± 0.17
628	0.6–2.5	11.9 ± 1.2
681	0.4–2.1	15.6 ± 1.1
685 ^a	0.11–0.55	21.1 ± 1.3
710	0.2–1.5	19.3 ± 1.3
832 ^a	0.05–0.50	32.5 ± 1.6

^aN₂O/H₂O mixture used as OH precursor instead of HONO.

summarized in Fig. 1. Our room temperature measurements are $\sim 40\%$ lower than the Atkinson *et al.*² recommendation based on pre-1997 data. The more recent measurements of Le Calvé *et al.*,⁴ Wollenhaupt *et al.*,⁵ and Vasvári *et al.*⁶ are more consistent with our measurements, all lying $\sim 12\%$ – 13% higher, and that of Tranter and Walker⁸ at 753 K, derived from the influence of acetone on H₂/O₂ chemistry, is 20% higher. Gierczak *et al.*⁹ recently published kinetic measurements of OH, OD, and ¹⁸OH with acetone and acetone-*d*₆. Their results also indicate 14% and 31% higher rate constants at 298 K compared to our results for acetone and acetone-*d*₆, respectively. Wollenhaupt *et al.* and Gierczak *et al.* conducted *in situ* optical measurements of the acetone concentration. These comparisons indicate that there may be some small systematic error in our rate measurements, perhaps associated with loss of acetone during transport through the reactor.

TABLE II. Absolute rate coefficients for OH+acetone-*d*₆.

Temperature K	Substrate conc. 10^{15} molecule cm^{-3}	$k_D \pm \sigma_{kD}$ 10^{-13} cm^3 molecule $^{-1}$ s $^{-1}$
298	2.8–6.9	0.229 ± 0.032
310	3.2–7.9	0.279 ± 0.017
324	1.6–8.1	0.330 ± 0.033
339	2.9–7.3	0.498 ± 0.056
355	4.6–7.7	0.640 ± 0.045
373	1.4–7.2	0.710 ± 0.045
389	1.7–8.6	0.815 ± 0.060
414	1.5–6.3	1.09 ± 0.02
439	0.7–4.4	1.26 ± 0.11
467	0.8–6.3	1.79 ± 0.12
498	0.7–3.7	2.81 ± 0.14
534	1.1–3.0	3.32 ± 0.27
578	0.7–4.3	4.10 ± 0.37
624	0.7–3.2	5.78 ± 0.39
681	1.5–3.9	9.06 ± 0.48
710	1.1–3.7	10.4 ± 0.57

FIG. 2. Potential energy diagram for OH+CH₃C(O)CH₃ showing enthalpies relative to reactants at 0 K, derived via the CBS–QB3 method. Energies of the abstraction transition states TS1 and TS2 were derived via the IRC-max approach (see text).

Our extended temperature measurements exhibit non-Arrhenius behavior with the data best fit by the following three-parameter expression (in units of cm^3 molecule $^{-1}$ s $^{-1}$):

$$k_H(298-832 \text{ K}) = (3.99 \pm 0.40) \times 10^{-24} T^{4.00} \times \exp(453 \pm 44)/T.$$

Error limits are 2σ values. Extrapolation to combustion temperatures is consistent with the shock-tube data of Bott and Cohen⁷ at 1200 K.

Measurements with acetone-*d*₆ indicated a substantial kinetic isotope effect as illustrated in Fig. 1. The modified Arrhenius equation also best describes these data and is given by (in units of cm^3 molecule $^{-1}$ s $^{-1}$):

$$k_D(298-710 \text{ K}) = (1.94 \pm 0.31) \times 10^{-21} T^{3.17} \times \exp(-529 \pm 68)/T.$$

IV. THEORETICAL ANALYSIS

A. Methodology

Geometries, and frequencies scaled by 0.99,²² of stationary points on the potential energy surface were characterized at the B3LYP/6-311G(*d,p*) level of theory (this information is listed in Table IS and the structures are shown in Fig. 1S), followed by single-point energy evaluations via CBS–QB3 theory,²² which includes zero-point vibrational energy (see Table IIS).²³ This methodology approximates a coupled cluster CCSD(T) calculation extrapolated to the complete basis set limit, and reproduces dissociation energies of neutral molecules in the G2 “test set” with a mean absolute deviation of 2.4 kJ mol $^{-1}$.²² The GAUSSIAN 98 program²⁴ was employed for the quantum calculations. The energy of OH was corrected by -0.8 kJ mol $^{-1}$ to account for spin–orbit splitting between the ²Π_{1/2,3/2} states. Reaction coordinates, and frequencies and energies along them, were obtained with the same methods. The highest point along the reaction path corresponds to the “IRCmax” barrier height at 0 K,²⁵ and these barriers and bound minima are summarized in Fig. 2. This approach avoids potential difficulties with poorly character-

ized single-point TS geometries, which will lead to underestimated barrier heights, and provides the information necessary to apply variational transition state theory and reliable tunneling corrections.

B. Reaction paths

Three reaction paths are identified in the present work. The first, (1), involves approach of the hydroxyl radical H-first towards the carbonyl oxygen in the plane of the carbon atoms and formation of a hydrogen bonded adduct, as described by Aloisio and Francisco.²⁶ The O atom in OH then swings towards a coplanar C–H bond and abstracts an H atom, to form ultimately $\text{H}_2\text{O} + \text{CH}_3\text{COCH}_2$. These same products can be reached via a second pathway, (2), where OH attacks one of the C–H bonds out of the plane of the carbon atoms. In this geometry the H in OH is too far away from the carbonyl O atom to form a hydrogen bond and no adduct is involved. The third pathway (3) is addition of OH to the central carbon atom and rupture of the carbonyl π bond, to form a covalently bonded adduct $\text{CH}_3\text{C}(\text{O})(\text{OH})\text{CH}_3$. This chemically activated adduct will have sufficient energy to eliminate CH_3 rapidly and form the most stable product, acetic acid.

As noted in the Introduction, past studies present a confusing picture of the reaction mechanism. Our computations support the general scheme proposed by Vandenberg *et al.*¹¹ We now make quantitative comparison with the measured kinetics.

C. Methyl elimination

First we consider the rate coefficient k_3 for addition to make $\text{CH}_3\text{C}(\text{O})(\text{OH})\text{CH}_3$, which will dissociate immediately to methyl plus acetic acid.¹¹ A conventional transition state theory (TST) analysis^{15,27}

$$k = \Gamma I^\ddagger \frac{Q_{\text{TS}}}{Q_{\text{reactants}}} \exp\left(-\frac{E_0}{RT}\right)$$

was applied, using CBS–QB3 information at the B3LYP/6-311G(*d,p*) saddle point along the reaction coordinate. The partition functions Q were obtained via the harmonic oscillator-rigid rotor approximation, except that internal rotors were identified and quantified according to the method of Ayala and Schlegel.²⁸ For the addition process the tunneling correction is negligible ($\Gamma \approx 1$) and the energy barrier (including zero-point energy) E_0 is 14.7 kJ mol^{-1} . Rotational symmetry numbers are ignored and instead symmetry is taken into account via the reaction path degeneracy $I^\ddagger$, equal to 2 here. This procedure gives an upper limit to the variational CBS–QB3 rate coefficient, and is negligibly small: $9 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature. This result confirms the value of k_3 calculated by Vandenberg *et al.*,¹¹ and like them we note that TS3 is particularly unfavorable in terms of entropy. Over 300–700 K the average pre-exponential factor for addition is only $2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This low value would make addition a minor channel even if the barrier were reduced by as much as 10 kJ mol^{-1} . Further, the kinetic isotope effect (KIE) is computed to increase from 0.7 at 200 K to 0.9 at

1000 K, at variance with the trend and magnitude of the measured KIE discussed below. At room temperature k_3 is computed to be $<0.1\%$ of the measured k_{H} and so the addition channel is not considered further.

Alternative paths to CH_3 formation were noted by Henon *et al.*¹⁴ These are based on decomposition of acetonyl complexed with water to $\text{CH}_3 + \text{CH}_2\text{CO}$. Very high barriers of around 90 kJ mol^{-1} were derived,¹⁴ so these channels cannot contribute to the observed kinetics.

D. Direct abstraction

The rate coefficient for the direct abstraction channel, k_2 , was obtained by evaluation of the TST equation at points along the reaction coordinate, with $I^\ddagger = 4$, followed at each temperature by interpolation to find the minimum, i.e., variational, canonical TST rate coefficient.¹⁵ A one-dimensional tunneling correction was derived by fitting an Eckart potential²⁹ to the CBS–QB3 energies along the reaction coordinate, which include zero-point vibrational energy. The Eckart potential provides a convenient extrapolation of the vibrationally adiabatic reaction coordinate to the asymptotic limits for reactants and products, in regions far from TS2. Transmission coefficients were derived using reduced masses of 1 and 2 amu for H- and D-atom transfer, respectively. This kind of procedure³⁰ avoids problems associated with imaginary frequencies obtained from the wrong curvature of a reaction coordinate computed at a low level of theory.³¹ The imaginary frequency for TS2 derived from CBS–QB3 energies is $901i \text{ cm}^{-1}$, significantly different from the B3LYP/6-311G(*d,p*) harmonic value of $513i \text{ cm}^{-1}$.

We refer to this pathway as “direct” meaning there is no strongly bound adduct in the entrance channel. Naturally, very weak van der Waals complexes may potentially exist between almost any pair of molecules. Henon *et al.* recently argued for an entrance adduct in path (2), bound by about 8 kJ mol^{-1} .¹⁴ We are unable to reproduce their given MP2/6-31G(*d,p*) structure for this complex “MC1b,”¹⁴ and instead optimizations starting from this geometry led ultimately to their “MC1” structure. Our own B3LYP/6-311G(*d,p*) searches did not reveal a bound intermediate in this region.

E. Abstraction via a complex

The rate coefficient k_1 for the abstraction channel involving a hydrogen-bonded adduct was initially analyzed according to the scheme advocated by Alvarez-Idaboy *et al.*³² for prereactive complexes

$$k_1 = \left(\frac{k_a}{k_{-a}}\right) k_b = K_{\text{eq}} k_b, \quad (1)$$

where k_a and k_{-a} describe formation and redissociation of the adduct and k_b describes rearrangement of the adduct to the H-abstraction TS1. k_b was evaluated as described for k_2 , with $I^\ddagger = 2$, and the ratio k_a/k_{-a} was evaluated as the equilibrium constant K_{eq} for adduct formation, derived from the partition functions and the computed 0 K binding enthalpy DH_0 of 20.1 kJ mol^{-1} .

FIG. 3. Comparison of experimental and variational transition state theory (VTST) rate coefficients for $\text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}_3$: dotted lines, k_1 , VTST for abstraction via hydrogen-bonded complex, and k_2 , VTST direct abstraction; dashed line, $k_{\text{TOT}} = k_1 + k_2$; solid lines, experimental k_{H} from this work (higher temperatures) and Wollenhaupt *et al.* (Ref. 5, lower temperatures).

The hydrogen-bonded adduct has been postulated as a possible final product for OH consumption by acetone.^{14,26} It is important to note that K_{eq} is small—at 200 K it is about $1.1 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1}$ —and K_{eq} decreases as the temperature is raised. Aloisio and Francisco²⁶ previously derived $\text{DH}_0 = 19.2 \text{ kJ mol}^{-1}$, with which we agree closely, but presented a much larger K_{eq} value at 200 K that appears to be in error, due in part to an incorrect temperature dependence for DH. Using computed $\text{H}_7 - \text{H}_0$ for fragments and complex we obtain DH_{200} of 22.0 kJ mol^{-1} , which may contrasted to the earlier value of 30.1 kJ mol^{-1} at this temperature.²⁶ The small value of K_{eq} means that even in an experiment with a very high (as compared to the troposphere) acetone partial pressure of 1 Torr, less than 1 part in 10^3 of OH radicals would be complexed by hydrogen bonding at 200 K. Even smaller fractions would be complexed at higher temperatures. Thus the hydrogen-bonded complex cannot be a final sink for OH and k_a , which may well have a negative temperature dependence, does not describe a rate-limiting step and does not contribute directly to the temperature dependence of k_1 at temperatures down to 200 K.

F. Comparison with experimental rate coefficients

Results for k_1 and k_2 are plotted on Fig. 3. TS1 is stabilized relative to TS2 by intramolecular hydrogen bonding (IRCmax barriers of 8.3 versus 11.6 kJ mol^{-1}), and so k_1 is dominant at low temperatures. This hydrogen bonding also lowers the entropy, and together with the greater reaction path degeneracy for direct abstraction, causes a switch in dominant pathway above about 450 K. Both channels of course lead to the same products, acetyl plus water, in accord with the more recent product studies.^{1,11} It may be seen that the sum $k_1 + k_2$ closely reproduces the measured temperature dependence of k_{H} , although the total rate coef-

ficient is around a factor of 3 too small. We have not attempted to adjust arbitrarily any computed parameters to loosen the TSs and improve this agreement.

k_2 exhibits a “conventional” temperature dependence, with moderate curvature in the Arrhenius plot similar to that found for example for $\text{OH} + \text{CH}_4$,^{33,34} whereas k_1 shows stronger non-Arrhenius behavior. This reflects (i) the temperature dependence of the partition functions in the region of TS1, (ii) greater tunneling through TS1 than TS2, particularly below room temperature, because of the former transition state’s greater curvature, and (iii) a role for the entrance complex. As noted by Alvarez-Idaboy *et al.*,³² for a classical treatment the influence of the complex exactly cancels in Eq. (1) and the overall rate coefficient depends only on properties of OH, acetone and TS1. However, if there is a possibility of quantum mechanical tunneling through TS1, then the existence of the complex means there are extra energy levels from where tunneling may occur so that the tunneling factor Γ increases. Alvarez-Idaboy *et al.*³² assumed that a thermal equilibrium distribution of energy levels was maintained, which corresponds to high-pressure limiting behavior. Thus energy levels from the bottom of the well of the complex up to the barrier might contribute to tunneling. Such extra levels are not available to the direct abstraction mechanism. With contributions of levels from energy $E = -20.1 \text{ kJ mol}^{-1}$ relative to $\text{OH} + \text{acetone}$ (i.e., from the bottom of the complex) on up, the calculated imaginary frequency for TS1 is 976 cm^{-1} for H transfer and Γ for k_1 at 200, 300, 500, and 700 K is 13.5, 2.7, 1.4, and 1.2, respectively.

If instead Γ is calculated using levels from $E = 0$ and up, then the corresponding values are 6.2, 2.3, 1.4, and 1.2, respectively. These two extremes correspond to the infinite and zero-pressure limiting cases, where in the latter situation the lack of collisional stabilization means that none of the OH + acetone entrance complexes can reach energies below that of the reactants. From this comparison we see that for our experimental temperature range the reactive contribution from levels with $E < 0$ (bound levels in the hydrogen-bonded complex) is minor.

G. Influence of pressure and the kinetic isotope effect

The tunneling factor Γ is sensitive to the occupation of energy levels at $E < 0$, and therefore to details of collisional energy transfer. Below room temperature, pressure effects could in principle change k_1 by up to factor of 2, although a large range in pressure would be needed to achieve this. Typical experimental conditions would likely not reveal a large pressure effect.

A sensitive test of the accuracy of our tunneling model is the kinetic isotope effect, $\text{KIE} = k_{\text{H}}/k_{\text{D}} = (k_1 + k_2)_{\text{H}} / (k_1 + k_2)_{\text{D}}$. The test can be extended to below room temperature with recent data from Ravishankara’s group,³⁵ and as shown in Fig. 4 there is excellent accord between theoretical and measured KIEs over a wide range of temperature. Deviations from the experimental KIE near 200 K might reflect the extreme sensitivity to minor variations in the barrier fitting to obtain transmission coefficients and/or the challenges of measuring the small k_{D} at the lowest temperatures.

FIG. 4. Comparison of experimental and theoretical kinetic isotope effects for $\text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}_3$: upper dashed line, variational transition state theory at the high-pressure limit; lower dotted line, calculations for low-pressure limit; solid lines, experiment from this work (higher temperatures) and presented by Smith and Ravishankara (Ref. 35, lower temperatures).

The KIE computed at the low-pressure limit (lower curve on Fig. 4) is in better accord with experiment than the high-pressure limiting values (the corresponding k_{H} values are smaller and further from experiment however). To test whether this is plausible we need to assess whether collisions with the bath gas are likely to stabilize energy levels of the adduct below the energy of the reactants. We do this through examination of adduct formation (k_a and k_{-a}) via a quantum RRK model.³⁶ We assumed a high-pressure limit for k_a of $10^{-10} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$. At 200 K, even at 10 bar pressure of Ar, we predict third-order behavior for k_a . This is further evidence that adduct formation per se does not contribute to the overall k_{H} which is observed to be pressure independent. This third-order behavior implies that the distribution of energy levels in the adduct is far from equilibrium.

V. CONCLUSIONS

New measurements of k_{H} bridge the gap between shock tube and lower temperature data, and data for the deuterated analog have been obtained at elevated temperatures. Computational analysis reproduces the observed temperature dependences and the kinetic isotope effect, and suggests that the dominant products are $\text{CH}_3\text{COCH}_2 + \text{H}_2\text{O}$ at all temperatures. Above about 450 K direct abstraction is most important, and below this temperature the dominant reaction channel involves a hydrogen-bonded complex and substantial quantum mechanical tunneling. This is in accord with the recent suggestion of Smith and Ravishankara.³⁵

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