



An experimental and theoretical study on the kinetic isotope effect of C_2H_6 and C_2D_6 reaction with OH



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ABSTRACT

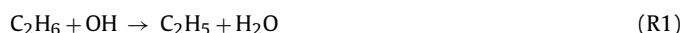
We report experimental and theoretical results for the deuterated kinetic isotope effect (DKIE) of the reaction of OH with ethane (C_2H_6) and deuterated ethane (C_2D_6). The reactions were investigated behind reflected shock waves over 800–1350 K by monitoring OH radicals near 306.69 nm using laser absorption. In addition, high level CCSD(T)/cc-pV(T,Q)Z//MP2/cc-pVTZ quantum chemical and statistical rate theory calculations were performed which agreed very well with the experimental findings. The results reported herein provide the first experimental evidence that DKIE asymptotes to a value of 1.4 at high temperatures.

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1. Introduction

Small alkanes (<C5) constitute almost all of the composition of natural and liquefied petroleum gas (LPG), whereas larger straight or branched alkanes ($\geq C_5$) are the primary constituents of gasoline, diesel and aviation fuels [1–4]. Hydrogen abstraction reactions from alkanes by hydroxyl radicals ($OH + RH \rightarrow R + H_2O$) are the primary oxidation pathways of these fuels at combustion conditions. Accurate modeling of combustion kinetics requires precise knowledge of total and site-specific rate coefficients over a wide range of temperatures and pressures. A conventional way to derive overall and site-specific rate coefficients is to start from small molecules and then use group additivity approximations to estimate rate coefficients for long chain molecules. Various approximations have been used in the literature, such as the Next-Nearest-Neighbor (NNN) [5,6] and Structure Activity Relationship (SAR) [7]. Tully et al. [8–13] pioneered the use of deuterium for the study of deuterium kinetic isotope effect (DKIE) to elucidate rules for the calculation of site-specific rates of H-abstraction from a variety of hydrocarbon molecules. This methodology has, for example, been used to discern the branching ratios of the two competing channels during the reaction of propane (C_3H_8) with OH at low temperatures [10] and high temperatures [14]. Recently, Badra et al. [15] published

experimental results and detailed kinetic analysis on the application of DKIE to extract branching ratios of the three competing channels during the reaction of propene (C_3H_6) with OH radicals at high temperatures [15]. The importance of DKIE of small molecules such as ethane, ethylene and acetylene in the determination of branching ratios of longer chain alkanes, alkenes and alkynes is demonstrated therein [15]. The aim of the current work is to extend low-temperature (290–800 K) DKIE data of ethane [9] to high temperatures (800–1350 K) using rate coefficient measurements of the reaction of ethane and deuterated ethane with OH radicals:



These results will be helpful in elucidating the competition of different H-abstraction channels during the reaction of larger alkanes with OH radicals. Moreover, a closer look into the database for the rate coefficients of R1 reveals that there are only three direct high-temperature ($T > 950$ K) measurements available in the literature [16–18]. Much of the earlier studies are limited to near room temperatures [9,16,17,19–23]; and in general they show excellent agreement to each other within overall uncertainties of $\pm 20\%$ at 298 K [19]. Surprisingly, there are not many reports of theoretical rate constant estimations using the electronic structure methods other than two studies from Krasnoperov and Michael [18] and Melissas and Truhlar [24]. The later employed PMP2//MP2/adj2-cc-pVTZ level of theory to compute the potential energy surface for the reaction of ethane with OH radicals. They computed the

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rate constants using *ab initio* and canonical variational transition state theory calculations with small curvature tunneling corrections. Their calculated values were found to agree well with the experiments within a factor of 2.3 over a wide range of temperatures. Krasnoperov and Michael [18] used B3LYP/6-31G* level of theory to map out the potential energy surface for ethane + OH reaction. They had to adjust the barrier height to 10.2 kJ/mol and one of the low bending mode was taken as 250 cm^{-1} to achieve good match with the available experimental data over $140 \leq T/K \leq 1600$. They further suggested that a high level theory should be used to study the reaction between ethane and OH. As for R2, there is only one experimental study from Tully et al. [9] at relatively low temperatures and no theoretical reports are found in literature. The current work thus aims to report the theoretical DKIE for ethane/d-ethane + OH reaction using high-level quantum chemical and statistical rate theory calculations.

2. Experimental setup

The low-pressure shock tube facility (LPST) at King Abdullah University of Science and Technology (KAUST) was used to conduct all experiments presented here. As the details of our experimental facility could be found elsewhere [25], only a brief description is provided here. The LPST has 9 m long driver and driven sections with an inner diameter of 14.2 cm. The length of the driver section is modifiable depending on the required test time. Optical windows were installed at the sidewall location, 20 mm from the end wall of the shock tube. Shock tube was pumped down to less than 10^{-5} mbar using turbo-molecular pump prior to each experiment to ensure high purity of the shock tube. The shock tube was found to have a leak rate of $<1 \times 10^{-6}$ mbar/min. All experiments reported here were conducted behind reflected shock waves, and the conditions (T_5 , P_5) were calculated by measuring the incident shock speed and using Rankine–Hugoniot shock-jump relations [26,27] embedded in the Frosh code [28].

Hydroxyl radicals were produced by rapid thermal decomposition of tert-butyl hydroperoxide (TBHP), which is known to be a clean thermolytic source of OH radicals and had been validated in many earlier studies [25,29,30]. Hydroxyl radicals were measured by using the well-characterized R1(5) absorption line in the (0,0) band of the $A^2 \Sigma^+ \leftarrow X^2 \Pi$ OH transition near 306.7 nm. Measured absorbance time–history was converted to OH concentration time–history using the Beer–Lambert law. A 70% TBHP in water solution was obtained from Sigma Aldrich. Ethane (99.99%), argon (99.999%), and helium (99.999%) were purchased from AH Gases. Ethane- d_6 (98%) was obtained from CDN Isotopes Inc. Several reflected-shock experiments were conducted for each fuel (C_2H_6 and C_2D_6) and the concentrations of reactants (fuel, TBHP) were chosen based on sensitivity analyses to achieve pseudo-first-order kinetics.

3. Quantum chemical calculations

Molecular and transition state geometries were optimized at the MP2/cc-pVTZ level of theory [31–33] applying the ‘tight’ convergence criterion of the GAUSSIAN09 program package [34]. The MP2/cc-pVTZ harmonic vibrational wavenumbers of the molecules and transition states were scaled by a factor of 0.95 adopted from CCCBDB database [35]. Similar to previous works [36–38], the accurate description of the electronic structures was approximated by extrapolation schemes. While Feller extrapolation [39] was utilized for HF energies (using cc-pVXZ basis sets, where $X=D, T$ and Q [31]), Helgaker extrapolation [40] for CCSD(T) correlation energies [41] was applied with cc-pVTZ and cc-pVQZ basis sets. Sum of these extrapolated energies manifested in

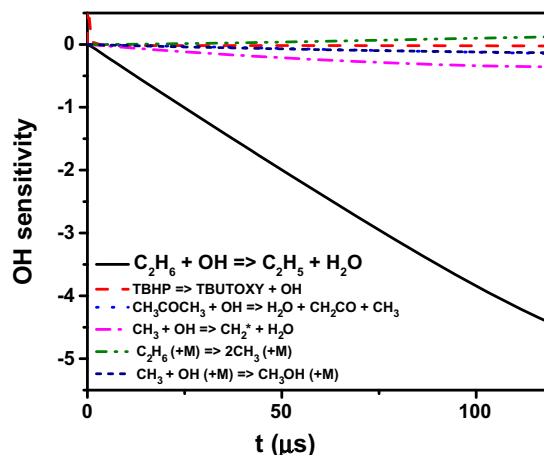


Figure 1. Hydroxyl sensitivity for $C_2H_6 + OH$ reaction at 1106 K and 1.38 atm. OH sensitivity is defined as $S_{OH} = (\partial X_{OH} / \partial k_i) \times (k_i / X_{OH})$, where X_{OH} is the local OH-mole fraction and k_i is the rate constant for the i th reaction. Initial mixture composition: 342 ppm ethane, 22.4 ppm TBHP (70 ppm water) diluted in argon.

CCSD(T)/cc-pV(T,Q)Z//MP2/cc-pVTZ level of theory which is chosen to establish high-level *ab initio* description of the zero-point corrected relative energies (ΔE_0) for both isotopologues (C_2H_6 and C_2D_6).

The rate constants for ethane + OH and ethane- d_6 + OH were calculated using canonical transition state theory (CTST) with the molecular parameters from our *ab initio* calculations. In these CTST calculations, all species were assumed to be in the electronic ground state except OH, for which the electronic partition function was calculated with a spin orbit splitting of 139.7 cm^{-1} [42]. One low lying bending mode corresponding to C–C rotation in the reactants and two of the low frequency torsional modes of the transition states corresponding to C–C and OH rotations were treated as hindered rotors within Pitzer–Gwinn [43] approximations. Rate calculations were carried out using ChemRate code [44].

4. Results and discussion

The JetSurf 1.0 mechanism [45] is used as the base mechanism and tert-butyl hydroperoxide (TBHP) chemistry from Pang et al. [46] is added to the base mechanism to simulate OH-time histories. Sensitivity analysis was performed to explore the role of secondary reactions that might affect OH concentration time-profile in our experimental conditions. As can be seen in Figure 1, the secondary chemistry has negligible contribution to OH-decay profile. Measurements for R1 were carried out in the temperature range of 847–1285 K using a mixture of 342 ppm of ethane with 22.4 ppm TBHP diluted in argon, whereas the measurements of R2 ranged from 805 to 1345 K using a mixture of 310 ppm of ethane- d_6 with 22.2 ppm TBHP diluted in argon. To ensure pseudo-first order kinetics, the concentration of TBHP was always kept at least 10 times smaller than that of ethane or ethane- d_6 . The rate coefficients of reactions R1 and R2 are obtained by fitting the simulated OH time profiles to the experimental OH time-profiles while varying the rate constant of the target reaction in the kinetic mechanism. Representative experimental and modeled OH profiles in addition to the effect of 20% deviation from the best fit for ethane and ethane- d_6 are shown in Figures 2 and 3, respectively. Measured values of the rate coefficients along with experimental conditions are compiled in Tables 1 and 2. Our data are plotted in Figure 4 along with the previous low-temperature data from Tully et al. [9] and three-parameter Arrhenius expression ($k_1 = 2.68 \times 10^{-18} (T/K)^{2.224} \exp(-373\text{ K}/T)\text{ cm}^{-3}\text{ molecule}^{-1}\text{ s}^{-1} \pm 13\%$) obtained by Krasnoperov and Michael [18] from fitting the entire database

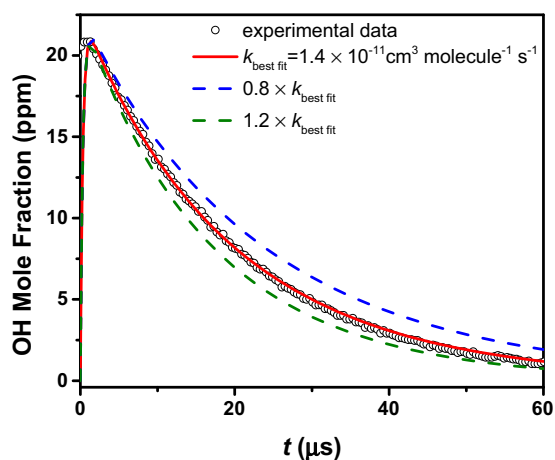


Figure 2. Hydroxyl mole fraction profile for ethane+OH reaction at $T=1106$ K, $P=1.38$ atm. The mixture composition was 342 ppm ethane, 22.4 ppm TBHP (70 ppm water) in argon. The best-fit to the experimental profile along with $\pm 20\%$ perturbations are also shown.

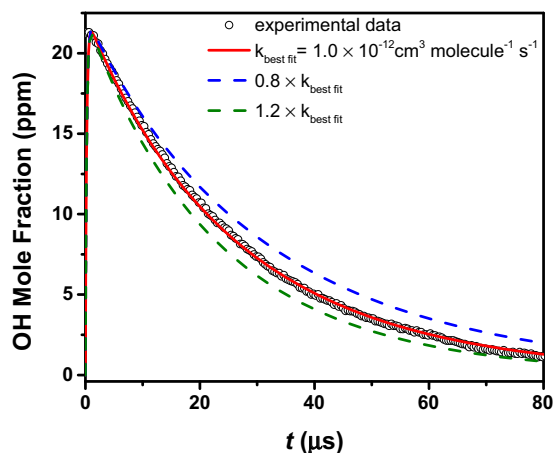


Figure 3. Hydroxyl mole fraction profile for ethane- d_6 +OH reaction at experimental conditions of $T=1133$ K, $P=1.44$ atm, 310 ppm ethane- d_6 , 22.2 ppm TBHP (80 ppm water) diluted in argon. Also presented are the best-fit simulated profile and perturbations of $\pm 20\%$.

Table 1
Measured rate coefficients of reaction R1 (ethane + OH).

Temperature (K)	Pressure (atm)	k_1 ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
847	1.68	6.81×10^{-12}
925	1.6	8.93×10^{-12}
970	1.46	1.06×10^{-11}
1034	1.4	1.23×10^{-11}
1106	1.38	1.39×10^{-11}
1142	1.31	1.54×10^{-11}
1275	1.31	1.94×10^{-11}
1277	1.08	2.08×10^{-11}
1285	1.21	1.96×10^{-11}

for ethane+OH reaction over 138–1367 K. As can be seen, the three-parameter expression [18] underpredicts our measured rate coefficients for R1 by a mean deviation of 20%. As for R2, there are no literature data available to compare with in the temperature range of our study. The best fit of our experimental data along with low temperature literature data for R1 and R2 resulted into

Table 2
Measured rate coefficient of reaction R2 (d-ethane + OH).

Temperature (K)	Pressure (atm)	k_2 ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
805	1.68	3.09×10^{-12}
875	1.63	4.47×10^{-12}
943	1.56	5.73×10^{-12}
997	1.34	7.40×10^{-12}
1030	1.62	8.25×10^{-12}
1133	1.44	1.00×10^{-11}
1190	1.44	1.14×10^{-11}
1240	1.28	1.30×10^{-11}
1254	1.42	1.32×10^{-11}
1345	1.37	1.60×10^{-11}

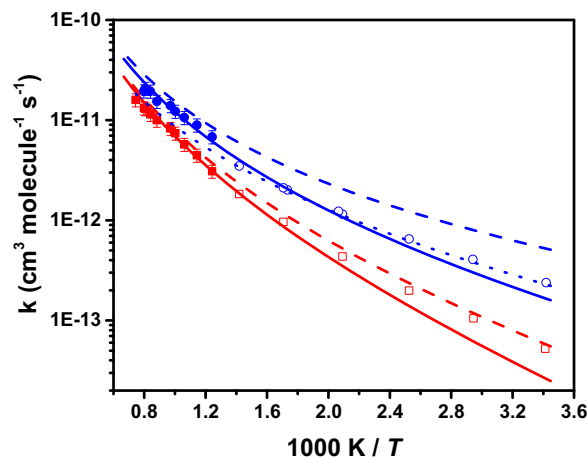


Figure 4. Comparison of the calculated rate coefficients with the experimental data. (●) this work for $\text{C}_2\text{H}_6 + \text{OH}$ reaction; (○) Tully et al. [9] for $\text{C}_2\text{H}_6 + \text{OH}$ reaction; (■) this work for $\text{C}_2\text{D}_6 + \text{OH}$; (□) Tully et al. [9] for $\text{C}_2\text{D}_6 + \text{OH}$ reaction. Blue and red lines represent the results of our *ab initio*/CTST calculations for C_2H_6 and C_2D_6 reactions with OH radicals, respectively. Solid lines represent the calculated rate coefficients without tunneling corrections, whereas the broken lines incorporate Wigner tunneling correction. Dotted lines are the results from fitting the entire database for $\text{C}_2\text{H}_6 + \text{OH}$ reaction over the T -ranges of 138–1367 K obtained by Krasnoperov and Michael [18].

the following three parameter Arrhenius expressions (in unit of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

$$k_1(T) = 1.02 \times 10^{-17} T^{2.083} \exp\left(\frac{-522.2 \text{ K}}{T}\right) \quad (290 - 1290 \text{ K}) \quad (1)$$

$$k_2(T) = 5.48 \times 10^{-17} T^{1.866} \exp\left(\frac{-1138.2 \text{ K}}{T}\right) \quad (290 - 1350 \text{ K}) \quad (2)$$

Our calculated energy profile of the reaction of ethane isotopologues with OH is shown in Figure 5. The *ab initio* reaction energy for ethane ($-75.9 \text{ kJ mol}^{-1}$) agrees within the uncertainty (1.70 kJ mol^{-1}) of the experimental value ($-76.01 \text{ kJ mol}^{-1}$) calculated from the data available in the CCBDB database. Our *ab initio* barrier height for R1 is found to be 9.3 kJ mol^{-1} which is consistent with the earlier report of 9.75 kJ mol^{-1} from Melissas and Truhlar [24]. These comparisons suggest that the energies calculated in the current work for the deuterated species are also highly accurate. The barrier height for R2 is calculated to be 13.3 kJ mol^{-1} . Based on the energy profile displayed in Figure 5 and molecular parameters listed in Table 3, we performed CTST calculations that are found to reproduce our experimental data very well (see Figures 4 and 6). However, the calculations underpredict experimental rate coefficients for both R1 and R2 in the low-temperature region. This subtle discrepancy may be attributed to the tunneling effect. As can be seen in Figure 4, the quantum tunneling effect is less pronounced for R1 as opposed to R2. This is expected as the reactions with small barriers contribute less to the quantum mechanical tunneling (κ). Tunneling

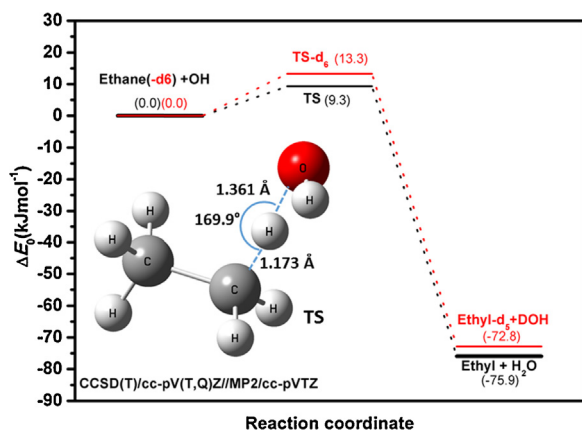


Figure 5. Potential energy surface (including zero-point energies) for the H-abstraction reaction of ethane and ethane-d₆ with OH radicals; energies are relative to the reactant energies.

(κ) was computed using Wigner formula that requires imaginary frequency (ν^\ddagger) corresponding to the reaction coordinate and the threshold energy (E_0) as given by:

$$\kappa = 1 - \frac{1}{24} \left(\frac{h\nu^\ddagger}{k_b T} \right)^2 \left(1 + \frac{RT}{E_0} \right) \quad (3)$$

After incorporating Wigner tunneling correction, the theoretical rate coefficients (dashed lines, Figure 4) for R2 showed excellent agreement with experimental data over the entire temperature range. But for R1, the tunneling correction appears to be quantitatively less reliable at low temperatures. The calculated rates were overestimated by roughly a factor of two in the low-temperature region. A similar behavior was reported by Melissas and Truhlar [24] where Wigner tunneling correction resulted in an overestimation of the rate coefficients by a factor of 2.3 at 300 K. The tunneling correction, however, is nearly negligible in our experimental conditions. Moreover, the contribution of tunneling is expected to be cancelled out to the large part when calculating the ratio of the rate coefficients (k_1/k_2). From the results of *ab initio* and transition state theory calculations, the ratio of the tunneling-uncorrected rate coefficients of reactions R1 and R2, i.e., DKIE, can be expressed over the temperature range of 290–1400 K:

$$\frac{k_1}{k_2}(T) = (0.38 \pm 0.10) \exp\left(-\frac{(3046 \pm 70)K}{T}\right) + (1.02 \pm 0.05) \exp\left(\frac{(527.5 \pm 0.2)K}{T}\right) \quad (4)$$

The best fit of experimental data (this work and Tully et al. [9]) yields the following expression for DKIE over the T range of

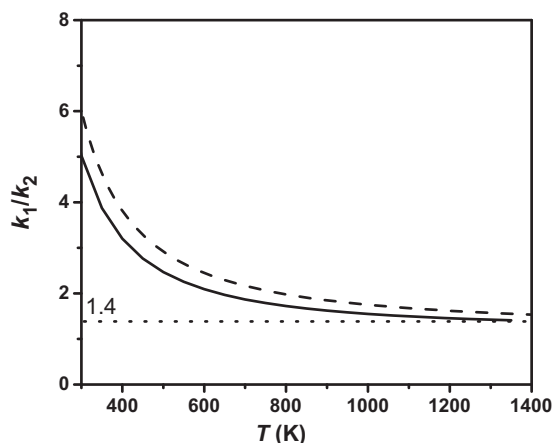


Figure 6. Comparison of the experimental and theoretical DKIE of ethane (H/D) + OH. (—) experimental results from this work and Tully et al. [9]; (---) calculated values from our *ab initio*/CTST methods. (.....) a horizontal line showing DKIE = 1.4.

293–1350 K:

$$\frac{k_1}{k_2}(T) = (0.5 \pm 0.10) \exp\left(-\frac{(2607 \pm 356)K}{T}\right) + (0.9 \pm 0.1) \exp\left(\frac{(526 \pm 1)K}{T}\right) \quad (5)$$

Both the experimental and calculated values for DKIE are displayed in Figure 6. As can be seen, the calculated and experimental DKIE values exhibit good agreement over the entire temperature range. Our calculated value for DKIE at 290 K is 6.4 which is close to that reported (4.61 ± 0.56) by Tully et al. [9]. At 850 K, we measured a DKIE value of 1.67 which agrees very well with the extrapolated value of 1.72 from the work of Tully et al. [9]. Our experimentally determined DKIE asymptotes to a value of 1.4 at high temperatures ($T > 1200$ K).

The high-temperature asymptoting behavior of DKIE can be explored using theoretical methods. From Arrhenius theory, DKIE can be written as:

$$\frac{k_1}{k_2}(T) = \frac{A_1}{A_2} \exp\left(\frac{\Delta E_a}{RT}\right) \quad (6)$$

where A is the pre-exponential factor and the subscripts identify the corresponding reactions; $\Delta E_a = E_a(D) - E_a(H)$ is the difference in the activation energies of the isotopes. As T approaches infinity, $k_1/k_2 \approx A_1/A_2$. The ratio of A_1 and A_2 can be approximated by taking the ratio of imaginary frequencies of the transition states ($\nu_1^\ddagger/\nu_2^\ddagger$) [47]. Using $\nu_1^\ddagger = 1303 \text{ cm}^{-1}$ and $\nu_2^\ddagger = 1003 \text{ cm}^{-1}$ (see Table 3), DKIE (k_1/k_2) comes out to be 1.3. On the other hand, *ab*

Table 3

Rotational constants (A , B , and C) and harmonic frequencies (ν_i) of the stationary points calculated at the MP2/cc-pVTZ level of theory. Frequencies are scaled by 0.95. Frequencies corresponding to the torsional modes are shown in bold.

Species	A , B , C (GHz)	ν_i (cm^{-1})
C ₂ H ₆	79.26966 19.81782 (2)	3045 (2), 3025.5 (2), 2951.7, 2950.3, 1437.7 (2), 1437.3 (2), 1358.9, 1331.0, 1166.8 (2), 990.3, 785 (2), 308.5
C ₂ D ₆	39.66530 13.70550 (2)	2254.5 (2), 2242 (2), 2127.4, 2116.6, 1135.5, 1041.8 (2), 1026 (2), 1017.4, 929.1 (2), 822.8, 567.4 (2), 218.4
TS	26.33548 4.80059 4.28371	1303i, 3621.5, 3073.8, 3047.0, 3032.1, 2992.8, 2949.2, 1432.6, 1427.5, 1412.7, 1342.1, 1311.6, 1266.5, 1196.0, 1154.4, 1019.5, 974.6, 809.9, 786.1, 630.4, 160.1, 114.6, 373.3, 51.2
TS-d ₆	17.78627 4.22738 3.74362	1003i, 3621.4, 2280.3, 2258.9, 2244.1, 2174.0, 2120.2, 1138.6, 1035.8, 1026.2, 1017.8, 991.5, 959.7, 937.9, 900.4, 888.9, 846.0, 673.2, 567.7, 537.5, 120.8, 101.5, 267.5, 49.5

initio/CTST calculations predict that DKIE asymptotes to 1.5 at high temperatures. These values are quite close to the experimentally determined DKIE of 1.4.

5. Conclusions

The deuterated kinetic isotope effect (DKIE) for the reaction of ethane and ethane- d_6 with OH radicals was determined experimentally between 800 and 1350 K. Additionally, high level CCSD(T)/cc-pV(T,Q)Z//MP2/cc-pVTZ quantum chemical and statistical rate theory calculations were performed to calculate the DKIE over 290–1400 K. The theoretical and experimental DKIE values are found to agree well over the entire temperature range of 290–1350 K. Our *ab initio*/CTST calculations predicted that DKIE asymptotes to 1.5 at high temperatures which is only 7% larger than the DKIE value determined experimentally in the current work. This work reports, to our knowledge, the first experimental evidence that DKIE asymptotes to 1.4 at high temperatures.

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