Isotopic Studies of Methane Oxidation Pathways on PdO Catalysts

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1. INTRODUCTION

Traces of methane are present in the untreated exhaust of automobiles and gas turbines fueled by natural gas. Methane removal via catalytic combustion requires the complete conversion of low methane concentrations (<1000 ppm) to CO2 and H2O at the temperatures of effluent streams. Also, low temperatures are required for the ignition of catalytic combustors used to reduce NOx emissions in power generation turbines. Catalytic combustion of methane occurs on metal oxides without side reactions. Catalysts based on supported PdO clusters are among the most active for methane combustion at low temperatures (1–3).

At low temperatures (<600 K), methane oxidation rates on PdO are proportional to CH4 concentration, independent of O2 concentration, and inversely proportional to the concentration of H2O (2–3). Rates also show a negative second-order dependence on CO2 when CO2 concentrations significantly exceed the concentration of H2O (2). A sequence of elementary steps consistent with these data has been proposed recently (3). The mechanism includes irreversible C–H bond activation on vacancy-oxygen site pairs and quasi-equilibrated desorption of CO2 and H2O. The measured rate expression cannot distinguish between quasi-equilibrated and irreversible O2 chemisorption, because this step is not kinetically significant when OH groups are the most abundant reactive intermediates (MAK1). A simple Langmuir–Hinshelwood kinetic equation based on the proposed sequence of elementary steps accurately describes the measured rate expression (3).

In this study, the details of the proposed mechanism were confirmed by measuring kinetic isotope effects (CH4/CD4) and the reversibility of the proposed steps. Predeuterated methane and 18O2 were used in isotopic equilibration studies during CH4 oxidation in order to establish the identity and reversibility of each proposed elementary step.

2. EXPERIMENTAL

A PdO/ZrO2 catalyst was prepared by incipient-wetness. ZrO2 (RC-100P, Daido Kigenso Kagaku Kogyo Co.) supports were heated in ambient air from room temperature to 1073 K at a rate of 0.33 K s−1, held at 1073 K for 24 h, and then cooled to room temperature. The surface area measured by N2 physisorption at its boiling point was 16–25 m2/g. ZrO2 was then impregnated to incipient wetness with an aqueous solution of Pd(NO3)2 (10 wt% Pd; 10 wt% nitric acid, Aldrich) and dried in ambient air for 1–2 h at room temperature (RT). The catalyst was heated from RT to 523 K in dry air at 0.0083 K s−1 in order to decompose
Pd(NO₃)₂ slowly. The temperature was then increased at 0.17 K s⁻¹ to 773 K and held for 10 h. The Pd concentration was measured by atomic absorption (7.9 wt% Pd).

A II catalytic measurements were carried out using a temperature-controlled flow reactor. The tubular reactor is 25 cm long with an inner diameter of 0.4 cm at both inlet and outlet. The center section is 0.8 cm in diameter and contains a porous quartz disk. Gas flow rates were monitored by electronic flow controllers (FC-280, R.O.-28, Tylan). A quadrupole mass spectrometer (Model 100C, UTI) was used in order to measure the chemical and isotopic composition of the reactor effluent.

Pd dispersion was measured by H₂–O₂ titration at 373 K (4). The catalyst was first treated at 373 K in a mixture of 25% H₂ (99.9% purity, Airco) in He at 1.7 cm³ s⁻¹ (Middleton Bay Airgas). At 373 K, a monolayer of chemisorbed oxygen forms on Pd metal at O₂ pressures below 46.7 kPa (4). Finally, H₂ pulses (0.4 cm³) were introduced in order to titrate chemisorbed oxygen until H₂ concentrations reached a constant value. Based on the reported titration stoichiometries (4)

Oxidation: Pdₙs + 1/2O₂(g) → PdO(s)
Reduction: PdO(s) + 3/2H₂(g) → Pd(s) + H₂O(g),

the Pd dispersion was calculated to be 13.5%. If we assume hemispherical crystallites, the corresponding average Pd metal crystallite radius is 6.4 nm.

Isothermal methane oxidation reactions were carried out using a mixture containing 1% CH₄ and 4% O₂ (UHP Grade, Middleton Bay A irgas) in He at 1.7 cm³ s⁻¹ and 373–623 K. A rgon (−1 mol%) was used as an internal standard. The catalyst (0.53 g) was first treated in 20% O₂ in He at 673 K for 3 h and then flushed with pure He for 1 h. The temperature was then decreased to 373 K, and the reactant stream was introduced. The catalyst temperature was increased to 623 K at a rate of 0.17 K s⁻¹, and methane oxidation rates were obtained by measuring CH₄ and CO₂ concentrations in the effluent using mass spectrometry. The experiment was repeated using CD₄ reactants in order to measure kinetic isotope effects for methane oxidation on PdO/ZrO₂.

H–D isotopic equilibration rates were measured for CH₄/CD₄ mixtures in order to determine the reversibility of C–H bond activation steps. These measurements were carried out using 0.5% CH₄, 0.5% CD₄ (99.9% purity, Isotec), 4% O₂, and He balance at a flow rate of 1.7 cm³ s⁻¹ between 473 and 623 K. The catalyst was pretreated as described above. A trap filled with ~10 g Drierite (CaSO₄) was placed after the reactor in order to remove water from the reaction products before mass spectrometric analysis. This was required in order to avoid interference between cracking fragments of H₂O, HD, and D₂O and those of deuterated methane isotopomers. Mass intensities at 15, 17, 18, 19, and 20 amu for CH₄ and at 40 amu for Ar were used to determine methane isotopomer concentrations. Mass 16 was not used because it contains fragments from O₂ and CO₂.

Mass fragmentation patterns for each CH₄–D₂, isotope, and the gas-phase concentrations of H₂O, HDO, and D₂O were measured, and those for the other isotopomers (CH₃D, CH₂D₂, and CHD₃) were calculated using reported methods (5). These patterns were then used along with those for Ar, CH₄, and CD₄ in order to obtain relative isotopomer concentrations using matrix inversion methods. Isotopic equilibration rates were measured using 16O₂/18O₂/CH₄ reactants (2%/2%/1%; 18O₂–Isotec, 99% purity; He balance) on 0.53 g PdO–ZrO₂ at a flow rate of 1.7 cm³ s⁻¹ in order to determine the reversibility of O₂ chemisorption during CH₄ combustion. The catalyst pretreatment and experimental procedures were similar to those described above. Gas-phase concentrations of 16O₂, 18O16O, and 18O₂ (32, 34, and 36 amu, respectively) and of C₁₆O₂, C₁₆O₁₈O, and C₁₈O₂ (44, 46, and 48 amu, respectively) were measured continuously by mass spectrometry.

Isotopic equilibration rates were measured on Pd₁₆O/Zr₁₆O₂ catalysts using CH₄/18O₂/C₁₆O₂ mixtures in order to probe the reversibility of CO₂ desorption. A Pd₁₆O/Zr₁₆O₂ catalyst was treated in 20% 18O₂/He at 673 K for 3 h and then flushed with pure He for 1 h. The temperature was decreased to 373 K, and a reactant mixture consisting of CH₄/18O₂/C₁₆O₂ (4%/2%/1%; 18O₂–Isotec, 99% purity; He balance) was introduced at 1.7 cm³ s⁻¹. The temperature was then increased from 373 to 623 K at 0.17 K s⁻¹ and the gas-phase concentrations of 16O₂, 18O16O, 18O₂, C₁₆O₂, C₁₆O₁₈O, and C₁₈O₂ in the effluent stream were measured continuously by mass spectrometry. The reversibility of CO₂ desorption was determined from the concentration of C₁₆O₁₈O in the effluent stream.

3. RESULTS AND DISCUSSION

The concentration of methane oxidation products (CO₂, H₂O) was measured on PdO/ZrO₂ between 473 and 623 K. Both CH₄ and CD₄ were converted completely at temperatures above 623 K, but CD₄ combustion rates were lower than CH₄ combustion rates at all lower temperatures. Using the kinetic rate equation proposed earlier for methane combustion on similar PdO/ZrO₂ catalysts (3) and the assumption of a plug-flow reactor, the measured rate constant can be expressed by

\[ k_{\text{eff}} = \frac{2F_{\text{CH}_4}}{n_s} \left( \ln \frac{1}{1-x} - x \right). \]

in which \( F_{\text{CH}_4} \), \( n_s \), and \( k_{\text{eff}} \) represent the inlet methane molar flow rate, the methane conversion, and the effective rate
FIG. 1. CH₄ and CD₄ combustion rates and measured kinetic isotope effects on PdO/ZrO₂ (1% CH₄ or CD₄, 4% O₂/He; 100 cm³/min; 0.53 g 7.9 wt% PdO/ZrO₂).

A semi-logarithmic plot of $k_{\text{eff}}$ as a function of inverse temperature is shown in Fig. 1. A least-square fit to these data between 536 and 586 K was used to determine activation energies. The activation energies for CH₄ and CD₄ oxidation reactions were 176 and 180 kJ/mol, respectively.

The values of $k_{\text{eff}}$ determined for CH₄–O₂ and CD₄–O₂ mixtures are denoted as $k_H$ and $k_D$, respectively, in Fig. 1. The kinetic isotope effect ($k_H/k_D$) is greater than unity at all temperatures and it decreases slightly with increasing temperature. At 573 K, the kinetic isotope effect is 2.4 while a theoretical treatment using partition functions predicts a value of 2.5 (see Appendix). The observation of a normal isotope effect ($k_H/k_D > 1$) suggests that rate-determining steps in the catalytic sequence involve H-atoms. In the mechanism proposed by Fujimoto et al. (3), there are only two elementary steps that involve H atoms, the activation of the C–H bond in CH₄ and the formation of water via recombination of hydroxyl groups. A more detailed discussion of these kinetic isotope effects is presented below and the detailed calculations are included in the Appendix.

The distribution of CH₄–CD₄ isotopomers formed during oxidation of CH₄/CD₄ iso-proportional scrambling with methane combustion rates. CH₄/CD₄ equilibration rates, defined as the sum of the rates of CH₃D, CH₂D₂, and CHD₃ formation, remained almost constant at about $1 \times 10^{-3}$ s⁻¹ below 573 K. Above 573 K, the concentrations of all CH₄–CD₄ isotopomers decreased as a consequence of their conversion to CO₂. The rate of isotopic CH₄–CD₄ equilibration was much smaller than the rate of methane combustion. At 573 K, the isotope exchange rate is $1.0 \times 10^{-3}$ s⁻¹ and the methane combustion rate is $9.5 \times 10^{-3}$ s⁻¹. Therefore, C–H bond activation is irreversible during CH₄ combustion on PdO-based catalysts at 573 K.

Isotopic scrambling rates for $^{16}$O₂/$^{18}$O₂ mixtures were also measured during CH₄ oxidation. Figure 3 shows Arrhenius plots for the molar rates of $^{16}$O₂, $^{16}$O$^{18}$O, and $^{18}$O₂ and of each CO₂ isotopomer exiting the reactor. $^{16}$O₂ is the first CO₂ isotopomer formed as methane combustion reactions begin to occur above 473 K (Fig. 3), suggesting that lattice $^{16}$O in PdO is used more efficiently than oxygen atoms from O₂ in methane combustion. As C$^{16}$O₂ desorbs from the catalytic surface, the resulting oxygen vacancies chemisorb $^{16}$O₂ and $^{18}$O₂ from the gas phase, leading to isotopically mixed oxygen atoms in the lattice and to the formation of all CO₂ isotopomers. Even at the highest temperature (625 K), equilibration of CO₂ isotopomers is incomplete and the equilibrium $^{16}$O₂:$^{16}$O$^{18}$O : $^{18}$O₂ composition (1:2:1) is not reached. The higher than equilibrium $^{16}$O content in the CO₂ isotopomers shows that the Pd$^{16}$O starting material retains an excess of $^{16}$O at the end of these experiments.

FIG. 2. Methane isotopomer distribution formed during reactions of CH₄–CD₄–O₂ mixtures on PdO/ZrO₂ (0.5% CH₄, 0.5% CD₄, 4% O₂, 1% Ar in He flowing at 100 cm³/min; 0.51 g 7.9 wt% PdO/ZrO₂).
FIG. 3. Oxygen and carbon dioxide isotopomer distributions formed in reactions of CH$_4$–$^{16}$O$_2$–$^{18}$O$_2$ mixtures on PdO/ZrO$_2$ (2% $^{16}$O$_2$, 2% $^{18}$O$_2$, and 1% CH$_4$ in He flowing at 100 cm$^3$/min; 0.52 g 7.9 wt% Pd/ZrO$_2$).

C$^{16}$O$^{18}$O is formed at significant rates during reactions of CH$_4$/$^{16}$O$_2$/18O$_2$ mixtures, but $^{16}$O$^{18}$O was not detected even at 625 K. These results differ from those obtained during isotopic equilibration of $^{16}$O$_2$/$^{18}$O$_2$ mixtures in the absence of CH$_4$ (10). Without CH$_4$, $^{16}$O$^{18}$O isotopomers were detected at 575 K when Pd$^{16}$O/ZrO$_2$ was contacted with a $^{16}$O/$^{18}$O$_2$ mixture. These results indicate that the rate of recombination of oxygen atoms on PdO surfaces is much slower than the rate at which such oxygen atoms react with methane to form CO$_2$. An alternate explanation is that the most abundant reactive intermediates (MARI) during CH$_4$ combustion are surface hydroxyls (3), which recombine to give water in quasi-equilibrated desorption steps. As a consequence, the concentration of surface lattice oxygens is much lower during methane combustion than under the conditions of chemical adsorption–desorption equilibrium prevalent during isotopic scrambling of $^{18}$O$_2$–$^{16}$O$_2$ in the absence of CH$_4$.

The reversibility of CO$_2$ desorption was established by labeling PdO with $^{18}$O, and then contacting the Pd$^{18}$O formed with a reactant stream containing $^{16}$O$_2$, CH$_4$, and C$^{16}$O$_2$. The formation of C$^{16}$O$^{18}$O would require reversible CO$_2$ desorption steps, because C$^{16}$O$_2$ is the only source of $^{16}$O in the reactant stream. The rates of formation of CO$_2$ and of its various isotopomers are shown as a function of temperature in Fig. 4. C$^{16}$O$_2$ in the feed exchanges with Pd$^{18}$O below 400 K. The concentration of C$^{16}$O$^{18}$O increases up to 475 K, at which point the C$^{18}$O$_2$ formed by methane combustion begins to contribute significantly to the CO$_2$ molecules present in the gas phase. The exchange of oxygen atoms between C$^{16}$O$_2$ and Pd$^{18}$O at temperatures well below those required for combustion shows that CO$_2$ adsorption–desorption steps are quasi-equilibrated during methane oxidation throughout the entire temperature range of this study.

The results of this study are consistent with the Mars–van Krevelen mechanism (11) proposed by Fujimoto et al. (3) for methane combustion on PdO/ZrO$_2$. The proposed mechanism (Steps 1–7) is consistent with the dependence of methane combustion rates on CH$_4$, O$_2$, H$_2$O, and CO$_2$ reported by Ribeiro et al. (2) and Fujimoto et al. (3), when surface hydroxyls are assumed to be the most abundant reaction intermediates (MARI).

\[
\begin{align*}
\text{Step 1:} & \quad \text{O}_2 + * \xrightarrow{k_1} \text{O}_2^* \\
\text{Step 2:} & \quad \text{O}_2^* + * \xrightarrow{k_2} \text{2O}^* \\
\text{Step 3:} & \quad \text{CH}_4 + * \xrightarrow{k_3} \text{CH}_4^* \\
\text{Step 4:} & \quad \text{CH}_4^* + \text{O}^* \xrightarrow{k_4} \text{CH}_3^* + \text{OH}^* \\
\text{Step 5:} & \quad \text{2O}^* \xrightarrow{k_5} \text{H}_2\text{O} + \text{O}^* + * \\
\text{Step 6:} & \quad \text{CO}_2^* \xrightarrow{k_6} \text{CO}_2 + * \\
\text{Step 7:} & \quad \text{CO}_3^* \xrightarrow{k_7} \text{CO}_2 + \text{O}^* 
\end{align*}
\]

A s discussed in detail below, the first steps in the mechanism are the molecular adsorption of O$_2$ and its subsequent dissociation to O atoms (Steps 1 and 2). The second step is assumed to be irreversible. Neither the kinetic rate
The observed isotopic effects support the above mechanism. The normal isotopic effect suggests either kinetic or thermodynamic relevance elementary steps with the participation of H atoms involved in one reaction cycle. From Eq. [3] one concludes that the rate constant \( k_{\text{eff}} \) is the combination of the methane adsorption equilibrium constant \( K_3 \), the C–H bond dissociation rate constant \( k_4 \), and the OH group recombination equilibrium constant \( K_5 \); all three steps involve the participation of H atoms. Step 4 is kinetically relevant, and Steps 3 and 5 are thermodynamically relevant. So the isotopic effects obtained reflect the combination of kinetic and thermodynamic effects. A theoretical treatment using partition functions shows that these isotopic effects reflect mainly the difference in zero point energy \( (\Delta E_0) \) between H- and D-containing species; for example, at 573 K, the contribution of the electronic partition function is 2.13, while that from isotopic effects on translational, rotational, and vibrational modes is only 1.19.

4. CONCLUSIONS

A normal kinetic isotope effect was measured for the combustion of methane on Pd/ZrO\(_2\) catalysts. Combustion rates for CD\(_4\)/O\(_2\) mixtures are significantly lower than those for CH\(_4\)/O\(_2\) reactants. Isotopic equilibrium rates in CH\(_4\)–CD\(_4\)–O\(_2\) are much lower than methane combustion rates. Thus, C–H bond activation steps are irreversible during methane combustion at 523 K on PdO/ZrO\(_2\) catalysts. Isotopic oxygen equilibration was not detected during combustion of \(^{16}\text{O}_2–^{18}\text{O}_2–\text{CH}_4\) reactant mixtures, showing that dissociative oxygen chemisorption steps are also irreversible. The reversibility of CO\(_2\) desorption steps was confirmed by the rapid scrambling of oxygen atoms between gas-phase \(^{16}\text{O}_2\) and lattice oxygens in the Pd\(^{18}\text{O}\) lattice. These isotopic studies confirm the redox mechanism previously proposed in order to describe the measured dependence of methane oxidation rates on CH\(_4\), O\(_2\), CO\(_2\), and H\(_2\)O concentrations (3). In view of the kinetic resemblance among supported PdO methane combustion catalysts, these mechanistic conclusions on PdO/ZrO\(_2\) are likely to apply generally to combustion catalysts based on PdO.

APPENDIX

Theoretical Treatment of the KinetiC Isotope Efect

The appropriate equations for translational, rotational, electronic, and vibrational partition functions at 600 K

expression nor the results of our isotopic tracer studies can discern whether O\(_2\) dissociation is preceded by quasi-equilibrated molecular adsorption. The absence of \(^{16}\text{O}_2^{16}\text{O}\) during reactions of CH\(_4–^{16}\text{O}_2–^{18}\text{O}_2\) mixtures confirmed that Step 2 is indeed irreversible. C–H bonds in methane are activated in Step 4 using a vacancy-oxygen site pair, following the reversible molecular adsorption of methane in Step 3. The finding that isotopic scrambling rates of CH\(_4–\text{CD}_4–\text{O}_2\) mixtures were much slower than the rate of chemical conversion to CO\(_2\) confirms the assumption that C–H bond activation (Step 4) is irreversible. Steps after the first C–H bond activation reaction involve sequential reactions of lattice oxygens with CH\(_x\) species until CO\(_2\) is formed and desorbed. These steps are not kinetically important because they occur after the first irreversible step and they do not involve the most abundant surface intermediates. Water is proposed to form via recombination of surface hydroxyl groups (Step 5). While isotopic evidence for the reversibility of this step was not obtained in the course of this study, the reported inhibition of combustion rates by water requires that Step 5 be reversible, because otherwise gas-phase water could not affect the composition of surface species or the rate of the reaction. The observed inverse dependence of the rate on water concentration requires that this desorption step be quasi-equilibrated. Steps 6 and 7 in the mechanism are the reversible desorption of CO\(_2\) adsorbed on vacant sites or lattice oxygen atoms. The rapid exchange of C\(^{16}\text{O}_2\) with Pd\(^{18}\text{O}\) during CH\(_4\) combustion confirmed that Step 7 is quasi-equilibrated.

Applying the pseudo-steady-state approximation to Steps 1 through 7 leads to a Langmuir–Hinshelwood-type kinetic expression.

\[
\text{rate} = \frac{K_1k_2P_{\text{CH}_4}}{3\left(1 + \frac{K_1k_2P_{\text{H}_2\text{O}}}{2K_3K_4P_{\text{CH}_4}} + K_1P_{\text{CH}_4} + K_3P_{\text{CH}_4} + \left(\frac{K_1k_2[H_2\text{O}]P_{\text{H}_2\text{O}}}{2K_3K_4K_5P_{\text{CH}_4}}\right)^{1/2} + \frac{P_{\text{CH}_4}}{K_1} + \frac{K_1k_2P_{\text{H}_2\text{O}}P_{\text{CH}_4}}{2K_3K_4K_5P_{\text{CH}_4}}\right)^{1/2}}
\]

When OH* is the most abundant reactive intermediate (MAR1), the term in the denominator containing the water concentration becomes much larger than the others and Eq. [2] reduces to the experimentally observed rate expression (2, 3)

\[
r = \frac{K_3k_4K_5P_{\text{CH}_4}}{P_{\text{H}_2\text{O}}} = k_{\text{eff}}P_{\text{CH}_4}/P_{\text{H}_2\text{O}}.
\]

When CO\(_2\) concentrations become significantly higher than H\(_2\)O concentrations, the rate given by Eq. [2] becomes proportional to \((P_{\text{CO}_2})^{-2}\), as observed experimentally (3). Since H\(_2\)O and CO\(_2\) are always formed in a 2 : 1 molar ratio during methane combustion, CO\(_2\) inhibition is unlikely to be observed in practical applications of methane oxidation reactions.
are

\[ Q_{\text{trans}} = \frac{(2\pi m k_B T)^{3/2} V}{h^3} \propto (mT)^{3/2} \]  \hspace{1cm} \text{[A 1.1]}

\[ Q_{\text{rot}} = \frac{8\pi^2}{\sigma h^3} (2\pi k_B T)^{3/2} (I_x, I_y, I_z)^{1/2} \propto T^{5/2} (I_x, I_y, I_z)^{1/2} \]  \hspace{1cm} \text{[A 1.2]}

\[ Q_{\text{elec}} = g_0 + g_1 e^{-\epsilon_0/k_BT} + g_2 e^{-\epsilon_2/k_BT} + \ldots \approx g_0 = e^{-\epsilon_0/RT} \]  \hspace{1cm} \text{[A 1.3]}

\[ Q_{\text{vib}} = \sum_{\nu=0}^{\infty} e^{-\theta_v/RT} \approx \frac{1}{1 - e^{-\theta_v/RT}} \text{, where } \theta_v = \frac{h}{2\pi k_B} \sqrt{\frac{k}{\mu}} \]  \hspace{1cm} \text{[A 1.4]}

The constants and variables that appear in the equations above are defined as

- \( h \): Planck’s constant
- \( I_x, I_y, I_z \): moment of inertia
- \( k \): force constant
- \( k_B \): Boltzmann’s constant
- \( m \): mass of molecules or atoms
- \( T \): temperature (K)
- \( V \): volume
- \( \mu \): reduced mass
- \( \epsilon_0 \): zero point energy
- \( \sigma \): symmetry number
- \( \theta_v \): characteristic temperature for vibration (K)

For gas phase molecules all four modes of the partition functions are important. However, the translational partition function is always unity for immobile adsorbed species since there are zero degrees of freedom. Values of \( \theta_v \) are needed to determine the vibrational partition function. Although \( \theta_v \) for isolated molecules can be found from the literature, values for adsorbed species are scarce. Values of \( \theta_v \) for isolated molecules in this study are shown in Table A1.1 (12).

Differences in zero point energy (\( \Delta \epsilon_0 \)) between isotopes are also available from the literature (13). Values of \( \Delta \epsilon_0 \) for species encountered in this study are shown in Table A1.2.

For methane combustion, the rate of combustion is proportional to

\[ \text{rate} \propto K_3 k_4 K_5. \]  \hspace{1cm} \text{[A 1.5]}

### Table A1.2
**Zero Point Energy Difference between Isotopomers (\( \Delta \epsilon_0 \))**

<table>
<thead>
<tr>
<th>Isotopomers</th>
<th>( \Delta \epsilon_0 ) (J mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)/CD(_4)</td>
<td>29350</td>
</tr>
<tr>
<td>H(_2)O/D(_2)O</td>
<td>14910</td>
</tr>
<tr>
<td>OH(^+)/OD(^+)</td>
<td>5860</td>
</tr>
</tbody>
</table>

Therefore, the kinetic isotope effect (KIE), which is defined as the ratio of the combustion rate for CH\(_4\)/O\(_2\) to that of CD\(_4\)/O\(_2\), equals

\[ \text{KIE} = \left( \frac{K_{3,CH_4}}{K_{3,CD_4}} \right) \left( \frac{k_{4,CH_4}}{k_{4,CD_4}} \right) \left( \frac{k_{5,CH_4}}{k_{5,CD_4}} \right). \]  \hspace{1cm} \text{[A 1.6]}

Each ratio in parentheses in Eq. [A 1.6] is examined separately below.

1. \( k_{4,CH_4}/k_{4,CD_4} = \left( \frac{Q_{CH_4}^0}{Q_{CD_4}^0} \right) \left( \frac{Q_{CH_4}^0}{Q_{CD_4}^0} \right)^2 \)  \hspace{1cm} \text{[A 1.7]}

2. \( K_{3,CH_4}/K_{3,CD_4} = \left( \frac{Q_{CH_4}}{Q_{CD_4}} \right) \left( \frac{Q_{CD_4}}{Q_{CH_4}} \right) \)  \hspace{1cm} \text{[A 1.8]}

3. \( K_{5,CH_4}/K_{5,CD_4} = \left( \frac{Q_{CH_4}}{Q_{CD_4}} \right) \left( \frac{Q_{CD_4}}{Q_{CH_4}} \right) \)  \hspace{1cm} \text{[A 1.9]}

Combining Eqs. [A 1.6] through [A 1.9] results in

4. \( \text{KIE} = \left( \frac{Q_{CH_4}^0}{Q_{CD_4}^0} \right)^2 \left( \frac{Q_{CD_4}^0}{Q_{CH_4}^0} \right)^2 \left( \frac{Q_{OD_4}^0}{Q_{OH_4}^0} \right)^2 \)  \hspace{1cm} \text{[A 1.10]}

Each ratio of the partition functions is evaluated as follows.

1. Translational partition function contribution:

\[ \frac{Q_{CD_4}^0}{Q_{CH_4}^0} \propto \left( \frac{m_{CD_4}}{m_{CH_4}} \right)^{3/2} = \left( \frac{20}{16} \right)^{3/2} = 1.398 \]  \hspace{1cm} \text{[A 1.11]}

\[ \frac{Q_{H_2O}^0}{Q_{D_2O}^0} \propto \left( \frac{m_{H_2O}}{m_{D_2O}} \right)^{3/2} = \left( \frac{18}{20} \right)^{3/2} = 0.854 \]  \hspace{1cm} \text{[A 1.12]}

### Table A1.1
**Characteristic Temperature (\( \theta_v \)) from the Literature**

<table>
<thead>
<tr>
<th>Isolated molecules</th>
<th>( \theta_v ) (K) (degeneracy in parentheses)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>4193, 2196 (2), 4345 (3), 1879 (3)</td>
</tr>
<tr>
<td>O(_2)</td>
<td>2274</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>5254, 2295, 5404</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>1997, 3380, 960 (2)</td>
</tr>
</tbody>
</table>
adsorbed species are approximately the same. Therefore,
\[
\left( \frac{Q_{\text{CH}_3\text{OH}^+}}{Q_{\text{CD}_3\text{OD}^+}} \right)_{\text{trans}} \approx 1 \tag{A 1.13}
\]
\[
\left( \frac{Q_{\text{OD}^+}}{Q_{\text{OH}^+}} \right)_{\text{trans}} \approx 1 \tag{A 1.14}
\]

2. Rotational partition function contribution:
\[
\left( \frac{Q_{\text{CD}_4}}{Q_{\text{CH}_4}} \right)_{\text{rot}} \approx (8)^{1/2} \tag{A 1.15}
\]
\[
\left( \frac{Q_{\text{H}_2\text{O}}}{Q_{\text{D}_2\text{O}}} \right)_{\text{rot}} \approx \left( \frac{1}{8} \right)^{1/2} \tag{A 1.16}
\]

The CH₃OH⁺, CD₃OD⁺, OH⁺, and OD⁺ are adsorbed species; therefore,
\[
\left( \frac{Q_{\text{CH}_3\text{OH}^+}}{Q_{\text{CD}_3\text{OD}^+}} \right)_{\text{rot}} \approx 1 \tag{A 1.17}
\]
\[
\left( \frac{Q_{\text{OD}^+}}{Q_{\text{OH}^+}} \right)_{\text{rot}} \approx 1. \tag{A 1.18}
\]

3. Vibrational partition function contribution: At low temperature, when T < 1000 K,
\[
\left( \frac{Q_{\text{CD}_4}}{Q_{\text{CH}_4}} \right)_{\text{vib}} \approx 1 \tag{A 1.19}
\]
\[
\left( \frac{Q_{\text{H}_2\text{O}}}{Q_{\text{D}_2\text{O}}} \right)_{\text{vib}} \approx 1 \tag{A 1.20}
\]
\[
\left( \frac{Q_{\text{CH}_3\text{OH}^+}}{Q_{\text{CD}_3\text{OD}^+}} \right)_{\text{vib}} \approx 1 \tag{A 1.21}
\]
\[
\left( \frac{Q_{\text{OD}^+}}{Q_{\text{OH}^+}} \right)_{\text{vib}} \approx 1. \tag{A 1.22}
\]

4. Electronic partition function contribution:
\[
\left( \frac{Q_{\text{CD}_4}}{Q_{\text{CH}_4}} \right)_{\text{elec}} = e^{29350/RT} \tag{A 1.23}
\]
\[
\left( \frac{Q_{\text{H}_2\text{O}}}{Q_{\text{D}_2\text{O}}} \right)_{\text{elec}} = e^{-14910/RT} \tag{A 1.24}
\]
\[
\left( \frac{Q_{\text{CH}_3\text{OH}^+}}{Q_{\text{CD}_3\text{OD}^+}} \right)_{\text{elec}} = e^{\Delta E_{\text{CD}_3\text{OD}^-}-\Delta E_{\text{CH}_3\text{OH}^-}} \tag{A 1.25}
\]
\[
\left( \frac{Q_{\text{OD}^+}}{Q_{\text{OH}^+}} \right)_{\text{elec}} = e^{11720/RT} \tag{A 1.26}
\]

Combining Eqs. (A 1.10) through (A 1.26), the kinetic isotopic effect (KIE) can be approximated as
\[
\text{KIE} = 1.19e^{-\frac{20160-(\Delta E_{\text{CD}_3\text{OD}^-}-\Delta E_{\text{CH}_3\text{OH}^-})}{RT}} = 1.19e^{-\Delta E/RT}, \tag{A 1.27}
\]

and the resulting pre-exponential factor of 1.19 is very similar to that found experimentally, 1.14. Experimental results show the \( \Delta E \) is equal to 3.6 kJ/mol. Using this value the calculated zero point energy difference between transition state species CD₃OD⁺ and CH₃OH⁺ is 22560 J/mol. This value is a little bit smaller than that between CH₄ and CD₄ (29350 J/mol) but much larger than that between OH⁺ and OD⁺ (5860 J/mol), suggesting that the transition state species structure looks more like CH₄ and CD₄. Assuming that \( \Delta E \) is equal to 3.6 kJ/mol, the predicted KIE is shown as a function of temperature in Fig. A1 along with the experimental values of the KIE.

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REFERENCES