Role of C–H Bond Strength in the Rate and Selectivity of Oxidative Dehydrogenation of Alkanes

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The oxidative dehydrogenation of alkanes (C₂H₆, C₃H₈, i-C₄H₁₀, and n-C₅H₁₀) was investigated on VOₓ supported on Al₂O₃. Rate constants for alkane dehydrogenation (k₁), alkane combustion (k₂), and alkene combustion (k₃) were measured, and a model was developed to describe the effects of alkane composition on these rate constants. The proposed model accounts for the effects of the number of C–H bonds available for activation and the relative strengths of these bonds in both the reactant and the product molecules. The Brønsted–Evans–Polanyi (BEP) relationship is used to relate activation energies of secondary and tertiary C–H bonds to that of primary C–H bonds. The model gives a reasonable approximation of the relative order of alkane reactivity, expressed by k₁ + k₂, and the relative ranking of alkanes with respect to combustion versus oxidative dehydrogenation, expressed by k₃/k₁. The ratio of k₃/k₁ is described by the product of two components; one that depends on the nature, number, and relative strength of C–H bonds of surface alkoxydes, and a second one that is independent of the alkoxyde composition and structure but depends on the difference in the entropy of activation for CO₂ precursor versus alkene formation. The model also explains the observed variation of k₃ with alkenic composition by considering two precursor states for alkenes. One is strongly bound through π-orbital interactions with Lewis acid centers, and the second weakly binds via H bonding and van der Waals interactions, similar to the binding of alkanes. As a result, the rate of alkenic combustion depends strongly on the large heats of adsorption of alkenes and only slightly on the presence of weak allylic C–H bonds. The high rate of C₂H₄ combustion is thus a consequence of its high heat of adsorption.

Introduction

Oxidative dehydrogenation (ODH) provides an alternate route for the conversion of alkanes to alkenes. It avoids the energy inefficiencies and ubiquitous deactivation of nonoxidative processes. Alkenic yields are typically below 50%, even for C₂H₆, the alkane that leads to the most selective ODH reactions.¹ Yield limitations reflect the sequential nature of the pathways involved and the higher reactivity of allylic C–H bonds, ubiquitous in alkanes, compared with C–H bonds in alkane reactants. Investigations carried out with VOₓ-based catalysts have shown that alkane ODH reaction rates are proportional to alkane pressure but independent of O₂ pressure,² consistent with C–H bond activation as the sole kinetically relevant step. Detailed kinetic and isotopic methods have confirmed these conclusions for VOₓ and MoOₓ catalysts.³–⁸

Hodnett et al.⁹,¹⁰ proposed empirical relations between selectivity and the strength of C–H bonds in reactant and products for reactions involving the activation of these bonds. These relations predict that achievable selectivities at a given reactant conversion depend on the differences in dissociation energies between the weakest C–H bonds in reactants and in products for a broad range of catalytic oxidation reactions.⁹ This approach does not include, however, any effects of the expected differences in the adsorption of reactants and products or any contributions to reactivity from C–H bonds other than the weakest one in each molecule. Low heats of adsorption (∆H_{ads}) for alkenes reflect predominant interactions via hydrogen-bonding or van der Waals forces. Alkenes interact with surfaces via similar interactions but also bind more strongly onto Lewis acid sites via their electron-rich π orbitals. The stronger binding of alkenes can lead to reactivities much greater than those predicted from their weakest C–H bond, consistent with the modest yields (~20%)¹ often observed for C₂H₄ in spite of its strong C–H bonds (464 kJ mol⁻¹; ref 11) relative to those in C₂H₆ reactants (421 kJ mol⁻¹; ref 11). Differences in C–H bond strength between the strongest and the weakest C–H bonds in alkanes are generally less than 20 kJ mol⁻¹, and ubiquitous linear free energy relations¹²,¹³ suggest their differences in activation barriers are even smaller. As a result, stronger bonds increasingly contribute to measured rates as temperatures increase and must be considered in all relations between catalytic reactivity and C–H bond energies.

The effects of C–H bond dissociation energy on activation energies are typically described by Brønsted–Evans–Polanyi (BEP) relations;¹²,¹³ these relations express activation energies as a linear function of enthalpy changes for a given elementary step. This approach has proven useful, in spite of its empirical basis, for homogeneous and catalytic reactions, such as in acid catalysis,¹² reactions of benzene derivatives,¹⁴ formate and methoxide decomposition on metals,¹⁵ CO, N₂, O₂, and NO activation on metal surfaces,¹⁶ and C–H bond formation and dissociation on metals.¹⁷ For reactions limited by homolytic bond cleavage steps, ∆Hₖ will depend sensitively on C–H bond dissociation energies, thus allowing C–H bond activation barriers to be related to the strength of individual C–H bonds.

Here, we address apparent inconsistencies between measured activation energies and weakest C–H bond energies and also the low C₂H₄ yields and preferential activation of the weakest...
**Experimental Methods**

**Catalyst Synthesis.** Vanadia domains supported on alumina were prepared via incipient-wetness impregnation of fumed silica with V=O-alkoxide (Degussa AG, 119 m² g⁻¹) with a solution of vanadium(V) oxy-tri-isopropoxide (Sigma-Aldrich, 99%) in 2-propanol (Sigma-Aldrich, 99.9%). This sample contained ~3% wt V₂O₅. Preparation details have been described previously. Catalyst characterization. Samples were characterized by N₂ physisorption and Raman and UV–vis spectroscopies using methods reported in the Supporting Information. Surface areas (per mass of support) measured by N₂ physisorption were 8 and 6 kPa, respectively. The catalyst bed was diluted with acid-washed quartz powder (250–500 µm) to maintain plug-flow hydrodynamics and to avoid temperature gradients. Rates were unaffected by quartz/catalyst mass ratios between 1 and 4. Space velocities were varied between 0.1 to 1.0 cm³ (g-cat s⁻¹) at constant inlet reactant pressures. Conversion data were corrected at all conversions greater than 5% using plug-flow formalisms and previously measured alkane ODH rate equations. Reactant and product concentrations were measured by gas chromatography (Agilent 6890) using a capillary column (HP-1, 50 m, 32 mm, 1.05 µm) connected to a flame ionization detector and a packed column (Hayesep-DB, 100/120, 30 ft × 1/8 in.) connected to a thermal conductivity detector.

**Results and Discussion**

Previous work has suggested that the rate of C–H activation for a given alkane is governed by the rate of activation of the weakest C–H bond. This implies that an Arrhenius plot of (k₁ + k₂)nₚ where nₚ is the number of weakest C–H bonds, would give a systematic trend between the apparent activation energy and the energy of the weakest C–H bond for various alkanes. Figure 1a shows an Arrhenius plot of (k₁ + k₂)nₚ for various alkanes; Table 1 reports apparent activation energies and pre-exponential factors derived from Figure 1a. As can be seen from the inset in Figure 1a, a semilogarithmic plot of (k₁ + k₂)nₚ at 648 K as a function of the energy of the weakest C–H bond shows the expected effects of the bond strength of the weakest C–H bond on alkane reactivity. However, while (k₁ + k₂)nₚ decreased exponentially with the energy of the weakest C–H bond at a fixed reaction temperature, the apparent activation energy (see Table 1) did not vary systematically with the energy of the weakest C–H bond for a given alkane. We conclude, therefore, that the effects of C–H bond energies on activation energies for C–H bond activation cannot account for the observed differences in reactivity reflected in the measured values of (k₁ + k₂)nₚ for the various alkanes.

These apparent inconsistencies can be resolved by considering the combined reactivity of all C–H bonds in a given alkane and the effects of temperature on their respective contributions to overall rates. First, we relate all apparent rate constants in eq 1 to those for the elementary steps in Scheme 2. Alkane reactions involve their initial quasi-equilibrated physisorption followed by the kinetically relevant C–H activation step that forms alkoxide intermediates. Subsequent reactions of alkoxides can form an alkene via H abstraction reactions (1') or CO₂ reactions (2') via a sequence of irreversible steps involving
including alkane physisorption ($K_{ads}$) and C–H bond activation ($k_0$).

Figure 1. (a) Alkane reaction rate constant ($k_1 + k_2$) divided by the number of weakest C–H bonds ($n_w$) in C$_2$H$_6$, C$_3$H$_8$, n-C$_4$H$_{10}$, and i-C$_4$H$_{10}$, 6, 2, 4, and 1, respectively. (Inset) Normalized C–H bond activation rate constant at 648 K as a function of the weakest C–H bond strength in the alkane. (b) Estimate of $(k_1 + k_2)/n_w$ as a function of inverse temperature from eq 7.

TABLE 1: Apparent Activation Energies and Pre-Exponential Factors for the Normalized Alkane Consumption Rate Constants, $(k_1 + k_2)/n_w$a

<table>
<thead>
<tr>
<th>alkane</th>
<th>$E_{app}$, kJ mol$^{-1}$</th>
<th>$A_{app}$, cm$^3$ (mol V-s)$^{-1}$</th>
<th>weakest C–H bond strength, kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_6$</td>
<td>99 ± 9</td>
<td>1.8 × 10$^6$ (4.4 × 10$^6$, 7.2 × 10$^6$)</td>
<td>421</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>112 ± 6</td>
<td>3.2 × 10$^6$ (1.1 × 10$^6$, 9.7 × 10$^6$)</td>
<td>411</td>
</tr>
<tr>
<td>n-C$<em>4$H$</em>{10}$</td>
<td>96 ± 5</td>
<td>2.2 × 10$^6$ (8.0 × 10$^6$, 5.9 × 10$^6$)</td>
<td>411</td>
</tr>
<tr>
<td>i-C$<em>4$H$</em>{10}$</td>
<td>104 ± 3</td>
<td>1.5 × 10$^6$ (5.3 × 10$^6$, 3.9 × 10$^6$)</td>
<td>400</td>
</tr>
</tbody>
</table>

a Confidence intervals are included at the 95% level.

SCHEME 2: Alkane Activation Pathways in ODH with Additional Mechanistic Detailsa

In eq 3, $K_{ads}$ is the alkane physisorption constant, $k_0$ is the rate constant for C–H activation in physisorbed alkanes, and $k_1'$ and $k_2'$ are the rate constants for alkoxide reactions to form alkenes and CO$_2$ precursors, respectively. $K_{ads}$ depends on the adsorption enthalpy, $\Delta H_{ads}$, and adsorption entropy, $\Delta S_{ads}$:

$$K_{ads} = e^{\Delta S_{ads}/R} e^{-\Delta H_{ads}/RT}$$

(4)

All alkanes investigated, except C$_2$H$_6$, have more than one type of C–H bond (e.g., primary, secondary, and tertiary). Overall rate constants for C–H bond activation therefore contain contributions from each type of C–H bond in a manner that reflects their respective reactivities, activation barriers ($E_i$), pre-exponential factors ($A_i$), and number of equivalent bonds C–H bonds ($n_i$). The value of $k_0$ then becomes

$$k_0 = \sum_i n_i A_i e^{-E_i/RT}$$

(5)

Each $E_i$ in eq 5 can be related to the bond dissociation energy of the $i$th type of C–H bond ($D_i$) using a Brønsted–Evans–Polanyi relation, 12, 13 which relates barriers for primary C–H bonds ($E_1$) to those for other types by

$$E_i = E_1 + \alpha (D_i - D_1)$$

(6)

In eq 6, $E_1$ and $E_2$ refer to barriers for secondary and tertiary C–H bonds, respectively, and $\alpha$ is a constant for homologous series of reactants.

Equations 5 and 6, together with the assumption that pre-exponential factors are independent of bond type ($A_1 = A_1$, for all $i$), lead to an equation for $k_0$ in terms of the reactive properties of primary C–H bonds and the differences in energy among the various available C–H bonds

$$\frac{k_0}{n_w} = \frac{A_1}{n_w} e^{-E_1/RT} \sum_i n_i e^{-\alpha (D_i - D_1)/RT}$$

(7)

Equations 3, 4, and 7 can be used to describe the effects of temperature on $(k_1 + k_2)/n_w$ for different alkanes. $K_{ads}$ in eq 4 was estimated by using condensation enthalpies to represent $\Delta H_{ads}$ for each alkane (Table 2; ref 22), and $\Delta S_{ads}$ was determined from the partition functions for alkanes in physisorbed and gaseous states, assuming that physisorbed species retain two degrees of translation and three degrees of rotation. The values of $E_1$ and $A_1$ in eq 7 were obtained from rate data for C$_2$H$_6$ reactants, which contain only primary C–H bonds. $A_1$ was estimated by dividing the apparent pre-exponential factor ($1.8 \times 10^6$ cm$^3$ (g-atom V-s)$^{-1}$; Table 1) by the estimate for $e^{\Delta S_{ads}/R}$, which led to a value of $2.0 \times 10^7$ cm$^3$ (g-atom V-s)$^{-1}$ for $A_1$. $E_1$ was estimated by subtracting alkane adsorption...
TABLE 3: Apparent Activation Energy and Pre-Exponential Factors Determined from the Estimated Values of \( (k_1 + k_2)/n_w \) Presented in Figure 1b

<table>
<thead>
<tr>
<th>alkane</th>
<th>( E_{app} ) kJ mol(^{-1} )</th>
<th>( A_{app} ) cm(^3)(mol V-s(^{-1} ))(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_6 )</td>
<td>99</td>
<td>( 1.8 \times 10^9 )</td>
</tr>
<tr>
<td>( \text{C}_3\text{H}_8 )</td>
<td>94</td>
<td>( 5.9 \times 10^9 )</td>
</tr>
<tr>
<td>( \text{n-C}<em>4\text{H}</em>{10} )</td>
<td>90</td>
<td>( 3.2 \times 10^9 )</td>
</tr>
<tr>
<td>( \text{i-C}<em>4\text{H}</em>{10} )</td>
<td>92</td>
<td>( 1.3 \times 10^9 )</td>
</tr>
</tbody>
</table>

enthalpies from measured activation energies (99 kJ mol\(^{-1} \); Table 1) to give an intrinsic barrier of 114 kJ mol\(^{-1} \) for \( E_i \). The value of \( \alpha \) in eq 7 was assumed to be 0.24, the value of \( \alpha \) for H-atom transfer reactions\(^{23} \) and a typical \( \alpha \) value for BEP relations.\(^{24} \)

The Arrhenius plots for \( (k_1 + k_2)/n_w \) obtained from eqs 3, 4, and 7 and the assumptions described above (leading to the parameters in Table 2) are shown in Figure 1b. The Arrhenius plot for \( \text{C}_2\text{H}_6 \) is the same as in Figure 1a, because experimental \( A_i \) and \( E_i \) values are used for this molecule. Equation 7 is fundamentally non-Arrhenius for \( \text{C}_2\text{H}_6 \), \( \text{n-C}_4\text{H}_{10} \), and \( \text{i-C}_4\text{H}_{10} \), but this behavior cannot be detected in an experimentally accessible temperature range. The predicted values of \( (k_1 + k_2)/n_w \) for \( \text{C}_2\text{H}_6 \), \( \text{n-C}_4\text{H}_{10} \), and \( \text{i-C}_4\text{H}_{10} \), without additional assumptions, agree qualitatively with those determined from the experimental data (see Figure 1); however, the ordering of \( \text{C}_2\text{H}_6 \) and \( \text{n-C}_4\text{H}_{10} \) is inverted, and the predicted apparent activation energies are somewhat lower than those determined from experimental data. Table 3 shows that estimated activation energies decrease with alkane size and are lower for \( \text{n-C}_4\text{H}_{10} \) than \( \text{i-C}_4\text{H}_{10} \) while estimated pre-exponential factors increase in the order \( \text{C}_2\text{H}_6 < \text{n-C}_4\text{H}_{10} < \text{C}_3\text{H}_8 < \text{i-C}_4\text{H}_{10} \).

The observed differences between the model and the experimental results are likely due to errors in the estimated heats of physisorption. An error of 3 kJ mol\(^{-1} \) could cause an underestimate of the activation energy for the alkane size increases observed in Table 3 as well as the inversion of the ordering of \( \text{C}_2\text{H}_6 \) and \( \text{n-C}_4\text{H}_{10} \) in Figure 1b.

While it may be attractive to attribute the 30-fold difference in reactivity of the alkanes to the 20 kJ mol\(^{-1} \) difference in weakest C–H bond energies (see inset, Figure 1a), this conclusion is not supported by the measured apparent activation energies of the alkanes. There are no clear differences in measured activation energies that can account for the 30-fold increase in rates at 648 K. The interpretation presented above demonstrates that the trends in the measured data likely reflect differences in adsorption enthalpies and the number of C–H bonds in the alkane and not simply the differences in bond energies for the weakest bonds.

Measured ratios of the rate constant for alkane combustion to alkane dehydrogenation \( (k_2/k_1) \) are shown as functions of temperature in Figure 2a. This ratio is only weakly dependent on temperature for all alkanes, indicating that activation energies for \( k_1 \) and \( k_2 \) are similar and suggesting that the transition states for the formation of alkene precursors reactions (1'; Scheme 2) and CO, precursors reactions (2'; Scheme 2) are nearly identical in energy.

Previous studies suggest that alkene formation and initiation of CO, formation involve a common intermediate, an alkoxide.\(^{3,4,6} \)

We propose that the transition states for alkene formation and the first step toward CO, formation involve H abstraction from the intermediate I* shown in Scheme 2 and that all H atoms are candidates for abstraction from this intermediate.

We assume that \( k_2/k_1 \) ratios result from the product of two factors, one sensitive to alkane identity and one not. The former factor accounts for the nature, number, and relative strength of C–H bonds available to form combustion precursors or alkynes, and the latter factor accounts for entropic differences in the transition states for the formation of alkynes and combustion precursors. The activation energies of C–H bonds in alkoxides will vary with bond strength and are estimated using BEP relations with the same parameters as those used for alkane C–H bond activation. C–H bond energies in surface alkoxides are assumed to be equal to those in the corresponding alkane, and...
H atoms at the α position relative to the C–O surface bond are assumed to have lower C–H bond energies, equal to the energy of a C–H bond with the next higher carbon substitution, e.g., a surface ethoxide has the equivalent of 3 primary C–H bonds (421 kJ mol\(^{-1}\)) and 2 secondary C–H bonds (411 kJ mol\(^{-1}\)). It is assumed that the activation entropy for formation of alkene and CO\(_x\) precursor is independent of the structure of the alkoxide from which these products originate; however, the activation entropy for alkene formation is considered to be larger than that for CO\(_x\) precursor formation because the entropy gained upon formation of a loosely bound molecule, leading to an alkene, is larger than that for a tightly bound surface intermediate, resulting in a precursor to CO\(_x\). On this basis, the ratio \(k_2/k_1\) is given by

\[
\frac{k_2}{k_1} = \frac{\left(\sum_i f_i \sum_{ij} n_{ij,A} e^{-E_{ij}/RT}\right)}{\left(\sum_i f_i \sum_{ij} n_{ij,C} e^{-E_{ij}/RT}\right)} (e^{\Delta \Delta S/R})
\]

where \(f_i\) is the fraction of molecules that react via alkoxide type \(i\); \(n_{ij,A}\) and \(n_{ij,C}\) are the number of C–H bonds of type \(j\) yielding alkenes and combustion precursors, respectively, from the \(i\)th alkoxide type; \(E_{ij}\) is the activation energy for activation of the \(j\)th of C–H bond in the \(i\)th alkoxide; and \(\Delta \Delta S\) is the difference in the activation entropies for combustion precursor and alkene formation. From an analysis of the data presented in Figure 2, we estimate that \(e^{\Delta \Delta S/R}\) is \(\sim 0.2\), corresponding to \(\Delta \Delta S = -13\) J (mol K\(^{-1}\)) consistent with the expectation that the activation entropy for alkene formation is higher than that for combustion.

When more than one type of C–H bond is present in the reacting alkane, several surface alkoxide intermediates can be formed. With the exception of C\(_2\)H\(_6\), each alkane forms two types of alkoxide: a primary alkoxide and a secondary or tertiary alkoxide. C\(_2\)H\(_6\) forms only primary alkoxides. The fraction of each intermediate, \(f_i\), depends on the ratio of the C–H bond activation rate constants for each type of bond involved in their formation, \((k_1 + k_2)/k_i + k_2)_{\text{total}}\) (column 3; Table 4). The values of \(n_{ij,A}\) and \(n_{ij,C}\) are calculated for each alkane from the following assumptions about C–H activation in the alkoxide intermediates. After an alkoxide has been formed, in subsequent elementary steps H atoms will be abstracted from the alkoxide to produce an alkene or CO\(_x\) precursor. To estimate these H abstraction rates and their effect on product selectivity, we assume H abstraction rates are dependent on the C–H bond energy and that the position of the H atom abstracted determines the selectivity between combustion and alkene products. We propose that H abstraction at the β carbon in alkoxides forms alkynes and at the α or γ carbons forms precursors to CO\(_x\). For butoxides formed from n-C\(_4\)H\(_8\), H abstraction may lead to an alkoxide bound at two nonadjacent carbon atoms. Butoxides bound in two positions may undergo intramolecular H-atom transfer to release alkynes or abstraction of additional H atoms to form butadiene or CO\(_x\) precursors. We assume that internal H-atom transfers have comparable activation barriers to H abstraction and therefore conclude that one-half of the γ- and δ-H abstraction events lead to alkynes and one-half to CO\(_x\) precursors. The values of \(n_{ij,A}\) and \(n_{ij,C}\) are summarized in Table, where nonintegral values of \(n_{ij,A}\) and \(n_{ij,C}\) for n-butane-derived alkoxides are averages.

The values of \(k_2/k_1\) estimated using eq 8 are shown in Figure 2b. These estimates are almost independent of temperature even though temperature appears explicitly in eq 8 and also affects the values of \(f_i\) appearing in this expression. The ratio \(k_2/k_1\) predicted by eq 8 captures semiquantitatively the trends in measured values with alkane composition shown in Figure 2a. Differences in the sign of the slopes of the lines appearing in Figure 2b versus those appearing in Figure 2a are most likely due to the values of \(E_{ij}\) used in eq 8. These findings indicate that alkane C–H bond energies do not have a strong effect on \(k_2/k_1\), but do influence this ratio by determining which alkoxides are formed upon initial activation of an alkane molecule. Therefore, the primary selectivity of an alkane is determined by the fraction of alkane molecules passing through each alkoxide intermediate, and the selectivity of each alkoxide to products is determined by the number of C–H bonds activated to form a given product.

Figure 3a shows Arrhenius plots for alkene combustion rate constants \((k_3)\) for the alkenes formed from the respective alkanes examined in this study. Apparent activation energies are similar for all alkenes (90 ± 25 kJ mol\(^{-1}\)), but combustion rate constants decrease in the sequence i-C\(_2\)H\(_8\) > n-C\(_3\)H\(_8\) > C\(_3\)H\(_6\) > C\(_2\)H\(_4\) with \(k_3\) being 23 times larger for i-C\(_2\)H\(_8\) than C\(_2\)H\(_4\) at 648 K.

We consider next how \(k_3\) depends on the rate of C–H bond activation in alkenes. All C–H bonds in the alkene are assumed to be active, and activation energies are estimated on the basis of C–H bond energies (see eq 6). Alkenes have vinylic and allylic C–H bonds which are not found in alkanes. The bond energies for all vinylic C–H bonds are assumed to be 464 kJ mol\(^{-1}\) (C\(_2\)H\(_4\), ref 11) regardless of substitution at the carbon center. The bond energy for all allylic C–H bonds is 369 kJ mol\(^{-1}\) (C\(_3\)H\(_6\), ref 11), and we will use 2-C\(_2\)H\(_4\) as the model for all normal butenes because it is ~65% of all butene products; however, this will lead to an underestimate of \(k_3\) for n-C\(_3\)H\(_8\) of ~10%.

Alkenes C–H bond strengths vary to a significantly greater degree than alkane C–H bond strengths (95 kJ mol\(^{-1}\) versus 20 kJ mol\(^{-1}\) in i-C\(_2\)H\(_10\)), and therefore, it may be expected that
only the weakest C–H bonds will contribute to the reactivity of alkenes. The ratio of \( k_i \) for \( i-C_2H_4 \) to \( C_2H_4 \) estimated solely using BEP relations for activation energies is \( \sim 100 \) at 648 K, which is significantly larger than the actual ratio of 23 at 648 K. Activation energies for \( C_3H_6 \), \( i-C_2H_6 \), and \( n-C_3H_6 \) would also be expected to be lower than that for \( C_2H_4 \) by 20 kJ mol\(^{-1}\). Since these expectations differ significantly from the observed rate constants we consider an alternative approach.

For alkenes other than \( C_2H_4 \), we assume that there are two physisorbed precursors for C–H bond activation. One is a weakly bound state for allylic C–H bond activation which interacts via H-bonding and van der Waals interactions. The second is a precursor for vinylic C–H bond activation which interacts with Lewis acid centers via \( \pi \) bonds of the alkene. The former will represent a relatively weak binding and hence weaker than Lewis acid bond activation in alkanes. The subscript notation has been predicted values of \( k \).

\[
K_{i,ads,all} = \sum_{i,j} n_{ij}A_{ij}e^{-E_{ij}/RT}
\]

where \( K_{i,ads} \) is the adsorption constant for the \( i \)th precursor state and \( n_{ij}, A_{ij}, \) and \( E_{ij} \) retain their previous definitions for C–H bond activation in alkanes. The subscript notation has been expanded to identify the precursor state, \( i \), and the C–H bond activated in the \( i \)th precursor state, \( j \).

Activation energies, \( E_{ij} \) for H abstraction from alkenes were estimated using eq 6. The pre-exponential factor for allylic C–H bond activation was estimated as \( 2.0 \times 10^7 \) cm\(^2\) (mol V-s)\(^{-1}\) under the assumption that the interactions of these species are similar to those for alkenes. The pre-exponential factor for vinylic C–H bond activation was determined to be \( 3.0 \times 10^5 \) cm\(^2\) (g-atom V-s)\(^{-1}\) from the apparent pre-exponential factor for \( C_2H_4 \) because it has only vinylic C–H bonds.

Heats of adsorption for allylic C–H bond activation precursors were estimated using the enthalpy change occurring upon condensation of the alkene (for \( C_2H_4 \), \( i-C_2H_4 \), and \( n-C_3H_6 \) they are 18.5, 22.4, and 23 kJ mol\(^{-1}\), respectively; ref 22). The adsorption enthalpy for all species adsorbed as precursors to vinylic C–H bond activation was estimated from the difference between the activation energy of \( H \) abstraction from \( C_2H_4 \) from eq 6 (117 kJ mol\(^{-1}\)) and its apparent activation energy for combustion (89 kJ mol\(^{-1}\)). Therefore, our estimate that the adsorption enthalpy of \( C_2H_4 \) is 13 kJ mol\(^{-1}\) lower than that of \( C_2H_4 \) (15 kJ mol\(^{-1}\)) is not unreasonable given available information.

Estimates of \( k_3 \) based on eq 9 are shown in Figure 3b. The predicted values of \( k_3 \) for \( C_2H_4 \) and \( i-C_2H_4 \) agree well with the measured values shown in Figure 3a, but the estimated values of \( k_3 \) for \( C_3H_6 \) and \( n-C_3H_6 \) are \( \sim 1.5 \) times larger than those measured. This is likely due to underestimation of the adsorption enthalpies for precursors to vinylic C–H activation for larger molecules, which in this temperature range corresponds to a difference of less than 5 kJ mol\(^{-1}\).

The estimates of \( k_3 \) show that an important factor in limiting the selectivity of ODH is the strong binding of alkenes. The presence of allylic C–H bonds does not increase the reactivity of alkenes significantly because activation energies for \( k_3 \) are \( \sim 90 \) kJ mol\(^{-1}\) for all alkenes, regardless of the number of allylic C–H bonds. Precursors for allylic C–H bond activation are weakly bound, and the net effect is that the apparent activation energies for both vinylic and allylic C–H bonds are nearly identical.

Conclusions

Observed differences in the rates of \( C_2H_6 \), \( C_3H_6 \), \( n-C_3H_6 \), and \( i-C_2H_4 \) oxidative dehydrogenation occurring on VO/Al\(_2\)O\(_3\) can be interpreted using a limited set of assumptions in combination with reasonable estimates of the kinetic parameters appearing in Scheme 2. The initial step in the reaction sequence, the activation of a C–H bond, depends on the strength of the C–H bond, and all C–H bonds within the molecule are candidates for activation. Thus, the apparent activation energy is a rate-weighted average over all C–H bonds in the molecule. Alkenes and CO\(_2\) are assumed to be produced by a series of irreversible reactions that start from alkoxide species formed upon activation of a C–H bond in the reactant alkane. The ratio of the rate coefficients for alkane combustion to alkene formation (\( k_3/k_1 \)) is found to depend on the composition and structure of the alkane but is nearly independent of temperature. The ratio \( k_3/k_1 \) is directly influenced by the number and type of C–H bonds present in each alkoxide intermediate; however, \( k_3/k_1 \) is also indirectly affected by the strengths of the C–H bonds in the alkane because they determine the relative rates of formation of different alkoxide intermediates. The rate constant for alkene combustion (\( k_3 \)) is influenced more strongly by the strength of alkene adsorption than by the strength of the C–H bonds in the alkene. While the presence of allylic C–H bonds in alkenes suggests high reactivity, the stronger binding of alkenes plays a more important role in determining the rate of alkene combustion. \( C_2H_4 \) has no allylic C–H bonds, and hence, its reactivity is expected to be negligible; however, it has significant reactivity relative to other alkenes because it has relatively strong binding via its \( \pi \) bonds, which explains the low yields observed for \( C_2H_4 \).

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Supporting Information Available: Description of the methods used to prepare and characterize the catalyst used in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


