

Selective C–H Bond Activation via NO_x-Mediated Generation of Strong H-Abstractors

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Supporting Information

ABSTRACT: Mechanistic details and product distributions for C₃H₈–O₂ reactions catalyzed by gas-phase NO_x species are compared to reactions on solid V₂O₅ catalysts. C₃H₈ conversions are greatly enhanced by addition of small concentrations of NO to C₃H₈–O₂ mixtures without solid catalysts because homogeneous catalytic redox cycles involving oxidation of NO to NO₂, reduction by H-addition to form HONO and release of OH radicals facilitate abstraction of H-atoms from strong C–H bonds in C₃H₈. NO_x-mediated conversions exhibit C₃H₆ selectivity values among the highest reported at similar oxidative conditions because OH radicals are strong abstractors that activate C–H bonds via early transition states that do not exhibit significant bond elongation, which dampens bond-strength sensitivity and the preference to activate weak allylic C–H bonds in C₃H₆ products over strong bonds in C₃H₈. C₃H₈ conversion rates increase with residence time and NO, O₂, and H₂O pressures and exhibit supra-linear dependence on C₃H₈ pressure with trends analogous to homogeneous systems involving H-abstraction by OH radicals but significantly different from V₂O₅ catalysts that exhibit linear C₃H₈ pressure dependence and weak sensitivity to the other parameters. Temperature dependencies of rate-constant-ratios representing activation energy differences between primary and secondary C₃H₈ and allylic C₃H₆ C–H bonds in NO_x-catalyzed routes are much weaker than V₂O₅, consistent with dampened bond-strength sensitivity that is also observed in density functional theory estimates of these differences for OH radicals. NO_x mediation enables efficient alkane activation providing high productivity and yields at moderate temperatures, which is important for chemical transformations requiring rate-limiting C–H activation.

KEYWORDS: C–H activation, nitric oxide, OH radicals, strong abstractors, oxidative dehydrogenation, selective oxidation, H-atom addition energy

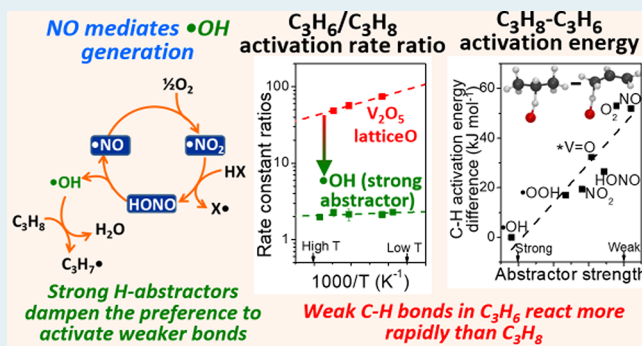
1. INTRODUCTION

Selective formation of alkenes and oxygenates via alkane activation in exothermic oxidative routes remains challenging because products undergo more facile secondary C–H bond activation or C–O bond formation than reactants.^{1,2} Systems reported to exhibit high propene (C₃H₆) yields in oxidative dehydrogenation (ODH) of propane (C₃H₈) on metal oxide catalysts and in gas-phase homogeneous reactions are summarized in Table S1 and Figure S1. Most oxide catalysts exhibit single-pass C₃H₆ yields below 20% and approach with increasing temperature values attainable in gas-phase C₃H₈–O₂ reactions in empty reactors;³ some alkali and halogen promoted oxides lead to 20–30% C₃H₆ yields at high temperatures via routes that tend to involve both homogeneous and heterogeneous contributions.⁴ Improvements in C₃H₆ selectivity with increasing temperatures in heterogeneous reactions are attributed to the lower activation energy for secondary reactions.¹ These studies show significant differences in kinetic details between solid catalysts and homogeneous gas-phase reactions.⁵ The reactions on solid oxides are typically first- and zero-order in alkane and O₂ pressures, respectively, while rates

on the latter systems tend to exhibit higher-order dependence on pressures of these reactants.⁵

Recent reports of high selectivity to C₃H₆ and C₂H₄ in C₃H₈–O₂ reactions on boron-based catalysts^{6–15} have attracted significant interest in understanding the origins of the reactivity of these materials previously considered inert. The boron nitride systems were shown to require treatments that restore nitrogen content for sustained performance, suggesting that nitrogen atoms are important,¹⁰ but reactions were also reported to proceed efficiently in other boron-based starting materials without nitrides.^{7,14} In spite of the requirement of solid-boron-based surfaces, these systems seem to exhibit supra-linear reaction orders in C₃H₈ and nonzero orders in O₂ pressures similar to homogeneous systems,⁶ pointing to some uniqueness in reaction steps involved.

Here, we report alternative selective dehydrogenation pathways involving homogeneous C₃H₈–O₂ reactions enhanced by



Weak C–H bonds in C₃H₆ react more rapidly than C₃H₈

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addition of trace concentrations of NO and assess how mechanistic details and selectivity limitations for this system compare with solid catalysts. In these reactions, the NO and NO₂ (NO_x) species undergo oxidation reduction catalytic cycles to release highly reactive OH radicals, which provide an important practical route to selective oxidative conversion of hydrocarbons at moderate temperatures. The effects of pressures of reactants and cofed H₂O on measured alkane conversion rates and energies of reactive species and transition states from density functional theory (DFT) are used to infer mechanistic details of NO_x catalysis, identify the types of radicals and reactive species involved, and determine conditions important for maximizing selectivity to desired products. The OH radicals generated in NO_x catalytic cycles are strong abstractors of H-atoms in strong C–H bonds, and therefore, they activate C–H bonds via exothermic steps with early C–H activation transition states that cannot differentiate between strong and weak bonds in alkanes and product alkenes, respectively. Such dampening of bond-strength effects on activation rates and its relation to selectivity improvements in C₃H₈ ODH are probed via temperature dependences of rate constant ratios relevant to selectivity and DFT calculations for C–H activation energy differences between C₃H₈ and the C₃H₆ product.

2. C₃H₈ ACTIVATION RATES AND SELECTIVITIES IN C₃H₈–O₂–NO REACTIONS

Figure 1 shows the effect of NO pressure on C₃H₈ conversion and product selectivity in empty flow reactors of two different

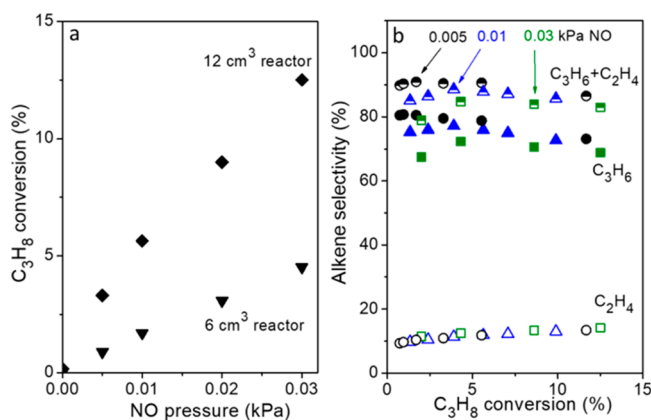


Figure 1. (a) C₃H₈ conversion in 6 and 12 cm³ reactors as a function of NO pressure at 30 cm³ min^{−1} flow rate, and (b) alkene selectivity as a function of C₃H₈ conversion for different residence times in 12 cm³ quartz reactor (773 K, 3 kPa C₃H₈, 10 kPa O₂, 0–0.03 kPa NO).

sizes (6 and 12 cm³ volumes; details in Figure S3). At the given reaction conditions (773 K, 3 kPa C₃H₈, 10 kPa O₂, 30 cm³ min^{−1}), C₃H₈ exhibits conversions below 0.1% in the absence of NO, but the introduction of 0.005 kPa NO increases the conversion by factors of 35 and 20 for the 6 and 12 cm³ reactors, respectively. The incorporation of NO leads to additional C₃H₈ reactions that are up to two or more orders of magnitude higher than the number of NO molecules added, depending on residence times and alkane pressures used, which suggests that NO acts as a catalyst instead of getting stoichiometrically consumed in the reaction. This catalytic role of NO_x in hydrocarbon conversion has been proposed and probed mechanistically in many previous studies.^{16–25} Such large

enhancements lead to homogeneous reactions rates comparable to those on solid catalysts, as shown in the Supporting Information via comparisons of productivity of NO_x-mediated reactions with several previously reported catalytic reactions (Table S2), which may make it practical to run these reactions at large scales. The C₃H₈ conversion increases with increasing NO pressure and is greater for the larger reactor, suggesting that reactions proceed in the gas-phase via homogeneous pathways enabled by NO or its oxidation products. The conversions increase more significantly than reactor volumes (Figure 1a) because rates are higher at longer residence times; such nonlinear residence time effects are further probed in section 4. C₃H₈–O₂ reactions at 0.005 kPa NO and conversions below 5% exhibit C₃H₆ and C₂H₄ selectivity near 80% and 10%, respectively (Figure 1b), total C1–C3 oxygenates selectivities near 7%, and total CO and CO₂ selectivity below 3% (detailed product selectivities in Figure S6a). The C₃H₆ selectivity decreases weakly with conversion, consistent with higher yields than those typically attained on oxide catalysts, as also reported in the case of boron nitride catalysts.⁶ The formation of C₂H₄ is consistent with C–C bond cleavage typically observed when homogeneous pathways mediate C₃H₈ activation, which point to mechanistic similarities between NO-catalyzed reactions and the homogeneous reactions previously reported.^{3,4,26} Higher NO feed concentrations enhance C₃H₈ conversion rates more significantly but cause a slight decrease in C₃H₆ selectivity at low conversions (Figure 1b), suggesting that an optimum low NO concentration maximizes the alkene selectivity at a given conversion.

Large enhancements in rates of alkane activation by NO_x have been studied previously for the direct conversion of CH₄ to oxygenate such as HCHO.^{19,27} The NO_x-catalyzed reactions led to greater HCHO selectivity than heterogeneous routes, but the yields remained well below 10% and significant side reactions that introduced nitrogen into hydrocarbons were observed due to large NO_x feed concentrations up to 5 kPa. We show here that much smaller NO concentrations can be used to selectively convert C₃H₈ to alkenes (Figure 1b; Section S4). Such small concentrations of NO are present as impurities in industrial exhaust gases^{28–30} that may be added to hydrocarbons and O₂ to carry out the desired oxidative conversions. For example, power plant boilers and other sources such as industrial boilers, incinerators, and gas turbines operating at high temperatures produce NO_x by oxidizing N₂ or nitrogen-containing fuels, leading to concentrations up to 300 and 1000 ppm at operating temperatures of 1350 K³⁰ and 1750 K,³¹ respectively. Flue gases from these sources can be mixed with C₃H₈–O₂ mixtures for production of alkenes and other oxygenates using NO_x at much lower temperatures and for potentially avoiding more expensive NO_x treatments.

The mechanism of NO_x-catalyzed conversions of hydrocarbons such as CH₄ involve the generation of OH radicals. These radicals have been detected by laser-induced fluorescence measurements³² for CH₄/O₂/NO_x reactions and their role as predominant abstractors of H-atoms from strong C–H bonds has been determined from kinetic simulations.^{19,27,32} The OH radicals generated from H₂O and O₂ in alkali promoted oxides and molten salt catalysts at high temperatures have also been shown to activate hydrocarbons.^{4,33,34} Therefore, we probe the role of H₂O in further enhancing NO_x-mediated C₃H₈ conversions by cofeeding H₂O to C₃H₈–O₂ reactants with and without NO_x catalysts, as shown in Figure 2. When no H₂O is cofed (0 kPa H₂O in Figure 2a), the C₃H₈ conversion is near

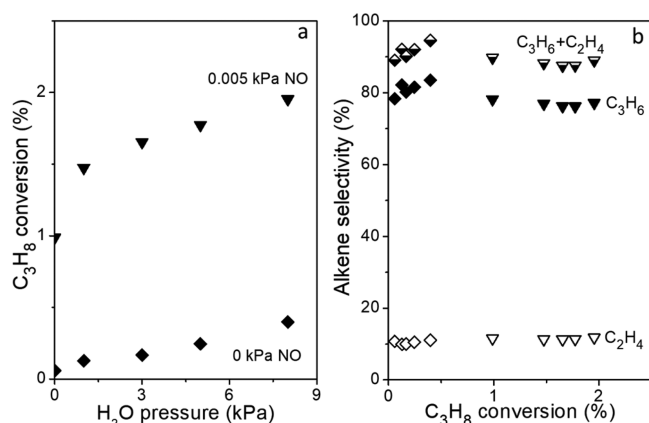


Figure 2. (a) C₃H₈ conversion as a function of cofed H₂O pressure (at 30 cm³ min⁻¹), and (b) alkene selectivity as a function of C₃H₈ conversion at different residence times (diamonds, 0 kPa NO; triangles, 0.005 kPa NO; 773 K, 3 kPa C₃H₈, 10 kPa O₂, 0–8 kPa H₂O, 6 cm³ reactor).

1% for 0.005 kPa NO_x, which is much higher than conversion without NO_x. At this conversion, the average pressure of H₂O produced from C₃H₈–O₂ reactions are near 0.01 kPa H₂O, which is much less than the cofed water pressures. The addition of 1 kPa H₂O for 0.005 kPa NO_x increases the conversions to nearly 1.5%; for reactions without NO_x, the conversion increase is much smaller. Further increase in cofed H₂O pressure increases the C₃H₈ conversion with slightly greater sensitivity for reactions with NO_x. Thus, H₂O enhances reaction rates more significantly when NO_x is present, suggesting that it acts as a promoter or a cocatalyst for NO_x-catalyzed OH radical generation. The alkene selectivities remain similar for reactions with and without NO_x and exhibit weak sensitivity to conversion (Figure 2b), suggesting that similar reactive species can be responsible for alkane activations in both cases. These reactive species have been proposed and shown to be OH radicals in previous homogeneous reaction studies.^{19,27,32}

Next, we propose mechanistic details involving catalytic reactions of NO_x and H₂O that lead to rate enhancements in gas-phase C₃H₈–O₂ reactions shown in Figures 1 and 2. We probe the feasibility of these reactions using DFT-derived H-abstraction strengths of gaseous reactive species, C–H bond strengths for different types of bonds in C3 hydrocarbons and organic radicals, C–H bond activation energies and experimental activation energies available in the literature, and electronic energies and Gibbs free energies for reactions involved in catalytic steps. These assessments are used to establish the nature of active species relevant for the selective gas-phase oxidative dehydrogenations.

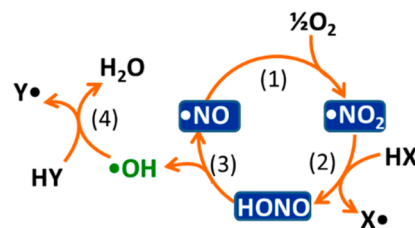
3. OH RADICAL GENERATION VIA NO_x CATALYSIS AND MECHANISTIC CONNECTIONS OF RATE AND SELECTIVITY ENHANCEMENTS TO STRENGTHS OF H-ABSTRACTORS AND C–H BONDS

3.1. H-Abstractors Generated in NO_x Catalytic Cycles.

Previous kinetic simulations for CH₄–O₂–NO_x reactions suggest that NO₂ formed via NO oxidation facilitates pathways that generate OH radicals, which are strong abstractors of H-atoms in CH₄, and reform NO to complete NO_x catalytic cycles,¹⁶ without NO getting stoichiometrically consumed in the process.^{19,27} Dehydrogenations of saturated hydrocarbons and oxygenates occur via homolytic C–H activation steps at H-

abstracting oxidants,^{2,35} indicating that mechanisms similar to CH₄ activation are also relevant to C₃H₈ dehydrogenation. Scheme 1 shows such catalytic cycles involving interactions of

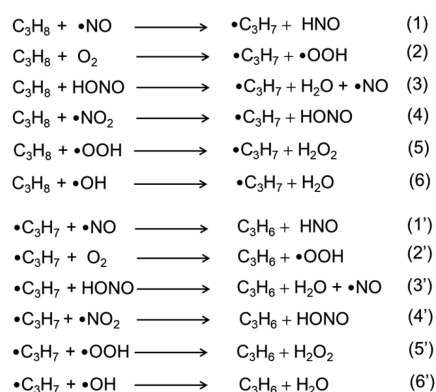
Scheme 1. NO_x Catalytic Cycles Generating OH Radicals^a



^aHX and HY represent organic molecules activated by C–H activation.

NO_x with oxidant O₂ and reductant hydrocarbons. The oxidation of NO to •NO₂ (step 1, Scheme 1) can occur via well-established kinetics with rates proportional to O₂ pressure and the square of NO pressure, and with slightly negative activation energy that indicates facile nature of this step.³⁶ This reaction is mediated by a kinetically relevant step involving a trimolecular transition state.^{37–40} The NO₂ molecule abstracts an H-atom from a saturated organic molecule (HX; e.g., C₃H₈) to form HONO and an organic radical species (X•, step 2, Scheme 1). The HONO species dissociates to form OH radical and NO molecule (step 3). The OH radicals generated in this cycle also abstract H-atoms from organic molecules (HY) to form organic radical species (Y•) and H₂O (step 4). These cycles are analogous to Mars van Krevelen (MvK) redox cycles ubiquitous in selective oxidation of organic molecules on oxides where facile O₂ activation forms an oxidized form of the catalyst, which is reduced via kinetically relevant C–H activation steps to form surface OH species that dehydroxylate to form H₂O and O-vacancies.^{41–44} The redox cycles for NO_x however, can generate highly energetic gaseous OH species instead of surface oxygen species.

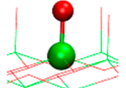
The OH radicals exhibit a strong tendency to abstract H-atoms from strong C–H bonds, as proposed in many previous studies.^{4,16,17,19,21,26,34,45} Their formation according to Scheme 1, however, requires a sacrificial H-abstraction by NO₂ to generate HONO precursors. The HX and HY molecules in Scheme 1 represent different or the same organic molecules depending on the types of species present during reactions and the reactivity preferences dictated by the strengths of the abstractors and C–H bonds. HX represents a sacrificial species with weak C–H bonds that can activate C–H bonds by NO₂ as an abstractor for facile HONO formation. Previous kinetic simulations for CH₄–O₂–NO_x reactions found that CH₄ itself acts as the sacrificial species near zero conversion during the induction period when weaker C–H bonds are not present, but at finite conversions oxygenate species such as HCHO molecules and HCO radicals with very weak C–H bonds can be the sacrificial H-donors.^{18,19,22–24,27} The organic radicals (X• and Y•) further react with oxidants to form unsaturated or oxidized organic molecules (e.g., C₃H₆, HCHO). Species with weak C–H bonds may activate on weaker abstractors, leading to several possibilities including C–H bond activation in organic species occurring directly at HONO, NO, or O₂ to form H₂O + NO, HNO, and •OOH species, respectively. These plausible steps for the activation of C₃H₈ and C₃H₇ radicals by different oxidants are shown in Scheme 2.

Scheme 2. C–H Activations in C₃H₈ and C₃H₇ Radical by Different Oxidant Species Involved in NO_x Catalytic Cycles

These possibilities lead to complex reaction networks in which only some of the many steps contribute to most of the observed rates and to selectivity limitations.^{18,19,22–24,27} Kinetic analyses for such systems require knowledge of rate constants for all possible steps. Many of these constants for CH₄ oxidation are available from experiments but require further modifications for kinetic simulations. Analogous analyses for C₃H₈ oxidation are more complex than CH₄ and involve greater uncertainty in values of rate constants due to the significantly greater number and structural complexity of possible organic species involved as minor products. Yet, trends in reactivity of the catalytic species present in reaction can be determined using thermodynamic properties reflected in bond strengths in reactants and abstractors derived from DFT calculations. Analyses based on these reactivity trends are used here to derive mechanistic insights and assess relevance of reactive species to rates and selectivity, instead of numerical data based on tabulated rate constants and activation energies. We probe which of the possible steps may prevail at reaction conditions by examining the strengths of C–H bonds and abstractors involved in the steps shown in Scheme 2.

3.2. Strengths H-Abstractors and C–H Bonds. The H-abstraction strengths of the various molecular species involved in catalytic cycles of NO_x (Schemes 1 and 2) and of lattice O-atoms of the V₂O₅(001) surface used as a representative solid oxide catalyst are given by the DFT-derived values of H-atom addition energy (HAE) shown in Table 1. The DFT calculations

Table 1. DFT (PBE-D3BJ)-Derived Electronic Energies for H-Atom Addition to H-Abstractors

H-abstractor	Structures	HAE (kJ mol ^{−1})
•NO		−179
O ₂		−221
HONO		−256
•NO ₂		−319
•OOH		−365
•OH		−520
V=O*		−292

were performed using PBE-D3BJ DFT functionals⁴⁶ within the Vienna Ab-Initio Simulation Package. Gas molecules were simulated in a 20 Å cubic box with dipole corrections, and V₂O₅(001) surface were simulated using two layers of orthorhombic oxide repeating periodically in lateral directions and vacuum separation in (001) direction. Additional details of computational methods and catalyst models are provided in Section S2.4. More negative HAE values represent stronger H-abtractors that tend to be more reactive for C–H bond activation.

The HAE values range from −179 kJ mol^{−1} to −520 kJ mol^{−1} for the weakest (NO) to the strongest (OH) abstractor in Schemes 1 and 2. The HAE value for the O-atom in terminal V=O* species in V₂O₅, the most reactive site on this oxide, is −292 kJ mol^{−1}. Weak H-abtractors NO, O₂, and HONO exhibit HAE values less negative than the lattice O-atoms of V₂O₅. As a result, these species are unlikely to directly abstract strong C–H bonds in alkanes. NO₂ and OOH radical species are stronger abstractors than V₂O₅, while OH radicals are much stronger than even OOH (Table 1). These values are consistent with the catalytic cycle proposed in Scheme 1, where C–H bonds are abstracted from NO₂ and OH radicals instead of the weak abstractors such as NO. The strong H-abstraction propensity of OH radicals leads to high reactivity of this abstractor for strong C–H bonds.

Table 2 shows the strength of C–H bonds in C₃H₈, in dehydrogenation product C₃H₆, and in radicals formed by first

Table 2. C–H Bond Dissociation Enthalpy (ΔH_{C–H}⁰ at 298.15 K) and Electronic Energy (ΔE_{C–H}⁰) in C3 Hydrocarbons and Radicals

molecule	C–H bond	ΔH _{C–H} ⁰ (kJ mol ^{−1})		ΔE _{C–H} ⁰ (kJ mol ^{−1}) (PBE-D3BJ)
		measured ⁴⁷	DFT-derived (PBE-D3BJ)	
C ₃ H ₈	CH ₃ CH ₂ CH ₃	411	391	421
	CH ₃ CH ₂ CH ₃	422	408	438
C ₃ H ₆	CH ₂ =CHCH ₃	363	345	371
	CH ₂ =CHCH ₃		452	478
	CH ₂ =CHCH ₃		427	454
•C ₃ H ₇	CH ₃ •CHCH ₃		159	174
	•CH ₂ CH ₂ CH ₃		142	157
•C ₃ H ₅	CH ₂ =CH•CH ₂		235	256

C–H activation in these molecules, as reflected in their experimental and PBE-D3BJ-derived bond dissociation enthalpies and electronic energies (BDE). Larger BDE values represent stronger C–H bonds that exhibit higher C–H activation energy for a given H-abstractor. The DFT-derived enthalpies are slightly lower than experimental values but exhibit similar differences among different types of C–H bonds as observed in measurements.^{35,47}

The electronic C–H BDE values for different types of C–H bonds in C₃H₈ and C₃H₆ range from +371 kJ mol^{−1} to +478 kJ mol^{−1}. The BDE value is higher for the primary C–H bond in C₃H₈ (438 kJ mol^{−1}) than the secondary C–H bond (421 kJ mol^{−1}, Table 2), suggesting that the secondary bonds are more reactive for homolytic C–H activations. The vinylic C–H bonds of the C₃H₆ are much stronger than both primary and secondary bonds in C₃H₈ (478 and 454 kJ mol^{−1}, Table 2), suggesting that these bonds are much less reactive. In contrast, the allylic C–H bonds in C₃H₆ are weaker than the bonds in C₃H₈ (371 kJ mol^{−1}, Table 2), which indicates that the C₃H₆ molecule can

undergo facile C–H activations at the allylic position and is more reactive for C–H activations than the reactants. Such allylic C–H activations are often rate-limiting steps in oxidation of C_3H_6 .^{48–51} C_3H_6 is the desired product in C_3H_8 oxidative dehydrogenation, and therefore, these facile C–H activations represent the most significant limitations to the selectivity to this product on typical transition metal oxide catalysts such as V_2O_5 because they lead to more facile activation of weaker C–H bonds.

The C–H BDE values for propyl radical species formed by first C–H activation in C_3H_8 are much lower than all bonds in C_3H_8 and C_3H_6 (157 and 174 kJ mol^{-1} for primary and secondary radicals, respectively; Table 2), which is indicative of the much more reactive nature of these radicals. The C–H BDE for the allyl radical formed from C_3H_6 is higher than propyl radicals, but it remains much lower than C_3H_8 and C_3H_6 molecules suggesting their reactive nature.

Next, we probe the effect of the BDE and the HAE values on DFT-derived C–H activation energies given by differences in electronic energy between the C–H activation transition state and the isolated abstractor and hydrocarbon. These trends are used to determine preferences for the abstractors for the activation of the different organic molecules and radicals in Table 2 and the most likely abstractors involved in C_3H_8 activation in the NO_x -mediated catalytic cycles shown in Scheme 1.

3.3. Effects of Abstractor Strengths and C–H Bond Strengths on C–H Activation Energies. The C–H activation energies derived from PBE-D3BJ calculations for a secondary C–H bond in C_3H_8 ($CH_3CH_2CH_3$, Table 2) to form a secondary C_3H_7 radical, for a C–H bond in the secondary C_3H_7 radical ($\dot{C}H_3CHCH_3$) to form the desired C_3H_6 product, and for an allylic C–H bond in C_3H_6 ($CH_2=CHCH_3$), as a function of HAE of the H-abstractors in Table 1 are shown in Figure 3. These C–H activations shown here represent the sequence of steps required to form the desired C_3H_6 product and its secondary reactions ($C_3H_8 \rightarrow \dot{C}C_3H_7 \rightarrow C_3H_6 \rightarrow \dot{C}C_3H_5$); thus, activation energy differences among these steps are relevant to C_3H_6 selectivity.

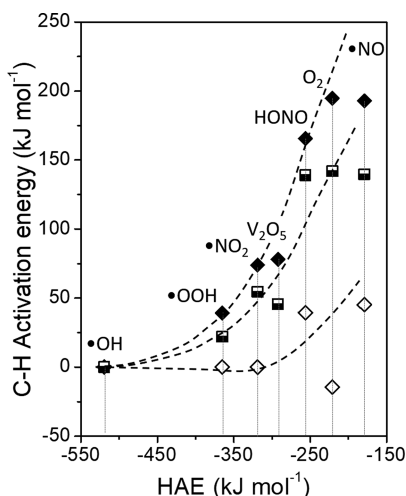


Figure 3. Activation energies derived from PBE-D3BJ calculations for C–H bonds in $CH_3CH_2CH_3$ (◆), $\dot{C}H_3CHCH_3$ (◇) and $CH_2=CHCH_3$ (half-filled squares) as a function of H-atom addition energies for abstractors shown in Table 1. Dashed lines show trends.

The C–H activation energies for a secondary C–H bond in C_3H_8 are lower for stronger H-abstractors with more negative HAE values ($CH_3CH_2CH_3$, Figure 3). This C–H bond is weaker and more reactive among the two types of C–H bonds in C_3H_8 (Table 2). The activation energy is greater than 150 kJ mol^{-1} for weak abstractors NO , O_2 , and $HONO$, near 75 kJ mol^{-1} for NO_2 and V_2O_5 abstractors of intermediate strength, and 39 kJ mol^{-1} for the OOH radical. The OH radicals are much stronger H-abstractors than all other abstractors. The energy of the system decreases monotonically as the C_3H_8 molecule approaches this abstractor and does not exhibit a local maximum indicative of a transition state (nudged elastic band calculation shown in Figure S20), which leads to an activation energy of zero. These trends in C_3H_8 activation energy are consistent with experimental values reported in the literature for the different oxidants, which are shown in Table S4. The measured activation energies in literature are 200, 95, and 58 kJ mol^{-1} for O_2 , NO_2 , and the OOH radical and nearly zero for the OH radical.^{52–55} These predicted and measured activation energies suggest that the activation rates for OH radicals are much higher than the other abstractors. Estimates from Arrhenius expression suggests that C_3H_8 activation rates at 773 K for OH radical are larger than OOH radical by 3 orders of magnitude for the DFT-derived activation energy (+39 kJ mol^{-1} for OOH , Figure 3) and by 4 orders of magnitude to measured values in the literature (+58 kJ mol^{-1} for OOH ⁵⁴); other abstractors are much less reactive than both OH and OOH radicals. Thus, C_3H_8 molecules will be activated preferentially by OH radicals even if the concentration of these radicals were much smaller than the concentrations of other abstractors. These estimates are consistent with the predominant role of OH radicals in homogeneous oxidations catalyzed by NO_x as well as alkali promoted and molten salt oxides.^{4,16–21,34}

The C–H bond in the C_3H_7 radical is much weaker than C_3H_8 , leading to much lower activation energy for a given abstractor ($\dot{C}H_3CHCH_3$, Figure 3). The C–H activation energy for this radical is 45 and 40 kJ mol^{-1} , for weak abstractors NO and $HONO$, respectively. For NO_2 and OOH and OH radicals, the energies decrease monotonically as the C_3H_7 radical approaches the abstractors, leading to zero activation energies. O_2 forms a stable physisorbed complex with the C_3H_7 radical which undergoes C–H activation via a transition state with -14 kJ mol^{-1} activation energy relative to the isolated precursors. This negative activation energy is consistent with the experimental value of -9 kJ mol^{-1} reported in the literature⁵⁶ (Table S4). Thus, in contrast to the C_3H_8 molecule, the C_3H_7 radical does not exhibit a strong preference for OH radicals as abstractors. The activation energy is near zero for several abstractors and it can be activated on several abstractor species, depending on the abundance of these species. The C_3H_7 radical can also act as a sacrificial H-atom donor required to form $HONO$ (Scheme 1). O_2 exhibits slightly negative activation energies and is fed at much higher concentrations than NO in the measurements (typical conditions: 3, 10, and 0.005 kPa C_3H_8 , O_2 , and NO , respectively); thus, O_2 is likely to activate most of the C_3H_7 radicals.

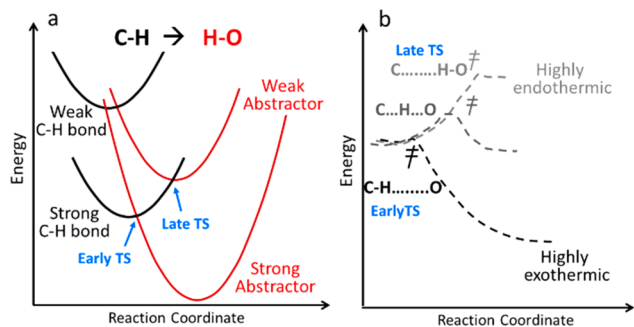
The C–H activation energies as a function of HAE were also calculated for a primary C–H bond in C_3H_8 ($\dot{C}H_3CH_2CH_3$, Table 2), and subsequent C–H activation in the primary radical to form C_3H_6 are shown in Figure S14 and Table S6. These activation energies exhibit similar overall trends as that shown for the secondary C–H bond activation and the subsequent alkene formation (Figure 3). The activation energies for

$\text{CH}_3\text{CH}_2\text{CH}_3$ are zero for OH radicals and 12–17 kJ mol⁻¹ higher than $\text{CH}_3\text{CH}_2\text{CH}_3$ for other abstractors, consistent with the less reactive nature of stronger primary C–H bonds. OH radicals, however, suppress these bond strength differences, leading to no activation energy difference between primary and secondary C–H bonds. The activation energies for both types of C_3H_7 radicals are similar within 6 kJ mol⁻¹ (Figure 3, Figure S14, and Table S7).

Figure 3 also shows the activation energies for the allylic C–H bond in C_3H_6 . This C–H bond is weaker than the bonds in C_3H_8 by about 50 kJ mol⁻¹ but nearly 200 kJ mol⁻¹ stronger than the bonds in C_3H_7 radicals (Table 2). As a result, the activation energies for C_3H_6 are intermediate between the two species. The lower activation energies of C_3H_6 than C_3H_8 is consistent with low selectivity to the desired C_3H_6 product observed on most oxide catalysts. The difference between the two activation energies diminishes as the abstractors become stronger and nearly zero for OH radicals, suggesting that stronger abstractors are more selective to C_3H_6 .

The decrease in activation energies with increasing abstractor strength exhibits a curved trend with a smaller local slope for stronger abstractors (Figure 3), consistent with deviations from linear Brønsted–Evans–Polanyi (BEP) relations^{57,58} that have been observed for C–H and O_2 activations and C–O bond formation reactions on oxides.^{35,59–61} Such trends can be described by crossing-potential models that represent C–H activation transition state structures and their energies via the intersection point between harmonic potentials for C–H bond cleavage and O–H bond formation, as shown in Scheme 3.

Scheme 3. Effect of C–H Bond Strength and H-Abstractor Strength on C–H Bond Activation^a



^a(a) Crossing of harmonic potentials for C–H cleavage and O–H formation, and (b) changes in lateness of transition state (TS) with reaction energies.

The stretching of a C–H or an O–H bond beyond its equilibrium length increases the potential energy of the species, which is represented here by parabolic shape of the harmonic potential energy surface for these bonds (Scheme 3a). A lower vertical position of the minimum energy point of a parabola represents stronger bond strength. C–H activation requires breaking of a C–H bond and formation of an O–H bond, which can be represented by overlapping the potentials (parabolas) for a reactant C–H bond and a product O–H bond. The *x*-axis here represents the position of H-atom moving away from the C-atom and toward the O-atom. The intersection point of the two potentials represents the C–H activation transition state.

For a given C–H bond, the minimum energy point of the OH potential shifts to lower energy while keeping the same distance with the C–H bond minimum position along the *x*-direction as

the H-abstractor becomes stronger (stronger O–H bond) and the C–H activation step becomes more exothermic. As a result, the intersection-point appears at lower energies (*y*-axis) and at earlier points along the C–H stretching coordinate (*x*-axis). When the abstractors are very strong, the intersection occurs near the flat part of the C–H parabola near the equilibrium C–H bond position where the energy of the intersection point decreases weakly with lowering of the O–H parabola (Scheme 3a). These intersection points represent early transition states with barely stretched C–H bonds and activation energies near zero.

The crossing potential models accurately capture the general shape of the activation energy versus HAE trends in Figure 3. Some deviations from the trendlines appear because activation energies depend not only on bond-making and -breaking shown by crossing potentials but also on additional attractive radical–radical or dispersive van der Waals interactions between reacting species in the reactant and the product state, as shown recently.³⁵ The functional form of the dependence of activation energies on the reaction energies derived from such crossing potential models are analogous to the activation energy term in Marcus theory,⁶² which accounts for the curvatures neglected in linear BEP relations.³⁵ Predictions from such models are also consistent with Hammond's postulate that more exothermic reactions occur via earlier transition states that are more reactant-like (Scheme 3b).⁶³ The small C–H bond elongation at early transition states, in turn, leads to activation energies insensitive to bond strengths.

For the C–H activation steps shown in Scheme 2 and the corresponding activation energies in Figure 3, the final state reaction energy is given by the summation of the C–H BDE in Table 2 and HAE in Table 1. The C–H BDE in C_3H_8 and C_3H_6 are larger than negative of the HAE of all abstractors except the OH radical. As a result, these reactions are endothermic for these weaker abstractors and highly exothermic for the OH radicals. As the reactions become less endothermic, the transition states appear earlier along the reaction coordinate and become less sensitive to bond strength. The DFT-derived bond-lengths of the transition states are shown in the Supporting Information, and they indeed exhibit shorter C–H and longer H–O bonds for more exothermic reactions (Figure S15). For OH radicals, the reaction is very exothermic, and the transition states are very early, leading to nearly complete insensitivity to bond strength and suppression of high reactivity for the weaker bonds. For weak C–H bonds in C_3H_7 radicals, the reaction is exothermic and is mediated by early transition states for both strong and weak abstractors which leads several abstractors with near-zero activation energies (Figure 3). Thus, both calculated activation energies and fundamental conceptual assessments of the bond activation process point to the importance of OH radicals in selectively activating strong C–H bonds.

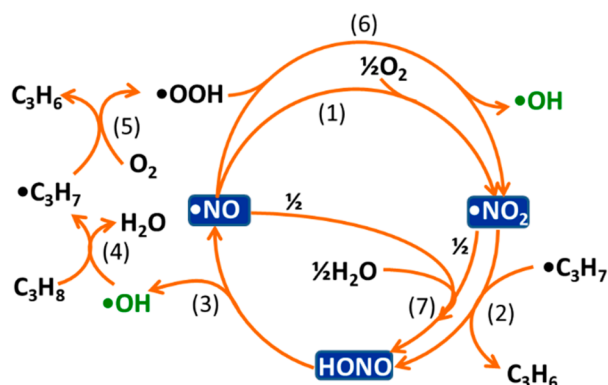
These analyses establish that (i) OH radicals can be generated from redox catalytic routes consisting of NO_x reduction oxidation steps reported in many past studies on NO_x -mediated hydrocarbon oxidations, (ii) OH radicals are very strong H-abstractors that activate strong C–H bonds in C_3H_8 at rates several orders of magnitude higher than any other reactive species, which makes them the predominant C_3H_8 activating species even when they are present at lower concentrations than other species, (iii) weak C–H bonds in C_3H_7 radicals do not require strong H-abstractors and can be activated by NO_2 and O_2 , with O_2 being more abundant, and (iv) OH radicals can

improve selectivity by dampening the preference exhibited by all other abstractors for activating C_3H_6 over C_3H_8 .

Next, we combine these insights with additional steps for consumption of OOH radicals and the role of H_2O in OH radical generation and use DFT calculations to assess energies of steps in a proposed reaction network for C_3H_8 activation in NO_x -mediated routes.

3.4. Role of H_2O and Alternative OH Radical Generation Paths. Scheme 4 shows more complete steps

Scheme 4. Primary C_3H_8 Activation Routes in NO_x Catalytic Cycles



involved in NO_x -mediated catalytic mechanism for OH radical generation and C_3H_8 activation. Electronic energies, enthalpies, and Gibbs free energies derived from DFT calculations for the steps in this mechanism are shown in Table 3. NO_2 formation via $NO-O_2$ reaction is highly exothermic, but its stoichiometry leads to fewer products than reactants, which results in entropy loss and slightly positive Gibbs free energies (22 kJ mol^{-1} , step 1, Table 3; $\Delta G = \Delta H - T\Delta S$). The mildly endoergic nature of this step (i.e., slightly positive ΔG) suggests that it will form a small but significant concentration of NO_2 to reach equilibrium. Higher O_2 concentrations push this equilibrium toward the NO_2 product. C_3H_7 radicals donate a H-atom to NO_2 to form HONO and C_3H_6 (step 2 in Scheme 4) because this step was found to be facile based on calculated C–H activation energies in Figure 3; this step is also highly exothermic and exoergic. The OH radical formation by HONO dissociation (step 3) is highly endothermic but only mildly endoergic due to entropy gain from the formation of two molecules from one ($\Delta G = +12 \text{ kJ mol}^{-1}$, step 3, Table 3). The OH radical activates C_3H_8 to form

the C_3H_7 radical and H_2O , in highly facile exothermic and exoergic steps (step 4). The C_3H_7 radical activates an O_2 molecule to form a OOH radical (step 5), which is also facile. This OOH radical can react with NO to form NO_2 and OH radical (step 6), which is much more facile than NO oxidation by O_2 (step 1). Previous kinetic simulations have shown that step 6 can lead to rapid NO oxidation, forming NO_2 in greater concentrations than the equilibrium value for step 1.¹⁹ These details show that NO_x can catalyze OH radical generation and C_3H_8 activation in a series of facile steps.

H_2O enhances C_3H_8 conversion in $C_3H_8-O_2$ reaction and does so to a much greater extent for NO_x -catalyzed reactions than reactions without NO_x (Figure 2). These enhancements are consistent with the role of water in generating OH radicals in molten salt catalysts and the facile reactions of NO_x to form HONO even at room temperature.⁶⁴ The HONO formation via the $NO-NO_2-H_2O$ reaction is exothermic and moderately endoergic at the reaction temperature (step 7, Scheme 4 and Table 3, $\Delta H = -35 \text{ kJ mol}^{-1}$, $\Delta G = +53 \text{ kJ mol}^{-1}$, 773 K), suggesting formation of small but significant concentrations of HONO using high H_2O pressures to push equilibrium toward products. DFT calculations for this reaction are shown in Figure S22. These calculations show that NO, NO_2 , and H_2O form a trimolecular complex and form HONO via a transition state with negative electronic activation relative to isolated molecules. Lower temperatures lead to a less exoergic nature of this step due to lesser contribution of entropy loss to free energy. The HONO molecules then dissociate to form OH radicals (step 3). Another step involving HONO and HONO₂ from NO_2 and H_2O is shown in Table 3 (step 8). This step is also mildly endoergic and suggests another route to a species that dissociates to form OH radicals. This reaction was also found to be facile in experiments reported in the literature.^{65,66} Thus, several steps involved in catalytic redox cycles of NO_x generate OH radicals (Scheme 4). These radicals can also be quenched to form O_2 and H_2O (step 9, Table 3), which leads to low concentration of these radicals. This highly potent nature of these radicals leads to enhanced C_3H_8 activations even at these low concentrations. Formation of such abstractors without NO_x would require direct initial alkane activation on O_2 , which has very high activation energies (Figure 3, Scheme 2). NO_x facilitates OH radical generation at moderate temperature by forming stable NO_x -derived species that enhance OH radical formation at moderate temperature. At finite C_3H_8 conversions organic species other than C_3H_8 exist in the reaction mixture, including alkenes and oxygenate formed as minor products. Plausible steps for formation of these products

Table 3. Electronic Energies, Enthalpies, and Gibbs Free Energies at 773 K, Derived from PBE-D3BJ Level of Theory,^a for Reaction Steps in Scheme 4

no.	reaction	$\Delta E \text{ (kJ mol}^{-1}\text{)}$	$\Delta H \text{ (kJ mol}^{-1}\text{)}$	$\Delta G \text{ (kJ mol}^{-1}\text{)}$
1	$\bullet NO + \frac{1}{2} O_2 \rightarrow \bullet NO_2$	−111	−121	22
2	$\bullet NO_2 + i\text{-}C_3H_7 \rightarrow C_3H_6 + HONO$	−144	−140	−99
3	$HONO \rightarrow \bullet OH + \bullet NO$	267	271	12
4	$C_3H_8 + \bullet OH \rightarrow i\text{-}C_3H_7 + H_2O$	−99	−106	−121
5	$i\text{-}C_3H_7 + O_2 \rightarrow C_3H_6 + \bullet OOH$	−46	−45	−58
6	$\bullet NO + \bullet OOH \rightarrow \bullet NO_2 + \bullet OH$	−52	−66	14
7	$\frac{1}{2} \bullet NO + \frac{1}{2} \bullet NO_2 + \frac{1}{2} H_2O \rightarrow HONO$	−33	−35	53
8	$\bullet NO_2 + \frac{1}{2} H_2O \rightarrow \frac{1}{2} HNO_2 + \frac{1}{2} HNO_3$	−21	−13	39
9	$\bullet OOH + \bullet OH \rightarrow H_2O + O_2$	−299	−297	−159

^aPressures of C_3H_8 , O_2 , H_2O , C_3H_6 , $\bullet NO$, and $\bullet NO_2$: 3, 10, 10, 1, 0.01, and 0.01 kPa, respectively, based on typical feed and moderate conversion; $\bullet OOH$, HONO, $i\text{-}C_3H_7$: 0.001 kPa; $\bullet OH$: 0.0001 kPa.

and some activation energies from experimental measurements of these steps reported in the literature are shown in Schemes S1,2 and Table S5. These products also contain weak C–H bonds and can promote H-abstraction by NO₂ to further enhance concentrations of HONO and OH radicals, as shown via experiments and kinetic simulations for HCHO formations in CH₄–O₂–NO_x reactions.^{18,19,22–24,27}

Next, we compare reaction rates and selectivity in this NO_x-mediated OH radical based reactions with V₂O₅ catalysts to assess the effect of abstractor strength on rates and selectivity.

4. DIFFERENCES IN RATES AND SELECTIVITY BETWEEN NO_x-MEDIATED PATHWAYS AND V₂O₅ CATALYSTS

C₃H₈ activation on vanadium-based oxide catalysts occurs via MvK redox cycles, where lattice oxygen species shown in Table 2 (V=O* species) act as predominant H-abstractors. C–H activations at these sites lead to reduced centers existing as OH pairs or as O-vacancies formed by dihydroxylations at OH pairs. These reduced centers are reoxidized by rapid O₂ activations to restore the V=O* sites. The rapid nature of the reoxidation steps leads to most of the catalyst existing as V=O* and nearly fixed number of these abstractors at different reaction conditions.^{1,42,67} In contrast, the NO_x-mediated cycles lead to OH radicals as predominant abstractors of strong C–H bonds in C₃H₈. The concentration of these abstractors varies with reaction conditions due to changes in concentrations of sacrificial H-atom donors to NO₂ (step 2 in Schemes 1 and 4) and presence of H₂O (step 7 in Scheme 4). These differences influence how change in C₃H₈ conversion via changing residence time affects reaction rates in the two types of reactions. Figure 4 shows C₃H₈ activation rates and product

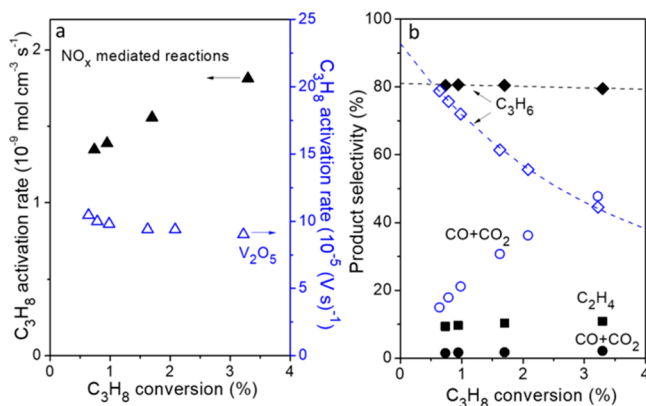


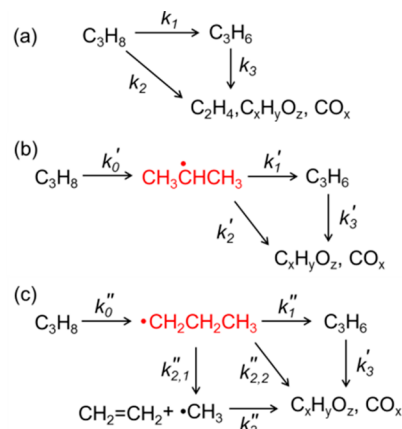
Figure 4. (a) C₃H₈ activation rates and (b) selectivity to alkenes, CO, and CO₂ as a function of C₃H₈ conversion, in 12 cm³ empty reactor with 0.005 kPa NO (closed symbols) and on V₂O₅ catalyst without NO (open symbols) (773 K, 3 kPa C₃H₈, 10 kPa O₂, 30–150 cm³ min^{−1}). The balance selectivity corresponds to C1–C3 oxygenates shown in Figure S7. Dashed curves represent best-fits to the form of eq 2.

selectivity as a function of C₃H₈ conversion for different flow rates (30–150 cm³ min^{−1}) in an empty reactor with 0.005 kPa NO and on a V₂O₅ catalyst without NO at identical temperature and reactant pressures (773 K, 3 kPa C₃H₈, 10 kPa O₂). Rates on V₂O₅ decreased slightly with increased conversion (Figure 4a), consistent with the inhibition of C–H activation by products such as H₂O via their adsorption on active lattice oxygens.⁶⁷ In contrast, the C₃H₈ activation rates in NO_x-promoted homogeneous reactions increased with conversion, suggesting a

corresponding increase in the concentration of OH radical species that abstract H-atoms from alkanes.¹⁹

The homogeneous and heterogeneous systems also exhibit large differences in selectivity trends (Figure 4b), which can be interpreted using the likely sequence of product formation shown in Scheme 5. The selectivity to C₃H₆ product at zero

Scheme 5. Products Formed in Oxidative Conversion of C₃H₈ via (a) All, (b) Secondary, and (c) Primary •C₃H₇ Radicals



conversion represents the fraction of primary C₃H₈ activations that branch to this product. The decrease in C₃H₆ selectivity with increasing conversion represents sequential conversion of C₃H₆ to secondary products (Scheme 5a). A balance over the moles of products, when their formation rates can be represented by lumped first-order rate constants for parallel conversions of C₃H₈ (k_1 , k_2 , Scheme 5a) and sequential conversion of C₃H₆ (k_3), lead to selectivity at zero conversion ($S_{C_3H_6}^0$) given by derivations in Section S8.1:⁶⁸

$$S_{C_3H_6}^0 = \frac{k_1}{k_1 + k_2} = \frac{1}{1 + \frac{k_2}{k_1}} \quad (1)$$

and the selectivity ($S_{C_3H_6}$) at finite conversions ($X_{C_3H_8}$) given by

$$S_{C_3H_6} = \frac{S_{C_3H_6}^0}{\left(1 - S_{C_3H_6}^0 \frac{k_3}{k_1}\right) X_{C_3H_8} - (1 - X_{C_3H_8})} \quad (2)$$

Regression of $S_{C_3H_6}$ data in Figure 4b to the form of eqs 1 and 2 provides rate-constant-ratios that represent numerical descriptors of the selectivity trends, where smaller k_2/k_1 and k_3/k_1 values represent higher selectivity at zero conversion and weaker selectivity decrease with increasing conversion, respectively.

For the data shown in Figure 4, the k_3/k_1 values are much smaller in NO_x-mediated reactions than on V₂O₅ (2.1 ± 0.19 and 56.7 ± 0.8 for NO_x and V₂O₅, respectively), suggesting that lattice O-atoms of V₂O₅ favor sequential reactions of C₃H₆ (k_3) over primary C₃H₈ activations (k_1) more than the radicals generated in NO_x-based pathways. These details are consistent with the weaker allylic C–H bond in C₃H₆ (bond dissociation enthalpy, BDE, 411 and 363 kJ mol^{−1} for CH₃CH₂CH₃ and CH₂CHCH₃, respectively; Table 2), the preference of lattice oxygens to activate these weaker bonds (Figure 3) or form C–O bonds in alkenes, and the ability of strong abstractors to dampen

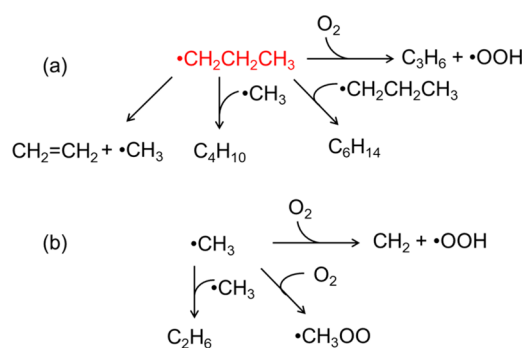
such preference due to formation of early C–H activation transition states (as shown in Scheme 3 and Figure 3).

The NO_x-mediated reactions exhibit larger k_2/k_1 values than V₂O₅ (0.23 ± 0.01 and 0.08 ± 0.01 , respectively, for data in Figure 4) and form significant amounts of C₂H₄ at zero conversion, instead of CO and CO₂ (Figure 4b). On the basis of the atomic connectivity in the radicals, the C₂H₄ products can form via C–C bond cleavage in primary •CH₂CH₂CH₃ radicals^{69,70} but not in the more stable secondary CH₃•CHCH₃ radicals resulting from C₃H₈ activations (Scheme 5b,c; BDE: 422 and 411 kJ mol^{−1} for CH₃CH₂CH₃ and CH₃CH₂CH₃, respectively, Table 2). Weaker abstractors such as lattice V=O* species in V₂O₅ prefer to activate weaker C–H bonds at a much higher rate (Figure 3) and, therefore, form predominantly CH₃•CHCH₃ radicals that cannot crack to form C₂H₄. The •CH₂CH₂CH₃ radical formation in NO_x-mediated homogeneous reactions shows that the OH radicals generated in these routes activate both weak and strong C–H bonds in C₃H₈ and generate both primary and secondary radicals, which is consistent with the dampening of bond-strength discrimination by OH radicals. The C₂H₄ selectivity remains near 10% in Figure 4b, which suggests that not all C₃H₇ radicals formed are primary •CH₂CH₂CH₃ radicals and not all of them crack to give C₂H₄. A majority of the radicals formed are either CH₃•CHCH₃ or •CH₂CH₂CH₃ radicals that proceed via dehydrogenation or O-insertion pathways to form oxygenates, with minority cracking products forming from the primary radicals. In contrast, the O-atoms in V₂O₅ only activate the weaker secondary C–H bond in C₃H₈ to form the secondary radical, which leads to higher C₃H₆ selectivity at zero conversion and lower k_2/k_1 values. Thus, the formation of C₂H₄ is an important evidence of the involvement of strong abstractors such as •OH radicals in the homogeneous reactions.

The formation of C₂H₄ via C–C cleavage in primary •CH₂CH₂CH₃ radicals also results in •CH₃ radicals (Scheme 5c). These radicals can either form C–O bonds with the O-atom containing gaseous species or couple with other •CH₃ radicals to form C₂H₆, and C₂H₄ upon further dehydrogenation. The coupling of radicals can be tested using ratios of carbon moles in C2 hydrocarbons to C1 products, which should be less than two if no coupling occurred and some C₂H₄ molecules formed in C–C cleavage steps oxidized further to C1 products. The measured C2 hydrocarbons to C1 product ratios are, however, much greater than two at low residence times, suggesting that significant coupling of •CH₃ radicals does occur despite low concentrations of these radicals (details in Section S6 and Figure S9). In contrast, direct coupling products of a primary C₃H₇ radical with another C₃H₇ radical or cross coupling with CH₃ radical is not observed. These details are analyzed further by examining the reactive preferences for primary C₃H₇ and CH₃ radicals via plausible steps shown in Scheme 6 and electronic energy, enthalpy, and free energy of these steps in Table 4.

The cracking of primary radicals •CH₂CH₂CH₃ is endothermic but highly exoergic (step 1, Table 4 and Scheme 6), due to entropy gain from the formation of two species from one. This step becomes even more exoergic if radical concentrations are lower than the arbitrary low concentration chosen in Table 4 and if temperatures are higher. In contrast, the coupling steps from propyl radicals (steps 2 and 3, Table 4, Scheme 6) are highly endothermic, but they require entropy loss from formation of a single product to form two species present in very low concentrations, which lead to more free energy penalty for lower pressures and higher temperatures. H-abstraction from

Scheme 6. Products Formed from (a) Primary •C₃H₇ and (b) •CH₃ Radicals



primary C₃H₇ radicals is also favored by enthalpy and free energy (step 4, Table 4), and it is very facile with slightly negative electronic activation energy (Figure 3; Figure S14). In contrast to radical coupling, this step also involves reaction of a radical present in low concentrations with an O₂ molecule fed at a much higher concentration leading to a much lower entropy penalty and higher rate compared to coupling reactions with near-zero activation energy but an entropy penalty to bring two species of low concentrations together. These details suggest that, when propyl radicals are present at low concentrations, its cracking and dehydrogenation by O₂ will be preferred over coupling reactions.

In contrast to propyl radicals, methyl radicals contain only one C atom and its reactions must involve coupling or reactions with O₂ (Scheme 6). The electronic energies and free energies in Table 4 show that the coupling of two methyl radicals (step 5) is more favorable than the coupling of two propyl radicals of the cross-coupling (steps 2,3) at the same concentration of all radicals. In contrast, the reactions of methyl radicals with O₂ are much less favorable (steps 6, 7) than such reactions for propyl radicals (step 4). The free energy difference between coupling of two propyl radicals and two methyl radicals is even more positive than the corresponding electronic energies (electronic energy and free energy difference +20 and +45 kJ mol^{−1}, respectively, in steps 3 and 5; similar differences exist but are less prominent for cross-coupling). The enthalpy and entropy contributions to these differences are shown in Section S14. The coupling of radicals is highly exothermic, suggesting that it likely proceeds via early transition states with insignificant enthalpy barriers. The Gibbs free energy for activation, however, also involves entropy contributions. The •CH₂CH₂CH₃ radicals exhibit significantly greater rotational entropy than •CH₃ radicals leading to more significant entropy loss in the longer chain radicals because of the coupling. This greater entropy loss leads to higher Gibbs free energy and lower coupling preference for •CH₂CH₂CH₃ for both self-coupling and cross-coupling because the molecule must align at the transition states to undergo coupling. The secondary propyl radicals are also formed as shown in Scheme 5b, but these species cannot crack and exhibit weaker coupling preferences than primary radicals, resulting in their contributions only to dehydrogenation or O-insertion events. Thus, these energies confirm that methyl radicals have significantly greater preference for coupling over other preferences favored by propyl radicals, consistent with measured selectivity for C2/C1 products and lack of observed C6 and C4 products, which was also observed recently for boron nitride catalysts.⁷¹

Table 4. Electronic Energies, Enthalpies, and Gibbs Free Energies at 773 K, Derived from PBE-D3BJ Level of Theory, for Conversions of $\bullet\text{C}_3\text{H}_7$ and $\bullet\text{CH}_3$ Radicals Shown in Scheme 6^a

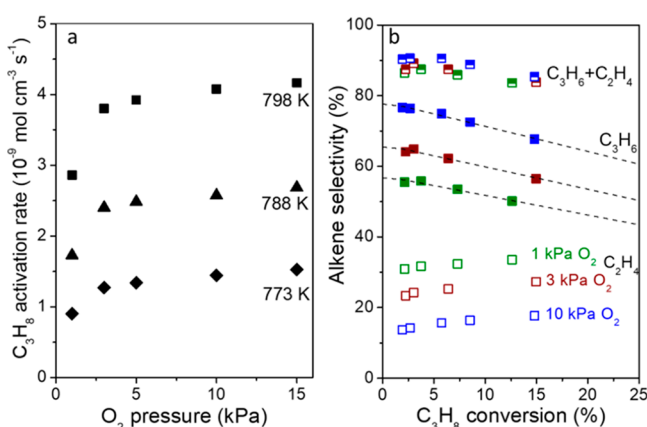
no.	reaction	ΔE (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)
1	$n\text{-}\bullet\text{C}_3\text{H}_7 \rightarrow \text{C}_2\text{H}_4 + \bullet\text{CH}_3$	123	108	-66
2	$n\text{-}\bullet\text{C}_3\text{H}_7 + \bullet\text{CH}_3 \rightarrow \text{C}_4\text{H}_{10}$	-392	-369	-150
3	$2n\text{-}\bullet\text{C}_3\text{H}_7 \rightarrow \text{C}_6\text{H}_{14}$	-382	-359	-124
4	$n\text{-}\bullet\text{C}_3\text{H}_7 + \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \bullet\text{OOH}$	-62	-63	-82
5	$2\bullet\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	-401	-378	-169
6	$\bullet\text{CH}_3 + \text{O}_2 \rightarrow \bullet\text{CH}_3\text{OO}$	-159	-144	-26
7	$\bullet\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_2 + \bullet\text{OOH}$	260	260	146

^aPressures: 0.001 kPa for radical species, 10 kPa for O₂.

The residence time effects highlight significant differences between reactions at lattice O-atoms and the pathways mediated by strong gas-phase H-abstractors. Next, we further probe these differences by examining the effect of reactant pressures on rates and selectivity.

5. EFFECTS OF REACTANT PRESSURES ON RATES AND SELECTIVITY

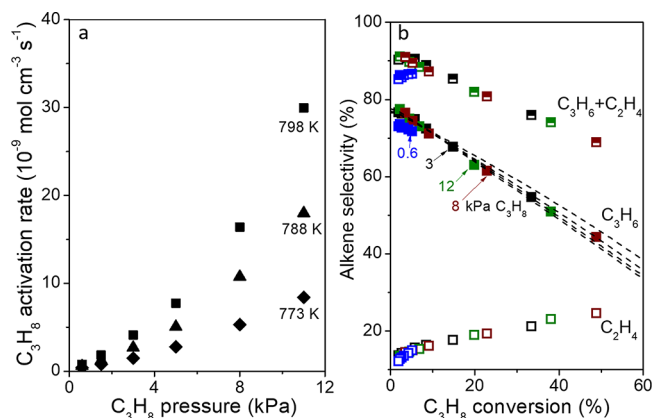
The effect of O₂ pressure on C₃H₈ activation rates in the 12 cm³ quartz reactor at different temperatures is shown in Figure 5a

**Figure 5.** (a) C₃H₈ activation rates as a function of O₂ pressure at a 60 cm³ min⁻¹ flow rate and at 773, 788, and 798 K, and (b) alkene selectivity as a function of conversion for 30–100 cm³ min⁻¹ flow rates at 798 K and 1, 3, and 10 kPa O₂ (0.005 kPa NO, 3 kPa C₃H₈, 12 cm³ reactor). Dashed curves represent best-fits to the form of eq 2.

(773, 788, and 798 K; 60 cm³ min⁻¹, 0.005 kPa NO, 3 kPa C₃H₈, 1–15 kPa O₂). At each of these temperatures, rates increase with O₂ pressure at pressures less than 5 kPa O₂ but become nearly insensitive to O₂ pressure at higher pressures. Figure 5b shows product selectivities as a function of conversion for different O₂ pressures at 798 K. Higher O₂ pressures lead to higher C₃H₆ selectivity and correspondingly lower C₂H₄ selectivity, such that the sum of C₃H₆ and C₂H₄ selectivity remains nearly independent of O₂ pressure (Figure 5b; 798 K). The slopes of trend-lines for the effect of conversion on selectivity are affected less significantly by O₂ pressures than the intercepts. These results suggest that higher O₂ pressures increase the C₃H₈ activation rates slightly (Figure 5a) and exhibit only small effects on the rates of activation of C₃H₆ relative to C₃H₈ greatly (k_3/k_1 values indicated by slopes of dashed curves in Figure 5b). Instead, the most significant effect of O₂ involves altering the branching between C–H activation and C–C bond cleavage in primary $\bullet\text{CH}_2\text{CH}_2\text{CH}_3$ radicals (steps represented by constants

k'_1 and $k''_{2,1}$ in Scheme 5c). These primary radicals are unstable and undergo a second C–H activation to form C₃H₆ even by weak abstractors such as O₂ (Figure 3). Higher O₂ pressures increase the rate of this bimolecular C–H activation over monomolecular C–C cleavage. Such results are counterintuitive in the light of attempts to improve selectivity on oxide catalysts by staging the O₂ feed to maintain low O₂ concentrations. They also present opportunities for increasing C₃H₆ yields beyond values reported here using O₂ pressures much higher than that required by reaction stoichiometry.

The effect of C₃H₈ pressure on C₃H₈ activation rates in a 12 cm³ quartz reactor at different temperatures is shown in Figure 6a (773, 788, and 798 K; 60 cm³ min⁻¹, 0.005 kPa NO, 0.6–11

**Figure 6.** (a) C₃H₈ activation rates as a function of C₃H₈ pressure at 60 cm³ min⁻¹ flow rate, 773, 788 and 798, and (b) alkene selectivity as a function of conversion for 20–150 cm³ min⁻¹ at 798 K, 0.6–12 kPa C₃H₈ (0.005 kPa NO, 10 kPa O₂, 12 cm³ reactor). Dashed curves represent best-fits to the form of eq 2.

kPa C₃H₈, 10 kPa O₂). C₃H₈ activation rates exhibit a supra-linear increase with C₃H₈ pressure, suggesting that higher alkane concentrations increase concentrations of OH radicals that activate alkanes because more sacrificial species for activating NO₂ (step 2, Schemes 1 and 4) and more H₂O is present at a given conversion when the alkane pressure is higher. Figure 6b shows that C₃H₆ and C₂H₄ selectivities remain nearly independent of C₃H₈ pressure above 3 kPa at 798 K.

The effect of H₂O pressure from H₂O cofed with reactants and formed from C₃H₈–O₂ conversions on rates and selectivity are shown in Figure 7. The reaction rates increase significantly with added H₂O pressure (Figure 7a), as also shown by increasing conversions in Figure 2. The rate enhancements by added H₂O are much more significant at higher temperature (Figure 7a; 773 and 798 K, 30 cm³ min⁻¹, 0.005 kPa NO, 0–10

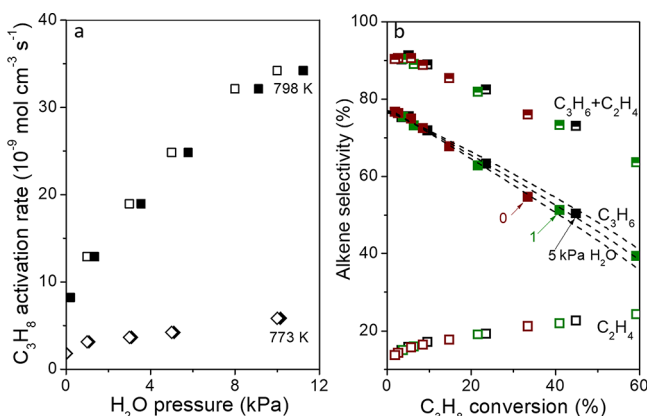


Figure 7. (a) C_3H_8 activation rates as a function of added H_2O pressure (open symbols) and sum of added and formed H_2O pressure (closed symbols) at $30 \text{ cm}^3 \text{ min}^{-1}$ flow rate, 773, and 798 K, and (b) alkene selectivity as a function of conversion for $20\text{--}100 \text{ cm}^3 \text{ min}^{-1}$ at 798 K, $0\text{--}5 \text{ kPa}$ added H_2O (0.005 kPa NO , $3 \text{ kPa C}_3\text{H}_8$, 10 kPa O_2 , 12 cm^3 reactor). Dashed curves represent best-fits to the form of eq 2.

$\text{kPa H}_2\text{O}$, $3 \text{ kPa C}_3\text{H}_8$, 10 kPa O_2). H_2O formed from the reaction shifts the trends only slightly, and the nonzero intercepts in these trends suggest that rate enhancement from NO_x catalysis, which is further enhanced by H_2O . These results are consistent with the role of H_2O in forming HONO from NO and NO_2 in proposed mechanisms (Schemes 1 and 4), and the facile nature of these steps reported from experimental studies in literature.^{65,66} Figure 7b shows product selectivities as a function of conversion for added H_2O pressures at 798 K. The C_3H_6 and C_2H_4 selectivities remain nearly independent of added H_2O (Figure 7b).

These effects of reactant pressures deviate significantly from ODH reactions on oxide catalysts that involve MvK cycles with rate-limiting C–H activation at lattice O-atoms of oxides and fast O_2 activation.⁴¹ Such mechanisms invariably exhibit a first-order dependence on alkane pressure and zero-order dependence on O_2 pressure.^{1,72–75} The ODH rates in MvK cycles show a small decrease in rates with H_2O pressures due to its adsorption at active sites.^{1,67} The results in NO_x -mediated reactions (Figures 5–7) and their deviations from heterogeneous reactions on oxides are also observed in trends reported recently for boron nitride^{6,11} and previously for systems in which catalysts generate radicals for homogeneous reactions;⁵ they likely originate here from higher concentrations of $\bullet\text{OH}$ species in NO_x -mediated routes at higher alkane, O_2 , and H_2O pressures (Schemes 1 and S3; Supporting Information).

The C_3H_6 selectivity data as a function of conversion for the different reactant pressures and reaction temperatures shown in Figures 5–7 and Figure S11 are regressed to the form of eq 2 to determine rate constant ratios, which are shown as a function of reactant pressures and reciprocal temperature in Figures 8 and 9, respectively. These data are used to summarize the effect of reactant pressure on selectivity and derive activation energy differences relevant to selectivity via effects of temperature on the ratios.

Figure 8 shows the rate constant ratios as a function of reactant pressures. C_3H_8 and H_2O pressures do not have significant effects on k_2/k_1 values (Figure 8a). Higher O_2 pressures lead to much smaller k_2/k_1 values, which correspond to lesser C–C cleavage and greater C_3H_6 selectivity (Figure 5b). These effects suggest that primary $\bullet\text{C}_3\text{H}_7$ species responsible for C_2H_4 formation undergo C–H activation more preferentially

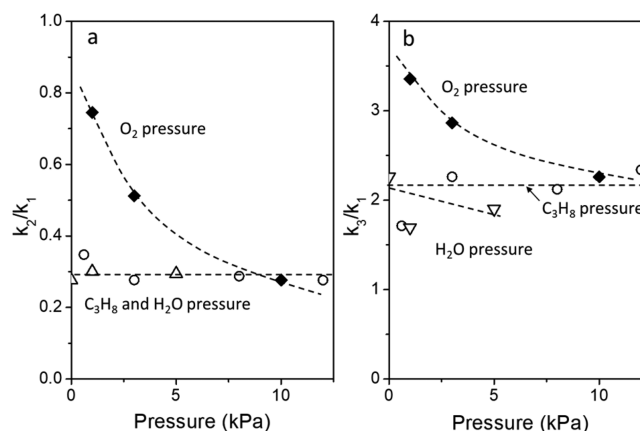


Figure 8. Ratios of rate constants (a) k_2/k_1 and (b) k_3/k_1 , as a function of C_3H_8 pressure (circles, 10 kPa O_2 , $0 \text{ kPa H}_2\text{O}$), O_2 pressure (diamonds, $3 \text{ kPa C}_3\text{H}_8$, $0 \text{ kPa H}_2\text{O}$), and H_2O pressure (triangles, $3 \text{ kPa C}_3\text{H}_8$, 10 kPa O_2) at 798 K and 0.005 kPa NO . Dashed curves represent trends.

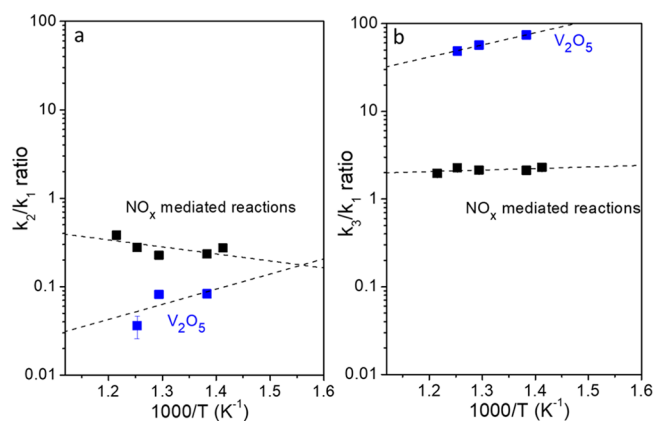


Figure 9. Ratios of rate constants (a) k_2/k_1 and (b) k_3/k_1 , as a function of reciprocal temperature at 0.005 kPa NO , $3 \text{ kPa C}_3\text{H}_8$, and 10 kPa O_2 . Dashed lines represent exponential best-fits for the values. Uncertainties represent standard errors.

than C–C activation when more O_2 is present (Scheme 5c). The k_3/k_1 values are nearly unaffected by C_3H_8 or H_2O pressures (Figure 8b) but decrease slightly (implying higher selectivity) at higher O_2 pressure. These data suggest that using denser feeds with high alkane and H_2O pressures will significantly enhance the rates (Figures 6a and 7a) and productivity (Table S2), while retaining high selectivity and yields. Furthermore, high O_2 pressures can be used to decrease C_2H_4 selectivity and increase C_3H_6 selectivity to values higher than that shown here (Figure 5b).

6. EFFECT OF ABSTRACTOR STRENGTH ON ACTIVATION ENTHALPY DIFFERENCES FOR STEPS INVOLVING C–H BONDS OF DIFFERENT STRENGTHS

Figure 9 shows the rate constant ratios k_2/k_1 and k_3/k_1 , representing selectivity for C_3H_6 formation over parallel and sequential reactions, respectively, as a function of reciprocal temperature for identical reactant pressures on V_2O_5 catalyst and in NO_x -catalyzed reactions. NO_x -mediated reactions exhibit larger k_2/k_1 values than V_2O_5 (Figure 9a) because generation of primary radicals leads to significant C–C bond cleavage, which

results in high C₂H₄ selectivity at zero conversion (Figure 4b). The k_3/k_1 values are much larger in V₂O₅ than in NO_x-mediated reactions because the latter reactions dampen the secondary reactions of C₃H₆ (Figure 9b).

The effects of temperature on rate constant ratios, at identical reactant pressures in Figure 9 (k_2/k_1 , and k_3/k_1 at 0.005 kPa NO, 3 kPa C₃H₈, and 10 kPa O₂), are expressed as activation enthalpy differences between the parallel or sequential undesired reactions and the C₃H₆ formation reaction using the following relations (details in section S8.2):

$$\frac{k_2}{k_1} = \exp\left(\frac{\Delta S_2^{\text{act}} - \Delta S_1^{\text{act}}}{R}\right) \exp\left(-\frac{\Delta H_2^{\text{act}} - \Delta H_1^{\text{act}}}{RT}\right) \\ = \exp\left(\frac{\Delta \Delta S_{21}}{R}\right) \exp\left(-\frac{\Delta \Delta H_{21}}{RT}\right) \quad (3)$$

$$\frac{k_3}{k_1} = \exp\left(\frac{\Delta S_3^{\text{act}} - \Delta S_1^{\text{act}}}{R}\right) \exp\left(-\frac{\Delta H_3^{\text{act}} - \Delta H_1^{\text{act}}}{RT}\right) \\ = \exp\left(\frac{\Delta \Delta S_{31}}{R}\right) \exp\left(-\frac{\Delta \Delta H_{31}}{RT}\right) \quad (4)$$

where, ΔH_1^{act} and ΔH_2^{act} represent ensemble averaged activation enthalpy for C₃H₆ formation and all steps mediating parallel C₃H₈ oxidation steps relative to gaseous C₃H₈ (Scheme 5a), respectively, ΔH_3^{act} represents activation enthalpy for C₃H₆ oxidation steps relative to gaseous C₃H₆, and ΔS^{act} values represent corresponding activation entropies. The values of activation enthalpy differences relevant to rate constant ratios k_2/k_1 ($\Delta \Delta H_{21} = \Delta H_2^{\text{act}} - \Delta H_1^{\text{act}}$) and k_3/k_1 ($\Delta \Delta H_{31} = \Delta H_3^{\text{act}} - \Delta H_1^{\text{act}}$) derived from slopes of regressed lines in Figure 9 are shown in Table 5.

Table 5. Activation Enthalpy Differences between the Parallel or Sequential Reactions and the Primary C–H Activations Derived from Regression of Rate Constants Ratios in Figure 9 to the Form of eqs 3 and 4^a

reaction system	$\Delta H_2^{\text{act}} - \Delta H_1^{\text{act}}$ (kJ mol ^{−1})	$\Delta H_3^{\text{act}} - \Delta H_1^{\text{act}}$ (kJ mol ^{−1})
V ₂ O ₅	−33 ± 34	−26 ± 1
NO _x -mediated	15 ± 10	−3 ± 3

^aUncertainties represent the standard errors.

The rate constant ratios on the V₂O₅ catalyst decrease with increasing temperature (Figure 9), suggesting that the activation enthalpy for parallel and sequential undesired reactions are lower than the primary reaction in Scheme 5a ($\Delta \Delta H_{21} = -33 \pm 34$ kJ mol^{−1} and $\Delta \Delta H_{31} = -26 \pm 1$ kJ mol^{−1}; Table 5). In contrast, NO_x-mediated homogeneous reactions exhibit increasing k_2/k_1 values with temperature, which shows that the activation enthalpy for the C₂H₄ formation step is higher than for the C–H activation in C₃H₈ ($\Delta \Delta H_{21} = 15 \pm 10$ kJ mol^{−1}; Table 5). The C₂H₄ formation step can only occur via C–C cleavage in primary •C₃H₇ radicals (Scheme 5c), suggesting that NO_x reactions involve significant formation of such primary radicals, in spite of the stronger C–H bonds involved in forming these radicals (Table 2). The activation of primary and secondary C–H bonds in C₃H₈ cannot be differentiated from Figure 9, because the k_1 values represent an ensemble average of all C–H activations occurring in C₃H₈. Therefore, the positive $\Delta \Delta H_{21}$ values indicate that the C–C bond cleavage in primary

•C₃H₇ radical, which does not involve strong H-abstractors, has higher activation enthalpy than the C–H activation required to form this radical.

The k_3/k_1 values in NO_x reactions are much lower than V₂O₅ and exhibit a much weaker temperature dependence ($\Delta \Delta H_{31} = -3 \pm 3$ and -26 ± 1 kJ mol^{−1} for NO_x and V₂O₅, respectively; Table 5). The steps for C₃H₆ reactions involve kinetically relevant activation of weak allylic C–H bonds prior to C–O bond formation that leads to oxygenates.^{49,76} Therefore, $\Delta \Delta H_{31}$ represents activation enthalpy differences for C–H activation in C₃H₆ and C₃H₈, and its negative values indicate that C₃H₆ activation is more facile due to weaker C–H bonds (Table 2). However, the $\Delta \Delta H_{31}$ values in NO_x reactions are much closer to zero than V₂O₅, which means that the H-abstractors involved in NO_x-mediated reactions can activate the two bonds with only slightly different rates despite the large difference in bond strength. This difference between C₃H₈ and C₃H₆ activation energies derived from DFT is described next for C–H activation using the H-abstractors of different strengths shown in Table 1.

Figure 10 shows the DFT-derived difference between electronic energies for C–H activation at a secondary C–H

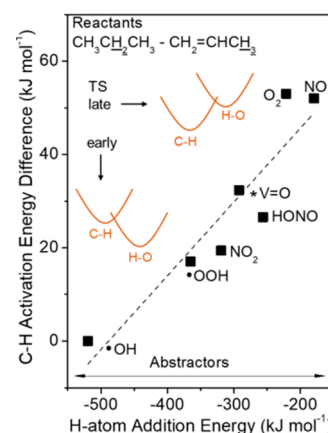


Figure 10. DFT-derived C–H activation energy differences between C₃H₈ and C₃H₆ as a function of HAE on different H-abstractors.

bond in C₃H₈ (BDE 411 kJ mol^{−1}, Table 2) and an allylic C–H bond in C₃H₆ (BDE 363 kJ mol^{−1}, Table 2) as a function of the HAE of H-abstractors. When the abstractor is weak (less negative HAE; e.g., NO in Table 1), the product state is less stable than the reactant. This scenario can be shown using a crossing potential for C–H cleavage and O–H formation, in which the product O–H potential is higher in energy than the reactant (inset in Figure 10). Such cases lead to high activation energies and the transition state represented by the crossing point of the potentials is “late” because it requires nearly full cleavage of the C–H bond and formation of the O–H bond. The lateness is to be confirmed by the structures and energies of transition states shown in Section S13. Such late transition states are highly sensitive to C–H bond strength, because the bond is nearly broken at the transition state. As a result, the C–H activation energy is very different in the stronger C₃H₈ C–H bond and the weaker C₃H₆ C–H bond. However, when the abstractor is strong (more negative HAE; e.g., OOH and OH in Table 1), the product state potential shifts to lower energies and leads to “early” transition states. Very early transition states do not involve significant C–H bond stretching and are insensitive to the C–H bond strength, leading to small differences between activation energy for strong and weak bonds in Figure 10. Thus,

the DFT-derived energies confirm that strong abstractors would lead to improvement in selectivity by suppression of bond-strength effects. Notably, the activation energy difference is fairly significant for V_2O_5 O-atoms ($+32 \text{ kJ mol}^{-1}$, Figure 10), and even for OOH radicals ($+17 \text{ kJ mol}^{-1}$, Figure 10), suggesting that only OH radicals, the strongest abstractor among those shown in Figure 10, can account for the $\Delta\Delta H_{31}$ values near zero in the measured data ($\Delta\Delta H_{31} = -3 \pm 3 \text{ kJ mol}^{-1}$, Table 5).

Thus, we conclude that the generation of OH radicals for C–H activation and the dampening of bond-strength discrimination by such strong abstractors lead to high selectivity and yield for alkenes. The OH radicals generated in NO_x -mediated reaction paths abstract both primary and secondary C–H bonds in C_3H_8 . The primary alkyl radicals can undergo C–C bond cleavage, which leads to significant C_2H_4 formation in addition to the dehydrogenation product C_3H_6 . The yields attained in this process are shown in Table S1 and Figure S1, along with yields reported in the literature. At 798 K, 24% maximum C_3H_6 yield was attained, and the corresponding maximum alkene ($\text{C}_3\text{H}_6 + \text{C}_2\text{H}_4$) and alkene + C3-oxygenates yields are 43% and 47%, respectively. An important consequence of strong abstractors and the low activation energy differences is that the yields are quite insensitive to temperature. As a result, the C_3H_6 yields $>22\%$ are attained even at temperatures much lower than previously reported in any other systems (723 K, Figure S1). These lower temperature conditions lead to a lower fraction of C_2H_4 (combined $\text{C}_3\text{H}_6 + \text{C}_2\text{H}_4$ yield 31%) with a greater fraction of additional valuable C3 oxygenate products that are not observed in other systems. The lower C–C cleavage at lower temperature (k_2/k_1 , Figure 9) corresponds to increased fractions of C3 oxygenate (Figure S1) without affecting C_3H_6 yields and leads to a combined alkene and C3 oxygenate yields of 40% at 723 K.

The NO_x mediation can also enhance other reactions limited by C–H bond activation. Examples of such reactions shown in Section S15 include: (i) C_2H_6 dehydrogenation with high C_2H_4 selectivity and (ii) formation of C3 hydrocarbons via C–C coupling in $\text{C}_2\text{H}_4\text{--CH}_3\text{OH--O}_2\text{--NO}$ reactions. Such facile C–H activations may also be useful for other reactions such as C–C coupling or oxygenate formations that require organic radical intermediates formed via rate-limiting C–H activation steps.^{2,77–80}

7. CONCLUSIONS

NO_x -mediated generation of OH radical species selectively activates strong C–H bonds in alkanes with high alkene productivity and yields at moderate temperatures by weakening the bond-strength-based discrimination of activation rates. The kinetic details and selectivity trends in these reactions resemble boron nitride and alkali promoted oxides that facilitate homogeneous reactions^{5,6,13} but differ markedly from reactions at lattice oxygens of oxide catalysts. NO_x helps overcome the high temperature requirements for the generation of OH radicals in alkali-based catalysts^{5,34,45} and, in turn, produces alkyl radicals and dehydrogenated products more efficiently.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b03862.

Alkene yields and productivities; methods; definitions of rates and selectivity; effects of time on stream, conversion

and reactant pressures, temperatures and reactor volumes on rates and selectivity; C2/C1 selectivity ratios; plausible elementary steps; selectivity trends derivations; structures and energies of transition states; C_2H_6 activation and C–C coupling in $\text{C}_2\text{H}_4\text{--CH}_3\text{OH--O}_2\text{--NO}$ reactions (PDF)

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Notes

The authors declare no competing financial interest.

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