

## Are Spin-Forbidden Crossings a Bottleneck in Methanol Oxidation?

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The rate of spin-surface crossing from the singlet to the triplet potential energy surface during methanol oxidation has been examined for classically spin-forbidden crossings. The Landau–Zener equation has been used to calculate the thermally-averaged spin transition probabilities for the nonadiabatic surface crossing reaction. Two active sites have been investigated: isolated vanadate species supported on silica (VO<sub>x</sub>/SiO<sub>2</sub>) and titania (VO<sub>x</sub>/TiO<sub>2</sub>). The results show that the rate of spin-surface crossing is much faster than the rate-limiting H-abstraction step on both active sites and is therefore not kinetically relevant.

### Introduction

Nonadiabatic reactions require movement between two different interacting potential energy surfaces and typically involve electronically excited species. In the analysis of many catalytic mechanisms, the details of nonadiabatic reactions have been largely ignored and have thus been assumed to either occur rapidly<sup>1–3</sup> or be spin-forbidden.<sup>4</sup>

An example of a nonadiabatic reaction is the rate-limiting step of H-abstraction in the oxidation of methanol to formaldehyde on isolated vanadate sites supported on silica (VO<sub>x</sub>/SiO<sub>2</sub>) and titania (VO<sub>x</sub>/TiO<sub>2</sub>). The reactant species on both supported metal oxides consists of an isolated VO<sub>x</sub> species with adsorbed methanol, forming a H<sub>3</sub>CO–V=O/M–OH (M = Si, Ti) pair.<sup>1–3,5,6</sup> The most energetically stable electronic state for the reactant is the singlet spin state ( $M = 1$ ) with V containing zero unpaired d electrons.<sup>1–3</sup> During the H-abstraction step, one of the three adsorbed methoxy H atoms is transferred to the vanadyl O to form a H<sub>2</sub>CO–V–OH group in the product species.<sup>1–3,5,6</sup> The transition state and product species are in the triplet electronic state ( $M = 3$ ) with V containing two unpaired d electrons.<sup>1–3</sup> In previous studies,<sup>1–3</sup> the broken symmetry approach<sup>7,8</sup> was used to calculate the activation energy of the transition state, thereby accounting for the change in spin state; however, these studies did not consider the probability that such a classically spin-forbidden transition occurs. The crossing from one potential energy surface to another has also recently been shown to play a role in the oxidative dehydrogenation of propane on VO<sub>x</sub> supported on TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.<sup>9</sup> In the present work, the probabilities and rate constants have been calculated for crossing from the singlet to the triplet potential energy surface during the rate-limiting step in methanol oxidation catalyzed on VO<sub>x</sub>/SiO<sub>2</sub> and VO<sub>x</sub>/TiO<sub>2</sub>. This study examines whether classically spin-forbidden transitions are a bottleneck in methanol oxidation.

### Theoretical Methods

The Landau–Zener formula,<sup>10–15</sup> eq 1, has been used to calculate the thermally-averaged spin transition probabilities,  $\bar{P}_{LZ}$ , between two different electronic states. In eq 1,  $H_{12}$  is the spin–orbit coupling energy between the two states, and  $\nabla E_1$  and  $\nabla E_2$  are the mass-weighted gradients of the two potential energy surfaces at the point of crossing. Equation 1 is integrated over  $v$ , the mass-weighted velocity of the system,<sup>13</sup> and evaluated using numerical integration. Alternatively, eq 1 can be integrated over the reaction coordinate velocity, where  $|\nabla E_1 - \nabla E_2|$  is replaced with

$$\left| \frac{dE}{ds} \Big|_{M=1} - \frac{dE}{ds} \Big|_{M=3} \right|$$

at the point of crossing.

$$\bar{P}_{LZ} = \frac{\int_0^\infty dv \left( 1 - \exp \left\{ \frac{-4\pi^2 H_{12}^2}{hv \|\nabla E_1 - \nabla E_2\|} \right\} \right) \exp \left\{ \frac{-v^2}{2k_B T} \right\}}{\int_0^\infty dv \exp \left\{ \frac{-v^2}{2k_B T} \right\}} \quad (1)$$

The Landau–Zener model has been successfully applied to a number of nonadiabatic systems involving excited species and near-resonant electronic-energy-transfer reactions, such as those involved in the chemical oxygen–iodine laser.<sup>16</sup> The classical trajectory method<sup>14</sup> can be used when a more exact treatment of electronically nonadiabatic processes is desired.

There are two traversals of the avoided crossing region during a nonadiabatic reaction that lead to the product species being on a different potential energy surface than the reactant species. One traversal involves crossing in the forward direction with a probability of  $\bar{P}_{LZ}$ , and the second traversal involves crossing in the reverse direction with a probability of  $\bar{P}_{LZ}^*(1 - \bar{P}_{LZ})$ .<sup>14</sup>

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The spin transmission coefficient,  $\kappa_{LZ}$ , represents the net transition probability for spin-forbidden transitions and is analogous to the quantum tunneling probability.<sup>14</sup> The parameter  $\kappa_{LZ}$  is defined in eq 2 as the sum of the two probabilities for crossing in the forward and reverse directions.

$$\kappa_{LZ} = 2\bar{P}_{LZ} - \bar{P}_{LZ}^2 \quad (2)$$

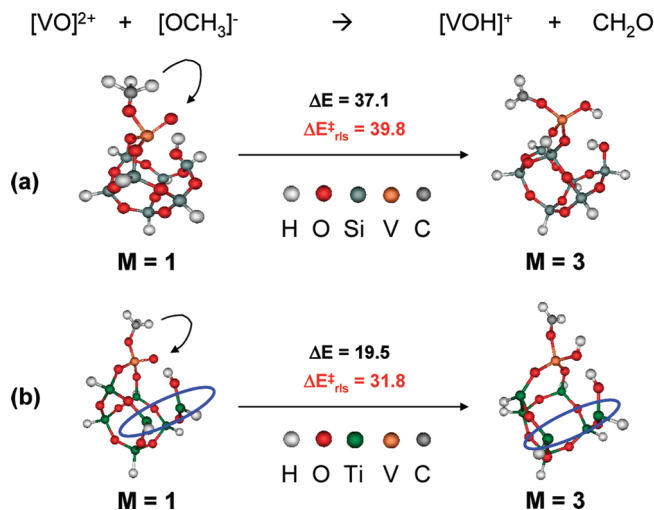
The rate constant for spin-surface crossing is equal to  $\bar{P}_{LZ}$  multiplied by an Arrhenius expression and is given in eq 3. The factor  $\bar{P}_{LZ}$  is used instead of  $\kappa_{LZ}$  because no recrossing is assumed to occur in the reverse direction under the assumption of absolute rate theory. Since the nonadiabatic reactions considered in this work involve crossing from a singlet to a triplet potential energy surface, the ratio of the electronic partition functions in eq 3 is  $q_{elec,M=3}/q_{elec,M=1} = 3$ . The translational, rotational, and vibrational partition functions were assumed to be identical for the same species with different spin states and have been omitted in eq 3, consistent with previous work.<sup>17</sup> Lastly,  $\Delta E_{M=1\rightarrow 3}$  is the difference in energy between the intersection of the two potential energy surfaces and the reactant state.

$$k_{M=1\rightarrow 3} = \bar{P}_{LZ} \cdot \frac{k_B T}{h} \frac{q_{elec,M=3}}{q_{elec,M=1}} \exp\left(\frac{-\Delta E_{M=1\rightarrow 3}}{RT}\right) \quad (3)$$

The spin-orbit coupling energies  $H_{12}$  for the systems in the present study were estimated from previous work on  $\text{FeO}^+$ .<sup>18</sup> During the oxidative activation of  $\text{H}_2$  by  $\text{FeO}^+$ , Danovich and Shaik<sup>18</sup> calculated  $H_{12}([\text{FeO}]^+)$ , which varied from  $9.44 \times 10^{-2}$  to  $1.97 \times 10^{-1}$  kcal/mol, depending on the calculation approach used. Since the spin-orbit coupling energies scale with the fourth-power of the atomic number,  $Z$ , the value for  $H_{12}([\text{VO}]^{2+})$  was estimated from  $H_{12}([\text{FeO}]^+)$  using eq 4, and calculated to vary from  $5.78 \times 10^{-2}$  kcal/mol to  $1.21 \times 10^{-1}$  kcal/mol.

$$H_{12}([\text{VO}]^{2+}) = H_{12}([\text{FeO}]^+) \cdot \left(\frac{Z_V}{Z_{\text{Fe}}}\right)^4 \quad (4)$$

All geometry optimizations and force calculations were performed using QChem 3.0<sup>20</sup> at the B3LYP/6-31G\* level of theory. The transition metals V and Ti were treated using the LANL2DZ basis sets and effective core potentials. All singlet spin state calculations were closed-shell, and the triplet spin states showed negligible spin contamination ( $\langle S^2 \rangle < 0.02$ ). The modified growing string method (GSM) was used with 11 nodes to determine an initial estimate of the transition state.<sup>21</sup> The hybrid strategy<sup>21,22</sup> was used to determine the minimum energy pathway on the singlet potential energy surface. The modified GSM calculations were initiated at the HF/STO-3G level of theory and further refined at the B3LYP/6-31G\* level of theory. The transition state estimate was further optimized by performing a transition state search calculation in QChem 3.0 at the B3LYP/6-31G\* level of theory, consisting of an initial Hessian calculation and a transition state optimization. The crossing point was determined by performing single-point energy calculations on the triplet potential energy surface using the geometries determined from the modified-GSM on the singlet potential energy surface. This approach underestimates the rate of spin-surface crossing because the intersection of the two potential



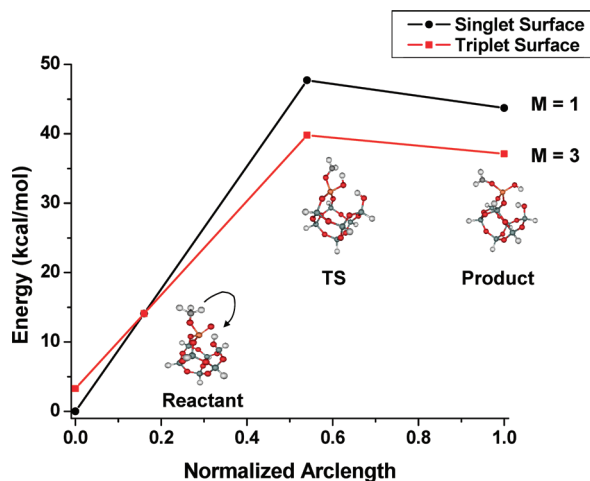
**Figure 1.** Rate-limiting H-abstraction step in methanol oxidation on (a)  $\text{VO}_x/\text{SiO}_2$  and (b)  $\text{VO}_x/\text{TiO}_2$  (the O-vacancy is circled). All reaction energies ( $\Delta E$ ) and activation energies ( $\Delta E^\ddagger$ ) are in kcal/mol.

energy surfaces occurs at a higher energy than if the geometries of the optimized triplet potential energy surface were used. At the point of intersection, the geometries and energies on the singlet and triplet potential energy surfaces were shown to be identical. It is important to note that the Born–Oppenheimer approximation may not be valid at the point of intersection because the nuclei may move rapidly from the singlet to the triplet potential energy surface; however, this is not the purpose of the present study, which instead is to examine a nonadiabatic transition driven by spin–orbit coupling. The SCF energy was considered converged when the energy of successive iterations differed by less than  $10^{-7}$  hartrees. The threshold value was set to  $10^{-10}$  for neglecting two electron integrals. All final energies reported were determined by setting the SCF convergence to  $10^{-8}$  and the threshold value to  $10^{-11}$  and by using the more refined SG-1 integration grid.

## Results and Discussion

**Methanol Oxidation on  $\text{VO}_x/\text{SiO}_2$ .** The rate-limiting step in methanol oxidation to formaldehyde on  $\text{VO}_x/\text{SiO}_2$  involves transferring one of the three H atoms from an adsorbed methoxy group to the vanadyl O atom,<sup>1,2</sup> as shown in Figure 1a. As mentioned previously, the lowest-energy structure of the reactant is a singlet spin state, whereas the lowest-energy structures for the transition and product states are triplet spin states. Modified-GSM calculations were performed on the singlet and triplet potential energy surfaces, and the spin-surface crossing was shown to occur before the transition state, as seen in Figure 2. The Landau–Zener probabilities,  $\bar{P}_{LZ}$ , were calculated using eq 1, and the values are shown in Table 1. These values are calculated for spin–orbit coupling energies,  $H_{12}([\text{VO}]^{2+})$ , of  $5.78 \times 10^{-2}$  and  $1.21 \times 10^{-1}$  kcal/mol, and for temperatures from 450 to 750 K. The norm of the difference in the gradient at the crossing point (which occurs at a normalized arclength value of  $\hat{s} = 0.16$ ) between the two electronic states,  $\|\nabla E_1 - \nabla E_2\|$ , is 165.8 kcal/mol·Å. The difference in energy between these two states,  $\Delta E_{M=1\rightarrow 3}$ , is 14.1 kcal/mol.

The maximum rate of formaldehyde production on  $\text{VO}_x/\text{SiO}_2$  occurs at 650 K.<sup>5</sup> At this temperature,  $\bar{P}_{LZ}$  ranges from 2.0 to 3.5%. Using eq 3, the rate constant  $k_{M=1\rightarrow 3}$  at 650 K is equal to  $1.49 \times 10^7 \text{ s}^{-1}$  (for  $\bar{P}_{LZ} = 2.03\%$ ) and  $2.56 \times 10^7 \text{ s}^{-1}$  (for  $\bar{P}_{LZ} = 3.47\%$ ). Comparing  $k_{M=1\rightarrow 3}$  to the rate constant for the rate-limiting H-abstraction step at 650 K,  $k_{\text{ris}} = 7.95 \times 10^{-2} \text{ s}^{-1}$ ,<sup>2</sup> it



**Figure 2.** Reaction pathway for H-abstraction on  $\text{VO}_x/\text{SiO}_2$  shown for the singlet ( $M = 1$ ) and triplet ( $M = 3$ ) surfaces. There is a spin-surface crossing from the singlet to the triplet surface with  $\Delta E_{M=1 \rightarrow 3} = 14.1$  kcal/mol at a normalized arclength value of  $\hat{s} = 0.16$ .

**TABLE 1: Thermally-Averaged Landau–Zener Spin Transition Probabilities ( $\bar{P}_{LZ}$ ) for H-Abstraction in  $\text{VO}_x/\text{SiO}_2$  (see Figure 1a)**

temperature (K)	$P_{LZ}, H_{12} = 5.78 \times 10^{-2}$ kcal/mol	$P_{LZ}, H_{12} = 1.21 \times 10^{-1}$ kcal/mol
450	0.0230	0.0389
550	0.0216	0.0368
650	0.0203	0.0347
750	0.0189	0.0327

**TABLE 2: Thermally-Averaged Landau–Zener Spin Transition Probabilities ( $\bar{P}_{LZ}$ ) for H-Abstraction in  $\text{VO}_x/\text{TiO}_2$  (see Figure 1b)**

temperature (K)	$P_{LZ}, H_{12} = 5.78 \times 10^{-2}$ kcal/mol	$P_{LZ}, H_{12} = 1.21 \times 10^{-1}$ kcal/mol
450	0.0497	0.156
550	0.0471	0.149
650	0.0446	0.142
750	0.042	0.134

is concluded that the rate of spin-surface crossing is rapid and hence not rate-limiting. Alternatively, if the reaction coordinate velocity is used instead of the mass-weighted system velocity in eq 1, then the values for  $\bar{P}_{LZ}$  in Table 1 are reduced slightly and range from 1.8 to 2.5% at 650 K, but are still not small enough to be rate-limiting.

**Methanol Oxidation on  $\text{VO}_x/\text{TiO}_2$ .** Similar to  $\text{VO}_x/\text{SiO}_2$ , the rate-limiting step in methanol oxidation on  $\text{VO}_x/\text{TiO}_2$  involves H-abstraction,<sup>3</sup> as shown in Figure 1b. Previous work has suggested that the active site involved in this reaction contains an O-vacancy, shown in Figure 1b, which serves to reduce the activation energy by H-bond stabilization of the transition state.<sup>3</sup> The lowest-energy structure of the reactant was  $M = 1$ , whereas the lowest-energy structures for the transition state and product were  $M = 3$ . A plot of the reaction pathway on the  $M = 1$  and  $M = 3$  surfaces is similar to that seen in Figure 2 for  $\text{VO}_x/\text{SiO}_2$  and shows that the spin-surface crossing also occurs before the transition state. The Landau–Zener probabilities,  $\bar{P}_{LZ}$ , were calculated using eq 1, and the values are shown in Table 2. The values are calculated for spin–orbit coupling energies of  $5.78 \times 10^{-2}$  and  $1.21 \times 10^{-1}$  kcal/mol and for temperatures from 450 to 750 K. The norm of the difference in the gradient at the crossing point (which occurs at a normalized arclength value of  $\hat{s} = 0.24$ ),  $\|\nabla E_1 - \nabla E_2\|$ , is 24.9 kcal/mol·Å, and  $\Delta E_{M=1 \rightarrow 3}$  is 21.8 kJ/mol.

The maximum rate of formaldehyde production on  $\text{VO}_x/\text{TiO}_2$  occurs at 450 K.<sup>6</sup> At this temperature,  $\bar{P}_{LZ}$  ranges from 5.0 to 15.6%. It is interesting to note that the values of  $\bar{P}_{LZ}$  for  $\text{VO}_x/\text{TiO}_2$  are about two to three times greater than those for  $\text{VO}_x/\text{SiO}_2$  at the same temperature. Using eq 3, the rate constant  $k_{M=1 \rightarrow 3}$  at 450 K is equal to  $3.60 \times 10^1 \text{ s}^{-1}$  (for  $\bar{P}_{LZ} = 4.97\%$ ) and  $1.13 \times 10^2 \text{ s}^{-1}$  (for  $\bar{P}_{LZ} = 15.6\%$ ). Comparing  $k_{M=1 \rightarrow 3}$  to the rate constant for the rate-limiting H-abstraction step at 450 K for 1% surface O-vacancies,  $k_{\text{rls}} = 1.46 \times 10^{-4} \text{ s}^{-1}$ ,<sup>3</sup> it is concluded that here too the rate of spin-surface crossing is rapid and hence not rate-limiting. Alternatively, if the reaction coordinate velocity is used instead of the mass-weighted system velocity in eq 1, then the values for  $\bar{P}_{LZ}$  in Table 2 are reduced and range only from 2.1 to 3.0% at 450 K, but are still not small enough to be rate-limiting.

## Conclusions

A spin-surface crossing from the singlet to the triplet potential energy surface occurs during methanol oxidation on  $\text{VO}_x/\text{SiO}_2$  and  $\text{VO}_x/\text{TiO}_2$ . Classically, the transition from  $M = 1 \rightarrow 3$  is spin-forbidden as the spin state must be preserved from reactant to product. The Landau–Zener model has been used to determine the spin transmission coefficient (using the mass-weighted system velocity or the reaction coordinate velocity) and a lower estimate of the rate constant for nonadiabatic spin-surface crossing processes. In the reaction considered, the ratio of the rate constant for spin-surface crossing,  $k_{M=1 \rightarrow 3}$ , to the rate constant for the rate-limiting step,  $k_{\text{rls}}$ , is on the order of  $10^8$  for  $\text{VO}_x/\text{SiO}_2$  and  $10^5$  for  $\text{VO}_x/\text{TiO}_2$ . The spin-surface crossing was also shown to occur well before the transition state. Thus, even though surface crossing reactions are classically spin-forbidden, they are still important in catalytic mechanisms, especially in the present example in which the rate of crossing is not kinetically-limiting.

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