

# Nitrous Oxide Decomposition over Fe-ZSM-5 in the Presence of Nitric Oxide: A Comprehensive DFT Study

Andreas Heyden,<sup>\*,†,‡</sup> Niels Hansen,<sup>†</sup> Alexis T. Bell,<sup>\*,§</sup> and Frerich J. Keil<sup>†</sup>

Department of Chemical Engineering, Hamburg University of Technology, D-21073 Hamburg, Germany, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455-0431, and Department of Chemical Engineering, University of California, Berkeley, California 94720-1462

Received: May 8, 2006

A number of experimental studies have shown recently that ppm-level additions of nitric oxide (NO) enhance the rate of nitrous oxide (N<sub>2</sub>O) decomposition catalyzed by Fe-ZSM-5 at low temperatures. In the present work, the NO-assisted N<sub>2</sub>O decomposition over mononuclear iron sites in Fe-ZSM-5 was studied on a molecular level using density functional theory (DFT) and transition-state theory. A reaction network consisting of over 100 elementary reactions was considered. The structure and energies of potential-energy minima were determined for all stable species, as were the structures and energies of all transition states. Reactions involving changes in spin potential-energy surfaces were also taken into account. In the absence of NO and at temperatures below 690 K, most active single iron sites (Z<sup>−</sup>[FeO]<sup>+</sup>) are poisoned by small concentrations of water in the gas phase; however, in the presence of NO, these poisoned sites are converted into a novel active iron center (Z<sup>−</sup>[FeOH]<sup>+</sup>). These latter sites are capable of promoting the dissociation of N<sub>2</sub>O into a surface oxygen atom and gas-phase N<sub>2</sub>. The surface oxygen atom is removed by reaction with NO or nitrogen dioxide (NO<sub>2</sub>). N<sub>2</sub>O dissociation is the rate-limiting step in the reaction mechanism. At higher temperatures, water desorbs from inactive iron sites and the reaction mechanism for N<sub>2</sub>O decomposition becomes independent of NO, reverting to the reaction mechanism previously reported by Heyden et al. [*J. Phys. Chem. B* 2005, 109, 1857].

## Introduction

Large amounts of nitrous oxide (N<sub>2</sub>O) are emitted from industrial processes used to produce nitric and adipic acid. Since N<sub>2</sub>O is the third most important greenhouse gas following CO<sub>2</sub> and CH<sub>4</sub>, there has been increasing interest in developing methods for its abatement. Considerable research has shown that N<sub>2</sub>O can be decomposed into N<sub>2</sub> and O<sub>2</sub> by passage over Fe-ZSM-5 at elevated temperatures.<sup>1–4</sup> One peculiarity of the tail gas streams from nitric acid plants is the presence of both N<sub>2</sub>O and nitric oxide (NO). While most catalytic systems active for N<sub>2</sub>O decomposition are inhibited by NO,<sup>5,6</sup> it has been reported that NO significantly enhances the rate of N<sub>2</sub>O decomposition over Fe-ZSM-5. This increase in the reaction rate is especially pronounced at low temperatures (<700 K).

The positive effect of NO on N<sub>2</sub>O decomposition over Fe-ZSM-5 was first reported by Kapteijn et al.,<sup>3</sup> who proposed that NO in the gas phase scavenged adsorbed oxygen deposited by N<sub>2</sub>O during the oxidation of active sites, thereby leading to the formation of NO<sub>2</sub> and regeneration of active sites. While this mechanism explains the overall increase in the N<sub>2</sub>O decomposition rate due to NO, it fails to explain the observations reported by Kögel et al.,<sup>7</sup> Mul et al.,<sup>4</sup> Pérez-Ramírez et al.,<sup>8</sup> Boutarouch et al.,<sup>9</sup> and Sang et al.<sup>10</sup> who report that relatively small amounts of NO are sufficient to induce a dramatic change in the N<sub>2</sub>O decomposition activity. Pérez-Ramírez et al.<sup>8</sup> also observed that for NO/N<sub>2</sub>O feed ratios higher than 0.25 the rate of N<sub>2</sub>O decomposition does not increase significantly, confirming the catalytic nature of NO on N<sub>2</sub>O decomposition. Since these authors did not observe NO inhibition at a feed molar ratio of

NO/N<sub>2</sub>O = 10, they suggested that NO adsorption and oxygen deposition by N<sub>2</sub>O occur at different sites in Fe-ZSM-5, and they proposed that two neighboring Fe sites are required to account for NO-assisted N<sub>2</sub>O decomposition. Pérez-Ramírez et al.<sup>8,11,12</sup> attributed the catalytic effect of NO to its action on O-atoms released during the decomposition of N<sub>2</sub>O. The adsorbed NO<sub>2</sub> formed in this way is proposed to react with a second O-atom from a neighboring site, thus accelerating the recombination of oxygen from N<sub>2</sub>O and the subsequent desorption of O<sub>2</sub>. The occurrence of this process was used to explain the promotional effect of NO under the assumption that the rate-determining process in N<sub>2</sub>O decomposition is O-atom recombination. Recently, Sang et al.<sup>10</sup> have observed a positive effect of NO on the rate of N<sub>2</sub>O decomposition on isolated Fe cations in Fe-ZSM-5. This observation requires a mechanistic interpretation that is different from those proposed by Mul et al.<sup>4</sup> and Pérez-Ramírez et al.<sup>8</sup> which involve di-iron sites.

While numerous investigators have studied the relationship between the structure of Fe-ZSM-5 and its activity for N<sub>2</sub>O decomposition, the nature of the active site and the mechanism of N<sub>2</sub>O decomposition both in the absence and in the presence of NO are not fully understood. Both, mononuclear and dinuclear iron sites have been proposed as the principal active site,<sup>13–36</sup> and either N<sub>2</sub>O dissociation or O<sub>2</sub> desorption has been suggested as the rate-limiting step in the overall process of N<sub>2</sub>O decomposition.<sup>37–47</sup>

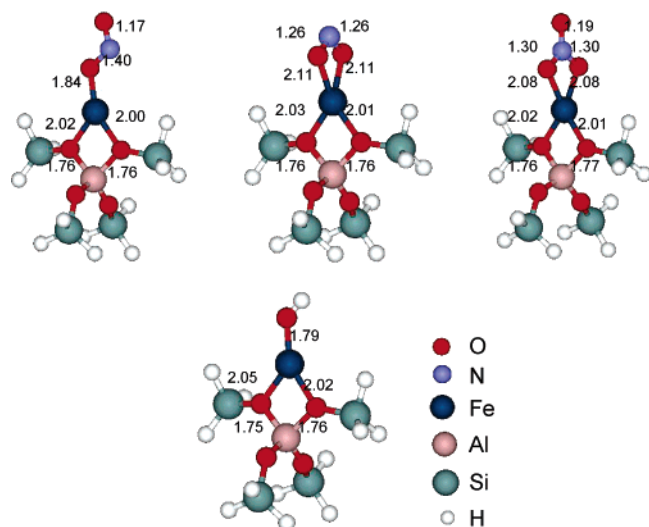
Recently, we reported the results of a detailed theoretical investigation of N<sub>2</sub>O decomposition occurring on mononuclear iron sites in Fe-ZSM-5 in the absence of NO.<sup>21</sup> The proposed reaction mechanism together with the rate coefficients calculated for each step was able to explain and reproduce various transient and steady-state experiments.<sup>22</sup> This work showed that the rate-limiting step in N<sub>2</sub>O decomposition is N<sub>2</sub>O dissociation and that O<sub>2</sub> desorption is very fast.<sup>22</sup> Isolated iron cations bound to a

\* To whom correspondence should be addressed. E-mail: heyden@chem.umn.edu (A.H.); bell@cchem.berkeley.edu (A.T.B.).

<sup>†</sup> Hamburg University of Technology.

<sup>‡</sup> University of Minnesota.

<sup>§</sup> University of California, Berkeley.



**Figure 1.** Iron nitrite, nitrate, and hydroxo zeolite cluster. Structures are potential-energy minima on the potential-energy surface with a spin multiplicity of  $M_S = 5$ . Atomic distances are indicated in angstroms.

single oxygen atom (viz.,  $Z^-[\text{FeO}]^+$ ) were identified as the active sites for N<sub>2</sub>O decomposition under the reaction conditions ( $T > 690$  K). Neighboring iron sites were not required to explain any of the experimental observations. The presence of H<sub>2</sub>O in the feed gas was found to inhibit the rate of N<sub>2</sub>O decomposition by deactivating active sites via the process  $Z^-[\text{FeO}]^+ + \text{H}_2\text{O} \rightleftharpoons Z^-[\text{Fe}(\text{OH})_2]^+$ . Since this process is reversible, the concentration of active sites ( $Z^-[\text{FeO}]^+$ ) was found to increase with increasing reaction temperature.

The present study is an extension of our previous work and focuses on the energetics and kinetics of the NO-assisted N<sub>2</sub>O decomposition occurring on single iron sites in Fe-ZSM-5. Of particular interest is understanding the interaction of NO with  $Z^-[\text{FeO}]^+$ ,  $Z^-[\text{FeO}_2]^+$ ,  $Z^-[\text{OFeO}]^+$ , and  $Z^-[\text{Fe}(\text{OH})_2]^+$ , the principal iron-containing species identified in our earlier study of N<sub>2</sub>O decomposition in the absence of NO.<sup>21,22</sup> It is shown that such interactions can lead to the formation of iron hydroxo, nitrite, and nitrate species,  $Z^-[\text{FeOH}]^+$ ,  $Z^-[\text{FeONO}]^+$ ,  $Z^-[\text{FeO}_2\text{N}]^+$ , and  $Z^-[\text{FeO}_2\text{NO}]^+$ , and that this opens up new pathways for N<sub>2</sub>O decomposition at temperatures below 700 K. The present investigation also illustrates how the nature of the active sites can change with temperature, both in the presence and in the absence of NO. Yet another objective of this study was to examine how NO might be formed directly from N<sub>2</sub>O at low temperatures. This part of the work was motivated by the spectroscopic results of Chen et al.,<sup>48</sup> Grubert et al.,<sup>49</sup> El-Malki et al.,<sup>50</sup> and the experimental observations of Sang and Lund,<sup>51,52</sup> Kiwi-Minsker et al.,<sup>46,53</sup> and Nováková and Sobalík,<sup>54</sup> who suggested that NO might be formed on the catalyst from N<sub>2</sub>O in the absence of NO in the feed stream.

We report here the results of theoretical calculations for a large number of elementary processes that are envisioned to occur during N<sub>2</sub>O decomposition on isolated mononuclear Fe sites in Fe-ZSM-5 in the presence of NO. In a companion paper, we use the calculated rate parameters of the present study to simulate the effects of NO on N<sub>2</sub>O decomposition under both steady-state and non-steady-state conditions.

## Theory

The catalytically active center and a portion of the zeolite framework are represented by a 23–27 atom cluster. This model is identical to that used in our earlier work.<sup>21</sup> As shown in Figure 1, the portion of the cluster describing the zeolite contains an Al-atom in the T12 position of the framework surrounded by shells of O- and Si-atoms. The terminal Si-atoms are fixed in

their crystallographic positions, as reported by Olson et al.<sup>55</sup> Dangling bonds are terminated by H-atoms located 1.48 Å from each terminal Si-atom oriented in the direction of the next O-atom in the zeolite matrix. This corresponds to the Si–H distance in SiH<sub>4</sub>. Heyden<sup>23</sup> has demonstrated that extended charge transfer occurs to a very limited extent over the zeolite matrix, so that the constrained T5 cluster model used in this work gives reliable results for electronic energy differences. To study the influence of nitric oxide on the active iron site, the anionic cluster is charge-compensated by a metal hydroxo, nitrite, or nitrate species,  $[\text{FeOH}]^+$ ,  $[\text{FeONO}]^+$ ,  $[\text{FeO}_2\text{N}]^+$ , or  $[\text{FeO}_2\text{NO}]^+$ , placed between two of the four O-atoms surrounding the Al-atom (see Figure 1).

Quantum chemical calculations of the geometry and energies of potential-energy minima were performed for spin surfaces with spin multiplicities of  $M_S = 2–8$ , using gradient-corrected spin density functional theory (DFT). To represent the effects of exchange and correlation, Becke's three-parameter exchange functional and the correlation functional of Lee, Yang, and Parr (B3LYP)<sup>56</sup> were used with a very fine numerical grid size (m5).<sup>57</sup> The B3LYP functional has proven to be effective for a number of reactions involving iron oxide molecules, leading us to conclude that a DFT-B3LYP approach can also be used successfully to investigate N<sub>2</sub>O decomposition on isolated Fe sites present in Fe-ZSM-5.<sup>58–62</sup> To speed up the calculation of potential-energy minima, all structures were preoptimized with the pure density functional BP86<sup>63,64</sup> using the resolution of identity (RI) approach for computing the electronic Coulomb interaction.<sup>65,66</sup> Basis sets at the triple- $\zeta$  level with polarization functions (TZVP)<sup>67</sup> were used for all atoms, including iron. Heyden<sup>23</sup> has demonstrated that, for the TZVP basis set, relative electronic energies are converged with respect to the basis set size. No corrections were made for the basis set superposition error (BSSE).<sup>68,69</sup> All calculations were carried out using the TURBOMOLE V5.7 suite of programs<sup>70,71</sup> in  $C_1$  symmetry.

Calculations on different spin potential-energy surfaces (PESs) revealed that the energy difference between different spin surfaces is usually significant so that only energies of PES minima for the ground state are reported. To approximate elementary reaction rates, first-order saddle points and minima on the seam of two PESs had to be determined. Saddle-point structures were determined only for the spin PES on which both reactant and product states have the lowest electronic energy. Likewise, minimum energy structures on the seam of two PESs were only determined for the two lowest spin PESs if the reactant and product state had ground electronic states on different spin PESs. Spin contamination was negligible for ground-state minimum structures. Some spin contamination was observed for transition states and minimum structures on a seam of two PESs. Nevertheless, in all cases, it was possible to distinguish clearly between states of different spin multiplicities.

Minimizations of the constrained cluster were performed in Cartesian coordinates with an energy convergence criterion of at least  $10^{-7}$  Ha and a gradient norm convergence criterion of  $10^{-4}$  Ha/bohr. At the end of all minimizations or saddle-point searches, a frequency calculation was done to confirm that all frequencies are positive for minima and only one frequency is imaginary for saddle points.

To accelerate the search for transition states, a combination of interpolation and local methods was used. The growing-string method<sup>72</sup> was used in mass-weighted coordinates with a maximum of 13–16 nodes. After the two ends of the growing string joined, the growing-string method was terminated and an approximate saddle point was obtained. To refine the position of the saddle point, the modified dimer method<sup>73</sup> was employed. A convergence criterion of the gradient norm of  $5 \times 10^{-4}$  Ha/bohr was used for transition states.

Minimum potential-energy structures on the seam of two PESs were determined with a multiplier penalty function algorithm (see Heyden et al.<sup>21</sup> and Heyden<sup>23</sup> for details). Converged minimum energy crossing point structures had a maximum energy difference on both PESs of less than  $10^{-6}$  Ha.

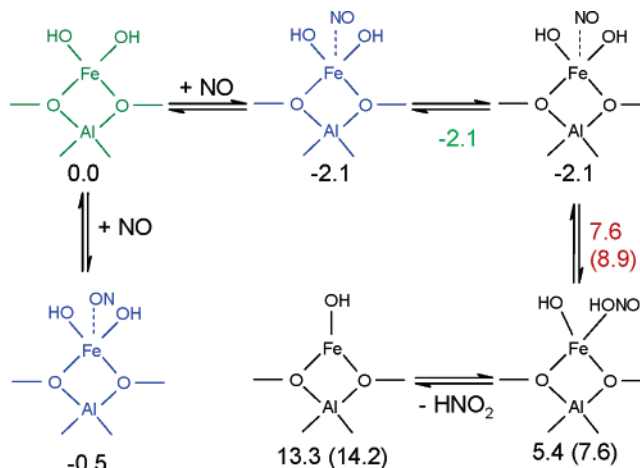
Overall equilibrium constants and reaction rate constants were computed using standard statistical mechanics and absolute rate theory.<sup>74</sup> We used the harmonic approximation, and included the contributions of the translational, rotational, vibrational, and electronic partition functions of all gaseous species participating in the reaction and the vibrational and electronic contribution of the zeolite cluster. Since the zeolite cluster is part of a solid, translational and rotational partition functions for the zeolite were assumed to be equal in the reactant and transition state. To calculate rates of spin-surface crossing, for example, desorption rates of oxygen, absolute rate theory was used under the assumption that the partition functions of the hypothetical transition state (minimum on the seam of two PESs) and the minimum on the PES with lower spin multiplicity (adsorbed state) are identical except for the electronic energy. This procedure completely neglects a low spin-surface crossing probability. To estimate if very low spin-surface crossing probabilities could have a significant effect on the reaction rate constants, thermally averaged spin transition probabilities are calculated with the Landau–Zener formula,<sup>75</sup> using a spin–orbit coupling energy,  $H_{12}$ , of 395 and 825 J/mol, as calculated by Danovich and Shaik<sup>76</sup> for the oxidative activation of  $H_2$  by  $FeO^+$ . Additional details concerning the calculations of rate parameters and the estimation of errors can be found in refs 21 and 23.

It is important to note that the necessary correction for the reaction rates to account for a spin-inversion probability smaller than 1 is comparable to the error inherent in the DFT calculations of activation energies. In addition, the rates of spin-surface crossing were never rate limiting in this work and, hence, spin-surface crossing should not have an influence on the overall kinetics of the reaction network studied.

## Results and Discussion

Most explanations of the promotional effect of NO on the  $N_2O$  decomposition over Fe-ZSM-5 are based on the assumption that NO adsorbs on an iron oxide species, that is, that it interacts with the same iron species responsible for  $N_2O$  decomposition in the absence of NO. Our recent theoretical work has shown that iron oxide species can indeed serve as the active species for temperatures above 700 K and in the absence of NO.<sup>21,22</sup> However, below this temperature, the majority of the iron sites are poisoned by water in the feed via the process  $Z^- [FeO]^+ + H_2O \rightleftharpoons Z^- [Fe(OH)_2]^+$  and our work has shown that the iron-dihydroxide species are inactive for  $N_2O$  decomposition.<sup>21</sup>

As noted in the Introduction, the promotional effect of NO on  $N_2O$  decomposition is especially pronounced at low temperatures ( $T < 700$  K) (where iron-dihydroxide species are calculated to be the majority iron species in the absence of NO) and disappears at high temperatures (where iron oxide species are calculated to be the majority iron species in the absence of NO). As a result, an explanation for NO-assisted  $N_2O$  decomposition that is based on the assumption that NO interacts with iron oxide species seems improbable. An alternative explanation is that NO converts the catalytically inactive iron-dihydroxide species into active species. In what follows, we first present calculations showing how NO can convert catalytically inactive  $Z^- [Fe(OH)_2]^+$  into catalytically active  $Z^- [FeOH]^+$  sites. Second, we present a reaction mechanism for  $N_2O$  decomposition utilizing  $Z^- [FeOH]^+$  sites. Third, we show that while NO can interact with iron oxide species at low temperatures to form various iron nitrite and nitrate species, these species do not



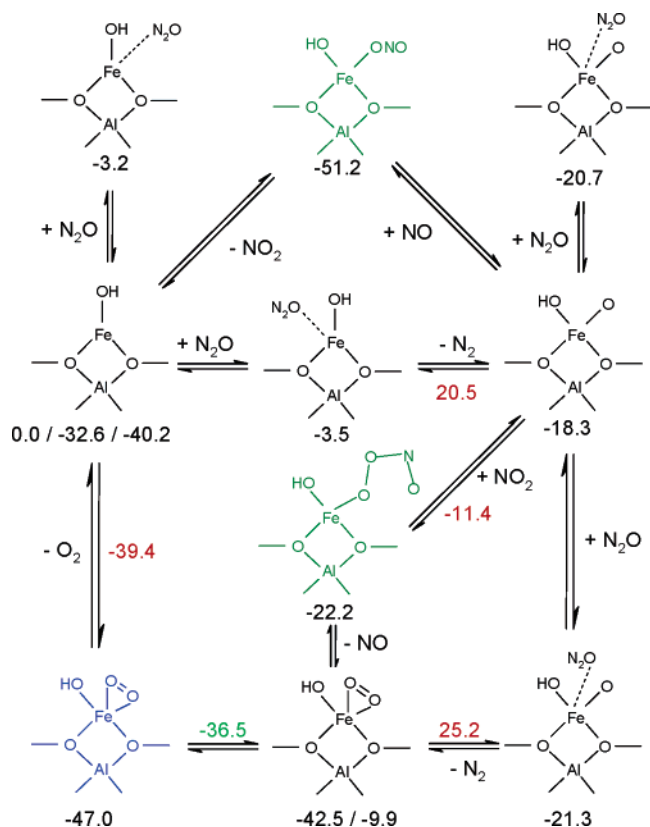
**Figure 2.** Activation of poisoned  $Z^- [Fe(OH)_2]^+$  sites. All energies are zero-point corrected, in kcal/mol and with reference to  $Z^- [Fe(OH)_2]^+$  with the appropriate amounts of NO, *trans*- $HNO_2$ , and *cis*- $HNO_2$ . The numbers in parentheses correspond to *cis*- $HNO_2$ . Energies of potential-energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PESs are in green. Black structures are on the PES with  $M_S = 5$ . Green structures are on the PES with  $M_S = 6$ . Structures in blue are on the PES with  $M_S = 7$ .

contribute significantly to  $N_2O$  decomposition either in the presence or absence of NO. Fourth, we examine several pathways for the formation of NO from  $N_2O$  on single iron sites. All quantum chemical calculations are summarized in Table 1 of the Appendix. Thermally averaged Landau–Zener transition probabilities are summarized for spin–orbit coupling energies of 395 and 825 J/mol for several temperatures in Table 2 of the Appendix. Failure to correct reaction rates for spin-inversion probabilities smaller than 1 creates errors smaller than an error in the activation barrier of 4 kcal/mol (at 700 K).

**Activation of  $Z^- [Fe(OH)_2]^+$  Sites.** Figure 2 illustrates a mechanism by which NO converts  $Z^- [Fe(OH)_2]^+$  sites into  $Z^- [FeOH]^+$  sites, which Nobukawa et al.<sup>77</sup> have proposed recently to be active for selective catalytic reduction of  $N_2O$  with  $CH_4$  in Fe-BEA zeolites. Nitric oxide can adsorb from the N-end on the septet spin PES with an enthalpy of adsorption of  $\Delta H_{ads} = -0.9$  kcal/mol (averaged from 600 to 800 K) and  $\Delta H_{ads} = 1.1$  kcal/mol for  $N_2O$  adsorption from the O-end. There is a negligible spin-change barrier of 0.1 kcal/mol from  $Z^- [Fe(OH)_2]^+ (NO) \{M_S = 7\}$  to  $Z^- [Fe(OH)_2]^+ (NO) \{M_S = 5\}$  sites. The spin-change process involves an enthalpy change of  $\Delta H_R = -0.01$  kcal/mol. Once adsorbed on the quintet PES, NO interacts with one hydroxo group to form adsorbed *cis*- or *trans*- $HNO_2$ . The transition state is characterized by a N–O distance of the N-atom from the nitric oxide and one O-atom from one of the hydroxo groups on the Fe-atom of 1.87 Å for the formation of *trans*- $HNO_2$  and 1.75 Å for the formation of *cis*- $HNO_2$ . The Fe–OH bond length increases in the transition state from 1.80 to 1.97 Å (*trans*- $HNO_2$ ) or 2.05 Å (*cis*- $HNO_2$ ). The activation barrier for the formation of  $HNO_2$  is  $E^\ddagger = 9.7$  kcal/mol (*trans*- $HNO_2$ ) or  $E^\ddagger = 11.0$  kcal/mol (*cis*- $HNO_2$ ). The imaginary frequency associated with the transition-state mode is  $196i$   $cm^{-1}$  (*trans*- $HNO_2$ ) or  $101i$   $cm^{-1}$  (*cis*- $HNO_2$ ). The enthalpy of reaction is  $\Delta H_R(\text{trans-}HNO_2) = 6.4$  kcal/mol or  $\Delta H_R(\text{cis-}HNO_2) = 8.7$  kcal/mol, respectively.  $HNO_2$  desorbs readily from  $Z^- [FeOH]^+ (HNO_2)$  sites to form mono-hydroxo-Fe sites. The enthalpy of desorption is  $\Delta H_R(\text{trans-}HNO_2) = 5.9$  kcal/mol or  $\Delta H_R(\text{cis-}HNO_2) = 4.3$  kcal/mol. Thus, in the presence of NO (and the absence of large amounts of  $HNO_2$ ),  $Z^- [FeOH]^+$  species can be formed readily from  $Z^- [Fe(OH)_2]^+$  sites.

**$N_2O$  Decomposition on  $Z^- [FeOH]^+$  Sites.** Figure 3 illustrates the catalytic cycle for  $N_2O$  decomposition on  $Z^- [FeOH]^+$





**Figure 3.** Catalytic cycle of the N<sub>2</sub>O dissociation on mononuclear Z-[FeOH]<sup>+</sup>{M<sub>S</sub> = 5} sites. All energies are zero-point corrected, in kcal/mol and with reference to Z-[FeOH]<sup>+</sup> with the appropriate amounts of N<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, NO, and NO<sub>2</sub>. Energies of potential-energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PESs are in green. Black structures are on the PES with M<sub>S</sub> = 5. Structures in green are on the PES with M<sub>S</sub> = 6. Structures in blue are on the PES with M<sub>S</sub> = 7. Multiple numbers under a PES minimum structure correspond to different catalytic cycles (see Table 1).

sites. N<sub>2</sub>O adsorbs through the N-end with an enthalpy of adsorption of  $\Delta H_{\text{ads}} = -1.4$  kcal/mol and through the O-end with an enthalpy of adsorption of  $\Delta H_{\text{ads}} = -1.8$  kcal/mol. The transition state for the reaction of Z-[FeOH]<sup>+</sup>(ON<sub>2</sub>) to form Z-[OFeOH]<sup>+</sup> and N<sub>2</sub> is characterized by a bending of the N<sub>2</sub>O molecule from 180° in the adsorbed state to 137.4° in the transition state, whereas the length of the N'-O'' bond of the N<sub>2</sub>O molecule increases from 1.20 to 1.38 Å. The activation barrier for the decomposition is  $E^\ddagger = 24.0$  kcal/mol. The imaginary frequency associated with the transition-state mode is 473i cm<sup>-1</sup>. Because the enthalpy of reaction is moderately exothermic,  $\Delta H_{\text{R}} = -16.1$  kcal/mol, the reverse reaction has a significant barrier and should not occur readily. Z-[OFeOH]<sup>+</sup> sites are possible active sites for the N<sub>2</sub>O dissociation. N<sub>2</sub>O adsorbs on Z-[OFeOH]<sup>+</sup> centers through the N-end with an enthalpy of adsorption of  $\Delta H_{\text{ads}} = -0.8$  kcal/mol and through the O-end with an enthalpy of adsorption of  $\Delta H_{\text{ads}} = -1.5$  kcal/mol. Hardly any N<sub>2</sub>O can be expected to adsorb on Z-[OFeOH]<sup>+</sup> sites under reaction conditions. The transition state for the reaction of Z-[OFeOH]<sup>+</sup>(ON<sub>2</sub>) to form Z-[O<sub>2</sub>FeOH]<sup>+</sup> and N<sub>2</sub> is characterized by a bending of the N<sub>2</sub>O molecule from 180° in the adsorbed state to 136.8° in the transition state, whereas the length of the N'-O'' bond of the N<sub>2</sub>O molecule increases from 1.20 to 1.34 Å. The O-atom from N<sub>2</sub>O forms a bond with the lone oxygen atom from Z-[OFeOH]<sup>+</sup>. The Fe-O bond increases along the reaction coordinate from 1.62 to 1.83 Å in the transition state. The O-O bond length is 1.59 Å. The activation barrier for N<sub>2</sub>O decomposition is  $E^\ddagger = 46.5$  kcal/

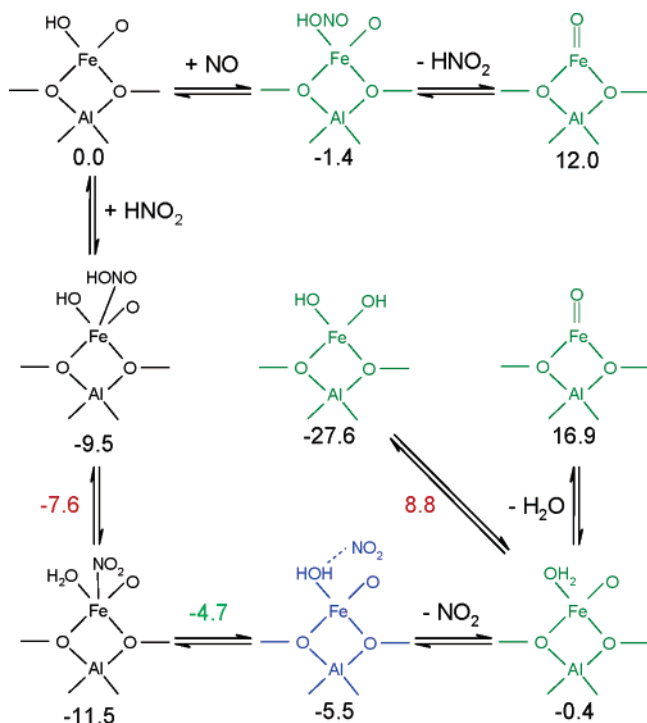
mol. The imaginary frequency associated with the transition-state mode is 710i cm<sup>-1</sup>. Because the enthalpy of reaction is  $\Delta H_{\text{R}} = -20.5$  kcal/mol, the reverse reaction has an even higher barrier and should not occur. Z-[O<sub>2</sub>FeOH]<sup>+</sup> species are more stable on the septet PES than on the quintet PES. A negligible spin-change barrier of about  $E^\ddagger = 6.0$  kcal/mol was found for the spin-inversion process. The enthalpy of reaction is  $\Delta H_{\text{R}} = -4.5$  kcal/mol, suggesting that Z-[O<sub>2</sub>FeOH]<sup>+</sup> species on the quintet and septet PES are in equilibrium. Z-[O<sub>2</sub>FeOH]<sup>+</sup>{M<sub>S</sub> = 7} species consist of a superoxide O<sub>2</sub><sup>-</sup> anion and a OH group associated with an Fe<sup>3+</sup> cation. The Fe-O bond distance of the superoxide anion to the iron cation is 2.06 Å. The O-O bond distance is 1.31 Å, and the O-O vibrational frequency is 1202 cm<sup>-1</sup>, confirming the superoxide character of the two adsorbed O-atoms.<sup>78</sup> Oxygen can desorb from Z-[O<sub>2</sub>FeOH]<sup>+</sup>{M<sub>S</sub> = 7}. The O<sub>2</sub> desorption barrier is  $E^\ddagger = 7.6$  kcal/mol, and the enthalpy of desorption is  $\Delta H_{\text{des}} = 5.8$  kcal/mol. The imaginary frequency associated with the transition-state mode is 58i cm<sup>-1</sup>. As in all catalytic cycles reported in this study, O<sub>2</sub> desorption is fast and, hence, oxygen inhibition is not projected to occur.

The highest barrier in the catalytic cycle involving Z-[FeOH]<sup>+</sup> sites is the second N<sub>2</sub>O decomposition on Z-[OFeOH]<sup>+</sup>, which has an activation barrier of over 43 kcal/mol with respect to the gas phase, making this catalytic cycle unlikely to occur except at elevated temperatures. The second N<sub>2</sub>O dissociation barrier on Z-[OFeOH]<sup>+</sup>/Z-[FeO<sub>2</sub>]<sup>+</sup> sites was previously calculated to be 12 and 17.3 kcal/mol, respectively.<sup>21</sup> The reason that the second N<sub>2</sub>O dissociation barrier on Z-[OFeOH]<sup>+</sup> is significantly higher than that on Z-[OFeO]<sup>+</sup> or Z-[FeO<sub>2</sub>]<sup>+</sup> is because superoxide species cannot be formed on Z-[OFeOH]<sup>+</sup> before the third oxygen atom is loaded on the iron atom, as is possible on Z-[OFeO]<sup>+</sup> or Z-[FeO<sub>2</sub>]<sup>+</sup> sites.

Figure 3 illustrates alternative reaction pathways for completing the catalytic cycle in the presence of NO. To bypass the second N<sub>2</sub>O dissociation on Z-[OFeOH]<sup>+</sup> sites, NO can adsorb on Z-[OFeOH]<sup>+</sup> sites, forming Z-[ONFeOH]<sup>+</sup> species. NO<sub>2</sub> can then desorb from these species. The enthalpy of NO adsorption is  $\Delta H_{\text{ads}} = -31.6$  kcal/mol. The enthalpy of NO<sub>2</sub> desorption is  $\Delta H_{\text{des}} = 16.8$  kcal/mol. The highest barrier in this catalytic cycle is the N<sub>2</sub>O decomposition,  $E^\ddagger = 24.0$  kcal/mol, suggesting a fast reaction mechanism in the presence of NO. This catalytic cycle involves the dissociation of one N<sub>2</sub>O molecule and the consumption of one NO molecule (one NO<sub>2</sub> molecule and one N<sub>2</sub> molecule are formed). Considering that high N<sub>2</sub>O conversion rates can be achieved over Fe-ZSM-5 at low temperatures in the presence of small amounts of NO and that significant amounts of O<sub>2</sub> are observed experimentally during N<sub>2</sub>O decomposition, NO<sub>2</sub> should be able to interact with Z-[OFeOH]<sup>+</sup> sites.

A reaction pathway that bypasses N<sub>2</sub>O decomposition on Z-[OFeOH]<sup>+</sup> sites and involves dissociation of one N<sub>2</sub>O molecule, consumption of one NO<sub>2</sub> molecule, and production of one NO, O<sub>2</sub>, and N<sub>2</sub> molecule is illustrated in Figure 3. NO<sub>2</sub> adsorption on Z-[OFeOH]<sup>+</sup> sites involves surmounting a small barrier of  $E^\ddagger = 6.9$  kcal/mol. The enthalpy of adsorption is  $\Delta H_{\text{ads}} = -1.4$  kcal/mol. The imaginary frequency associated with the transition-state mode is 400i cm<sup>-1</sup>. The transition state is characterized by a O-O bond distance of 1.84 Å. In the Z-[HOFeO]<sup>+</sup>(NO<sub>2</sub>) adsorption complex, the O-O bond length is 1.40 Å and the N-O bond length increases to 1.53 Å. NO can readily desorb from Z-[HOFeO]<sup>+</sup>(NO<sub>2</sub>) to form Z-[O<sub>2</sub>FeOH]<sup>+</sup>. Oxygen can desorb from Z-[O<sub>2</sub>FeOH]<sup>+</sup>, as described above. The net effect of both catalytic cycles is the dissociation of N<sub>2</sub>O molecules into N<sub>2</sub> and O<sub>2</sub>, thereby bypassing the dissociation of N<sub>2</sub>O on Z-[OFeOH]<sup>+</sup> sites.

In principle, NO and HNO<sub>2</sub> formed in situ can also interact with the hydroxyl group on Z-[OFeOH]<sup>+</sup> to form HNO<sub>2</sub> or NO<sub>2</sub>

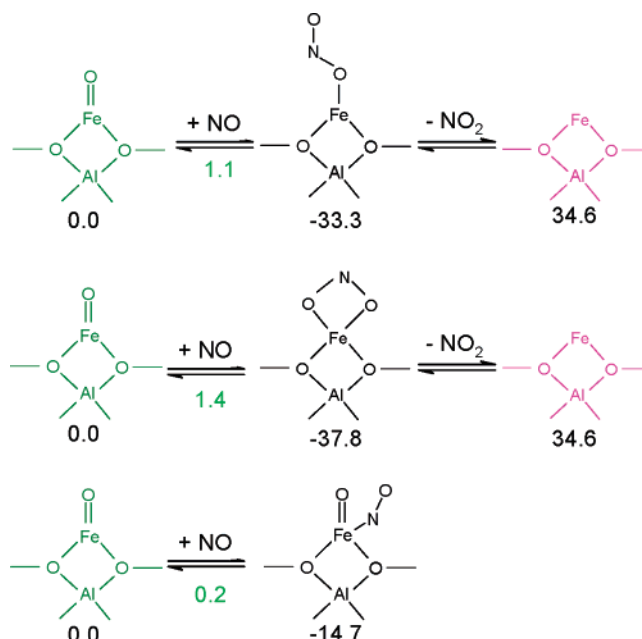


**Figure 4.** Two pathways from  $Z^{-}[\text{OFeOH}]^{+}$  sites to active  $Z^{-}[\text{FeO}]^{+}$  ( $M_S = 6$ ) sites. All energies are zero-point corrected, in kcal/mol and with reference to  $Z^{-}[\text{OFeOH}]^{+}$  with the appropriate amounts of  $\text{H}_2\text{O}$ , *trans*- $\text{HNO}_2$ ,  $\text{NO}$ , and  $\text{NO}_2$ . Energies of potential-energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PESs are in green. Black structures are on the PES with  $M_S = 5$ . Structures in green are on the PES with  $M_S = 6$ . Structures in blue are on the PES with  $M_S = 7$ .

and  $\text{H}_2\text{O}$  and a catalytically active  $Z^{-}[\text{FeO}]^{+}$  site. Figure 4 illustrates these reaction pathways and shows that these processes are endothermic and should therefore not be favored over those processes involving  $\text{NO}$  or  $\text{NO}_2$  reaction with the oxygen atom in  $Z^{-}[\text{OFeOH}]^{+}$ . As a result, these pathways are not discussed further.

To summarize, in the absence of  $\text{NO}$  and at temperatures below 650 K, the majority of the active sites in Fe-ZSM-5 are in the form of  $Z^{-}[\text{Fe}(\text{OH})_2]^{+}$ . The zero-point corrected energy barrier for water to desorb and to form catalytically active  $Z^{-}[\text{FeO}]^{+}$  sites is about 44.5 kcal/mol. Owing to the entropy gain in desorbing a water molecule, this process occurs at high temperatures but does not occur at low temperatures (<650 K). If  $\text{NO}$  is present in the gas stream and in contact with Fe-ZSM-5, the zero-point corrected energy barrier for the formation of active  $Z^{-}[\text{FeOH}]^{+}$  sites is about 13.3 kcal/mol, which is significantly lower than the activation barrier for the desorption of  $\text{H}_2\text{O}$  from  $Z^{-}[\text{Fe}(\text{OH})_2]^{+}$ . As a result, if large amounts of nitric oxide are added to an Fe-ZSM-5 catalyst at low temperatures, as done by Bulushev et al.,<sup>79</sup> the catalyst is activated immediately. Active  $Z^{-}[\text{FeOH}]^{+}$  sites are formed much more rapidly than active  $Z^{-}[\text{FeO}]^{+}$  species. The highest barrier for  $\text{N}_2\text{O}$  decomposition on  $Z^{-}[\text{FeOH}]^{+}$  is 20.5 kcal/mol with respect to the gas phase, which is about 3.5 kcal/mol lower than the activation barrier for  $\text{N}_2\text{O}$  decomposition on  $Z^{-}[\text{FeO}]^{+}$  sites. On the other hand, at elevated temperatures (>700 K), water desorption becomes the dominant process for activating  $Z^{-}[\text{Fe}(\text{OH})_2]^{+}$  sites. No net gas species are formed in the process of producing  $Z^{-}[\text{FeOH}]^{+}$  sites, so that at high temperatures the entropy increase associated with desorption of  $\text{H}_2\text{O}$  should offset the higher activation barrier for the water desorption process,  $Z^{-}[\text{Fe}(\text{OH})_2]^{+} \rightleftharpoons Z^{-}[\text{FeO}]^{+} + \text{H}_2\text{O}$ .

**Interaction of  $\text{NO}$  with  $Z^{-}[\text{FeO}]^{+}$ ,  $Z^{-}[\text{FeO}_2]^{+}$ , and  $Z^{-}[\text{OFeO}]^{+}$  Sites.** At elevated temperatures ( $T > 700$  K),

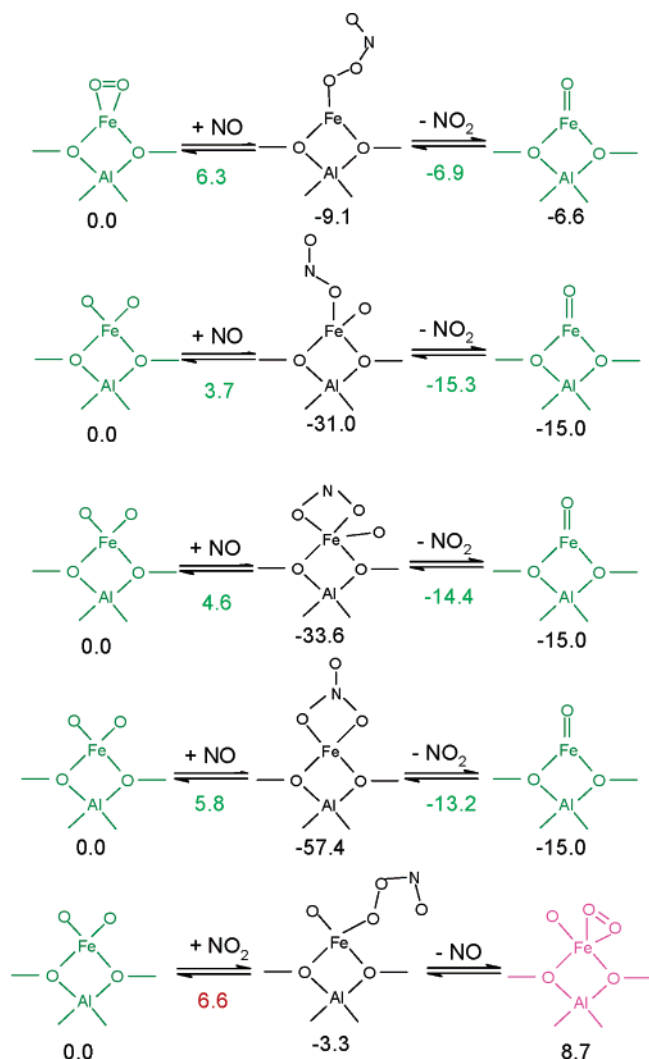


**Figure 5.** Interaction of nitric oxide with  $Z^{-}[\text{FeO}]^{+}$  ( $M_S = 6$ ) sites. All energies are zero-point corrected, in kcal/mol and with reference to  $Z^{-}[\text{FeO}]^{+}$  ( $M_S = 6$ ). Energies of potential-energy minima are in black. Energies of minima on the seam of two PESs are in green. Structures in green are on the PES with  $M_S = 6$ . Black structures are on the PES with  $M_S = 5$ . Structures in magenta are on the PES with  $M_S = 4$ .

isolated Fe cations are predicted to be present primarily as  $Z^{-}[\text{FeO}]^{+}$ ,  $Z^{-}[\text{FeO}_2]^{+}$ , and  $Z^{-}[\text{OFeO}]^{+}$  sites.<sup>21,22</sup> In what follows, the interaction of these iron oxide species with  $\text{NO}$  to form iron nitrite and nitrate species is investigated. The purpose of this section is to show that  $\text{NO}$  has very little effect on the overall  $\text{N}_2\text{O}$  decomposition activity of single iron sites in Fe-ZSM-5 at temperatures where iron nitrite and nitrate species might be formed.

Figure 5 illustrates the interaction of  $\text{NO}$  with  $Z^{-}[\text{FeO}]^{+}$  sites. Nitric oxide adsorbs on  $Z^{-}[\text{FeO}]^{+}$  centers from the nitrogen end with an enthalpy of adsorption of  $\Delta H_{\text{ads}} = -32.9$  kcal/mol (averaged over 600–800 K), forming  $Z^{-}[\text{FeONO}]^{+}$  species. During the adsorption process, spin pairing occurs. The ground state of  $Z^{-}[\text{FeO}]^{+}$  is on the sextet PES, whereas the ground state of  $Z^{-}[\text{FeONO}]^{+}$  is on the quintet PES. The adsorption process involves a negligible spin-change barrier of  $\sim 1.1$  kcal/mol. The bonding of  $Z^{-}[\text{FeONO}]^{+}$  is illustrated in Figure 1, the Fe–O bond increases during the adsorption process from 1.66 to 1.84 Å. The O–N′–O′′ bond angle is calculated to be 112.9° in the adsorbed state on the PES with a spin multiplicity of  $M_S = 5$ . The characteristic vibrational frequency of adsorbed nitric oxide is calculated to be 1701  $\text{cm}^{-1}$ . In principle, nitrogen dioxide can desorb from  $Z^{-}[\text{FeONO}]^{+}$ ; however, the enthalpy of desorption for this process is  $\Delta H_{\text{des}} = 66.0$  kcal/mol, making this process unlikely to occur.

A second potential-energy minimum was found for adsorbed  $\text{NO}$ ,  $Z^{-}[\text{FeO}_2\text{N}]^{+}$ , illustrated in Figures 1 and 5. The enthalpy of adsorption was calculated to be  $\Delta H_{\text{ads}} = -37.8$  kcal/mol. The adsorption process involves a spin-change barrier of 1.4 kcal/mol. The reason for the difference in the spin-change barriers for the formation of  $Z^{-}[\text{FeONO}]^{+}$  and  $Z^{-}[\text{FeO}_2\text{N}]^{+}$  is attributable to the assumption that the zero-point energies of the adsorbed state and transition state are equivalent. The Fe–O bond length in  $Z^{-}[\text{FeO}_2\text{N}]^{+}$  is 2.11 Å, and the O–N′–O′′ bond angle is 111.3°. The characteristic vibrational frequencies of adsorbed nitric oxide are 1238 and 1330  $\text{cm}^{-1}$ . The enthalpy of  $\text{NO}_2$  desorption from  $Z^{-}[\text{FeO}_2\text{N}]^{+}$  is  $\Delta H_{\text{des}} = 70.9$  kcal/mol, making  $\text{NO}_2$  desorption very unlikely to occur.



**Figure 6.** Interaction of nitric oxide with  $Z^{-}[\text{FeO}_2]^+$  ( $M_S = 6$ ) and  $Z^{-}[\text{OFeO}]^+$  ( $M_S = 6$ ) sites. All energies are zero-point corrected, in kcal/mol and with reference to  $Z^{-}[\text{FeO}_2]^+$  or  $Z^{-}[\text{OFeO}]^+$ . Energies of potential-energy minima are in black. Energies of minima on the seam of two PESs are in green. Structures in green are on the PES with  $M_S = 6$ . Black structures are on the PES with  $M_S = 5$ . Structures in magenta are on the PES with  $M_S = 4$ .

Nitric oxide might also adsorb on  $Z^{-}[\text{FeO}]^+$  from the nitrogen end of the molecule. The enthalpy of adsorption for this process is calculated to be  $\Delta H_{\text{ads}} = -13.6$  kcal/mol, a value significantly lower than that for the formation of  $Z^{-}[\text{FeONO}]^+$  and  $Z^{-}[\text{FeO}_2\text{N}]^+$  species. Adsorption of NO through the nitrogen end of the molecule involves surmounting a negligible spin-change barrier of 0.2 kcal/mol. The N'-O' bond length is 1.15 Å and is essentially the same as that for gaseous NO. The characteristic harmonic vibrational frequency of adsorbed nitric oxide is calculated to be 1895 cm<sup>-1</sup>, in good agreement with the experimental values of 1884 and 1874 cm<sup>-1</sup> reported by Mul et al.<sup>4</sup> Owing to the low adsorption enthalpy, -13.6 kcal/mol,  $Z^{-}[\text{OFeNO}]^+$  species (or similar ones) are unlikely to play a role in N<sub>2</sub>O decomposition at reaction temperatures above 500 K. Therefore, iron species on which NO is weakly adsorbed through the N-end are not discussed further. No other, more stable, potential-energy minimum with a nitrogen atom in direct contact with the iron atom was found in this study.

Figure 6 illustrates the interaction of NO with  $Z^{-}[\text{FeO}_2]^+$  and  $Z^{-}[\text{OFeO}]^+$  sites. Simulations of N<sub>2</sub>O decomposition on Fe-ZSM-5 reveal that  $Z^{-}[\text{FeO}_2]^+$  and  $Z^{-}[\text{OFeO}]^+$  are always in equilibrium. While  $Z^{-}[\text{FeO}_2]^+$  is the more abundant species,

$Z^{-}[\text{OFeO}]^+$  is the more active center for N<sub>2</sub>O decomposition. Nitric oxide adsorbs from the N-end with an enthalpy of adsorption of  $\Delta H_{\text{ads}} = -9.0$  kcal/mol on  $Z^{-}[\text{FeO}_2]^+$  centers, forming  $Z^{-}[\text{FeOONO}]^+$  sites. The spin-change barrier for adsorption in this manner is 6.3 kcal/mol, suggesting a fast NO adsorption process. Nitrogen dioxide readily desorbs from  $Z^{-}[\text{FeOONO}]^+$ . The spin-change barrier from the quintet PES back to the sextet PES of the active site is below the zero-point corrected energy of  $Z^{-}[\text{FeO}]^+$  and NO<sub>2</sub>. The enthalpy of desorption averaged over 600–800 K is calculated to be  $\Delta H_{\text{des}} = 1.0$  kcal/mol. As a result, in the presence of NO,  $Z^{-}[\text{FeO}_2]^+$  sites are rapidly reduced to  $Z^{-}[\text{FeO}]^+$ .

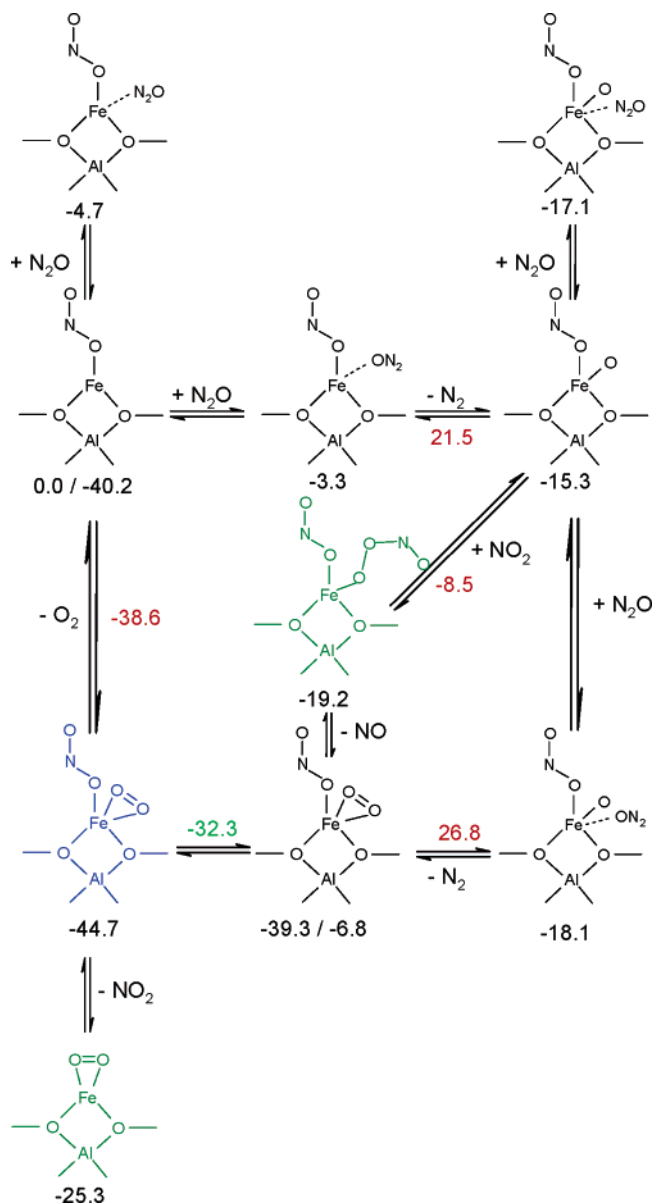
Our results for the reaction  $Z^{-}[\text{FeO}_2]^+ + \text{NO} \rightleftharpoons Z^{-}[\text{FeO}]^+ + \text{NO}_2$  can be compared with those of Sang et al.<sup>10</sup> These authors reported a change in electronic energy for this reaction of about -1.5 kcal/mol, a number in reasonable agreement with the zero-point corrected energy difference of -6.6 kcal/mol calculated in this work. The differences between the calculated values are attributable to the use of a cluster located in the T1 position by Sang et al.<sup>10</sup> rather than the T12 position used in this work and the use of a double- $\zeta$  basis set (LACVP\*\*) rather than a triple- $\zeta$  basis set.

Nitric oxide can also adsorb on  $Z^{-}[\text{OFeO}]^+$  sites to form  $Z^{-}[\text{OFeONO}]^+$  or  $Z^{-}[\text{OFeO}_2\text{N}]^+$  species. The spin-change barrier for adsorption is 3.7 or 4.6 kcal/mol, respectively, suggesting that the adsorption process is fast. The corresponding enthalpies of adsorption are  $\Delta H_{\text{ads}} = -30.5$  kcal/mol and  $\Delta H_{\text{ads}} = -34.0$  kcal/mol, respectively. The characteristic harmonic vibrational frequency of adsorbed nitric oxide on  $Z^{-}[\text{OFeO}]^+$  sites is calculated to be 1797 cm<sup>-1</sup> for  $Z^{-}[\text{OFeONO}]^+$  and 1256 and 1308 cm<sup>-1</sup> for  $Z^{-}[\text{OFeO}_2\text{N}]^+$ . Nitrogen dioxide can desorb from  $Z^{-}[\text{OFeONO}]^+$  and  $Z^{-}[\text{OFeO}_2\text{N}]^+$ . The desorption barrier is 16.0 kcal/mol from  $Z^{-}[\text{OFeONO}]^+$  sites and 19.2 kcal/mol from  $Z^{-}[\text{OFeO}_2\text{N}]^+$  sites, suggesting that NO<sub>2</sub> desorption should be fast at reaction temperatures. The enthalpy of desorption is  $\Delta H_{\text{des}} = 14.4$  kcal/mol from  $Z^{-}[\text{OFeONO}]^+$  sites and  $\Delta H_{\text{des}} = 17.9$  kcal/mol from  $Z^{-}[\text{OFeO}_2\text{N}]^+$  centers. Consequently,  $Z^{-}[\text{OFeO}]^+$  sites are reduced rapidly in the presence of NO to  $Z^{-}[\text{FeO}]^+$ .

Nitric oxide can also adsorb on  $Z^{-}[\text{OFeO}]^+$  sites to form stable iron nitrate species,  $Z^{-}[\text{FeO}_2\text{NO}]^+$ . The spin-change barrier for adsorption is 5.8 kcal/mol, and the enthalpy of adsorption is  $\Delta H_{\text{ads}} = -58.3$  kcal/mol. The desorption barrier is 63.2 kcal/mol, suggesting that iron nitrate species once formed will be difficult to eliminate. The bonding of  $Z^{-}[\text{FeO}_2\text{NO}]^+$  is illustrated in Figure 1; the Fe-O bond increases during the adsorption process from 1.68 Å in  $Z^{-}[\text{OFeO}]^+$  to 2.08 Å in the iron nitrate species. The characteristic harmonic vibrational frequency of adsorbed NO in  $Z^{-}[\text{FeO}_2\text{NO}]^+$  is calculated to be 1641 cm<sup>-1</sup>. Mul et al.<sup>4</sup> and Pérez-Ramírez et al.<sup>11</sup> observed a sharp infrared band at 1635 and 1632 cm<sup>-1</sup>, respectively, suggesting that iron nitrate species might be formed during N<sub>2</sub>O decomposition on Fe-ZSM-5. Nitrogen dioxide can desorb from  $Z^{-}[\text{FeO}_2\text{NO}]^+$  sites with an activation barrier of 44.2 kcal/mol, which is equal to the enthalpy of NO<sub>2</sub> desorption. The spin-change barrier for NO<sub>2</sub> adsorption on  $Z^{-}[\text{FeO}]^+$  sites is 1.8 kcal/mol.

Nitrogen dioxide adsorption on  $Z^{-}[\text{OFeO}]^+$  sites was also considered. The adsorption process involves spin pairing and subsequent surmounting of a small activation barrier of  $E^\ddagger = 6.6$  kcal/mol on the quintet PES. The enthalpy of adsorption is  $\Delta H_{\text{ads}} = -2.0$  kcal/mol. The imaginary frequency associated with the transition-state mode is 510i cm<sup>-1</sup>. The transition state is characterized by an O-O bond distance of 1.79 Å (one oxygen bond to Fe, the other oxygen bond to N) and a slight elongation of the N-O bond length to 1.22 Å. Nitric oxide can desorb from  $Z^{-}[\text{OFeO}]^+(\text{NO}_2)$  sites to form  $Z^{-}[\text{OFeO}_2]^+$

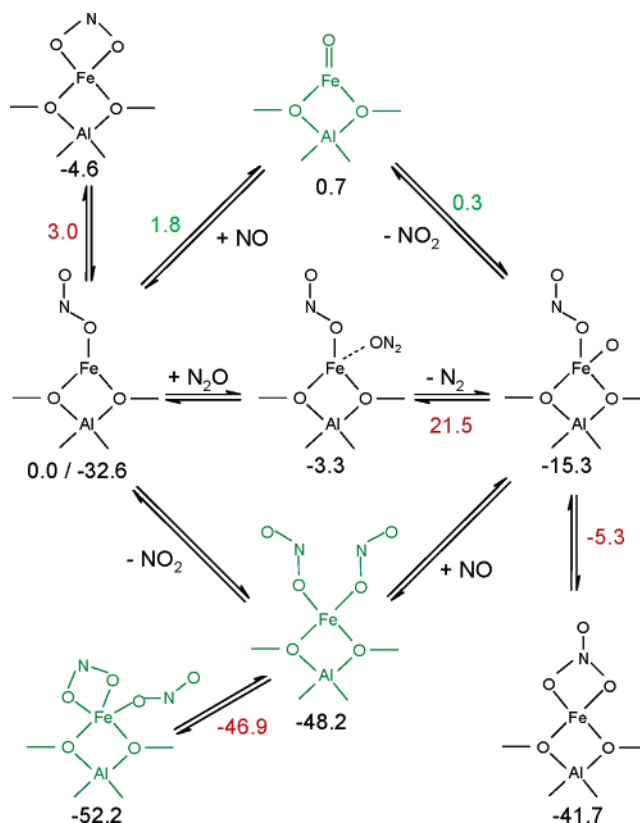




**Figure 7.** Catalytic cycle of the  $\text{N}_2\text{O}$  dissociation on mononuclear  $\text{Z}^-\text{[FeONO]}^+\{M_S = 5\}$  sites. All energies are zero-point corrected, in kcal/mol and with reference to  $\text{Z}^-\text{[FeONO]}^+$  with the appropriate amounts of  $\text{N}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{NO}$ , and  $\text{NO}_2$ . Energies of potential-energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PESs are in green. Black structures are on the PES with  $M_S = 5$ . Green structures are on the PES with  $M_S = 6$ . Structures in blue are on the PES with  $M_S = 7$ . Multiple numbers under a PES minimum structure correspond to different catalytic cycles (see Table 1).

species. The desorption barrier for this process is 12.0 kcal/mol. The enthalpy of desorption at reaction temperature is  $\Delta H_{\text{des}} = 12.2$  kcal/mol. Since  $\text{O}_2$  can readily desorb from  $\text{Z}^-\text{[OFeO}_2]^+$  species (see Heyden et al.<sup>21</sup>), the reduction of  $\text{Z}^-\text{[OFeO}_2]^+$  sites with  $\text{NO}_2$  is a fast, entropy driven process (two gas molecules are produced from one  $\text{NO}_2$  molecule).

To summarize, exposure of  $\text{Z}^-\text{[FeO]}^+$ ,  $\text{Z}^-\text{[FeO}_2]^+$ , and  $\text{Z}^-\text{[OFeO]}^+$  sites to  $\text{NO}$  leads to the formation of three new stable species,  $\text{Z}^-\text{[FeONO]}^+$ ,  $\text{Z}^-\text{[FeO}_2\text{N]}^+$ , and  $\text{Z}^-\text{[FeO}_2\text{NO]}^+$ . The enthalpy of desorption of  $\text{NO}$  or  $\text{NO}_2$  from these sites is  $\Delta H_{\text{des}} = 32.9$ , 37.8, and 42.2 kcal/mol, respectively. These results suggest that if iron oxide species were present in Fe-ZSM-5 at low temperatures, small amounts of nitric oxide in the feed gas of the  $\text{N}_2\text{O}$  decomposition would result in the formation of significant amounts of  $\text{Z}^-\text{[FeONO]}^+$ ,  $\text{Z}^-\text{[FeO}_2\text{N]}^+$ ,

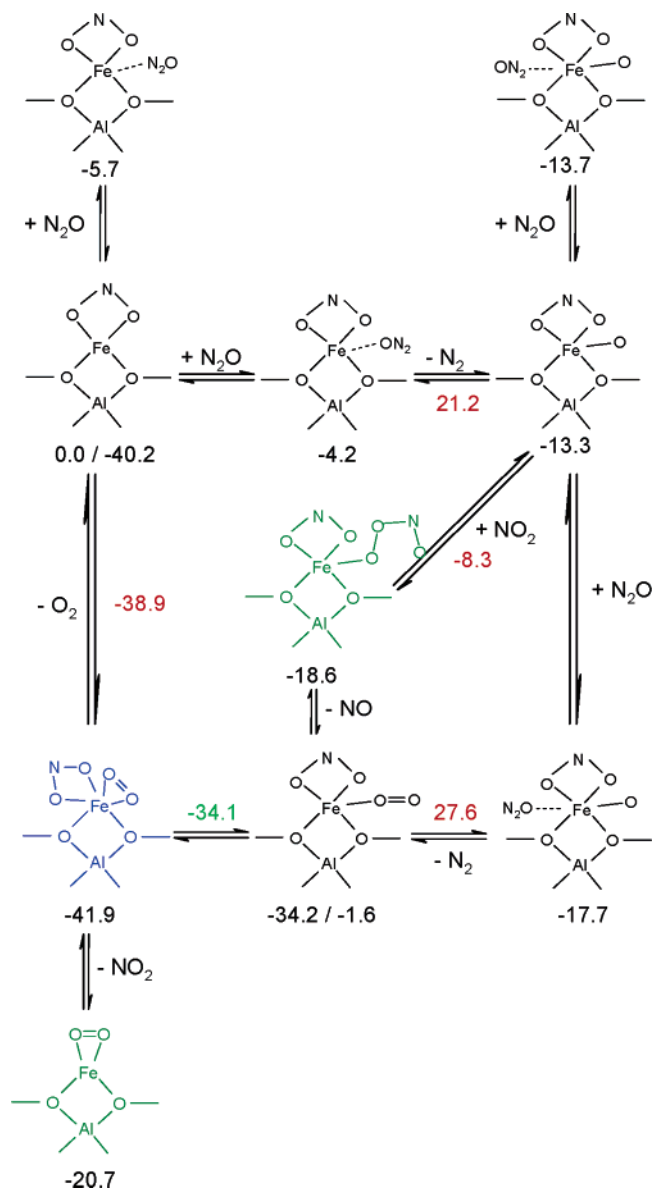


**Figure 8.** Alternative catalytic cycle of the  $\text{N}_2\text{O}$  dissociation on mononuclear  $\text{Z}^-\text{[FeONO]}^+\{M_S = 5\}$  sites. All energies are zero-point corrected, in kcal/mol and with reference to  $\text{Z}^-\text{[FeONO]}^+$  with the appropriate amounts of  $\text{N}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{NO}$ , and  $\text{NO}_2$ . Energies of potential-energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PESs are in green. Black structures are on the PES with  $M_S = 5$ . Structures in green are on the PES with  $M_S = 6$ .

and  $\text{Z}^-\text{[FeO}_2\text{NO]}^+$  species. However, our earlier work on the simulation of  $\text{N}_2\text{O}$  decomposition on isolated Fe sites in Fe-ZSM-5 indicates that iron oxide species will not be present at low temperatures ( $< 650$  K) because such sites will react very rapidly with  $\text{H}_2\text{O}$  to form  $\text{Z}^-\text{[Fe(OH)}_2]^+$  sites. Therefore, iron nitrite and nitrate species can only be formed at higher temperatures where water desorbs. The enthalpy of water desorption,  $\Delta H_{\text{des}} = 43.4$  kcal/mol ( $\text{Z}^-\text{[Fe(OH)}_2]^+ \rightleftharpoons \text{Z}^-\text{[FeO]}^+ + \text{H}_2\text{O}$ ), is higher than the enthalpy of  $\text{NO}_x$  desorption from iron nitrite or nitrate species. As a result,  $\text{NO}_x$  desorption begins at lower temperatures than  $\text{H}_2\text{O}$  desorption, and large amounts of nitric oxide are necessary to displace  $\text{H}_2\text{O}$  at lower temperatures or to form iron nitrite or nitrate species at higher temperatures.

Figures 7–12 illustrate the catalytic cycle of the  $\text{N}_2\text{O}$  decomposition on iron nitrite and nitrate species. The reaction mechanism, reaction intermediates, and transition states are very similar to those shown for  $\text{N}_2\text{O}$  decomposition on  $\text{Z}^-\text{[FeOH]}^+$  species (see Figure 3). As a result, these pathways are not discussed further. More information about these reaction pathways can be found in ref 23.

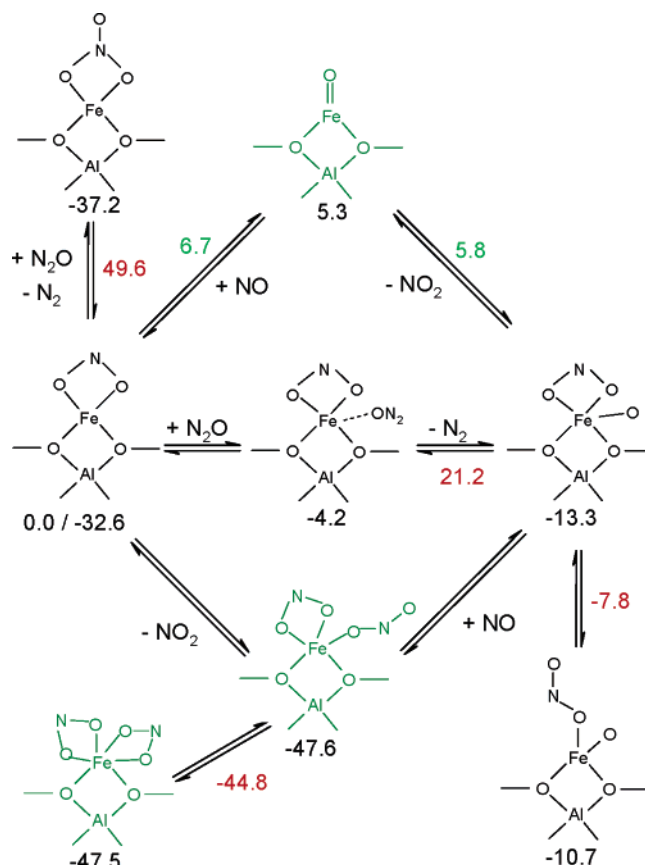
In industrial tail gases, the  $\text{H}_2\text{O}$  concentration is significantly larger than the  $\text{NO}_x$  concentration.<sup>80</sup> As a result, iron nitrite and nitrate species should not be present under industrial conditions. In some experimental studies,<sup>79</sup> the  $\text{NO}_x$  concentration is very large so that iron nitrite and nitrate species might contribute to the  $\text{N}_2\text{O}$  decomposition. On iron nitrite and nitrate species, the first  $\text{N}_2\text{O}$  dissociation barrier with respect to the gas phase is calculated to be 21.5, 21.2, and 22.4 kcal/mol, respectively. This elementary reaction step is the rate-limiting step in the reaction



**Figure 9.** Catalytic cycle of the N<sub>2</sub>O dissociation on mononuclear Z-[FeO<sub>2</sub>N]<sup>+</sup>{M<sub>S</sub> = 5} sites. All energies are zero-point corrected, in kcal/mol and with reference to Z-[FeO<sub>2</sub>N]<sup>+</sup> with the appropriate amounts of N<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, NO, and NO<sub>2</sub>. Energies of potential-energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PESs are in green. Black structures are on the PES with M<sub>S</sub> = 5. Green structures are on the PES with M<sub>S</sub> = 6. Structures in blue are on the PES with M<sub>S</sub> = 7. Multiple numbers under a PES minimum structure correspond to different catalytic cycles (see Table 1).

mechanism of the NO-assisted N<sub>2</sub>O decomposition on iron nitrite and nitrate species. On Z-[FeOH]<sup>+</sup> species, we calculated in this study a rate-limiting barrier of 20.5 kcal/mol, and for Z-[FeO]<sup>+</sup> sites, Heyden et al.<sup>21</sup> computed an only marginally larger barrier of 24–24.3 kcal/mol. As a result, iron nitrite and nitrate species are not more active than Z-[FeOH]<sup>+</sup> and Z-[FeO]<sup>+</sup> species and large amounts of nitric oxide cannot significantly increase the N<sub>2</sub>O decomposition rate.

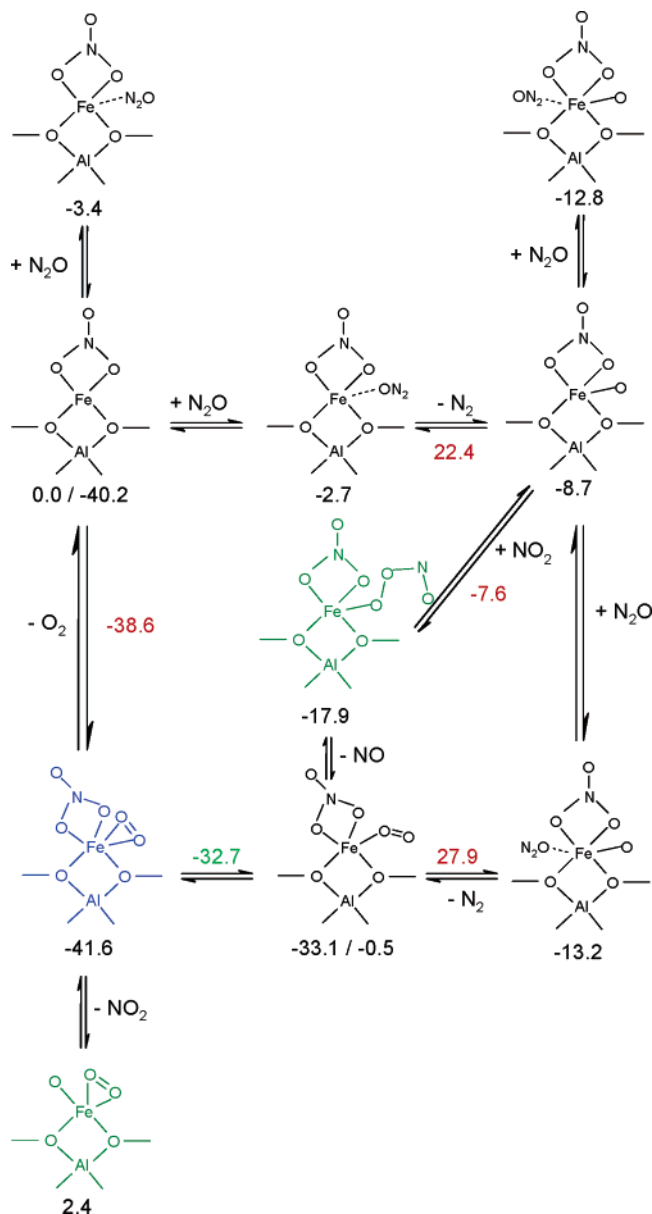
**Formation of NO from N<sub>2</sub>O.** El-Malki et al.,<sup>50</sup> Bulushev et al.,<sup>79</sup> Kiwi-Minsker et al.,<sup>46,53</sup> Sang and Lund,<sup>51,52</sup> and Nováková and Sobalík<sup>54</sup> have proposed that NO formed from N<sub>2</sub>O could facilitate the decomposition of N<sub>2</sub>O at low temperatures in the absence of NO in the feed. Figure 13 illustrates reaction pathways for the formation of NO on Z-[OFeO]<sup>+</sup>, Z-[ONFeO]<sup>+</sup>, Z-[OFeO<sub>2</sub>N]<sup>+</sup>, Z-[OFeO<sub>2</sub>NO]<sup>+</sup>, and Z-[OFeOH]<sup>+</sup>. Since these pathways are very similar, we will only discuss that for the



**Figure 10.** Alternative catalytic cycle of the N<sub>2</sub>O dissociation on mononuclear Z-[FeO<sub>2</sub>N]<sup>+</sup>{M<sub>S</sub> = 5} sites. All energies are zero-point corrected, in kcal/mol and with reference to Z-[FeO<sub>2</sub>N]<sup>+</sup> with the appropriate amounts of N<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, NO, and NO<sub>2</sub>. Energies of potential-energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PESs are in green. Black structures are on the PES with M<sub>S</sub> = 5. Structures in green are on the PES with M<sub>S</sub> = 6.

formation of NO on Z-[OFeO]<sup>+</sup> sites. Nitrous oxide interacts via the N-end with the O-atom on the mononuclear iron site and forms an adsorbed NO dimer. The transition state for the reaction, Z-[OFeO]<sup>+</sup> + N<sub>2</sub>O ⇌ Z-[FeO]<sup>+</sup>(*cis*-(NO)<sub>2</sub>), is characterized by a decrease in the bond angle of the N<sub>2</sub>O molecule from 180 to 152.8° in the transition state, whereas the length of the N–N' bond increases from 1.12 to 1.17 Å. The N–O (oxygen bond to the iron atom) bond length is 1.67 Å in the transition state. The activation barrier for the nitric oxide dimer is E<sup>‡</sup> = 28.2 kcal/mol, and the enthalpy of reaction is ΔH<sub>R</sub> = 24.4 kcal/mol. The activation barrier for NO formation on Z-[ONFeO]<sup>+</sup>, Z-[OFeO<sub>2</sub>N]<sup>+</sup>, Z-[OFeO<sub>2</sub>NO]<sup>+</sup>, and Z-[OFeOH]<sup>+</sup> and the enthalpy of reaction involving these species is slightly smaller than that for Z-[OFeO]<sup>+</sup> (see Table 1 in the Appendix). The imaginary frequency associated with the transition-state mode is 614i cm<sup>-1</sup>. The activation barrier calculated for the reaction Z-[OFeO]<sup>+</sup> + N<sub>2</sub>O ⇌ Z-[FeO]<sup>+</sup>(*cis*-(NO)<sub>2</sub>), 28.2 kcal/mol, is similar to that found by Gonzalez et al.<sup>81</sup> for the reaction O(<sup>3</sup>P) + N<sub>2</sub>O ⇌ 2 NO, 27.7 kcal/mol. The geometry of the transition-state structure is also quite similar with an O–N distance of 1.66 Å, an N–N' distance of 1.17 Å, and a N<sub>2</sub>O bending of 157.3° in the transition state. Nitric oxide can desorb from Z-[FeO]<sup>+</sup>(*cis*-(NO)<sub>2</sub>) sites. The transition state for the reaction of Z-[FeO]<sup>+</sup>(*cis*-(NO)<sub>2</sub>) to form Z-[FeO]<sup>+</sup>(ON) and NO is characterized by an increase in the N–N' bond length from 1.23 Å in the adsorbed state to 1.44 Å in the transition state. The activation barrier for the dissociation is E<sup>‡</sup> = 9.2 kcal/mol, and the imaginary frequency associated with the transition-state mode is 677i cm<sup>-1</sup>. The enthalpy of reaction is ΔH<sub>R</sub> =

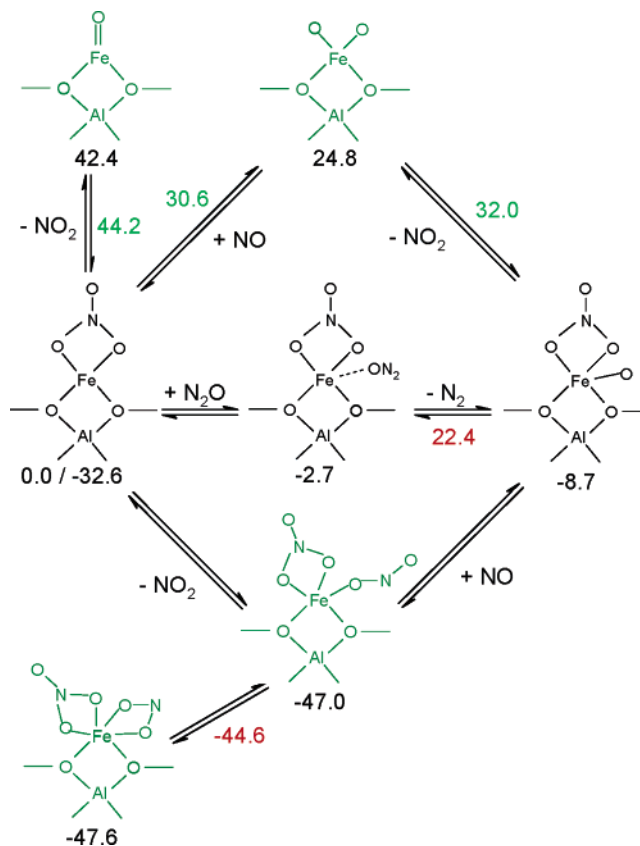




**Figure 11.** Catalytic cycle of the  $\text{N}_2\text{O}$  dissociation on mononuclear  $\text{Z}^+[\text{FeO}_2\text{NO}]^+\{M_S = 5\}$  sites. All energies are zero-point corrected, in kcal/mol and with reference to  $\text{Z}^+[\text{FeO}_2\text{NO}]^+$  with the appropriate amounts of  $\text{N}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{NO}$ , and  $\text{NO}_2$ . Energies of potential-energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PESs are in green. Black structures are on the PES with  $M_S = 5$ . Green structures are on the PES with  $M_S = 6$ . Structures in blue are on the PES with  $M_S = 7$ . Multiple numbers under a PES minimum structure correspond to different catalytic cycles (see Table 1).

−6.1 kcal/mol. Therefore, at temperatures where  $\text{N}_2\text{O}$  decomposition occurs, the dissociation of the NO dimer will be fast. Nitric oxide rapidly desorbs from  $\text{Z}^+[\text{FeO}]^+(\text{ON})$  sites. The spin-change barrier for desorption is  $E^\ddagger = 4.8$  kcal/mol, and the enthalpy of desorption is  $\Delta H_{\text{des}} = 3.3$  kcal/mol. Thus, if under reaction conditions a significant fraction of surface sites is present in the form of  $\text{Z}^+[\text{OFeO}]^+$ ,  $\text{Z}^+[\text{ONFeO}]^+$ ,  $\text{Z}^+[\text{OFeO}_2\text{N}]^+$ ,  $\text{Z}^+[\text{OFeO}_2\text{NO}]^+$ , and  $\text{Z}^+[\text{OFeOH}]^+$  sites, NO can be formed from nitrous oxide. The energetically most demanding step is the formation of an adsorbed NO dimer; once formed, NO production occurs readily.

Since  $\text{NO}_x$  (NO and  $\text{NO}_2$ ) rapidly reduces once-oxidized iron sites (e.g.,  $\text{Z}^+[\text{OFeO}]^+$ ,  $\text{Z}^+[\text{OFeOH}]^+$ ), NO production is not likely to occur in the presence of significant amounts of  $\text{NO}_x$ . Therefore, the only scenario in which NO produced from  $\text{N}_2\text{O}$



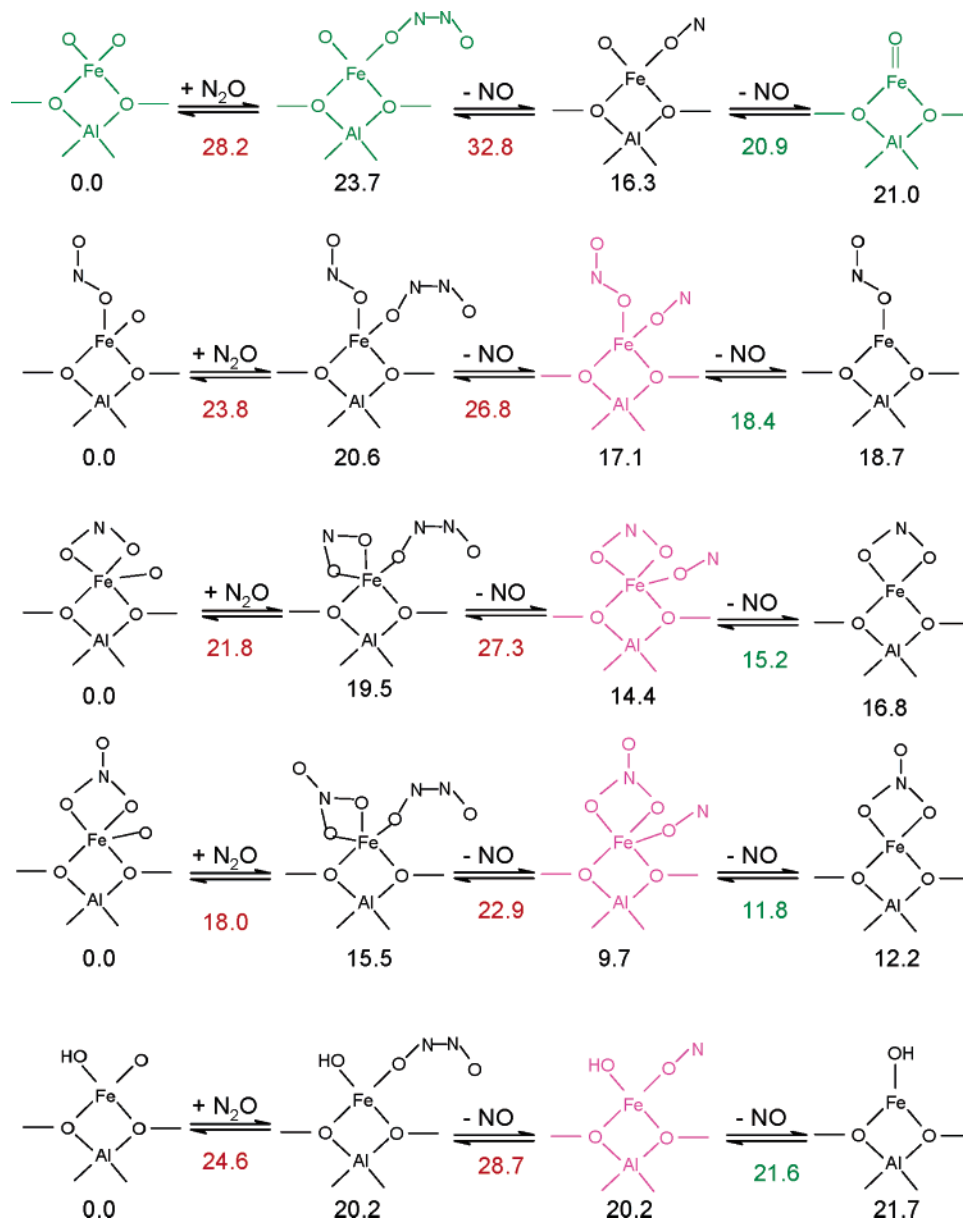
**Figure 12.** Alternative catalytic cycle of the  $\text{N}_2\text{O}$  dissociation on mononuclear  $\text{Z}^+[\text{FeO}_2\text{NO}]^+\{M_S = 5\}$  sites. All energies are zero-point corrected, in kcal/mol and with reference to  $\text{Z}^+[\text{FeO}_2\text{NO}]^+$  with the appropriate amounts of  $\text{N}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{NO}$ , and  $\text{NO}_2$ . Energies of potential-energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PESs are in green. Black structures are on the PES with  $M_S = 5$ . Structures in green are on the PES with  $M_S = 6$ .

could significantly influence the rate of  $\text{N}_2\text{O}$  decomposition on Fe-ZSM-5 would be at low temperatures, where most iron sites are poisoned by water (i.e., are in the form of  $\text{Z}^+[\text{Fe}(\text{OH})_2]^+$ ) and the activity of Fe-ZSM-5 for  $\text{N}_2\text{O}$  decomposition is low.

## Conclusions

Rate coefficients have been determined using a combination of density functional theory and transition-state theory for an ensemble of over 100 elementary reactions that might be involved in NO-promoted decomposition of  $\text{N}_2\text{O}$  on Fe-ZSM-5 at temperatures below 700 K. Under these conditions, highly active  $\text{Z}^+[\text{FeO}]^+$  sites react with small amounts of water vapor to form  $\text{Z}^+[\text{Fe}(\text{OH})_2]^+$  sites, which are inactive for  $\text{N}_2\text{O}$  decomposition. NO can react with such species to form  $\text{HNO}_2$  and  $\text{Z}^+[\text{FeOH}]^+$  sites. These newly formed sites are catalytically active for  $\text{N}_2\text{O}$  decomposition to  $\text{N}_2$  and  $\text{O}_2$ . The reaction pathway involves the formation and decomposition of  $\text{NO}_2$  and is illustrated in Figure 3. Since the activation barrier for the formation of  $\text{Z}^+[\text{FeOH}]^+$  sites is low (13.3 kcal/mol), the number of active iron sites for the  $\text{N}_2\text{O}$  decomposition increases significantly in the presence of small amounts of NO, as does the  $\text{N}_2\text{O}$  decomposition rate. At elevated temperatures, on the other hand, water desorbs from inactive  $\text{Z}^+[\text{Fe}(\text{OH})_2]^+$  sites, forming active  $\text{Z}^+[\text{FeO}]^+$  sites. No net gas species are formed in the process of  $\text{Z}^+[\text{FeOH}]^+$  formation, so that at high temperatures the entropy gain in splitting off an adsorbed water molecule from  $\text{Z}^+[\text{Fe}(\text{OH})_2]^+$  centers outweighs the higher energy barrier for the water desorption reaction.

While iron nitrite and nitrate species were also considered as possible intermediates in  $\text{N}_2\text{O}$  decomposition, these species



**Figure 13.** Possible pathways for the formation of nitric oxide. All energies are zero-point corrected, in kcal/mol and with reference to  $Z^{-}[\text{OFeO}]^{+}$ ,  $Z^{-}[\text{OFeONO}]^{+}$ ,  $Z^{-}[\text{OFeO}_2\text{N}]^{+}$ , or  $Z^{-}[\text{OFeO}_2\text{NO}]^{+}$ , or  $Z^{-}[\text{OFeOH}]^{+}$  with the appropriate amounts of N<sub>2</sub>O and NO. Energies of potential-energy minima are in black. Energies of transition states are in red. Energies of minima on the seam of two PESs are in green. Structures in magenta are on the PES with  $M_S = 4$ . Black structures are on the PES with  $M_S = 5$ . Green structures are on the PES with  $M_S = 6$ .

were not found to play a significant role in N<sub>2</sub>O decomposition over Fe-ZSM-5. H<sub>2</sub>O adsorbs on  $Z^{-}[\text{FeO}]^{+}$  species more strongly than NO, and as a result, small amounts of NO cannot displace H<sub>2</sub>O at low temperatures in order to form iron nitrite or nitrate species. At higher temperatures, both H<sub>2</sub>O and NO desorb. In general, iron nitrite and nitrate species are about as active for N<sub>2</sub>O decomposition as  $Z^{-}[\text{FeO}]^{+}$  and  $Z^{-}[\text{FeOH}]^{+}$  species. Consequently, large amounts of NO cannot increase the overall activity for N<sub>2</sub>O decomposition by forming iron nitrite and nitrate species.

Finally, the possibility of NO formation from N<sub>2</sub>O over Fe-ZSM-5 was investigated. Only at low temperatures, where most iron sites are poisoned by water and the overall catalyst activity for N<sub>2</sub>O decomposition is low, it is possible for NO produced from N<sub>2</sub>O to significantly influence the overall activity of Fe-ZSM-5 for N<sub>2</sub>O decomposition.

**Acknowledgment.** The authors would like to thank Dr. Jens Döbler and Dr. Bernd Kallies for support with the TURBO-MOLE V5.6/7 software package. Computations were carried

out at the “Norddeutscher Verbund für Hoch- und Höchstleistungsrechnen” (HLRN)<sup>82</sup> on an IBM p690-Cluster. This work was supported by the Methane Conversion Cooperative funded by BP, the “Fonds der chemischen Industrie”, and the Max-Buchner-Forschungsförderung.

## Appendix

All rate parameters computed from quantum chemical data are summarized in Table 1. Calculated enthalpies of reaction are averaged over 600–800 K. To estimate if low spin-inversion probabilities could result in a significant reduction of the rates of spin-surface crossing, thermally averaged Landau–Zener transition probabilities were calculated and are summarized in Table 2 for spin–orbit coupling energies of 395 and 825 J/mol for several temperatures. All spin-inversion transmission coefficients are larger than 0.05 (at 700 K). As a result, failure to correct reaction rates for spin-inversion probabilities smaller than 1 creates errors smaller than an error in the activation barrier of 4 kcal/mol (at 700 K).

**TABLE 1: Computed Rate Parameters for Elementary Steps in NO-Assisted Nitrous Oxide Dissociation over Fe-ZSM-5**

reaction	$E^\ddagger, \Delta H^b$ (kcal/mol)	constant	$T$ (K)		
			600	700	800
1. $Z^-[\text{FeO}]^+\{M=6\} + \text{NO(g)} \leftrightarrow Z^-[\text{FeONO}]^+\{M=5\}$	$\Delta H_1 = -32.9$ $E_1^\ddagger = 1.1$	$K_1, \text{bar}^{-1}$ $A_1, \text{s}^{-1} \text{bar}^{-1}$ $k_1, \text{s}^{-1} \text{bar}^{-1}$	$1.54 \times 10^4$ $1.43 \times 10^5$ $5.93 \times 10^4$	$2.87 \times 10^2$ $1.68 \times 10^5$ $7.91 \times 10^4$	$1.49 \times 10^1$ $1.98 \times 10^5$ $1.02 \times 10^5$
	$E_{-1}^\ddagger = 34.3$	$A_{-1}, \text{s}^{-1}$ $k_{-1}, \text{s}^{-1}$	$1.25 \times 10^{13}$ $3.85 \times 10^0$	$1.46 \times 10^{13}$ $2.76 \times 10^2$	$1.67 \times 10^{13}$ $6.90 \times 10^3$
2. $Z^-[\text{FeONO}]^+\{M=5\} \leftrightarrow Z^-[\text{Fe}]^+\{M=4\} + \text{NO}_2(\text{g})$	$\Delta H_2 = 66.0$ $E_2^\ddagger = 67.9$	$K_2, \text{bar}$ $A_2, \text{s}^{-1}$ $k_2, \text{s}^{-1}$	$5.56 \times 10^{-18}$ $1.25 \times 10^{13}$ $2.25 \times 10^{-12}$	$1.56 \times 10^{-14}$ $1.46 \times 10^{13}$ $9.01 \times 10^{-9}$	$5.81 \times 10^{-12}$ $1.67 \times 10^{13}$ $4.61 \times 10^{-6}$
	$E_{-2}^\ddagger = 0.0$	$A_{-2}, \text{s}^{-1} \text{bar}^{-1}$ $k_{-2}, \text{s}^{-1} \text{bar}^{-1}$	$4.05 \times 10^5$ $4.05 \times 10^5$	$5.76 \times 10^5$ $5.76 \times 10^5$	$7.93 \times 10^5$ $7.93 \times 10^5$
3. $Z^-[\text{FeO}]^+\{M=6\} + \text{NO(g)} \leftrightarrow Z^-[\text{FeO}_2\text{N}]^+\{M=5\}$	$\Delta H_3 = -37.8$ $E_3^\ddagger = 1.4$	$K_3, \text{bar}^{-1}$ $A_3, \text{s}^{-1} \text{bar}^{-1}$ $k_3, \text{s}^{-1} \text{bar}^{-1}$	$3.07 \times 10^5$ $6.19 \times 10^4$ $1.85 \times 10^4$	$3.18 \times 10^3$ $7.00 \times 10^4$ $2.49 \times 10^4$	$1.06 \times 10^2$ $7.98 \times 10^4$ $3.23 \times 10^4$
	$E_{-3}^\ddagger = 39.3$	$A_{-3}, \text{s}^{-1}$ $k_{-3}, \text{s}^{-1}$	$1.25 \times 10^{13}$ $6.04 \times 10^{-2}$	$1.46 \times 10^{13}$ $7.81 \times 10^0$	$1.67 \times 10^{13}$ $3.05 \times 10^2$
4. $Z^-[\text{FeO}_2\text{N}]^+\{M=5\} \leftrightarrow Z^-[\text{Fe}]^+\{M=4\} + \text{NO}_2(\text{g})$	$\Delta H_4 = 70.9$ $E_4^\ddagger = 72.5$	$K_4, \text{bar}$ $A_4, \text{s}^{-1}$ $k_4, \text{s}^{-1}$	$2.78 \times 10^{-19}$ $1.25 \times 10^{13}$ $4.88 \times 10^{-14}$	$1.41 \times 10^{-15}$ $1.46 \times 10^{13}$ $3.37 \times 10^{-10}$	$8.16 \times 10^{-13}$ $1.67 \times 10^{13}$ $2.60 \times 10^{-7}$
	$E_{-4}^\ddagger = 0.0$	$A_{-4}, \text{s}^{-1} \text{bar}^{-1}$ $k_{-4}, \text{s}^{-1} \text{bar}^{-1}$	$1.75 \times 10^5$ $1.75 \times 10^5$	$2.39 \times 10^5$ $2.39 \times 10^5$	$3.19 \times 10^5$ $3.19 \times 10^5$
5. $Z^-[\text{FeO}]^+\{M=6\} + \text{NO(g)} \leftrightarrow Z^-[\text{OFeNO}]^+\{M=5\}$	$\Delta H_5 = -13.6$ $E_5^\ddagger = 0.2$	$K_5, \text{bar}^{-1}$ $A_5, \text{s}^{-1} \text{bar}^{-1}$ $k_5, \text{s}^{-1} \text{bar}^{-1}$	$1.05 \times 10^{-2}$ $5.75 \times 10^5$ $4.98 \times 10^5$	$1.99 \times 10^{-3}$ $7.38 \times 10^5$ $6.51 \times 10^5$	$5.84 \times 10^{-4}$ $9.29 \times 10^5$ $8.34 \times 10^5$
	$E_{-5}^\ddagger = 14.9$	$A_{-5}, \text{s}^{-1}$ $k_{-5}, \text{s}^{-1}$	$1.25 \times 10^{13}$ $4.72 \times 10^7$	$1.46 \times 10^{13}$ $3.28 \times 10^8$	$1.67 \times 10^{13}$ $1.43 \times 10^9$
6. $Z^-[\text{FeO}_2]^+\{M=6\} + \text{NO(g)} \leftrightarrow Z^-[\text{FeOONO}]^+\{M=5\}$	$\Delta H_6 = -9.0$ $E_6^\ddagger = 6.3$	$K_6, \text{bar}^{-1}$ $A_6, \text{s}^{-1} \text{bar}^{-1}$ $k_6, \text{s}^{-1} \text{bar}^{-1}$	$3.90 \times 10^{-5}$ $2.25 \times 10^5$ $1.13 \times 10^3$	$1.28 \times 10^{-5}$ $2.59 \times 10^5$ $2.77 \times 10^3$	$5.71 \times 10^{-6}$ $3.00 \times 10^5$ $5.65 \times 10^3$
	$E_{-6}^\ddagger = 15.5$	$A_{-6}, \text{s}^{-1}$ $k_{-6}, \text{s}^{-1}$	$1.25 \times 10^{13}$ $2.89 \times 10^7$	$1.46 \times 10^{13}$ $2.15 \times 10^8$	$1.67 \times 10^{13}$ $9.89 \times 10^8$
7. $Z^-[\text{FeOONO}]^+\{M=5\} \leftrightarrow Z^-[\text{FeO}]^+\{M=6\} + \text{NO}_2(\text{g})$	$\Delta H_7 = 1.0$ $E_7^\ddagger = 2.5$	$K_7, \text{bar}$ $A_7, \text{s}^{-1}$ $k_7, \text{s}^{-1}$	$1.14 \times 10^7$ $1.25 \times 10^{13}$ $1.50 \times 10^{12}$	$1.32 \times 10^7$ $1.46 \times 10^{13}$ $2.37 \times 10^{12}$	$1.42 \times 10^7$ $1.67 \times 10^{13}$ $3.40 \times 10^{12}$
	$E_{-7}^\ddagger = 0.0$	$A_{-7}, \text{s}^{-1} \text{bar}^{-1}$ $k_{-7}, \text{s}^{-1} \text{bar}^{-1}$	$1.32 \times 10^5$ $1.32 \times 10^5$	$1.80 \times 10^5$ $1.80 \times 10^5$	$2.40 \times 10^5$ $2.40 \times 10^5$
8. $Z^-[\text{OFeO}]^+\{M=6\} + \text{NO(g)} \leftrightarrow Z^-[\text{OFeONO}]^+\{M=5\}$	$\Delta H_8 = -30.5$ $E_8^\ddagger = 3.7$	$K_8, \text{bar}^{-1}$ $A_8, \text{s}^{-1} \text{bar}^{-1}$ $k_8, \text{s}^{-1} \text{bar}^{-1}$	$6.27 \times 10^3$ $4.05 \times 10^5$ $1.86 \times 10^4$	$1.57 \times 10^2$ $4.84 \times 10^5$ $3.45 \times 10^4$	$1.01 \times 10^1$ $5.75 \times 10^5$ $5.70 \times 10^4$
	$E_{-8}^\ddagger = 34.6$	$A_{-8}, \text{s}^{-1}$ $k_{-8}, \text{s}^{-1}$	$1.25 \times 10^{13}$ $2.97 \times 10^0$	$1.46 \times 10^{13}$ $2.20 \times 10^2$	$1.67 \times 10^{13}$ $5.67 \times 10^3$
9. $Z^-[\text{OFeONO}]^+\{M=5\} \leftrightarrow Z^-[\text{FeO}]^+\{M=6\} + \text{NO}_2(\text{g})$	$\Delta H_9 = 14.4$ $E_9^\ddagger = 16.0$	$K_9, \text{bar}$ $A_9, \text{s}^{-1}$ $k_9, \text{s}^{-1}$	$1.88 \times 10^2$ $1.25 \times 10^{13}$ $1.84 \times 10^7$	$1.09 \times 10^3$ $1.46 \times 10^{13}$ $1.46 \times 10^8$	$3.89 \times 10^3$ $1.67 \times 10^{13}$ $7.04 \times 10^8$
	$E_{-9}^\ddagger = 0.0$	$A_{-9}, \text{s}^{-1} \text{bar}^{-1}$ $k_{-9}, \text{s}^{-1} \text{bar}^{-1}$	$9.78 \times 10^4$ $9.78 \times 10^4$	$1.35 \times 10^5$ $1.35 \times 10^5$	$1.81 \times 10^5$ $1.81 \times 10^5$
10. $Z^-[\text{OFeO}]^+\{M=6\} + \text{NO(g)} \leftrightarrow Z^-[\text{OFeO}_2\text{N}]^+\{M=5\}$	$\Delta H_{10} = -34.0$ $E_{10}^\ddagger = 4.6$	$K_{10}, \text{bar}^{-1}$ $A_{10}, \text{s}^{-1} \text{bar}^{-1}$ $k_{10}, \text{s}^{-1} \text{bar}^{-1}$	$3.60 \times 10^3$ $2.61 \times 10^4$ $5.48 \times 10^2$	$5.96 \times 10^1$ $2.82 \times 10^4$ $1.03 \times 10^3$	$2.80 \times 10^0$ $3.10 \times 10^4$ $1.71 \times 10^3$
	$E_{-10} = 38.2$	$A_{-10}, \text{s}^{-1}$ $k_{-10}, \text{s}^{-1}$	$1.25 \times 10^{13}$ $1.52 \times 10^{-1}$	$1.46 \times 10^{13}$ $1.73 \times 10^1$	$1.67 \times 10^{13}$ $6.11 \times 10^2$
11. $Z^-[\text{OFeO}_2\text{N}]^+\{M=5\} \leftrightarrow Z^-[\text{FeO}]^+\{M=6\} + \text{NO}_2(\text{g})$	$\Delta H_{11} = 17.9$ $E_{11}^\ddagger = 19.2$	$K_{11}, \text{bar}$ $A_{11}, \text{s}^{-1}$ $k_{11}, \text{s}^{-1}$	$3.27 \times 10^2$ $1.25 \times 10^{13}$ $1.27 \times 10^6$	$2.85 \times 10^3$ $1.46 \times 10^{13}$ $1.48 \times 10^7$	$1.40 \times 10^4$ $1.67 \times 10^{13}$ $9.51 \times 10^7$
	$E_{-11}^\ddagger = 0.6$	$A_{-11}, \text{s}^{-1} \text{bar}^{-1}$ $k_{-11}, \text{s}^{-1} \text{bar}^{-1}$	$6.31 \times 10^3$ $3.89 \times 10^3$	$7.86 \times 10^3$ $5.19 \times 10^3$	$9.77 \times 10^3$ $6.80 \times 10^3$
12. $Z^-[\text{OFeO}]^+\{M=6\} + \text{NO(g)} \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+\{M=5\}$	$\Delta H_{12} = -58.3$ $E_{12}^\ddagger = 5.8$	$K_{12}, \text{bar}^{-1}$ $A_{12}, \text{s}^{-1} \text{bar}^{-1}$ $k_{12}, \text{s}^{-1} \text{bar}^{-1}$	$1.89 \times 10^{12}$ $2.87 \times 10^4$ $2.18 \times 10^2$	$1.70 \times 10^9$ $2.93 \times 10^4$ $4.47 \times 10^2$	$8.95 \times 10^6$ $3.07 \times 10^4$ $7.90 \times 10^2$
	$E_{-12}^\ddagger = 63.2$	$A_{-12}, \text{s}^{-1}$ $k_{-12}, \text{s}^{-1}$	$1.25 \times 10^{13}$ $1.15 \times 10^{-10}$	$1.46 \times 10^{13}$ $2.63 \times 10^{-7}$	$1.67 \times 10^{13}$ $8.83 \times 10^{-5}$
13. $Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} \leftrightarrow Z^-[\text{FeO}]^+\{M=6\} + \text{NO}_2(\text{g})$	$\Delta H_{13} = 42.2$ $E_{13}^\ddagger = 44.2$	$K_{13}, \text{bar}$ $A_{13}, \text{s}^{-1}$ $k_{13}, \text{s}^{-1}$	$6.23 \times 10^{-7}$ $1.25 \times 10^{13}$ $9.67 \times 10^{-4}$	$9.99 \times 10^{-5}$ $1.46 \times 10^{13}$ $2.26 \times 10^{-1}$	$4.37 \times 10^{-3}$ $1.67 \times 10^{13}$ $1.37 \times 10^1$
	$E_{-13}^\ddagger = 1.8$	$A_{-13}, \text{s}^{-1} \text{bar}^{-1}$ $k_{-13}, \text{s}^{-1} \text{bar}^{-1}$	$6.94 \times 10^3$ $1.55 \times 10^3$	$8.16 \times 10^3$ $2.26 \times 10^3$	$9.66 \times 10^3$ $3.14 \times 10^3$
14. $Z^-[\text{FeONO}]^+\{M=5\} + \text{N}_2\text{O(g)} \leftrightarrow Z^-[\text{FeONO}]^+(\text{N}_2\text{O})\{M=5\}$	$\Delta H_{14} = -3.1$ $E_{14}^\ddagger = 0.0$	$K_{14}, \text{bar}^{-1}$ $A_{14}, \text{s}^{-1} \text{bar}^{-1}$ $k_{14}, \text{s}^{-1} \text{bar}^{-1}$	$4.87 \times 10^{-5}$ $1.17 \times 10^7$ $1.17 \times 10^7$	$3.28 \times 10^{-5}$ $1.61 \times 10^7$ $1.61 \times 10^7$	$2.50 \times 10^{-5}$ $2.15 \times 10^7$ $2.15 \times 10^7$
	$E_{-14}^\ddagger = 4.7$	$A_{-14}, \text{s}^{-1}$ $k_{-14}, \text{s}^{-1}$	$1.25 \times 10^{13}$ $2.39 \times 10^{11}$	$1.46 \times 10^{13}$ $4.91 \times 10^{11}$	$1.67 \times 10^{13}$ $8.58 \times 10^{11}$



TABLE 1: (Continued)

reaction	$E^\ddagger, {}^a \Delta H^b$ (kcal/mol)	constant	T (K)		
			600	700	800
15. Z <sup>-</sup> [FeONO] <sup>+</sup> {M = 5} + N <sub>2</sub> O(g) ↔ Z <sup>-</sup> [FeONO] <sup>+</sup> (ON <sub>2</sub> ) {M = 5}	$\Delta H_{15} = -1.5$	$K_{15}, \text{bar}^{-1}$	$5.00 \times 10^{-5}$	$4.09 \times 10^{-5}$	$3.61 \times 10^{-5}$
	$E_{15}^\ddagger = 0.0$	$A_{15}, \text{s}^{-1} \text{bar}^{-1}$	$3.99 \times 10^7$	$5.64 \times 10^7$	$7.65 \times 10^7$
		$k_{15}, \text{s}^{-1} \text{bar}^{-1}$	$3.99 \times 10^7$	$5.64 \times 10^7$	$7.65 \times 10^7$
	$E_{-15}^\ddagger = 3.3$	$A_{-15}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
16. Z <sup>-</sup> [FeONO] <sup>+</sup> (ON <sub>2</sub> ) {M = 5} ↔ Z <sup>-</sup> [OFeONO] <sup>+</sup> {M = 5} + N <sub>2</sub> (g)	$\Delta H_{16} = -12.7$	$K_{16}, \text{bar}$	$5.21 \times 10^9$	$1.16 \times 10^9$	$3.66 \times 10^8$
	$E_{16}^\ddagger = 24.8$	$A_{16}, \text{s}^{-1}$	$3.39 \times 10^{13}$	$3.97 \times 10^{13}$	$4.52 \times 10^{13}$
		$k_{16}, \text{s}^{-1}$	$3.08 \times 10^4$	$7.07 \times 10^5$	$7.49 \times 10^6$
	$E_{-16}^\ddagger = 36.8$	$A_{-16}, \text{s}^{-1} \text{bar}^{-1}$	$1.58 \times 10^8$	$1.97 \times 10^8$	$2.40 \times 10^8$
17. Z <sup>-</sup> [OFeONO] <sup>+</sup> {M = 5} + N <sub>2</sub> O(g) ↔ Z <sup>-</sup> [OFeONO] <sup>+</sup> (N <sub>2</sub> O) {M = 5}	$\Delta H_{17} = -0.5$	$K_{17}, \text{bar}^{-1}$	$1.84 \times 10^{-6}$	$1.71 \times 10^{-6}$	$1.66 \times 10^{-6}$
	$E_{17}^\ddagger = 0.0$	$A_{17}, \text{s}^{-1} \text{bar}^{-1}$	$5.24 \times 10^6$	$7.03 \times 10^6$	$9.15 \times 10^6$
		$k_{17}, \text{s}^{-1} \text{bar}^{-1}$	$5.24 \times 10^6$	$7.03 \times 10^6$	$9.15 \times 10^6$
	$E_{-17}^\ddagger = 1.8$	$A_{-17}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
18. Z <sup>-</sup> [OFeONO] <sup>+</sup> {M = 5} + N <sub>2</sub> O(g) ↔ Z <sup>-</sup> [OFeONO] <sup>+</sup> (ON <sub>2</sub> ) {M = 5}	$\Delta H_{18} = -1.5$	$K_{18}, \text{bar}^{-1}$	$1.41 \times 10^{-6}$	$1.16 \times 10^{-6}$	$1.03 \times 10^{-6}$
	$E_{18}^\ddagger = 0.0$	$A_{18}, \text{s}^{-1} \text{bar}^{-1}$	$1.72 \times 10^6$	$2.30 \times 10^6$	$3.00 \times 10^6$
		$k_{18}, \text{s}^{-1} \text{bar}^{-1}$	$1.72 \times 10^6$	$2.30 \times 10^6$	$3.00 \times 10^6$
	$E_{-18}^\ddagger = 2.8$	$A_{-18}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
19. Z <sup>-</sup> [OFeONO] <sup>+</sup> (ON <sub>2</sub> ) {M = 5} ↔ Z <sup>-</sup> [O <sub>2</sub> FeONO] <sup>+</sup> {M = 5} + N <sub>2</sub> (g)	$\Delta H_{19} = -20.7$	$K_{19}, \text{bar}$	$2.79 \times 10^{15}$	$2.35 \times 10^{14}$	$3.60 \times 10^{13}$
	$E_{19}^\ddagger = 44.9$	$A_{19}, \text{s}^{-1}$	$1.80 \times 10^{14}$	$2.16 \times 10^{14}$	$2.51 \times 10^{14}$
		$k_{19}, \text{s}^{-1}$	$7.76 \times 10^{-3}$	$2.03 \times 10^0$	$1.33 \times 10^2$
	$E_{-19}^\ddagger = 66.2$	$A_{-19}, \text{s}^{-1} \text{bar}^{-1}$	$3.64 \times 10^6$	$4.05 \times 10^6$	$4.53 \times 10^6$
20. Z <sup>-</sup> [O <sub>2</sub> FeONO] <sup>+</sup> {M = 5} ↔ Z <sup>-</sup> [O <sub>2</sub> FeONO] <sup>+</sup> {M = 7}	$\Delta H_{20} = -5.4$	$K_{20}, -$	$4.83 \times 10^1$	$2.52 \times 10^1$	$1.54 \times 10^1$
	$E_{20}^\ddagger = 7.1$	$A_{20}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{20}, \text{s}^{-1}$	$3.31 \times 10^{10}$	$9.02 \times 10^{10}$	$1.95 \times 10^{11}$
	$E_{-20}^\ddagger = 12.4$	$A_{-20}, \text{s}^{-1}$	$2.22 \times 10^{13}$	$2.64 \times 10^{13}$	$3.05 \times 10^{13}$
21. Z <sup>-</sup> [O <sub>2</sub> FeONO] <sup>+</sup> {M = 7} ↔ Z <sup>-</sup> [FeONO] <sup>+</sup> {M = 5} + O <sub>2</sub> (g)	$\Delta H_{21} = 3.3$	$K_{21}, \text{bar}$	$1.35 \times 10^5$	$2.05 \times 10^5$	$2.72 \times 10^5$
	$E_{21}^\ddagger = 6.0$	$A_{21}, \text{s}^{-1}$	$1.11 \times 10^{14}$	$1.22 \times 10^{14}$	$1.30 \times 10^{14}$
		$k_{21}, \text{s}^{-1}$	$7.12 \times 10^{11}$	$1.60 \times 10^{12}$	$2.94 \times 10^{12}$
	$E_{-21}^\ddagger = 1.5$	$A_{-21}, \text{s}^{-1} \text{bar}^{-1}$	$1.92 \times 10^7$	$2.37 \times 10^7$	$2.85 \times 10^7$
22. Z <sup>-</sup> [O <sub>2</sub> FeONO] <sup>+</sup> {M = 7} ↔ Z <sup>-</sup> [FeO <sub>2</sub> ] <sup>+</sup> {M = 6} + NO <sub>2</sub> (g)	$\Delta H_{22} = 17.3$	$K_{22}, \text{bar}$	$1.68 \times 10^0$	$1.37 \times 10^1$	$6.40 \times 10^1$
	$E_{22}^\ddagger = 19.4$	$A_{22}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{22}, \text{s}^{-1}$	$1.07 \times 10^6$	$1.28 \times 10^7$	$8.34 \times 10^7$
	$E_{-22}^\ddagger = 0.0$	$A_{-22}, \text{s}^{-1} \text{bar}^{-1}$	$6.38 \times 10^5$	$9.29 \times 10^5$	$1.30 \times 10^6$
23. Z <sup>-</sup> [OFeONO] <sup>+</sup> {M = 5} + NO(g) ↔ Z <sup>-</sup> [Fe(ONO) <sub>2</sub> ] <sup>+</sup> {M = 6}	$\Delta H_{23} = -31.7$	$K_{23}, \text{bar}^{-1}$	$1.31 \times 10^6$	$2.83 \times 10^4$	$1.64 \times 10^3$
	$E_{23}^\ddagger = 0.0$	$A_{23}, \text{s}^{-1} \text{bar}^{-1}$	$1.73 \times 10^7$	$2.24 \times 10^7$	$2.84 \times 10^7$
		$k_{23}, \text{s}^{-1} \text{bar}^{-1}$	$1.73 \times 10^7$	$2.24 \times 10^7$	$2.84 \times 10^7$
	$E_{-23}^\ddagger = 32.9$	$A_{-23}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
24. Z <sup>-</sup> [Fe(ONO) <sub>2</sub> ] <sup>+</sup> {M = 6} ↔ Z <sup>-</sup> [FeONO] <sup>+</sup> {M = 5} + NO <sub>2</sub> (g)	$\Delta H_{24} = 13.2$	$K_{24}, \text{bar}$	$2.20 \times 10^0$	$1.10 \times 10^1$	$3.53 \times 10^1$
	$E_{24}^\ddagger = 15.6$	$A_{24}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{24}, \text{s}^{-1}$	$2.60 \times 10^7$	$1.97 \times 10^8$	$9.13 \times 10^8$
	$E_{-24}^\ddagger = 0.0$	$A_{-24}, \text{s}^{-1} \text{bar}^{-1}$	$1.18 \times 10^7$	$1.79 \times 10^7$	$2.59 \times 10^7$
25. Z <sup>-</sup> [Fe(ONO) <sub>2</sub> ] <sup>+</sup> {M = 6} ↔ Z <sup>-</sup> [ONOF <sub>2</sub> O <sub>2</sub> N] <sup>+</sup> {M = 6}	$\Delta H_{25} = -4.7$	$K_{25}, -$	$1.39 \times 10^0$	$7.98 \times 10^{-1}$	$5.24 \times 10^{-1}$
	$E_{25}^\ddagger = 1.3$	$A_{25}, \text{s}^{-1}$	$8.12 \times 10^{11}$	$8.05 \times 10^{11}$	$7.99 \times 10^{11}$
		$k_{25}, \text{s}^{-1}$	$2.80 \times 10^{11}$	$3.23 \times 10^{11}$	$3.60 \times 10^{11}$
	$E_{-25}^\ddagger = 5.3$	$A_{-25}, \text{s}^{-1}$	$1.65 \times 10^{13}$	$1.77 \times 10^{13}$	$1.87 \times 10^{13}$
26. Z <sup>-</sup> [OFeONO] <sup>+</sup> {M = 5} ↔ Z <sup>-</sup> [FeO <sub>2</sub> NO] <sup>+</sup> {M = 5}	$\Delta H_{26} = -27.8$	$K_{26}, -$	$3.02 \times 10^8$	$1.09 \times 10^7$	$8.89 \times 10^5$
	$E_{26}^\ddagger = 10.0$	$A_{26}, \text{s}^{-1}$	$3.51 \times 10^{12}$	$3.69 \times 10^{12}$	$3.83 \times 10^{12}$
		$k_{26}, \text{s}^{-1}$	$7.69 \times 10^8$	$2.69 \times 10^9$	$6.90 \times 10^9$
	$E_{-26}^\ddagger = 36.5$	$A_{-26}, \text{s}^{-1}$	$4.95 \times 10^{13}$	$6.08 \times 10^{13}$	$7.19 \times 10^{13}$
27. Z <sup>-</sup> [FeONO] <sup>+</sup> {M = 5} ↔ Z <sup>-</sup> [FeO <sub>2</sub> N] <sup>+</sup> {M = 5}	$\Delta H_{27} = -4.9$	$K_{27}, -$	$2.00 \times 10^1$	$1.11 \times 10^1$	$7.12 \times 10^0$
	$E_{27}^\ddagger = 3.0$	$A_{27}, \text{s}^{-1}$	$2.84 \times 10^{13}$	$2.97 \times 10^{13}$	$3.07 \times 10^{13}$
		$k_{27}, \text{s}^{-1}$	$2.36 \times 10^{12}$	$3.52 \times 10^{12}$	$4.75 \times 10^{12}$
	$E_{-27}^\ddagger = 7.5$	$A_{-27}, \text{s}^{-1}$	$6.57 \times 10^{13}$	$7.14 \times 10^{13}$	$7.62 \times 10^{13}$
28. Z <sup>-</sup> [FeO <sub>2</sub> N] <sup>+</sup> {M = 5} + N <sub>2</sub> O(g) ↔ Z <sup>-</sup> [FeO <sub>2</sub> N] <sup>+</sup> (N <sub>2</sub> O) {M = 5}	$\Delta H_{28} = -4.2$	$K_{28}, \text{bar}^{-1}$	$3.19 \times 10^{-5}$	$1.89 \times 10^{-5}$	$1.31 \times 10^{-5}$
	$E_{28}^\ddagger = 0.0$	$A_{28}, \text{s}^{-1} \text{bar}^{-1}$	$3.41 \times 10^6$	$4.66 \times 10^6$	$6.15 \times 10^6$
		$k_{28}, \text{s}^{-1} \text{bar}^{-1}$	$3.41 \times 10^6$	$4.66 \times 10^6$	$6.15 \times 10^6$
	$E_{-28}^\ddagger = 5.7$	$A_{-28}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{-28}, \text{s}^{-1}$	$1.07 \times 10^{11}$	$2.47 \times 10^{11}$	$4.69 \times 10^{11}$

TABLE 1: (Continued)

reaction	$E^\ddagger, {}^a \Delta H^\ddagger$ (kcal/mol)	constant	$T$ (K)		
			600	700	800
29. $Z^-[\text{FeO}_2\text{N}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeO}_2\text{N}]^+(\text{ON}_2)\{M=5\}$	$\Delta H_{29} = -2.5$	$K_{29}, \text{bar}^{-1}$	$4.22 \times 10^{-5}$	$3.06 \times 10^{-5}$	$2.47 \times 10^{-5}$
	$E_{29}^\ddagger = 0.0$	$A_{29}, \text{s}^{-1} \text{bar}^{-1}$	$1.60 \times 10^7$	$2.23 \times 10^7$	$2.99 \times 10^7$
		$k_{29}, \text{s}^{-1} \text{bar}^{-1}$	$1.60 \times 10^7$	$2.23 \times 10^7$	$2.99 \times 10^7$
30. $Z^-[\text{FeO}_2\text{N}]^+(\text{ON}_2)\{M=5\} \leftrightarrow Z^-[\text{OFeO}_2\text{N}]^+\{M=5\} + \text{N}_2(\text{g})$	$\Delta H_{30} = -10.2$	$K_{30}, \text{bar}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
	$E_{30}^\ddagger = 25.4$	$A_{30}, \text{s}^{-1}$	$3.79 \times 10^{11}$	$7.28 \times 10^{11}$	$1.21 \times 10^{12}$
		$k_{30}, \text{s}^{-1}$	$1.78 \times 10^8$	$5.30 \times 10^7$	$2.09 \times 10^7$
31. $Z^-[\text{OFeO}_2\text{N}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{OFeO}_2\text{N}]^+(\text{N}_2\text{O})\{M=5\}$	$\Delta H_{31} = 1.6$	$K_{31}, \text{bar}^{-1}$	$1.42 \times 10^{13}$	$1.63 \times 10^{13}$	$1.83 \times 10^{13}$
	$E_{31}^\ddagger = 0.0$	$A_{31}, \text{s}^{-1} \text{bar}^{-1}$	$7.73 \times 10^3$	$1.87 \times 10^5$	$2.07 \times 10^6$
		$k_{31}, \text{s}^{-1} \text{bar}^{-1}$	$1.77 \times 10^8$	$2.27 \times 10^8$	$2.83 \times 10^8$
32. $Z^-[\text{OFeO}_2\text{N}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{OFeO}_2\text{N}]^+(\text{ON}_2)\{M=5\}$	$\Delta H_{32} = -2.7$	$K_{32}, \text{bar}^{-1}$	$4.35 \times 10^{-5}$	$3.54 \times 10^{-3}$	$9.88 \times 10^{-2}$
	$E_{32}^\ddagger = 0.0$	$A_{32}, \text{s}^{-1} \text{bar}^{-1}$	$1.74 \times 10^{-4}$	$2.07 \times 10^{-4}$	$2.42 \times 10^{-4}$
		$k_{32}, \text{s}^{-1} \text{bar}^{-1}$	$1.64 \times 10^9$	$2.37 \times 10^9$	$3.27 \times 10^9$
33. $Z^-[\text{OFeO}_2\text{N}]^+(\text{ON}_2)\{M=5\} \leftrightarrow Z^-[\text{O}_2\text{FeO}_2\text{N}]^+\{M=5\} + \text{N}_2(\text{g})$	$\Delta H_{33} = -16.1$	$K_{33}, \text{bar}$	$1.64 \times 10^9$	$2.37 \times 10^9$	$3.27 \times 10^9$
	$E_{33}^\ddagger = 45.2$	$A_{33}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{33}, \text{s}^{-1}$	$9.45 \times 10^{12}$	$1.15 \times 10^{13}$	$1.35 \times 10^{13}$
34. $Z^-[\text{O}_2\text{FeO}_2\text{N}]^+\{M=5\} \leftrightarrow Z^-[\text{O}_2\text{FeO}_2\text{N}]^+\{M=7\}$	$\Delta H_{34} = -7.7$	$K_{34}, \text{bar}^{-1}$	$1.45 \times 10^{-5}$	$1.03 \times 10^{-5}$	$8.17 \times 10^{-6}$
	$E_{34}^\ddagger = 0.1$	$A_{34}, \text{s}^{-1}$	$4.90 \times 10^6$	$6.79 \times 10^6$	$9.08 \times 10^6$
		$k_{34}, \text{s}^{-1}$	$4.90 \times 10^6$	$6.79 \times 10^6$	$9.08 \times 10^6$
35. $Z^-[\text{O}_2\text{FeO}_2\text{N}]^+\{M=7\} \leftrightarrow Z^-[\text{FeO}_2\text{N}]^+\{M=5\} + \text{O}_2(\text{g})$	$\Delta H_{35} = 0.7$	$K_{35}, \text{bar}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
	$E_{35}^\ddagger = 3.0$	$A_{35}, \text{s}^{-1} \text{bar}^{-1}$	$3.38 \times 10^{11}$	$6.60 \times 10^{11}$	$1.11 \times 10^{12}$
		$k_{35}, \text{s}^{-1} \text{bar}^{-1}$	$3.81 \times 10^{13}$	$5.61 \times 10^{12}$	$1.31 \times 10^{12}$
36. $Z^-[\text{O}_2\text{FeO}_2\text{N}]^+\{M=7\} \leftrightarrow Z^-[\text{FeO}_2\text{N}]^+\{M=6\} + \text{NO}_2(\text{g})$	$\Delta H_{36} = 19.6$	$K_{36}, \text{bar}$	$1.59 \times 10^{14}$	$1.89 \times 10^{14}$	$2.18 \times 10^{14}$
	$E_{36}^\ddagger = 21.2$	$A_{36}, \text{s}^{-1}$	$5.15 \times 10^{-3}$	$1.39 \times 10^0$	$9.36 \times 10^1$
		$k_{36}, \text{s}^{-1}$	$4.58 \times 10^6$	$5.07 \times 10^6$	$5.65 \times 10^6$
37. $Z^-[\text{OFeO}_2\text{N}]^+\{M=5\} + \text{NO}(\text{g}) \leftrightarrow Z^-[\text{ONFeO}_2\text{N}]^+\{M=6\}$	$\Delta H_{37} = -32.9$	$K_{37}, \text{bar}^{-1}$	$1.35 \times 10^{-16}$	$2.48 \times 10^{-13}$	$7.15 \times 10^{-11}$
	$E_{37}^\ddagger = 0.0$	$A_{37}, \text{s}^{-1} \text{bar}^{-1}$	$5.97 \times 10^2$	$2.37 \times 10^2$	$1.19 \times 10^2$
		$k_{37}, \text{s}^{-1} \text{bar}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
38. $Z^-[\text{ONFeO}_2\text{N}]^+\{M=6\} \leftrightarrow Z^-[\text{FeO}_2\text{N}]^+\{M=5\} + \text{NO}_2(\text{g})$	$\Delta H_{38} = 12.9$	$K_{38}, \text{bar}$	$1.11 \times 10^{13}$	$1.32 \times 10^{13}$	$1.52 \times 10^{13}$
	$E_{38}^\ddagger = 15.0$	$A_{38}, \text{s}^{-1}$	$1.31 \times 10^{13}$	$1.53 \times 10^{13}$	$1.76 \times 10^{13}$
		$k_{38}, \text{s}^{-1}$	$1.86 \times 10^{10}$	$5.55 \times 10^{10}$	$1.28 \times 10^{11}$
39. $Z^-[\text{ONFeO}_2\text{N}]^+\{M=6\} \leftrightarrow Z^-[\text{Fe}(\text{O}_2\text{N})_2]^+\{M=6\}$	$\Delta H_{39} = -0.6$	$K_{39}, \text{bar}^{-1}$	$2.70 \times 10^6$	$2.99 \times 10^6$	$3.14 \times 10^6$
	$E_{39}^\ddagger = 2.8$	$A_{39}, \text{s}^{-1}$	$1.30 \times 10^{13}$	$1.38 \times 10^{13}$	$1.44 \times 10^{13}$
		$k_{39}, \text{s}^{-1}$	$1.08 \times 10^{12}$	$1.64 \times 10^{12}$	$2.23 \times 10^{12}$
40. $Z^-[\text{OFeO}_2\text{N}]^+\{M=5\} \leftrightarrow Z^-[\text{OFeONO}]^+\{M=5\}$	$\Delta H_{40} = 3.5$	$K_{40}, \text{bar}^{-1}$	$1.13 \times 10^6$	$1.33 \times 10^6$	$1.55 \times 10^6$
	$E_{40}^\ddagger = 5.6$	$A_{40}, \text{s}^{-1}$	$4.01 \times 10^5$	$5.47 \times 10^5$	$7.11 \times 10^5$
		$k_{40}, \text{s}^{-1}$	$1.68 \times 10^0$	$1.81 \times 10^1$	$1.04 \times 10^2$
41. $Z^-[\text{FeO}_2\text{N}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} + \text{N}_2(\text{g})$	$\Delta H_{41} = -37.1$	$K_{41}, \text{bar}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
	$E_{41}^\ddagger = 49.6$	$A_{41}, \text{s}^{-1}$	$2.34 \times 10^5$	$3.47 \times 10^6$	$2.67 \times 10^7$
		$k_{41}, \text{s}^{-1}$	$1.39 \times 10^5$	$1.92 \times 10^5$	$2.57 \times 10^5$
42. $Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+(\text{N}_2\text{O})\{M=5\}$	$\Delta H_{42} = -1.8$	$K_{42}, \text{bar}^{-1}$	$3.19 \times 10^6$	$5.94 \times 10^4$	$3.08 \times 10^3$
	$E_{42}^\ddagger = 0.0$	$A_{42}, \text{s}^{-1} \text{bar}^{-1}$	$1.32 \times 10^7$	$1.74 \times 10^7$	$2.24 \times 10^7$
		$k_{42}, \text{s}^{-1} \text{bar}^{-1}$	$1.32 \times 10^7$	$1.74 \times 10^7$	$2.24 \times 10^7$
43. $Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+(\text{N}_2\text{O})\{M=5\}$	$\Delta H_{43} = -37.1$	$K_{43}, \text{bar}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
	$E_{43}^\ddagger = 49.6$	$A_{43}, \text{s}^{-1}$	$4.14 \times 10^0$	$2.93 \times 10^2$	$7.28 \times 10^3$
		$k_{43}, \text{s}^{-1}$	$3.15 \times 10^1$	$1.53 \times 10^2$	$4.80 \times 10^2$
44. $Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+(\text{N}_2\text{O})\{M=5\}$	$\Delta H_{44} = -37.1$	$K_{44}, \text{bar}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
	$E_{44}^\ddagger = 49.6$	$A_{44}, \text{s}^{-1}$	$4.24 \times 10^7$	$2.99 \times 10^8$	$1.32 \times 10^9$
		$k_{44}, \text{s}^{-1}$	$1.35 \times 10^6$	$1.96 \times 10^6$	$2.75 \times 10^6$
45. $Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+(\text{N}_2\text{O})\{M=5\}$	$\Delta H_{45} = -0.6$	$K_{45}, \text{bar}^{-1}$	$1.35 \times 10^6$	$1.96 \times 10^6$	$2.75 \times 10^6$
	$E_{45}^\ddagger = 2.8$	$A_{45}, \text{s}^{-1}$	$4.14 \times 10^{-2}$	$3.87 \times 10^{-2}$	$3.67 \times 10^{-2}$
		$k_{45}, \text{s}^{-1}$	$3.65 \times 10^{11}$	$3.56 \times 10^{11}$	$3.50 \times 10^{11}$
46. $Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+(\text{N}_2\text{O})\{M=5\}$	$\Delta H_{46} = -0.6$	$K_{46}, \text{bar}^{-1}$	$3.46 \times 10^{10}$	$4.72 \times 10^{10}$	$5.97 \times 10^{10}$
	$E_{46}^\ddagger = 2.7$	$A_{46}, \text{s}^{-1}$	$8.13 \times 10^{12}$	$8.58 \times 10^{12}$	$8.96 \times 10^{12}$
		$k_{46}, \text{s}^{-1}$	$8.35 \times 10^{11}$	$1.22 \times 10^{12}$	$1.63 \times 10^{12}$
47. $Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+(\text{N}_2\text{O})\{M=5\}$	$\Delta H_{47} = 3.5$	$K_{47}, \text{bar}^{-1}$	$1.74 \times 10^0$	$2.63 \times 10^0$	$3.59 \times 10^0$
	$E_{47}^\ddagger = 5.6$	$A_{47}, \text{s}^{-1}$	$3.73 \times 10^{13}$	$4.20 \times 10^{13}$	$4.61 \times 10^{13}$
		$k_{47}, \text{s}^{-1}$	$3.50 \times 10^{11}$	$7.68 \times 10^{11}$	$1.39 \times 10^{12}$
48. $Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+(\text{N}_2\text{O})\{M=5\}$	$\Delta H_{48} = 3.5$	$K_{48}, \text{bar}^{-1}$	$2.41 \times 10^{12}$	$2.45 \times 10^{12}$	$2.49 \times 10^{12}$
	$E_{48}^\ddagger = 5.6$	$A_{48}, \text{s}^{-1}$	$2.01 \times 10^{11}$	$2.92 \times 10^{11}$	$3.86 \times 10^{11}$
		$k_{48}, \text{s}^{-1}$	$2.01 \times 10^{11}$	$2.92 \times 10^{11}$	$3.86 \times 10^{11}$
49. $Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+(\text{N}_2\text{O})\{M=5\}$	$\Delta H_{49} = -37.1$	$K_{49}, \text{bar}^{-1}$	$3.94 \times 10^{12}$	$4.63 \times 10^{10}$	$1.65 \times 10^9$
	$E_{49}^\ddagger = 49.6$	$A_{49}, \text{s}^{-1}$	$2.53 \times 10^8$	$3.44 \times 10^8$	$4.50 \times 10^8$
		$k_{49}, \text{s}^{-1}$	$2.11 \times 10^{-10}$	$1.10 \times 10^{-7}$	$1.24 \times 10^{-5}$
50. $Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+(\text{N}_2\text{O})\{M=5\}$	$\Delta H_{50} = -37.1$	$K_{50}, \text{bar}^{-1}$	$2.25 \times 10^9$	$3.03 \times 10^9$	$3.92 \times 10^9$
	$E_{50}^\ddagger = 49.6$	$A_{50}, \text{s}^{-1}$	$5.35 \times 10^{-23}$	$2.37 \times 10^{-18}$	$7.51 \times 10^{-15}$
		$k_{50}, \text{s}^{-1}$	$2.61 \times 10^{-5}$	$2.05 \times 10^{-5}$	$1.76 \times 10^{-5}$
51. $Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+(\text{N}_2\text{O})\{M=5\}$	$\Delta H_{51} = -1.8$	$K_{51}, \text{bar}^{-1}$	$1.82 \times 10^7$	$2.52 \times 10^7$	$3.37 \times 10^7$
	$E_{51}^\ddagger = 0.0$	$A_{51}, \text{s}^{-1} \text{bar}^{-1}$	$1.82 \times 10^7$	$2.52 \times 10^7$	$3.37 \times 10^7$
		$k_{51}, \text{s}^{-1} \text{bar}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
52. $Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+(\text{N}_2\text{O})\{M=5\}$	$\Delta H_{52} = -1.8$	$K_{52}, \text{bar}^{-1}$	$6.97 \times 10^{11}$	$1.23 \times 10^{12}$	$1.91 \times 10^{12}$
	$E_{52}^\ddagger = 0.0$	$A_{52}, \text{s}^{-1} \text{bar}^{-1}$			
		$k_{52}, \text{s}^{-1} \text{bar}^{-1}$			

TABLE 1: (Continued)

reaction	$E^\ddagger, {}^a \Delta H^b$ (kcal/mol)	constant	$T$ (K)		
			600	700	800
43. $Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+(\text{ON}_2)\{M=5\}$	$\Delta H_{43} = -1.0$	$K_{43}, \text{bar}^{-1}$	$9.10 \times 10^{-6}$	$7.89 \times 10^{-6}$	$7.28 \times 10^{-6}$
	$E_{43}^\ddagger = 0.0$	$A_{43}, \text{s}^{-1} \text{bar}^{-1}$	$1.14 \times 10^7$	$1.61 \times 10^7$	$2.17 \times 10^7$
		$k_{43}, \text{s}^{-1} \text{bar}^{-1}$	$1.14 \times 10^7$	$1.61 \times 10^7$	$2.17 \times 10^7$
	$E_{-43}^\ddagger = 2.7$	$A_{-43}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
44. $Z^-[\text{FeO}_2\text{NO}]^+(\text{ON}_2)\{M=5\} \leftrightarrow Z^-[\text{OFeO}_2\text{NO}]^+\{M=5\} + \text{N}_2(\text{g})$	$\Delta H_{44} = -7.0$	$K_{44}, \text{bar}$	$2.50 \times 10^7$	$1.10 \times 10^7$	$5.79 \times 10^6$
	$E_{44}^\ddagger = 25.2$	$A_{44}, \text{s}^{-1}$	$3.42 \times 10^{13}$	$3.99 \times 10^{13}$	$4.52 \times 10^{13}$
		$k_{44}, \text{s}^{-1}$	$2.27 \times 10^4$	$5.41 \times 10^5$	$5.91 \times 10^6$
	$E_{-44}^\ddagger = 31.2$	$A_{-44}, \text{s}^{-1} \text{bar}^{-1}$	$2.13 \times 10^8$	$2.75 \times 10^8$	$3.43 \times 10^8$
45. $Z^-[\text{OFeO}_2\text{NO}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{OFeO}_2\text{NO}]^+(\text{N}_2\text{O})\{M=5\}$	$\Delta H_{45} = -2.6$	$K_{45}, \text{bar}^{-1}$	$8.56 \times 10^{-6}$	$6.17 \times 10^{-6}$	$4.95 \times 10^{-6}$
	$E_{45}^\ddagger = 0.0$	$A_{45}, \text{s}^{-1} \text{bar}^{-1}$	$3.45 \times 10^6$	$4.73 \times 10^6$	$6.27 \times 10^6$
		$k_{45}, \text{s}^{-1} \text{bar}^{-1}$	$3.45 \times 10^6$	$4.73 \times 10^6$	$6.27 \times 10^6$
	$E_{-45}^\ddagger = 4.1$	$A_{-45}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
46. $Z^-[\text{OFeO}_2\text{NO}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{OFeO}_2\text{NO}]^+(\text{ON}_2)\{M=5\}$	$\Delta H_{46} = -2.9$	$K_{46}, \text{bar}^{-1}$	$3.87 \times 10^{-6}$	$2.67 \times 10^{-6}$	$2.07 \times 10^{-6}$
	$E_{46}^\ddagger = 0.0$	$A_{46}, \text{s}^{-1} \text{bar}^{-1}$	$1.14 \times 10^6$	$1.57 \times 10^6$	$2.08 \times 10^6$
		$k_{46}, \text{s}^{-1} \text{bar}^{-1}$	$1.14 \times 10^6$	$1.57 \times 10^6$	$2.08 \times 10^6$
	$E_{-46}^\ddagger = 4.5$	$A_{-46}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
47. $Z^-[\text{OFeO}_2\text{NO}]^+(\text{ON}_2)\{M=5\} \leftrightarrow Z^-[\text{O}_2\text{FeO}_2\text{NO}]^+\{M=5\} + \text{N}_2(\text{g})$	$\Delta H_{47} = -19.2$	$K_{47}, \text{bar}$	$6.52 \times 10^{15}$	$6.60 \times 10^{14}$	$1.16 \times 10^{14}$
	$E_{47}^\ddagger = 41.1$	$A_{47}, \text{s}^{-1}$	$1.02 \times 10^{13}$	$1.18 \times 10^{13}$	$1.32 \times 10^{13}$
		$k_{47}, \text{s}^{-1}$	$1.05 \times 10^{-2}$	$1.67 \times 10^0$	$7.60 \times 10^1$
	$E_{-47}^\ddagger = 61.0$	$A_{-47}, \text{s}^{-1} \text{bar}^{-1}$	$2.67 \times 10^4$	$2.82 \times 10^4$	$3.02 \times 10^4$
48. $Z^-[\text{O}_2\text{FeO}_2\text{NO}]^+\{M=5\} \leftrightarrow Z^-[\text{O}_2\text{FeO}_2\text{NO}]^+\{M=7\}$	$\Delta H_{48} = -8.7$	$K_{48}, -$	$6.26 \times 10^2$	$2.20 \times 10^2$	$1.01 \times 10^2$
	$E_{48}^\ddagger = 0.4$	$A_{48}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{48}, \text{s}^{-1}$	$9.24 \times 10^{12}$	$1.13 \times 10^{13}$	$1.33 \times 10^{13}$
	$E_{-48}^\ddagger = 8.9$	$A_{-48}, \text{s}^{-1}$	$2.63 \times 10^{13}$	$3.12 \times 10^{13}$	$3.62 \times 10^{13}$
49. $Z^-[\text{O}_2\text{FeO}_2\text{NO}]^+\{M=7\} \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} + \text{O}_2(\text{g})$	$\Delta H_{49} = 0.4$	$K_{49}, \text{bar}$	$1.86 \times 10^6$	$1.98 \times 10^6$	$2.01 \times 10^6$
	$E_{49}^\ddagger = 3.0$	$A_{49}, \text{s}^{-1}$	$1.91 \times 10^{13}$	$2.04 \times 10^{13}$	$2.15 \times 10^{13}$
		$k_{49}, \text{s}^{-1}$	$1.57 \times 10^{12}$	$2.40 \times 10^{12}$	$3.30 \times 10^{12}$
	$E_{-49}^\ddagger = 1.5$	$A_{-49}, \text{s}^{-1} \text{bar}^{-1}$	$3.07 \times 10^6$	$3.68 \times 10^6$	$4.32 \times 10^6$
50. $Z^-[\text{O}_2\text{FeO}_2\text{NO}]^+\{M=7\} \leftrightarrow Z^-[\text{OFeO}_2]^+\{M=6\} + \text{NO}_2(\text{g})$	$\Delta H_{50} = 43.2$	$K_{50}, \text{bar}$	$3.88 \times 10^{-9}$	$8.05 \times 10^{-7}$	$4.34 \times 10^{-5}$
	$E_{50}^\ddagger = 44.0$	$A_{50}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{50}, \text{s}^{-1}$	$1.16 \times 10^{-3}$	$2.65 \times 10^{-1}$	$1.58 \times 10^1$
	$E_{-50}^\ddagger = 0.0$	$A_{-50}, \text{s}^{-1} \text{bar}^{-1}$	$3.00 \times 10^5$	$3.29 \times 10^5$	$3.64 \times 10^5$
51. $Z^-[\text{OFeO}_2\text{NO}]^+\{M=5\} \leftrightarrow Z^-[\text{OFeO}]^+\{M=6\} + \text{NO}_2(\text{g})$	$\Delta H_{51} = 33.6$	$K_{51}, \text{bar}$	$1.75 \times 10^{-3}$	$1.00 \times 10^{-1}$	$2.02 \times 10^0$
	$E_{51}^\ddagger = 40.8$	$A_{51}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{51}, \text{s}^{-1}$	$1.71 \times 10^{-2}$	$2.65 \times 10^0$	$1.18 \times 10^2$
	$E_{-51}^\ddagger = 7.2$	$A_{-51}, \text{s}^{-1} \text{bar}^{-1}$	$4.22 \times 10^3$	$4.81 \times 10^3$	$5.55 \times 10^3$
52. $Z^-[\text{OFeO}_2\text{NO}]^+\{M=5\} + \text{NO}(\text{g}) \leftrightarrow Z^-[\text{ONFeO}_2\text{NO}]^+\{M=6\}$	$\Delta H_{52} = -37.0$	$K_{52}, \text{bar}^{-1}$	$8.49 \times 10^7$	$9.67 \times 10^5$	$3.46 \times 10^4$
	$E_{52}^\ddagger = 0.0$	$A_{52}, \text{s}^{-1} \text{bar}^{-1}$	$1.18 \times 10^7$	$1.55 \times 10^7$	$1.98 \times 10^7$
		$k_{52}, \text{s}^{-1} \text{bar}^{-1}$	$1.18 \times 10^7$	$1.55 \times 10^7$	$1.98 \times 10^7$
	$E_{-52}^\ddagger = 38.3$	$A_{-52}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
53. $Z^-[\text{ONFeO}_2\text{NO}]^+\{M=6\} \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} + \text{NO}_2(\text{g})$	$\Delta H_{53} = 12.3$	$K_{53}, \text{bar}$	$3.90 \times 10^1$	$1.76 \times 10^2$	$5.23 \times 10^2$
	$E_{53}^\ddagger = 14.5$	$A_{53}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{53}, \text{s}^{-1}$	$6.76 \times 10^7$	$4.46 \times 10^8$	$1.87 \times 10^9$
	$E_{-53}^\ddagger = 0.0$	$A_{-53}, \text{s}^{-1} \text{bar}^{-1}$	$1.73 \times 10^6$	$2.54 \times 10^6$	$3.57 \times 10^6$
54. $Z^-[\text{ONFeO}_2\text{NO}]^+\{M=6\} \leftrightarrow Z^-[\text{NO}_2\text{FeO}_2\text{NO}]^+\{M=6\}$	$\Delta H_{54} = -1.3$	$K_{54}, -$	$5.53 \times 10^{-2}$	$4.75 \times 10^{-2}$	$4.22 \times 10^{-2}$
	$E_{54}^\ddagger = 2.5$	$A_{54}, \text{s}^{-1}$	$5.32 \times 10^{11}$	$5.20 \times 10^{11}$	$5.10 \times 10^{11}$
		$k_{54}, \text{s}^{-1}$	$6.70 \times 10^{10}$	$8.80 \times 10^{10}$	$1.08 \times 10^{11}$
	$E_{-54}^\ddagger = 3.0$	$A_{-54}, \text{s}^{-1}$	$1.52 \times 10^{13}$	$1.61 \times 10^{13}$	$1.70 \times 10^{13}$
55. $Z^-[\text{Fe}(\text{OH})_2]^+\{M=6\} + \text{NO}(\text{g}) \leftrightarrow Z^-[\text{Fe}(\text{OH})_2]^+(\text{ON})\{M=7\}$	$\Delta H_{55} = 1.1$	$K_{55}, \text{bar}^{-1}$	$3.00 \times 10^{-5}$	$3.29 \times 10^{-5}$	$3.62 \times 10^{-5}$
	$E_{55}^\ddagger = 0.0$	$A_{55}, \text{s}^{-1} \text{bar}^{-1}$	$2.46 \times 10^8$	$3.34 \times 10^8$	$4.39 \times 10^8$
		$k_{55}, \text{s}^{-1} \text{bar}^{-1}$	$2.46 \times 10^8$	$3.34 \times 10^8$	$4.39 \times 10^8$
	$E_{-55}^\ddagger = 0.5$	$A_{-55}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
56. $Z^-[\text{Fe}(\text{OH})_2]^+\{M=6\} + \text{NO}(\text{g}) \leftrightarrow Z^-[\text{Fe}(\text{OH})_2]^+(\text{NO})\{M=7\}$	$\Delta H_{56} = -0.9$	$K_{56}, \text{bar}^{-1}$	$2.37 \times 10^{-5}$	$2.05 \times 10^{-5}$	$1.89 \times 10^{-5}$
	$E_{56}^\ddagger = 0.0$	$A_{56}, \text{s}^{-1} \text{bar}^{-1}$	$5.01 \times 10^7$	$6.52 \times 10^7$	$8.28 \times 10^7$
		$k_{56}, \text{s}^{-1} \text{bar}^{-1}$	$5.01 \times 10^7$	$6.52 \times 10^7$	$8.28 \times 10^7$
	$E_{-56}^\ddagger = 2.1$	$A_{-56}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{-56}, \text{s}^{-1}$	$2.11 \times 10^{12}$	$3.17 \times 10^{12}$	$4.39 \times 10^{12}$



TABLE 1: (Continued)

reaction	$E^\ddagger, {}^a \Delta H^\ddagger$ (kcal/mol)	constant	$T$ (K)		
			600	700	800
57. $Z^-[\text{Fe}(\text{OH})_2]^+(\text{NO})\{M=7\} \leftrightarrow Z^-[\text{Fe}(\text{OH})_2]^+(\text{NO})\{M=5\}$	$\Delta H_{57}^\ddagger = -0.01$ $E_{57}^\ddagger = 0.1$ $E_{-57}^\ddagger = 0.03$	$K_{57}, -$	$5.20 \times 10^{-1}$	$5.20 \times 10^{-1}$	$5.19 \times 10^{-1}$
		$A_{57}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{57}, \text{s}^{-1}$	$1.19 \times 10^{13}$	$1.40 \times 10^{13}$	$1.61 \times 10^{13}$
		$A_{-57}, \text{s}^{-1}$	$2.35 \times 10^{13}$	$2.76 \times 10^{13}$	$3.16 \times 10^{13}$
58. $Z^-[\text{Fe}(\text{OH})_2]^+(\text{NO})\{M=5\} \leftrightarrow Z^-[\text{FeOH}]^+(\text{trans-HNO}_2)\{M=5\}$	$\Delta H_{58}^\ddagger = 6.4$ $E_{58}^\ddagger = 9.7$ $E_{-58}^\ddagger = 2.3$	$K_{58}, -$	$2.16 \times 10^{-5}$	$4.68 \times 10^{-5}$	$8.29 \times 10^{-5}$
		$A_{58}, \text{s}^{-1}$	$3.72 \times 10^{12}$	$3.75 \times 10^{12}$	$3.77 \times 10^{12}$
		$k_{58}, \text{s}^{-1}$	$1.05 \times 10^9$	$3.40 \times 10^9$	$8.20 \times 10^9$
		$A_{-58}, \text{s}^{-1}$	$3.22 \times 10^{14}$	$3.68 \times 10^{14}$	$4.09 \times 10^{14}$
59. $Z^-[\text{Fe}(\text{OH})_2]^+(\text{NO})\{M=5\} \leftrightarrow Z^-[\text{FeOH}]^+(\text{cis-HNO}_2)\{M=5\}$	$\Delta H_{59}^\ddagger = 8.7$ $E_{59}^\ddagger = 11.0$ $E_{-59}^\ddagger = 1.3$	$K_{59}, -$	$7.12 \times 10^{-6}$	$2.04 \times 10^{-5}$	$4.45 \times 10^{-5}$
		$A_{59}, \text{s}^{-1}$	$1.13 \times 10^{11}$	$1.06 \times 10^{11}$	$1.00 \times 10^{11}$
		$k_{59}, \text{s}^{-1}$	$1.09 \times 10^7$	$3.82 \times 10^7$	$9.76 \times 10^7$
		$A_{-59}, \text{s}^{-1}$	$4.49 \times 10^{12}$	$4.72 \times 10^{12}$	$4.91 \times 10^{12}$
60. $Z^-[\text{FeOH}]^+(\text{trans-HNO}_2)\{M=5\} \leftrightarrow Z^-[\text{FeOH}]^+\{M=5\} + \text{trans-HNO}_2(\text{g})$	$\Delta H_{60}^\ddagger = 5.9$ $E_{60}^\ddagger = 7.9$ $E_{-60}^\ddagger = 0.0$	$K_{60}, \text{bar}$	$4.84 \times 10^4$	$1.01 \times 10^5$	$1.68 \times 10^5$
		$A_{60}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{60}, \text{s}^{-1}$	$1.61 \times 10^{10}$	$4.87 \times 10^{10}$	$1.14 \times 10^{11}$
		$A_{-60}, \text{s}^{-1} \text{ bar}^{-1}$	$3.33 \times 10^5$	$4.84 \times 10^5$	$6.76 \times 10^5$
61. $Z^-[\text{FeOH}]^+(\text{cis-HNO}_2)\{M=5\} \leftrightarrow Z^-[\text{FeOH}]^+\{M=5\} + \text{cis-HNO}_2(\text{g})$	$\Delta H_{61}^\ddagger = 4.3$ $E_{61}^\ddagger = 6.6$ $E_{-61}^\ddagger = 0.0$	$K_{61}, \text{bar}$	$6.45 \times 10^4$	$1.11 \times 10^5$	$1.61 \times 10^5$
		$A_{61}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{61}, \text{s}^{-1}$	$5.06 \times 10^{10}$	$1.30 \times 10^{11}$	$2.68 \times 10^{11}$
		$A_{-61}, \text{s}^{-1} \text{ bar}^{-1}$	$7.85 \times 10^5$	$1.17 \times 10^6$	$1.66 \times 10^6$
62. $Z^-[\text{FeOH}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeOH}]^+(\text{N}_2\text{O})\{M=5\}$	$\Delta H_{62}^\ddagger = -1.4$ $E_{62}^\ddagger = 0.0$ $E_{-62}^\ddagger = 3.2$	$K_{62}, \text{bar}^{-1}$	$1.40 \times 10^{-4}$	$1.17 \times 10^{-4}$	$1.05 \times 10^{-4}$
		$A_{62}, \text{s}^{-1} \text{ bar}^{-1}$	$1.21 \times 10^8$	$1.73 \times 10^8$	$2.35 \times 10^8$
		$k_{62}, \text{s}^{-1} \text{ bar}^{-1}$	$1.21 \times 10^8$	$1.73 \times 10^8$	$2.35 \times 10^8$
		$A_{-62}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
63. $Z^-[\text{FeOH}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeOH}]^+(\text{ON}_2)\{M=5\}$	$\Delta H_{63}^\ddagger = -1.8$ $E_{63}^\ddagger = 0.0$ $E_{-63}^\ddagger = 3.5$	$K_{63}, \text{bar}^{-1}$	$3.61 \times 10^{-5}$	$2.85 \times 10^{-5}$	$2.45 \times 10^{-5}$
		$A_{63}, \text{s}^{-1} \text{ bar}^{-1}$	$2.45 \times 10^7$	$3.42 \times 10^7$	$4.60 \times 10^7$
		$k_{63}, \text{s}^{-1} \text{ bar}^{-1}$	$2.45 \times 10^7$	$3.42 \times 10^7$	$4.60 \times 10^7$
		$A_{-63}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
64. $Z^-[\text{FeOH}]^+(\text{ON}_2)\{M=5\} \leftrightarrow Z^-[\text{OFeOH}]^+\{M=5\} + \text{N}_2(\text{g})$	$\Delta H_{64}^\ddagger = -16.1$ $E_{64}^\ddagger = 24.0$ $E_{-64}^\ddagger = 38.8$	$K_{64}, \text{bar}$	$2.31 \times 10^{10}$	$3.42 \times 10^9$	$7.95 \times 10^8$
		$A_{64}, \text{s}^{-1}$	$8.07 \times 10^{11}$	$8.76 \times 10^{11}$	$9.40 \times 10^{11}$
		$k_{64}, \text{s}^{-1}$	$1.49 \times 10^3$	$2.85 \times 10^4$	$2.64 \times 10^5$
		$A_{-64}, \text{s}^{-1} \text{ bar}^{-1}$	$8.52 \times 10^6$	$1.06 \times 10^7$	$1.30 \times 10^7$
65. $Z^-[\text{OFeOH}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{OFeOH}]^+(\text{N}_2\text{O})\{M=5\}$	$\Delta H_{65}^\ddagger = -0.8$ $E_{65}^\ddagger = 0.0$ $E_{-65}^\ddagger = 2.5$	$K_{65}, \text{bar}^{-1}$	$1.25 \times 10^{-4}$	$1.11 \times 10^{-4}$	$1.04 \times 10^{-4}$
		$A_{65}, \text{s}^{-1} \text{ bar}^{-1}$	$1.92 \times 10^8$	$2.68 \times 10^8$	$3.60 \times 10^8$
		$k_{65}, \text{s}^{-1} \text{ bar}^{-1}$	$1.92 \times 10^8$	$2.68 \times 10^8$	$3.60 \times 10^8$
		$A_{-65}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
66. $Z^-[\text{OFeOH}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{OFeOH}]^+(\text{ON}_2)\{M=5\}$	$\Delta H_{66}^\ddagger = -1.5$ $E_{66}^\ddagger = 0.0$ $E_{-66}^\ddagger = 3.1$	$K_{66}, \text{bar}^{-1}$	$5.86 \times 10^{-5}$	$4.83 \times 10^{-5}$	$4.29 \times 10^{-5}$
		$A_{66}, \text{s}^{-1} \text{ bar}^{-1}$	$5.59 \times 10^7$	$7.76 \times 10^7$	$1.04 \times 10^8$
		$k_{66}, \text{s}^{-1} \text{ bar}^{-1}$	$5.59 \times 10^7$	$7.76 \times 10^7$	$1.04 \times 10^8$
		$A_{-66}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
67. $Z^-[\text{OFeOH}]^+(\text{ON}_2)\{M=5\} \leftrightarrow Z^-[\text{O}_2\text{FeOH}]^+\{M=5\} + \text{N}_2(\text{g})$	$\Delta H_{67}^\ddagger = -20.5$ $E_{67}^\ddagger = 46.5$ $E_{-67}^\ddagger = 67.7$	$K_{67}, \text{bar}$	$6.27 \times 10^{13}$	$5.42 \times 10^{12}$	$8.53 \times 10^{11}$
		$A_{67}, \text{s}^{-1}$	$5.48 \times 10^{12}$	$6.52 \times 10^{12}$	$7.54 \times 10^{12}$
		$k_{67}, \text{s}^{-1}$	$6.10 \times 10^{-5}$	$1.92 \times 10^{-2}$	$1.45 \times 10^0$
		$A_{-67}, \text{s}^{-1} \text{ bar}^{-1}$	$4.70 \times 10^6$	$5.09 \times 10^6$	$5.56 \times 10^6$
68. $Z^-[\text{O}_2\text{FeOH}]^+\{M=5\} \leftrightarrow Z^-[\text{O}_2\text{FeOH}]^+\{M=7\}$	$\Delta H_{68}^\ddagger = -4.5$ $E_{68}^\ddagger = 6.0$ $E_{-68}^\ddagger = 10.5$	$K_{68}, -$	$6.09 \times 10^1$	$3.57 \times 10^1$	$2.39 \times 10^1$
		$A_{68}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{68}, \text{s}^{-1}$	$8.19 \times 10^{10}$	$1.96 \times 10^{11}$	$3.84 \times 10^{11}$
		$A_{-68}, \text{s}^{-1}$	$8.75 \times 10^{12}$	$1.02 \times 10^{13}$	$1.16 \times 10^{13}$
69. $Z^-[\text{O}_2\text{FeOH}]^+\{M=7\} \leftrightarrow Z^-[\text{FeOH}]^+\{M=5\} + \text{O}_2(\text{g})$	$\Delta H_{69}^\ddagger = 5.8$ $E_{69}^\ddagger = 7.6$ $E_{-69}^\ddagger = 0.8$	$K_{69}, \text{bar}$	$3.58 \times 10^4$	$7.30 \times 10^4$	$1.21 \times 10^5$
		$A_{69}, \text{s}^{-1}$	$7.23 \times 10^{13}$	$7.93 \times 10^{13}$	$8.50 \times 10^{13}$
		$k_{69}, \text{s}^{-1}$	$1.22 \times 10^{11}$	$3.32 \times 10^{11}$	$7.05 \times 10^{11}$
		$A_{-69}, \text{s}^{-1} \text{ bar}^{-1}$	$6.59 \times 10^6$	$8.03 \times 10^6$	$9.58 \times 10^6$
70. $Z^-[\text{OFeOH}]^+\{M=5\} + \text{NO}(\text{g}) \leftrightarrow Z^-[\text{ONFeOH}]^+\{M=6\}$	$\Delta H_{70}^\ddagger = -31.6$ $E_{70}^\ddagger = 0.0$ $E_{-70}^\ddagger = 32.9$	$K_{70}, \text{bar}^{-1}$	$2.09 \times 10^5$	$4.56 \times 10^3$	$2.66 \times 10^2$
		$A_{70}, \text{s}^{-1} \text{ bar}^{-1}$	$2.60 \times 10^6$	$3.42 \times 10^6$	$4.42 \times 10^6$
		$k_{70}, \text{s}^{-1} \text{ bar}^{-1}$	$2.60 \times 10^6$	$3.42 \times 10^6$	$4.42 \times 10^6$
		$A_{-70}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{-70}, \text{s}^{-1}$	$1.24 \times 10^1$	$7.51 \times 10^2$	$1.66 \times 10^4$

TABLE 1: (Continued)

reaction	$E^\ddagger, {}^a \Delta H^\ddagger$ (kcal/mol)	constant	$T$ (K)		
			600	700	800
71. $Z^-[\text{ONFeOH}]^+\{M=6\} \leftrightarrow Z^-[\text{FeOH}]^+\{M=5\} + \text{NO}_2(\text{g})$	$\Delta H_{71}^\ddagger = 16.8$	$K_{71}, \text{bar}$	$4.32 \times 10^0$	$3.32 \times 10^1$	$1.47 \times 10^2$
	$E_{71}^\ddagger = 18.6$	$A_{71}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{71}, \text{s}^{-1}$	$2.08 \times 10^6$	$2.25 \times 10^7$	$1.37 \times 10^8$
	$E_{-71}^\ddagger = 0.0$	$A_{-71}, \text{s}^{-1} \text{bar}^{-1}$	$4.81 \times 10^5$	$6.80 \times 10^5$	$9.32 \times 10^5$
72. $Z^-[\text{OFeOH}]^+\{M=5\} + \text{NO}(\text{g}) \leftrightarrow Z^-[\text{FeO}]^+(\text{trans-HNO}_2)\{M=6\}$	$\Delta H_{72}^\ddagger = -0.2$	$K_{72}, \text{bar}^{-1}$	$1.14 \times 10^{-6}$	$1.07 \times 10^{-6}$	$1.05 \times 10^{-6}$
	$E_{72}^\ddagger = 0.0$	$A_{72}, \text{s}^{-1} \text{bar}^{-1}$	$4.28 \times 10^6$	$5.56 \times 10^6$	$7.07 \times 10^6$
		$k_{72}, \text{s}^{-1} \text{bar}^{-1}$	$4.28 \times 10^6$	$5.56 \times 10^6$	$7.07 \times 10^6$
	$E_{-72}^\ddagger = 1.4$	$A_{-72}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
73. $Z^-[\text{FeO}]^+(\text{trans-HNO}_2)\{M=6\} \leftrightarrow Z^-[\text{FeO}]^+\{M=6\} + \text{trans-HNO}_2(\text{g})$	$\Delta H_{73}^\ddagger = 11.2$	$K_{73}, \text{bar}$	$3.08 \times 10^2$	$1.21 \times 10^3$	$3.25 \times 10^3$
	$E_{73}^\ddagger = 13.5$	$A_{73}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{73}, \text{s}^{-1}$	$1.55 \times 10^8$	$9.06 \times 10^8$	$3.47 \times 10^9$
	$E_{-73}^\ddagger = 0.0$	$A_{-73}, \text{s}^{-1} \text{bar}^{-1}$	$5.01 \times 10^5$	$7.48 \times 10^5$	$1.07 \times 10^6$
74. $Z^-[\text{OFeOH}]^+\{M=5\} + \text{trans-HNO}_2(\text{g}) \leftrightarrow Z^-[\text{OFeOH}]^+(\text{trans-HNO}_2)\{M=5\}$	$\Delta H_{74}^\ddagger = -8.8$	$K_{74}, \text{bar}^{-1}$	$7.84 \times 10^{-6}$	$2.68 \times 10^{-6}$	$1.23 \times 10^{-6}$
	$E_{74}^\ddagger = 0.0$	$A_{74}, \text{s}^{-1} \text{bar}^{-1}$	$3.33 \times 10^4$	$4.16 \times 10^4$	$5.15 \times 10^4$
		$k_{74}, \text{s}^{-1} \text{bar}^{-1}$	$3.33 \times 10^4$	$4.16 \times 10^4$	$5.15 \times 10^4$
	$E_{-74}^\ddagger = 9.5$	$A_{-74}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
75. $Z^-[\text{OFeOH}]^+(\text{trans-HNO}_2)\{M=5\} \leftrightarrow Z^-[\text{OFeOH}_2]^+(\text{NO}_2)\{M=5\}$	$\Delta H_{75}^\ddagger = -1.4$	$K_{75}, -$	$7.07 \times 10^0$	$5.99 \times 10^0$	$5.30 \times 10^0$
	$E_{75}^\ddagger = 1.9$	$A_{75}, \text{s}^{-1}$	$2.06 \times 10^{12}$	$2.14 \times 10^{12}$	$2.22 \times 10^{12}$
		$k_{75}, \text{s}^{-1}$	$4.02 \times 10^{11}$	$5.27 \times 10^{11}$	$6.51 \times 10^{11}$
	$E_{-75}^\ddagger = 3.9$	$A_{-75}, \text{s}^{-1}$	$1.52 \times 10^{12}$	$1.47 \times 10^{12}$	$1.44 \times 10^{12}$
76. $Z^-[\text{OFeOH}_2]^+(\text{NO}_2)\{M=5\} \leftrightarrow Z^-[\text{OFeOH}_2]^+(\text{NO}_2)\{M=7\}$	$\Delta H_{76}^\ddagger = 7.3$	$K_{76}, -$	$6.63 \times 10^0$	$1.59 \times 10^1$	$3.06 \times 10^1$
	$E_{76}^\ddagger = 6.8$	$A_{76}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{76}, \text{s}^{-1}$	$4.22 \times 10^{10}$	$1.11 \times 10^{11}$	$2.33 \times 10^{11}$
	$E_{-76}^\ddagger = 0.8$	$A_{-76}, \text{s}^{-1}$	$1.29 \times 10^{10}$	$1.28 \times 10^{10}$	$1.30 \times 10^{10}$
77. $Z^-[\text{OFeOH}_2]^+(\text{NO}_2)\{M=7\} \leftrightarrow Z^-[\text{FeO}]^+(\text{OH}_2)\{M=6\} + \text{NO}_2(\text{g})$	$\Delta H_{77}^\ddagger = 3.7$	$K_{77}, \text{bar}$	$1.04 \times 10^5$	$1.66 \times 10^5$	$2.30 \times 10^5$
	$E_{77}^\ddagger = 5.2$	$A_{77}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{77}, \text{s}^{-1}$	$1.64 \times 10^{11}$	$3.56 \times 10^{11}$	$6.47 \times 10^{11}$
	$E_{-77}^\ddagger = 0.0$	$A_{-77}, \text{s}^{-1} \text{bar}^{-1}$	$1.58 \times 10^6$	$2.14 \times 10^6$	$2.82 \times 10^6$
78. $Z^-[\text{FeO}]^+(\text{OH}_2)\{M=6\} \leftrightarrow Z^-[\text{FeO}]^+\{M=6\} + \text{H}_2\text{O}(\text{g})^c$	$\Delta H_{78}^\ddagger = 16.3$	$K_{78}, \text{bar}$	$1.01 \times 10^0$	$7.35 \times 10^0$	$3.14 \times 10^1$
	$E_{78}^\ddagger = 17.3$	$A_{78}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{78}, \text{s}^{-1}$	$6.13 \times 10^6$	$5.70 \times 10^7$	$3.09 \times 10^8$
	$E_{-78}^\ddagger = 0.0$	$A_{-78}, \text{s}^{-1} \text{bar}^{-1}$	$6.04 \times 10^6$	$7.75 \times 10^6$	$9.82 \times 10^6$
79. $Z^-[\text{FeO}]^+(\text{OH}_2)\{M=6\} \leftrightarrow Z^-[\text{Fe}(\text{OH})_2]^+\{M=6\}$	$\Delta H_{79}^\ddagger = -27.1$	$K_{79}, -$	$1.83 \times 10^9$	$7.10 \times 10^7$	$6.26 \times 10^6$
	$E_{79}^\ddagger = 9.2$	$A_{79}, \text{s}^{-1}$	$2.28 \times 10^{12}$	$2.18 \times 10^{12}$	$2.13 \times 10^{12}$
		$k_{79}, \text{s}^{-1}$	$1.03 \times 10^9$	$2.97 \times 10^9$	$6.60 \times 10^9$
	$E_{-79}^\ddagger = 36.4$	$A_{-79}, \text{s}^{-1}$	$1.08 \times 10^{13}$	$1.02 \times 10^{13}$	$9.69 \times 10^{12}$
80. $Z^-[\text{OFeO}]^+\{M=6\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeO}]^+(\text{cis-(NO)}_2)\{M=6\}$	$\Delta H_{80}^\ddagger = 24.4$	$K_{80}, \text{bar}^{-1}$	$2.43 \times 10^{-16}$	$4.46 \times 10^{-15}$	$4.07 \times 10^{-14}$
	$E_{80}^\ddagger = 28.2$	$A_{80}, \text{s}^{-1} \text{bar}^{-1}$	$2.55 \times 10^6$	$3.08 \times 10^6$	$3.65 \times 10^6$
		$k_{80}, \text{s}^{-1} \text{bar}^{-1}$	$1.39 \times 10^{-4}$	$4.91 \times 10^{-3}$	$7.33 \times 10^{-2}$
	$E_{-80}^\ddagger = 4.5$	$A_{-80}, \text{s}^{-1}$	$2.45 \times 10^{13}$	$2.76 \times 10^{13}$	$3.01 \times 10^{13}$
81. $Z^-[\text{FeO}]^+(\text{cis-(NO)}_2)\{M=6\} \leftrightarrow Z^-[\text{FeO}]^+(\text{ON})\{M=5\} + \text{NO}(\text{g})$	$\Delta H_{81}^\ddagger = -6.1$	$K_{81}, \text{bar}$	$3.40 \times 10^{12}$	$1.70 \times 10^{12}$	$9.85 \times 10^{11}$
	$E_{81}^\ddagger = 9.2$	$A_{81}, \text{s}^{-1}$	$4.78 \times 10^{13}$	$5.62 \times 10^{13}$	$6.40 \times 10^{13}$
		$k_{81}, \text{s}^{-1}$	$2.18 \times 10^{10}$	$7.69 \times 10^{10}$	$2.00 \times 10^{11}$
	$E_{-81}^\ddagger = 16.6$	$A_{-81}, \text{s}^{-1} \text{bar}^{-1}$	$7.02 \times 10^3$	$6.82 \times 10^3$	$6.87 \times 10^3$
82. $Z^-[\text{FeO}]^+(\text{ON})\{M=5\} \leftrightarrow Z^-[\text{FeO}]^+\{M=6\} + \text{NO}(\text{g})$	$\Delta H_{82}^\ddagger = 3.3$	$K_{82}, \text{bar}$	$2.60 \times 10^4$	$4.01 \times 10^4$	$5.41 \times 10^4$
	$E_{82}^\ddagger = 4.8$	$A_{82}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{82}, \text{s}^{-1}$	$2.28 \times 10^{11}$	$4.72 \times 10^{11}$	$8.28 \times 10^{11}$
	$E_{-82}^\ddagger = 0.0$	$A_{-82}, \text{s}^{-1} \text{bar}^{-1}$	$8.78 \times 10^6$	$1.17 \times 10^7$	$1.53 \times 10^7$
83. $Z^-[\text{ONFeO}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeONO}]^+(\text{cis-(NO)}_2)\{M=5\}$	$\Delta H_{83}^\ddagger = 22.2$	$K_{83}, \text{bar}^{-1}$	$5.95 \times 10^{-14}$	$8.33 \times 10^{-13}$	$6.22 \times 10^{-12}$
	$E_{83}^\ddagger = 23.8$	$A_{83}, \text{s}^{-1} \text{bar}^{-1}$	$4.06 \times 10^7$	$5.31 \times 10^7$	$6.71 \times 10^7$
		$k_{83}, \text{s}^{-1} \text{bar}^{-1}$	$8.37 \times 10^{-2}$	$1.91 \times 10^0$	$2.05 \times 10^1$
	$E_{-83}^\ddagger = 3.2$	$A_{-83}, \text{s}^{-1}$	$2.07 \times 10^{13}$	$2.29 \times 10^{13}$	$2.48 \times 10^{13}$
84. $Z^-[\text{FeONO}]^+(\text{cis-(NO)}_2)\{M=5\} \leftrightarrow Z^-[\text{FeONO}]^+(\text{ON})\{M=4\} + \text{NO}(\text{g})$	$\Delta H_{84}^\ddagger = -3.0$	$K_{84}, \text{bar}$	$1.02 \times 10^{10}$	$7.42 \times 10^9$	$5.69 \times 10^9$
	$E_{84}^\ddagger = 6.1$	$A_{84}, \text{s}^{-1}$	$2.59 \times 10^{13}$	$2.94 \times 10^{13}$	$3.25 \times 10^{13}$
		$k_{84}, \text{s}^{-1}$	$1.51 \times 10^{11}$	$3.59 \times 10^{11}$	$6.89 \times 10^{11}$
	$E_{-84}^\ddagger = 9.7$	$A_{-84}, \text{s}^{-1} \text{bar}^{-1}$	$4.92 \times 10^4$	$5.05 \times 10^4$	$5.31 \times 10^4$
		$k_{-84}, \text{s}^{-1} \text{bar}^{-1}$	$1.48 \times 10^1$	$4.83 \times 10^1$	$1.21 \times 10^2$

TABLE 1: (Continued)

reaction	$E^{\ddagger,a} \Delta H^b$ (kcal/mol)	constant	$T$ (K)		
			600	700	800
85. $Z^-[\text{FeONO}]^+(\text{ON})\{M=4\} \leftrightarrow Z^-[\text{FeONO}]^+\{M=5\} + \text{NO}(\text{g})$	$\Delta H_{85} = 0.04$	$K_{85}, \text{bar}$	$8.65 \times 10^4$	$9.01 \times 10^4$	$9.05 \times 10^4$
	$E_{85}^{\ddagger} = 1.7$	$A_{85}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{85}, \text{s}^{-1}$	$3.12 \times 10^{12}$	$4.44 \times 10^{12}$	$5.89 \times 10^{12}$
	$E_{-85}^{\ddagger} = 0.0$	$A_{-85}, \text{s}^{-1} \text{bar}^{-1}$	$3.61 \times 10^7$	$4.93 \times 10^7$	$6.51 \times 10^7$
86. $Z^-[\text{OFeO}_2\text{N}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeO}_2\text{N}]^+(\text{cis-}(\text{NO})_2)\{M=5\}$	$\Delta H_{86} = 21.2$	$K_{86}, \text{bar}^{-1}$	$1.58 \times 10^{-13}$	$1.95 \times 10^{-12}$	$1.33 \times 10^{-11}$
	$E_{86}^{\ddagger} = 21.8$	$A_{86}, \text{s}^{-1} \text{bar}^{-1}$	$4.88 \times 10^7$	$6.48 \times 10^7$	$8.29 \times 10^7$
		$k_{86}, \text{s}^{-1} \text{bar}^{-1}$	$5.64 \times 10^{-1}$	$1.02 \times 10^1$	$9.24 \times 10^1$
	$E_{-86}^{\ddagger} = 2.3$	$A_{-86}, \text{s}^{-1}$	$2.47 \times 10^{13}$	$2.73 \times 10^{13}$	$2.95 \times 10^{13}$
87. $Z^-[\text{FeO}_2\text{N}]^+(\text{cis-}(\text{NO})_2)\{M=5\} \leftrightarrow Z^-[\text{FeO}_2\text{N}]^+(\text{ON})\{M=4\} + \text{NO}(\text{g})$	$\Delta H_{87} = -4.2$	$K_{87}, \text{bar}$	$1.07 \times 10^{11}$	$6.68 \times 10^{10}$	$4.58 \times 10^{10}$
	$E_{87}^{\ddagger} = 7.9$	$A_{87}, \text{s}^{-1}$	$2.19 \times 10^{13}$	$2.51 \times 10^{13}$	$2.80 \times 10^{13}$
		$k_{87}, \text{s}^{-1}$	$2.96 \times 10^{10}$	$8.73 \times 10^{10}$	$1.98 \times 10^{11}$
	$E_{-87}^{\ddagger} = 12.9$	$A_{-87}, \text{s}^{-1} \text{bar}^{-1}$	$1.40 \times 10^4$	$1.40 \times 10^4$	$1.45 \times 10^4$
88. $Z^-[\text{FeO}_2\text{N}]^+(\text{ON})\{M=4\} \leftrightarrow Z^-[\text{FeO}_2\text{N}]^+\{M=5\} + \text{NO}(\text{g})$	$\Delta H_{88} = 0.8$	$K_{88}, \text{bar}$	$1.09 \times 10^5$	$1.25 \times 10^5$	$1.34 \times 10^5$
	$E_{88}^{\ddagger} = 2.3$	$A_{88}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{88}, \text{s}^{-1}$	$1.76 \times 10^{12}$	$2.72 \times 10^{12}$	$3.84 \times 10^{12}$
	$E_{-88}^{\ddagger} = 0.0$	$A_{-88}, \text{s}^{-1} \text{bar}^{-1}$	$1.62 \times 10^7$	$2.18 \times 10^7$	$2.86 \times 10^7$
89. $Z^-[\text{OFeO}_2\text{NO}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+(\text{cis-}(\text{NO})_2)\{M=5\}$	$\Delta H_{89} = 17.2$	$K_{89}, \text{bar}^{-1}$	$4.73 \times 10^{-12}$	$3.65 \times 10^{-11}$	$1.74 \times 10^{-10}$
	$E_{89}^{\ddagger} = 18.0$	$A_{89}, \text{s}^{-1} \text{bar}^{-1}$	$4.92 \times 10^7$	$6.55 \times 10^7$	$8.40 \times 10^7$
		$k_{89}, \text{s}^{-1} \text{bar}^{-1}$	$1.41 \times 10^1$	$1.61 \times 10^2$	$1.04 \times 10^3$
	$E_{-89}^{\ddagger} = 2.4$	$A_{-89}, \text{s}^{-1}$	$2.29 \times 10^{13}$	$2.55 \times 10^{13}$	$2.76 \times 10^{13}$
90. $Z^-[\text{FeO}_2\text{NO}]^+(\text{cis-}(\text{NO})_2)\{M=5\} \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+(\text{ON})\{M=4\} + \text{NO}(\text{g})$	$\Delta H_{90} = -5.0$	$K_{90}, \text{bar}$	$1.24 \times 10^{11}$	$7.08 \times 10^{10}$	$4.54 \times 10^{10}$
	$E_{90}^{\ddagger} = 7.4$	$A_{90}, \text{s}^{-1}$	$1.60 \times 10^{13}$	$1.80 \times 10^{13}$	$1.99 \times 10^{13}$
		$k_{90}, \text{s}^{-1}$	$3.26 \times 10^{10}$	$8.92 \times 10^{10}$	$1.91 \times 10^{11}$
	$E_{-90}^{\ddagger} = 13.2$	$A_{-90}, \text{s}^{-1} \text{bar}^{-1}$	$1.65 \times 10^4$	$1.63 \times 10^4$	$1.67 \times 10^4$
91. $Z^-[\text{FeO}_2\text{NO}]^+(\text{ON})\{M=4\} \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} + \text{NO}(\text{g})$	$\Delta H_{91} = 0.8$	$K_{91}, \text{bar}$	$1.03 \times 10^5$	$1.18 \times 10^5$	$1.27 \times 10^5$
	$E_{91}^{\ddagger} = 2.4$	$A_{91}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{91}, \text{s}^{-1}$	$1.61 \times 10^{12}$	$2.52 \times 10^{12}$	$3.58 \times 10^{12}$
	$E_{-91}^{\ddagger} = 0.0$	$A_{-91}, \text{s}^{-1} \text{bar}^{-1}$	$1.57 \times 10^7$	$2.14 \times 10^7$	$2.82 \times 10^7$
92. $Z^-[\text{OFeOH}]^+\{M=5\} + \text{N}_2\text{O}(\text{g}) \leftrightarrow Z^-[\text{FeOH}]^+(\text{cis-}(\text{NO})_2)\{M=5\}$	$\Delta H_{92} = 22.2$	$K_{92}, \text{bar}^{-1}$	$5.03 \times 10^{-14}$	$7.00 \times 10^{-13}$	$5.21 \times 10^{-12}$
	$E_{92}^{\ddagger} = 24.6$	$A_{92}, \text{s}^{-1} \text{bar}^{-1}$	$1.18 \times 10^7$	$1.60 \times 10^7$	$2.08 \times 10^7$
		$k_{92}, \text{s}^{-1} \text{bar}^{-1}$	$1.33 \times 10^{-2}$	$3.42 \times 10^{-1}$	$4.03 \times 10^0$
	$E_{-92}^{\ddagger} = 4.3$	$A_{-92}, \text{s}^{-1}$	$9.79 \times 10^{12}$	$1.08 \times 10^{13}$	$1.16 \times 10^{13}$
93. $Z^-[\text{FeOH}]^+(\text{cis-}(\text{NO})_2)\{M=5\} \leftrightarrow Z^-[\text{FeOH}]^+(\text{ON})\{M=4\} + \text{NO}(\text{g})$	$\Delta H_{93} = 0.9$	$K_{93}, \text{bar}$	$3.25 \times 10^8$	$3.72 \times 10^8$	$4.03 \times 10^8$
	$E_{93}^{\ddagger} = 8.5$	$A_{93}, \text{s}^{-1}$	$7.34 \times 10^{12}$	$8.14 \times 10^{12}$	$8.83 \times 10^{12}$
		$k_{93}, \text{s}^{-1}$	$5.96 \times 10^9$	$1.83 \times 10^{10}$	$4.25 \times 10^{10}$
	$E_{-93}^{\ddagger} = 8.5$	$A_{-93}, \text{s}^{-1} \text{bar}^{-1}$	$2.30 \times 10^4$	$2.22 \times 10^4$	$2.22 \times 10^4$
94. $Z^-[\text{FeOH}]^+(\text{ON})\{M=4\} \leftrightarrow Z^-[\text{FeOH}]^+\{M=5\} + \text{NO}(\text{g})$	$\Delta H_{94} = -0.1$	$K_{94}, \text{bar}$	$1.01 \times 10^6$	$1.04 \times 10^6$	$1.04 \times 10^6$
	$E_{94}^{\ddagger} = 1.5$	$A_{94}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{94}, \text{s}^{-1}$	$3.70 \times 10^{12}$	$5.14 \times 10^{12}$	$6.69 \times 10^{12}$
	$E_{-94}^{\ddagger} = 0.0$	$A_{-94}, \text{s}^{-1} \text{bar}^{-1}$	$3.67 \times 10^6$	$4.94 \times 10^6$	$6.46 \times 10^6$
95. $Z^-[\text{OFeO}]^+\{M=6\} + \text{NO}_2(\text{g}) \leftrightarrow Z^-[\text{OFeO}]^+(\text{NO}_2)\{M=5\}$	$\Delta H_{95} = -2.0$	$K_{95}, \text{bar}^{-1}$	$1.41 \times 10^{-7}$	$1.09 \times 10^{-7}$	$9.28 \times 10^{-8}$
	$E_{95}^{\ddagger} = 6.6$	$A_{95}, \text{s}^{-1} \text{bar}^{-1}$	$1.74 \times 10^5$	$2.13 \times 10^5$	$2.56 \times 10^5$
		$k_{95}, \text{s}^{-1} \text{bar}^{-1}$	$6.61 \times 10^2$	$1.79 \times 10^3$	$3.91 \times 10^3$
	$E_{-95}^{\ddagger} = 10.0$	$A_{-95}, \text{s}^{-1}$	$2.03 \times 10^{13}$	$2.15 \times 10^{13}$	$2.25 \times 10^{13}$
96. $Z^-[\text{OFeO}]^+(\text{NO}_2)\{M=5\} \leftrightarrow Z^-[\text{OFeO}_2]^+\{M=4\} + \text{NO}(\text{g})$	$\Delta H_{96} = 12.2$	$K_{96}, \text{bar}$	$6.31 \times 10^3$	$2.82 \times 10^4$	$8.49 \times 10^4$
	$E_{96}^{\ddagger} = 12.0$	$A_{96}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{96}, \text{s}^{-1}$	$5.09 \times 10^8$	$2.52 \times 10^9$	$8.50 \times 10^9$
	$E_{-96}^{\ddagger} = 0.0$	$A_{-96}, \text{s}^{-1} \text{bar}^{-1}$	$8.07 \times 10^4$	$8.92 \times 10^4$	$1.00 \times 10^5$
97. $Z^-[\text{OFeONO}]^+\{M=5\} + \text{NO}_2(\text{g}) \leftrightarrow Z^-[\text{OFeONO}]^+(\text{NO}_2)\{M=6\}$	$\Delta H_{97} = -1.8$	$K_{97}, \text{bar}^{-1}$	$9.32 \times 10^{-7}$	$7.29 \times 10^{-7}$	$6.31 \times 10^{-7}$
	$E_{97}^{\ddagger} = 6.8$	$A_{97}, \text{s}^{-1} \text{bar}^{-1}$	$9.95 \times 10^5$	$1.28 \times 10^6$	$1.62 \times 10^6$
		$k_{97}, \text{s}^{-1} \text{bar}^{-1}$	$3.30 \times 10^3$	$9.62 \times 10^3$	$2.23 \times 10^4$
	$E_{-97}^{\ddagger} = 10.7$	$A_{-97}, \text{s}^{-1}$	$2.81 \times 10^{13}$	$2.90 \times 10^{13}$	$2.98 \times 10^{13}$
98. $Z^-[\text{OFeONO}]^+(\text{NO}_2)\{M=6\} \leftrightarrow Z^-[\text{O}_2\text{FeONO}]^+\{M=5\} + \text{NO}(\text{g})$	$\Delta H_{98} = 12.3$	$K_{98}, \text{bar}$	$5.60 \times 10^3$	$2.54 \times 10^4$	$7.70 \times 10^4$
	$E_{98}^{\ddagger} = 12.4$	$A_{98}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
		$k_{98}, \text{s}^{-1}$	$3.65 \times 10^8$	$1.89 \times 10^9$	$6.62 \times 10^9$
	$E_{-98}^{\ddagger} = 0.0$	$A_{-98}, \text{s}^{-1} \text{bar}^{-1}$	$6.51 \times 10^4$	$7.45 \times 10^4$	$8.59 \times 10^4$



TABLE 1: (Continued)

reaction	$E^{\ddagger,a} \Delta H^b$ (kcal/mol)	constant	$T$ (K)		
			600	700	800
99. $Z^-[\text{OFeO}_2\text{N}]^+\{M=5\} + \text{NO}_2(\text{g}) \leftrightarrow Z^-[\text{OFeO}_2\text{N}]^+(\text{NO}_2)\{M=6\}$	$\Delta H_{99} = -2.9$	$K_{99}, \text{bar}^{-1}$	$6.22 \times 10^{-5}$	$4.30 \times 10^{-5}$	$3.39 \times 10^{-5}$
	$E_{99}^{\ddagger} = 5.1$	$A_{99}, \text{s}^{-1} \text{bar}^{-1}$	$1.21 \times 10^7$	$1.63 \times 10^7$	$2.13 \times 10^7$
		$k_{99}, \text{s}^{-1} \text{bar}^{-1}$	$1.70 \times 10^5$	$4.22 \times 10^5$	$8.67 \times 10^5$
	$E_{-99}^{\ddagger} = 10.3$	$A_{-99}, \text{s}^{-1}$	$1.56 \times 10^{13}$	$1.63 \times 10^{13}$	$1.68 \times 10^{13}$
100. $Z^-[\text{OFeO}_2\text{N}]^+(\text{NO}_2)\{M=6\} \leftrightarrow Z^-[\text{O}_2\text{FeO}_2\text{N}]^+\{M=5\} + \text{NO}(\text{g})$	$\Delta H_{100} = 16.8$	$K_{100}, \text{bar}$	$2.73 \times 10^9$	$9.81 \times 10^9$	$2.56 \times 10^{10}$
	$E_{100}^{\ddagger} = 16.9$	$A_{100}, \text{s}^{-1}$	$1.18 \times 10^1$	$9.12 \times 10^1$	$4.13 \times 10^2$
		$k_{100}, \text{s}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
	$E_{-100}^{\ddagger} = 0.0$	$A_{-100}, \text{s}^{-1} \text{bar}^{-1}$	$8.48 \times 10^6$	$7.53 \times 10^7$	$3.94 \times 10^8$
101. $Z^-[\text{OFeO}_2\text{NO}]^+\{M=5\} + \text{NO}_2(\text{g}) \leftrightarrow Z^-[\text{OFeO}_2\text{NO}]^+(\text{NO}_2)\{M=6\}$	$\Delta H_{101} = -6.8$	$K_{101}, \text{bar}^{-1}$	$7.19 \times 10^5$	$8.25 \times 10^5$	$9.54 \times 10^5$
	$E_{101}^{\ddagger} = 1.2$	$A_{101}, \text{s}^{-1} \text{bar}^{-1}$	$2.91 \times 10^{-3}$	$1.25 \times 10^{-3}$	$6.89 \times 10^{-4}$
		$k_{101}, \text{s}^{-1} \text{bar}^{-1}$	$1.91 \times 10^7$	$2.56 \times 10^7$	$3.31 \times 10^7$
	$E_{-101}^{\ddagger} = 10.3$	$A_{-101}, \text{s}^{-1}$	$7.24 \times 10^6$	$1.11 \times 10^7$	$1.60 \times 10^7$
102. $Z^-[\text{OFeO}_2\text{NO}]^+(\text{NO}_2)\{M=6\} \leftrightarrow Z^-[\text{O}_2\text{FeO}_2\text{NO}]^+\{M=5\} + \text{NO}(\text{g})$	$\Delta H_{102} = 17.4$	$K_{102}, \text{bar}$	$1.45 \times 10^{13}$	$1.51 \times 10^{13}$	$1.55 \times 10^{13}$
	$E_{102}^{\ddagger} = 17.5$	$A_{102}, \text{s}^{-1}$	$2.49 \times 10^9$	$8.92 \times 10^9$	$2.32 \times 10^{10}$
		$k_{102}, \text{s}^{-1}$	$1.15 \times 10^1$	$9.58 \times 10^1$	$4.58 \times 10^2$
	$E_{-102}^{\ddagger} = 0.0$	$A_{-102}, \text{s}^{-1} \text{bar}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
103. $Z^-[\text{HOFeO}]^+\{M=5\} + \text{NO}_2(\text{g}) \leftrightarrow Z^-[\text{HOFeO}]^+(\text{NO}_2)\{M=6\}$	$\Delta H_{103} = -1.4$	$K_{103}, \text{bar}^{-1}$	$5.44 \times 10^6$	$5.15 \times 10^7$	$2.83 \times 10^8$
	$E_{103}^{\ddagger} = 6.9$	$A_{103}, \text{s}^{-1} \text{bar}^{-1}$	$4.73 \times 10^5$	$5.38 \times 10^5$	$6.17 \times 10^5$
		$k_{103}, \text{s}^{-1} \text{bar}^{-1}$	$1.90 \times 10^{-5}$	$1.56 \times 10^{-5}$	$1.41 \times 10^{-5}$
	$E_{-103}^{\ddagger} = 10.9$	$A_{-103}, \text{s}^{-1}$	$1.12 \times 10^7$	$1.55 \times 10^7$	$2.08 \times 10^7$
104. $Z^-[\text{HOFeO}]^+(\text{NO}_2)\{M=6\} \leftrightarrow Z^-[\text{HOFeO}_2]^+\{M=5\} + \text{NO}(\text{g})$	$\Delta H_{104} = 12.2$	$K_{104}, \text{bar}$	$3.50 \times 10^4$	$1.11 \times 10^5$	$2.76 \times 10^5$
	$E_{104}^{\ddagger} = 12.3$	$A_{104}, \text{s}^{-1}$	$1.67 \times 10^{13}$	$1.75 \times 10^{13}$	$1.82 \times 10^{13}$
		$k_{104}, \text{s}^{-1}$	$1.84 \times 10^9$	$7.12 \times 10^9$	$1.96 \times 10^{10}$
	$E_{-104}^{\ddagger} = 0.0$	$A_{-104}, \text{s}^{-1} \text{bar}^{-1}$	$2.56 \times 10^2$	$1.14 \times 10^3$	$3.40 \times 10^3$
		$k_{-104}, \text{s}^{-1} \text{bar}^{-1}$	$1.25 \times 10^{13}$	$1.46 \times 10^{13}$	$1.67 \times 10^{13}$
			$4.13 \times 10^8$	$2.11 \times 10^9$	$7.27 \times 10^9$
			$1.61 \times 10^6$	$1.85 \times 10^6$	$2.14 \times 10^6$
			$1.61 \times 10^6$	$1.85 \times 10^6$	$2.14 \times 10^6$

<sup>a</sup> Calculated activation energy including zero-point energy correction. <sup>b</sup> Calculated enthalpy averaged over 600–800 K. <sup>c</sup> The numbers presented in refs 21 and 22 for this reaction are wrong.

TABLE 2: Norm of the Gradient Difference at the Point of Spin-Surface Crossing and Thermally Averaged Landau–Zener Transition Probabilities at a Temperature of 600, 700, and 800 K<sup>a</sup>

reaction	$ \text{grad}(E_1) - \text{grad}(E_2) $ (kJ/mol/Å)	$P_{\text{LZ}}(H_{12} = 395 \text{ J/mol})$			$P_{\text{LZ}}(H_{12} = 825 \text{ J/mol})$		
		$T = 600 \text{ K}$	$T = 700 \text{ K}$	$T = 800 \text{ K}$	$T = 600 \text{ K}$	$T = 700 \text{ K}$	$T = 800 \text{ K}$
1. $Z^-[\text{FeO}]^+\{M=6\} + \text{NO}(\text{g}) \leftrightarrow Z^-[\text{FeONO}]^+\{M=5\}$	0.446	0.992	0.990	0.988	1.000	1.000	1.000
3. $Z^-[\text{FeO}]^+\{M=6\} + \text{NO}(\text{g}) \leftrightarrow Z^-[\text{FeO}_2\text{N}]^+\{M=5\}$	0.446	0.992	0.990	0.988	1.000	1.000	1.000
5. $Z^-[\text{FeO}]^+\{M=6\} + \text{NO}(\text{g}) \leftrightarrow Z^-[\text{OFeNO}]^+\{M=5\}$	0.446	0.992	0.990	0.988	1.000	1.000	1.000
6. $Z^-[\text{FeO}_2]^+\{M=6\} + \text{NO}(\text{g}) \leftrightarrow Z^-[\text{FeOONO}]^+\{M=5\}$	141	0.070	0.066	0.062	0.205	0.195	0.186
7. $Z^-[\text{FeOONO}]^+\{M=5\} \leftrightarrow Z^-[\text{FeO}]^+\{M=6\} + \text{NO}_2(\text{g})$	1.47	0.906	0.893	0.882	0.998	0.998	0.997
8. $Z^-[\text{OFeO}]^+\{M=6\} + \text{NO}(\text{g}) \leftrightarrow Z^-[\text{OFeONO}]^+\{M=5\}$	514	0.026	0.025	0.024	0.086	0.081	0.077
9. $Z^-[\text{OFeONO}]^+\{M=5\} \leftrightarrow Z^-[\text{FeO}]^+\{M=6\} + \text{NO}_2(\text{g})$	1.47	0.906	0.893	0.882	0.998	0.998	0.997
10. $Z^-[\text{OFeO}]^+\{M=6\} + \text{NO}(\text{g}) \leftrightarrow Z^-[\text{OFeO}_2\text{N}]^+\{M=5\}$	514	0.026	0.025	0.024	0.086	0.081	0.077
11. $Z^-[\text{OFeO}_2\text{N}]^+\{M=5\} \leftrightarrow Z^-[\text{FeO}]^+\{M=6\} + \text{NO}_2(\text{g})$	1.47	0.906	0.893	0.882	0.998	0.998	0.997
12. $Z^-[\text{OFeO}]^+\{M=6\} + \text{NO}(\text{g}) \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+\{M=5\}$	514	0.026	0.025	0.024	0.086	0.081	0.077
13. $Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} \leftrightarrow Z^-[\text{FeO}]^+\{M=6\} + \text{NO}_2(\text{g})$	1.47	0.906	0.893	0.882	0.998	0.998	0.997
20. $Z^-[\text{O}_2\text{FeONO}]^+\{M=5\} \leftrightarrow Z^-[\text{O}_2\text{FeONO}]^+\{M=7\}$	454	0.034	0.032	0.030	0.108	0.102	0.097
34. $Z^-[\text{O}_2\text{FeO}_2\text{N}]^+\{M=5\} \leftrightarrow Z^-[\text{O}_2\text{FeO}_2\text{N}]^+\{M=7\}$	164	0.072	0.068	0.064	0.211	0.201	0.192
48. $Z^-[\text{O}_2\text{FeO}_2\text{NO}]^+\{M=5\} \leftrightarrow Z^-[\text{O}_2\text{FeO}_2\text{NO}]^+\{M=7\}$	185	0.065	0.061	0.058	0.192	0.182	0.174
51. $Z^-[\text{OFeO}_2\text{NO}]^+\{M=5\} \leftrightarrow Z^-[\text{OFeO}]^+\{M=6\} + \text{NO}_2(\text{g})$	1.05	0.953	0.945	0.937	1.000	1.000	0.999
57. $Z^-[\text{Fe}(\text{OH})_2]^+(\text{NO})\{M=7\} \leftrightarrow Z^-[\text{Fe}(\text{OH})_2]^+(\text{NO})\{M=5\}$	1.87	0.671	0.742	0.725	0.981	0.977	0.973
68. $Z^-[\text{O}_2\text{FeOH}]^+\{M=5\} \leftrightarrow Z^-[\text{O}_2\text{FeOH}]^+\{M=7\}$	129	0.082	0.078	0.074	0.237	0.225	0.215
76. $Z^-[\text{OFeOH}_2]^+(\text{NO}_2)\{M=5\} \leftrightarrow Z^-[\text{OFeOH}_2]^+(\text{NO}_2)\{M=7\}$	10.1	0.399	0.382	0.367	0.771	0.752	0.736
82. $Z^-[\text{FeO}]^+(\text{ON})\{M=5\} \leftrightarrow Z^-[\text{FeO}]^+\{M=6\} + \text{NO}(\text{g})$	0.446	0.992	0.990	0.988	1.000	1.000	1.000
85. $Z^-[\text{FeONO}]^+(\text{ON})\{M=4\} \leftrightarrow Z^-[\text{FeONO}]^+\{M=5\} + \text{NO}(\text{g})$	11.7	0.400	0.383	0.368	0.772	0.753	0.737
88. $Z^-[\text{FeO}_2\text{N}]^+(\text{ON})\{M=4\} \leftrightarrow Z^-[\text{FeO}_2\text{N}]^+\{M=5\} + \text{NO}(\text{g})$	5.92	0.567	0.546	0.529	0.907	0.894	0.883
91. $Z^-[\text{FeO}_2\text{NO}]^+(\text{ON})\{M=4\} \leftrightarrow Z^-[\text{FeO}_2\text{NO}]^+\{M=5\} + \text{NO}(\text{g})$	12.4	0.381	0.364	0.350	0.751	0.732	0.715
94. $Z^-[\text{FeOH}]^+(\text{ON})\{M=4\} \leftrightarrow Z^-[\text{FeOH}]^+\{M=5\} + \text{NO}(\text{g})$	2.14	0.815	0.797	0.782	0.991	0.988	0.985

<sup>a</sup> Landau–Zener probabilities are calculated for spin–orbit coupling energies of  $H_{12} = 395$  and  $825 \text{ J/mol}$ . The reaction numbers are the same as those in Table 1.

## References and Notes

(1) Kapteijn, F.; Rodriguez-Mirasol, J.; Moulijn, J. A. *Appl. Catal., B* **1996**, 9, 25.

(2) Mul, G.; Pérez-Ramírez, J.; Kapteijn, F.; Moulijn, J. A. *Catal. Lett.* **2001**, 77, 7.

(3) Wood, B. R.; Reimer, J. A.; Bell, A. T. *J. Catal.* **2002**, 209, 151.

- (4) Zhu, Q.; van Teeffelen, R. M.; van Santen, R. A.; Hensen, E. J. *M. J. Catal.* **2004**, 221, 575.
- (5) Oi, J.; Obuchi, A.; Bamwenda, G. R.; Ogata, A.; Yagita, H.; Kushiya, S.; Mizuno, K. *Appl. Catal., B* **1997**, 12, 277.
- (6) Centi, G.; Galli, A.; Montanari, B.; Perathoner, S.; Vaccaria, A. *Catal. Today* **1997**, 35, 113.
- (7) Kögel, M.; Abu-Zied, B. M.; Schwefer, M.; Turek, T. *Catal. Commun.* **2001**, 2, 273.
- (8) Pérez-Ramírez, J.; Kapteijn, F.; Mul, G.; Moulijn, J. A. *J. Catal.* **2002**, 208, 211.
- (9) Boutarouch, M. N. D.; Cortés, J. M. G.; El Beggani, M. S.; de Lecea, C. S. M.; Pérez-Ramírez, J. *Appl. Catal., B* **2004**, 54, 115.
- (10) Sang, C.; Kim, B. H.; Lund, C. R. F. *J. Phys. Chem. B* **2005**, 109, 2295.
- (11) Pérez-Ramírez, J.; Mul, G.; Kapteijn, F.; Moulijn, J. A. *Kinet. Catal.* **2003**, 44, 639.
- (12) Pérez-Ramírez, J.; Kumar, M. S.; Brückner, A. *J. Catal.* **2004**, 223, 13.
- (13) Lobree, L. J.; Hwang, I. C.; Reimer, J. A.; Bell, A. T. *J. Catal.* **1999**, 186, 242.
- (14) Kucherov, A. V.; Shelef, M. *J. Catal.* **2000**, 195, 106.
- (15) Choi, S. H.; Wood, B. R.; Bell, A. T.; Janicke, M. T.; Ott, K. C. *J. Phys. Chem. B* **2004**, 108, 8970.
- (16) Choi, S. H.; Wood, B. R.; Ryder, J. A.; Bell, A. T. *J. Phys. Chem. B* **2003**, 107, 11843.
- (17) Pirngruber, G. D.; Luechinger, M.; Roy, P. K.; Cecchetto, A.; Smirniotis, P. J. *Catal.* **2004**, 224, 429.
- (18) Berlier, G.; Ricchiardi, G.; Bordiga, S.; Zecchina, A. *J. Catal.* **2005**, 229, 127.
- (19) Dubkov, K. A.; Ovanesyan, N. S.; Shteinman, A. A.; Starokon, E. V.; Panov, G. I. *J. Catal.* **2002**, 207, 341.
- (20) Overweg, A. R.; Cragg, M. W. J.; van der Kraan, A. M.; Arends, I. W. C. E.; Ribera, A.; Sheldon, R. A. *J. Catal.* **2004**, 223, 262.
- (21) Heyden, A.; Peters, B.; Bell, A. T.; Keil, F. J. *J. Phys. Chem. B* **2005**, 109, 1857.
- (22) Heyden, A.; Bell, A. T.; Keil, F. J. *J. Catal.* **2005**, 233, 26.
- (23) Heyden, A. Theoretical investigation of the nitrous oxide decomposition over iron zeolite catalysts. Ph.D. Thesis, Department of Chemical Engineering, Hamburg University of Technology, 2005.
- (24) Zhu, Q.; Mojet, B. L.; Janssen, R. A. J.; Hensen, E. J. M.; van Grondelle, J.; Magusin, P. C. M. M.; van Santen, R. A. *Catal. Lett.* **2002**, 81, 205.
- (25) Kiwi-Minsker, L.; Bulushev, D. A.; Renken, A. *Catal. Today* **2004**, 91, 165.
- (26) Joyner, R.; Stockenhuber, M. *J. Phys. Chem. B* **1999**, 103, 5963.
- (27) Hensen, E. J. M.; Zhu, Q.; Hendrix, M. M. R. M.; Overweg, A. R.; Kooyman, P. J.; Sychev, M. V.; van Santen, R. A. *J. Catal.* **2004**, 221, 560.
- (28) Battiston, A. A.; Bitter, J. H.; Koningsberger, D. C. *Catal. Lett.* **2000**, 66, 75.
- (29) Battiston, A. A.; Bitter, J. H.; de Groot, F. M. F.; Overweg, A. R.; Stephan, O.; van Bokhoven, J. A.; Kooyman, P. J.; van der Spek, C.; Vankó, G.; Koningsberger, D. C. *J. Catal.* **2003**, 213, 251.
- (30) Battiston, A. A.; Bitter, J. H.; Heijboer, W. M.; de Groot, F. M. F.; Koningsberger, D. C. *J. Catal.* **2003**, 215, 279.
- (31) Battiston, A. A.; Bitter, J. H.; Koningsberger, D. C. *J. Catal.* **2003**, 218, 163.
- (32) Marturano, P.; Drozdová, L.; Kogelbauer, A.; Prins, R. *J. Catal.* **2000**, 192, 236.
- (33) Marturano, P.; Drozdová, L.; Pirngruber, G. D.; Kogelbauer, A.; Prins, R. *Phys. Chem. Chem. Phys.* **2001**, 3, 5585.
- (34) Jia, J.; Sun, Q.; Wen, B.; Chen, L. X.; Sachtler, W. M. H. *Catal. Lett.* **2002**, 82, 7.
- (35) Sun, K.; Xia, H.; Hensen, E.; van Santen, R.; Li, C. *J. Catal.* **2006**, 238, 186.
- (36) Krishna, K.; Makkee, M. *Catal. Lett.* **2006**, 106, 183.
- (37) Panov, G. I.; Sobolev, V. I.; Kharitonov, A. S. *J. Mol. Catal.* **1990**, 61, 85.
- (38) Chang, Y.-F.; McCarty, J. G.; Zhang, Y. L. *Catal. Lett.* **1995**, 34, 163.
- (39) Nobukawa, T.; Tanaka, S.; Ito, S.; Tomishige, K.; Kameoka, S.; Kunimori, K. *Catal. Lett.* **2002**, 83, 5.
- (40) El-Malki, E. M.; van Santen, R. A.; Sachtler, W. M. H. *Microporous Mater.* **2000**, 35–36, 235.
- (41) Kiwi-Minsker, L.; Bulushev, D. A.; Renken, A. *J. Catal.* **2003**, 219, 273.
- (42) Pirngruber, G. D. *J. Catal.* **2003**, 219, 456.
- (43) Wood, B. R.; Reimer, J. A.; Bell, A. T.; Janicke, M. T.; Ott, K. C. *J. Catal.* **2004**, 224, 148.
- (44) Pérez-Ramírez, J.; Kapteijn, F. *Catal. Commun.* **2003**, 4, 333.
- (45) Kaucký, D.; Sobalík, Z.; Schwarze, M.; Vondrová, A.; Wichterlová, B. *J. Catal.* **2006**, 238, 293.
- (46) Bulushev, D. A.; Renken, A.; Kiwi-Minsker, L. *J. Phys. Chem. B* **2006**, 110, 305.
- (47) Pirngruber, G. D.; Pieterse, J. A. Z. *J. Catal.* **2006**, 237, 237.
- (48) Chen, H.-Y.; Voskoboinikov, T.; Sachtler, W. M. H. *J. Catal.* **1998**, 180, 171.
- (49) Grubert, G.; Hudson, M. J.; Joyner, R. W.; Stockenhuber, M. *J. Catal.* **2000**, 196, 126.
- (50) El-Malki, E. M.; van Santen, R. A.; Sachtler, W. M. H. *J. Catal.* **2000**, 196, 212.
- (51) Sang, C.; Lund, C. R. F. *Catal. Lett.* **2000**, 70, 165.
- (52) Sang, C.; Lund, C. R. F. *Catal. Lett.* **2001**, 73, 73.
- (53) Kiwi-Minsker, L.; Bulushev, D. A.; Renken, A. *Catal. Today* **2005**, 110, 191.
- (54) Nováková, J.; Sobalík, Z. *Catal. Lett.* **2005**, 105, 169.
- (55) Olson, D. H.; Kokotailo, G. T.; Lawton, S. L.; Meier, W. M. *J. Phys. Chem.* **1981**, 85, 2238.
- (56) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, 98, 11623.
- (57) Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, 102, 346.
- (58) Koch, W.; Holthausen, M. C. *A chemist's guide to density functional theory*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2001.
- (59) Yoshizawa, K.; Shiota, Y.; Yamabe, T. *J. Chem. Phys.* **1999**, 111, 538.
- (60) Zilberberg, I.; Gora, R. W.; Zhidomirov, G. M.; Leszczynski, J. *J. Chem. Phys.* **2002**, 117, 7153.
- (61) Zygmunt, S. A.; Mueller, R. M.; Curtiss, L. A.; Iton, L. E. *THEOCHEM* **1998**, 430, 9.
- (62) Furche, F.; Perdew, J. P. *J. Chem. Phys.* **2006**, 124, 044103.
- (63) Becke, A. D. *Phys. Rev. A* **1988**, 38, 3098.
- (64) Perdew, J. P. *Phys. Rev. B* **1986**, 33, 8822.
- (65) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, 242, 652.
- (66) Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. *Theor. Chem. Acc.* **1997**, 97, 119.
- (67) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, 100, 5829.
- (68) Kestner, N. R.; Combariza, J. E. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; Wiley-VCH: New York, 1999; Vol. 13.
- (69) Van Duijneveldt, F. B.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Lenthe, J. H. *Chem. Rev.* **1994**, 94, 1873.
- (70) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, 162, 165.
- (71) Ahlrichs, R. v.; Armin, M. In *Methods and Techniques in Computational Chemistry: METECC-95*; Clementi, E., Corongiu, G., Eds.; STEF: Cagliari, 1995.
- (72) Peters, B.; Heyden, A.; Bell, A. T.; Chakraborty, A. *J. Chem. Phys.* **2004**, 120, 7877.
- (73) Heyden, A.; Bell, A. T.; Keil, F. J. *J. Chem. Phys.* **2005**, 123, 224101.
- (74) McQuarrie, D. A. *Statistical Mechanics*; Harper Collins Publisher: New York, 1973.
- (75) Stern, A. E.; Eyring, H. *J. Chem. Phys.* **1935**, 3, 778.
- (76) Danovich, D.; Shaik, S. *J. Am. Chem. Soc.* **1997**, 119, 1773.
- (77) Nobukawa, T.; Yoshida, M.; Kameoka, S.; Ito, S.; Tomishige, K.; Kunimori, K. *Stud. Surf. Sci. Catal.* **2004**, 154, 2514.
- (78) Che, M.; Tench, A. *J. Adv. Catal.* **1983**, 32, 1.
- (79) Bulushev, D. A.; Kiwi-Minsker, L.; Renken, A. *J. Catal.* **2004**, 222, 389.
- (80) Pérez-Ramírez, J. Catalyzed N<sub>2</sub>O activation. Promising (new) catalysts for abatement and utilization; Ph.D. Thesis, Technische Universiteit Delft, 2002.
- (81) Gonzalez, M.; Valero, R.; Sayos, R. *Chem. Phys. Lett.* **2001**, 343, 119.
- (82) <http://www.hlrn.de>.