The Molecular Origins of NO Selectivity in the Thermal Reduction of NO_x by NH_3

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Introduction

Thermal deNO_x process is an effective way for "lean" NO_x (x= 1, 2) control for stationary sources and attracting serious attention for selective catalytic reduction of NO_x by NH_3 from mobile-sources. The fundamental mechanism underlying the thermal deNO_x chemistry is the selective reduction of NO_x over a large excess of O_2. This mechanism involves generation of the amino (NH_2) radical through chain reactions that involve O atoms and OH radicals,[1, 2] and the NH_2 is reacting directly with NO to ultimately produce N_2. Competition between NO and O_2 for the "activated" NH_2 reductant is thus inherent to the overall chemistry. The reactions of NH_2 with NO and O_2 have been studied extensively both theoretically and experimentally: [3,4,5,6,7,8,9,10,11]

$$NH_2 + NO \rightarrow \text{Products} \qquad (1)$$
$$NH_2 + O_2 \rightarrow \text{Products} \qquad (2)$$

Fortunately, the rate of reaction (1) (10^{-12} cm^3 molecule^{-1} s^{-1} at 2000 K) is observed to be 10 orders of magnitude faster than that of reaction (2) (10^{-21} cm^3 molecule^{-1} s^{-1} at room temperature) although they proceed through topologically similar channels. The primary channels of reaction (1) are: [4,5,7,12]

$$NH_2 + NO \rightarrow N_2 + H_2O \qquad (3)$$
$$\rightarrow HN_2 + OH \qquad (4)$$

The reaction (2) analogs to channels (3) and (4) are:

$$NH_2 + O_2 \rightarrow NO + H_2O \qquad (5)$$
$$\rightarrow HNO + OH \qquad (6)$$

Although reactions (1) and (2) have been studied individually in great detail, little attention has been paid to understanding the origins of the very different kinetics of these superficially similar reactions. In this paper, the potential energy surfaces of these two reactions have been analyzed and the origin of the NO selectivity is attributed to the much greater stability of the initial H_2NNO adduct relative to H_2NOO radical with analysis of their electronic structures.

Computational Method

DFT calculations were performed with the Amsterdam Density Functional (ADF) package with the spin-polarized BLYP approximation. [13,14,15,16] A valence double-ζ plus polarization Slater-type basis was used on all atoms.

Results and Discussion

Figures 1 and 2 summarize the key potential energy surface for reactions (1) and (2) in which analogous steps of both reactions are considered together in parallel for comparison.

The mechanistic origins of the NO selectivity that underpin thermal deNO_x are readily apparent from Figure 1. NH_3 itself is unreactive towards NO and O_2; rather, NH_3 is activated for reaction by removal of an H atom to produces NH_2 radicals. NH_2 radical forms a relatively strongly bound (54 kcal mol^{-1} from BLYP) adduct with NO. Particularly favorable electronic interactions produce strong σ and π bonding in the molecular structure of H_2NNO. In contrast, NH_2 radical forms a relatively weakly bound adduct with O_2 (15 kcal mol^{-1} from BLYP): O_2 has one more electron and less accessible 2π acceptor levels than NO, and H_2NOO radical has neither the strong σ nor π bonds of H_2NNO. As seen in Figures 1 and 2, beyond the adduct formation step the potential energy surfaces for the two reactions are superficially quite similar. The paths to the thermodynamic products involve a sequence of H-transfer, isomerization, and decomposition steps, the most highly activated of which is the initial $H_2NXO \rightarrow HNXOH$ H-transfer (X=N, O). These steps compete with backwards decomposition to reactants, and the balance between forward and backward steps controls the overall reaction rate. For strongly bound H_2NNO, the forward reaction steps are all at lower energy than the entrance channel, and essentially all H_2NNO formed react forward to products in what is in effect a single elementary step. [17] In contrast, weakly bound H_2NOO radical is shifted upwards in energy such that the forward reaction channels involve energy barriers greater than the energy to decompose back to reactants, and only at high temperatures do any of the forward reaction channels occur at an appreciable rate. [18] Remarkably, then, the difference in initial adduct stability alone accounts for the much different rates of the NH_2 + NO and NH_2 + O_2 reactions.

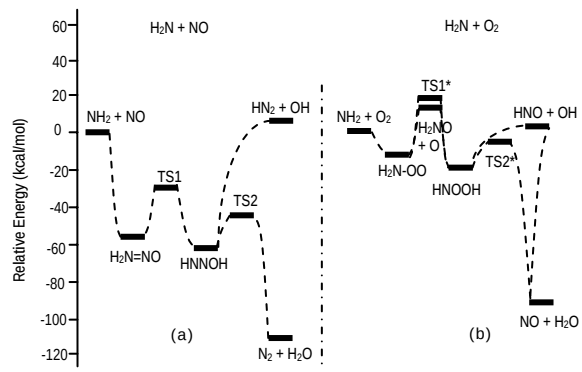

Figure 1. BLYP-calculated potential energy surfaces for reactions (a) NH_2 + NO and (b) NH_2 + O_2. HNXOH (X = N, O) isomerization details hidden for clarity

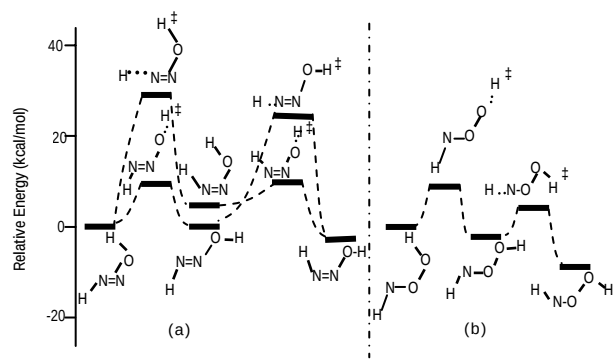

Figure 2. BLYP-calculated potential energy surfaces for isomerization of (a) HNNOH and (b) HNOOH.

It is interesting to consider the generality of this difference in reactivity between NO and O_2. Table 2 compares the R–NO and R–O_2 bond dissociation energies for a number of common alkyl and heteroatomic free radicals R for which data is available. NO is found to readily bind to all the radicals within this sample set: bond strengths range from around 40 to less than 60 kcal mol^{-1}, with the strongest bonds tending to be π donor radicals, such as NH_2 or OH radical. For practical purposes NO does not thermochemically discriminate within this set, and consistent with the behavior typical

Table 1. Comparison of 298 K R–NO and R–O_2 bond strengths (kcal mol^{-1}). All experimental values from ref. [19]

	R–NO	R–O_2	Δ
H	47	49	–2
CH_3	40	33	7
i-C_3H_7	37	37	0
CF_3	43	37[a]	6
HO	49	7[b]	42
CH_3O	42	–4[c]	46
F	57	13	44
Cl	38	6	33
NH_2	48[d]/54[e]	0[e]/15[f]	~40-50

a. Calculated, ref. [20] b. Calculated, ref. [21] c. Calculated, ref. [22] d. Calculated, ref. e. Calculated, ref. f. Calculated, this work.

for free radical combination reactions, the corresponding R + NO high pressure limiting rate constants are large — typically within an order of magnitude of the gas-kinetic limit.[19] O_2 presents an interesting contrast. Within the H and alkyl radical group, the R–O_2 and R–NO bond strengths are comparable and the difference between the two is uniformly small. Consistent with this, the R + O_2 reaction rate constants are comparable to those for R + NO, and thus these R-radicals exhibit little inherent selectivity in reactions with NO over O_2; i.e. neither CH_3 radical nor H radical will selectively combine with or reduce NO in the presence of O_2.

The heteroatom (halogen, O, and N)-centered radicals behave much differently. Here the R–O_2 bond energies are very small—so small that accurate experimental determination is difficult, and the most reliable estimates tend to come from first-principles calculations. While there are uncertainties in some of these R–O_2 bond energies, what is not uncertain is that the bonds are on the order of 40 kcal mol^{-1} weaker the R–NO ones. Because these are association reactions, the relative bond energies dominate the relative reaction rate constants, and the corresponding R + O_2 reactions are similarly much slower than the R + NO ones.[23] (Precise reaction rate comparisons are complicated by the existence of multiple reaction channels, large sensitivities to pressure, temperature, and diluent, and the limited availability of data for the slow R + O_2 reactions.) Thus, these heteroatomic radicals are selective in their reactions with NO over O_2, not because of some inherent preference for NO but rather because of inherent unreactivity towards O_2. While we have only considered in detail the NH_2 radical case here, it is likely that the slow reactions of the other heteroatomic radicals with O_2 have similar explanations in terms of π repulsions and poor σ bonding. Any of these heteroatomic radicals will selectively combine with NO in the presence of O_2; NH_2 radical is particularly useful because reaction with NO ultimately leads to reduction to N_2.

Conclusions

Any useful system for catalytically reducing NO_x in lean exhaust must have as its basis very high selectivity for reactions of reductant with NO_x over O_2, both to counterbalance the great thermodynamic driving force for oxidation reactions and to overcome the large disparities in concentration between small amounts of NO_x and large amounts of background O_2. Within a limited range of conditions, this selectivity is achieved without catalysts in the thermal deNO_x process. NH_2 radicals generated in situ from NH_3 are many orders of magnitude more reactive towards NO than O_2. NH_2 radicals form a strong bond with NO to produce H_2NNO, which provides an entrance into rearrangement channels ultimately yielding the desired products N_2 and H_2O. What is unusual in this system, though, is not the fast rate of the NH_2 + NO reaction—in fact, this reaction proceeds at rates comparable to other radical + NO reactions. Rather, the key feature that underpins thermal deNO_x is the very slow reaction of NH_2 radical with O_2. The H_2NOO adduct is weakly bound, and fragmentation back to reactants competes very effectively with channels ultimately leading to NO and H_2O. This weak binding and slow reaction is characteristic of O_2 reactions with heteroatomic radicals, such as F, OH or NH_2, but not of reactions with H or carbon-centered radicals. Its origins lie in π repulsions and weak σ bonding between O_2 and electron-rich radicals.

These observations provide a different perspective on the selective catalytic reduction of NO_x with NH_3 or hydrocarbons. Effective catalysts clearly must be able to bind and activate reductants and to maintain or enhance selectivity in reductant reactivity between NO and O_2. While mechanistic emphasis tends to be placed on understanding the reactivity of NO_x, the absence of reactivity with O_2 is at least as important to understand.

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References

1 Miller, J. A.; Bowman C. T. *Progress in Energy and Combustion Science*, **1989**, *15,* 287.
2 Lyon, R. K. *Diesel Engine Emissions Reduction (DEER) Workshop*, **2001**.
3 Wolf , M.; Yang, D. L.; Durant J. L. *J. Phys. Chem. A* **1997**, 101, 6243.
4 Vandooren , J.; Bian, J.; Tiggelen, P. J. *Combustion & Flame,* **1994,** 98, 402.
5 Diau, E. W.-G; Smith, S. C. *J. Chem. Phys.*, **1997,** 106, 9263.
6 Sumathi , R.; Peyerimhoff, S. D. *J. Chem. Phys.*, **1998**, 108, 5510.
7 Marcy, P. T.; Heard , E. D.; Leone, R. S. *J. Phys. Chem. A,* **2002**, 106, 8249.
8 Park, J.; Lin, M. C. *J. Phys. Chem. A*, **1997**, 101, 5.
9 Miller, J. A.; Glarborg, P. *Int J. Chem. Kinet.*, **1999**, 31, 757.
10 Diau, E. W.; Yu, T.; Wagner, M. A. G.; Lin, M. C. *J. Phys. Chem.*, **1994**, 98, 4034.
11 Yamasaki , K.; Watanabe, A.; Tanaka, A.; Sato, M.; Tokue, I. *J. Phys. Chem.*, **2002**, 106, 6563.
12 Votsmeier, M.; Song, S.; Hanson, R. K.; Bowman, C. T. *J. Phys. Chem. A*, **1999**, 103, 1566.
13 Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.*, **1973**, 41, 1.
14 Becke, A. D. *Phys. Rev. A*, **1998**, 38, 3098.
15 Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B, 1988, 37, 785.
16 Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.*, **1989**, 157, 200.
17 Miller, J. A.; Klippenstein, S. J. *J. Phys. Chem. A*, **2000**, 104, 2061.
18 Bozzelli, J. W.; Dean, A. M. *J. Phys. Chem.*, **1989**, 93, 1058.
19 NIST Chemical Kinetics Database, Hhttp://kinetics.nist.govH.
20 Schneider, W. F.; Wallington, T. J. **J. Phys. Chem.**, **1993**, 97, 12783.
21 Denis, P. A.; Kieninger, M. O.; Ventura, N.; Cachau, R. E.; Diercksen, G. H. F. *Chem. Phys. Lett.*, **2002**, 365, 440.
22 Jungkamp, P. W.; Seinfeld, J. H. *Chem. Phys. Lett.*, **1996**, 257, 15.
23 Ruscic, B.; Berkowitz, J. *J. Chem. Phys.*, **1991**, 95, 4378.