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COMMUNICATION

On The Selective Cleavage of Nitrous Oxide by Metal-Amide Complexes

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Abstract Computational investigation of nitrous oxide cleavage by metal-amide systems has shown that a bimetallic mechanism is compatible with the remarkable experimental observation of selective N-N scission by a di-molybdenum system, and that the interplay between the bonding energetics of reactants and products can both provide an explanation for the observed cleavage selectivity and be utilized to modify and design chemical behaviour.

The chemistry of nitrous oxide has attracted considerable attention, since this triatomic molecule plays a significant environmental role as a potent greenhouse gas and a contributor to stratospheric ozone depletion [1]. The fact that both processes mediated by the enzyme nitrous oxide reductase and potential remediation methods using heterogeneous catalysts involve transition elements in a central capacity "has stimulated great interest in developing and understanding [N_2O] decomposition, particularly through the use of transition metal promoters" [1]. Also, research focusing on the chemistry of nitrous oxide in the presence of transition metal systems has been described as particularly important in the sense that these investigations are "likely to inform efforts to design more effective catalysts for remediation [purposes]" [1].

Experimental data [2] indicate that the N-N bond (dissociation energy ~481 kJ mol^{-1}) is significantly stronger than the N-O bond (dissociation energy ~167 kJ mol^{-1}), and metal-mediated decomposition of nitrous oxide typically involves preferential activation and scission of the N-O over N-N bond [1]. A surprising exception to this observation was first reported by Cummins and coworkers in 1995 [3] and subsequently thoroughly described in 2001 [4]. These researchers showed that, in the presence of molybdenum-amide complexes with the [$Mo(NRAr)_3$ – R = $C(CD_3)_2CH_3$, Ar = 3,5-$C_6H_3Me_2$] composition, nitrous oxide undergoes selective N-N bond cleavage and the exclusive products of the reaction are molybdenum nitride [N-$Mo(NRAr)_3$] and nitrosyl [ON-$Mo(NRAr)_3$] complexes. The experimental evidence presented by Cummins and coworkers suggests that the "simplest mechanism consistent with all the data is a post-rate-determining bimetallic scission of the nitrous oxide molecule" [4]. These authors also described their conclusion as "intriguing when juxtaposed with the contrary results" of the computational study performed by Morokuma and coworkers [5], whose calculations favour a monometallic mechanism as explanation for the observed N-N selective cleavage, and also indicate that a bimetallic mechanism should favour N-O over N-N scission.

In this work, we have investigated the activation and scission of nitrous oxide by a di-molybdenum tris-amide system by means of an approach successfully employed in our previous computational studies of metal-mediated functionalization of a variety of small molecules [6-11]. Our results show that a bimetallic mechanism can lead to selective N-N cleavage of nitrous oxide provided certain specific structural and bonding properties are present, and that the interplay between the bonding energetics of reactants and products can both provide an explanation for the observed cleavage selectivity and be utilized to modify and design chemical behaviour. The latter case is exemplified by use of a molybdenum-niobium system, which leads to reversal of the cleavage selectivity and thus preferential scission of the N-O over N-N bond in nitrous oxide.

Results and Discussion

Our calculations have focused on a "bimetallic mechanism" for the selective cleavage of nitrous oxide by metal-amide complexes, which can be described in terms of the following reaction sequence,

(1) $L_3M + NNO \leftrightarrow L_3M\text{-}NNO$ [encounter complex]

(2) $L_3M\text{-}NNO + ML_3 \leftrightarrow L_3M\text{-}NNO\text{-}ML_3$ [dinuclear species]

(3) $L_3M\text{-}NNO\text{-}ML_3 \leftrightarrow L_3M\text{-}NN + O\text{-}ML_3$ [N-O selective cleavage]
$L_3M\text{-}NNO\text{-}ML_3 \leftrightarrow L_3M\text{-}N + ON\text{-}ML_3$ [N-N selective cleavage]

in which the ligand [L] corresponds to [NH_2], [NMe_2], [NMePh], or [NRAr, R = ^{t}Bu, Ar = 3,5-$C_6H_3Me_2$]. In this work, we have not considered the "monometallic mechanism" explored in previous studies of the reactions of nitrous oxide with metal-amide complexes [5,12], since this pathway is not supported by experimental evidence [4], but some details are given as supplementary material.

Our initial calculations used simple [NH_2] models in order to test the effects of methodological variables on the calculated results. A more extensive description is given as supplementary material, but the most significant outcome of these tests can be summarized by noting that, on a qualitative level, the general characteristics of the

reaction profile, including structural and spin-state details, are not affected by the choice of density functional methodology. Although individual numerical results may exhibit some variation, the overall trends and conclusions are not dependent on the technical aspects of the approach used in performing the calculations.

These [NH_2] model calculations indicate that all steps in the reaction profile are characterized by favourable energetics, and a bimetallic mechanism does lead to selective cleavage of the N-N bond, and thus exclusively to molybdenum-nitride and molybdenum-nitrosyl products, provided the molecular geometry of each product is not allowed to undergo complete relaxation but constrained to possess trigonal (C_{3v}) symmetry, which represents a realistic approximation to the configurations imposed by the large-sized terminal groups in the actual [NRAr] case.

Detailed calculations for the reaction sequence described by equations (1) through (3) were carried out using [NMe_2] and [NMePh] ligands, which represent satisfactory models for experimental systems involving, respectively, bis-alkyl amide or alkyl-aryl amide complexes. Also, although an investigation of the complete reaction profile was not feasible for the actual experimental system, some calculations were nonetheless performed using [NRAr] ligands, with full optimizations achieved for all mononuclear species, but with some constraints required for the dinuclear species due to the large size and geometric complexity resulting from the six [NRAr] groups.

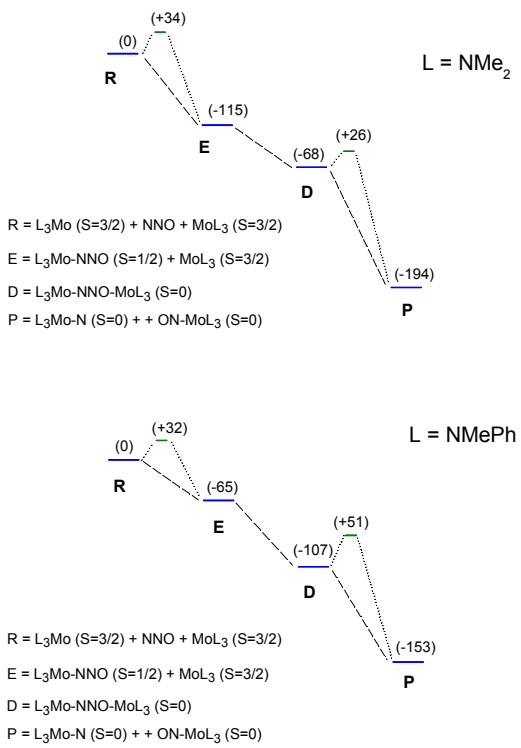

Figure 1. Reaction profile energetics (in kJ mol^{-1}) from calculations involving [NMe_2] and [NMePh] ligand systems.

The general characteristics of the reaction profiles obtained with the [NMe_2] and [NMePh] models (Figure 1) are consistent with the experimental results and analysis reported by Cummins and coworkers [4], if the structural properties of the various [NMe_2] and [NMePh] species are constrained to be compatible with those of the actual [NRAr] species, which exhibit geometric configurations that are either close to or deviate moderately from trigonal symmetry. Relevant structural schemes are given as supplementary material.

All individual reactions are energetically favourable and N-N over N-O scission is preferred at the cleavage step. Barriers of similar magnitude are found for encounter complex formation and N-N bond breaking, whereas formation of the dinuclear species appears barrierless. The encounter complex step involves intersystem crossing from the spin-quartet to spin-doublet potential energy surfaces with a barrier of ~33 kJ mol^{-1}, whilst the barrier for N-N bond breaking ranges between ~26 kJ mol^{-1} (for a more constrained geometry in the [NMe_2] case) and ~51 kJ mol^{-1} (for a more relaxed geometry in the [NMePh] case). Additional results in the form of selected potential energy curves are given as supplementary material.

Results corresponding to selective cleavage energetics are summarized in Table 1. In agreement with experimental observations, unconstrained calculations on the actual [NRAr] system favour N-N over N-O scission (by ~24 kJ mol^{-1}). Also, results for the [NMe_2] and [NMePh] model systems highlight the central effects arising from the structural properties of the terminal groups, since selective N-N cleavage is predicted only if trigonal (C_{3v}) symmetry constraints are imposed on the geometry of the products. In contrast, unconstrained calculations involving [NMe_2] and [NMePh] ligands slightly favour N-O over N-N scission. It should be noted that the greater difference between N-N and N-O cleavage energetics calculated in the [NMe_2] and [NMePh] (C_{3v}) cases, relative to the [NRAr] (C_1) case, is due to the fact that, for the latter system, geometric configurations are relatively close to, but do not strictly show, trigonal symmetry. Additional results including zero-point and entropy contributions are given as supplementary material.

Table 1. Energetics (in kJ mol^{-1}) of the [L_3M + NNO + ML_3 ↔ Products] process for [NMe_2], [NMePh], and [NRAr] ligand systems.

Ligand	Products	Energy	Symmetry
NMe_2	L_3Mo-NN + O-MoL_3	-301	C_{3v}
	L_3Mo-N + ON-MoL_3	-377	C_{3v}
NMePh	L_3Mo-NN + O-MoL_3	-245	C_{3v}
	L_3Mo-N + ON-MoL_3	-325	C_{3v}
NRAr	L_3Mo-NN + O-MoL_3	-391	C_1
	L_3Mo-N + ON-MoL_3	-415	C_1
NRAr	L_3Mo-NN + O-NbL_3	-526	C_1
	L_3Mo-N + ON-NbL_3	-405	C_1

Analyses [13,14] of thermochemical results for metal-mediated diatomic-molecule cleavage have suggested that the thermodynamic driving force for these processes is provided by the strength of the metal-element bonds in the products. This concept can also be applied to the present case, as shown by the bond energy analysis presented in Table 2. These results indicate that, although (in isolated nitrous oxide) the calculated bond energy of the N-N interaction is ~268 kJ mol^{-1} greater than that of the N-O interaction, the rather stronger N-N bond is selectively cleaved by a di-molybdenum system because much larger bonding stabilization is provided by the products of N-N than N-O cleavage. Given that the

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Mo-O and Mo-N bonding interactions exhibit similar strength, the primary reason appears to lie in the notably weak bonding nature of the Mo-NN product, compared to the Mo-NO product.

The fact that the bonding stabilization provided by the products has a strong influence on small-molecule cleavage thermochemistry can be used to modify the composition of the metal-based system and achieve a different outcome for the overall process. This concept is illustrated by the results (also included in Tables 1 and 2) for a molybdenum-niobium system, which favours selective N-O over N-N scission (by ~121 kJ mol^{-1} in the [NRAr] case), in contrast to the preferred N-N over N-O scission in the experimentally known di-molybdenum system. Reversal of the cleavage selectivity can be predicted on the basis that the strength of Nb-O bonding is known to be significantly greater than that of Mo-O bonding [14] (thereby leading to similar overall stabilization for the products of N-O and N-N scission) and that intrinsic bond breaking energetics are much more favourable in the N-O than N-N case.

Table 2. Bonding Energetics (in kJ mol^{-1}) of the N-N and N-O cleavage products for [NRAr] ligand systems (from calculations using Becke 1988 exchange and Perdew 1986 correlation functionals).

Metal System	Products	Bond Energy	Symmetry
Mo, Mo	L_3Mo-NN	40	C_1
	L_3Mo-O	644	C_1
	L_3Mo-N	628	C_1
	L_3Mo-NO	348	C_1
Mo, Nb	L_3Mo-NN	40	C_1
	L_3Nb-O	870	C_1
	L_3Mo-N	628	C_1
	L_3Nb-NO	357	C_1

Additional results describing the effects of intrinsic bonding stability on product selectivity, which were obtained from an energy decomposition analysis conducted for the both the di-molybdenum and molybdenum-niobium [NMePh] systems (using C_{3v} symmetry), are given as supplementary material.

Conclusion

We have used density functional methodology to investigate the cleavage of nitrous oxide by metal-amide systems, and shown that a bimetallic mechanism is compatible with the remarkable experimental observation of selective N-N scission by a di-molybdenum system if certain structural requirements are satisfied, namely, the geometric configuration of the amide terminal groups is close to or deviates only moderately from trigonal symmetry. An analysis of bonding energetics has indicated that N-N scission is favoured over N-O scission because, in the former case, the [L_3Mo-N] and [L_3Mo-NO] products provide considerably greater stabilization, thereby compensating for the much stronger nature of the N-N than N-O bond in nitrous oxide. The strength of metal-element bonding in the products can also be used to design systems that lead to reversed cleavage selectivity, namely, N-O over N-N scission, as illustrated by the results for a molybdenum-niobium system. In this case, selective N-O cleavage is achieved as a consequence of the significantly greater stabilization provided by Nb-O than Mo-O bonding in conjunction with the intrinsic relative weakness of the N-O bond in nitrous oxide.

Computational Methodology

All calculations were performed with the Amsterdam Density Functional package, http://www.scm.com [15,16]. Calculations were performed in an unrestricted fashion using default convergence parameters and the GGA Becke-Perdew density functional and the TZP all-electron basis set. Relativistic corrections were incorporated using the Zeroth-Order Regular Approximation (ZORA). The Conductor-like Screening Model (COSMO) was used for the treatment of solvation effects, with toluene as the solvent All relevant details are given as supplementary material.

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Notes and references

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Electronic Supplementary Information (ESI) available: methodology details, structural diagrams, free energy calculations, potential energy curves, bond energy decomposition analysis, monometallic mechanism, cartesian coordinates. See DOI: 10.1039/c000000x/

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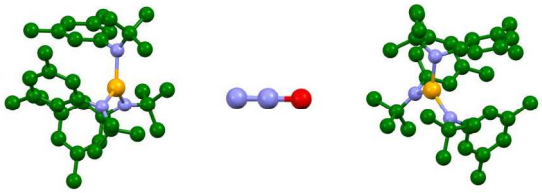
Graphical Abstract

On the Selective Cleavage of Nitrous Oxide by Metal-Amide Complexes

G.Cavigliasso, A. Criddle, H-S. Kim, R. Stranger, B. F. Yates

The remarkable selective cleavage of nitrous oxide by metal-amide systems, involving a bimetallic mechanism, has been investigated using computational methodology and rationalized on the basis of the interplay of structural and bonding factors.



$(NRAr)_3Mo + NNO + Mo(NRAr)_3$

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