



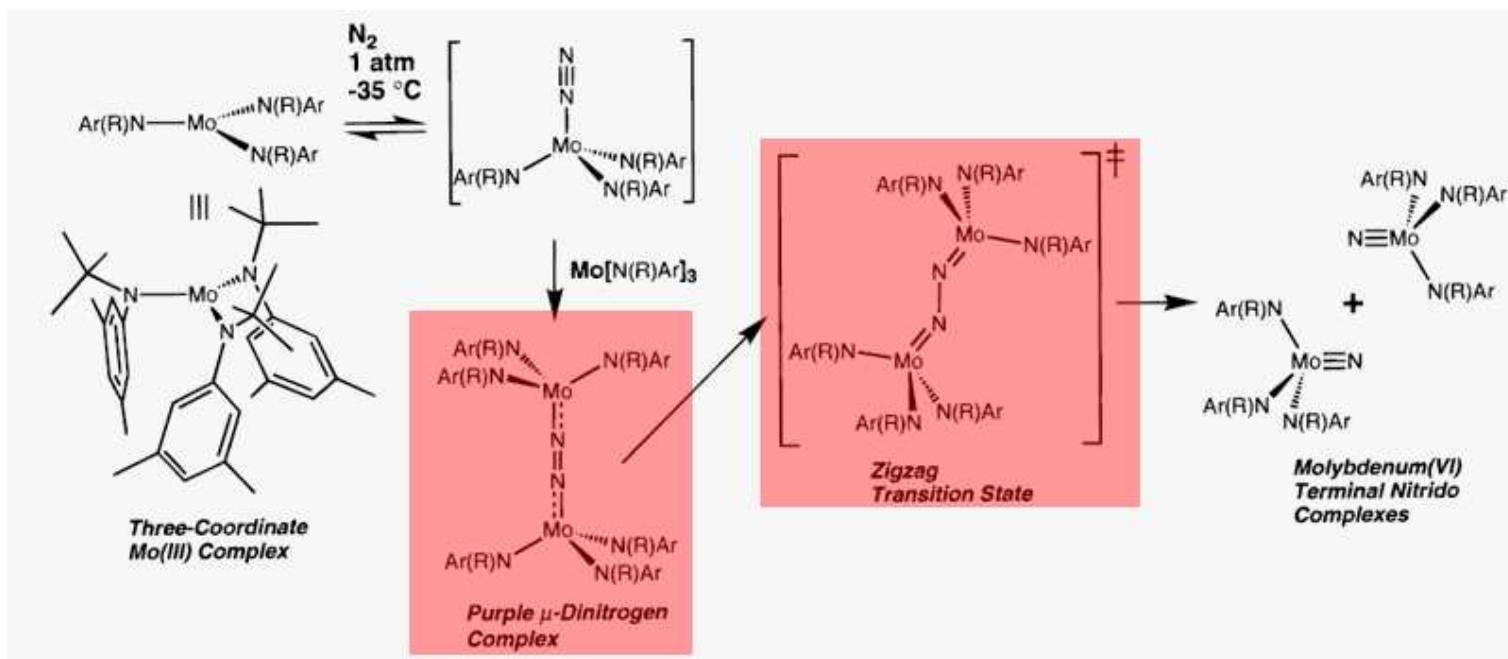
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Cleavage of Three-Coordinate Molybdenum(III) Complexes

Consult Laplaza, C.; Johnson, M.; Peters, J.; Odom, A.; Kim, E; Cummins, C. C.; George, G; Pickering, I., Dinitrogen Cleavage by Three-Coordinate Molybdenum(III) Complexes: Mechanistic and Structural Data. *Journal of the American Chemical Society* **1996**, 118, 8623-8638.

Scheme I, page 8623

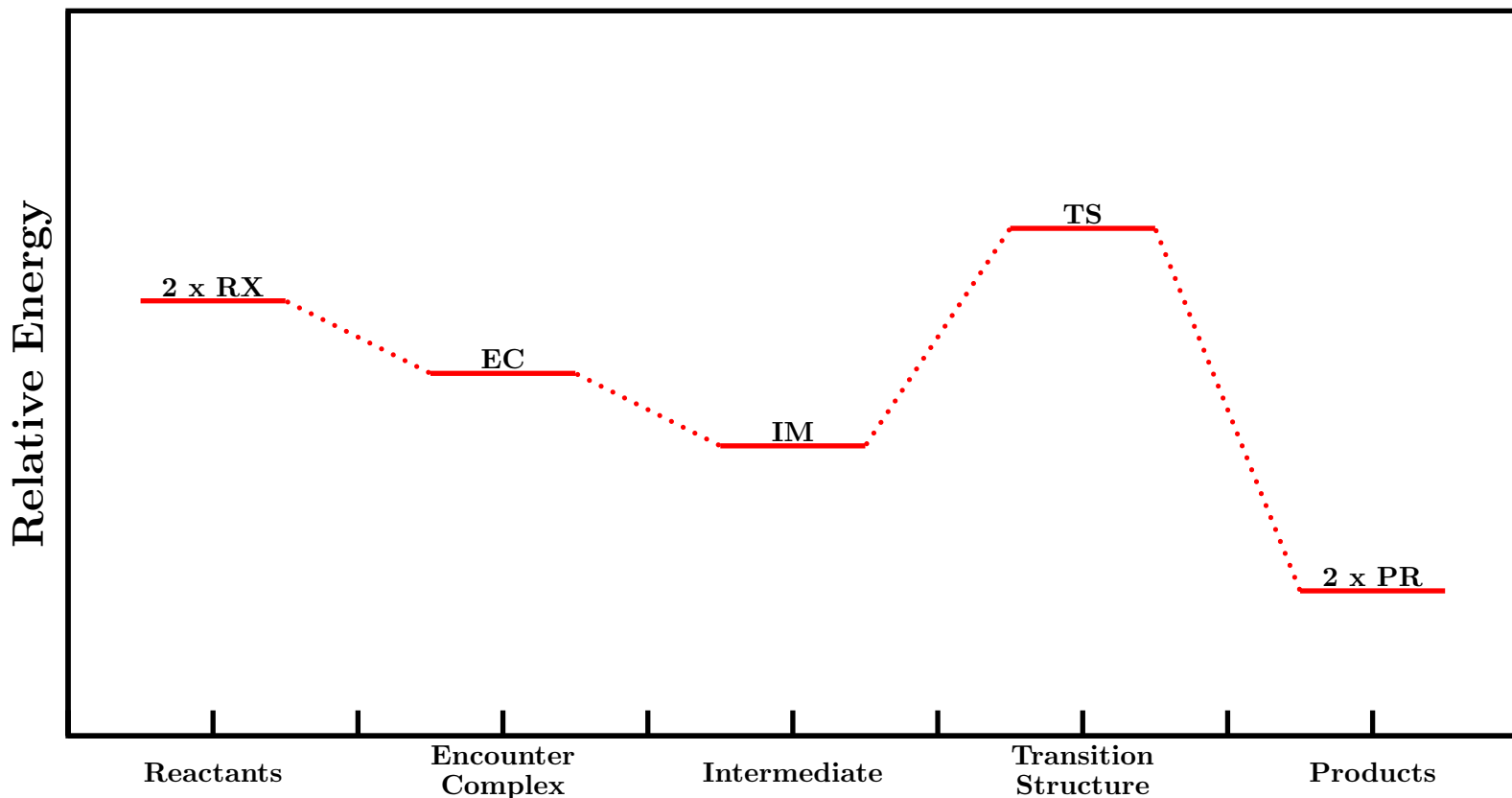
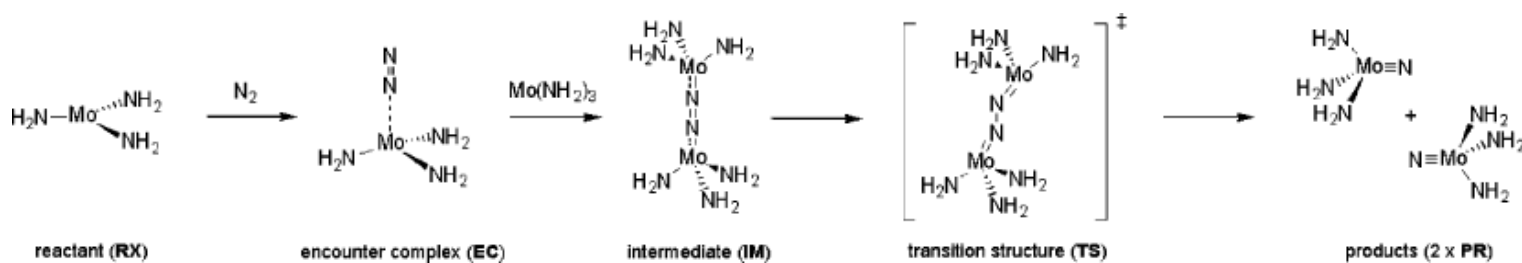


shows the formation of a terminal nitrido complex $\text{NMo}[\text{N}(\text{R})\text{Ar}]_3$ from $\text{Mo}[\text{N}(\text{R})\text{Ar}]_3 + \text{N}_2$ via an intermediate, $\mu - \text{N}_2\{[\text{N}(\text{R})\text{Ar}]_3\}_2$.



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Questions

1. Optimize all structures given on Page 2, and compare calculated structural parameters to the experimental values presented in the paper.
2. Determine whether the singlet or triplet states of **IM** are reactive intermediates (i.e. high-energy minima) or transition states.
If they are minima, find the transition state structure for dissociation.
3. Determine whether **TS** is really a transition state or a reactive intermediate.
If **TS** is a minimum, find the transition-state structure between reactant and product, and the transition state structure for dissociation.
4. Compare the calculated values of ΔH^\ddagger and ΔS^\ddagger to the experimental values given in the paper.
5. Using whatever transition state you determine to be relevant, calculate the Kinetic Isotope Effect. It is possible to use a calculated ΔG^\ddagger to predict a unimolecular rate constant, k_i by using the equation

$$k_i = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}}$$

where k_B is the Boltzmann constant, and ΔG^\ddagger is the free energy of activation.

Rates of reaction are determined, in part, by the energy barrier for the reaction (ΔG^\ddagger) which involves changes in both the potential energy surface and the zero point energy.

$$\Delta G^\ddagger \approx (\text{PE}^\ddagger - \text{PE}_{\text{Reactant}}) + (\text{ZPE}^\ddagger - \text{ZPE}_{\text{Reactant}})$$

Since the zero point energy is isotope sensitive, the magnitude of the barrier may also be isotope dependent, and a kinetic isotope effect may be observed.

The potential energy surface is the same for all isotopic derivatives, and the kinetic isotope effect can be given as

$$\frac{k_{^{14}\text{N}}}{k_{^{15}\text{N}}} = e^{-\frac{[\Delta\text{ZPE}(^{14}\text{N}) - \Delta\text{ZPE}(^{15}\text{N})]}{RT}}$$

where

$$\Delta\text{ZPE}(\text{isotope}) = \text{ZPE}^\ddagger(\text{isotope}) - \text{ZPE}_{\text{Reactant}}(\text{isotope})$$

Calculate the kinetic isotope effect, $\frac{k_{^{14}\text{N}}}{k_{^{15}\text{N}}}$, for the reaction in **Scheme I**, at 300 K, 320 K, and 340 K, and compare your calculated values **KIE** to the experimentally derived one.



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Questions Continued

6. Calculate the Intrinsic Reaction Coordinate (**IRC**) pathway from reactants to products.

The **IRC** is related to the minimum energy path (**MEP**) which is defined as the steepest descent path starting from the TS and going in either the backward direction (i.e. to reactants) or forward direction (i.e. to products).

Following this path can indicate if a TS was found that connects the two minima of interest.

7. Do your errors seem reasonable given the method and basis set used? Correct your electronic energies by doing single point calculations at the B3LYP + a higher level basis set.

Are things improved by comparison to experiment?

8. While it is always possible that deviations between theory and experiment represent inaccuracy in the modelling, what physical effects might be responsible for differences between theory and experiment?



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Quick Reminders with Respect to Gaussian 09

- To find transition states in the absence of a symmetry constraint, use **opt=(ts,calcfc)**.
If you have a symmetry constraint, you need to decide whether the reaction coordinate for the TS structure breaks the symmetry, in which case, use neither **ts** nor **calcfc** as keywords. If you preserve symmetry, then use both key words.
If you are looking for a TS, you may often find it helpful to use **opt=(ts,calcfc,noeigentest)**. The other keywords besides **ts** request calculation of analytic force constants on the first step (**calcfc**), and that the job not die if other than exactly one negative force constant is found at some step (**noeigentest**).
- You can save a lot of time by using useful information from previous calculations stored in the checkpoint file. Plan your calculations to try to save time. You can also save a lot of time by using symmetry when appropriate.
- The keywords **guess=read** and **geom=checkpoint** read the wave function and geometry, respectively, from the last completed calculation. So, if you have just performed an optimization, and want to follow-up with a frequency calculation, you will certainly want to use these keywords.
If you know ahead of time that you will want frequencies after a given optimization, you can simply include the **freq** keyword in the same job as **opt**.
Note: Frequencies must be calculated using the same level of theory with which the geometry was optimized to correspond to true IR frequencies!
- If you just optimized a geometry at one level of theory, and want to repeat that optimization at a different level, include the keyword **opt=(readfc)**, or **opt=(ts,readfc)** for a second pass at a transition-state optimization. This causes G09 to start with the force constants from the previous calculation, which is efficient.
It is usually a good idea to work your way up in a geometry optimization so you don't waste a lot of computer time because of a bad initial guess.
- To obtain the Zero Point Energy (ZPE) from the thermochemistry part of the frequency calculation, look for the line **Thermal correction to Energy = xxx** where xxx is a number in Hartree. Use the following conversion factor: 1 Hartree = 627.509 kcal/mol = 2625.50 kJ/mol
- An example of the G09 keyword for IRC is **irc=(forward,maxpoints=20,stepsize=10)** which means to take 20 steps in the product (forward) direction from the TS.



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Sample G09 Input File for Project III

```
%chk=triplet_intermediate.chk  
# b3lyp/gen pseudo(read) opt scf gfinput gfprint
```

Triplet Intermediate - D3D Symmetry

```
0 3  
N 0.000000 0.000000 0.610116  
N 0.000000 0.000000 -0.610116  
Mo 0.000000 0.000000 2.465316  
Mo 0.000000 0.000000 -2.465316  
N 0.000000 1.955665 2.750165  
H 0.000000 2.645066 1.999623  
H 0.000000 2.403644 3.668749  
N 1.693655 -0.977832 2.750165  
H 2.081617 -1.201822 3.668749  
H 2.290694 -1.322533 1.999623  
N -1.693655 -0.977832 2.750165  
H -2.290694 -1.322533 1.999623  
H -2.081617 -1.201822 3.668749  
N -1.693655 0.977832 -2.750165  
H -2.081617 1.201822 -3.668749  
H -2.290694 1.322533 -1.999623  
N 1.693655 0.977832 -2.750165  
H 2.290694 1.322533 -1.999623  
H 2.081617 1.201822 -3.668749  
N 0.000000 -1.955665 -2.750165  
H 0.000000 -2.645066 -1.999623  
H 0.000000 -2.403644 -3.668749
```

```
N H Mo 0  
LANL2DZ  
****
```

```
Mo 0  
LANL2DZ
```