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Conformation-Dependent State Selectivity in O−O Cleavage of ONOONO: An “Inorganic Cope Rearrangement” Helps Explain the Observed Negative Activation Energy in the Oxidation of Nitric Oxide by Dioxygen

Leif P. Olson,* Keith T. Kuwata, Michael D. Bartberger, and K. N. Houk*

Contribution from Eastman Kodak Research Laboratories, Rochester, New York 14650-2102, Department of Chemistry, Macalester College, St. Paul, Minnesota 55105-1899, and Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569

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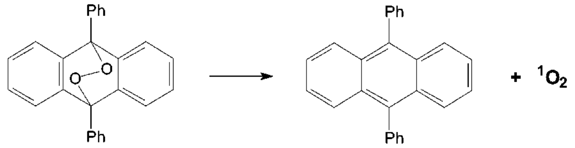
Abstract: ONOONO has been proposed as an intermediate in the oxidation of nitric oxide by dioxygen to yield nitrogen dioxide. The O−O bond breaking reactions of this unusual peroxide, and subsequent rearrangements, were evaluated using CBS-QB3 and B3LYP/6-311G* hybrid density functional theory. The three stable conformers (*cis*,*cis*-, *cis*,*trans*-, and *trans*,*trans*-ONOONO, based on the O−N−O−O dihedral angles of either ∼0° or ∼180°) are predicted to have very different O−O cleavage barriers: 2.4, 13.0, and 29.8 kcal/mol, respectively. These large differences arise because bond breaking leads to correlation of the nascent NO_2 fragments with either the ground $^2A_1$ state or the excited $^2B_2$ state of NO_2, depending on the starting ONOONO conformation. A *cis*-oriented NO_2 fragment correlates with the $^2A_1$ state, whereas a *trans*-oriented NO_2 fragment correlates with the $^2B_2$ state. Each NO_2 fragment that correlates with $^2A_1$ lowers the O−O homolysis energy by ∼15 kcal/mol, similar to the ∼17−25 kcal/mol $^2A_1 \rightarrow {}^2B_2$ energy difference in NO_2. Hence, this provides an unusual example of conformation-dependent electronic state selectivity. The O−O bond homolysis of *cis,cis*-ONOONO is particularly interesting because it has a very low barrier and arises from the most stable ONOONO conformer, and also due to obvious similarities to the well-known {3,3}-sigmatropic shift of 1,5-hexadiene, i.e., the Cope rearrangement. As an additional proof of our state selectivity postulate, a comparison is also made to breakage of the O−O bond of *cis,cis*-formyl peroxide, where no significant stabilization of the transition state is available because the $^2A_1$ and $^2B_2$ states of formyloxy radical are near-degenerate in energy. In the case of *trans,trans*-ONOONO, the O−O bond breaking transition state is a concerted rearrangement yielding O_2NNO_2, whereas for *cis,cis*- and *cis,trans*-ONOONO, the initially formed NO_2 radical pairs can undergo further rearrangement to yield $ONONO_2$. It is proposed that previous spectroscopic observations of certain N═O stretching frequencies in argon-matrix-isolated products from the reaction of NO with O_2 (or $^{18}O_2$) are likely from $ONONO_2$, not the OONO radical as reported.

Introduction

A curious aspect of the chemistry of peroxides is their tendency to yield electronically excited products from thermal decomposition.[1] This tendency is related to the exothermicity of decomposition of these fragile molecules and the relatively low energies of the excited states of the products, as well as orbital and state symmetry considerations. For example, the symmetry-allowed retro-Diels−Alder reaction of 9,10-diphenylanthracene *endo*-peroxide yields singlet oxygen as one of the products[2] (Scheme 1), while the symmetry-forbidden 2 + 2 retrocyclization of 1,2-dioxetanes yields excited-state carbonyl products,[3] which occurs in at least some instances with state selectivity (Scheme 2), i.e., the formation of n−π* triplet states.[4]

Scheme 1



Herein we report a variation on the themes of thermally accessible excited states and state selectivity. An important inorganic peroxide reaction intermediate decomposes with

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* Address correspondence to these authors at the University of California, Los Angeles. E-mail (K.N.H.): houk@chem.ucla.edu.

(1) (a) Adam, W. *Pure Appl. Chem.* **1980**, *52*, 2591. (b) Schuster, G. B. *Acc. Chem. Res.* **1979**, *12*, 366. (c) Givens, R. S.; Schowen, R. L. The Peroxyoxalate Chemiluminescence Reaction. In *Chemiluminescence and Photochemical Reaction Detection in Chromatography*; Birks, J. W., Ed.; VCH: New York, 1989; pp 125−147.

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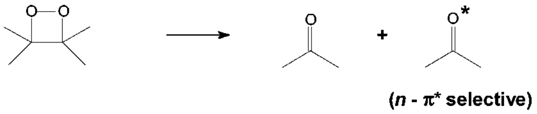
Scheme 2



smooth evolution into ground states of products in one conformation, but into excited states in other conformations. In the latter cases, significantly higher barriers to decomposition are predicted. This manifests itself as a large conformational dependence on the activation barriers for breaking the peroxide bond.

CBS-QB3 and B3LYP hybrid density functional methods[5] were used to investigate rearrangements of the geometric isomers of the peroxide ONOONO,[6] a proposed intermediate in the oxidation of nitric oxide by dioxygen (eq 1).

$$2NO + O_2 \rightarrow 2NO_2 \qquad (1)$$

Ground-state and transition-state structures and energies were evaluated for the three ONOONO conformers, the bond rotations that interconvert them, the O−O cleavage reactions for each isomer, and subsequent rearrangements of the NO_2 fragments. The three different O−O bond breaking reactions display state selectivity: depending on the starting conformation, either zero, one, or two of the nascent NO_2 fragments in the transition state correlate electronically with the lower $^2A_1$ state of NO_2 rather than the excited $^2B_2$ state of the starting material. This leads to very large differences in the barriers for O−O bond breaking for the three ONOONO conformers. Notably, the O−O bond breaking rearrangement of *cis,cis*-ONOONO occurs via a novel and previously unrecognized "inorganic Cope" rearrangement with a small barrier, indicating a favored pathway for NO_2 formation.

The chemistry of nitric oxide (NO) is of considerable significance, not only in medical research for its numerous physiological roles,[7] but also as a reactive atmospheric NO_x species.[8] The direct oxidation of NO by O_2 to give nitrogen dioxide (NO_2) (eq 1) is thought to play a critical role in processes such as combustion, and can contribute to atmospheric chemistry under conditions of high NO concentration, such as in emissions from power plants or automobiles.[8] A significant step forward in understanding the mechanism of this reaction was made in an ab initio study of the N_2O_4 potential energy surface by McKee,[6a] in which it was suggested that the previously unconsidered N_2O_4 isomer ONOONO plays a key role in the NO oxidation process.[9] ONOONO could arise from initial association of NO and O_2 to give the weakly bound OO•NO ($^2A_2$) (eq 2), followed by addition of a second NO to give ONOONO (eq 3).

$$NO + O_2 \rightarrow OO{\cdot}NO \qquad (2)$$

$$NO + OO{\cdot}NO \rightarrow ONOONO \qquad (3)$$

Alternatively, OO•NO could rearrange to the $^2A_1$ radical (eq 4), followed by addition of a second NO to form ONOONO (eq 5).

$$OO{\cdot}NO \rightarrow OONO \qquad (4)$$

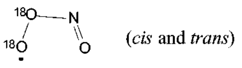
$$NO + OONO \rightarrow ONOONO \qquad (5)$$

McKee's MP2, DFT, and QCISD(T) calculations predicted a 28−36 kcal/mol barrier for O−O bond cleavage from the *trans,trans* isomer of ONOONO (eq 6). From these data, O−O bond breakage in ONOONO was predicted to be the rate-determining step in NO_2 formation.

$$ONOONO \rightarrow ONO\text{---}ONO \qquad (6)$$

While an enthalpy barrier of about 30−35 kcal/mol would not be unexpected for the homolysis of most simple peroxides,[10] the computed barrier for ONOONO is puzzlingly high for an O−O bond dissociation reaction involving formation of two NO_2 radicals, considering the large and energetically favorable reorganization energy[6a] that must be involved, as well as the known weak O−O bonds of peroxynitrous acid and similar compounds.[11] A negative activation energy generally requires not only a highly reversible initial step, like eq 2, but also that any subsequent steps leading to product must have low kinetic barriers. While McKee did partially address this problem by computing the energy of the *trans,trans*-ONOONO O−O bond breaking transition state in several different ways which gave smaller barriers, we considered the approach used as questionable (especially inasmuch as the energy barrier predicted by a fully optimized transition state was discounted as being an overestimate),[6a] and furthermore, no investigation was made of other ONOONO conformations. Meanwhile, we were surprised by another report: infrared spectroscopic studies of argon-matrix-trapped products from the reaction of NO with unlabeled O_2 and with $^{18}O_2$ showed species (interpreted as OONO) with 50 cm^{-1} different N=O stretching frequencies.[12] Although the assertion was made that $^{18}O{-}^{18}O{-}N{=}^{16}O$ could give a 50 cm^{-1} lower N=O stretching frequency than $^{16}O{-}^{16}O{-}N{=}^{16}O$ (Scheme 3), our vibrational frequency calculations[13] on these two isotopomers indicate a less than 1 cm^{-1} difference. Simple calculations reveal, however, that a variety of $R{-}N{=}^{16}O$ vs $R{-}N{=}^{18}O$ species (including, but not limited to, OONO) have the requisite ∼50 cm^{-1} different N=O stretches.[14] Hence, an initial hypothesis to explain the spectroscopic results was that ^{18}O isotope migration might occur by a {1,3}-sigmatropic shift occurring from *cis*-ONOO (Scheme 4). However, the putative four-membered cyclic OONO (trioxazetidinyl) radical interme-

Scheme 3



Frequency for N=O stretch 50 cm^{-1} lower than unlabeled material?

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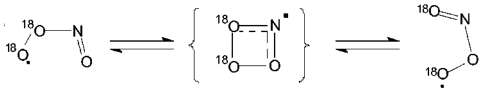
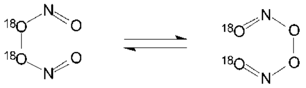
diate is predicted to be very high in energy relative to other NO_3 isomers.[15]

Scheme 4



While the {1,3}-sigmatropic shift hypothesis was rejected on energetic grounds, a similar line of reasoning led to another, more interesting hypothesis: the trapped species observed by IR might not be OONO at all, but rather the product of addition of a second NO molecule to OONO (eq 5). If McKee's proposed ONOONO intermediate has a *cis,cis* isomer, this might undergo a novel {3,3}-sigmatropic shift, i.e., a Cope rearrangement (Scheme 5), that would provide the requisite mixture of R$-$N$=^{16}$O and R$-$N$=^{18}$O material when $^{18}O_2$ reacts with 2NO. While such a pathway might be difficult to study experimentally, its existence might be revealed by theoretical calculations.

Scheme 5



Computational Methods

All calculations on ONOONO were performed using Gaussian 98, revision A.9.[16] Some exploratory CASSCF calculations on OONO (mentioned in the Introduction) were done using the PC Gamess version[17a] of the GAMESS(US) software.[17b] Initial identification of stationary points was done at the B3LYP/6-311G* level, prior to recalculation at the CBS-QB3 level. As a check on the surprisingly different relative energies of the O$-$O bond breaking transition states of ONOONO geometric isomers, QCISD(T) single-point calculations were done on the B3LYP/6-311G* geometries.[18] These relative energies agreed well with the CBS-QB3 and DFT results.

All structures were true minima or transition states (zero or one imaginary vibrational frequency) with the exception of **CT-TS2**, which is a second-order saddle point. The second imaginary frequency of this C_s-symmetric structure is a symmetry-breaking mode. Attempts to follow this mode downhill to locate a true first-order saddle point with C_1 symmetry were not successful, due to the extreme flatness of this potential energy surface.

All structures were tested for spin contamination using a broken-symmetry singlet UB3LYP wave function. Only two structures showed any spin contamination, with $\langle S^2 \rangle$ values of 0.6907 (0.0256 after annihilation of the triplet spin contaminant) for **CT-TS1** and 0.9983 (0.0510 after annihilation) for **CT-INT**. The CBS-QB3 method includes procedures for projecting out unwanted spin states, so its energetic predictions are generally to be preferred relative to those of "unadorned" DFT in such cases. Because of the high accuracy of the CBS-QB3 method,[5a−c] relative energies in the text refer to the CBS-QB3 results.

Results

ONOONO Geometric Isomers and Interconversions. During the course of our work, DFT and MP2 computations[6b] were reported that indicated the existence of three ground-state isomers of ONOONO (Figure 1; structures in Figures 3$-$5), each with a ~90° N$-$O$-$O$-$N dihedral angle and two O$-$N$-$O$-$O dihedral angles of ~0° (*cis*) and/or ~180° (*trans*).

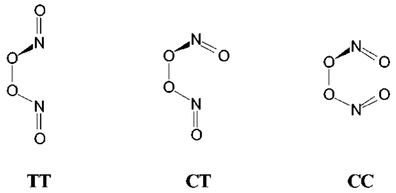


Figure 1. *trans,trans* (**TT**), *cis,trans* (**CT**), and *cis,cis* (**CC**) isomers of ONOONO.

The predicted order of thermodynamic stability is *cis,cis*-ONOONO (**CC**) > *cis,trans*-ONOONO (**CT**) > *trans,trans*-ONOONO (**TT**), with differences of a few kilocalories per mole. Our computations agree closely with these findings. However, we prefer an interpretation different from that of Wang and Qin, who ascribe the origin of these differences in energy as resulting from weak 1,6 and/or 1,4 O$-$O bonds. While such weak interactions might exist in ONOONO, the conformational energy differences are better ascribed to relief of 1,3 interactions between oxygen lone pairs when an $-$OONO fragment is in an *s-cis* conformation. The conformational preferences seen here are similar in direction, magnitude, and cause to the well-known *s-cis* conformational preference of carboxylic esters and acids.[19]

Additionally, we find that **CT** can convert to either **CC** or **TT** via simple O$-$N$-$O$-$O bond rotations (Figure 2), with transition states 13$-$15 kcal/mol higher in energy than **CT** (Table 1).

These isomerization reactions can occur with rotation of one OONO fragment in either an *exo* or *endo* sense relative to the rest of the molecule. For steric reasons, the *exo* rotations are slightly favored relative to their *endo* counterparts. Presumably N$-$O$-$O$-$N bond rotations could occur which would interconvert enantiomers of each conformation (all of which are chiral), but these were not explored.

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(14) For example, CASSCF and DFT (B3LYP/6-311G*) calculations show that ^{18}O substitution into the N═O groups of NO, $ONONO_2$, OONO, and ONOONO results in a ~50 cm^{-1} lower frequency N═O stretch than that of the ^{16}O isotopomers.

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(16) Gaussian 98, revision A.9: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.

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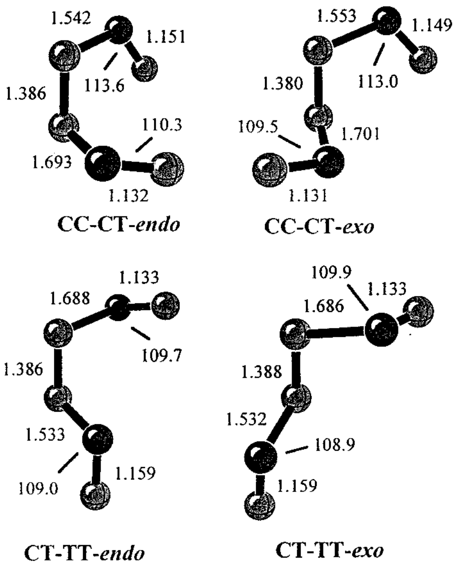

Figure 2. Bond rotation transition structures for ONOONO.

Table 1. CBS-QB3 and B3LYP/6-311G* Energetics of N_2O_4 Species (no ZPE Corrections for B3LYP)

structure	CBS-QB3 energy, hartrees	CBS-QB3 E_{rel}, kcal/mol	B3LYP/6-311G* E_{rel}, kcal/mol
$2NO_2$	−409.699078	−11.16	−19.41
trans,trans-ONOONO (**TT**)	−409.669478	+7.41	+3.64
TT-TS	−409.622071	+37.16	+36.07
O_2**NNO**$_2$	−409.719579	−24.03	−34.41
cis,trans-ONOONO (**CT**)	−409.678521	+1.74	+1.79
CT-TS1	−409.657770	+14.76	+16.45
CT-INT	−409.681178	+0.07	+11.31
CT-TS2	−409.692288	−6.90	+15.53
trans-ONONO$_2$	−409.714122	−20.60	−22.14
cis,cis-ONOONO (**CC**)	−409.681290	0.00	0.00
CC-TS1	−409.677410	+2.43	+2.45
CC-INT	−409.698283	−10.66	−10.57
CC-TS2	−409.689572	+5.20	−1.50
cis-ONONO$_2$ (90° twist of NO_2)	−409.707778	−16.62	−19.76
CC−CT isomerization **TS1** (*exo*)	−409.658423	+14.35	+11.95
CC−CT isomerization **TS2** (*endo*)	−409.657376	+15.01	+12.95
CT-TT isomerization **TS1** (*exo*)	−409.655355	+16.27	+14.56
CT−TT isomerization **TS2** (*endo*)	−409.655176	+16.39	+14.89

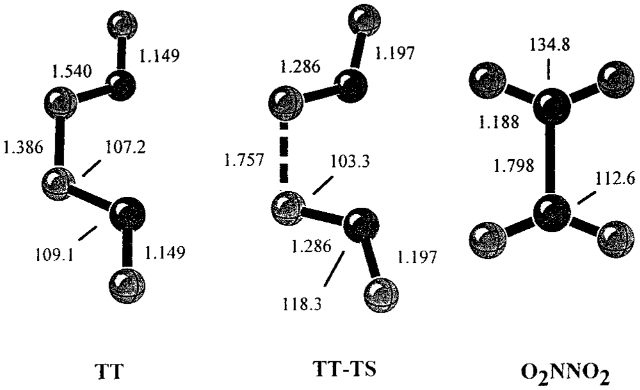

Figure 3. **TT**, **TT-TS**, and ONONO$_2$.

O−O Homolysis and Rearrangements of TT, CT, and CC. For **TT**, the O−O bond breaking transition state **TT-TS** (Figure 3) was previously reported by McKee.[6a] We find a similar structure, with a 29.8 kcal/mol energy barrier (Table 1) similar to that found previously for this transition state.

However, this is not a simple dissociation reaction, as was previously suggested:[6a] Instead, by following the evolution of **TT-TS** along an irc to product, we find that the overall reaction is a concerted formation of O_2NNO_2. This product is 31.4 kcal/mol more stable than **TT**.

For **CT**, the picture is rather different; bond cleavage is considerably more facile at 13.0 kcal/mol (energy of **CT-TS1** relative to **CT**), and yields a perpendicularly arranged NO_2 radical pair, **CT-INT** (Figure 4), as an intermediate, 1.7 kcal/mol lower in energy than the starting material. **CT-INT** sits on a very flat energy surface with respect to subsequent N−O bond formation to yield ONONO$_2$, and may not be a real intermediate at all. The best structure we found for rearrangement to ONONO$_2$ is **CT-TS2**, a C_s-symmetric second-order saddle point which is 4 kcal/mol uphill from **CT-INT** at the B3LYP/CBSB7 level,[20] but 6.9 kcal/mol *downhill* after full CBS-QB3 energy corrections. (Other pathways for rearrangement of **CT-INT** might exist. For example, we unsuccessfully sought a pathway for O_2NNO_2 formation from this intermediate. Such flat potential energy surfaces may be subject to factors such as dynamic effects[21] which can control product formation.[22]) The final product, *trans*-ONONO$_2$, is 22.4 kcal/mol lower in energy than **CT**.

Finally, not only is **CC** the most stable conformer of ONOONO, but it also has the lowest (2.4 kcal/mol) barrier for O−O bond breaking. This occurs via the very early transition state **CC-TS** (Figure 5). The first product that forms is the planar, hexagon-shaped NO_2 radical pair intermediate **CC−INT**. Although this species represents a minimum rather than a saddle point, it clearly resembles the coupled bis(allyl)radical transition state for the Cope rearrangement of 1,5-hexadiene,[23] for which ONOONO can be considered an inorganic analogue. The ONO• •ONO coupled radical pair intermediate **CC−INT** is 10.7 kcal/mol lower in energy than the starting material. A second rearrangement step with a transition state (**CC-TS2**, Figure 3) 15.9 kcal/mol uphill from this hexagon-shaped radical intermediate yields *cis*-ONONO$_2$ as the final product, in a conformation with the −NO$_2$ fragment perpendicular to the ONO− fragment. This species is 16.6 kcal/mol lower in energy than **CC**, and 5.9 kcal/mol below the cyclic coupled radical pair **CC-INT**.

Dependence of Selectivity for the $^2A_1$ or $^2B_2$ States of NO_2 on the ONOONO Conformation. The dramatic differences in activation energies for the O−O bond cleavage reactions of **TT**, **CT**, and **CC** may be explained by comparing the electronic states of the constituent NO_2 fragments in the reactant and the product. All three ONOONO conformers involve the formal coupling of two NO_2 units that are both in the excited $^2B_2$ state, a state with the unpaired electron localized on the two terminal oxygens (Figure 6). The SOMO is largely localized on the oxygen atoms in an in-plane orbital that is antisymmetric with respect to the C_2 axis. In the $^2A_1$ state, the SOMO is largely

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(20) The CBSB7 basis set is used to obtain geometries in the CBS-QB3 compound method.

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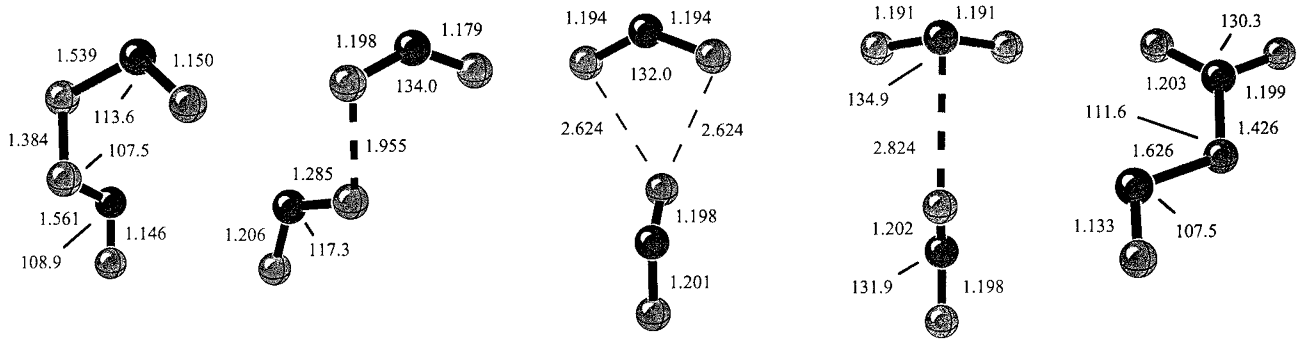
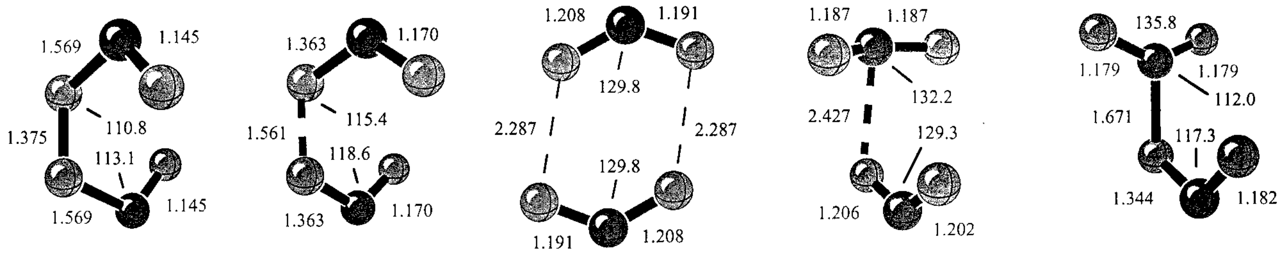


CT **CT-TS1** **CT-INT** **CT-TS2** ***trans*-ONONO$_2$**

Figure 4. **CT**, **CT-TS1**, **CT-INT**, **CT-TS2**, and *trans*-ONONO$_2$.



CC **CC-TS1** **CC-INT** **CC-TS2** ***cis,90*-ONONO$_2$**

Figure 5. **CC**, **CC-TS1**, **CC-INT**, **CC-TS2**, and *cis,90*-ONONO$_2$.

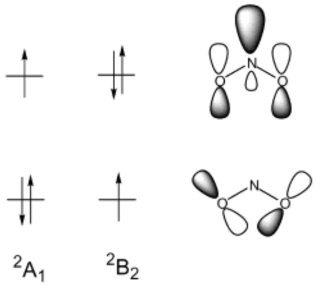


Figure 6. Orbital occupation of the ground ($^2A_1$) and excited ($^2B_2$) states of NO$_2$.

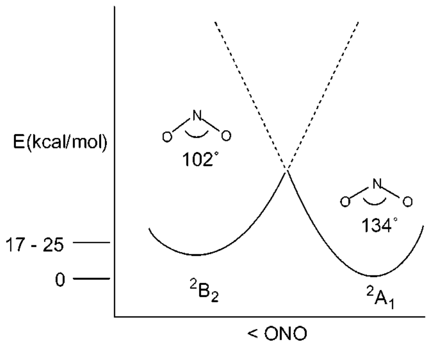


Figure 7. The $^2B_2$ state of ONO, with a smaller ONO angle, is ca. 17−25 kcal/mol higher in energy than the $^2A_1$ state.

localized on an in-plane orbital on the nitrogen atom, and two $^2A_1$ NO$_2$ radicals can form a covalent bond linking the N atoms.

As a result of the classic studies of Jaeckels and Davidson, as well as more recently Blahous et al., the natures of these states are quite well established.[24] The $^2B_2$ state of NO$_2$ is 17−25 kcal/mol higher in energy than the $^2A_1$ state. The radical geometry is significantly different as well, with a smaller ONO angle (~102°) in the $^2B_2$ state compared to the $^2A_1$ state (~134°) (Figure 7).

Meanwhile, inspection of the ground-state structures of **TT**, **CT**, and **CC** (Figures 3−5) reveals that the *trans*-oriented OONO fragments have ONO angles of 107−109°, whereas the *cis*-oriented OONO fragments have ONO angles of 113−114°. Presumably this difference is due to overlap of the N=O π orbital with the O−O σ^* orbital, similar to the C=O/O−C interaction often cited to explain why carboxylic esters are *syn* rather than *anti*.[19] Our postulate is that the ONO angle difference permits correlation of the nascent NO$_2$ fragments in the O−O bond breaking transition states with the lower energy $^2A_1$ state in the case of a *cis*-oriented OONO fragment, but maintains the $^2B_2$ state in the case of a *trans*-oriented OONO fragment (Figure 8). This results in a ~15 kcal/mol lowering of the enthalpy barrier for each *cis*-oriented fragment.

In the transition state **TT-TS**, the OO bond cleaves to form two excited-state $^2B_2$ NO$_2$ radicals. As shown in Figure 8, the HOMO in the **TT-TS** resembles two interacting SOMOs of the NO$_2$ radicals in $^2B_2$ states. Because both **TT** and **TT-TS** correlate with the same electronic state, the dissociation energy of about 30 kcal/mol is similar to that of an ordinary peroxide, such as CH$_3$OOCH$_3$.[10] The radical pairs do both eventually relax to the $^2A_1$ state to couple to form the O$_2$N−NO$_2$ isomer, after the transition state.

For **CT**, as the reactant evolves into **CT-TS1**, the *trans*-oriented NO$_2$ fragment simply continues to correlate with the $^2B_2$ state, whereas the *cis*-oriented NO$_2$ fragment relaxes directly into the ground $^2A_1$ state, since the breaking O−O bond is

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[24] (a) Blahous, C. P.; Yates, B. F.; Xie Y.; Schaefer H. F. *J. Phys. Chem.* **1990**, *93*, 8105. (b) Kaldor, U. *Chem. Phys. Lett.* **1991**, *185*, 131. (c) Jackels, C. F.; Davidson, E. R. *J. Chem. Phys.* **1976**, *64*, 2908. (d) Jackels, C. F.; Davidson, E. R. *J. Chem. Phys.* **1976**, *65*, 2941.

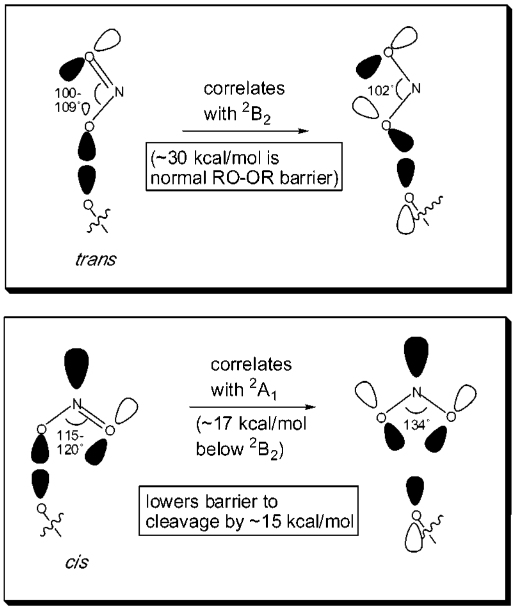


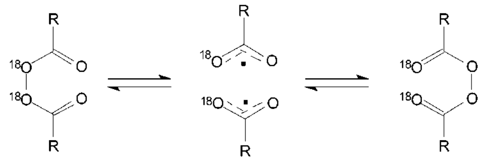
Figure 8. Effect on O−O bond breakage of a *trans*-oriented ONO fragment (top) vs a *cis*-oriented ONO fragment (bottom). In the case of the *cis*-oriented fragment, the wider ONO angle, and overlap of the developing SOMO with the breaking O−O bond, favors the $^2A_1$ state.

antiperiplanar to the N lone pair. This is reflected in the barrier, which is about 15 kcal/mol lower than that for **TT-TS**. This radical pair collapses to the $ONONO_2$ isomer with a very small barrier (or no barrier, as predicted by CBS-QB3 following energy corrections), because of the correlation with $^2B_2$ and $^2A_1$, an O-centered radical and an N-centered radical. Note that the barrier for the reaction **CT** → **CT-TS1** accords well with the experimental free energy of activation (17 kcal/mol) for the rearrangement of peroxynitrous acid (HOONO), a *syn*-peroxide isomer of nitric acid ($HONO_2$). For this system, the dissociation energy is also about 15 kcal/mol less than expected for a normal peroxide.[10,11]

Finally, in **CC** both NO_2 fragments are *cis*-oriented, so they both evolve into the lower energy $^2A_1$ state in **CC-TS1**. The essentially negligible barrier for this process is consistent with our postulate; i.e., the ~30 kcal/mol "normal" peroxide bond dissociation energy is compensated by having both NO_2 fragments correlate with a lower electronic state. (While the NO_2 fragments in **CC-INT** interact through their oxygen atoms, and the ONO bond angles are relatively small at 117°, examination of the HOMO for this species shows that the fragments are both $^2A_1$.) The subsequent isomerization of **CC-INT** to $ONONO_2$ via **CC-TS2** has an activation barrier of 15.9 kcal/mol. One explanation for the 15.9 kcal/mol barrier is simply that it is about the same as the energy required to "re-excite" one $^2A_1$ radical back to a $^2B_2$ oxygen-centered NO_2 radical.

Comparison to Formyl Peroxide Theoretical Results. As another proof of our state selectivity postulate for the O−O bond cleavage reactions of **CC**, **CT**, and **TT**, it is instructive to compare the present results with Uchimaru et al.'s B3LYP/6-311+G* study[25a] of the mechanism of decomposition of formyl peroxide (OHCOOCHO), used as a model for experimental observations of oxygen isotope scrambling in larger diacyl peroxides (Scheme 6).[25b−h] Formyl peroxide is isoelectronic with ONOONO, and both of these peroxides have a global minimum conformation with a *cis,cis* orientation of their OONO (structure **CC**) or OOCHO groups. The two peroxides are also similar in that both are formally composed of two radical fragments (NO_2 or formyloxy) bound in the $^2B_2$ state. Like NO_2, formyloxy radical has a $^2A_1$ ground state, and in both cases the $^2A_1$ ground states and $^2B_2$ excited states have different bond angles and distances. However, unlike NO_2, the ground state of formyloxy radical is only about 0.3 kcal/mol lower in energy than the $^2B_2$ state; i.e., *the ground state and first excited state are nearly degenerate in energy*. This difference is critical. Uchimaru et al. find that *cis,cis*-formyl peroxide has a {3,3}-sigmatropic shift transition state that is thermally accessible, and correlates (e.g., bond distances and angles) with two formyloxy fragments in the $^2A_1$ state. (In their strict usage, this structure is referred to as a "σ-acyloxy transition state" to distinguish it from a true Cope rearrangement, which can be considered as correlating with the $^2A_2$ π-radical state of the constituent fragments.) This formyl peroxide saddle point is an unmistakable electronic analogue of our **CC-INT**. But because the formyloxy fragments gain very little stabilization by changing from $^2B_2$-like in the starting material to $^2A_1$-like in the transition state, the energy barrier (29.4 kcal/mol at the B3LYP/6-311+G* level) is not much lower than that of a simple peroxide bond dissociation. This also explains why the formyl peroxide rearrangement structure is a saddle point while **CC-INT** is a potential energy minimum.

Scheme 6



The Importance of CC-INT. The inorganic Cope rearrangement of **CC** via **CC-TS1** and **CC-INT** seems particularly noteworthy. This is because it is the most facile bond breaking reaction arising from the most stable ONOONO isomer, and also because of its obvious relationship to the six-electron pericyclic Cope rearrangement of 1,5-hexadiene. The inorganic Cope cannot be strictly considered a genuine Cope rearrangement, in the sense that the {3,3}-sigmatropic shift of 1,5-hexadiene correlates electronically with the $^2A_2$ (π-radical) state of its allyl radical fragments. Furthermore, despite controversy over the mechanism of Cope (and Claisen) rearrangements,[23] the bulk of the evidence clearly supports a concerted pathway,[23b] whereas **CC-INT** is a true intermediate. Still, it is intriguing to note that part of the reason a Cope rearrangement is facile has to do with transition-state aromaticity (as delineated by the Woodward−Hoffmann rules for orbital symmetry).[26] One useful quantitative measure of aromaticity is the nucleus-independent

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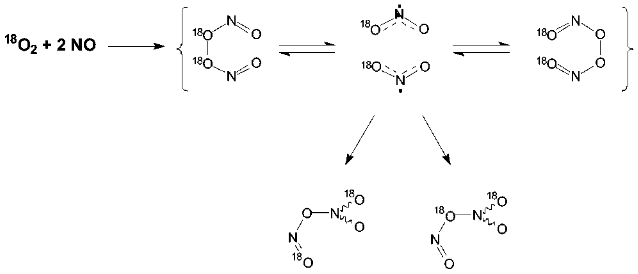
(26) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970.

chemical shift (NICS),[27] which employs an NMR calculation of the chemical shift of a chosen point in space, typically a ghost atom at the center of a ring, to evaluate the strength of the ring current. A significantly negative NICS value indicates an aromatic ring current (whereas a significantly positive NICS value indicates an antiaromatic ring current); for example, benzene has an NICS value of −9.7 ppm (HF/GIAO/6-31+G*//B3LYP/6-311G*) at the center of the ring. When an NICS calculation is performed at this same level for **CC-INT**, the value obtained is −13.9 ppm for the center of the ring, which seems to indicate strong aromaticity (perhaps using σ- rather than π-electrons).

CC-INT is in equilibrium with **CC**, and could thereby accomplish scrambling of isotopically labeled O_2 as in Scheme 3. As such, the part of our hypothesis stating that **CC** might undergo a Cope-like rearrangement is supported. On the other hand, the part of the hypothesis stating that isotopically labeled **CC** might be the species responsible for the $N{=}^{18}O$ IR absorbance observed when $^{18}O_2$ reacts with nitric oxide[12] seems unlikely. Continued reaction to eventually yield $ONONO_2$ as a more kinetically and thermodynamically stable (and hence trappable) product seems more reasonable. Note that trapping $ONONO_2$ as a product from the reaction of NO with O_2 would provide the requisite N=O stretch observed experimentally,[12] and also when this reaction is performed using $^{18}O_2$, the observed ca. 50:50 mixture of $N{=}^{16}O$ and $N{=}^{18}O$ IR absorbances would be expected (Scheme 7).

Scheme 7



Conclusions

Although the present work constitutes a significant proposed revision to the mechanism of oxidation of NO to NO_2 by O_2, the overall picture reinforces the basic framework laid out by McKee.[6a] The proposal that ONOONO could be a key intermediate in the oxidation pathway is supported by the CBS-QB3 calculations. The key differences are with regard to which step(s) might be rate-determining. These calculations suggest that the rate-determining step is very likely the addition of NO to either OONO or $O_2{\cdot}NO$, since we have found that ONOONO has a significantly more facile pathway for rearrangement to lower-energy species than was previously thought. This is consistent with the rate dependence on $[NO]^2[O_2]$ and the negative energy of activation for eq 1. A negative energy of activation is, of course, generally harder to rationalize if one of the elementary mechanistic steps of the reaction (e.g., O−O bond breaking in this case) has a large barrier.

It is unknown what conformation of ONOONO might be most favorably formed by addition of NO to $O_2{\cdot}NO$ (eq 3) or OONO (eq 5). It seems reasonable to suppose that a mixture of isomers might form. The calculations suggest that if **TT** is formed, it will more likely undergo bond rotation to give **CT** than rearrange to give O_2NNO_2. If **CT** is formed, its stepwise rearrangement to $ONONO_2$ should be competitive with bond rotation to give **CC**. If **CC** is formed, it should most rapidly undergo the inorganic Cope rearrangement and ultimately give $ONONO_2$. We cannot be certain about which matrix-isolated products were observed experimentally by IR spectroscopy. However, on the basis of our vibrational frequency calculations of isotopomers of OONO, it seems extremely unlikely that OONO was the trapped product with the 50 cm^{-1} isotopic frequency shift when $^{18}O_2$ was reacted with NO. Given the likely kinetic instability of ONOONO, we propose that the species observed is most likely $ONONO_2$, with the ^{18}O label partially scrambled by the inorganic Cope rearrangement.

ONOONO is a very unusual compound in that it has very pronounced, conformation-dependent state selectivity for O−O bond cleavage. One might expect in the gas phase that some fraction of ONOONO (for example, **TT** and **CT**) could, if sufficiently thermally activated, dissociate into free $^2B_2$ NO_2. This might occur with emission of near-IR radiation as the $^2B_2$ NO_2 undergoes radiative decay to the $^2A_1$ state,[28] which would place ONOONO as yet another example of a chemiluminescent peroxide.[1]

It is striking that a reaction with the importance of that in eq 1 might occur largely via a previously unsuspected {3,3}-sigmatropic shift as part of the mechanism, i.e., an inorganic Cope rearrangement.

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