Ab Initio Study of the N_2O_4 Potential Energy Surface. Computational Evidence for a New N_2O_4 Isomer

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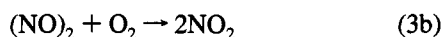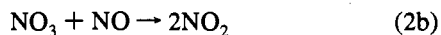
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Abstract: Density functional theory with nonlocal corrections (Becke3LYP) and Hartree−Fock theory with perturbative electron correlation (QCISD(T)) are used to study the nitrogen oxides. With few exceptions, DFT calculations with a small basis set (6-31G(d)) are in good agreement with QCISD(T) calculations with a moderate basis set (6-31+G-(2df)). A new isomer of N_2O_4 is calculated which involves the coupling of two NO_2 radicals through oxygens. The O−O bond in ONOONO is similar to other peroxide bonds except that the bond dissociation energy is negative (−17.5 kcal/mol) due to the large reorganization energy of NO_2. The ONOONO intermediate is suggested to play a key role in the reaction $2NO + O_2 \rightarrow 2NO_2$. The stepwise mechanism for formation of ONOONO, adding NO to O_2 (endothermic by 11.5 kcal/mol) followed by adding NO to ONOO (exothermic by 21.6 kcal/mol), is not consistent with experimental observations. Rather, a new mechanism is proposed in which ONOONO is formed in a concerted step from NO plus NO•O_2, a weakly bound complex of NO and O_2. Assuming O−O cleavage as the rate determining step gives the correct rate law ($[O_2][NO]^2$) and an overall activation barrier consistent with experiment.

Introduction

While the oxidation of NO in the presence of O_2 to NO_2 (reaction 1) is a significant atmospheric reaction, the mechanism is poorly understood.[1,2] The reaction is known to be second

$$2NO + O_2 \rightarrow 2NO_2 \qquad (1)$$
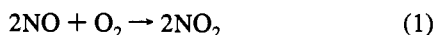
order in NO and first order in O_2, and most studies have concluded that the overall activation barrier is slightly negative.[1] Four mechanisms have been presented to account for the oxidation. The concerted termolecular mechanism (reaction 1) was assumed by Gershinowitz and Eyring[3] in 1935 to make an empirical fit with experimental data using transition state theory. Two bonds form and one bond breaks simultaneously in the activated complex. Mechanisms 2 and 3 were considered to

$$NO + O_2 \rightleftharpoons NO_3 \qquad (2a)$$

$$NO_3 + NO \rightarrow 2NO_2 \qquad (2b)$$

$$2NO \rightleftharpoons (NO)_2 \qquad (3a)$$

$$(NO)_2 + O_2 \rightarrow 2NO_2 \qquad (3b)$$

account for the observation that temperature dependence fits better to a multistep mechanism than a concerted mechanism; however, there was not a preference for one over the other.[1] It is interesting that mechanism 3 has been used in several introductory textbooks as a pedagogical example of a multistep reaction involving a reactive intermediate.[4−6]

On the basis of an identified ONOO intermediate in the reaction of NO with O_2, Bhatia and Hall[7] suggested mechanism 4. In step 4b, one bond forms and one bond breaks, while step

$$NO + O_2 \rightarrow ONOO \qquad (4a)$$

$$ONOO + NO \rightarrow 2NO_2 \qquad (4b)$$

$$2NO + O_2 \rightarrow 2NO_2 \qquad (4c)$$
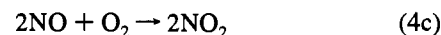
4c may involve concerted NO_2 formation.

Method

Both Hartree−Fock (HF) and density functional theory (DFT)[10−12] have been applied in this study. With an appropriate choice of gradient correction and modest basis set, DFT has been shown to give results of near chemical quality.[13−18] In addition, spin contamination does not seem to be as serious for DFT compared to

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Table 1. Total Energy (hartrees) and Zero-Point Energies (kcal/mol) of Species on the N_2O_4 Potential Energy Surface[a]

	PG	state	//Becke3LYP/a			//MP2/a			
			Becke3LYP/a	ZPE[b]	⟨S²⟩[c]	MP2/a	⟨S²⟩[c]	QCISD(T)/a	MP2/b
NO	$C_{\infty v}$	²Π	-129.888 16	2.85 (0)	0.75	-129.558 90	0.77	-129.579 18	-129.639 02
O₂	$D_{\infty h}$	³Σg⁻	-150.320 04	2.37 (0)	2.01	-149.949 73	2.04	-149.961 87	-150.041 51
NO₂	C_{2v}	²A₁	-205.072 18	5.53 (0)	0.75	-204.560 25	0.78	-204.577 06	-204.693 40
cis-(NO)₂	C_{2v}	¹A₁	-259.774 34	7.78 (0)		-259.132 46		-259.158 61	-259.293 98
trans-(NO)₂	C_{2h}	¹Ag	-259.766 52	7.28 (0)		-259.112 42		-259.153 62	-259.275 16
cis-(NO)₂	C_{2v}	³B₁	-259.777 46	7.17 (0)	2.01	-259.118 78	2.03	-259.143 95	-259.280 32
O=N-N=O	C_{2h}	¹Ag	-259.753 70	8.03 (0)		-259.126 41		-259.127 41	-259.291 12
cis-NO•O₂	C_s	²A″	-280.210 22	5.93 (0)	1.64	-279.509 72[d]	1.81	-279.542 43	-279.681 94
NO₃	D_{3h}	²A₂′	-280.216 79	6.64 (0)	0.75	-279.524 43	0.78	-279.533 46	-279.711 87
cis-ONOO	C_s	²A″	e			-279.473 65	0.78	-279.520 13	-279.651 81
trans-ONOO	C_s	²A″	e			-279.469 36	0.77	-279.514 78	-279.648 03
ONOONO	C_2	¹A	-410.112 91	12.06 (0)		-409.080 39		-409.131 62	-409.342 90
O₂N-NO₂	D_{2h}	¹Ag	-410.168 18	14.72 (0)		-409.154 85		-409.172 12	-409.428 51
O₂N-NO₂	D_{2d}	¹A₁	-410.156 66	14.39 (1)		-409.140 20		-409.159 58	-409.415 19
cis-ONONO₂	C_s	¹A′	-410.146 66	13.34 (1)		-409.125 90		-409.159 40	-409.396 59
trans-ONONO₂	C_s	¹A′	-410.151 26	13.38 (0)		-409.128 03		-409.163 72	-409.398 13
trans-ONONO₂	C_1	¹A	-410.151 26	13.42 (0)		-409.128 06		-409.163 74	-409.398 11
[NO⁺][NO₃⁻]	C_{2v}	¹A₁	-410.089 88	12.41 (2)		-409.050 26		-409.081 73	-409.327 13
TS ONO--ONO	C_2	¹A	-410.062 85	10.97 (1)		-409.023 74		-409.082 82	-409.288 49
TS ON--OO--NO	C_2	¹A	f			-409.055 83		-409.095 08	-409.321 10
TS O₂N--NO₂	D_{2h}	¹Ag	g			-409.131 57		-409.146 72	-409.402 64

[a] Basis set "a" is 6-31G(d). Basis set "b" is 6-31+G(2df). [b] Zero-point energies in kcal/mol. Number of imaginary frequencies in parentheses. [c] Before spin projection. [d] Optimization of the NO•O₂ complex was not carried out to completion due to difficulties in calculating the search direction at the MP2 level. [e] Molecule dissociates to NO + O₂ at the Becke3LYP/6-31G(d) level. [f] Geometry did not converge to a stationary point. [g] During search for a stationary point at the Becke3LYP/6-31G(d) level, the NO₂ moieties separate to a very large distance.

Table 2. Relative Energies (kcal/mol) on the N_2O_4 Potential Energy Surface[a]

	//DFT/a		//MP2/a				
	DFT/a	+ZPC	MP2/a	QCISD(T)/a	MP2/b	[QCI/b][b]	+ZPC[c]
2NO + O₂	10.4	6.6	8.1	7.1	14.6	13.7	9.9
NO + cis-ONOO			30.0	20.3	32.7	23.0	21.6
NO + trans-ONOO			32.7	23.6	35.0	26.0	24.4
O₂ + cis-(NO)₂ ¹A₁	11.6	9.8	-1.1	7.0	4.6	12.8	11.0
O₂ + trans-(NO)₂ ¹Ag	16.5	14.2	11.4	10.1	16.4	15.1	12.8
O₂ + cis-(NO)₂ ³B₁	9.7	7.4	7.4	16.2	13.2	22.0	19.6
O₂ + trans-O=N-N=O ¹Ag	24.6	23.2	2.7	26.6	6.4	30.3	28.7
NO + NO•O₂	9.2	6.1	7.4	6.3	13.8	12.7	9.6
ONOONO	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TS ONO--ONO	31.4	30.4	35.5	30.6	34.1	29.2	28.0
TS ON--OO--NO			15.4	22.9	13.7	21.2	17.4
2NO₂	-19.7	-20.7	-25.2	-14.1	-27.5	-16.5	-17.5
O₂NNO₂ (D_{2h})	-34.7	-32.2	-46.7	-25.4	-53.7	-32.4	-29.9
O₂NNO₂ (D_{2d})	-27.4	-25.2	-37.5	-17.5	-45.4	-25.4	-23.2
TS O₂N--NO₂			-32.1	-9.5	-37.5	-14.8	-15.8
cis-ONONO₂	-21.2	-20.0	-28.6	-17.4	-33.7	-22.6	-21.4
trans-ONONO₂	-24.1	-22.9	-29.9	-20.1	-34.6	-24.9	-23.7
NO + NO₃	5.0	2.6	-1.8	11.9	-5.0	8.7	6.3
[NO⁺][NO₃⁻]	14.4	14.7	18.9	31.3	9.9	22.3	22.6

[a] Basis set "a" is 6-31G(d). Basis set "b" is 6-31+G(2df). [b] Additivity approximation. Reference 20. [c] Zero-point corrections (weighted by a 0.95 factor) are taken from vibrational frequency calculations at the Becke3LYP/6-31G(d) level. For ONOO, zero-point correction (weighted by a 0.90 factor) is taken at the UHF/6-31G(d) level. For TS O₂N- -NO₂ and ON- -OO—NO, the zero-point correction is taken from NO + O₂ and NO₂.

HF theory.[19] Geometries were calculated with the Becke3LYP algorithm (Becke3LYP/6-31G(d)) which has been shown to be effective in reproducing atomization energies (±2.4 kcal/mol of experimental atomization energies).[8,14] At optimized MP2/6-31G(d) geometries, single-point calculations were made at the MP2/6-31+G(2df) and QCISD(T)/6-31G(d) levels and combined to estimate relative energies at the [QCISD(T)/6-31+G(2df)] level.[20] Vibrational frequencies were calculated at both MP2/6-31G(d) and Becke3LYP/6-31G(d) levels. For several molecules (NO, ONOO, (NO)₂), frequencies at the MP2/6-31G(d) level were unrealistic due to the effect of symmetry breaking on the CPHF equations.[21] For that reason, Becke3LYP/6-31G(d) frequencies were used to make zero-point corrections (0.95 weighting factor) for both the MP2 and DFT geometries.

While the unrestricted QCISD(T) wave function was not spin-projected, a recent study[22] showed that spin contamination in NO, NO₂, and NO₃ at the unrestricted CCSD level (to which QCISD is related) was not significant.

This paper is divided into three sections. Section A deals with a comparison between theory and experiment for N₂O₄ species and related fragments, section B deals with calculations of the N₂O₄ isomer, ONOONO, and section C is an evaluation of the N₂O₄ potential energy surface. Absolute energies (hartrees) and zero-point energies (kcal/mol) of N₂O₄ isomers and fragments are presented in Table 1. Energies (kcal/mol) relative to the new ONOONO isomer are given in Table 2, while geometric parameters at the MP2/6-31G(d) and Becke3LYP/6-31G(d) levels are given in Figure 1. Unless otherwise indicated, "DFT" energies will refer to Becke3LYP/6-31G(d)+ZPC and "QCI" will refer

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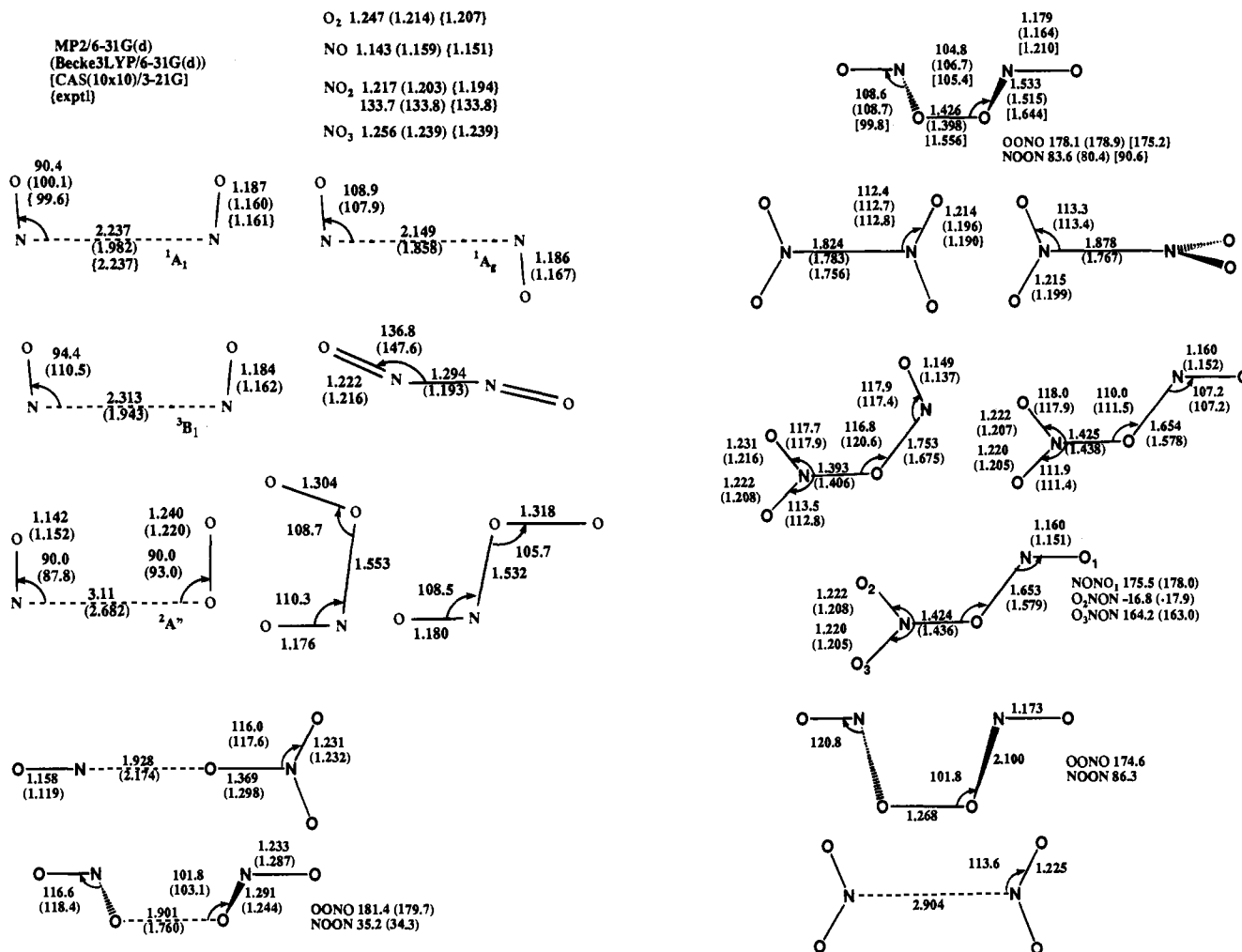(22) Stanton, J. F. *J. Chem. Phys.* **1994**, *101*, 371.

MP2/6-31G(d)
(Becke3LYP/6-31G(d))
[CAS(10x10)/3-21G]
{exptl}

O_2 1.247 (1.214) {1.207}

NO 1.143 (1.159) {1.151}

NO_2 1.217 (1.203) {1.194}
133.7 (133.8) {133.8}

NO_3 1.256 (1.239) {1.239}

Figure 1. Geometric parameters for N₂O₄ isomers and fragments at the MP2/6-31G(d) and (in parentheses) Becke3LYP/6-31G(d) levels. Parameters at the CAS(10×10)/3-21G level are given for ONOONO in brackets. The experimental values for NO, NO₂, NO₃, (NO)₂, and O₂NNO₂ (except the N—N distance of O₂NNO₂ which is taken from refs 42 and 43) are taken from ref 23.

to [QCISD(T)/6-31+G(2df)]+DFT/ZPC. Multiconfigurational SCF calculations on ONOONO were made at the CAS(10×10)/3-21G level and are further described in section B.

Results and Discussion

A. Comparison of NO, O₂, NO₂, NO₃, (NO)₂, NO·O₂, O=N–N=O, ONOO, O₂NNO₂, ONONO₂, and [NO⁺][NO₃⁻]. Johnson et al.[13] have reported calculations on O₂ and NO at the B-LYP/6-31G(d) level, where B-LYP refers to Becke's exchange correction with Lee, Yang, and Parr's correlation function (LYP) which includes local and nonlocal terms. The Becke3 correction (used in this study) is a hybrid exchange correction consisting of a linear combination of Slater's exchange (LSD), Becke's exchange, and nonlocal exchange terms.[14]

Density functional theory was used recently by Stirling et al.[23] in a study of nitrogen oxides up to N₂O₅. Three different functionals were used, one with local spin density exchange and two with nonlocal exchange corrections to Perdew's gradient-corrected correlation functional.[24] It was concluded that bond dissociation energies were in better agreement with experiment using nonlocal functionals but were still over-estimated by about 10 kcal/mol. For other properties, geometries, and frequencies, both local and nonlocal functionals performed equally well.

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Table 3. Becke3LYP/6-31G(d) and MP2/6-31G(d) Calculated Frequencies (cm⁻¹) and IR Intensities (km) of NO, O₂, NO₂, and NO₃

		Becke3LYP		MP2		exptl[a]
NO	σ	1992 (31)	σ	3915 (2724)	σ	1904
$O_2(^3\Sigma_g^-)$	σ	1656 (0)	σ	1998 (0)	σ	1556[b]
NO₂	a₁	1402 (0)	a₁	1380 (17)	a₁	1353
		749 (8)		752 (7)		760
	b₂	1717 (324)	b₂	2271 (1967)	b₂	1671
NO₃	a₁′	1139 (0)	a₁′	1339 (0)	a₁′	1060
	a₂″	790 (16)	a₂″	937 (37)	a₂″	762
	e′	1150 (24)	e′	2217 (3854)	e′	1492
	e″	207 (33)	e″	790 (40)	e″	380

[a] Unless otherwise indicated, taken from ref 23. [b] Taken from ref 55.

In the present study, geometries calculated by Becke3LYP/6-31G(d) are in better agreement with experimental geometries for all nitrogen oxides (when known) than those calculated by MP2/6-31G(d) with the exception of (NO)₂ (Figure 1). The Becke3LYP functional also gave better geometries than the DFT functionals used by Stirling et al.[23] In Table 3, a comparison is made with MP2, Becke3LYP, and experimental frequencies for NO, NO₂, and NO₃. Particularly important is the fact that the Becke3LYP functional avoids the exaggerated NO stretch found at the MP2 level which is probably due to the effect of symmetry breaking on the CPHF equations (note that the stretch in NO is too large by a factor of 2 by MP2). Due to the unreasonable frequencies calculated by MP2 for several of the

nitrogen oxides studied, zero-point corrections were made using DFT frequencies.

Besides the known NO_3 radical, two other species of the same formula are considered: ONOO, a peroxide radical, and $NO\cdot O_2$, a weakly bound complex of NO and triplet O_2. Two different N_2O_2 species are considered, $(NO)_2$ species, which are spin-coupled complexes of two NO radicals, and a molecular N_2O_2 species, which is higher in energy than $(NO)_2$ but separated by a HOMO/LUMO crossing.

The $(NO)_2$ complex is relevant to the present study since it is a steady state species in mechanism 3. The experimental N−N distance[25] (2.237 Å) and binding energy (1.5−3.7 kcal/mol)[23,26] both indicate a weak interaction. The computational predictions of the complex varies widely with the method used.[23,27] The N−N distance is predicted to be shorter than experiment by Becke3LYP/6-31G(d) and other DFT functionals while the MP2 geometry is in very good agreement. The functionals used by Stirling et al.[23] greatly overestimate the binding energy, particularly that of the triplet which is predicted to be the ground state. This is inconsistent with the general assumption from experiment[26] that the complex is a singlet. The Becke3LYP functional also overestimates the stability of the $(NO)_2$ triplet complex relative to the singlet complex. At the DFT level, the triplet is 2.4 kcal/mol more stable than the singlet while at the QCI level the triplet is 8.6 kcal/mol less stable than the singlet. It appears that DFT theory (with a small basis set) overestimates the stability of the triplet $(NO)_2$ complex, perhaps due to excessive exchange correlation in weakly bound complexes.

Another oddity is the predicted energy difference between the cis and trans singlet complex at the DFT level. The 6.8 kcal/mol difference (Table 2) in favor of the cis complex appears to be too large for such a weakly bound complex (1.8 kcal/mol at QCI).

The $(NO)_2$ complex is difficult to describe accurately.[27] At the QCI level, the complex is still calculated to be unbound by 1.1 kcal/mol with respect to two NO radicals (unbound by 3.2 kcal/mol at DFT). Considering the experimental binding energy (1.5−3.7 kcal/mol),[23,26] QCI underestimates the $(NO)_2$ binding energy by 3−7 kcal/mol.

A complex similar to $(NO)_2$ can be envisioned between NO and O_2 ($^3\Sigma_g^-$) where the stabilizing interaction is the singlet coupling of the unpaired spin of NO with an unpaired spin of triplet O_2 to give an overall doublet ($NO\cdot O_2$). While there is no experimental evidence for the complex, it is discussed presently because the complex will play a role in the proposed mechanism for oxidation of NO. The cis complex, located at the DFT level, has a N−O radical separation of 2.682 Å which is 0.70 Å more than the N−N separation in $(NO)_2$. At both the DFT and MP2 levels, the complex was characterized by severe spin contamination [$\langle S^2 \rangle$ = 1.81 (MP2), 1.61 (DFT)]. In fact, a precise stationary point could not be located at the MP2 level due to difficulties in determining a search direction in the optimization procedure. At the lowest-energy point, the N−O separation is 3.11 Å, 0.87 Å longer than the N−N separation in $(NO)_2$. At the QCI level, the $NO\cdot O_2$ complex is bound by 0.3 kcal/mol which is close to the DFT value of 0.5 kcal/mol. These calculations demonstrate that the $NO\cdot O_2$ complex has a stability comparable to the $(NO)_2$ complex.

A molecular N_2O_2 species (O=N−N=O trans geometry) was also calculated with DFT and MP2. The short N−N bond (1.294 Å, MP2; 1.193 Å, DFT; Figure 1) is indicative of multiple

bond character. At the QCI level, the trans O=N−N=O isomer is a minimum and only 17.7 kcal/mol higher in energy than the cis singlet $(NO)_2$ complex which is similar to the calculated value at the DFT level (13.4 kcal/mol). Although not experimentally reported,[28] the trans O=N−N=O isomer could form by promotion of an electron from a doubly occupied σ-type orbital to the singly occupied π^* orbital, thus allowing the formation of a N−N σ bond. Collapse to the lower-energy *trans*-$(NO)_2$ complex is prevented by a LUMO/LUMO crossing along the reaction coordinate. Since the energy is higher for O=N−N=O than two NO radicals, the present results show that the N−N bond strength does not compensate for the promotion energy.

The anion $ONOO^-$ has received recent attention as a possible biological intermediate.[29] It is possible that its cousin, the ONOO radical, may also play an important role as an atmospheric intermediate,[30] even though the more symmetrical species (NO_3, D_{3h}) is lower in energy.[31] Several researchers[30,32,33] have found a new IR absorption (1838−1840 cm^{-1}) during the reaction of NO with O_2 and O_3 and identified it as the asym-NO_3 radical (ONOO). Theoretical calculations have been reported by Morris, Bhatia, and Hall[32] in an effort to confirm the ONOO identification. They found that the trans form of ONOO was more stable than the cis form ($^2A''$), but their calculated N=O stretch (1518 cm^{-1}, DZP; 1659 cm^{-1}, 6-31G*) was much lower than experiment (1838−1840 cm^{-1}). Boehm and Lohr[33] also reported ab initio energies and geometries for ONOO and NO_3. Interestingly, they found that inclusion of electron correlation (MP4/DZP) reversed the relative stability of the cis and trans isomer. At the MP4/DZP level, the *cis*-ONOO isomer was 2.0 kcal/mol more stable than the trans isomer and 10.7 kcal/mol less stable than sym-NO_3 ($^2A_2'$). In the present study, the cis conformer is also predicted to be more stable; the comparable numbers at the QCI level are 2.8 and 15.3 kcal/mol. The *cis*-ONOO isomer is predicted to be 11.7 kcal/mol less stable than NO + O_2 ($^3\Sigma_g^-$) which is somewhat higher than the experimental estimate of 7 ± 2 kcal/mol.[30] The ON−OO bond in ONOO appears to be very sensitive to the level of optimization. At the UHF/DZP level, the N−O distance is 1.411 Å, which increases to 1.553 Å at the UMP2/6-31G(d) level. The *cis*-ONOO radical was subjected to 20 cycles of optimization at the UQCISD/6-31G(d) which yielded a "nearly optimized" value of ~1.71 Å.[34] Unfortunately, the DFT method failed to find a bound complex, dissociating instead into NO plus O_2. The calculated N=O stretch in *cis*-ONOO at the MP2 level is much higher than experiment (2432 vs 1866 cm^{-1})[35,36] due to the effect of symmetry breaking on the CPHF equations.

The most familiar and well-studied N_2O_4 isomer is the N−N bonded O_2N-NO_2 structure of D_{2h} symmetry.[37−45] The struc-

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Table 4. Becke3LYP/6-31G(d) and MP2/6-31G(d) Calculated Frequencies (cm⁻¹) and IR Intensities (km) of *cis*-ONONO₂ and *trans*-ONONO₂ᵃ

cis-ONONO₂				trans-ONONO₂					
Becke3LYP		MP2		Becke3LYP		MP2		exptlᶜ	
a′	1986 (401)	a′	2165 (441)	a′	1906 (282)	a′	1871 (183)	a′	1871
	1722 (216)		1905 (493)		1769 (337)		1839 (273)		1839
	1338 (275)		1568 (327)		1353 (291)		1315 (332)		1315
	872 (193)		1055 (304)		954 (24)		926 (82)		926
	791 (34)		965 (23)		797 (237)		778 (241)		778
	620 (210)		802 (235)		636 (139)		636 (176)		636
	588 (9)		674 (138)		477 (181)		489 (159)		489
	270 (136)		286 (0)		322 (251)		310 (208)		310ᵈ
	206 (26)		250 (329)		214 (1)		205 (4)		
a″	769 (17)	a″	902 (38)	a″	760 (15)	a″	751 (12)		
	169 (10)		145 (1)		140 (0)		123 (0)		
	−55 (0)		−90 (0)		29 (0)		−31ᵇ (1)		

ᵃ IR intensities are given in parentheses. ᵇ Imaginary frequency. The C_s structure is lower than the C_1 structure when zero-point corrections are included. ᶜ Reference 36. ᵈ Reassigned in ref 23.

ture and frequencies of the D_{2h} minimum as well as the D_{2d} transition state for rotation have been calculated previously at the MP2/6-31G(d) level.[41] The experimental N−N distance is 1.756 Å, a value obtained by both a neutron diffraction study[42] and a rotational analysis of spectroscopic constants.[43] The DFT N−N distance (1.783 Å) and the MP2 N−N distance (1.824 Å) are both too long. The N−N distances calculated by Stirling et al.[23] in their DFT study are also somewhat too long depending on the functional used (1.774−1.854 Å). The DFT functional without nonlocal corrections gave the best agreement with experiment, in contrast to the Becke3LYP functional used here which gave a N−N distance close to experiment. The QCI (12.4 kcal/mol) and MP2 (11.5 kcal/mol) values for dissociation of O₂NNO₂ into 2NO₂ are in good agreement with experiment (13.6 kcal/mol).[39,40] Another point of contact between experiment and theory is the energy difference between the D_{2h} and D_{2d} symmetry structures. The experimental difference is 5.4 kcal/mol,[45] in good agreement with QCI (6.7 kcal/mol), DFT (7.0 kcal/mol), and previous theoretical calculations (6−7 kcal/mol).[37d]

A second N₂O₄ isomer is the ONONO₂ isomer where two NO₂ radicals are linked by an O−N bond. If NO₂ is localized in one of its resonance forms with one O−N bond and one N=O bond (•O−N=O), asym-N₂O₄ can form by coupling the unpaired electron on the oxygen of •O−N=O and the unpaired electron on nitrogen on the second NO₂. The asym-N₂O₄ isomer has only been reported in the condensed phase,[46−50] and the only theoretical calculation is the DFT study by Stirling et al.[23] on the *trans*-ONONO₂ isomer.

Two planar conformers were considered in this study, *cis*-ONONO₂ and *trans*-ONONO₂. At both the MP2 and DFT

levels, the cis planar structure was a transition structure, while at the MP2 level, the trans planar structure was a transition structure. A C_1 minimum was found at both the MP2 and DFT levels for the trans structure, but it was only marginally more stable than the C_s structure (less than 0.1 kcal/mol). In their DFT study of the *trans*-ONONO₂ isomer, Stirling et al.[23] reported the symmetry of *trans*-ONONO₂ as C_s and the electronic state as ¹A′, yet they reported dihedral angles which would indicate a C_1 symmetry structure. Since the energy difference between the C_s and C_1 symmetry structures is very small, the more symmetric C_s structure will be used in further discussions. The heat of formation of ONONO₂ has been estimated from experiment to be 6.7 ± 1 kcal/mol[51] which is only 4.5 kcal/mol less stable than O₂NNO₂. At the QCI level, *trans*-ONONO₂ is 6.2 kcal/mol less stable than O₂NNO₂ (9.3 kcal/mol at the DFT level), in fair agreement with the experimental estimate.

On the basis of a longer ON−ONO₂ bond in the trans isomer relative to the ONO−NO₂ bond, Stirling et al.[23] surmised that the preferred products of dissociation would be NO and NO₃. Calculations at the MP2 and QCI levels agree with the relative ordering of NO bond lengths [1.753 and 1.393 Å (MP2) versus 1.675 and 1.406 Å (DFT)] but predict that NO + NO₃ are 23.8 kcal/mol higher than 2NO₂ at the QCI level and 23.3 kcal/mol higher at the MP2 level (21.2 kcal/mol, exptl).[52] It does appear odd that the NO bond in ON−ONO₂ which is longer (0.23 Å, MP2; 0.14 Å, DFT) than the adjacent NO bond (ONO−NO₂) would also be over 20 kcal/mol stronger. The origin of the difference is due to the very large stabilization that the •O−N=O fragment undergoes which makes the NO bond in ONO−NO₂ very weak. On the other hand, the fragments which result from breaking the NO bond in ON−ONO₂ are not strongly resonance stabilized and the bond is not unusually weak.

As indicated below, the cis isomer of ONOO is more stable than the trans isomer by 2.8 kcal/mol (QCI). If the ONOO radical is an indicator, the cis isomer of ONONO₂ might be predicted to be more stable than the trans. However, additional steric repulsion in the cis isomer shifts the stability toward the trans isomer, making it more stable by 2.3 kcal/mol at QCI and 2.9 kcal/mol at DFT.

In Table 4 calculated vibrational frequencies are reported for the C_s structures of the cis and trans isomer of ONONO₂ as well as the experimental frequencies for the trans isomer. The

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DFT calculated frequencies are in good agreement with experiment[23,26] for the trans isomer as well as density functional calculations reported by Stirling et al.[23] At the MP2 level, the N=O stretch for the cis isomer (2165 cm⁻¹) is much higher than the same stretch (1871 cm⁻¹) of the trans isomer. Since the calculated N=O frequencies at the DFT level do not show a large increase for trans → cis (1906 → 1986 cm⁻¹), it may be that MP2 frequencies are not reliable. More extreme cases of unrealistic frequencies at the HF levels have been reported.[21]

The closed shell ions, NO⁺ and NO₃⁻, are expected to have strong mutual Coulombic attraction. A C_{2v}-symmetry supermolecule calculation was made for the [NO⁺][NO₃⁻] complex and, indeed, the inter-ion separation is relatively short (1.928 Å (MP2) 2.174 Å (DFT); Figure 1). The energy for electron transfer in the reaction NO + NO₃ → [NO⁺][NO₃⁻] is only 16.3 kcal/mol at QCI and 12.1 kcal/mol at DFT. In the [NO⁺][NO₃⁻] complex, 0.44 e⁻ have been transferred from NO⁺ to NO₃⁻ at the HF/6-31+G(2df) level and 0.59 e⁻ at the Becke3LYP/6-31G(d) level. At the MP2 and DFT levels, the [NO⁺][NO₃⁻] complex has two imaginary frequencies. An inspection of the corresponding transition vectors indicates that the complex is unstable with respect to distortion toward the ONONO₂ isomer.

B. New Isomer, ONOONO. The ONOONO isomer can be thought of as the missing isomer in the N₂O₄ series. Coupling the two nitrogen centers forms the well-known O₂-NNO₂ isomer and a very weak N−N bond but does not require any promotion energy. Formation of the known ONONO₂ isomer couples a nitrogen-centered radical to an oxygen-centered radical and requires the promotion of one NO₂ radical to a higher energy resonance form (•O−N=O). The missing N₂O₄ isomer is the unknown oxygen−oxygen coupled isomer (ONOONO) which requires the promotion of two NO₂ radicals to their higher-energy resonance form. It can be pointed out that molecules similar to ONOONO, for example, HOONO and ClOONO (where one NO is replaced with H or Cl), are well-known.[53] While it is unlikely that this isomer could form directly from NO₂, a plausible mechanism can be written which forms ONOONO as an intermediate in the oxidation of NO.

Since this isomer is rather unusual, preliminary calculations were carried out at the MCSCF level to determine the feasibility of calculations based upon a single reference. A large active space with the relatively small 3-21G basis set was chosen to allow the simultaneous description of the NO, O₂, and NO₂ portions of the molecule. The 10-electrons in 10-orbitals active space (CAS(10×10)) was composed of the σ and σ* orbitals in the N−O−O−N portion of the molecule (6-electrons in 6-orbitals) and four π electrons in four π orbitals in the O=N portion. Preliminary calculations performed at the HF/6-31G(d) level showed that the most stable structure had C_2 symmetry with a NOON dihedral angle of about 90°. At the MCSCF level, the optimized ONOONO structure has a long central O−O bond *and* two long adjacent NO bonds (Figure 1). Out of 9752 configurations, the SCF configuration accounts for 71% of the wave function with one configuration contributing 5%, two configurations each contributing 4%, and eight configurations each contributing 1%. Since the QCISD(T) level of electron correlation would be used,[54] the wave function was considered to be sufficiently dominated by one configuration to continue with perturbative methods of introducing electron correlation.

At the MP2 and DFT levels, the optimized geometries of ONOONO are very similar, with the central O−O bond and

the adjacent NO bonds somewhat shorter than the CAS(10×10)/3-21G results (Figure 1). At the MP2 level, the ONOO portion of ONOONO exhibits a strong similarity to the trans-ONOO radical (Figure 1). Except for the O−O distance, which is 0.11 Å shorter in the ONOO radical, all other distances are within a few thousandths of an angstrom and all angles are within a few tenths of a degree. The lowest electronic state of trans-ONOO (²A″ state) contains an unpaired electron on the terminal oxygen furthest from nitrogen. This electron can couple with an unpaired electron in a π* orbital of NO to form a σ bond (ON−OONO) with very little activation.

Each •O−N=O fragment of ONO−ONO also bears a resemblance to the •O−N=O fragment of trans-ONONO₂. The long NO bond in ONONO₂ [1.654 (MP2), 1.578 Å (DFT)] is a bit shorter in ONOONO [1.553 (MP2), 1.515 Å (DFT)]. The NOON dihedral angle in ONOONO is a little less than 90° [83.6° (MP2), 80.4° (DFT)], while the OONO dihedral angle is close to 180° [178.1° (MP2), 178.9° (DFT)]. While the ONOONO isomer is predicted to be 9.9 kcal/mol more stable than 2NO + O₂ at the QCI level and 6.6 kcal/mol more stable at the DFT level, it is predicted to be 17.5 kcal/mol less stable than 2NO₂ at the QCI level and 20.7 kcal/mol at the DFT level. Thus, the O−O bond in ONOONO has a negative bond dissociation energy.

There are many compounds of formula XOOX, and it may be possible to take advantage of the substantial body of theoretical and experimental data to analyze the ONOONO bond.[55-73] For example, is the O−O bond in ONOONO more similar to FOOF, which is known to be difficult to describe by ab initio methods,[59-62] or more similar to CH₃OOCH₃? Experimental heats of formation of XOOX molecules and fragments are collected into Table 5. In Table 6, data are collected for XOOX molecules including the electronegativity of X, the O−O bond distance, and several bond dissociation energies (BDE). The O−O bond distance in XOOX and XOO shows a trend (except for X = CF₃) toward smaller distances as the electronegativity increases. At X = F there is an abrupt shortening of the O−O distance with a corresponding increase in the O−O BDE. What is the cause for this abrupt change between X = NO and F?

The explanation can be seen in the nature of the bonding between X = NO and F in XOO (Figure 2). For X = NO, the lone pair and π* orbitals in one plane of O₂ are rehybridized to sp² in preparation for forming a 2c-2e σ bond with NO. For X

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Ab Initio Study of the N_2O_4 Potential Energy Surface

J. Am. Chem. Soc., Vol. 117, No. 5, 1995 1635

Table 5. Heats of Formation (kcal/mol) of X, XO, XO$_2$, and XOOX[a]

X	$\Delta H_f(X)$	XO	$\Delta H_f(XO)$	XO$_2$	$\Delta H_f(XO_2)$	XOOX	$\Delta H_f(XOOX)$
H	52.1	HO	9.4	HO$_2$	3.5	HOOH	−32.6
CH$_3$	34.9	CH$_3$O	4.2	CH$_3$O$_2$	2.5	CH$_3$OOCH$_3$	−30.0
CF$_3$	−113[b]	CF$_3$O	−157[b]	CF$_3$O$_2$	−160[b]	CF$_3$OOCF$_3$	−361[b]
Cl	29.0	ClO	24.4	ClO$_2$	23.3	ClOOCl	31.1
ON	21.6	ONO	7.9	ONOO	33.3[c]	ONOONO	33.3[c]
F	19.0	FO	26.0[d]	FO$_2$	6.2[e,f]	FOOF	4.6[e]

[a] Unless otherwise stated, experimental heats of formation are taken from ref 52. [b] Reference 58. Alternative values from ref 64 give very similar BDE. [c] This work. Based on energies at the [QCISD(T)/6-31+G(2df)]//MP2/6-31G(d)+ZPC level. [d] A calculated value of 27.8 kcal/mol has been reported. Zhao, Y.; Francisco, J. S. *Chem. Phys. Lett.* **1990**, *167*, 285. [e] Reference 65. An alternative value of 5.5 kcal/mol is reported for the heat of formation of FO$_2$. [f] A calculated value of 8.9 kcal/mol has been reported. Francisco, J. S.; Zhao, Y.; Lester, W. A., Jr.; Williams, I. H. *J. Chem. Phys.* **1992**, *96*, 2861.

Table 6. Experimental O−O Bond Distances (Å) and Bond Dissociation Energies (kcal/mol) of XOOX Molecules

XOOX	$\chi(X)$[a]	O−O distance		BDE (kcal/mol)[b]			
		XO−OX	XO−O	XOOX → 2XO	XOOX → X + OOX	XOO → X + O$_2$	Δ
HOOH	2.20	1.464[c]	1.330[d]	51.4	88.2	48.6	39.6
CH$_3$OOCH$_3$	2.56	1.457[e]	1.312[f]	38.4	67.4	32.4	35.0
CF$_3$OOCF$_3$	2.71	1.419[c]	1.333[f]	47[g]	88	47	41
ClOOCl	3.05	1.426[h]	1.21[i]	17.7	21.2	5.7	15.5
ONOONO	3.12	1.426[j]	1.304[j]	−17.5	21.6	−11.7	33.3
FOOF	4.00	1.217[k]	1.200[k]	47.4[l]	20.6[m]	12.8[m]	7.8

[a] Group electronegativities: (a) Boyd, R. J.; Edgecombe, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 4182; (b) Boyd, R. J.; Boyd, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 1652. [b] For recent general references of peroxide BDE see refs 55−58. [c] Reference 55. [d] Lubic, K. G.; Amano, T.; Uehara, H.; Kawaguchi, K.; Hirota, E. *J. Chem. Phys.* **1984**, *81*, 4826. [e] Haas, B.; Oberhammer, H. *J. Am. Chem. Soc.* **1984**, *106*, 6146. [f] Calculated at the MP2/6-31G(d) level (ref 66). For recent additional computations on CH$_3$OO see: (a) Cheung, Y.-S.; Li, W.-K. *Chem. Phys. Lett.* **1994**, *223*, 383. (b) Sicilia, E.; Di Maio, F. P.; Russo, N. *Chem. Phys. Lett.* **1994**, *225*, 208. (c) Sicilia, E.; Di Maio, F. P.; Russo, N. *THEOCHEM* **1994**, *310*, 13. [g] A slightly lower value of 44.4 kcal/mol is obtained based on recent high-level calculations of COF$_2$. Schneider, W. F.; Wallington, T. J. *J. Phys. Chem.* **1994**, *98*, 7448. [h] Birk, M.; Freidl, R. R.; Cohen, E. A.; Pickett, H. M.; Sander, S. P. *J. Chem. Phys.* **1989**, *91*, 6588. [i] Estimated from theoretical calculations. Jensen, F. *Chem. Phys. Lett.* **1990**, *169*, 519. [j] Calculated MP2/6-31G(d) level. This work. [k] Yamada, C.; Hirota, E. *J. Chem. Phys.* **1994**, *80*, 4694. [l] The quoted O−O bond dissociation energies in FOOF range from 9.1 kcal/mol (Francisco, J. S. *J. Phys. Chem.* **1994**, *98*, 5650) to 62.1 kcal/mol (ref 63). [m] Similar values have been quoted for the first (19.9 kcal/mol) and second (13.5 kcal/mol) BDE of F from FOOF. Reference 61.
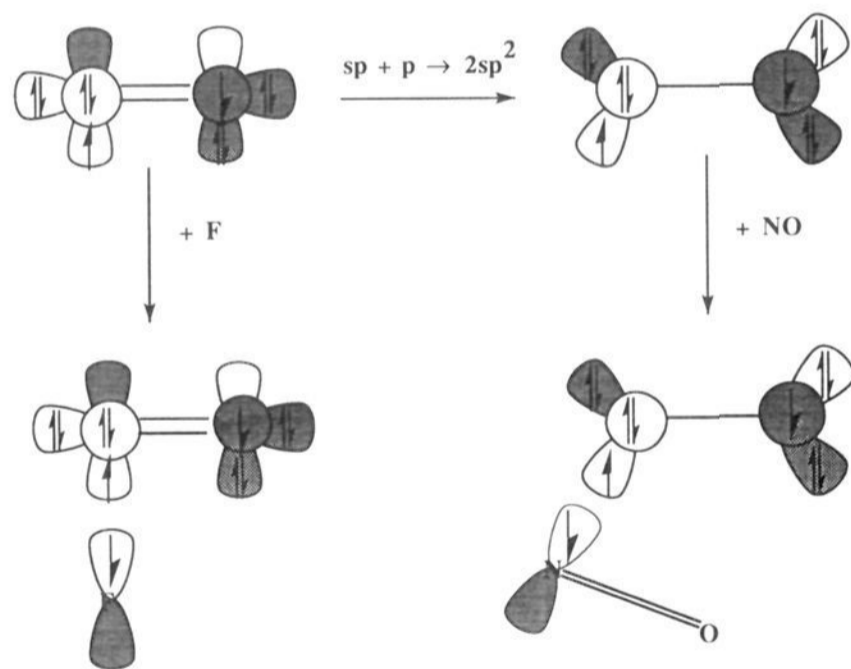

Figure 2. Sketch of the two different modes of bond formation with O$_2$. With F, the most stable interaction involves the formation of a three-center two-electron (3c-2e) bond without rehydridization of the O$_2$ orbitals. With NO, the most stable interaction involves the rehybridization of the O$_2$ orbitals to form a singly occupied sp^2 orbital at oxygen which can form a two-center two-electron (2c-2e) bond. Bond formation with ligands such as H, CH$_3$, and CF$_3$ will also involve promotion followed by 2c-2e bond formation.

= F, another mechanism of bond formation leads to a more stable system. The EA of F and the IP of O$_2$ are matched sufficiently that a stable 3c-2e bond forms between the π^* of O$_2$ (1 electron over two centers) and the F radical. While the 3c-2e F−O−O bond is not as strong as a 2c-2e F−O bond, no rehybridization is required.[74]

Table 6 bears out this interpretation. Since no rehydrization is required for X = F, the first and second X−O BDE's are

(74) For a related discussion on these types of molecules see refs 37, 54, and 60.

very similar. For all other X (except X = Cl), the first BDE is about 33−41 kcal/mol smaller than the second. The promotion (rehybridization) energy is required before the first bond is formed; the second bond can form with little or no rehybridization. For X = Cl, the difference between the first and second BDE is 15.5 kcal/mol, about twice the corresponding value for X = F. Adding the first NO to O$_2$ is endothermic because forming the ON−OO bond does not compensate for the energy required to rehybridize O$_2$. However, adding the second NO bond (ON−OONO) is exothermic because rehybridization is not required. Again, the BDE of the O−O bond in ONOONO is negative due to the large reorganization energy of the •O−N=O fragment.

It is possible to estimate the O−O BDE with respect to the hypothetical •O−N=O radical (i.e. in the absence of reorganization) by the use of standard bond energies. In Table 7, heats of formation of a series of XONO compounds are collected along with standard bond energies of the X−O bond. If the heat of formation of X is known, an estimate of the heat of formation of •O−N=O can be obtained. Averaging over four values leads to a heat of formation for the hypothetical •O−N=O isomer of 36 ± 4 which is 28 ± 4 kcal/mol larger than the heat of formation of NO$_2$. Therefore, with respect to the •O−N=O "isomer" the O−O BDE would be 56 kcal/mol larger, which would give a BDE of 38 kcal/mol (56 − 17.5) or about the same as the BDE of O−O in CH$_3$OOCH$_3$ (Table 6).

Calculated vibrational frequencies (cm^{-1}) and infrared intensities (km) for ONOONO are given in Table 8. The most intense bands are the N=O antisymmetric stretch (1711, MP2; 1832 cm^{-1}, DFT) and the NO antisymmetric stretch (833, MP2; 871 cm^{-1}, DFT). The O−O stretch (982, MP2; 1042 cm^{-1}, DFT) is larger than the experimental O−O stretch in HOOH (863 cm^{-1})[55] but smaller than the experimental O−O stretch in FOOF (1210 cm^{-1}).[65] All of the bends (O=N−O and O−O−

Table 7. Estimation of Heat of Formation (kcal/mol) of the Hypothetical ˙O−N=O Isomer

XONO	ΔH_f (XONO)[a]	av	BDE[b]	ΔH_f (˙O−N=O)[c]	stab energy[d]
HONO	−19.0	H−O	111.6	40.5	32.6
CH₃ONO	−15.6	C−O	85.4	35.1	27.2
FONO	10.9[e]	F−O	45.4	37.3	29.4
ClONO	13.4[f]	Cl−O	48.5	32.9	25.0
				av 36 ± 4	28 ± 4

[a] Unless otherwise indicated, experimental heats of formation are taken from ref 52. [b] Bond dissociation energies (kcal/mol) are from: Zumdahl, S. S. *Chemistry*, 3rd ed.; Heath: Toronto, 1993; p 365. [c] ΔH_f(˙O−N=O) = av BDE − ΔH_f(X) + ΔH_f(XONO). [d] The stabilization energy equals ΔH_f(˙O−N=O) − ΔH_f(NO₂, 7.9 kcal/mol). [e] The experimental ΔH_f(FONO) derived from the experimental ΔH_f(FNO₂) (ref 52) plus the calculated energy difference between FNO₂ and FONO. Lee, T. J.; Rice, J. E. *J. Chem. Phys.* **1992**, *97*, 4223. A value of 12.0 kcal/mol has been quoted for *trans*-FONO (ref 51). For a DFT study of FONO see ref 61. Also see: Lee, T. J.; Bauschlicher, C. W.; Dateo, C. E.; Rice, J. E. *Chem. Phys. Lett.* **1994**, *228*, 583. [f] A theoretical value of 14.5 kcal/mol at 298 K has been reported. Lee, T. J. *J. Phys. Chem.* **1994**, *98*, 111.

Table 8. Becke3LYP/6-31G(d) and MP2/6-31G(d) Calculated Frequencies (cm⁻¹) and IR Intensities (km) of ONOONO[a]

Becke3LYP		MP2		assignment
a	1861 (52)	a	1728 (46)	N=O sym stretch
	1042 (29)		982 (22)	O−O stretch
	766 (55)		736 (69)	N−O sym stretch
	417 (14)		370 (21)	O=N−O bend
	343 (6)		331 (12)	O−O−N bend
	202 (0)		200 (0)	NOON torsion
	71 (0)		80 (0)	OONO torsion
b	1832 (595)	b	1711 (372)	N=O asym stretch
	871 (255)		833 (200)	N−O asym stretch
	476 (304)		390 (249)	O−O−N bend
	394 (3)		358 (174)	O=N−O bend
	165 (1)		158 (2)	OONO torsion

[a] IR intensities are given in parentheses.

N) fall into a rather narrow range (331−390, MP2; 343−476 cm⁻¹, DFT). The averages of the symmetric and antisymmetric N=O and N−O stretches in ONOONO (1720 and 784 cm⁻¹, Table 8) are very close to the corresponding modes in *trans*-nitrous acid (*trans*-HONO) (1700 and 790 cm⁻¹)[75] which is an indication that the bonding in the O−N=O portion of both molecules is similar.
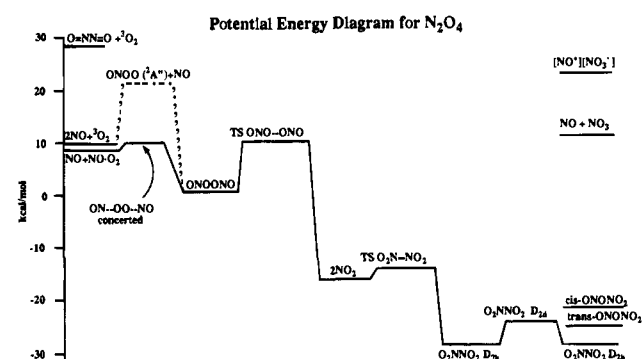
C. Potential Energy Surface for N₂O₄. Transition structures for homolytic bond-breaking processes are not well described by methods based on a single-configurational reference. Nevertheless, such calculations may provide qualitative information if used with care. It should also be kept in mind that the energy of the transition structure for a bond-breaking process is likely to be overestimated by methods based on a single configuration and that the calculated activation barrier is an upper limit. With these provisos in mind, the potential energy surface of N₂O₄ is discussed with emphasis on the mechanism of NO oxidation to NO₂ in the presence of O₂.

Three bond-breaking transition structures are calculated in this section: (1) the concerted fragmentation of ONOONO → 2NO + O₂, (2) the fragmentation of ONOONO → 2NO₂, and (3) O₂NNO₂ → 2NO₂. As fragmentation proceeds beyond the transition state, the breaking bond elongates and the forming radicals undergo electronic relaxation. In the reverse direction, it is assumed that once the radical fragments have been "activated" into the proper geometry, the bond will form without activation (i.e. the activation barrier is entirely due to geometric change of the radical fragments within the molecule).

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Table 9. Estimated Activation Barriers (kcal/mol) at QCI and DFT (in parentheses) Levels[a]

reactant → TS	radicals at //reactant[b]	TS[c]	radicals at //TS[d]
ONOONO → ON- -OO- -NO	32.1 (27.7)	17.4	10.1
ONOONO → ONO- -ONO	53.7 (50.1)	28.0 (30.4)	10.9 (2.7)
O₂NNO₂ → O₂N- -NO₂	−0.1 (0.1)	1.7	1.1

[a] The first energy is at QCI = [QCISD(T)/6-31+G(2df)]//MP2/6-31G(d)+ZPC. The value in parentheses is DFT = Becke3LYP/6-31G(d)//Becke3LYP/6-31G(d)+ZPC. [b] The energy of the transition structure is assumed to be equal to radicals frozen in the geometry of the reactant. The zero-point energies are taken from optimized NO, O₂, and NO₂. [c] The energy of the transition structure is evaluated at the optimized transition structure. [d] The energy of the transition structure is assumed to be equal to radicals frozen in the geometry of the transition structure. The zero-point energies are taken from optimized NO, O₂, and NO₂.

Figure 3. Potential energy surface for the formation of ONOONO and N₂O₄ from 2NO + O₂ at the QCI level of theory. The activation barriers for 2NO + O₂ → ONOONO and ONOONO → 2NO₂ were estimated by calculations on the radicals fragments frozen to the geometry in the transition structure. The scale on the left is energy in units of kcal/mol.

The barrier for fragmentation can be estimated in three ways (Table 9). First, no relaxation of the fragments can be assumed until after the transition state is reached. In that case, the barrier can be estimated as the sum of the radical fragments frozen in the reactant geometry (radicals//reactant). Second, the transition structure can be calculated and the barrier directly evaluated. While this method is preferable, as indicated above, activation barriers are expected to be overestimated. Third, the activation barrier can be assumed to be the sum of the radical fragments frozen to the geometry in the transition structure (radicals//TS). This approximation assumes that the degree of fragment "activation" in the transition structure is correct even though the energy of the transition structure is overestimated.

The three methods of estimating the activation barrier are compared in Table 9. When no relaxation of the fragments is permitted, the energy is usually higher than the transition structure calculation where relaxation does take place. The O₂-NNO₂ → 2NO₂ barrier at the QCI level is an exception because the energy (QCI) is evaluated at a different level than that used to calculate the geometry (MP2). However, all three methods are within 2 kcal/mol of each other. The third method gives lower activation barriers, which are probably more realistic, for the first two fragmentations. The intent of this section is not to provide an accurate description of the transition state or a quantitative estimate of the activation barrier but rather to attempt an evaluation of the possibility of a mechanism involving the ONOONO intermediate.

On the left-hand side of Figure 3, the reactants 2NO + O₂ are indicated with an energy relative to ONOONO. In a multistep mechanism, the first step is formation of the ONOO intermediate which is calculated to be endothermic by 11.7 kcal/mol at the QCI level. Once formed, the ONOO intermediate

should add a second NO with little or no activation to form ONOONO. Support for this mechanism comes from the reaction of peroxy radicals with NO. A proposed step in the observed reaction $5^{76,77}$ is the intermediate ROONO which is

$$\text{ROO} + \text{NO} \rightarrow \text{NO}_2 + \text{OR} \qquad (5)$$
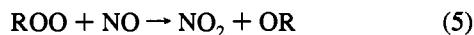
analogous to the addition of NO to the ONOO radical. However, this mechanism has a positive activation barrier which is not consistent with experiment (overall negative activation barrier).[1] The largest contribution to the barrier is the formation of the ONOO intermediate which contributes 11.7 kcal/mol.

While a termolecular reaction is unlikely due to a very unfavorable A-factor (simultaneous collision of three bodies in the gas phase), a concerted bimolecular reaction between $(\text{NO})_2$ and O_2 (mechanism 2) to form ONOONO would be more favorable from an entropic point of view.[78,79] However, such a concerted mechanism is not likely because the orbital overlap (bond formation) between the NO radicals and O_2 is not possible until the NO radicals have come apart since the same orbitals are being utilized.

Another possibility is that O_2 could displace a NO from the $(\text{NO})_2$ dimer or add directly to a free NO radical. The new NO·O_2 complex would be an overall doublet and would be stabilized by the singlet coupling of two unpaired electrons, the same mechanism which stabilizes $(\text{NO})_2$. If the NO·O_2 radical complex survived for a few vibrations, the complex could encounter another NO radical and could form the ONOONO molecule in a concerted fashion, with two new NO bonds (ON–OO–NO) forming simultaneously. The NO·O_2 complex, described in section B, is calculated to be bound by 0.3 kcal/mol at the QCI level, which suggests that a reaction between NO·O_2 and NO is possible.
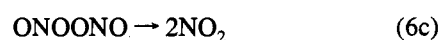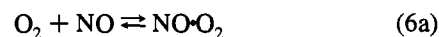
A transition structure for the concerted process $(\text{NO·O}_2 + \text{NO} \rightarrow \text{ONOONO})$ was calculated only at the MP2 level because the DFT calculation failed to converge to a stationary structure. Two negative eigenvalues were found at the MP2 level which indicates that a lower-energy stationary point exists on the MP2 surface. The forming/breaking NO bonds are 2.100 Å while the N=O and O=O distances are close to values in the isolated diatomics (Figure 1). The estimated activation barrier (Table 9, radical//TS) is only 0.2 kcal/mol at the QCI level or 9.7 kcal/mol lower than the stepwise reaction (2NO + O₂ → ONOO + NO → ONOONO).

The next transition structure studied was the O–O fragmentation in ONOONO. A C_2-symmetry transition structure was located with one imaginary frequency and an elongated O–O bond (1.901, MP2; 1.760 Å, DFT). At the QCI level, the activation barrier for O–O fission was 28.0 kcal/mol (30.4 kcal/mol, DFT); however, as pointed out above, methods based on a single-configurational reference may substantially overestimate the activation barrier. The NO bonds in ONOONO, which resemble the single and double bonds of the hypothetical ·O–N=O isomer, are more equal in the transition structure [1.291 and 1.233 Å, (MP2); 1.244 and 1.287 Å (DFT)], indicating a movement toward NO_2 radicals. The energy of two NO_2 fragments frozen to the geometry of the transition structure (radicals//TS) gives an estimated barrier for the reaction ONOONO → 2NO₂ of 10.1 kcal/mol at the QCI level and 2.7

kcal/mol at the DFT level. With respect to the 2NO + O₂ asymptote, the O–O fragmentation transition structure is 1.0 kcal/mol higher at QCI and 3.9 kcal/mol lower at DFT.

The NO_2 dimerization transition structure was calculated at the MP2 level with an assumed symmetry of D_{2h} (DFT failed to converge to a transition structure). All three methods of estimating the activation barrier predict the value to be less than 2 kcal/mol (Table 9). The last transition structure to be considered is the twisted NO_2 dimer which has D_{2d} symmetry. The present barrier of 6.7 kcal/mol at the QCI level (7.0 kcal/mol, DFT) is in good agreement with experiment[45] and previous theoretical estimates.[37b]

An overall mechanism incorporating the present computational results is given below as mechanism 6. The rate equation

$$\text{O}_2 + \text{NO} \rightleftharpoons \text{NO·O}_2 \qquad (6a)$$

$$\text{NO·O}_2 + \text{NO} \rightarrow \text{ONOONO (RDS)} \qquad (6b)$$

$$\text{ONOONO} \rightarrow 2\text{NO}_2 \qquad (6c)$$

$$\text{rate} = K_{6a}k_{6b}[\text{NO}]^2[\text{O}_2] \quad (k_{-6a} \gg k_{6b}[\text{NO}]) \qquad (6d)$$

for this mechanism can be derived by assuming step 6b is the rate determining step (RDS) and making a steady state approximation for NO·O_2 and ONOONO. The simplified rate equation (mechanism 6d) (made by assuming $k_{-6a} \gg k_{6b}[\text{NO}]$) is second order in [NO] and first order in [O₂]. If one uses the values in Tables 2 and 9, the overall activation barrier is −0.1 kcal/mol $(-0.3(\Delta H/6a) + 0.2(E_a/6b))$ which is in agreement with the experimental determinations of a slightly negative overall activation barrier.[1]

Conclusion

Two computational methods are applied to the study of nitrogen oxides. The first is density functional theory using the LYP correlation function and the nonlocal corrections by Becke (Becke3LYP/6-31G(d)//Becke3LYP/6-31G(d)+ZPC), and the second is Hartree–Fock theory with perturbative electron correlation ([QCISD(T)/6-31+G(2df)]//MP2/6-31G(d)+ZPC). Both methods yield very similar results and provide reassurance that the present results are reliable.

Computational evidence is presented for a new N_2O_4 isomer, the ONOONO molecule of C_2 symmetry. This new peroxide isomer has a negative O–O bond dissociation energy (−17.5 kcal/mol) which is due to the large electron reorganization that takes place as the unstable "hypothetical" ·O–N=O isomer rearranges to the known C_{2v} isomer. The bonding in ONOONO is more similar to HOOH, CH₃OOCH₃, and CF₃OOCF₃ than to FOOF or ClOOCl as judged by the difference in the first and second BDE to O₂. The O–O stretch in ONOONO (982 cm⁻¹, MP2; 1042 cm⁻¹, DFT) is higher than in HOOH but lower than in FOOF.

A new mechanism is presented for the overall reaction 2NO + O₂ → 2NO₂. After a fast equilibrium to form NO·O₂, a concerted step leads directly to the ONOONO intermediate. In turn, the intermediate undergoes exothermic O–O bond cleavage with an estimated activation barrier of 10.9 kcal/mol. The overall activation barrier is calculated to be slightly negative, which is in agreement with experimental observations.

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