N-Nitrosohydroxylamine-*N*-sulfonate: A Redetermination of Its X-ray Crystal Structure and an Analysis of Its formation from NO and SO_3^{2-} Using Ab Initio Molecular Orbital Calculations

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The synthesis, structure, and acid-catalyzed degradation of *N*-nitrosohydroxylamine-*N*-sulfonate has been subjected to analysis by ab initio molecular-orbital calculations using a cc-pVTZ basis set, further refined using density functional theory at the Becke 3LYP level using the 6-311+G(3d) basis set. The theoretical data is compared to the structural data obtained from the redetermination of the X-ray crystal structure of this seminal anion. This comparison allows a unique insight into the mechanism behind nitric oxide coupling and its reductive elimination as nitrous oxide. These processes are of direct relevance to the action of metalloenzymes such as nitrite reductase and the underlying mechanism of Wacker type catalysts for the dismutation of nitric oxide into nitrogen and oxygen ($2NO \rightarrow N_2O \rightarrow N_2 + {}^1/_2O_2$).

Introduction

Nitric oxide is one of the smallest heteronuclear molecules known. Although it contains an unpaired electron in the π^* antibonding orbital, its independent reactivity is low. For example, the molecule couples to form ONNO only at high pressures and low temperatures, and although it is unstable in air, the gas-phase reaction (leading to the formation of NO_2) is governed by third-order kinetics.[1−4] This moderate reactivity has enabled nitric oxide to assume a special role in chemistry and biology where it can act as a radical, an electrophile, or a π acid depending on the character of its coreactants[5−12] (eqs 1−3).

$$[O_2]^{\cdot-} + {}^{\cdot}NO \rightarrow [ONOO]^- \tag{1}$$

$$RS^- + NO \rightarrow [RSNO]^- \tag{2}$$

$$Cr(CO)_6 + 4NO \rightarrow Cr(NO)_4 + 6CO \tag{3}$$

One of the earliest known examples of the reactivity of nitric oxide is the coupling reaction effected at sulfite to form Pelouze's salt, *N*-nitrosohydroxylamine-*N*-sulfonate (eq 4).[13−16] Similar reactions are known to occur at cobalt(II) centers, forming bridged hyponitrito ($[N_2O_2]^{2-}$) complexes.[17,18] These motifs are unstable to acid, which facilitates the reduction of the coupled NO ligands and their release as N_2O (eq 5).[19−22] Similar behavior is observed in nitrosyl coordination chemistry when the nitric oxide ligand is not fully occupied as a three-electron π-acid ligand, allowing coupling, elimination[23−25] of N_2O, and subsequent oxidation of the metal center.

$$[SO_3]^{2-} + 2NO \rightarrow [O_3SNONO]^{2-} \tag{4}$$

$$[O_3SNONO]^{2-} + H_3O^+ \rightarrow [HSO_4]^- + H_2O + N_2O \tag{5}$$

We were intrigued by the contrast between the reluctance of nitric oxide to dimerize and the ease with which nitric oxide will couple at a center such as sulfite or cobalt(II).[13−18] As a result, we embarked on a study of the reactivity of nitric oxide with a range of sulfur oxoanions ($[S_2O_6]^{2-}$, $[SO_3]^{2-}$, $[S_2O_4]^{2-}$, $[S_2O_3]^{2-}$) to investigate the generality of the coupling reaction. Furthermore, we have re-evaluated the ligand coupling and acid-catalyzed degradation processes using ab initio molecular-orbital calculations. This has afforded us a unique view of a reaction

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which has played a special role in the formative studies on synthesis,[13−16] crystallography,[26−28] and molecular-orbital calculations[29] within inorganic chemistry. However, the reaction described (eqs 4 and 5) also generates an important model of the behavior of nitric oxide in complex systems which continue to be of wide interest, e.g., in microbial denitrification[30−32] and in the use of Wacker type catalysts for the dismutation of the chemical components of NO_x gases (eq 6).[22]

$$2NO \rightarrow N_2O \rightarrow N_2 + {}^1\!/_2O_2 \qquad (6)$$

Experimental Section

All chemicals were commercially obtained unless stated otherwise. Nitric oxide was generated using a published method.[33]

Two grams of each of the sulfur oxoanions ($[S_2O_6]^{2-}$, $[SO_3]^{2-}$, $[S_2O_4]^{2-}$, $[S_2O_3]^{2-}$) dissolved in aqueous potassium hydroxide (∼1 g/10 mL), and nitric oxide was passed through the solutions for 6 h or until the solution had stopped absorbing the gas. The product (*N*-nitrosohydroxylamine-*N*-sulfonate) of the reaction of nitric oxide with sulfite and dithionite was precipitated directly from solution upon cooling and recrystallized from aqueous potassium hydroxide.

Anal. Calcd for $K_2S_1N_2O_5$: N, 12.83; H, 0.00; S, 14.69. Found: (sulfite) N, 12.23; H, 0.00; S, 15.25. IR: 1320 cm^{-1} weak (ν_{ONNO}), 1280 cm^{-1} strong ($\nu_{N(2)O(4)}$), 1230 cm^{-1} medium (ν_{SO}), 1130 cm^{-1} strong (ν_{SN}), 1060 cm^{-1} ($\nu_{SO/ONNO}$ composite), 930 cm^{-1} medium (ν_{ONNO}), 620 cm^{-1} medium (ν_{SO}).[34]

Acid digestion using 2 M H_2SO_4 and infrared analysis of the resulting gas (ν_1, 2210 cm^{-1}; ν_2, 1280 cm^{-1}) provided clear evidence of N_2O production consistent with eq 5.

X-ray Crystallography. A colorless needle crystal (0.60 × 0.25 × 0.20 mm) was obtained directly from the mother liquor of the dithionite reaction[35] after refrigeration and mounted in a glass capillary. The cell parameters were determined from 25 accurately centered reflections ($51.55 \leq 2\theta \leq 54.29°$). Data were collected at room temperature using graphite monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) on a Rigaku AFC7S diffractometer. Nine hundred ninety-six unique reflections were measured, of which 786, with $I > 1.00\sigma(I)$, were used in structure solution and refinement. Lorentz-polarization and empirical ψ-scans absorption corrections were applied to the data. The structure was solved by direct methods,[36] and full-matrix least-squares refinement[37] (with all atoms anisotropic) converged with $R = 0.030$ and $R_w = 0.032$ for 786 reflections and 56 parameters (reflections/parameters = 14.04). The maximum shift/esd in the final cycle was <0.001, and residual electron density was in the range ± 0.53 e Å^{-3}. A summary of the crystallographic parameters is given in Table 1 and the refined atomic positions and equivalent isotropic temperature factors in Table 2.

Table 1: Crystallographic Data for Potassium *N*-Nitrosohydroxylamine-*N*-sulfonate

formula	$K_2N_2O_5S_1$
fw	218.27
space group	*Pnma* (No. 62)
a (Å)	9.951(1)
b (Å)	8.072(1)
c (Å)	7.075(1)
V (Å^3)	568.2(1)
Z	4
T (K)	293
λ (Mo Kα) (Å)	0.71071
D_{calcd} (g cm^{-3})	2.551
μ (cm^{-1})	19.97
R, R_w	0.030, 0.032

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Potassium *N*-Nitrosohydroxylamine-*N*-sulfonate

atom	*x*	y	z	*B*(eq)
K(1)	1.31024(06)	0.48826(07)	−0.05380(08)	1.78(2)
S(1)	1.00272(09)	1/4	0.14411(12)	1.13(3)
O(1)	1.1482(02)	1/4	0.1550(04)	1.9(1)
O(2)	0.9407(02)	0.4000(02)	0.2114(03)	1.87(7)
O(3)	0.8378(03)	1/4	−0.1396(04)	1.8(1)
O(4)	1.0271(03)	1/4	0.3889(04)	1.8(1)
N(1)	0.9667(03)	1/4	−0.0975(04)	1.2(1)
N(2)	1.0649(03)	1/4	−0.2142(04)	1.4(1)

No products were obtained from the remaining oxoanions ($[S_2O_6]^{2-}$, $[S_2O_3]^{2-}$). Isolation of solids by trituration revealed unchanged starting materials by IR spectroscopy.

Ab initio molecular-orbital calculations[38] were carried out on the *N*-nitrosohydroxylamine-*N*-sulfonate dianion and related species in order to shed light on its structure, possible mode of formation, and instability in acidic medium. The molecular species were subjected to geometry optimization initially at the Hartree−Fock level using the correlation-consistent basis set cc-pVTZ of Dunning[39−41] and further refined using density functional theory at the Becke 3LYP level[42] using the 6-311+G-(3d) basis set.[43] The results[44] are all reported at the higher level except for the two radical species ($[O_3SNO]^{2-\bullet}$ and $[O_3SON]^{2-\bullet}$) which had convergence problems at the higher level.

Results and Discussion

The reaction of nitric oxide with sulfite has been known for many years.[13−16] However, the potential for the other sulfur oxoanions in oxidation states III−IV (especially dithionite) seems to have been ignored. Whereas thiosulfate and dithionate

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(35) The elemental analysis found for the bulk product derived from dithionite was as follows: N, 8.5; H, 0.96; S, 13.70. As the analysis of these compound is made more difficult by their tendency to form mixed Na/K salts, the crystals obtained were immediately analyzed by X-ray methods. Due to the low precision of the original X-ray structure,[26−28] it was necessary to refine the new data set in order to obtain accurate structural parameters for use in the complementary theoretical study. Retrospective vibrational analysis indicates that the bulk solid is a mixture of $[O_3SNONO]^{2-}$ and $[SO_3]^{2-}$. Acid digestion of the bulk solid released N_2O, confirming the presence of the $[N_2O_2]^{2-}$ moiety.

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(44) Calculated energies in au for the species analyzed are as follows: I, −883.870299; II, −751.368784 (UHF); III, −751.327175 (UHF); IV, −883.898981; V, −884.561254; and VI, −885.096334.

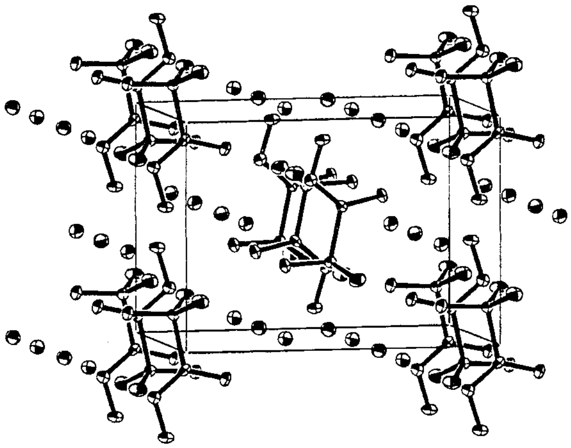

Figure 1. Bulk structure of $K_2[O_3S(NO)_2]$, showing the alternating orientations of the anions.

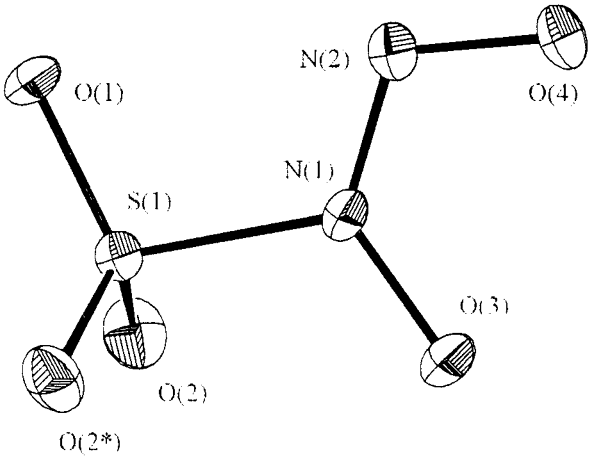

Figure 2. Structure of $K_2[O_3S(NO)_2]$. Bond angles and bond lengths are given in Table 3.

remain unreactive toward nitric oxide, dithionite reacts with it to form the *N*-nitrosohydroxylamine-*N*-sulfonate. The nature of these simple inorganic species makes it most difficult to definitively identify a product using NMR, IR, and microanalytical techniques alone. Thus, the product of the reaction of nitric oxide and dithionite (Figure 1) only became obvious once the crystal structure had been solved.[35] It would seem that prior to complexation nitric oxide oxidizes the dithionite to sulfite in a manner similar to that found for the reaction of oxygen with dithionite.

The bulk structure shows stacks of potassium ions and $[O_3S(NO)_2]^{2-}$ anions with alternating orientations as shown in Figure 1. Each K^+ ion is eight-coordinate, interacting with oxygen atoms from neighboring anions, with K−O distances in the range 2.839(2)−2.980(2) Å. Longer K and O (3.12 Å) and K and N (3.32 Å) distances are also noted. All the atoms of the anion except O(2) lie on a crystallographic mirror plane, and the structure (shown in Figure 2) corresponds in generality with the previously determined structures of the ammonium and potassium salts.[27,28] However, there are some marked deviations in the detailed structural parameters, and a comparison is drawn in Table 3.

Table 3. Comparison of Bond Lengths (Å) and Angles (deg) for Different Determinations of the Structure of the $[O_3S(NO)_2]^{2-}$ Ion[a]

structural parameter	$K_2O_3S(NO)_2$ this work	$K_2O_3S(NO)_2$[27]	$(NH_4)_2O_3S(NO)_2$[28]	calculated this work
S(1)−O(1)	1.450(3)	1.43(6)	1.464(12)	1.462
S(1)−O(2)	1.440(2)	1.43(6)	1.434(12)	1.465
S(1)−N(1)	1.746(3)	1.63(6)	1.791(12)	1.828
N(1)−O(3)	1.318(4)	1.35(6)	1.286(17)	1.288
N(1)−N(2)	1.279(4)	1.30(6)	1.327(17)	1.304
N(2)−O(4)	1.292(4)	1.35(6)	1.284(17)	1.287
O(1)−S(1)−O(2)	114.24(10)	108	114.2	113.9
O(2)−S(1)−O(2*)	114.5(2)	116	116.0	113.7
O(1)−S(1)−N(1)	104.9(2)	105	105.7	106.9
O(2)−S(1)−N(1)	103.63(9)	106	102.2	103.4
S(1)−N(1)−O(3)	114.9(2)	121	118.4	116.8
S(1)−N(1)−N(2)	118.4(2)	121	116.5	115.6
O(3)−N(1)−N(2)	126.7(3)	118	125.1	127.6
N(1)−N(2)−O(4)	113.3(3)	119	112.2	115.3

[a] Theoretical data for the $[O_3S(NO)_2{}^{2-}]$ ion was obtained using ab initio calculations using density functional theory at the Becke 3LYP level and the 6-311+G(3d) basis set.

Table 4. Comparison of the Vibrational Frequencies for the $[O_3S(NO)_2]^{2-}$ Ion

obsd vibrnl freq, cm^{-1}	intens	calcd vibrnl freq, cm^{-1}	calcd intens	assignmnt[b]	Figure 3 descrptn
1320	weak	1332	201	ONNO	**a**
1280	strong	1242	266	$N_{(2)}O_{(4)}$	**b**
1230	medium	1215	328	SO_3	**c**
		1203	363		
1130	strong	1075	154	SN	**d**
1060	strong	1002	124	SO_3/ ONNO composite band	**e**
930	medium	916	136	ONNO	**f**
620	strong	612	275	SO_3	**g**

[a] Obtained using ab initio calculations using density functional theory at the Becke 3LYP level and the 6-311+G(3d) basis set and the observed vibrational frequencies (Nujol mull). [b] The band assignments are described in relation to the displacement of the relevant atoms as described in Figure 3.

The structure shows a flattened tetrahedral environment for S(1), presumably minimizing O−O nonbonded interactions, and the S−N bond length at 1.746(3) Å is fairly typical of a S−N single bond (cf. 1.72 Å in $K_3N(SO_3)_3$).[45] The N_2O_2 group has an N−N bond length suggestive of a double bond (1.279 Å, cf. 1.264 Å in $4\text{-}MeC_6H_4N{=}N(O)Ph$),[46] while the N−O distances of 1.292 and 1.318 Å are also suggestive of appreciably more than single-bond character. There is some distortion around N(1), with O(3)−N(1)−N(2) = 126.7°, and although the origin of this effect is not certain, it probably arises from repulsion between O(3) and O(4).

After reevaluating the structure of *N*-nitrosohydroxylamine-*N*-sulfonate, we began to consider the mechanism underlying its formation and thus subjected the various possible components of the reaction scheme to analysis by ab initio molecular-orbital calculation methods including a comparison of the observed and calculated infrared spectrum of the product anion (Table 4). The optimized structure of the dianion (I) has the same gross features as the crystallographic structure presented in Figure 2 and Table 3. They show good agreement with the experimentally derived values especially those reported for the ammonium salt.[28] This is not surprising as in this salt the influence of the cation will be somewhat weaker than when the potassium is present. The parameter which seems to be most affected by the presence of the cation is the S−N bond length, which increases as the strength of the cation decreases. Analysis of the calculated population analysis reveals that the anionic charge is almost evenly divided between the SO_3 moiety which carries an overall

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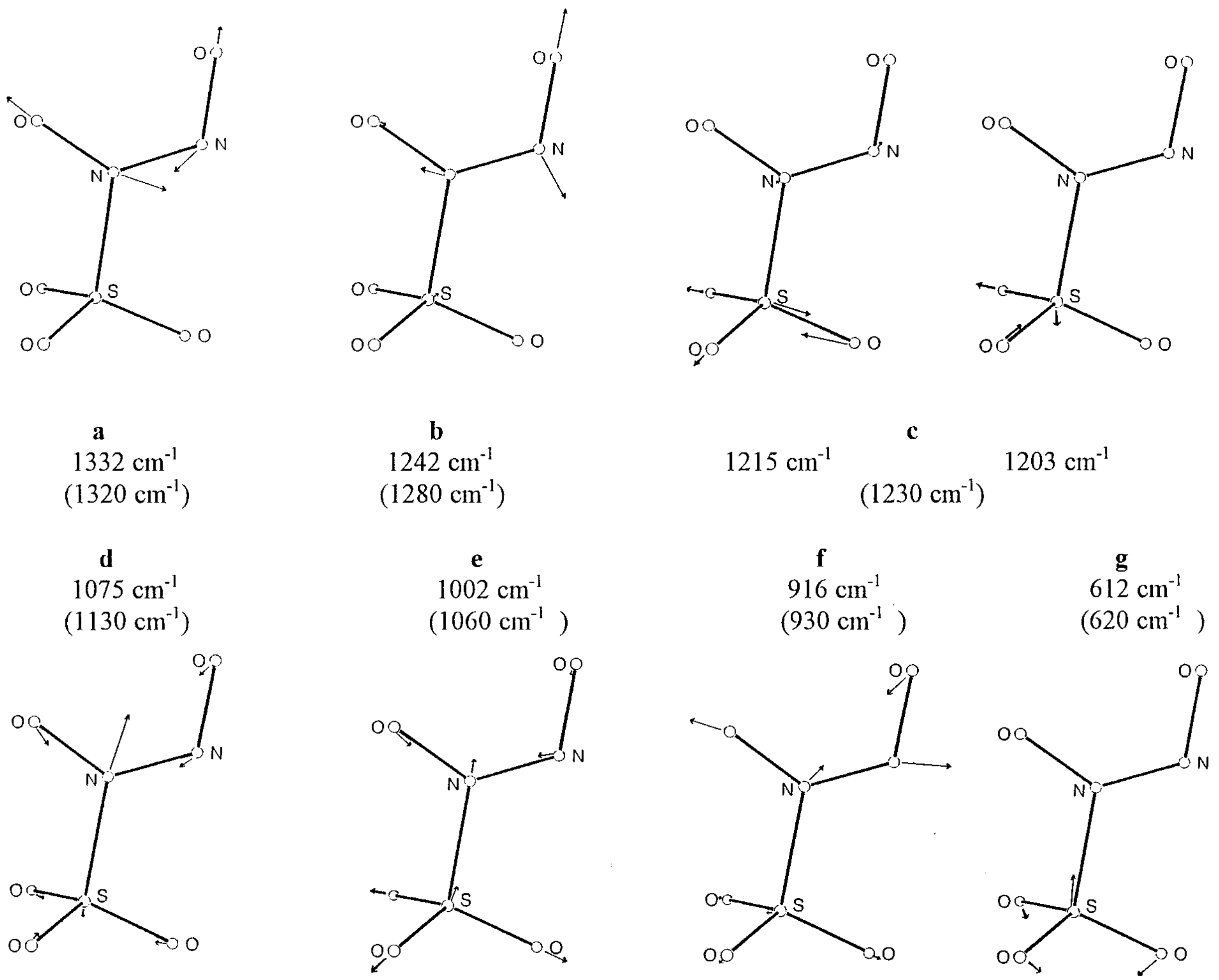
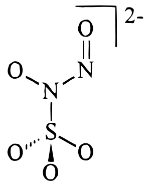


Figure 3. Diagrammatic representation of the vibrational frequencies identified using ab initio calculations. Values for the observed bands are given in parentheses. Vectors are drawn proportional to the atom displacements.

−0.9 charge and the ONNO fragment which bears the remaining −1.1 charge.

The calculated IR vibrational modes are given in Table 4 and portrayed in Figure 3. At this level of calculation, no correction factor to the frequencies of the bands was thought necessary. Agreement between the observed and calculated band frequencies is good, considering that the experimental data was obtained from a supporting medium (Nujol) and the theoretical data was calculated from the gas phase. The small deviation between the experimental and theoretical results can also be explained in terms of the influence of the cations on the experimental vibrations. Although the nature of the counterion and the phase do not seem to affect the agreement between the experimental and calculated frequencies, some discrepancies between the data sets begin to appear once the relative intensities of the bands are calculated (Table 4).

The calculated frequencies allow an instructive assignment to be made for each band, and these are displayed in Figure 3. The two highest frequency bands are associated exclusively with NO stretches followed by two bands related to the S−O stretches. The band at 1130 cm^{-1} involves movement by all the atoms connected by an SN stretch while the band at 1060 cm^{-1} is a composite mode with stretches in both the SO_3 and N_2O_2 portions of the ion. Finally, the two lowest frequency bands are associated with bending modes in the ion: the band at 930 cm^{-1} in the ONNO portion and the band at 620 cm^{-1} in the SO_3 moiety.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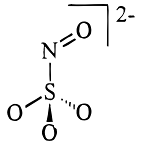
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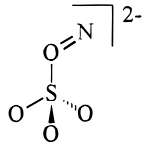
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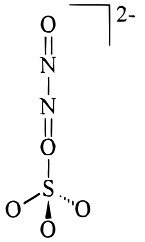
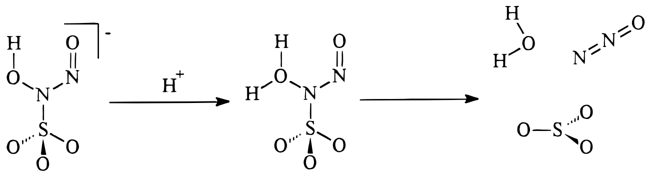

IV

That the ab initio calculations can generate a structure with the correct geometry and bond lengths (Table 3) and a vibrational spectrum with the correct number of bands in the observed regions (Table 4) shows that it is possible to model the *N*-nitrosohydroxylamine-*N*-sulfonate dianion and its associated species in a satisfactory manner. Thus, having successfully characterized the structure of *N*-nitrosohydroxylamine-*N*-sulfonate (I), the next logical step is to consider a possible mechanism underlying its formation. The calculations indicate a two-step mechanism for the addition of two NO molecules to the $[SO_3]^{2-}$ ion. Addition of the first NO molecule is found to favor (by 26.1 kcal/mol) isomer II, in which the nitrogen is bound to the sulfur rather than isomer III in which the oxygen is bound to sulfur. Binding of one molecule of NO to the sulfite anion in the manner described activates the unpaired electron, facilitating the coupling of the second NO moiety (I). The addition of the first NO species in this manner dictates that the second NO is predisposed to add at the coordinated NO via the nitrogen rather than the oxygen.

An alternative hypothetical mechanism by which I can form involves the coupling of the transient species ONNO with $[SO_3]^{2-}$. The product would initially adopt an arrangement (IV) whereby the nitric oxide would couple to sulfur through oxygen rather than nitrogen. However, the calculations show that should IV form via this process, it would rearrange further to $[SO_4]^{2-}$ and N_2O. The rearrangement of IV in this manner is energetically more favorable than rearrangement to the observed product (I) by 18.0 kcal/mol. Hence, our calculations predict that the formation of the *N*-nitrosohydroxylamine-*N*-sulfonate anion must be driven by the prior formation of II.

The *N*-nitrosohydroxylamine-*N*-sulfonate dianion I is only stable in alkaline medium. Under acidic conditions it decomposes to yield N_2O and the sulfate anion.[19−22] Calculations were invoked to study the addition of one proton followed by that of a second to the dianion I. They showed that protonation of the oxygen derived from the initial nitric oxide (V) is more favorable than addition of a proton either at the sulfite oxygens (by 38.4 kcal/mol) or at the oxygen derived from the second nitric oxide (by 4.8 kcal/mol). When the anion is offered a second proton, this adds at the same oxygen preferentially (VI) rather than the oxygen derived from the second NO moiety (by 32.0 kcal/mol) or at the sulfite oxygens (by 44.8 kcal/mol). The resulting geometry optimization of VI produces weakly bound nitrous oxide, sulfur trioxide, and water.[47]

By replacing the metal center and its ancillary ligands by the SO_3 moiety, we have been able to model the mechanism of formation of M-NONO species and their subsequent oxidative degradation.[23−25] We have thus generated a simple, instructive model for the behavior of a plethora of species which include enzymes such as nitrite reductase and Wacker catalysts for the dismutation of NO_x gases. Our study confirms that these reactions are best effected at a redox-active metal center with a vacant coordination site. Of some interest, however, is the requirement for the catalyst to preactivate the unpaired electron on the nitric oxide by inducing the molecule to coordinate to the metal in a bent configuration i.e., as a two-electron donor. Furthermore, although the degradation pathway may be assisted by the presence of electron-donating ligands, the process is initiated externally by protonation of the coupled ligand. It is this step which draws electrons from the metal center and collapses the complex (eq 6).



V VI

Supporting Information Available: A crystallographic information file (CIF) is available free of charge via the Internet at http://pubs.acs.org.

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(47) Many more species and reactions were investigated during the analysis of this system, all of which were observed to be unfavorable energetically.