Divergent Pathways for the Addition of Dioxygen to Sulfur in Nickel *cis*-Dithiolates: An Isotopomeric Analysis[1]

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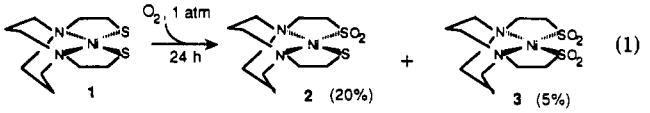
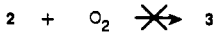
The selective addition of molecular O_2 to sulfur in transition metal thiolates has been an illusive goal of import to (1) the establishment of a wide range of chemical changes in complexes with catalytic and electrochemical abilities as well as (2) the potential of metal-promoted selective synthesis of sulfinic and sulfenic acids. Three recent reports[2-4] of well-characterized sulfur–oxygenates resulting from the reaction of O_2 with nickel(II) thiolates are encouraging for an eventual mechanistic understanding and thus control of such reactions.

Both mono- and bissulfinate complexes are isolated from the reaction of 1 atm of O_2 with the ca. square planar, diamagnetic, *cis*-dithiolate complex (bme-daco)Ni, **1**, eq 1.[1,2] The technique



(1)



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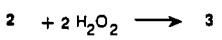
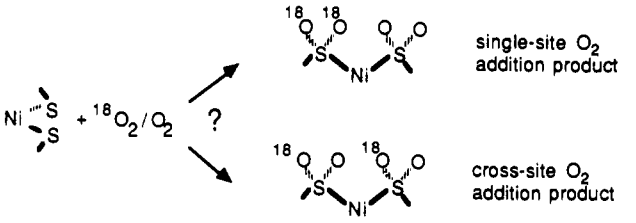


(3)

of MALD-FT ICR mass spectroscopy established that, when synthesized from $^{16}O_2/^{18}O_2$ mixtures in aprotic solvents, >90% of the isotopomers of both sulfinates, **2** and **3**, contained an even number of ^{16}O or ^{18}O atoms. This result implied that an O_2 pairwise addition, rather than single O-atom transfer (as seen when hydrogen peroxide was used as O-source),[2a] was involved in the dominant reaction pathway. Significantly, the *isolated* monosulfinate **2** is unreactive with O_2,[2a] even at pressures of 4000 kPa, eq 2.[2b]

Nevertheless the bissulfinate **3** can be prepared by reaction with the single O-atom source H_2O_2, eq 3. These observations raise the curious question of the pathway to **3** in the original reaction described by eq 1, which involves molecular addition of O_2, without the intermediacy of **2**! An electrochemical monitor of the reaction reveals the bissulfinate is formed early, concomitantly with **2**.[6] There is no apparent induction period for the formation of **3**.

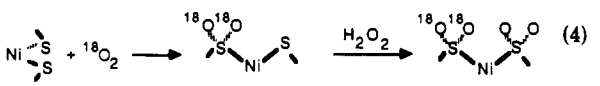
The initial labeling experiments for reaction 1 utilized a mass spectrometric analysis of parent ion abundances which did not differentiate between isotopomers of the same mass.[2] If there were single-site, molecular specificity in the O_2 addition (labeled "single-site addition product"), the isotopically pure SO_2 fragments, $S^{16}O_2$ and $S^{18}O_2$, might result from a mixture of $^{16}O_2$ and $^{18}O_2$. Alternatively, mixed isotope SO_2 fragments, $S^{16}O^{18}O$, would arise if two O_2 molecules were split between adjacent sulfur sites, the "cross-site addition product".



Theoretically, the infrared spectra of the isotopomers of **3** could be used to differentiate between the two possible labeled products; however, in practice, the breadth of the ν(SO) absorptions, as well as the presence of other unrelated, overlapping bands, makes such assessment difficult, especially in isotopomeric mixtures. Photoinduced decomposition/mass spectroscopy has permitted isotopomeric analysis based on the fragment SO_2^- derived from the sulfinate sites of **3** and provided an unequivocal indicator of reaction mechanism.

Laser desorption ionization was used to obtain Fourier transform ion cyclotron resonance (FT-ICR) mass spectra of pure samples of **3** deposited on the probe as methanolic solutions (~0.1 mM).[7] The experimental setup was essentially identical to that used in the previous labeling study,[2] except for the lack of matrix and the use of a double laser pulse to enhance photofragmentation. Mass spectra were obtained in the broad band mode, signal averaging data from 20 acquisitions. Time-domain data consisted of 32 K data points yielding a resolution of approximately 4 K for the SO_2^- ion. The error in ion abundances based on peak height or peak area is less than 8%.

To determine whether the conditions employed might induce O-atom exchange during desorption, a specifically labeled sample of **3**, containing no $S^{16}O^{18}O$, was prepared by making use of the reaction sequence in eq 4. The monosulfinate **2** isolated from



(4)

reaction with predominantly (85%) ^{18}O-labeled dioxygen (the remainder was $^{16}O_2$) was further reacted with natural-abundance H_2O_2 to produce a sample of **3** which would have a majority of the sulfinate sites isotopically homogeneous; i.e., each site would be either $RS^{16}O_2^-$ (~60%) or $RS^{18}O_2^-$ (~40%).[8] The FT-ICR MS spectrum for this sample of **3** is seen in Figure 1a. The predicted m/z absorptions 64($S^{16}O_2$):66($S^{16}O^{18}O$):68($S^{18}O_2$) are 100:0:74, respectively; the observed ratio is 100:0:75. Thus oxygen-label scrambling does not occur in the desorption process.

Mass spectra were then analyzed for samples of **3** isolated from reactions of **1** with natural-abundance $^{16}O_2$ as well as a

(1) Abbreviations used in this communication: bme-daco = *N*,*N*′-bis(mercaptoethyl)-1,5-diazacyclooctane; mese-daco = *N*-(mercaptoethyl)-*N*′-(sulfinatoethyl)-1,5-diazacyclooctane; bse-daco = *N*,*N*′-bis(sulfinatoethyl)-1,5-diazacyclooctane. A preliminary report of this research was given at the Fifth International Symposium on the Activation of Dioxygen and Homogeneous Catalytic Oxidation, March 14–19, 1993, College Station, TX.

(2) (a) Farmer, P. J.; Solouki, T.; Mills, D. K.; Soma, T.; Russell, D. H.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1992**, *114*, 4601. (b) Soma, T.; Farmer, P. J.; Darensbourg, M. Y. Unpublished results.

(3) (a) Kumar, M.; Colpas, G. J.; Day, R. O.; Colpas, G. J.; Maroney, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 8323. (b) Mizra, S. A.; Pressler, M. A.; Kumar, M.; Day, R. O.; Maroney, M. J. *Inorg. Chem.* **1993**, *32*, 977.

(4) Schrauzer, G. N.; Zhang, C.; Chadha, R. *Inorg. Chem.* **1990**, *29*, 4104.

(5) Farmer, P. J.; Lindahl, P. A.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1993**, *115*, 4665.

(6) Darensbourg, M. Y.; Farmer, P. J.; Soma, T.; Russell, D. H.; Solouki, T.; Reibenspies, J. H. *Proceedings of the 5th International Symposium on The Activation of Dioxygen and Homogeneous Catalytic Oxidation*; Plenum Publ. Corp.: New York, in press.

(7) Hanson, C. D.; Castro, M. E.; Kerley, E. L.; Russell, D. H. *Anal. Chem.* **1990**, *62*, 520. Karas, M.; Bachmann, D.; Hillenkamp, F. *Int. J. Mass Spectrom. Ion Processes* **1987**, *78*, 53. Solouki, T.; Russell, D. H. *Appl. Spectros.* **1993**, *47*, 211.

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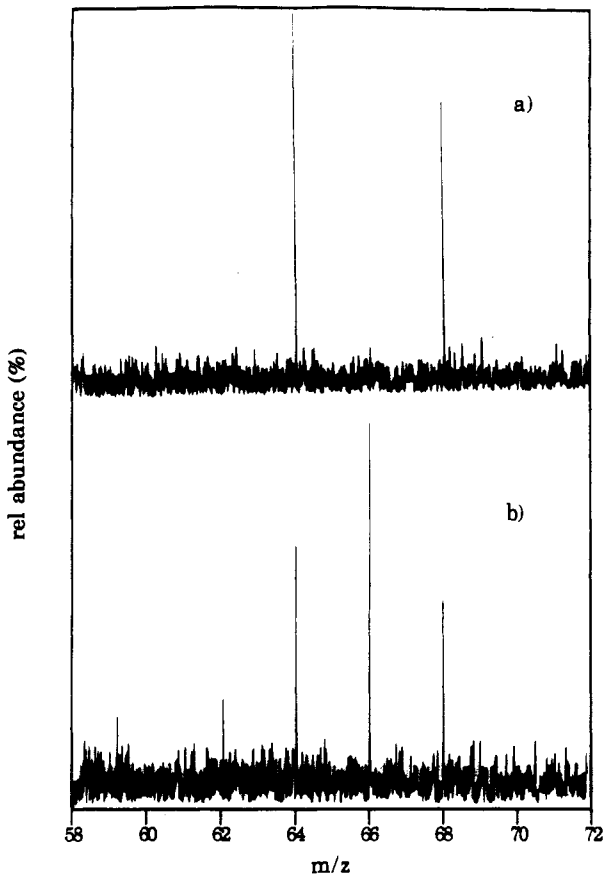
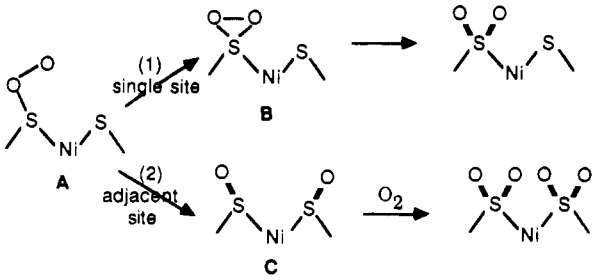


Figure 1. FT-ICR mass spectra in the SO_2^- region of (a) ^{18}O-dilabeled (bse-daco)Ni, **3**, isolated from the reaction of **2** (ca. 85% $RS^{18}O_2^-$) with natural-abundance H_2O_2 and (b) bse-daco)Ni, **3**, isotopomer mixture isolated from the reaction of **1** with a 53:47 mixture of $^{16}O_2$:$^{18}O_2$.

53:47 mixture of $^{16}O_2$:$^{18}O_2$.[9] The spectrum obtained on the mixed label sample, Figure 1b, shows the largest abundance at m/z 66, indicative of $S^{16}O^{18}O^-$ from the cross-site addition product. The observed m/z 64:66:68 ratio is 67:100:53. Since, for the isotopic mixture of O_2 used, a single-site addition would require abundance peak ratios at m/z 64:66:68 of 100:0:89, the cross-site addition with predicted ratios of 56:100:44 is clearly more consistent with the experimental results. A simple statistical fit, using the isotopic ratio observed in the mixed label spectrum, shows that pairwise O_2 addition across cis-sulfur sites is the major pathway (91%) operative in the production of the bissulfinate, **3**.

Comments on Mechanism. Whereas there should be (and *indeed may be*) a role for Ni–O_2 interaction in a precursor complex which serves to circumvent the spin-forbidden character of this reaction, we have no experimental evidence, direct or indirect, for the existence of such an adduct.[2] Since all previous chemistry

Scheme I



with **1** suggests great reactivity (nucleophilicity) at sulfur, including alkylation,[10] metalation,[11] and the formation of an S-bound SO_2 adduct,[12] our interpretation will focus on the binding of O_2 to sulfur, unavoidable entities along the reaction path regardless of mechanism or antecedent $^3O_2$ activation process.

The mechanism shown in Scheme I invokes a persulfoxidic species, **A**, as has been proposed in the reaction of $^1O_2$ with R_2S[13] and adopted for Ni–$SR/^3O_2$ reactions[3b,6] as the common precursor of both the mono- and bissulfinate products. Single-site collapse would yield the dioxirane, **B**, *en route* to the stable monosulfinate product. The bissulfinate formation would use **A** for intramolecular, adjacent-sulfur-site O-atom transfer, yielding a reactive bissulfenate $(RSO^-)_2$ intermediate, **C**. A second, similar cross-sulfur-site addition of O_2 yields the bissulfinate.

Such an internal collapse of persulfoxidic intermediate, **A**, is consistent with the isotopic labeling results of (1) molecular addition of O_2 in both products, (2) label homogeneity in the SO_2 of the monosulfinate, and (3) the distribution of four O-atoms between two S-sites in the disulfinate. The mechanism in Scheme I is also compatible with the observed concurrent formation of both the mono- and bissulfinate products. It implies that the intermediate sulfenate or metallosulfoxide, **C**, an appealing intermediate for the hydrogen peroxide reaction,[2,3b] should be further reactive with O_2, in keeping with the known instability/reactivity of such moieties in electron-rich metal environments.[14]

This mechanism, in the specific case of complex **1**, requires the presence of adjacent or cis-sulfur sites for formation of the bissulfinate. The factors which control the apportionment of pathways 1 and 2 in Scheme I and hence the generality of the mechanism await delineation in further study.

Acknowledgment. Financial support from the National Institutes of Health (Grant RO1 GM44865-01 to M.Y.D.), the National Science Foundation (Grant CHE 91-09579 to M.Y.D. and Grant CHE 91-40945 to D.H.R.), and the R. A. Welch Foundation is gratefully acknowledged.

Supplementary Material Available: A plot of the concentrations of **1–3** vs time for the reaction of **1** with O_2 in DMF (1 page). Ordering information is given on any current masthead page.

(8) The ca. 85% ^{18}O-labeled monosulfinate **2** was isolated from reaction of **1** with 90% $^{18}O_2$ that was unintentionally exposed to air over the course of reaction. The head gas was 21:79 $^{16}O_2$:$^{18}O_2$ at time of workup. The product **2** (26.0 mg or 0.080 mM) was dissolved in 20 mL of dry CH_3CN, and on addition of 20 μL of 30% H_2O_2 (0.195 mM), the solution immediately turned from brown to bright yellow. The reaction mixture was stirred for 30 min and then evaporated to dryness. Chromatography yielded only one yellow band of **3**, checked by comparison of its UV–vis spectra with an authentic sample. The yield of specifically labeled **3** after workup was 11.2 mg (39%).

(9) A 100-mL flask was seeded with **1** (0.100 g, 0.34 mM) in 30 mL of triply dried, degassed CH_3CN, evacuated and backfilled 3 times with Ar, and then left under slight vacuum. The reaction flask was charged with ca. 60 mL of 53:47 $^{16}O_2$:$^{18}O_2$, (2.68 nM), as checked by GC/MS, and then put under slight Ar pressure and left to stir for 1 week. The isotopic ratio was 55:45 $^{16}O_2$:$^{18}O_2$, with less than 0.1% $^{16/18}O_2$ prior to workup. The reaction mixture was evaporated and chromatographically separated as in ref 1. Yields (mg): **1** (37.7), **2** (41.9), **3** (7.8). Samples of **3** were washed with dry EtOH prior to submission for FT-ICR. Natural-abundance **3** was prepared as in ref 2.

(10) (a) Mills, D. K.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1990**, *29*, 4364. (b) Darensbourg, M. Y.; Font, I.; Mills, D. K.; Pala, M.; Reibenspies, J. H. *Inorg. Chem.* **1992**, *31*, 4965. (c) Goodman, D. C.; Tuntulani, T.; Farmer, P. J.; Darensbourg, M. Y.; Reibenspies, J. H. *Angew. Chem.* **1992**, *32*, 116.

(11) (a) Mills, D. K.; Hsiao, Y. M.; Farmer, P. J.; Atnip, E. V.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1991**, *113*, 1421. (b) Tuntulani, T.; Reibenspies, J. H.; Farmer, P. J.; Darensbourg, M. Y. *Inorg. Chem.* **1992**, *31*, 3497.

(12) Tuntulani, T.; Reibenspies, J. H.; Darensbourg, M. Y. Submitted for publication.

(13) For example: (a) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795. (b) Akasada, T.; Sakurai, A.; Ando, W. *J. Am. Chem. Soc.* **1991**, *113*, 2696. (c) Watanabe, Y.; Kuriki, N.; Ishiguro, K.; Sawaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2677.

(14) See for example: (a) Schenk, W. A.; Frisch, J.; Adam, W.; Prechtl, F. *Inorg. Chem.* **1992**, *31*, 3329. (b) Wienman, D. J.; Abrahmson, H. B. *Inorg. Chem.* **1987**, *26*, 3034. (c) Adamzli, I. K.; Lisbon, K. L.; Lyndon, J. D.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1979**, *18*, 303.