its associated $S = {}^5/_2$ iron atom, as well as zero-field splitting for iron, could all be important. Given this number of variables, a unique fit to the data cannot be assured. Our current best models have (i) strong coupling between the two radical spins ($-2J = -70$ cm^{-1}), slightly weaker coupling between each $S = {}^5/_2$ Fe(III) center and its associated radical ($-2J' = -63$ cm^{-1}), and a zero-field splitting constant of 35 cm^{-1} or (ii) strong coupling between high-spin iron and porphyrin radical ($-2J\vec{S}\cdot\vec{s}$, with $-2J = -49$ cm^{-1}, $D = 21$ cm^{-1}) and weak coupling of the total spins between the dimer units $-2J'(\vec{S} + \vec{s})\cdot(\vec{S}' + \vec{s}')$ with $-2J' = -3.5$ cm^{-1} (antiferromagnetic).[21] This latter model is similar to that used by Lang et al.[22] for a fit of the magnetic susceptibility data of [Fe(TPP$^\bullet$)(Cl)][SbCl$_6$]. Both models give an excellent fit to the susceptibility data over the entire temperature range as shown in Figure 2B. Detailed Mössbauer investigations are underway but are complicated by intermediate relaxation rate effects from 4 K up to 100 K. Magnetic ordering below 2 K in a 6-T applied field also occurs.

In summary, characterization of π-cation-radical derivatives of (octaethylporphinato)iron(III), [Fe(OEP$^\bullet$)(OClO$_3$)$_2$], and [Fe(OEP$^\bullet$)(Cl)]Y, Y = ClO$_4^-$ or SbCl$_6^-$, shows that the spin-state assignment and spin-coupling mechanisms are more complex than those of the analogous TPP$^\bullet$ species and more complex than those assumed by Nakashima et al.[2,3] An admixed intermediate-spin state for iron in a π-cation-radical derivative has been demonstrated for the first time. The question of the magnitude of the coupling between metal spins with a$_{1u}$ radicals (OEP$^\bullet$) compared to a$_{2u}$ radicals (TPP$^\bullet$) remains open.

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Supplementary Material Available: Tables SIII–SV, giving atomic coordinates, bond distances, and bond angles for [Fe(OEP$^\bullet$)(OClO$_3$)$_2$], Tables SVI–SVIII, giving atomic coordinates, bond distances, and bond angles for [Fe(OEP$^\bullet$)(Cl)]ClO$_4$, Figure S1, showing a formal diagram of the core of [Fe(OEP$^\bullet$)(OClO$_3$)$_2$], Figure S2, containing diagrams showing the temperature-dependent fits of the magnetic Mössbauer spectral data for [Fe(OEP$^\bullet$)(OClO$_3$)$_2$], Figure S3, showing an ORTEP drawing of the [Fe(OEP$^\bullet$)(Cl)]$_2^{2+}$ dimer viewed down the Fe$\cdots$Fe axis, Figure S4, showing the alternant bond distances in the inner 16-membered rings of [Fe(OEP$^\bullet$)(Cl)]$_2^{2+}$, and text giving the complete synthetic details (14 pages); Tables SI and SII, listing calculated and observed structure factors (×10) (31 pages). Ordering information is given on any current masthead page.

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[21] The ${}^5/_2$ iron spin system is represented by $\vec{S}$ and the radical spin system by $\vec{s}$.

[22] Lang, G.; Boso, B.; Erler, B. S.; Reed, C. A. *J. Chem. Phys.* **1986**, *84*, 2998.

[23] Work also performed at the Department of Physics, University of Illinois.

Articles

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Generation and Characterization of Dihydroxy Disulfide, HOSSOH: The Chainlike Isomer of Thiosulfurous Acid[1]

Heinar Schmidt,[2a] Ralf Steudel,*[,2a] Detlev Sülzle,[2b] and Helmut Schwarz[2b]

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Dissociative ionization of diisopropoxy disulfide (C$_3$H$_7$OSSOC$_3$H$_7$) by 70-eV electron impact gives rise to H$_2$S$_2$O$_2^{\bullet+}$ ions, whose collisional activation (CA) mass spectrum is in keeping with the connectivity of HOSSOH$^{\bullet+}$. This ion has been successfully neutralized and reionized in a two-stage collision experiment. This neutralization–reionization (NR) mass spectrum confirms previous theoretical predictions that HOSSOH resides in a potential minimum deep enough to prevent the species from isomerization–dissociation processes during the experiment (about 10^{-5} s). The experimental assignments are supported by the study of HOSSOD$^{\bullet+}$ and DOSSOD$^{\bullet+}$ generated accordingly by electron-impact-induced loss of propene from C$_3$H$_7$OSSOC$_3$D$_7$ and C$_3$D$_7$OSSOC$_3$D$_7$, respectively.

Introduction

Thiosulfurous acid is unstable in condensed phases, as it is common for all lower oxyacids of sulfur.[3] The free acid, H$_2$S$_2$O$_2$, or its anion is regarded to be the primary product in the reaction between sulfur dioxide and hydrogen sulfide,[4] well-known from the aqueous Wackenroder reaction and the industrially important Claus process, eq 1.

$$H_2S + SO_2 \rightarrow H_2S_2O_2 \qquad (1)$$

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[1] Sulfur Compounds. 148. Part 147: Miaskiewicz, K.; Steudel, R. *Angew. Chem.* **1992**, *104*, 87–89; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 58–59.

[2] (a) Institut für Anorganische und Analytische Chemie. (b) Institut für Organische Chemie.

[3] (a) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, U.K., 1984; p 834. (b) Holleman-Wiberg; *Lehrbuch der Anorganischen Chemie*; W. de Gruyter: Berlin, 1985; p 501. (c) Lyons, D.; Nickless, G. In *Inorganic Sulphur Chemistry*; Nickless, G., Ed.; Elsevier: Amsterdam, 1968; Chapter 14, p 509.

[4] (a) Stamm, H.; Goehring, M. *Z. Anorg. Allg. Chem.* **1939**, *242*, 413. (b) Schenk, P. W.; Steudel, R. *Angew. Chem.* **1965**, *77*, 437; *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 402. (c) *Gmelin Handbuch der Anorganischen Chemie*; Springer Verlag: Berlin, 1980; Schwefel, Ergänzungsband 3, p 195. (d) Ab-initio calculations on H$_2$S, SO$_2$, and (SOH)$_2$ at the HF/6-31G* level indicate that reaction 1 is exothermic by 13 kJ/mol: Miaskiewicz, K.; Steudel, R. Unpublished results, 1991.

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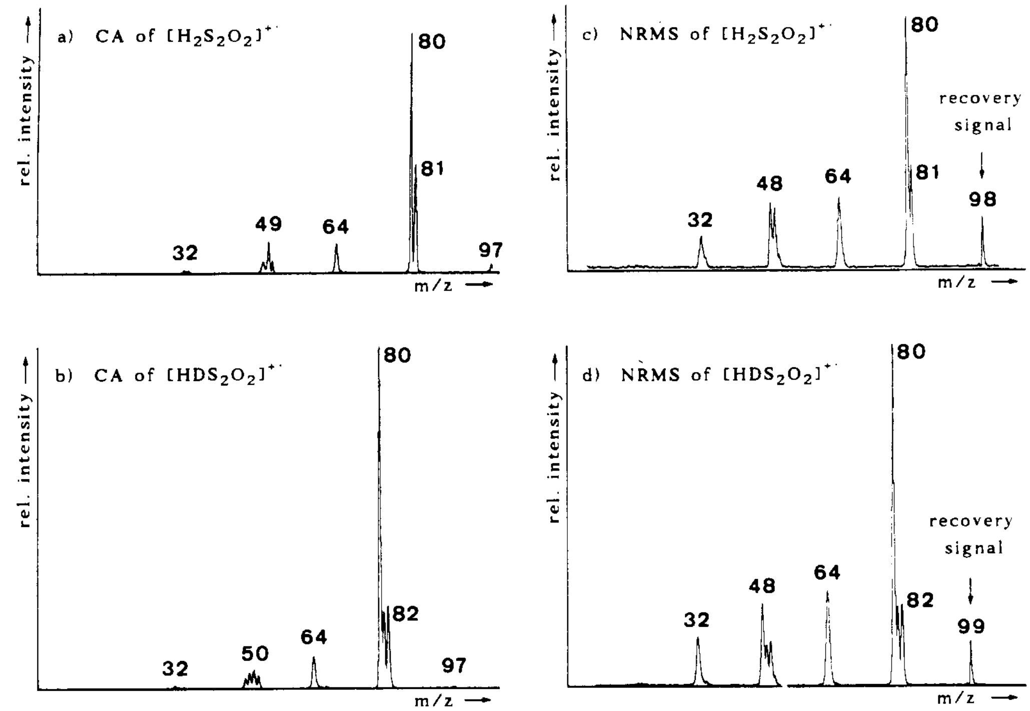
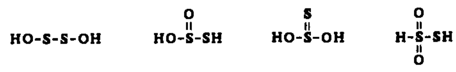


Figure 1. CA and NR mass spectra of $[H_2S_2O_2]^{\cdot+}$ (a, c) and $[HDS_2O_2]^{\cdot+}$ (b, d).

Chart I. Four Isomeric Structures of $H_2S_2O_2$ and Calculated Relative Stabilities in kJ/mol (from ref 7a)



$$\mathrm{HO{-}S{-}S{-}OH} \qquad \mathrm{HO{-}\overset{\overset{O}{\|}}{S}{-}SH} \qquad \mathrm{HO{-}\overset{\overset{S}{\|}}{S}{-}OH} \qquad \mathrm{H{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}SH}$$

0	13.4	16.2	98.4	MP4/6-31G*
0	-1.26	13.2	not refined	MP2/6-311G**+z.p.e.
I	II	III	IV	

While it was never possible to directly characterize the acid, aqueous solutions of saponified derivatives have been studied in the older literature.[5] Schenk and Ludwig claimed the preparation of thiosulfurous acid as a colorless solid from sulfur dioxide and hydrogen sulfide at −70 °C.[6] However, analytical data are scarce and no definite conclusions could be drawn concerning the structure of the material.[6] There are at least 11 isomeric structures conceivable for the molecule $H_2S_2O_2$. Among these, only four are considered to be chemically significant (Chart I). The stabilities and structures of eight isomers of neutral $H_2S_2O_2$ formed the subject of recent theoretical studies by ab-initio molecular orbital calculations,[7] which showed that the order of decreasing stability of the four most stable isomers is I > II > III > IV at the HF/6-31G*//MP4/6-31G* level.[7a] The energies of I–III differ by less than 16 kJ/mol, while IV is substantially higher in energy (98 kJ/mol with respect to I). When the calculations on I–III are refined at the HF/6-311G**//MP2/6-311G** level and zero-point vibrational energies calculated at the HF/6-311G** level are taken into account, structure II is favored as the most stable isomer, but the difference between I and II is only 1 kJ/mol.[7a]

For the related acid H_2SO_2, a chainlike structure of C_2 symmetry has been found by ab-initio calculations at the HF/6-31G*//MP4/6-31G* level to be most stable.[8a] On the other hand, photolysis of an H_2S/SO_2 mixture in an argon matrix at 12 K produced a molecule, the infrared spectrum of which has been ascribed to the isomer with a thiosulfinate structure, HS(O)OH.[8b,c]

Here, we report the generation and characterization of the chainlike isomer I of thiosulfurous acid by neutralization–reionization mass spectrometry (NRMS), after it has been observed that diisopropoxy disulfide yields $H_2S_2O_2^{\cdot+}$ ions on 70-eV electron impact.[9] NRMS has been successfully applied to generate and characterize numerous elusive sulfur compounds,[10] including the formal oxygen analogue of $H_2S_2O_2$, sulfurous acid (H_2SO_3).[10b]

Experimental Section

Preparation of Diisopropoxy-d_0, -d_7, and -d_{14} Disulfide. The preparation of diisopropoxy disulfide has been described elsewhere.[11] Diisopropoxy-d_{14} disulfide was synthesized accordingly by using 2-propanol-d_8 (Aldrich, 99 atom% D). Both compounds were purified by repeated vacuum distillation. Their purities were checked by ^{1}H-NMR and GC–MS analysis and were better than 99% and 97%, respectively.

The mass spectrum of $(C_3H_7O)_2S_2$ exhibits m/z peaks consistent with the following ions: $M^{\cdot+}$, 8; $C_3H_8O_2S_2^{\cdot+}$, 31; $C_2H_5O_2S_2^+$, 7; $H_2S_2O_2^{\cdot+}$, 56; $S_2O^{\cdot+}$, 4; HS_2^+, 1; $S_2^{\cdot+}$, 3; $C_3H_7^+$, 100.

The mass spectrum of $(C_3D_7O)_2S_2$ exhibits m/z peaks consistent with the following ions: $M^{\cdot+}$, 2; $C_3D_8O_2S_2^{\cdot+}$, 13; $C_2D_5O_2S_2^+$, 3; $D_2S_2O_2^{\cdot+}$, 51; $S_2O^{\cdot+}$, 4; DS_2^+, 3; $S_2^{\cdot+}$, 3; $C_3D_7^+$, 100.

Diisopropoxy-d_7 disulfide was synthesized in two steps because simple cocondensation of 2-propanol and 2-propanol-d_8 would produce a mixture of all three possible isotopomers which would be impossible to separate. A 120-mmol sample of diisopropoxy disulfide (21.9 g) was chlorinated with sulfur dichloride as described in ref 9. After a low-temperature

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[5] *Gmelin Handbuch der Anorganischen Chemie*; Verlag Chemie: Weinheim, Germany, 1960; Schwefel, Part B2, p 375 and references therein.

[6] Schenk, P. W.; Ludwig, R. *Z. Naturforsch., B* **1965**, *20*, 809.

[7] (a) Miaskiewicz, K.; Steudel, R. *J. Chem. Soc., Dalton Trans.* **1991**, 2395. (b) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1981**, *103*, 6232. (c) Freeman, F. *Chem. Rev.* **1984**, *84*, 117.

[8] (a) Steiger, T.; Steudel, R. *J. Mol. Struct.*, submitted for publication. (b) Fender, M. A.; Sayed, Y. M.; Prohaska, F. T. *J. Phys. Chem.* **1991**, *95*, 2811. (c) The infrared spectra reported in ref 8b are not in agreement with the spectra calculated for the geometry-optimized molecules HOSOH and HS(O)OH.[8a]

[9] Schmidt, H.; Steudel, R. *Z. Naturforsch., B* **1990**, *45*, 557.

[10] (a) Sülzle, D.; Drewello, T.; Schwarz, H. In *Sulfur-Centered Reactive Intermediates in Chemistry and Biology*; Chatiglialoglu, C., Asmus, K. D., Eds.; Plenum Press: New York, 1990; p 185. (b) Sülzle, D.; Verhoeven, M.; Terlouw, J. K.; Schwarz, H. *Angew. Chem.* **1988**, *100*, 1591; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1533. (c) McLafferty, F. W. *Science* **1990**, 925. (d) Holmes, J. L. *Mass Spectrom. Rev.* **1989**, *9*, 513. (e) Terlouw, J. K. *Adv. Mass Spectrom.* **1989**, *11*, 984. (f) Schwarz, H. *Pure Appl. Chem.* **1989**, *61*, 685.

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vacuum distillation of the reaction mixture, only the fraction which did not contain any sulfur monochloride was used for further synthesis. This was accurately checked by Raman spectroscopy. Isopropoxy chloro disulfide ($C_3H_7OS_2Cl$) is not stable at room temperature and should be used immediately after preparation or stored at liquid nitrogen temperature. For introduction of the C_3D_7O moiety, a fraction containing 51 mmol of isopropoxy chloro disulfide, besides the diisopropyl sulfite (^1H-NMR), was diluted with 20 mL of dry methylene chloride and added dropwise to a well-stirred mixture of 60 mmol of 2-propanol-d_8 (3 mL) and 60 mmol of triethylamine (8.4 mL) dissolved in 40 mL of methylene chloride. The reaction mixture was kept at −50 °C during the addition. After 30 min, the reaction was complete. The workup procedure was essentially the same as for the symmetrical compounds.[11] The crude product was subjected to a repeated vacuum distillation to remove the diisopropyl sulfite. GC–MS analysis proved the absence of $(C_3H_7O)_2S_2$ and $(C_3D_7O)_2S_2$. The purity was better than 98.5%.

$C_3H_7OS_2OC_3D_7$ is a colorless liquid, bp 63 °C/15 mbar. The 400-MHz ^1H-NMR spectrum in $CDCl_3$ shows an $A_3A'_3X$ pattern: $\delta_A = 1.27$ ppm, $\delta_{A'} = 1.30$ ppm, $\delta_X = 4.09$ ppm ($J_{AX} = J_{A'X} = 6$ Hz). The mass spectrum exhibits m/z peaks consistent with the following ions: $M^{\bullet+}$, 4; $C_3D_7HO_2S_2^{\bullet+}$, 26; $C_3H_7DO_2S_2^{\bullet+}$, 14; $C_2D_4HO_2S_2^+$, 3; $C_2H_4DO_2S_2^+$, 2; $HDO_2S_2^{\bullet+}$, 79; $S_2O^{\bullet+}$, 10; $S_2^{\bullet+}$, 11; $C_3D_7^+$, 100; ions with m/z <50 were not recorded.

Mass Spectrometric Experiment. The mass spectrometric experiments were carried out with a modified VG Instruments ZAB mass spectrometer. This is a four-sector instrument with BEBE configuration (B and E denote magnetic and electric sectors, respectively) which has been built by combining the BE part of an original ZAB-HF-3F instrument (MS I) with an AMD 604 double-focusing mass spectrometer (MS II).[12]

The ions $[H_{2-x}D_xS_2O_2]^{\bullet+}$ (x = 0–2) were generated by 70-eV electron impact ionization of the corresponding diisopropoxy-d_0, -d_7, and -d_{14} disulfides which were introduced into the ionization source via a heated septum inlet ($T \approx 250$ °C). The ion source conditions were as follows: temperature 200 °C, pressure $\approx 10^{-5}$ mbar, repeller voltage ≈ 10 V, accelerating voltage 8 kV.

Collision-induced dissociations,[13] used to characterize the ions were brought about by mass-selecting an 8-keV beam of the ions of interest by means of MS I and colliding it with helium in a collision chamber located in the field-free region between MS I and MS II at a transmission T of about 80%. Ionic products were recorded by scanning the second magnet.

$[H_{2-x}D_xS_2O_2]^{\bullet+}$ ions having 8-keV translational energy were neutralized in the first cell of a differentially pumped tandem collision cell located in the field-free region between MS I and MS II by colliding the beam with xenon (80% T). Unreacted ions were removed from the beam of neutral species by applying a voltage of 1 kV on the deflector electrode. Subsequent reionization occurred in the second collision cell by collision with oxygen (80% T). The resulting mass spectra were recorded by scanning B(2). The experimentally determined lifetime τ of the neutral species corresponds to the transit time from the first to the second collision cell and exceeds 10^{-5} s.

Results and Discussion

Upon electron impact ionization in the gas phase, diisopropoxy disulfide and its deuterated isotopomers eliminate two molecules of propene, leading to radical cations $[H_{2-x}D_xS_2O_2]^{\bullet+}$, $\mathbf{1}^{\bullet+}$, $\mathbf{1}\text{-}d_1^{\bullet+}$, and $\mathbf{1}\text{-}d_2^{\bullet+}$ for x = 0–2, respectively, (eq 2). Reduction of $\mathbf{1}\text{-}d_x^{\bullet+}$

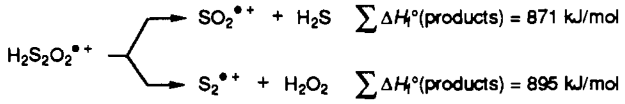
$$(CH_3)_2CH{-}OSSO{-}CH(CH_3)_2 \xrightarrow[-2C_3H_6]{EI/70\ eV} \underset{\mathbf{1}^{\bullet+}}{[H_2S_2O_2]^{\bullet+}} \xrightarrow{NRMS} \underset{\mathbf{1}}{H_2S_2O_2} \qquad (2)$$

in an NRMS experiment provides intense recovery signals for the neutral free acids $H_{2-x}D_xS_2O_2$, as shown in Figure 1.

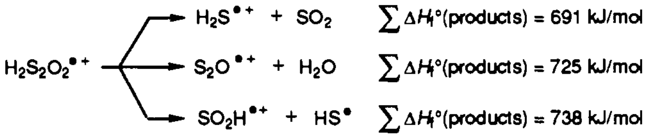
The spectra of collisional activated $\mathbf{1}\text{-}d_x^{\bullet+}$ ions (Figure 1a,b) are essentially identical with the NR mass spectra (Figure 1c,d), indicating that no rearrangement of the neutral free acid has taken place during the NR experiment. The relative intensities of the signals at m/z 32, 48, and 64 in the NR spectra are enhanced by reionization of neutral atoms and molecules, S, SO, and S_2, generated either by collision-induced dissociation of $\mathbf{1}\text{-}d_x^{\bullet+}$ ions (in the neutralization cell) or by decay of the energy-rich fraction of $\mathbf{1}\text{-}d_x$ molecules from the neutralization process. The structure of the ions $\mathbf{1}\text{-}d_x^{\bullet+}$ is the same as that for the corresponding neutral species due to the vertical nature of the collisional-induced charge-transfer process.[14]

The point of discussion is which isomer would be formed under these conditions. We will focus on the four relevant isomers I–IV. In fact, all fragments observed in the CA spectra are consistent with the chainlike structure I which is found in the precursor molecule too.[15]

The CA spectrum of $\mathbf{1}^{\bullet+}$ (Figure 1a) is dominated by the losses of H_2O and $OH^\bullet$, yielding $S_2O^{\bullet+}$ (m/z 80)[16] and S_2OH^+ (m/z 81), as might be anticipated from simple thermochemical considerations. However, these considerations are incomplete because no entire set of data for all conceivable products is available (e.g. $\Delta H_f°(HS_2O^+)$, $\Delta H_f°(HSO^+)$).[17] In addition, losses of H_2O and $OH^\bullet$ do not permit a distinction among isomers I–III. A strong argument in favor of structure I is provided by the m/z 64 fragment, which could be either $S_2^{\bullet+}$ or $SO_2^{\bullet+}$. Thermochemical data show both fragmentations to be of comparable enthalpy of formation,[17] slightly favoring $SO_2^{\bullet+}$:



Mass-selecting the isotopomer of $\mathbf{1}^{\bullet+}$ bearing one ^{34}S atom (m/z 100) convincingly demonstrates that only $S_2^{\bullet+}$ is formed from $\mathbf{1}^{\bullet+}$. In this CA spectrum (not shown) m/z 64 is quantitatively shifted to m/z 66. Since the S_2 unit is clearly present in structure I, we assign this connectivity to the radical cation $\mathbf{1}^{\bullet+}$. Isomers containing an OSO moiety (as in II and IV) are ruled out for the same reason, and isomer III is expected to generate both $S_2^{\bullet+}$ and $SO_2^{\bullet+}$. An even stronger argument against structure II (and IV) is the following. Thermodynamically,[17] the most probable decomposition products of $I^{\bullet+}$ are



The absence of $H_2S^{\bullet+}$ (m/z 34) and SO_2H^+ (m/z 65) from the spectra shown in Figure 1a unambiguously excludes structures II and IV, leaving I as the most probable. Further support comes from the relatively high intensity of the SOH^+ and $SO^{\bullet+}$ fragments indicating the cleavage of the sulfur–sulfur bond in $\mathbf{1}^{\bullet+}$. These assignments are completely confirmed by the spectra of the deuterated species $\mathbf{1}\text{-}d_1^{\bullet+}$ (Figure 1b) and $\mathbf{1}\text{-}d_2^{\bullet+}$ (not shown). Therefore, these spectra deserve no further discussion.

In addition, we have investigated *O,S*-diisopropyl thiosulfite, $^iC_3H_7O{-}S(O){-}S^iC_3H_7$ (**2**), *O,O'*-bicyclohexyl-1,1'-diyl thiosulfite $(C_6H_{10})_2O_2S(S)$ (**3**), and 2-propyl 2-propanethiosulfonate, $^iC_3H_7{-}S(O)_2{-}S^iC_3H_7$ (**4**), with the intention of generating the three other isomers of $H_2S_2O_2$ (II–IV respectively).[18]

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(12) For a full description of the instrument, see: (a) Srinivas, R.; Sülzle, D.; Koch, W.; DePuy, C. H.; Schwarz, H. *J. Am. Chem. Soc.* **1991**, *113*, 5970. (b) Srinivas, R.; Sülzle, D.; Weiske, T.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *107*, 369.

(13) Reviews: (a) Levsen, K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 509. (b) Cooks, R. G., Ed. *Collision Spectroscopy*; Plenum Press: New York, 1978. (c) Levsen, K.; Schwarz, H. *Mass Spectrom. Rev.* **1983**, *2*, 77. (d) Bordas-Nagy, J.; Jennings, K. R. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 105.

(14) (a) Durup, J.; Appell, J.; Fehsenfeld, F. C.; Fournier, P. *J. Phys. B* **1972**, *3*, L58. (b) Lorquet, J. C.; Leyh-Nihant, B.; McLafferty, F. W. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 465.

(15) Dimethoxy disulfide adopts a chainlike gauche conformation in the gaseous and the solid states: Buschmann, J.; Koritsanszky, T.; Luger, P.; Schmidt, H.; Steudel, R. *Z. Kristallogr., Suppl. Issue No. 3* **1991**, 40. Baumeister, E.; Oberhammer, H.; Schmidt, H.; Steudel, R.; *Heteroat. Chem.* **1991**, *2*, 633–642.

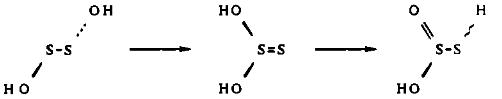
(16) The energies of S_2O, H_2O, and $(SOH)_2$ calculated at the HF/6-31G* level show that the reaction $(SOH)_2 \rightarrow S_2O + H_2O$ is endothermic by 63 kJ/mol: Miaskiewicz, K.; Steudel, R. Unpublished results, 1991.

(17) Lias, S. G.; Dartman, B. E.; Liebman, S. F.; Holmes, S. L.; Levin, R. D.; Maillard, W. G. *J. Phys. Chem. Ref. Data* **1988**, 17, Supplement 1.

However, all three precursors, **2**–**4**, provided only very small amounts of a radical cation with m/z 98, while this fragment represents the second most frequent ion in the case of **1**. Apparently, **2** decomposed under the applied experimental conditions and **3** predominantly formed CH-containing fragments with m/z 98 and 100. Only **4** produced $H_2S_2O_2^{\bullet+}$ in an abundance sufficient for an NRMS experiment. But, unfortunately, both the CA and NR spectra are beyond a detailed interpretation due to interfering decomposition products from the ion source.

Conclusion

Electron-impact-induced dissociation of diisopropoxy disulfide in the vapor phase yields propene and the chainlike radical cation $HOSSOH^{\bullet+}$, which was neutralized in a NRMS experiment to give the free acid HOSSOH. In the highly diluted gas phase, this molecule is stable against isomerization during the time of its observation (10^{-5} s), indicating that isomer I is separated from isomers of comparable energy, like HOS(O)SH (II), by a sufficiently high energy barrier. Isomerization of I to give II probably has to proceed via III (migration of an OH group from one sulfur to the other) followed by a proton shift from oxygen to the terminal sulfur atom which becomes two-valent (eq 3). This two-step mechanism may explain that under the experimental conditions only I was observed when diisopropoxy disulfide was used as a precursor. On the other hand, dissociation of I into S_2O and H_2O may be more favorable than the isomerization due to a possibly lower energy barrier, thus explaining that II was not observed.



(3)

Attempts to obtain other isomers (II–IV) from corresponding precursors have failed so far. This does not exclude II from being generated in a totally different experiment. For instance, reaction 1 probably leads primarily to the adduct $H_2S{\cdot}SO_2$, containing a weak SS bond[19] which may stabilize itself by a proton shift to oxygen, resulting in II. Work to identify the initial products of reaction 1 is in progress.

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(18) Compound **2** has been prepared from thionyl chloride, 2-propanol, and 2-mercaptopropane in the presence of triethylamine. It could not be obtained in pure form due to decomposition. **3** was kindly provided by D. N. Harpp. See also: Harpp, D. N.; Steliou, K.; Cheer, C. J. *J. Chem. Soc., Chem. Commun.* **1980**, 825. **4** has been prepared by the reaction of diisopropyl disulfide with sulfuryl chloride in the presence of acetic acid according to: Buckmann, J. D.; Bellas, M.; Kim, H. K.; Field, L.; *J. Org. Chem.* **1967**, *32*, 1626.

(19) See also the structure of the van der Waals molecule $H_2S{\cdot}SO_2$ in: Kukolich, S. G.; Pauley, D. J. *J. Chem. Phys.* **1990**, *93*, 871.

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Single-Crystal Polarized Absorption Spectroscopic Study of the Electronic Structure of μ-1,2-Peroxo Binuclear Cobalt Complexes

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Single-crystal polarized absorption spectra of five trans planar μ-peroxo cobalt systems are presented and interpreted. Ligand field (LF) transitions are assigned at energies typical for Co(III) systems. Charge-transfer (CT) transitions from the peroxide π^*_v orbital vertical with respect to the Co–O–O–Co plane to the cobalt dσ orbitals are found to be at lower energy than the LF transitions. This indicates that the highest occupied molecular orbital (HOMO) of planar monobridged cobalt peroxo complexes has peroxide π^*_v character. Due to the limited overlap between the orbitals involved, the intensity of these CT transitions is low ($\epsilon \approx 100$ M^{-1} cm^{-1}). The overlap between the peroxide π^*_σ orbital within the Co–O–O–Co plane and the cobalt d_{z^2} orbital is large. The intense band ($\epsilon = 14\,000$ M^{-1} cm^{-1}) at 300 nm is assigned to the $\pi^*_\sigma \rightarrow d_{z^2}$ CT transition, which is supported by the *A*-term Raman enhancement behavior observed for the intra-peroxide stretch. These results are related to the spectra of cis μ-1,2-peroxo cobalt the trans μ-1,2-superoxo cobalt complexes, and the photochemical implications of the different bonding schemes are discussed. A comparison of the spectra of the trans μ-peroxo cobalt and the trans μ-peroxo binuclear copper systems reveals characteristic differences with respect to dimer splitting in CT excited states.

Introduction

The reversible binding and activation of dioxygen by transition metal complexes has been of continued interest in biochemistry and in heterogeneous and homogeneous catalysis. Cobalt peroxo and superoxo complexes comprise a large number of structurally characterized monomers as well as cis and trans μ-1,2- and μ-1,1-hydroperoxo-bridged dimers. Thermodynamic, kinetic, and mechanistic aspects of interconversions between these species are well understood and have been reviewed.[1]

A comparison of the different binding modes of peroxide has gained considerable importance in connection with the question of which structural modes are involved in the binding and activation of oxygen in copper-containing enzymes. Hemocyanin and tyrosinase bind dioxygen as a bridge between two copper centers,[2a–c] and laccase reduces O_2 to H_2O via a peroxide-bridged intermediate at a trinuclear copper site.[2d] An understanding of the spectral features associated with different peroxide binding modes, particularly the peroxide to metal charge-transfer spectra, is of crucial importance for further mechanistic insight into binding and activation of oxygen in biomolecules. The variety of structurally characterized cobalt peroxo dimers allows a systematic comparison of these features. Spectroscopic studies along these lines are also of theoretical interest with respect to electronic interactions in dimers. Whereas attention has traditionally been focused on interactions in the electronic ground state, little has been done to investigate excited-state dimer interactions. In copper dimers, a detailed picture of dimer interactions in excited ligand

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