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Chemical Transformations and Disproportionation of Sulfur Dioxide on Transition Metal Complexes

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Aside from its renown as a source of acid precipitation, sulfur dioxide is remarkable in possessing physicochemical and coordination properties that are more diverse than those of any other small molecule. SO_2 is amphoteric, behaving as a Lewis acid or base, mild oxidant or reductant, or oxygen donor or acceptor. It is an excellent nonaqueous solvent[1] when liquefied at −10 °C and coordinates to many types of compounds, including metal complexes at both metal and ligand sites, strong Lewis acids, and virtually all nucleophiles, even halide ion (Figure 1). SO_2 can bind strongly to low-valent metals like CO or NO or completely reversibly like O_2 or H_2. The diversity of metal–SO_2 bonding geometries is unmatched and has been reviewed by us and others.[2]

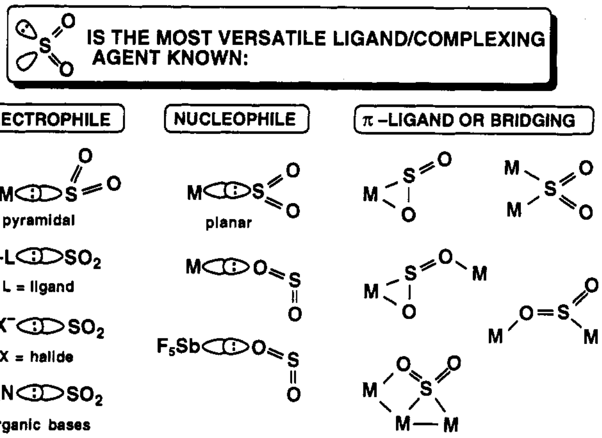
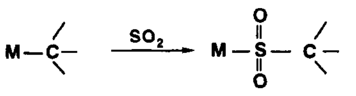


Figure 1. Coordination modes and geometries for SO_2.

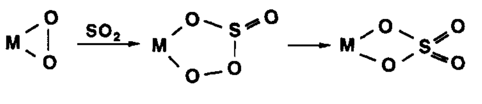
This Account will focus on the *reactivity* of SO_2, e.g., S=O bond cleavage, some of which has been reviewed[2] but not in depth. We have been developing homogeneous catalytic processes for reducing SO_2 to sulfur to address the problem of SO_2 abatement. In our studies, SO_2 has revealed surprisingly facile oxygen transfer and disproportionation reactions that may be central to its chemistry and valuable for SO_2 conversion to useful/innocuous species. The richness of SO_2 chemistry has recently dramatically increased, and it appears that any transformation imaginable is possible. Although mechanistic studies of SO_2 reactions have been sparse, we have now begun to identify likely intermediates and pathways in SO_2 reduction and disproportionation.

Insertion-Type Reactions of SO_2 and, Conversely, Attack at Bound SO_2

Historically, the first well-studied SO_2 reactions were insertion into M–C[3] and M–O:[4,5]



(1)



(2)

M–C insertion has been reviewed[3] and will not be

Gregory Kubas was born in Cleveland, OH, in 1945. He obtained his B.S. in chemistry at Case-Western Reserve University and Ph.D. from Northwestern University under Duward Shriver. After postdoctoral positions at Princeton with Thomas Spiro and at Los Alamos, he joined the staff at Los Alamos National Laboratory in 1974. He was appointed a Laboratory Fellow in 1987 and was the recipient of the 1993 American Chemical Society Award in Inorganic Chemistry for his discovery of metal–dihydrogen coordination. His research includes binding and reactions of environmentally related and energy-related small molecules such as SO_2 and H_2 on metal complexes, particularly group 6 metals and sulfide clusters, as well as studies of metal σ-bond coordination.

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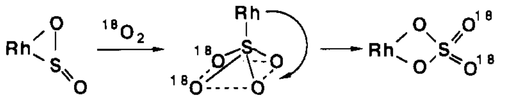
discussed further. The peroxysulfite intermediate in eq 2 was demonstrated by Collman[4e] by ^{18}O labeling and was supported theoretically.[4h] The sulfonate and bidentate[4d] (η^2) sulfate groups generally could not easily be removed from the metal to regenerate starting complex, a common problem in designing catalytic conversions of SO_2 to, e.g., H_2SO_4. Little work has been done on reactions of sulfate complexes, but Atwood[5a] has recently found that η^2-SO_4 can be displaced from the coordination sphere of an iridium complex by CO. Also, novel reversible addition of SO_2 across *cis*-oxo bonds in $L_3Tc(=O)_3$ to give $L_3Tc(=O)(\eta^2\text{-}SO_4)$ has now been observed.[5b] Insertions of SO_2 into the M–SO bond in $Pd(PPh_3)_2(SO)$ to give S,O-bound *thiosulfate*[6] and into other metal–ligand bonds (M–OR, M–H) or internal ligand bonds[7] have been found, as discussed below.

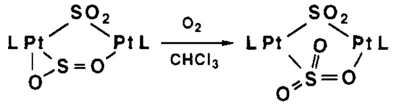
The converse reaction of M–SO_2 with O_2 or SO[6] also forms η^2-SO_4 or -S_2O_3 complexes.[4a–d,8–10] We identified at least two mechanisms by ^{18}O labeling: initial replacement of SO_2 in $Pt(SO_2)(PCy_3)_2$ by O_2,[9] followed by insertion as in eq 2, or attack of O_2 on sulfur in $Rh(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$ to form a Rh–SO_4 intermediate with square-pyramidal sulfur:[10]



(3)

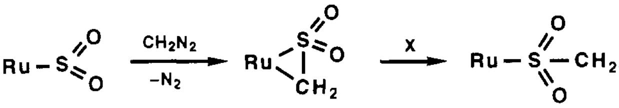
Shift of Rh to the equivalent basal edges gave the expected 1:2:1 ratio of isotopomers. The former mechanism is generally more likely since usually complexes with labile M–SO_2 form sulfates[2d] and some sulfates are accessible from either M–O_2 or M–SO_2.[4a–d,9]

Complexes with M=O bonds insert SO_2 to form bidentate *sulfites*.[11,12] Reaction of (tmtaa)Ti(η^2-SO_3) (tmtaa = 7,16-dihydro-6,8,15,17-tetramethyldibenzo-[*b,i*][1,4,8,11]tetraazacyclotetradecine dianion) with NH_4OH regenerated (tmtaa)Ti=O plus $[NH_4]_2SO_3$, suggesting that M=O compounds could be useful as reusable SO_2 scavengers.[11] Farrar found a novel sulfite bridge formed from oxidation of μ-SO_2:[13]



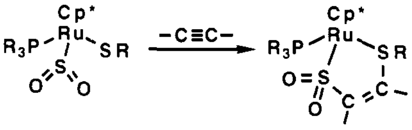
(4)

Other examples of electrophilic and nucleophilic attack at metal-bound SO_2 are known,[2c,14] e.g., silylation at oxygen of $Mo(CO)_3(PR_3)_2(\eta^1\text{-}SO_2)$ to give S-bound $O{=}S{-}OSiMe_3$ and alkylation at sulfur by LiR or ZnR_2 to give M—SO_2R.[14b] CH_2N_2 converts $[CpRu(Ph_2PCH_2PPh_2)(SO_2)]^+$ to a η^2-sulfene reactive with X = Br^-, CN^-, PR_3, or ROH:[14c]



(5)

Conversely, SO_2 had earlier been found to insert into $M(\mu\text{-}CH_2)M$ and $M{=}CH_2$ to also form η^2-CH_2SO_2.[15,16] The versatility of SO_2 is further highlighted by a remarkable cycloaddition of activated acetylenes across S^{IV} and S^{II} centers:[17]



(6)

SO_2 Reduction/Disproportionation by Transition Metal Hydride Complexes

About 20 years ago Taube[18] found the first example of reduction of metal-bound SO_2 by treating $RuCl(NH_3)_4(SO_2)^{2+}$ with zinc in aqueous HCl to produce the S_2-bridged dimer $[RuCl(NH_3)_4]_2(\mu\text{-}S_2)^{4+}$. Meyer[19] recently showed stepwise $6e^-$ electrochemical reduction of $Ru(NH_3)_5(SO_2)^{2+}$ to $Ru(NH_3)_5(H_2S)^{2+}$ via the intermediacy of an S_2 dimer. Our initial efforts in SO_2 reactivity focused on its reduction by hydride complexes to devise new synthetic/catalytic methodologies and probe reduction mechanisms. Although H and SO_2 ligands can coexist,[2b] many hydrides should reduce SO_2.

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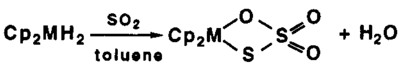
Table 1. IR and Structural Data for Metal-Coordinated Polyoxosulfido Ligands[a]

complex	SO frequencies, cm^{-1}	X-ray distances, Å[b] M–S	M–O	S–S	$S{=}O_t$[c]	$S{-}O_b$[d]	ref
$CpMo(CO)_3(SO_2H)$	990, 762	2.521(2)			1.515(6)	1.637(6)[e]	23
$CpW(CO)_3(SO_2H)$	970, 760 (937, 732)[f]						23
$Cp^*Ru(CO)_2(SO_3H)$	1180, 1080, 810	2.318(2)			1.459(3)	1.559(3)[e]	31
$CpFe(CO)_2(SO_3H)$	1184, 1084, 811						32a
$[Ru(bpy)_2(py)(SO_3H)]^+$		2.286(2)			1.467(5)	1.586(5)[e]	33b
$Ir(CO)(SO_2)(PPh_3)_2(SO_3H)$	1213,[g] 1072,[h] 1053,[g] 918[h]						25
$Fe(TPP)(OSO_3H)$			1.919(4)		1.446(5)	1.492(4) 1.521(5)[e]	35
$[CpMoO(S_2)MoO(\eta^2\text{-}SO_3)]^-$	1166, 646, 571, 502		2.077(10)[i]		1.441(9)	1.586(9)	67
$[CpMoO(S_2)MoO(\eta^2\text{-}SO_4)]^-$	1307, 1172, 669, 612, 572, 540		2.077(10)[i]		1.43(1)	1.540(6)	67
$[CpMoO(S_2)MoO(\eta^2\text{-}S_2O_3)]^-$	1277, 1172, 1150, 662, 542	2.302(6)	2.077(10)[i]	1.991(7)	1.429(10)	1.512(11)	67
$Cp_2Mo(\eta^2\text{-}S_2O_3)$	1247, 1137, 1128, 652, 545	2.450(2)	2.134(4)	2.051(2)	1.448(4)	1.536(4)	21
$Ni(tu)_4(\eta^2\text{-}S_2O_3)\cdot H_2O$	1152, 1090, 971, 665, 535	2.718(4)	2.107(9)	2.01(1)	1.45(1)	1.50(1)	22a,b
$[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$	1228, 1190, 1045, 1020, 505	2.395(2)		2.135(3)	1.44(1)		31
$Cp^*{}_2Mo_2(\mu\text{-}S)(\mu\text{-}S_2)(\mu\text{-}S_2O_3)$	1242, 1205, 1010, 604	2.441(3)		2.166(4)	1.436(8)		62
$Cp^*{}_2Cr_2(\mu\text{-}S)(\mu\text{-}S_2)(\mu\text{-}S_2O_3)$	1228, 1204, 1012, 610	2.367(2)		2.152(2)	1.441(6)		65
$[(S_2)OMoS_2MoO(\eta^2\text{-}S_3O_2)]^{2-}$[j]	1255, 598, 557	2.417(5)		2.047(11)	1.401(15)		22e
$[Cp^*Mo(CO)_3]_2(\mu\text{-}S_2O_4)$	1207, 1027	2.496(1)		2.266(1)	1.471(4)		23
$[CpFe(CO)_2]_2(\mu\text{-}S_2O_4)$	1223, 1040						28a
$[M(CO)_5]_2(\mu\text{-}S_2O_4)$ (M = Mn, Re)	1224, 1037;[k] 1212, 1031[l]						28a
$CH_2[CpRh(C_2H_4)]_2(\mu\text{-}S_2O_4)$	1219, 1051						28c
$Cp^*{}_2V(\eta^2\text{-}[O,O]\text{-}S_2O_4)$	1092, 942, 927		2.032(3)[m]	2.335(2)	1.472(4)[m]	1.534(3)[m]	29
$Fe(dieneN_4)(\eta^2\text{-}[O,O]\text{-}S_2O_5)$[j]			2.173(9)[m]	2.222(7)	1.37(2)[m]	1.490(8)[m]	8g

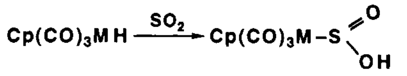
[a] Only representative examples of SO_3, SO_4, and SO_3H ligands are listed. Abbreviations: Cp = C_5H_5; Cp* = C_5Me_5; bpy = bipyridine; py = pyridine; TPP = tetraphenylporphyrinate; tu = thiourea; dieneN_4 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. [b] Unless noted otherwise, average values are given for each bond type. [c] Terminal S=O. [d] S–O with oxygen bound to another atom. [e] S–OH distance. [f] ^{18}O isotopomer. [g] SO_2. [h] SO_3H. [i] In ref 67, an average M–O distance was given for all three Mo complexes listed here (range: 2.060(7)–2.090(4) Å). [j] $\eta^2\text{-}S_3O_2$ = S,S-bound dithiosulfate, $\eta^2\text{-}S_2O_5$ = O_2SSO_3 bonded via one oxygen from each sulfur. [k] M = Mn. [l] M = Re. [m] Distances are symmetry-related.

However, we and others before were surprised to find that hydrides did not necessarily reduce SO_2 all the way to S^0 or S^{2-} and sometimes gave S^{VI} products indicative of sulfur *oxidation*. Several researchers[2a,20] reported perplexing SO_2 reactivity with $RuH_2(PR_3)_x$ (x = 3, 4) and related Ru species where sulfato complexes, e.g., $Ru(SO_4)(SO_2)(PPh_3)_2(H_2O)$,[20c] were identified to be among the products. At the time it was not clear whether traces of O_2 or H_2O were involved, and SO_2 disproportionation was proposed.[20c] Our findings below support this idea, and what has evolved is exceptionally rich SO_2 reactivity involving both insertion and O transfer.

We chose group 6 metals as targets because of their low cost and use in hydrodesulfurization. Two important reactions occurred rapidly in good yield (M = Mo, W):



(7)



$$Cp(CO)_3MH \xrightarrow{SO_2} Cp(CO)_3M{-}S(=O)OH \tag{8}$$

Equation 7 gave quantitative partial reduction to η^2-thiosulfate rather than S_8 or sulfide, even with excess hydride.[21] As will be further shown, $M{-}S_2O_3$[22] or similar $M{-}S_xO_y$ species often form and seem to be thermodynamic sinks (Table 1). Like ionic thiosulfates, $Cp_2M(S_2O_3)$ reacted with strong acids, e.g., HBr, to give SO_2, H_2O, and $Cp_2M(S)(Br)_2$.[21] Equation 8 (in toluene or Et_2O) demonstrated that SO_2 inserts into M–H bonds as in M–C bonds, except that the hydride attaches to oxygen rather than sulfur as in eq 1 to form the novel SO_2H ligand.[23] This was proven crystallographically (Table 1) and spectroscopically (ν(OH) = 2552 cm^{-1} in $CpW(CO)_3(SO_2H)$). Equation 8 is also unlike CO_2 insertion into M–H bonds, which gives η^2-O-bound HCO_2.[24] The solid SO_2H complexes are remarkable in that they completely dissociate back to $CpM(CO)_3H$ and SO_2 upon redissolving in the solvents from which they were crystallized. A broad ^1H NMR signal (δ 3.89) for the SO_2H in $Cp^*Mo(CO)_3(SO_2H)$ was observable only at −40 °C in liquid SO_2. The ephemeral nature of SO_2H is reiterated by the only recent substantiation[25] of the tautomeric equilibrium $IrH(SO_2)(CO)(PR_3)_2 \leftrightarrow Ir(SO_2H)(CO)(PR_3)_2$ proposed[8b] 22 years ago.

Like RSO_2H, $M{-}SO_2H$ complexes are thermally unstable toward auto-redox, even in the solid state where $(C_5R_5)M(CO)_3(SO_2H)$ gave a mixture of polynuclear sulfido and oxo–sulfido species in a day at 25 °C (M = Mo; R = H) or on mild heating (M = W).

$$(C_5R_5)M(CO)_3(SO_2H) \rightarrow [(C_5R_5)M(CO)_3]_2 + [(C_5R_5)MS_xO_y]_n + H_2O + CO \tag{9}$$

It is thus possible that SO_2 inserts into the M–H bonds of Cp_2MH_2 as the first step in eq 7, followed by elimination of H_2O to give S_2O_3. In eq 9, however, a

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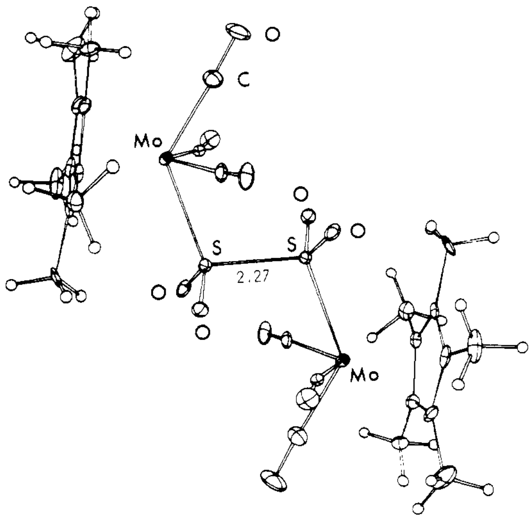
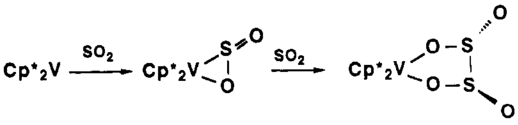


Figure 2. Structure of $[Cp^*Mo(CO)_3]_2(\mu\text{-}S_2O_4)$. Reprinted with permission from ref 23. Copyright 1985 American Chemical Society.

thiosulfate was not formed despite large variation in product composition depending on M and R. $[(C_5R_5)MO(\mu\text{-}S)]_2$ always formed, showing that total reduction of S^{IV} to S^{II-} can occur even in the solid. Prolonged *solution* reactions of the W hydrides with SO_2 in 4:1 ratio gave CO-containing sulfides such as $[Cp^*W(CO)_2(\mu\text{-}S\cdot SO_2)]_2$,[23] further illustrating the diversity of pathways. Tight binding of SO_2 to μ-S apparently stabilized the latter since attempts to remove SO_2 thermally gave decomposition. Ligand–SO_2 binding is normally reversible, e.g., in $L_nCu^I(SR\cdot SO_2)$, which can form a basis for SO_2 sensors.[27]

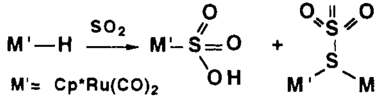
At -20 °C in SO_2-saturated CH_3CN, $Cp^*Mo(CO)_3H$ unexpectedly gave instead of the SO_2H complex a 31% yield of a dithionite-bridged complex (protons eliminated as water). $[Cp^*Mo(CO)_3]_2(S_2O_4)$ (Figure 2) is the first example of S-bound $S_2O_4^{2-}$ and a rare case of C_{2h} S_2O_4.[23] The S–S distance (2.266 Å) is shorter than in $Na_2S_2O_4$ and other C_{2v} $S_2O_4^{2-}$ ions (2.35–2.39 Å).[28] The dithionite is solution unstable, giving the same oxo–sulfido clusters as from $Cp^*Mo(CO)_3H$–SO_2 reaction. Reaction of SO_2 with $Na[Cp^*M(CO)_3]_2$ also gave the dithionite in 31% yield (plus $Na_2S_2O_4$), analogous to an iron system[28a,b] for which a mechanism involving coupling of $M(SO_2)^\bullet$ radicals was proposed. We subsequently found that O-bonded dithionite can be produced by coupling of two SO_2 at a vanadium center:



(10)

$Cp^*_2V(\eta^2\text{-}SO_2)$ had the lowest ν_{SO} bands ever observed for η^2-SO_2 (1076, 819 cm^{-1}), indicating activation of SO_2 via metal–ligand back-bonding, and indeed reacted further with SO_2 to yield the less soluble S_2O_4 complex.[29] The staggered coordination mode of the dithionite is unprecedented, and whether it is a kinetic product formed in the coupling of SO_2 ligands or the preferred coordination mode for dithionite is unknown. A similarly bonded disulfite ligand, $O_2S\text{-}SO_3^{2-}$, was prepared from an Fe macrocycle and HSO_3^-, possibly via $2HSO_3^- \leftrightarrow S_2O_5^{2-} + H_2O$.[8g] To complete the series of $S_2O_x^{2-}$ formations, a redox/disproportionation reaction of SO_2 with $Cr(C_6H_6)_2$ gave $[(C_6H_6)_2Cr]_2[S_2O_6\cdot 2SO_2]$ containing SO_2-solvated dithionate anion.[30]

A ruthenium analogue of the above hydrides, $Cp^*Ru(CO)_2H$, gave yet different reactivity with SO_2, yielding two soluble, crystallographically-characterized complexes, $Cp^*Ru(CO)_2(SO_3H)$ (25%) and dinuclear $[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$ (37%), plus unidentified species, in a variety of solvents.[31] In this case, SO_3H and bridging thiosulfate ligands are created by oxygen transfer. The source of the third oxygen in these ligands was confirmed to be SO_2 by $S^{18}O_2$ labeling and IR (Table 1). As for the Mo/W systems, varying the SO_2:hydride ratio of eq 11 did not change product ratios, indicating thermodynamic control. A mechanism is difficult to propose, but it is noteworthy that polar solvents and bases such as NEt_3 accelerated the reaction, a common feature of SO_2 disproportionations discussed later.



(11)

SO_3R ligands[32] are commonly formed by SO_2 insertion into M–OR[32c] or RO^- attack on M–SO_2.[14a] Usually they are S-bound,[32b] but an O-bound form has recently been shown in $Ir(CO)[OSO_2Me](SO_2)(PPh_3)_2$.[25] SO_3H ligands[25,32c,33] are rare (Table 1) and prior to our work had not been made directly from SO_2 ($CpFe(CO)_2(SO_3H)$ was synthesized by hydrolysis of the SO_3R species[32a]). X-ray[28a,31] and IR[31] studies showed attachment of the proton to oxygen ($\nu(OH)/\nu(^{18}OH)$ = 2460/2450) in $Cp^*Ru(CO)_2(SO_3H)$, which can readily be deprotonated by Et_3N. Theoretical work showed that the bisulfite isomers HSO_3^- and SO_3H^- are comparable in energy, with the latter containing a long S–OH bond (1.716 Å) suggesting assembly from weakly interacting SO_2 and OH^-.[34] Insertion of SO_2 into M–OH to form M–SO_3H has indeed been found for Rh[32c] and Ir.[25] The experimental S–OH distance in $Cp^*Ru(CO)_2(SO_3H)$, 1.559 Å, is much shorter than the theoretical, indicating that metal binding may stabilize SO_3H. To complete the SO_xH series, O-bonded *bisulfate* is formed in Fe-

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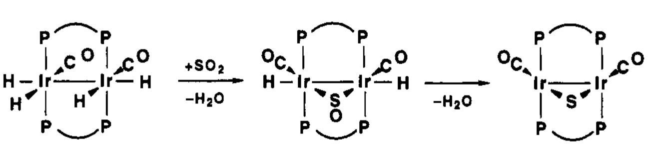
(TPP)(OSO_3H) from Fe(TPP) and SO_2 (TPP = tetraphenylporphyrinate), where trace O_2 is the oxidant.[35]

M–SO_xH may often be unobserved intermediates in SO_2 reduction. Prior to our work, reaction of Cp_2Fe with CF_3SO_3H in liquid SO_2 to give Cp_2Fe^+, H_2O, and S_8 had been proposed to occur via insertion of SO_2 into $Cp_2Fe–H^+$ followed by loss of unstable "HSO_2 radical".[36] A well-studied hydride which we also believe activates SO_2 by insertion is $Os_3(CO)_{10}(\mu\text{-}H)_2$. The latter forms an SO_2-bridged complex, $Os_3(CO)_{10}(\mu\text{-}H)_2(\mu\text{-}SO_2)$, as the first observable product, which gradually converts in solution to an unisolated species believed to be $Os_3(CO)_{10}(\mu\text{-}H)(SO_2H)$ based on NMR and isolation of the salt $[Bz_3NH][Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SO_2)]$ on addition of Bz_3N.[37] Reduction of SO_2 to H_2O and unidentified Os–CO species then occurs after several days in liquid SO_2.

An iridium polyhydride reduces SO_2 stepwise, initially to an unstable μ-SO complex and then to μ-S, which can later be protonated off as H_2S:[38]



(12)

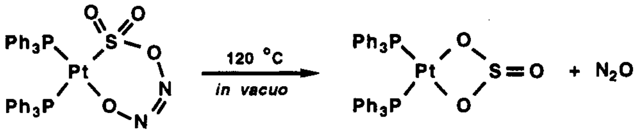
This is a rare example of complete reduction of SO_2 to sulfide and H_2O by hydrides.

Oxygen-Transfer Reactions of SO_2 on Metal Centers

Prior to our work, oxygen transfer to or from SO_2 had been rarely observed under mild conditions. Bennett found that reaction of SO_2 and $(Me_3Si)_2NH$ gave $(Me_3Si)_2O$, Me_3SiNSO, and $NH_4[Me_3SiOSO_2]$,[39] while Mingos demonstrated that SO_2 is able to function as both an oxygen donor and receptor on metal complexes:[8c,40]

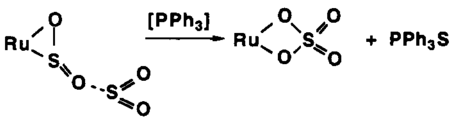
$$Pt(\eta^2\text{-}CS_2)(PPh_3)_2 + 2SO_2 \xrightarrow{\text{benzene}} Pt(CS_2O)(PPh_3)_2 + S + SO_3 \quad (13)$$

SO_2 addition to $Pt(N_2O_2)(PPh_3)_2$ gave a product proposed on the basis of IR ^{15}N-labeling studies to have the cyclic insertion-type structure shown below, which decomposed on heating to a sulfito complex.[8c]



(14)

At about the same time, we noted that $Ru(CO)_2(\eta^2\text{-}SO_4)(PPh_3)_2$, PPh_3S, and unidentified Ru species slowly formed from $Ru(CO)_2(\eta^2\text{-}SO_2)(PPh_3)_2$ in toluene containing excess SO_2 even with careful exclusion of O_2.[41] The structure at −60 °C revealed a second SO_2 weakly bonded to the terminal O of SO_2.



(15)

This suggested that *self-association of SO_2 molecules* was the first step in an O-transfer process to give SO_4 plus sulfur, scavenged by PPh_3 (free or coordinated), an important theme echoed by our later work on SO_2 disproportionation on sulfide complexes.

Several single oxygen-atom transfer reactions are known,[42] e.g., removal of oxygen from bound SO_2 to give bound SO[42a] and vice-versa (M = Fe, Ru, Rh, Ir):[42b–d]

$$CpRh(C_2H_4)(SO_2) + Si_2Cl_6 \rightarrow CpRh(SO) + (Cl_3Si)_2O + C_2H_4 \quad (16)$$

$$M\text{–}SO \xrightarrow{[O]} M\text{–}SO_2 \xrightarrow{2[O]} M\text{–}\eta^2\text{-}SO_4 \qquad [O] = p\text{-}ClC_6H_4CO_3H \quad (17)$$

RuCl(NO)(PPh_3)(SO) in eq 17 converted all the way to sulfate.[42d] On M = $[CpRu(PR_3)_2]^+$, SO disproportionated to give MSO_2 and MSSM.[42c] Many more examples of O transfer and disproportionation-type reactions are emerging, and in a sense all SO_2 bond-breaking reactions can be considered O transfer.

Activation of SO_2 on Metal Clusters To Give Sulfido and Oxo Ligands

Although reactions of SO_2 on metal clusters would be a good model for SO_2 reactions on surfaces,[43] little such work has been done.[44] While investigating potential catalysts for SO_2 reduction, we found that $Cp_2Mo_2(CO)_6$ catalyzed SO_2/H_2 reaction (10–100 atm of H_2, 100 °C, toluene) to give primarily S_8 and H_2O. Under 1 atm, reduction was not observed, and the same Mo-containing products resulted with or without H_2. Analysis of the products indicated that CO from $Cp_2Mo_2(CO)_6$ reduced SO_2 to give CO_2 and sulfido complexes. One early product that disappeared on longer reaction was characterized to be the first homonuclear butterfly cluster of a group 6 metal (Figure 3).[45] The complex contained the elements of reduced SO_2, and an overall reaction can be written:

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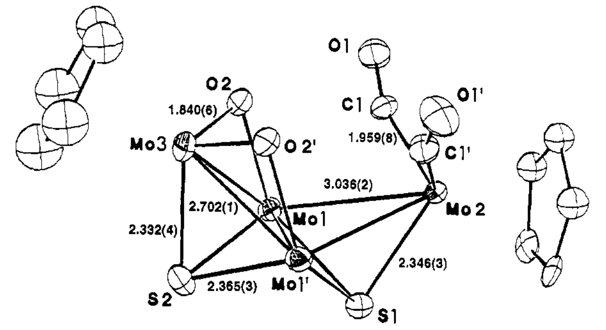

Figure 3. Structure of $Cp_4Mo_4(CO)_2(\mu\text{-}S)_2(\mu\text{-}O)_2$ (Cp rings on Mo1 and Mo1′ omitted). Distances not shown: Mo1–Mo1 = 2.845(2) Å; Mo1–O2 = 2.051(5) Å; Mo1–S1 = 2.364(2) Å; Mo1–C1 = 2.718(8) Å; dihedral angle between wings: 123°.

$$2Cp_2Mo_2(CO)_6 + 2SO_2 \rightarrow Cp_4Mo_4(CO)_2(\mu\text{-}S)_2(\mu\text{-}O)_2 + 8CO + 2CO_2 \quad (18)$$

The average Mo oxidation state changed from +1 to +3 (and sulfur from +4 to −2), but examination of the Mo environments individually led to assignments of +3 for Mo1 and Mo1′, +2 for Mo2, and +4 Mo3. The presence of three different metal oxidation states is rare in homonuclear clusters. More importantly, the structure provides a model for some of the intermediates that have been proposed for metal-catalyzed reduction of SO_2 with CO. SO_2 can be envisioned to coordinate to a metal surface or unsaturated cluster and dissociate into sulfido and oxo ligands (terminal or bridging). The oxo species could then react with nearby M–CO to give CO_2. In the Mo cluster, each oxo is 2.58 Å away from the carbon atom of a semibridging CO. This distance is less than the sum of the van der Waals radii (~3.0 Å), suggesting a weak interaction between the CO and oxo ligands.

Recently Shriver[46] found that cluster-bound SO_2 is reduced by $NaPh_2CO$ to sulfido or SO ligands in $[HFe_3(CO)_9(SO_2)]^-$, where prior acetylation is necessary for reductive cleavage of both oxygens from SO_2 (Figure 4). Both cluster-bound SO and formation of a stable SO complex by oxygen removal from bound SO_2 are rare.[38] Reaction with AcCl initially formed unstable $[HFe_3(CO)_9(SO_2Ac)]$, which then was reduced via a complex, multistep mechanism not involving $[HFe_3(CO)_9S]^-$ or $[Fe_3(CO)_9SO]^{2-}$ as intermediates.

Other examples reiterating the usefulness of SO_2 as a S/O-ligand source include Taube's Ru–S_2–Ru dimer[18] and $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ from reduction of $Rh(CO)_2(acac)$ and SO_2 with H_2/CO (300 atm, 160 °C).[47] Reactions of SO_2 with the dithiocarbamate $W(CO)_3(LL)_2$ (LL = S_2CNR_2) formed a mixture of $WO(S_2)(LL)_2$, $WS(S_2)(LL)_2$, and $W_2O_2S_2(LL)_2$, and with $MoCl(LL)_3$ reduced with Zn/Hg gave $Mo(SOCl_2)(LL)_3$, claimed to be the first $SOCl_2$ complex.[48] Noncluster building examples include Lorenz's reaction of SO_2 with *trans*-$Mo(N_2)_2(dppe)_2$ to give *trans*-Mo(=S)(=O)$(dppe)_2$ containing lattice H_2SO_4 (dppe = $Ph_2PC_2H_4PPh_2$).[49] It was speculated that SO_2 disproportionated to SO_3 (the source of H_2SO_4) and SO, which oxidatively added to a $14e^-$ $Mo(dppe)_2$ fragment. However, the mechanism and origin of H_2SO_4 were not well defined. A related system is $MoH_4(dppe)_2$ protonated with HBF_4 in THF that reacted with SO_2 to form *trans*-$[MoF(O)(dppe)_2]^+$ and *trans*-$[MoF(S)(dppe)_2]^+$.[50] These are rare examples of total cleavage of SO_2 to separate O/S ligands. We recently found novel removal of the oxygens of SO_2 at 25 °C by $U(OR)_3$ to give $(OR)_3U\text{–}S\text{–}U(OR)_3$ as the major uranium product.[51a] The fate of the oxygens is as yet unknown. Conversely, $W(CO)(phenanthroline)(SPh)_2(\eta^2\text{-}SO_2)$ spontaneously converts in solution to *cis*-W(=O)$_2$(phenanthroline)$(SPh)_2$ and S_8.[51b]

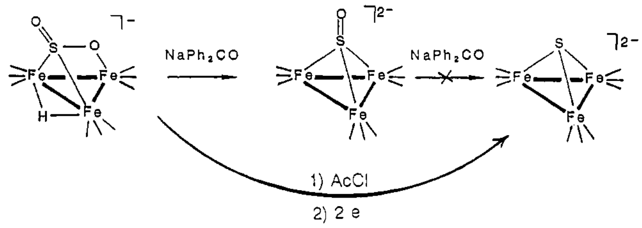

Figure 4. Structure and reactions of $[HFe_3(CO)_9(SO_2)]^-$ (three CO ligands on each iron; Ac = acetyl).

Catalytic Reduction and Disproportionation-Type Reactions of SO_2

Aside from commonly used limestone scrubbing, SO_2 abatement schemes can involve either oxidation to H_2SO_4 or reduction to sulfur, which is of greater research interest because methodology is less established and S_8 is often a more desirable product.[52] Numerous papers and patents have appeared on this subject, and a variety of reducing agents have been used including H_2, CH_4, and CO. An early concept for SO_2 removal from combustion gases was to reduce it with CO already present, but formation of toxic COS was a problem.[53] However, natural gas is currently employed to reduce SO_2 scrubbed from the flue gas of certain coal-fired utilities:

$$CH_4 + SO_2 \rightarrow S_8 + H_2S + CO_2 + H_2O \quad (19)$$

Vanadium–alumina[54] or metal sulfide[52] catalysts at 620–720 K can be used to produce sulfur and/or H_2S, which is then reacted with further SO_2 to give S_8 as the final product.

We chose to study SO_2 reduction by H_2, initially using very active heterogeneous catalysts such as 0.5% Ru/alumina under mild conditions (150–300 °C) to minimize formation of byproducts such as H_2S.[55] Typical experiments involved flask-heating of catalyst pellets and SO_2/H_2 in 1:2 ratio at ~1 atm. The only products obtained were S_8 and H_2O. Turnovers/h ranged up to 65 at 300 °C with no catalyst poisoning. Mixtures of

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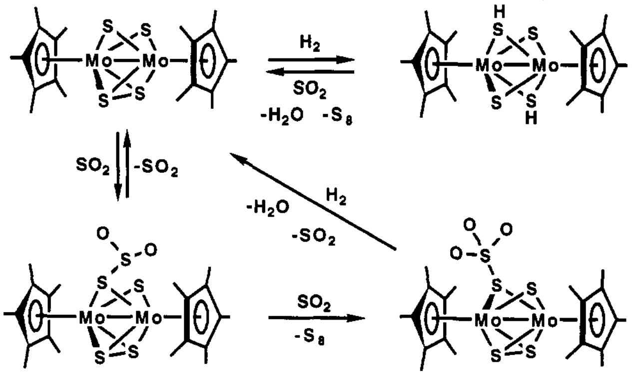


Figure 5. Reactions relating to catalytic SO_2 hydrogenation and disproportionation on Mo–S complexes. The S_8 produced from SO_2 reduction in the top reaction becomes incorporated into the clusters *to form* $[Cp^*MoS_3]_n$ *(ref 58).*

SO_2 and NO were simultaneously reduced to N_2, S_8, H_2O, and a trace of N_2O.

The next goal was to establish *homogeneous* catalytic reduction. As mentioned above, $Cp_2Mo_2(CO)_6$ catalyzed hydrogenation but decomposed. Clearly the major obstacle is sulfur poisoning, so we looked into sulfido complexes as catalysts. $[CpMoS(SH)]_2$ (Figure 5, top right) stood out because it catalyzed S_8 and H_2 to H_2S and contained reducing SH ligands uniquely regenerable from H_2.[56] Hydrogenation of SO_2 to S_8 and H_2O was found to occur cleanly at 25 °C in a closed flask containing a solution of $[CpMoS(SH)]_2$.[57] Optimization of conditions, including use of more soluble Cp* analogues in 1:1 PhCl–BuOH solvent with 0.1% Bu_3N promoter and ~3 atm of H_2 gave 350 turnovers/h at 75 °C. A 10-fold rate increase in the presence of weak bases such as alcohols and amines was a critical clue in postulating a mechanism for the catalysis, which initially was believed to include the top reactions in Figure 5, plus reduction of SO_2 by H_2S formed from H_2 reaction with $[Cp^*MoS_3]_n$[58] and/or S_8 product. It is important that the system be totally regenerable, i.e., that there be no dead-end species. Indeed $Cp^*{}_2Mo_2S_4$[59] formed from SO_2–$[Cp^*MoS(SH)]_2$ reaction (Figure 5, top) was an equally good catalyst.

Further research led to fascinating new chemistry where SO_2 was found to disproportionate on the clusters to S_8 and SO_3, forming the basis for new catalytic pathways. We found that reaction of SO_2 with $Cp^*{}_2Mo_2S_4$ initially yielded an adduct containing SO_2 weakly bound to μ-S (Figure 5, S–SO_2 = 2.60 Å).[60] Reversible Lewis acid binding of SO_2 to sulfur ligands is common,[61] but in this case further reaction with SO_2 unexpectedly occurred in solution to quantitatively give sulfur and $Cp^*{}_2Mo_2(\mu\text{-}S)(\mu\text{-}S_2)(\mu\text{-}SSO_3)$ containing an *SO_3 fragment* bound to the μ-S (Figure 5). ^{18}O labeling

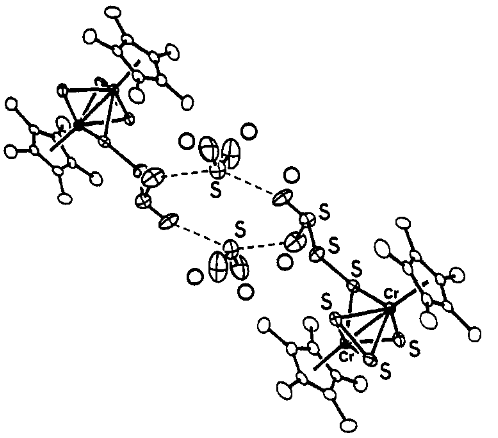
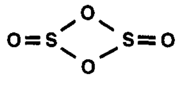


Figure 6. Structure of $2Cp^*{}_2Cr_2(\mu\text{-}S)(\mu\text{-}\eta^2\text{-}S_2)(\mu\text{-}\eta^1\text{-}SS{\cdot}SO_2){\cdot}2SO_2$, showing cyclic aggregation of SO_2. Reprinted with permission from ref 63. Copyright 1992 American Chemical Society.

established that the SO_3 is formed from SO_2 by oxygen transfer. The SSO_3 can be regarded as a reactive thiosulfate ligand (S–S = 2.17 Å) and is readily hydrogenated at 25–75 °C to regenerate $Cp^*{}_2Mo_2S_4$ (Figure 5). The relationship to the catalytic hydrogenation of SO_2 became apparent: rates of the disproportionation and catalytic reactions were similar, and both processes were promoted by Lewis bases nearly identically. A new mechanism for catalysis based on Figure 5 was proposed, where the rate-determining step is SO_2 disproportionation to sulfur and S-bound SO_3.[60]

We then found that $Cp^*{}_2Cr_2S_5$, with both η^1-S_2 and η^2-S_2 ligands,[62] is more active than the Mo sulfides in cleaving SO_2.[63] It initially bonded SO_2 at the η^1-S_2, and crystallography revealed a crucial finding: the oxygens of each bound SO_2 interacted further with the sulfurs of two *associated* SO_2 molecules to form a ring (Figure 6). In solution disproportionation then occurred to $Cp^*{}_2Cr_2S_4{\cdot}SO_3$ with one less core sulfur, isostructural with the Mo analogue. The structure of the SO_2 adduct suggested an oxygen-transfer mechanism initiated by *self-aggregation of SO_2 via weak Lewis acid–base interactions induced by electron donation from sulfide* (Figure 7). In support of this mechanism, reaction of ^{34}S-labeled $Cp^*{}_2Cr_2S_5$ with SO_2 produced labeled S_8 and unlabeled SO_3. The role of base promoters (B) is perhaps to stabilize transients, i.e., SO_3 and unstable S_2O[64] (bases also catalyze $SOCl_2$–SO_2 exchange[1]). SO_2 itself is slightly associated in liquid and gas,[1] although an X-ray[65] of the solid showed no close interactions. Self-exchange of oxygens occurs within minutes, possibly via a cyclic intermediate:[1]



Raman studies of SO_2 at high pressure indicated formation of a cyclic trimer at 25 kbar which produced free sulfur on photolysis.[66] The bimolecular dispro-

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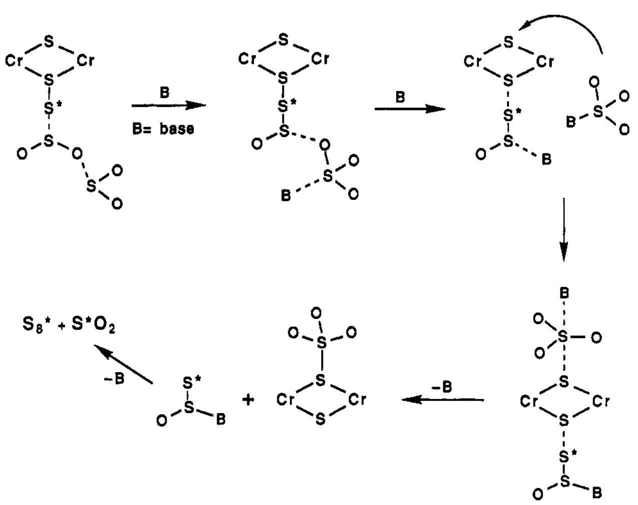


Figure 7. Possible mechanism for the disproportionation of SO_2 to sulfur and SO_3 on $Cp^*{}_2Cr_2(\mu\text{-}S)(\mu\text{-}\eta^2\text{-}S_2)(\mu\text{-}\eta^1\text{-}SS{\cdot}SO_2)$, where B is a Lewis base such as Et_3N. S* indicates positions of ^{34}S in the labeling experiment (metal-bound core sulfides also contained ^{34}S). The $\mu\text{-}\eta^2\text{-}S_2$ ligand is not shown for clarity. Reprinted with permission from ref 63. Copyright 1992 American Chemical Society.

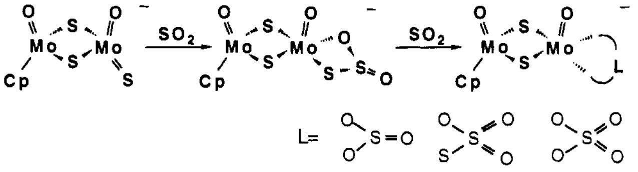
portionation $2SO_2 \rightarrow SO_3 + SO$ is thermodynamically unfavorable[63] and complicated by the instability of SO[64] and the strong oxidizing ability of SO_3. However, the latter can be stabilized by binding to bases, e.g., sulfide to give thiosulfate, and the resulting binding energy can then make the overall process thermodynamically favorable. The fact that SO and S_2O quickly go to S_8 (and SO_2) gives an easy kinetic pathway for attrition of SO_2 to sulfur. Thus, disproportionation may be a disguised mechanistic feature of many SO_2 reactions, and even apparent reduction of $S^{IV}O_2$ may actually go via $S^{VI}O_3$-containing intermediates from oxygen transfer between SO_2 (as in eq 11). It is important to note that the disproportionation is directly facilitated by the sulfide ligand rather than the spectating metal, and that sulfate was not formed as in the metal-bound case (eq 15).

Facile disproportionation of SO_2 has potential for use in SO_2 scavenging. A product such as $Cp^*{}_2Mo_2S_4{\cdot}SO_3$ can be considered to be a source of stabilized SO_3 (nucleophiles such as amines strip it off under mild conditions[60]). It is conceivable that catalytic cycles can be designed where SO_3 species are directly utilized to form organosulfonates or H_2SO_4. Indeed rapid hydrosulfination catalyzed by $[Pd(dppp)(MeCN)_2]^{2+}$ at 80 °C has recently been found,[67] analogous to hydroformylation:

$$RCH{=}CH_2 + SO_2 + H_2 \rightarrow [R'SO_2H] \rightarrow R'SO_2SR' + R'SO_3H + H_2O \quad (20)$$

Unstable sulfinic acids[26] formed via H_2 reaction with $Pd\text{-}SO_2R'$ were postulated as intermediates, but overall, many pathways to useful compounds may be possible.

A recent flurry of activity has occurred in the area of SO_2 disproportionation/oxygen transfer. Coucouvanis[68] showed even more diverse reactivity with a Mo oxo–sulfido cluster leading to formation of crystallographically-characterized sulfite, thiosulfate, or sulfate species depending on temperature and time:



(21)

The initial step was believed to be addition of SO_2 across the terminal Mo═S bond to give an unisolated η^2-thiosulfite complex, followed by further multistep reactions with SO_2. A related Mo oxo–sulfido dimer also produced sulfate ligands from SO_2 in the absence of oxygen in DMF at 100 °C, including an unprecedented $\mu_4\text{-}SO_4$ linking two $[(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]^{2-}$ subunits. In another remarkable variation on the same theme, *anionic* sulfate has been formed from reaction of O_2 with *ligand-bound* SO_2 in a nickel(II)–dithiolate.[69] Ligands also may participate in exposure of $MnX_2(OPPh_3)_n(SO_2)$ (X = Cl, Br, NCS) to moist air to give H_2SO_4, isolated as $(PPh_3O)(PPh_3OH)(HSO_4)$.[70]

Epilogue

There appear to be endless possibilities for SO_2 activation at both metal and ligand sites, both with and without oxygen present, to give either free or coordinated sulfur and oxysulfur species. SO_2 disproportionation to primarily thiosulfate-containing species is ubiquitous and may be the central step in much of known SO_2 reactivity, including catalytic hydrogenation or even reduction by methane on sulfide catalysts such as Re_2S_7 and MoS_2.[52,71] Indeed FeS is known to react with SO_2 in water to produce thiosulfate ion,[72] perhaps analogously to the $Cp^*{}_2Mo_2S_4$ system. Even well-established but mechanistically undefined processes not involving metals, such as Claus reaction of SO_2 and H_2S, may initially involve O transfer among SO_2 molecules to form unstable intermediates such as H_2SSO_3. A major question is, How susceptible are SO_2 and other amphoteric molecules such as NO_x to disproportionation processes? Further study of the conditions which promote this reactivity may lead to new strategies for chemical synthesis and abatement technology.

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