Lewis Acid Mediated Reactions of Organotransition Metal Complexes. A Marked Promotion of the Sulfur Dioxide Insertion in Alkyl(η^5-cyclopentadienyl)tricarbonyltungsten(II) by Boron(III) and Antimony(V) Fluorides[1]

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Abstract: The insertion of SO_2 into the W–R bond of η^5-$C_5H_5W(CO)_3R$ (R = CH_3, **1a**; R = $CH_2C_6H_5$, **1b**) in liquid SO_2 is markedly promoted by the Lewis acids BF_3 and SbF_5. Thus, at −26 °C the reaction of **1a** with SO_2–BF_3 appears to be at least 20 000 times faster than the reaction of **1a** with SO_2 alone. The promoted reaction proceeds to the corresponding Lewis acid stabilized *O*-sulfinato complexes, η^5-$C_5H_5W(CO)_3[OS(OBF_3$ or $OSbF_5)R]$ (BF_3: R = CH_3, **3a**; R = $CH_2C_6H_5$, **3b**. SbF_5: R = CH_3, **4a**; R = $CH_2C_6H_5$, **4b**), which were isolated and characterized by a combination of elemental analysis and infrared and ^1H NMR spectroscopy; by contrast, the insertion of SO_2 alone continues to the *S*-sulfinato complexes, η^5-$C_5H_5W(CO)_3S(O)_2R$ (R = CH_3, **2a**; R = $CH_2C_6H_5$, **2b**). Treatment of **3a** with NH_3, $C_6H_5NH_2$, or other Lewis bases affords **2a** in good yield, whereas storage of **3a** in benzene–pentane furnishes some isomeric η^5-$C_5H_5W(CO)_3[S(O)(OBF_3)CH_3]$ (**5a**). Complex **5a** also results upon treatment of **2a** with BF_3 in toluene at 25 °C or in SO_2 at −16 °C; this reaction may be reversed by the application of vacuum. Other similar 1:1 adducts of **2a** or **2b** and BF_3 or SbF_5 (or F_5SbOSO) were prepared by direct reaction of the appropriate components in SO_2 solution. The promotion of the reaction of the tungsten–alkyl complexes with SO_2 by BF_3 or SbF_5 is thought to derive from a stronger electrophilic character of the Lewis acid·SO_2 adduct than of the SO_2 alone. Mechanistic aspects of the promoted and unpromoted insertion of SO_2 are discussed, and possible extensions of this approach to other reactions at transition metal–carbon σ bonds are considered.

Introduction

One of the important reactions of transition metal–carbon σ bonds is cleavage promoted by electrophilic reagents.[2-8] Such a reaction occurs frequently in catalysis and stoichiometric synthesis; it also finds extensive use in the identification of organometallic compounds.

Transition metal alkyls generally exhibit a wide range of reactivity toward a given electrophile, E–X. This prompted us to explore a chemical means, ideally a catalytic one, of enhancing the reactivity of the more inert complexes. Our approach consisted of the use of a Lewis acid, A, in conjunction with the electrophile. This choice was made on the premise that the acid–base complex $E\text{–}X{\rightarrow}A$ would be a stronger electrophilic reagent than E–X alone. Although, to the best of our knowledge, such an approach has not yet been employed, reactions of Lewis acids with transition metal complexes have been investigated,[9-11] principally by Shriver and co-workers.[10,11] The use of Lewis acids to complex a dissociating ligand and thus promote the formation of catalytically active coordinatively unsaturated metal species has also been examined.[12]

In the present study, SO_2 was selected as E–X for initial tests because its reaction with coordinatively saturated transition metal carbonyl alkyl complexes is a reasonably well understood electrophilic cleavage process.[13] Furthermore, the reactivity of SO_2 varies markedly with the nature of the transition metal–carbon σ bond,[14] and thus offers a considerable choice of alkyl compounds suitable for the investigation in question.

The Lewis acids chosen for this study were SbF_5 and BF_3. The very strong acid SbF_5 forms a stable 1:1 adduct with SO_2. An X-ray diffraction study revealed Sb–O bonding therein, F_5SbOSO.[15] Boron(III) fluoride also yields a 1:1 adduct with SO_2; however, this compound is partly dissociated into its components above the melting point of −96 °C.[16] We assume that the SO_2 in $BF_3{\cdot}SO_2$ is also attached via oxygen. The labile $BF_3{\cdot}SO_2$ and the stable $SbF_5{\cdot}SO_2$ were considered possible representative electrophilic cleavage reagents whose reactions with metal–carbon σ bonds would be respectively catalytic and stoichiometric in Lewis acid.

Two examples of Lewis acid enhancement of electrophilic reactivity of SO_2 have recently been reported. Sulfur dioxide adds to cyclooctatetraene in the presence of SbF_5 at −70 °C;[17,18] by contrast, SO_2 alone appears unreactive.[17] In the presence of BF_3, SO_2 undergoes an addition reaction with η^4-$C_4H_4Fe(CO)_3$ to afford (η^3-$CH_2CHCHCH_2)Fe(CO)_3[OS(OBF_3)]$,[19] which was characterized by X-ray crystallography.[19,20] Antimony(V) fluoride behaves similarly to BF_3. There is no observable reaction in the absence of the Lewis acid.

We now report on the reaction of η^5-$C_5H_5W(CO)_3R$ (R = CH_3,$CH_2C_6H_5$) with SO_2 in the presence of BF_3 and SbF_5, the two tungsten complexes having been selected because of their relatively slow reaction with SO_2 alone.[21] Our study demonstrates a remarkable enhancement of the reactivity of SO_2 toward the tungsten–carbon σ bonds upon introduction of each of these Lewis acids. Certain aspects of this investigation were disclosed earlier in a preliminary form.[22]

Results

Reactions. The reaction of η^5-$C_5H_5W(CO)_3R$ (R = CH_3, $CH_2C_6H_5$) with SO_2, studied previously under synthetic conditions only,[21,23] was followed by ^1H NMR spectroscopy to provide a more quantitative measure of reactivity. An examination of a solution of η^5-$C_5H_5W(CO)_3CH_3$ (**1a**) in neat SO_2 at −15 °C shows that the formation of η^5-$C_5H_5W(CO)_3S(O)_2CH_3$ (**2a**) is ca. 16% complete after 27 days. At room temperature, approximately 10% of **1a** is converted to **2a** in 6 days, and the reaction appears substantially complete in 2 months. Similarly, after 6 days at room temperature, η^5-$C_5H_5W(CO)_3CH_2C_6H_5$ (**1b**) and SO_2 afford ca. 30% η^5-$C_5H_5W(CO)_3S(O)_2CH_2C_6H_5$ (**2b**), the insertion being virtually complete within 2 months. Both reactions proceed very cleanly to the respective *S*-sulfinates, and the *O*-sulfinato intermediates, observed earlier for several alkyl complexes

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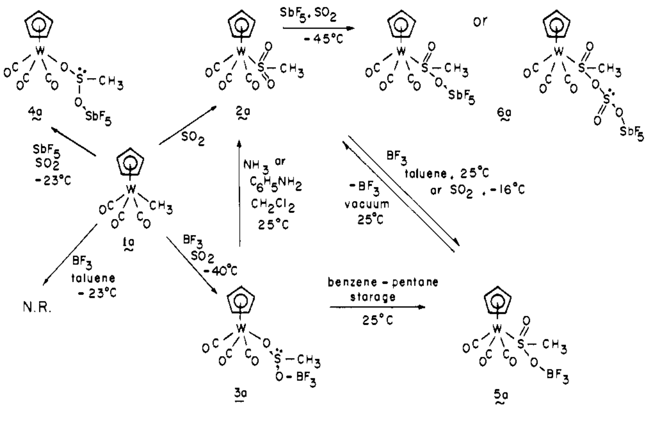
Scheme I



η^5-$C_5H_5Fe(CO)_2R$, η^5-$C_5H_5Mo(CO)_3R$, $Mn(CO)_5R$, and $Re(CO)_5R$,[24] are not seen in the spectra.

Addition of an equimolar amount of BF_3 to a solution of **1a** in SO_2 results in a dramatic enhancement of reactivity in the insertion. Although there is no evidence of reaction at −78 °C, upon warming to −40 °C the solution changes color from yellow to burgundy red. An examination of this solution by ^1H NMR spectroscopy at −26 °C reveals two new singlet resonances at τ 3.98 and 7.51 ppm with the relative intensities 5:3. These new signals are attributed to η^5-$C_5H_5W(CO)_3[OS(OBF_3)CH_3]$ (**3a**). The conversion of **1a** to **3a** at −26 °C requires less than 40 min for completion. In a separate, synthetic experiment involving **1a**, SO_2, and BF_3, a red, microcrystalline solid was isolated which exhibits an ^1H NMR spectrum matching that of the **3a** detected in solution. The rather elaborate isolation procedure of this moisture-sensitive compound is described fully in the Experimental Section. The composition of **3a** as a 1:1:1 adduct of **1a**, SO_2, and BF_3 was ascertained by analysis, and its structure was assigned from the IR and ^1H NMR spectroscopic data presented in the following subsection of this paper.

To determine whether reaction between **1a** and SO_2 would be promoted also by catalytic amounts of the Lewis acid, **1a** and SO_2 at reflux were allowed to interact with a deficiency (27%) of BF_3 for 2 h. The ^1H NMR spectrum of the reaction mixture showed the presence of **3a** and some (ca. 30%) unreacted **1a**, thus demonstrating that the BF_3 is assuming a stoichiometric rather than a catalytic role in the insertion. The observation that a mixture of approximately equimolar amounts of **1a** and **3a** in SO_2 at −20 °C retains its composition for at least 1 h points to quite a strong attachment of the Lewis acid in **3a**, thus supporting the aforementioned conclusion. In both experiments, complete consumption of **1a** and presence of **2a** in addition to **3a** would be expected if the promotion of the reaction by BF_3 were catalytic.

A tensimetric titration of **1a** with BF_3 in toluene at −23 °C was carried out to check for the possibility of interaction between the two compounds. Plotting the results as total pressure over the solution vs. mole ratio of added BF_3:**1a** yields a straight line. Thus, no adduct formation is indicated; unreacted **1a** was recovered virtually quantitatively upon removal of the solvent. The change of color from yellow to reddish orange during the titration probably reflects a minor side reaction or decomposition of **1a** effected by the BF_3. In view of this result it appears unlikely that the formation of **3a** from **1a** proceeds via initial activation of the alkyl complex by BF_3 to yield an adduct which would then react with SO_2 to furnish **3a**.

To test the generality of promotion of the SO_2 insertion by Lewis acids, reaction of **1a** and SO_2 was also examined in the presence of SbF_5. Since SbF_5 is an extremely reactive and difficult to manipulate substance, some of our experiments were performed by intercalating SbF_5 in graphite to form a free-flowing black powder.[25] When used in this form, SbF_5 is much less reactive and can be handled with relative ease. Both pure SbF_5 in SO_2 solution and SbF_5 intercalated in graphite react readily with **1a** in SO_2 even at −78 °C to yield deep orange crystals after workup. The product, characterized as η^5-$C_5H_5W(CO)_3[OS(OSbF_5)CH_3]$ (**4a**) by elemental analysis and IR and ^1H NMR spectroscopy (vide infra), is strictly analogous to the BF_3 derivative **3a**. However, it is easier to handle than **3a** and appears to be more stable when exposed to air in solution or in the solid.

The ease of formation of $SbF_5{\cdot}SO_2$ from the two components (at −60 to −50 °C[26]) and its considerable stability to dissociation[27] both provide support for a direct, very facile interaction between **1a** and $SbF_5{\cdot}SO_2$. With this system it is even less likely than with $BF_3{\cdot}SO_2$ that the insertion proceeds first by complexation between **1a** and the Lewis acid followed by reaction with SO_2.

The behavior of the benzyl complex **1b** toward SO_2 and BF_3 is strictly analogous to that of **1a**. Thus, addition of an equimolar amount of BF_3 to **1b** in SO_2 at −78 °C in an NMR tube, followed by warming to −26 °C, results in a virtually complete conversion of **1b** to η^5-$C_5H_5W(CO)_3[OS(OBF_3)CH_2C_6H_5]$ (**3b**). This is indicated by the appearance of new resonances at τ 2.60 (complex), 4.06 (singlet), and 5.98 and 6.14 (AB quartet) with the relative intensities 5:5:2. In a similar but larger scale experiment, complex **3b** was isolated as a red oil exhibiting an ^1H NMR spectrum identical with that presented above. It is noteworthy that addition of BF_3 to a solution of **1b** in SO_2 at −78 °C immediately resulted in the formation of a brown precipitate, which dissolved upon warming the reaction mixture. The precipitate could not be isolated for characterization.

A similar reaction of **1b** with SO_2 and SbF_5 in place of BF_3 at −78 °C for 48 h led to the isolation of a red powder. This solid is thought to be η^5-$C_5H_5W(CO)_3[OS(OSbF_5)CH_2C_6H_5]$ (**4b**) from the spectroscopic evidence presented later.

Complex **3a** can be converted to the *S*-sulfinate **2a** by reaction with Lewis bases under a variety of conditions. Accordingly, treatment of **3a** in CH_2Cl_2 with NH_3 affords **2a** in 85% yield along with $BF_3{\cdot}NH_3$. The reaction of **3a** with another nitrogen base, aniline, also gives **2a** in high yield; however, the boron-containing material could not be characterized, presumably owing to the known instability of BF_3–aniline reaction products.[28,29] Additionally, **2a** was obtained from **3a** by dissolution in THF or water, exposure in CH_2Cl_2 solution to alumina or Florisil, and grinding with KBr and compressing into a pellet. Thus, although the BF_3-promoted reaction of SO_2 with **1a** is arrested at an intermediate, *O*-sulfinato stage, the final, *S*-sulfinato product of the insertion, **2a**, may be conveniently obtained therefrom under ambient conditions. These and other reactions investigated herein of the tungsten complexes **1**-**4a** comprise Scheme I.

During an attempt at recrystallization of **3a** from benzene by slow addition of pentane, an orange, crystalline solid was isolated. The ^1H NMR signals of this product match exactly the singlet resonances appearing at τ 3.84 (5 H) and 6.31 (3 H) ppm when a solution of **2a** in SO_2 is allowed to react with approximately equimolar BF_3 at −16 °C. This latter reaction proceeds cleanly and reaches 80% completion in 45 min. The same substance was prepared by a tensimetric titration with BF_3 of **2a** in a heterogeneous mixture in toluene at 25 °C. The plot in Figure 1 shows coordination of 0.8 mol of BF_3 per mol of **2a**. We take this result to indicate the formation of a 1:1 complex of **2a** and BF_3, **5a**, the low value of BF_3 uptake undoubtedly deriving from the heterogeneous nature of the reaction mixture. This 1:1 complex was in fact isolated, quantitatively, following the titration. Thus, **5a**, formulated as η^5-$C_5H_5W(CO)_3[S(O)(OBF_3)CH_3]$ from spectroscopic data

Table I. Infrared Spectra of Organotungsten and Some Reference Compounds (cm^{-1})[a]

no.	compd	$\nu(C{\equiv}O)$[b]	$\nu(S{=}O)$[c]	$\nu(S{-}O)$[c,d]	$\nu(BF)$[c]	$\nu(SbF)$[c]
2a	η^5-$C_5H_5W(CO)_3S(O)_2CH_3$	2046, 1955	1188, 1054			
2b	η^5-$C_5H_5W(CO)_3S(O)_2CH_2C_6H_5$[e]	2053, 1975, 1955[j]	1201, 1951			
3a	η^5-$C_5H_5W(CO)_3[OS(OBF_3)CH_3]$	2052, 1960		870	1132 m, 1105 m, 870	
3b	η^5-$C_5H_5W(CO)_3[OS(OBF_3)CH_2C_6H_5]$	2056, 1970[k]		845[k]	1130, 845, 810 sh[k]	
4a	η^5-$C_5H_5W(CO)_3[OS(OSbF_5)CH_3]$	2058, 1967		990, 870 m, 845 sh		660, 645
4b	η^5-$C_5H_5W(CO)_3[OS(OSbF_5)CH_2C_6H_5]$	2060, 1970[j]		986 m		660
5a	η^5-$C_5H_5W(CO)_3[S(O)(OBF_3)CH_3]$	2050, 1964	1200	860	1142, 1117, 860, 820	
	η^5-$C_5H_5Fe(CO)[P(n\text{-}C_4H_9)_3]$-$[S(O)(OBF_3)CH_3]$[f]		1130	890	1165 sh, 1130, 1090 sh, 850 m	
	$(C_6H_5)_3P{\cdot}BF_3$[g]				1150–1100, 915, 888	
	$C_5H_5N{\cdot}BF_3$[h]				1165, 1125, 912, 893	
	F_5SbOSO[i]		1327[l]	1102[l]		695, 659[l]

[a] All strong unless otherwise noted. Abbreviations: m, medium; sh, shoulder. [b] CH_2Cl_2 solution. [c] Nujol mull. [d] Assignment tentative. [e] Reference 23. [f] Reference 32. [g] Scott, R. N.; Shriver, D. F.; Lehman, D. D. *Inorg. Chim. Acta* **1970**, *4*, 73–78. [h] Reference 31. [i] Reference 26. [j] $CHCl_3$ solution. [k] Neat. [l] Powder between AgCl plates.

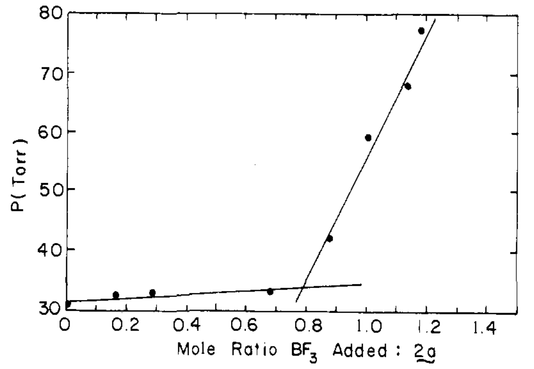


Figure 1. Tensimetric titration of **2a** with BF_3 in toluene at 25 ± 2 °C. *P* is the total pressure over the reaction mixture.

(vide infra), and **3a** are isomeric 1:1:1 adducts of **1a**, SO_2, and BF_3. Complex **5a** loses BF_3 under vacuum at 25 °C in ca. 10 h to regenerate **2a** quantitatively.

Adduct formation occurs also between **2a** and SbF_5 or F_5SbOSO as ascertained by ^1H NMR spectroscopy. When equimolar amounts of **2a** and SbF_5 intercalated in graphite are allowed to react in SO_2 at −45 °C, the solution changes color from yellow to yellow-brown. After 7 h, the ^1H NMR spectrum shows quantitative conversion of **2a** to η^5-$C_5H_5W(CO)_3[S(O)(OSbF_5)CH_3]$ or η^5-$C_5H_5W(CO)_3\{S(O)[O$-$S(O)OSbF_5]CH_3\}$ (**6a**), exhibiting singlet resonances at τ 3.95 (5 H) and 6.47 (3 H) ppm.

Complex **2b** reacts similary to **2a** with each of BF_3 and SbF_5 (intercalated in graphite) in SO_2 at −45 °C. The formation of η^5-$C_5H_5W(CO)_3[S(O)(OBF_3)CH_2C_6H_5]$ (**5b**) reaches completion within 1 h as the solution turns deep red, whereas the formation of η^5-$C_5H_5W(CO)_3[S(O)(OSbF_5)CH_2C_6H_5]$ or η^5-$C_5H_5W(CO)_3\{S(O)[OS(O)OSbF_5]CH_2C_6H_5\}$ (**6b**) was observed to be essentially complete in 7 h to give a yellow-brown solution. Both reactions, monitored by ^1H NMR spectroscopy, are quantitative.

Characterization of Complexes. Complexes **3–5a** and **3–4b** were isolated and characterized by a combination of elemental analysis, IR and ^1H NMR spectroscopy, and chemical reactions. IR and ^1H NMR spectral data, set out in Tables I and II, respectively, were especially helpful in making structural assignments.

All of the aforementioned complexes show IR $\nu(C{\equiv}O)$ spectra which are similar to those of the *S*-sulfinates **2a** and **2b**, as well as a characteristic singlet proton resonance for the η^5-C_5H_5 ring. These data indicate that the η^5-$C_5H_5W(CO)_3$ fragment remains intact and that the $BF_3{\cdot}SO_2$ or $SbF_5{\cdot}SO_2$ is inserted into the W–R bond. The IR spectra of **2–5a** in the 1300–650-cm^{-1} region, shown in Figure 2, are particularly informative with regard to the nature of the insertion linkages. Thus, complex **2a** exhibits two terminal SO stretching bands (1188 and 1054 cm^{-1}), in agreement with the presence of an *S*-sulfinato group.[30] By contrast, **5a** shows only one terminal SO stretching absorption (1200 cm^{-1}), and **3a** and **4a** display none. However, assignment of $\nu(S{=}O)$ bands for **3a** and **5a** from the two spectra alone is by no means unequivocal, since $\nu_{as}(BF)$ absorptions occur in the same region[31] (also see Table I for examples). For that reason, a comparison of the spectra of **4a** with those of **3a** (in particular) and **5a** becomes necessary. It is seen that substitution of SbF_5 in **4a** for BF_3 in **3a** eliminates the bands at 1132 and 1105 cm^{-1} present for the latter complex. Accordingly, these absorptions are assigned to ν_{as}(BF). The same assignment follows for the absorptions at 1142 and 1117 cm^{-1} in the spectrum of **5a**. Hence it is concluded that **5a** contains one terminal S=O, and **3a** and **4a** none.

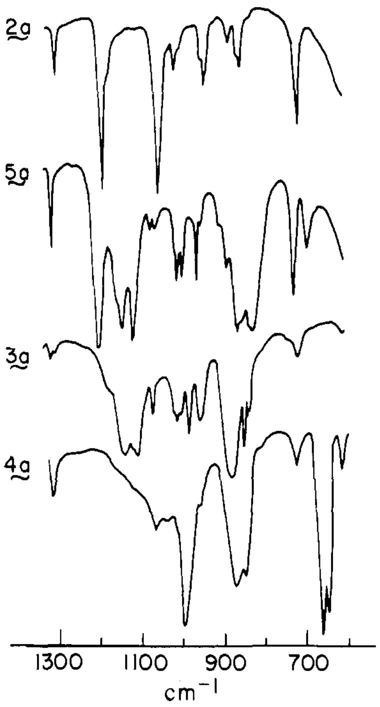


Figure 2. Infrared spectra in the 1300–650-cm^{-1} region of some organotungsten complexes in Nujol mull.

Table II. ^1H NMR Spectra of Organotungsten and Some Reference Compounds (τ, ppm)[a]

no.	compd	chemical shift of C_5H_5	chemical shift of CH_2	chemical shift of CH_3
1a	η^5-$C_5H_5W(CO)_3CH_3$	4.48		9.58
1b	η^5-$C_5H_5W(CO)_3CH_2C_6H_5$	4.48	7.12	
2a	η^5-$C_5H_5W(CO)_3S(O)_2CH_3$	4.02		6.76
2b	η^5-$C_5H_5W(CO)_3S(O)_2CH_2C_6H_5$	4.21	5.70	
3a	η^5-$C_5H_5W(CO)_3[OS(OBF_3)CH_3]$	3.98		7.51
3b	η^5-$C_5H_5W(CO)_3[OS(OBF_3)CH_2C_6H_5]$	4.06	5.98, 6.14 q_{AB}[f]	
4a	η^5-$C_5H_5W(CO)_3[OS(OSbF_5)CH_3]$	3.96		7.30
4b	η^5-$C_5H_5W(CO)_3[OS(OSbF_5)CH_2C_6H_5]$[b]	4.07	5.92, 5.99[g]	
5a	η^5-$C_5H_5W(CO)_3[S(O)(OBF_3)CH_3]$	3.84		6.31
5b	η^5-$C_5H_5W(CO)_3[S(O)(OBF_3)CH_2C_6H_5]$	3.93	4.89	
6a	η^5-$C_5H_5W(CO)_3[S(O)(OSbF_5)CH_3]$[c]	3.95		6.47
6b	η^5-$C_5H_5W(CO)_3[S(O)(OSbF_5)CH_2C_6H_5]$[d]	4.04	5.36	
	η^5-$C_5H_5Mo(CO)_3S(O)_2CH_2C_6H_5$[e]	4.32	5.78	
	η^5-$C_5H_5Mo(CO)_3[OS(O)CH_2C_6H_5]$[e]	4.29	6.31, 6.49 q_{AB}[h]	
	$Mn(CO)_5S(O)_2CH_3$[e]			6.91
	$Mn(CO)_5[OS(O)CH_3]$[e]			7.72

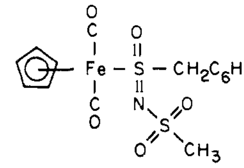
[a] In SO_2; C_6H_5 protons not included. All singlets unless otherwise noted. Abbreviation: q_{AB}, AB quartet. [b] $CDCl_3$ solution. [c] Alternative structure η^5-$C_5H_5W(CO)_3\{S(O)[OS(O)OSbF_5]CH_3\}$; see text. [d] Alternative structure η^5-$C_5H_5W(CO)_3\{S(O)[OS(O)OSbF_5]CH_2C_6H_5\}$; see text. [e] Reference 24. [f] J_{AB} = 13.2 Hz. [g] Inner peaks of a presumed AB quartet. [h] J_{AB} = 12.5 Hz.

Of several possible structures $W(BF_3 \cdot SO_2)CH_3$ with a single terminal S=O, e.g., $W[S(O)(OBF_3)CH_3]$, $W[S(O)(OCH_3)BF_3]$, and $W[OS(O)(BF_3)CH_3]$, the one present in **5a** is undoubtedly that listed first. This follows from the facile and reversible reaction of **2a** with BF_3 to yield **5a**. Complexes with an identical $S(O)(OBF_3)CH_3$ ligand, η^5-$C_5H_5Fe(CO)(PR_3)[S(O)(OBF_3)CH_3]$ (R = n-C_4H_9, C_6H_5), have been reported;[32] some of the IR spectral data for one of them (R = n-C_4H_9) are included in Table I for comparison. Several different arrangements are also possible for $W(A \cdot SO_2)CH_3$ (A = BF_3, SbF_5) without terminal S=O bonds, e.g., $W[OS(OA)CH_3]$ and $W[OS(OCH_3)A]$. There appears little doubt that the actual fragment in **3a** and **4a** is $W[OS(OA)CH_3]$. Support for this conclusion derives from the facile conversion of **3a** to **2a** by the action of NH_3, $C_6H_5NH_2$, and other Lewis bases; thus **3a** and **4a** almost certainly represent examples of a Lewis acid intercepted *O*-sulfinato intermediate in the SO_2 insertion.

The IR spectra in the 1300-650-cm^{-1} region of the benzyl derivatives **3b** and **4b** are very similar to those of **3a** and **4a**, respectively, suggesting analogous structures. These structures receive support from the ^1H NMR spectra which show nonequivalent CH_2 protons owing to the presence of a chiral sulfur. Furthermore, the ^1H NMR spectra reveal that all of **3-4a,b** show CH_2 or CH_3 signals upfield (0.22-0.75 ppm) from the corresponding resonances of the *S*-sulfinate **2a** or **2b**. Both the nonequivalence and the upfield shift were noted before in the spectra of the *O*-sulfinates derived from transition metal-methyl and -benzyl complexes by SO_2 insertion[24] (see Table II for examples). They thus lend further credence to the structures assigned in this study.

Although complexes **5-6b** and **6a** were only observed in SO_2 solution by ^1H NMR spectroscopy, their structures as Lewis acid adducts of **2b** and **2a**, respectively, may be assigned with reasonable confidence. These complexes were formed cleanly and quantitatively from **2a** or **2b** and BF_3 or SbF_5 (or F_5SbOSO). Since only a single product resulted in each case as the ratio of the *S*-sulfinate to the Lewis acid varied from 1:1 to ca. 1:2, this product is formulated as a 1:1 adduct of the reactants. By analogy with the inferred structure of the related **5a** (vide supra), the Lewis acid almost certainly adds to a sulfinate oxygen. The only unresolved question concerns the added acid in **6a** and **6b**, whether SbF_5 or F_5SbOSO; we cannot answer this from the ^1H NMR data alone.

The ^1H NMR spectra of **5-6a,b** all exhibit similar features which are consistent with the proposed structures. Thus, in direct contrast to **3-4a,b**, these complexes show CH_2 and CH_3 resonances downfield (0.29-0.81 ppm) from those of the parent *S*-sulfinate. Moreover, **5b** and **6b** do not exhibit a magnetic nonequivalence of the CH_2 protons even though the benzyl group is bonded to a chiral sulfur. This unexpected behavior may possibly arise from a rapid shift of the BF_3 or SbF_5 between the sulfinate oxygens. However, such a site exchange need not be occurring to give the observed singlet CH_2 resonance, as the complex below also shows magnetically equivalent methylene protons.[33]



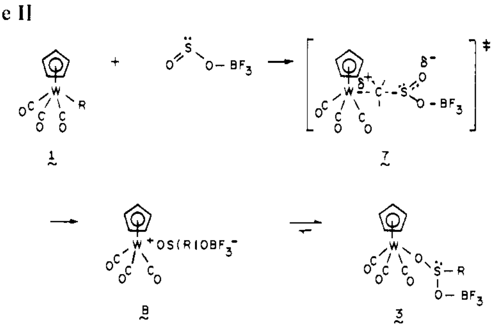
Discussion

First we wish to compare the reaction between the tungsten-methyl complex **1a** and neat SO_2 with that between **1a** and SO_2 in the presence of BF_3. The latter reaction proceeds cleanly to **3a**, which has been isolated and characterized as described earlier in the paper. A reasonable structural alternative to **3a**, **5a**, may be ruled out by virtue of two independent syntheses and a spectroscopic characterization of this isomeric compound. When SO_2 alone reacts with **1a**, the *S*-sulfinate **2a** has been observed, isolated, and characterized.

The insertion of SO_2 is very significantly promoted by the presence of BF_3. Considering the observations that the reaction of **1a** with neat SO_2 is 16% complete in 27 days at −15 °C and 10% complete in 6 days at 25 °C, a half-life of 152 days is calculated at −26 °C. At this temperature the conversion of **1a** to **3a** by SO_2 and BF_3 has a half-life of not more than 10-15 min. Thus the reaction of **1a** with SO_2 and BF_3 is at least 20 000 times faster than that of **1a** with SO_2 alone—a very significant enhancement indeed. The analogous reactions of **1a** with SO_2 and SbF_5 to give **4a** and of the tungsten-benzyl complex **1b** with each of SO_2-BF_3 and SO_2-SbF_5 to yield **3b** and **4b**, respectively, also experience a marked promotion by the added Lewis acid.

In the light of the aforementioned results, the possibility of a change of reaction mechanism on going from the insertion with neat SO_2 to that with SO_2 and BF_3 becomes an important consideration. To shed some light on this problem, stereochemical experiments were conducted in our laboratory on the

Scheme II



reactions of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$ with neat SO_2 and with SO_2 and BF_3.[34] In both cases, inversion of configuration at the α carbon of the $CHDCHDC_6H_5$ ligand was observed. Thus it appears that the insertion of SO_2 alone in **1** and in other coordinatively saturated transition metal carbonyl alkyl complexes, described fully elsewhere,[13,35] bear a close mechanistic analogy. Our inability to detect the *O*-sulfinato intermediates from **1a** and **1b** in all probability derives from their low concentration in solution owing to a relatively slow rate of cleavage of the W–R bond compared to *O*-sulfinato to *S*-sulfinato isomerization.

The insertion of $BF_3{\cdot}SO_2$ in **1** apparently follows a similar mechanism, shown in Scheme II. We attribute the marked enhancement of reactivity in the presence of BF_3 or SbF_5 to a more facile interaction of **1** with the stronger electrophile $BF_3{\cdot}SO_2$ or $SbF_5{\cdot}SO_2$ than with the weaker electrophile SO_2. Alternatively, the presence of BF_3 (or SbF_5) may help reduce the developing negative charge on the SO_2 oxygens in the transition state (**7**) and thus provide a driving force for the reaction. Arguments have already been advanced (vide supra) for the participation of the $BF_3{\cdot}SO_2$ adduct rather than the BF_3 and SO_2 components separately.

Another facet of the insertion which merits attention is its arrest at the *O*-sulfinato stage by the coordination of BF_3 or SbF_5 (**3** or the SbF_5 analogue in Scheme II). We believe that the formation in these reactions of the corresponding tungsten *S*-sulfinate is precluded by a decreased basicity of the sulfur in **3** compared to that in the uncomplexed tungsten *O*-sulfinate, owing to the coordination of the Lewis acid. This would disfavor isomerization either via a proposed[35] ion pair, **8**, or intramolecularly. However, removal of the coordinated BF_3 in **3a** by the action of NH_3, $C_6H_5NH_2$, or some other Lewis base rapidly leads to the formation of the *S*-sulfinate **2a**. It is possible that the previously observed[24] considerable stability of some transition metal *O*-sulfinates in liquid SO_2 derives from a similar interaction, but of the SO_2 acting as an acid, with the coordinated *O*-sulfinato ligand. Upon evaporation of the solvent, a rearrangement to the *S*-sulfinate occurs there as well.

Finally, the demonstrated ability of Lewis acids to promote SO_2 insertion in **1** raises the question of generality of such an acid assistance in enhancing reactions at transition metal–carbon σ bonds. Studies along these lines are underway in our laboratory. For example, reaction between η^5-$C_5H_5Fe(CO)_2CH_3$ and an analogue of SO_2, $C_6H_{11}NSO$, is appreciably speeded up by the presence of BF_3.[36] An extension to some common and useful unsaturated molecules such as olefins, acetylenes, and CO_2 is planned.

Experimental Section

General Procedures. All reaction of the Lewis acids BF_3 and SbF_5 were conducted in a grease-free (also Hg-free for SbF_5) vacuum line. Separation and purification of products were carried out using Schlenk-type glassware.[37] Sample preparation and various manipulations of nonvolatile air- and/or moisture-sensitive materials were conducted in a drybox filled with argon.

Chromatography was performed using columns packed either with neutral alumina (Ventron) deactivated by the addition of 10% H_2O or with 60–100 mesh Florisil. Melting points were measured in vacuo or under argon on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were done by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Physical Measurements. Infrared (IR) spectra of solutions were obtained on a Beckman IR-9 spectrophotometer, whereas IR spectra of solids as Nujol and Fluorolube mulls were recorded on a Perkin-Elmer Model 337 spectrophotometer.

^1H NMR spectra were measured on a Varian A-60A spectrometer equipped with low-temperature accessories. All SO_2 solutions were sealed in NMR tubes under vacuum and included Me_4Si as an internal reference. ^{19}F NMR spectra were obtained on a Bruker HX-90 spectrometer at 84.6 MHz with the assistance of Dr. C. E. Cottrell.

Materials. Commercially procured solvents were reagent grade quality and were purified further by reflux over and distillation from P_4O_{10} (CH_2Cl_2 and $CHCl_3$), CaH_2 (benzene), or $LiAlH_4$ (pentane, hexane, and toluene). They were deaerated by three freeze–thaw cycles or by purging with argon for at least 30 min.

Sulfur dioxide from Air Products was purified by passage through concentrated H_2SO_4 and a column packed with P_4O_{10} prior to use. Boron(III) fluoride (Matheson) was treated with NaF and then fractionally distilled. Antimony(V) fluoride (Columbia Organic Chemicals) was purified by trap to trap distillation. It was intercalated in graphite by the procedure of Lalancette[25] to yield a free-flowing black powder containing 65% SbF_5 by weight. The powder, which did not fume in moist air, was generally handled in a dry argon atmosphere, and its reactions were initiated by addition of solvent on a vacuum line. All other chemicals were procured in reagent grade or equivalent quality and were used as received.

The organotungsten complexes η^5-$C_5H_5W(CO)_3R$ where R = CH_3 and $CH_2C_6H_5$ were prepared by the general method of Piper and Wilkinson[38] and were purified as reported elsewhere.[39] The corresponding *S*-sulfinates, η^5-$C_5H_5W(CO)_3S(O)_2R$ where R = CH_3 and $CH_2C_6H_5$, were synthesized according to the literature.[23] The former was isolated in 45% yield whereas, by employing lower reaction temperatures (35–40 °C) and a longer time (8 days), the latter was obtained in 90% yield.

Tensimetric Titrations with BF_3. A. η^5-$C_5H_5W(CO)_3CH_3$ (1a). A degassed solution of **1a** (0.33 g, 0.95 mmol) in toluene (25 mL) was maintained at −23 °C with the aid of a CCl_4 slush bath. This solution was treated with a fivefold excess of BF_3 introduced in 11 aliquots from a reservoir cooled to −126 °C. Pressure readings were taken after allowing 30 min for equilibration following each addition. A small quantity of brown precipitate formed on addition of the first portion of BF_3, and the solution turned reddish orange during the titration. After all of the BF_3 had been added, volatile materials were removed under vacuum. An IR spectrum in the $\nu(C{\equiv}O)$ region of the residue showed a very weak absorption at 2060 cm^{-1} in addition to strong bands at 2020 and 1930 cm^{-1} (CH_2Cl_2 solution).

B. η^5-$C_5H_5W(CO)_3S(O)_2CH_3$ (2a). Preparation of η^5-$C_5H_5W(CO)_3[S(O)(OBF_3)CH_3]$ (5a). A heterogeneous mixture of partly dissolved **2a** (0.68 g, 1.7 mmol) in toluene (50 mL) was degassed and then treated with excess (2.0 mmol) BF_3. The BF_3 was introduced in aliquots from a flask at −196 °C and, after each addition, was allowed to equilibrate for 30-45 min to the temperature (25 ± 2 °C) of the reaction mixture for pressure measurements. At the conclusion of the titration volatile materials were removed under vacuum and the residue was washed with CH_2Cl_2 to leave a yellow powder, **5a**, mp (under Ar) 100–105 °C dec, in essentially quantitative yield: ^1H NMR ($CDCl_3$) τ 4.08 s (C_5H_5), 6.64 s (CH_3) ppm; IR (Nujol) 3115 m, 2060 s, 1980 s, 1950 s, 1312 m, 1200 vs, 1142 s, 1117 s, 1070 vw, 1060 vw, 1010 m, 998 m, 960 m, 890 sh, 860 s br, 820 s br, 725 m, 690 w cm^{-1}.

Reaction of η^5-$C_5H_5W(CO)_3CH_3$ (1a) with SO_2 and BF_3. Preparation of η^5-$C_5H_5W(CO)_3[OS(OBF_3)CH_3]$ (3a). The reaction and subsequent workup were carried out in Schlenk-type apparatus consisting of a fritted filter tube attached at both ends to round-bottom flasks and equipped with appropriate vacuum and inert atmosphere connectors.

Sulfur dioxide (50 mL liquid) was introduced to the evacuated round-bottom reaction flask containing 2.54 g (7.30 mmol) of **1a** at −78 °C. After the tungsten-methyl complex had dissolved the flask was placed in liquid nitrogen (−196 °C) and treated with 7.29 mmol of BF_3 (four 57.64-mL aliquots, 2343 Torr total, 23.7 °C). The resulting mixture changed color from yellow to deep burgundy red upon slow warming with stirring to -23 °C (CCl_4 slush bath). After 45 min of reaction time, the solution was cooled to -196 °C and treated with 20 mL of CH_2Cl_2 on a vacuum line. The reaction mixture was allowed to warm and then was concentrated to 20 mL under vacuum. An additional 40 mL of CH_2Cl_2 was added and the volume was further reduced to 10 mL. The mixture was then filtered to remove some unidentified brown decomposition product. Addition of 50 mL of pentane to the clear burgundy red filtrate afforded a large amount of red precipitate. This microcrystalline solid was collected by back-filtration on the clean side of the.frit, washed with pentane, dried in vacuo, and transferred to a Schlenk tube for storage, approximate yield 70–85%.

The product was recrystallized from a 50:50 mixture of CH_2Cl_2–C_6F_6 by partial removal of solvent on a rotary evaporator, mp (in vacuo) 97 °C with gas evolution. Anal. Calcd for $C_9H_8BF_3O_5SW$: C, 22.52; H, 1.68; F, 11.88. Found: C, 22.48, 23.10; H, 1.90, 1.83; F, 10.87, 11.07.

^1H NMR ($CDCl_3$): τ 4.01 s (C_5H_5), 7.52 s (CH_3) ppm. ^{19}F NMR (50:50 CH_2Cl_2–C_6F_6): ϕ 147.64 s br ppm (relative to $CFCl_3$, ϕ 0 ppm). IR (Nujol): 3031 w, 2055 s, (1960 s, 1940 s), 1318 vw, 1308 vw, (1132 m, 1105 m), 1068 w, (1018 w, 1010 w, 1000 w), 978 w, 950 w, 870 s br, 845 w, (835 w, 830 w), 713 w, 580 w, 550 w, 510 w, 462 w cm^{-1}.

The product is soluble in $CHCl_3$ and CH_2Cl_2, moderately soluble in C_6H_6, sparingly soluble in C_6F_6, and insoluble in pentane. When pure, it is stable under argon or in vacuo at 25 °C for at least 2 years. Moreover, it shows no sign of decomposition when exposed to dry air for 3 h. However, it rapidly turns to a dark, gummy material in a stream of water-saturated nitrogen.

Reaction of η^5-$C_5H_5W(CO)_3CH_2C_6H_5$ (1b) with SO_2 and BF_3. Preparation of η^5-$C_5H_5W(CO)_3[OS(OBF_3)CH_2C_6H_5]$ (3b). The reaction between **1b** (0.722 g, 1.70 mmol), SO_2 (45 mL liquid), and BF_3 (57.64 mL, 345.8 Torr, 20.50 °C and 57.64 mL, 188.9 Torr, 20.10 °C; 1.68 mmol) was conducted similarly to the corresponding reaction of **1a**. Addition of BF_3 to the solution of **1b** in SO_2 resulted in the formation of brown, plate-like crystals. This precipitate dissolved upon warming the reaction mixture, and the solution acquired a deep red color. Removal of volatile materials under vacuum left a red oil, **3b**, which underwent partial decomposition during attempts at purification and crystallization: ^1H NMR ($CDCl_3$) τ 2.8 c (C_6H_5), 4.16 s (C_5H_5), 5.98, 6.29 q_{AB} (CH_2, $J_{AB} = 13.4$ Hz) ppm; IR (neat) 2055 vs, 1960 vs br, 1130 vs br, 1060 m, 1000 m, 950 m, 910 s, 845 s br, 810 sh, 770 w, 730 s, 698 m, 645 w, 615 w, 548 m, 510 m, 460 m cm^{-1}.

Reaction of η^5-$C_5H_5W(CO)_3CH_3$ (1a) with SO_2 and SbF_5. Preparation of η^5-$C_5H_5W(CO)_3[OS(OSbF_5)CH_3]$ (4a). A colorless solution of SbF_5 (0.382 g, 1.76 mmol) in SO_2 was added to ca. 30 mL of a yellow solution of **1a** in SO_2 at -78 °C. Immediately the mixture turned red. Reaction was allowed to proceed at -78 °C for 2 h, after which time volatile materials were removed under vacuum. The reddish brown residue was extracted with CH_2Cl_2 and filtered in a drybox to give a deep red solution. Addition of pentane and concentration of the resulting solution on a rotary evaporator afforded small, plate-like crystals which were isolated by decantation of the mother liquor. These deep orange crystals of **4a**, mp 110 °C dec, could be handled in air for a short time without any noticeable decomposition. Anal. Calcd for $C_8H_8F_5O_5SSbW$: C, 17.19; H, 1.28; Sb, 19.36. Found: C, 17.16; H, 1.98; Sb, 19.65.

^1H NMR ($CDCl_3$): τ 4.02 s (C_5H_5), 7.39 s (CH_3) ppm. IR (Nujol and Fluorolube): 3121 w, 2933 vw, 2050 s, 1955 vs br, 1310 w, 1070–1030 m br, 990 s, 870 m, 845 sh, 835 sh, 720 w, 660 vs, 645 s, 610 w, 545 w, 505 w, 465 w cm^{-1}.

The above reaction was also carried out using SbF_5 intercalated in graphite in place of pure SbF_5. Sulfur dioxide (15 mL liquid) was condensed onto a mixture of **1a** (0.167 g, 0.480 mmol) and excess SbF_5 intercalated in graphite at -78 °C. The resulting mixture was allowed to warm until vapor pressure of the SO_2 reached ca. 400 Torr. The reaction was allowed to proceed for 2 h, after which time volatile materials were removed under vacuum and the residue was dissolved in 10 mL of CH_2Cl_2 and filtered to give a clear red solution. An IR spectrum of this solution showed absorptions at 2058 m, 2020 vs, 1967 m br, and 1930 vs br cm^{-1}, attributed to **1a** and **4a**. The two complexes were separated by crystallization from CH_2Cl_2–hexane to give 0.073 g of unreacted **1a** and 0.032 g (11% yield) of **4a**.

Reaction of η^5-$C_5H_5W(CO)_3CH_2C_6H_5$ (1b) with SO_2 and SbF_5. Preparation of η^5-$C_5H_5W(CO)_3[OS(OSbF_5)CH_2C_6H_5]$ (4b). In a reaction very similar to that of its methyl analogue, **1b** (1.16 g, 2.73 mmol) was allowed to interact with SbF_5 (0.593 g, 2.74 mmol) in 10 mL of SO_2 at -78 °C for 48 h. Materials volatile at -78 °C were then removed and the residue was extracted with CH_2Cl_2 at -23 °C, leaving 0.938 g of a brown, insoluble solid with IR absorptions at 2120 m, 2060 s, 1970 s, 865 m br, and 665 vs cm^{-1} (Nujol mull). Further attempts at purification of this solid were unsuccessful. Upon treatment of the extract with pentane, a red powder precipitated. This mixture was filtered and solvent was removed from the filtrate resulting in a recovery of 0.201 g of **1b**. The red precipitate (0.53 g, 28% yield), which is slightly soluble in $CHCl_3$, was identified as **4b**: IR (Nujol) 3140 w, 2070 s, 1980 s br, 986 m, 890 w br, 850 w br, 770 w, 700 w, 668 sh, 660 s cm^{-1}.

Reactions of η^5-$C_5H_5W(CO)_3[OS(OBF_3)CH_3]$ (3a). A. With NH_3. A solution of **3a** (0.584 g, 1.30 mmol) in 30 mL of CH_2Cl_2 was treated with NH_3 (57.64 mL, 414.1 Torr, 25.6 °C; 1.28 mmol) at -196 °C. When the resulting mixture was allowed to warm to room temperature with stirring, a precipitate formed and the solution changed color from red to orange. After 45 min of reaction time, the precipitate was filtered off and washed with CH_2Cl_2. This white solid was shown to be $BF_3 \cdot NH_3$ by comparison of its IR spectrum with that of an authentic sample of $BF_3 \cdot NH_3$, prepared according to the literature.[40] The filtrate and the wash were combined, concentrated to 10 mL on a rotary evaporator, and slowly treated with pentane. The resulting yellow precipitate, **2a**, was collected on a filter, yield 0.419 g (85%).

B. With Aniline. A large excess of aniline was added dropwise to a solution of **3a** in CH_2Cl_2 at room temperature. The white precipitate (adduct of aniline and BF_3[28,29]) was filtered off, and **2a** was isolated from the filtrate as in the preceding reaction.

C. Isomerization to η^5-$C_5H_5W(CO)_3[S(O)(OBF_3)CH_3]$ (5a). A closed glass system consisting of an inner tube containing a saturated solution of **3a** in benzene (ca. 5 mL) and an outer tube filled with pentane under argon was set aside at room temperature in the dark. Pentane slowly collected in the inner tube, and within 12 h a colorless layer had formed over the red solution of **3a**. After 15 days, the benzene and pentane solutions were decanted from the crystals which had deposited on the sides of the tube. Three different compounds were identified by IR spectroscopy: yellow **2a** (primarily in contact with the upper pentane layer), orange **5a** (primarily near the interface of the pentane and benzene layers), and red **3a** (a few crystals near the bottom of the benzene layer). The overall yield of the crystalline products was low.

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A Comparison of the Rates of Electron Exchange Reactions of Ammine Complexes of Ruthenium(II) and -(III) with the Predictions of Adiabatic, Outer-Sphere Electron Transfer Models

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Abstract: The rate constants for the $Ru(NH_3)_6{}^{3+/2+}$, $Ru(NH_3)_4(bpy)^{3+/2+}$, and $Ru(NH_3)_2(bpy)_2{}^{3+/2+}$ electron exchange reactions have been measured by a technique involving subtle modifications of the ligands. The rate constants ($M^{-1}\ s^{-1}$, medium) at 25 °C are 3.2×10^3, 0.1 M CF_3SO_3H, for the $Ru(NH_3)_6{}^{3+/2+}$ exchange; 7.7×10^5, 0.1 M CF_3SO_3H, and 2.2×10^6, 0.1 M $HClO_4$, for the $Ru(NH_3)_4(bpy)^{3+/2+}$ exchange; 8.4×10^7, 0.1 M $HClO_4$, for the $Ru(NH_3)_2(bpy)_2{}^{3+/2+}$ exchange. The rate constants and activation parameters for the $Ru(NH_3)_4(bpy)^{3+/2+}$ exchange reaction were determined as a function of ionic strength ($k = 4.1 \times 10^4\ M^{-1}\ s^{-1}$, $\Delta H^\ddagger = 4.0$ kcal mol^{-1}, and $\Delta S^\ddagger = -24$ cal deg^{-1} mol^{-1} at zero ionic strength and 25 °C). The rate constants determined in this work together with those for the analogous $Ru(NH_3)_5py^{3+/2+}$ and $Ru(bpy)_3{}^{3+/2+}$ exchange reactions are compared with the predictions of theoretical models. Good linearity was found for a plot of log k_{ex} vs. $1/\bar{r}$, where $\bar{r}$ is the mean separation of the ruthenium centers in the activated complex. The Marcus model derived on the basis of a reactive collision formulation gives better agreement with the observed rate constants and activation parameters at zero ionic strength than the conventional ion-pair preequilibrium model. Contrary to prediction, the increase in exchange rate with increasing ionic strength is reflected primarily in a decreased enthalpy of activation.

Introduction

Outer-sphere electron exchange reactions constitute the simplest class of electron transfer reactions.[1] The rates and activation energetics of such reactions are therefore of considerable interest. The currently accepted model for bimolecular electron exchange between $M^{(III)}L_6{}^{3+}$ and $M^{(II)}L_6{}^{2+}$ involves the reaction sequence[2]

$$M^{(III)}L_6{}^{3+} + M^{(II)}L_6{}^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [M^{(III)}L_6|M^{(II)}L_6]^{5+} \quad (1)$$

$$[M^{(III)}L_6|M^{(II)}L_6]^{5+} \xrightarrow{k_{et}} [M^{(II)}L_6|M^{(III)}L_6]^{5+} \quad (2)$$

$$[M^{(II)}L_6|M^{(III)}L_6]^{5+} \rightarrow M^{(II)}L_6{}^{2+} + M^{(III)}L_6{}^{3+} \quad (3)$$

In this scheme the reactants first form a precursor complex (eq 1). The electron transfer takes place within this complex to form a successor complex (eq 2). Dissociation of the successor complex yields the observed electron transfer products (eq 3). In this paper we treat the case in which precursor complex formation is a rapidly established preequilibrium with the subsequent electron transfer within this complex being rate determining ($k_{-1} \gg k_{et}$). Under these conditions the observed second-order rate constant is equal to $K_0 k_{et}$ where $K_0 = k_1/k_{-1}$. We will also assume that the electron transfer is adiabatic, that is, that the interaction between the reactants is large enough for the electron transfer to occur with unit probability in the activated complex. In other words, we assume for the time being that the probability factor $\langle \kappa \rangle$ in the expression

$$k_{et} = \langle \kappa \rangle \frac{k_B T}{h} \exp[-\Delta G_\lambda{}^\ddagger/RT]$$

is equal to unity. Under these circumstances the Franck-Condon barrier to electron transfer should account for $\Delta G_\lambda{}^\ddagger$. For a M(II)/M(III) exchange reaction, the Franck-Condon barrier arises because the metal-ligand bond lengths must rearrange to some common value intermediate between that characteristic for the metal ion in oxidation states II and III before electron transfer can occur. Likewise, the solvent polarization around the reactants, which is sensitive to the charge of the reactant, must rearrange prior to electron transfer. These rearrangements are required to satisfy conservation of energy.[1,3-10] Therefore if the equilibrium constants for precursor complex formation (k_1/k_{-1}) and the Franck-Condon rearrangement barriers are known, the rate constants for electron-exchange reactions can be calculated.

In this paper the exchange rate constants of the Ru(III)/Ru(II) redox couple in a series of ruthenium ammine complexes are compared with the predictions of various models. The exchange rate constants for the ruthenium complexes were

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