

Catalysis of the Sulfur Dioxide Insertion by Boron(III) Fluoride

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Transition metal alkyl-complexes display a wide range of reactivity in the insertion reaction with sulfur dioxide¹. Since this insertion is an electrophilic bond cleavage process, we considered the use of SO₂-Lewis acid adducts to promote the reactivity of the more inert complexes.

The alkyls η^5 -C₅H₅W(CO)₃R (R = CH₃ and CH₂C₆H₅) react very slowly with neat SO₂ at reflux (-10 °C)², and at 50-55 °C in 72 hr afford the appropriate *S*-sulfinates in 10-25% yield.³ They thus represent excellent candidates for a test of the proposed catalysis of the insertion.

Sulfur dioxide forms a structurally well-characterized, *O*-bonded, 1:1 adduct with SbF₅,⁴ and the same mode of bonding is assumed to be present in an unstable 1:1 adduct of SO₂ with BF₃.⁵ The system SO₂-BF₃ was found to react with η^5 -C₄H₆Fe(CO)₃ to yield [(η^3 -C₄H₆)S(OBF₃)O]Fe(CO)₃ although SO₂ alone is unreactive.⁶

Reaction of η^5 -C₅H₅W(CO)₃CH₃, I, with equimolar BF₃ in liquid SO₂ at -26 °C for 30 min affords II in good yield as a deep red solid decomposing at 95-100 °C (Calcd for C₉H₈WBF₃O₅S: C, 22.53; H, 1.68; F, 11.88. Found: C, 22.79; H, 1.84; F, 11.02). Treatment with NH₃ in CH₂Cl₂ at 25 °C converts II to the known³ *S*-sulfinato, III, in 85% yield. III reacts with BF₃ in toluene at 25 °C to yield an orange solid, IV, which is structurally analogous to the previously reported⁷ iron complexes η^5 -C₅H₅Fe(CO)(PR₃)[S(O)(OBF₃)CH₃] (R = C₆H₅ or *n*-C₄H₉). IV is also obtainable by slow addition of pentane to a benzene solution of II over one week at 25 °C. On pumping *in vacuo* IV reverts to III. These transformations are summarized below.

The infrared spectra of II-IV in the 1300-700 cm⁻¹ region are shown in Fig. 1. Whereas two terminal SO stretching frequencies are observed for

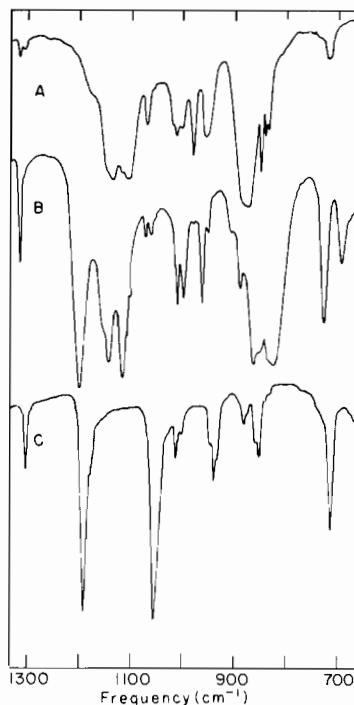
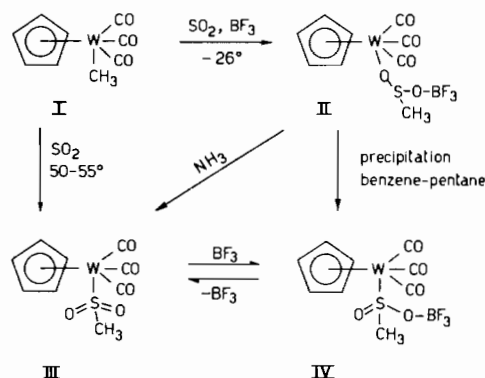


Fig. 1. Infrared spectra of complexes II (A), IV (B), and III (C) in Nujol mull.

III (1188, 1054 cm⁻¹), only one is apparent for IV (1198 cm⁻¹) and none for II, as expected for the proposed structures. The carbonyl stretching frequencies for II (2052, 1960 cm⁻¹; CH₂Cl₂ soln) and IV (2050, 1964 cm⁻¹; CHCl₃ soln) rule out coordination of BF₃ to CO. In the PMR spectrum of II the CH₃ resonance occurs at τ 7.52 (SO₂, -26 °C), which is 0.72 ppm upfield from the corresponding resonance in III. A similar difference

in chemical shift was noted earlier for some *S*-sulfinates and precursor *O*-sulfinates.⁸

Preliminary experiments show that $\text{SO}_2 \cdot \text{BF}_3$ reacts readily also with $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_2\text{C}_6\text{H}_5$ to afford $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3[\text{OS}(\text{OBF}_3)\text{CH}_2\text{C}_6\text{H}_5]$ with a structure strictly equivalent to II.

The above-noted enhancement of the rate of the cleavage of W–C bonds most likely arises from an increase in electrophilic strength of SO_2 upon complexation with BF_3 . The arrest of the insertion at the intermediate, *O*-sulfinato, stage almost certainly derives from a stabilizing effect exerted by the coordinated BF_3 . Accordingly, removal of the latter from II with NH_3 rapidly yields the *S*-sulfinato, III. It is possible that the previously observed⁸ substantial stability of some transition metal *O*-sulfinates in liquid sulfur dioxide results from a similar interaction, but of the SO_2 , with the coordinated OS(O)R ligand. Upon evaporation of the solvent, rearrangement to the *S*-sulfinato occurs there as well.

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