

Preliminary Communication

Preparation of An Ambident S-Sulfinate Complex from Dicarbonyl
(η^5 -cyclopentadienyl)ferrate and Sulfur Dioxide

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SUMMARY

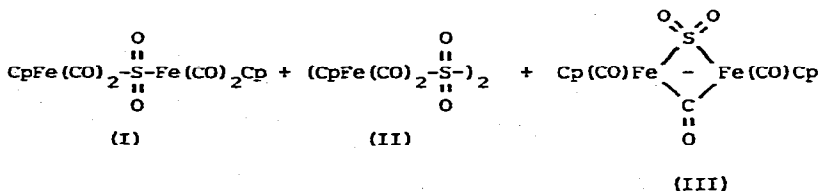
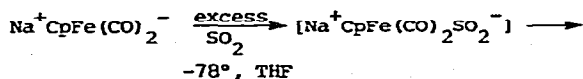
Nucleophilic addition of $K^+(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2^-$ rather than the corresponding sodium salt to THF solutions of sulfur dioxide precipitates $K^+(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{S}(\text{O})_2^-$, the first example of an isolable transition metal sulfinate anion. Reaction of the ambident sulfinate ion with CH_3I or $\text{CH}_3\text{OSO}_2\text{F}$ leads to S or O alkylated products respectively.

Many S-bonded transition metal-sulfur dioxide complexes are known where SO_2 , in either a terminal or bridging environment, acts as a formal 2 electron donor^{1,2} in the same sense as carbon monoxide. Sulfur dioxide also exhibits weak Lewis acid properties with both main group^{2,3} and transition elements^{3,4}. We report here an example of a transition metal complex wherein SO_2 acts as a formal Lewis acid.

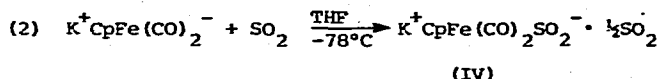
Churchill and Wojcicki^{5,6} recently reported a rather remarkable

reaction of sodium dicarbonyl(η^5 -cyclopentadienyl)ferrate with sulfur dioxide which ultimately produced several neutral complexes (I,II,III) containing bridging SO_2 . The neutral complexes, I,II,III were proposed to result from 1 electron oxidation of an intermediate sulfinate ion complex^{5,8} under the reaction conditions.

(1)



We find that addition of excess or equimolar quantities of SO_2 at low temperature (-78°C) to THF solutions of potassium dicarbonyl(η^5 -cyclopentadienyl)ferrate rather than the corresponding sodium salt^{5,6}, produces a bright orange precipitate. The neutral compounds I, II, III could not be isolated on Florisil chromatography of the deep red filtrates.* The orange precipitate appears to be the sulfinate complex IV alluded to by Wojcicki^{5,8}, the logical result of addition of the highly nucleophilic $\text{CpFe}(\text{CO})_2^-$ anion to sulfur dioxide (eq. 2). Yields of up to 85% have



been routinely obtained. The reaction is analogous to the preparation of organic sulfinate salts via Grignard addition to sulfur dioxide⁹ and

* We thank a referee for the suggestion that the relative insolubility of the K^+ vs. Na^+ salts precludes further oxidation of IV $-\text{K}^+$ to I, II, III.

closely parallels the formation of metallothiocarboxylate anion complexes by addition of metal carbonyl anions to carbon disulfide¹⁰.

The thermally and oxidatively labile complex IV (dec. > 60°C under N₂) is very soluble in water and methanol, moderately soluble in nitromethane but sparingly soluble in tetrahydrofuran, methylene chloride or chloroform. It is a strong electrolyte in aqueous solution with $\Lambda = 120 \text{ ohm}^{-1} \text{ cm}^2$ (10^{-3} M) and forms as a finely divided glass of approximate composition $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2\text{K} \cdot \frac{1}{2}\text{SO}_2^{\ddagger}$. Attempts to obtain a crystalline form by addition of large cations have thus far been unsuccessful.

Table 1

Carbonyl Stretching Frequencies for Some Metal Carbonyl Anions and Derivatives

Cpd.	$\nu_{\text{CO}} (\text{cm}^{-1})$		Ref.
$\text{CpFe}(\text{CO})_2^-$	1865, 1788	(nBu_4N^+ , THF)	7
	1862, 1786, 1770	(Na^+ , THF, dibenzo-18-crown-6)	11
$[\text{CpFe}(\text{C})_2]_2\text{Mg} \cdot 2\text{THF}$	2015, 1921, 1854	(benzene)	12
$\text{CpFe}(\text{CO})_2\text{CS}_2^-$	2002, 1950	(K^+ , THF)	10
$\text{CpFe}(\text{CO})_2\text{SO}_2 \cdot \frac{1}{2}\text{SO}_2$ (IV)	2052, 2018	(K^+ , CH_2Cl_2 , dibenzo-18-crown-6)	This work
	2041, 2020, 1984	(K^+ , Nujol)	

Infrared spectra of the sulfinate ion complex (IV) as the potassium salt in nitromethane show extensive splitting of the carbonyl stretching frequencies due to ion pair formation. Removal of ion paired species¹¹ by addition of dibenzo-18-crown-6 gave a simplified spectrum with frequencies given in Table 1. It is apparent from the increase in ν_{CO} frequencies (Table 1) as one proceeds from the dicarbonyl-

[‡] Required for $\text{C}_7\text{H}_5\text{FeO}_5\text{S}_{1.5}\text{K}$; C:26.9, H:1.60. Found; C:27.3, H:1.9

(η^5 -cyclopentadienyl)ferrate anion through the covalent magnesium derivative to the dithiocarboxylate and sulfinate salts that less negative charge resides on iron. Thus structure IVa contributes a minor role.

Table 2
PMR Spectra of MSO_2CH_3 Derivatives

cpd.	τ			Ref.
	Cp	CH_3		
$\text{CpFe}(\text{CO})_2\text{OS}(\text{O})\text{CH}_3$, (VII)	4.75	7.85	(liq SO_2 , -37°C)	14
$\text{CpFe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$ (V)	-	6.95	(liq. SO_2 , -30°C)	14
	4.75	6.85	(CDCl_3)	15
$\text{CpFe}(\text{CO})_2\text{S}(\text{O})\text{OCH}_3$ (VI)	4.80	6.43	(CDCl_3)	This work
$(\text{PPh}_2\text{CH}_3)_2(\text{CO})\text{Cl}_2\text{IrS}(\text{O})\text{OCH}_3$	-	7.08	(CDCl_3)	16
$(\text{PPh}_2\text{CH}_3)_2(\text{CO})\text{Cl}_2\text{IrS}(\text{O})_2\text{CH}_3$	-	7.82	(CDCl_3)	16

Evidence for the S-alkoxysulfenate structure VI is provided by PMR and IR data. Table 2 shows PMR shifts for several $\text{M-SO}_2\text{CH}_3$ derivatives. As expected^{14,16}, O-bonded methyl is observed at lower fields than S-bonded methyl and the S-methoxysulfenate, (VI), has a lower chemical shift than either V or VII.

The IR spectrum of VI (Fig. 1) exhibits a more complicated ν_{SO_2} and δ_{SO_2} region than V which shows two strong bands at 1193, 1051 cm^{-1} assigned to the asymmetric and symmetric ν_{SO} modes. A strong four band pattern at 1218, 1096, 972, 682 cm^{-1} (KBr pellet) assigned to $\nu_{\text{S-O}}$, $\nu_{\text{(C-O)}}$, and $\nu_{\text{(S-O)}}$ similar to that reported for some Ir(III) S-alkoxysulfenato complexes¹⁶ is observed. Carbonyl stretching frequencies for V (2059, 2002 cm^{-1} , KBr) are higher than those of VI (2043, 1972 cm^{-1} , KBr) indicating that S-methoxysulfenato is better pi acceptor than the S-methylsulfinato ligand.

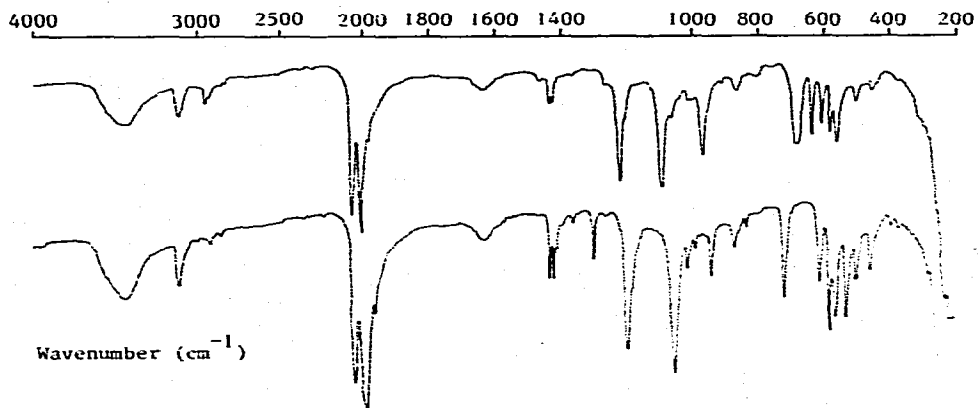
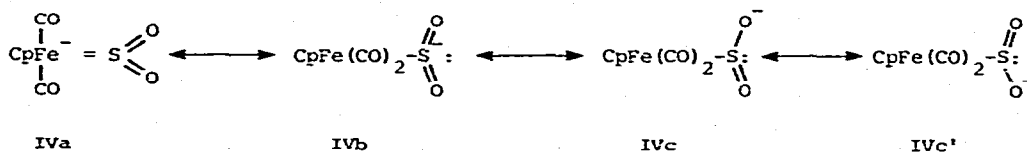


Fig. 1. Top. Infrared Spectrum of VI (KBr disk)

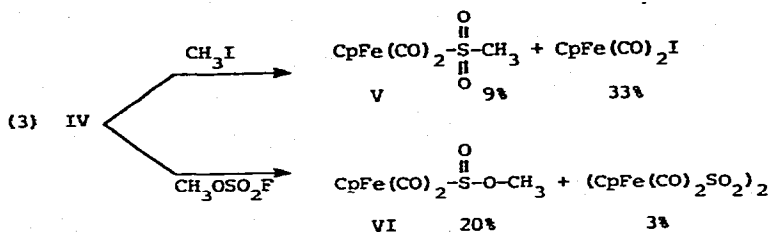
Bottom. Infrared Spectrum V (KBr disk)

Contributions of structures IVa-c led to the expectation of ambident properties¹³ for the sulfinate ion complex. The importance of IVb,c,c' are



reflected in the products obtained from alkylation with methyl iodide or methylfluorosulfonate. The former results in S-alkylation to produce a low yield of the known S-methyl sulfinate complex $\text{CpFe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$ while the harder acid O-alkylates giving the S-methoxysulfenate complex $\text{CpFe}(\text{CO})_2\text{S}(\text{O})\text{OCH}_3^*$ (m.p. dec. > 145 under N_2). We note here that previous attempts to prepare the S-methoxysulfenate complex by treatment of dicarbonyl(η^5 -cyclopentadienyl)ferrate with chloromethylsulfinate have been unsuccessful¹⁴.

* Analysis: Required for $\text{C}_8\text{H}_8\text{O}_4\text{SFe}$; C, 37.5, H 3.13, S 12.5. Found C, 36.6; H, 2.98; S, 12.5.



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