Volume 12
Number 4
April 1973

Inorganic Chemistry

Contribution from the McPherson Chemical Laboratory,
The Ohio State University, Columbus, Ohio 43210

Sulfur Dioxide Insertion. XVII. Linkage Isomerism of Transition Metal-Sulfinato Complexes. The Intermediacy of *O*-Sulfinates in Sulfur Dioxide Insertion Reactions[1]

STEPHEN E. JACOBSON, PETER REICH-ROHRWIG,[2] and ANDREW WOJCICKI*

Received August 10, 1972

An investigation is reported on the constitution of solutions of transition metal alkyls and aryls of the type h^5-$C_5H_5Fe(CO)_2R$, h^5-$C_5H_5Mo(CO)_3R$, $Mn(CO)_5R$, and $Re(CO)_5R$ in liquid SO_2 and in organic solvents containing SO_2. Spectroscopic (^1H nmr and infrared), electrical conductivity, and chemical evidence indicates that reactions of the foregoing compounds with SO_2 proceed *via* the intermediacy of the oxygen-bonded sulfinates, which subsequently rearrange to the thermodynamically stable and isolable sulfur-bonded sulfinates. These *O*-sulfinato complexes are reasonably stable in the presence of sulfur dioxide, with the stability being highest when $R = CH_3$. However, complete removal of SO_2 during attempts at their isolation causes immediate isomerization to the corresponding *S*-sulfinates.

Introduction

Linkage isomerism of the anions of sulfinic acids is still a rare phenomenon in transition metal chemistry. It has been reported only for $M(bipy)_2(p\text{-}SO_2C_6H_4CH_3)_2$ (M = Fe, Ni, Co).[3] When M = Fe or Ni, the *O*-sulfinato complex isomerizes to the *S*-sulfinate upon heating at 115° in pyridine.[4]

Low-valent transition metals generally show preference for the more polarizable donor atom of an ambidentate ligand.[5,6] Therefore, it is not surprising that most of the sulfinato complexes isolated from the reaction between transition metal alkyls[7] and sulfur dioxide exhibit metal-sulfur bonding.[8] The only systems that do not conform to this behavior are h^5-cyclopentadienyl complexes of titanium(IV) and zirconium(IV), which insert SO_2 to yield *O*-sulfinates.[9] A metal-oxygen linkage is also found in the carbonyl *trans*-$Ir(CO)[P(C_6H_5)_3]_2(p\text{-}O_2SC_6H_4CH_3)$, prepared from $Ir(CO)(CH_3CN)[P(C_6H_5)_3]_2^+$ and $p\text{-}CH_3C_6H_4SO_2^-$.[10] However, a rearrangement to $IrS(O)_2C_6H_4CH_3$ occurs upon reaction of this square-planar complex with O_2 or CH_3I. A substituted manganese(I) carbonyl, $[Mn(CO)_3(py)O_2SCH_2C_6H_5]_n$, very likely contains a bidentate, O,O′-bonded sulfinate.[11]

In the course of our studies on the mechanism of the sulfur dioxide insertion of h^5-$C_5H_5Fe(CO)_2R$, we noticed that the carbonyl stretching frequencies of the isolated *S*-sulfinates differ slightly from those of the initial products of the reaction. This observation was followed by a detailed examination of the constitution of solutions of transition metal alkyls in SO_2 using infrared and ^1H nmr spectroscopy in conjunction with chemical reactivity and electrical conductivity measurements. Results of the foregoing studies are best interpreted in terms of the initial formation of the metal *O*-sulfinates and their isomerization to the thermodynamically stable and isolable *S*-sulfinates. The intermediacy of the *O*-sulfinato complexes clarifies several mechanistic aspects concerned with the sulfur dioxide insertion, as will be reported in a subsequent paper.[12] Described now is our complete investigation on the characterization in solution of the kinetically favored products of the reaction between various transition metal alkyls and sulfur dioxide and on attempts at isolation of these species. A preliminary account of this work was published earlier.[13]

Experimental Section

Materials. Anhydrous grade SO_2, from Matheson, was passed through concentrated H_2SO_4 and a 24-in. column of $CaCl_2$-P_4O_{10} before condensation in a trap at *ca* −75°. $(n\text{-}C_4H_9)_4NI$, purchased from Eastman Chemical Co., was used without further purification. Tetrahydrofuran (THF) was distilled from CaH_2 under a nitrogen atmosphere immediately before use. Benzene and pentane were also purified by distillation from CaH_2. All other solvents and chemicals were of reagent grade or equivalent quality and were used as received. Ventron alumina, deactivated with distilled water (6–10%), and Florisil (60–100 mesh), from Fisher Scientific Co., were employed in chromatographic separations and purifications.

Metal Alkyls and *S*-Sulfinates. The alkyls h^5-$C_5H_5Fe(CO)_2CH_3$,[14]

---

[1] Part XVI: S. E. Jacobson, P. Reich-Rohrwig, and A. Wojcicki, *Chem. Commun.*, 1526 (1971).

[2] Postdoctoral Fellow of the Ohio State University Graduate School, 1970–1971.

[3] (a) G. Vitzthum and E. Lindner, *Angew. Chem.*, 83, 315 (1971); (b) E. Konig, E. Lindner, I.-P. Lorenz, and G. Ritter, *Inorg. Chim. Acta*, 6, 123 (1972).

[4] (a) E. Lindner, I.-P. Lorenz, and G. Vitzthum, *Angew. Chem.*, 83, 213 (1971); (b) E. Lindner and I.-P. Lorenz, *Chem. Ber.*, 105, 1032 (1972).

[5] A. H. Norbury and A. I. P. Sinha, *Quart. Rev., Chem. Soc.*, 24, 69 (1970).

[6] J. L. Burmeister, *Coord. Chem. Rev.*, 3, 225 (1968).

[7] Unless qualified, in this paper *alkyl* stands for both alkyl and aryl groups.

[8] A. Wojcicki, *Accounts Chem. Res.*, 4, 344 (1971).

[9] P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organometal. Chem.*, 33, 181 (1971); 34, 155 (1972).

[10] C. A. Reed and W. P. Roper, *Chem. Commun.*, 1556 (1971).

[11] F. A. Hartman and A. Wojcicki, *Inorg. Chim. Acta*, 2, 351 (1968).

[12] S. E. Jacobson and A. Wojcicki, in preparation.

[13] S. E. Jacobson, P. Reich-Rohrwig, and A. Wojcicki, *Chem. Commun.*, 1526 (1971).

[14] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3, 104 (1956).

h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$,[15] h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$,[16] h^5-$C_5H_5Fe(CO)_2CH_2Si(CH_3)_3$,[17] h^5-$C_5H_5Mo(CO)_3CH_3$,[14] h^5-$C_5H_5Mo(CO)_3CH_2C_6H_5$,[18] $Mn(CO)_5CH_3$,[19] $Mn(CO)_5CH_2C_6H_5$,[19] and $Re(CO)_5CH_3$[20] and the *S*-sulfinates h^5-$C_5H_5Fe(CO)_2SO_2CH_3$,[15] h^5-$C_5H_5Fe(CO)_2SO_2CH_2C_6H_5$,[15] h^5-$C_5H_5Fe(CO)_2$(p-$SO_2C_6H_4CH_3$),[15] h^5-$C_5H_5Mo(CO)_3SO_2CH_3$,[21] h^5-$C_5H_5Mo(CO)_3SO_2CH_2C_6H_5$,[21] $Mn(CO)_5SO_2CH_3$,[22] $Mn(CO)_5SO_2CH_2C_6H_5$,[22] and $Re(CO)_5SO_2CH_3$[22] were prepared as described in the literature. h^5-$C_5H_5Fe(CO)_2$(p-$C_6H_4CH_3$) was synthesized according to an adaptation of the general method of King and Bisnette.[23] The reaction of Na[h^5-$C_5H_5Fe(CO)_2$] with p-$ClCOC_6H_4CH_3$ yielded h^5-$C_5H_5Fe(CO)_2$(p-$COC_6H_4CH_3$) which was then decarbonylated photochemically in THF using a Hanovia 450-W high-pressure quartz mercury-vapor lamp. The orange product melted at 78°. *Anal.* Calcd for $C_{14}H_{12}O_2Fe$: C, 62.69; H, 4.47. Found: C, 62.72; H, 4.56.

The *S*-sulfinates h^5-$C_5H_5Fe(CO)_2SO_2CH(CH_3)_2$ and h^5-$C_5H_5Fe(CO)_2SO_2CH_2Si(CH_3)_3$ were obtained by dissolving the corresponding alkyls in liquid SO_2 and allowing the solutions to reflux for 1 and 5 hr, respectively. The reaction of the isopropyl complex was found to be very exothermic and requires caution. Removal of the SO_2 and chromatography on alumina yielded yellow h^5-$C_5H_5Fe(CO)_2SO_2CH(CH_3)_2$ (57% yield, mp 100–103°) and h^5-$C_5H_5Fe(CO)_2SO_2CH_2Si(CH_3)_3$ (80% yield, mp 112°). The isopropylsulfinate has been also obtained (69% yield) by dissolving the alkyl in SO_2-saturated $CHCl_3$ at 25° and bubbling SO_2 through the resulting solution for 1 hr. *Anal.* Calcd for $C_{10}H_{12}O_4SFe$: C, 42.26; H, 4.23. Found: C, 42.38; H, 4.53. Calcd for $C_{11}H_{16}SiO_4SFe$: C, 50.01; H, 6.06. Found: C, 50.15; H, 6.23.

Reactions of Metal Alkyls and Sulfinates with Iodide (or Bromide) in Presence of SO_2. (a) In Liquid SO_2. A varying quantity of KI (1–100 parts of KI per 1 part of the alkyl complex) was dissolved in 30 ml of SO_2 at reflux. The alkyl (~1 mmol) was introduced into the resulting red solution which was then allowed to reflux for *ca.* 2 hr. After the SO_2 was removed under a stream of nitrogen, the residue was dissolved in CH_2Cl_2 and chromatographed on alumina (h^5-$C_5H_5Fe(CO)_2$ derivatives) or Florisil (h^5-$C_5H_5Mo(CO)_3$ derivatives). In each case the iodo complex (identified by infrared spectroscopy[24]) was eluted off before the *S*-sulfinato complex. The reaction of h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ (1.1 mmol) with KBr (8.4 mmol) in SO_2 was conducted analogously.

The addition was also carried out in the reverse order. The alkyl was dissolved in *ca.* 25 ml of liquid SO_2 and the solution was kept at reflux for 2–4 hr. After introduction of KI the reflux conditions were maintained for additional 2 hr. The work-up was the same as in the previous procedure.

Results of these experiments are summarized in Table I. The *S*-sulfinates h^5-$C_5H_5Fe(CO)_2SO_2R$ were found to give no reaction with KI in liquid SO_2, whereas h^5-$C_5H_5Mo(CO)_3SO_2CH_3$ gave 1% h^5-$C_5H_5Mo(CO)_3I$.

(b) In Dichloromethane and Benzene. Liquid SO_2 (9.2 g, 141 mmol) and (n-C_4H_9)$_4$NI (2.1 g, 5.8 mmol) were added to CH_2Cl_2 (35 ml) at 0°, and the resulting solution was treated with h^5-$C_5H_5Fe(CO)_2CH_2Si(CH_3)_3$ (0.30 g, 1.1 mmol) under nitrogen. After stirring for 1 hr, the solvent was removed. Chromatography on alumina yielded h^5-$C_5H_5Fe(CO)_2I$ (0.05 g, 15% yield) and h^5-$C_5H_5Fe(CO)_2SO_2CH_2Si(CH_3)_3$ (~70% yield). The latter contained an impurity of (n-C_4H_9)$_4$NI, which proved difficult to remove by chromatography or crystallization.

When the above reaction was carried out without the SO_2, only the alkyl was obtained upon work-up. No h^5-$C_5H_5Fe(CO)_2I$ was detected.

Sulfur dioxide was bubbled into a mixture of h^5-$C_5H_5Fe(CO)_2CH_2Si(CH_3)_3$ (0.30 g, 1.1 mmol) and (n-C_4H_9)$_4$NI (1.0 g, 2.7 mmol) in 400 ml of benzene at 25°. After a few minutes all of the insoluble material went into solution. Passage of SO_2 was continued for 23 hr. Removal of the solvent and chromatography on alumina with CH_2Cl_2 afforded h^5-$C_5H_5Fe(CO)_2I$ (0.05 g, 13% yield) and impure h^5-$C_5H_5Fe(CO)_2SO_2CH_2Si(CH_3)_3$ (~60% yield).

Attempts at Isolation of the *O*-Sulfinato Intermediate. (a) h^5-$C_5H_5Fe(CO)_2OS(O)CH_3$. h^5-$C_5H_5Fe(CO)_2CH_3$ (0.04 g) was dissolved in 5–10 ml of SO_2 and allowed to react for 5 min at −30°. The bulk of the solvent was removed under reduced pressure (−30°, 0.05 mm) in 5 hr. Further pumping (15 min) at 25° afforded a red oil. Upon application of pressure between two infrared KBr plates, the oil started turning yellow. After 5 min the change was complete, and the infrared spectrum showed the presence of only the S-bonded h^5-$C_5H_5Fe(CO)_2SO_2CH_3$.

(b) $Re(CO)_5OS(O)CH_3$. $Re(CO)_5CH_3$ (0.04 g) was dissolved in 10 ml of SO_2 and allowed to react for 30 min at −30°. Removal of the solvent at −30° (0.1 mm) in 2 hr furnished a white crystalline material. These crystals started to collapse upon warming to 25°, suggesting occlusion of free SO_2 therein. Attempts to record the infrared spectrum in the ν(SO) region of the white intermediate as a Nujol mull, neat between two KBr plates, or as a KBr disk were all unsuccessful. Only the spectrum of the *S*-sulfinate was obtained. However, the spectrum of the intermediate in the ν(SO) region could be obtained by dissolving the crystals in 1:5 $CDCl_3$–CS_2 at −40° and injecting the resulting solution into the low-temperature cell (*vide infra*).

The results were the same when a longer time (5 hr) was used for the removal of free SO_2 after completion of the insertion.

Infrared Measurements. All infrared absorption bands reported in this paper have been recorded on a Beckman Model IR-9 spectrophotometer. Solution spectra at 25° were obtained using NaCl sample cells of 0.05-, 0.10-, and 0.50-mm thickness in conjunction with matched reference cells. Solid-state spectra were obtained as Nujol mulls on KBr pellets. For routine spectra, a Perkin-Elmer Model 337 spectrophotometer was used.

Low-temperature (<25°) spectra in liquid SO_2 or organic solvents were obtained using a VLT-2 variable-temperature unit manufactured by the Research and Industrial Instruments Co., London, England (a subsidiary of Beckman Instruments, Inc.). The sample cell (0.5-mm thickness) was fitted with an AgCl window. Suitable adaptations were made in this unit for work with liquid SO_2; they will be described elsewhere.[12] A syringe cooled with Dry Ice served to introduce samples into the cell.

^{1}H Nmr Measurements. The spectra were recorded on a Varian A-60 or A-60A spectrometer using tetramethylsilane (TMS) as an internal standard. For measurements on solutions in liquid sulfur dioxide, 1 ml of SO_2 was condensed onto 50–60 mg of the alkyl and TMS in an nmr tube. The tube was then sealed under vacuum at −196°. Standard vacuum techniques were employed throughout.

Other Measurements and Analyses. Molar conductivities were determined in liquid SO_2 at −32° with an Industrial Instruments, Inc., Model RC 16B2 conductivity bridge. A cell with platinum electrodes was used. Melting points were measured either in capillaries using a mineral oil bath or with a Thomas-Hoover capillary melting point apparatus; they are uncorrected. Elemental analyses were performed by Dr. F. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany, and by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results and Discussion

Characterization of the Reaction Intermediate. (i) Nmr Spectra. Changes in the constitution of solutions of several benzyl and methyl complexes in liquid SO_2 were followed by proton nmr spectroscopy. In the spectrum of h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$, recorded at −18°, the CH_2 resonance of the parent alkyl at τ 7.31 diminishes in intensity and an AB quartet and a singlet appear and grow at τ 6.49 (center) and 5.79, respectively. The latter signal is due to the CH_2 protons of the isolable h^5-$C_5H_5Fe(CO)_2SO_2CH_2C_6H_5$. Accompanying these changes is a diminution in intensity of the h^5-C_5H_5 absorption of the alkyl at τ 5.20 and a simultaneous growth of the corresponding peak of the sulfinate at τ 4.91. The spectra recorded in the CH_2 and h^5-C_5H_5 proton region 3, 20, and 60 min after preparation of the solution, as well as that of the *S*-sulfinate, are shown in Figure 1. After storage of the solution for *ca.* 24 hr at −25°, the quartet at τ 6.49 is barely discernible, the CH_2 resonance at τ 7.31

---

(15) J. P. Bibler and A. Wojcicki, *J. Amer. Chem. Soc.*, **88**, 4862 (1966).

(16) M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963).

(17) R. B. King, K. H. Pannell, C. R. Bennett, and M. Ishaq, *J. Organometal. Chem.*, **19**, 327 (1969).

(18) R. B. King and A. Fronzaglia, *J. Amer. Chem. Soc.*, **88**, 709 (1966).

(19) R. D. Closson, J. Kozikowski, and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957).

(20) W. Hieber, G. Braun, and W. Beck, *Chem. Ber.*, **93**, 901 (1960).

(21) M. Graziani, J. P. Bibler, R. M. Montesano, and A. Wojcicki, *J. Organometal. Chem.*, **16**, 507 (1969).

(22) F. A. Hartman and A. Wojcicki, *Inorg. Chem.*, **7**, 1504 (1968).

(23) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964).

(24) T. E. Sloan and A. Wojcicki, *Inorg. Chem.*, **7**, 1268 (1968).

Table I. Reactions of h^5-$C_5H_5Fe(CO)_2R$ and h^5-$C_5H_5Mo(CO)_3R$ ([M]-R) with KI or KBr in Liquid SO_2 at −10°

R[a]	Order of addn[c]	Reaction time, hr	KI (KBr)[d]: [M]-R ratio	Isolated product, %: [M]-I(Br)	Isolated product, %: [M]-SO_2R
$CH_2C_6H_5$	A	2	1:1	13	75
$CH_2C_6H_5$	A	2	10:1	16	70
$CH_2C_6H_5$	A	2	100:1	23	48
$CH_2C_6H_5$	B	3	10:1	3	78
$CH_2C_6H_5$	B	3	100:1	4	73
$CH_2C_6H_5$	A′	2	8:1	6	77
$SO_2CH_2C_6H_5$	A	4	10:1	0	75
$SO_2CH_2C_6H_5$	A	4	100:1	0	69
p-$C_6H_4CH_3$	A	3	100:1	44	40
p-$C_6H_4CH_3$	B	4	100:1	46	38
p-$SO_2C_6H_4CH_3$	A	4	100:1	0	77
CH_3	A	2	100:1	75	15
CH_3	B	2	100:1	52	38
SO_2CH_3	A	1	10:1	0	85
SO_2CH_3	A	4	100:1	0	67
$CH_2Si(CH_3)_3$	A	2	100:1	64	32
CH_3[b]	A	2	1:1	3	92
CH_3[b]	B	2	100:1	4	74
CH_3[b]	B	3	100:1	5	72
SO_2CH_3[b]	B	3	100:1	1	73

[a] h^5-$C_5H_5Fe(CO)_2R$ (~3 × 10^{-2} M) unless otherwise stated. [b] h^5-$C_5H_5Mo(CO)_3R$ (~3 × 10^{-2} M). [c] A, [M]-R added to KI in SO_2; A′, [M]-R added to KBr in SO_2; B, KI added to [M]-R in SO_2; see Experimental Section for details. [d] Concentration of KI ~3 × 10^{-2} to 3 M.

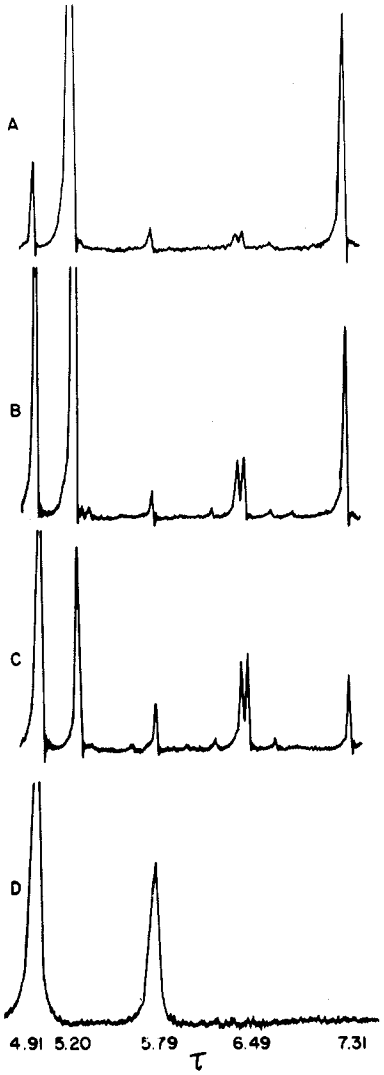


Figure 1. Proton magnetic resonance spectra of a solution of h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ in liquid SO_2: A, after storage for ~3 min at −18°; B, after storage for 20 min at −18°; C, after storage for 60 min at −18°; D, after complete conversion to h^5-$C_5H_5Fe(CO)_2SO_2CH_2C_6H_5$.

has disappeared, and the intensity of the peak at τ 5.79 has considerably increased. Interestingly, there is no detectable change in the position of the h^5-C_5H_5 resonance at τ 4.91 during the reaction. Removal of the SO_2 at this stage leads to isolation of the S-bonded h^5-$C_5H_5Fe(CO)_2SO_2CH_2C_6H_5$. A qualitatively similar behavior is observed for $Mn(CO)_5CH_2C_6H_5$ in SO_2 at −18 and −37°; however, the amount of the intermediate present at any one time is less than for h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$. After the manganese alkyl has reacted for 1 half-life (*ca.* 70 min) at −18°, the intermediate comprises 60% of the total sulfinate.

By way of contrast, in the nmr spectrum of h^5-$C_5H_5Mo(CO)_3CH_2C_6H_5$ in SO_2 at −37° a very low-intensity quartet centered at τ 6.40 appears at the start, remains barely visible throughout the reaction, and finally disappears. Thus the concentration of the intermediate is very low during the entire reaction. The absorption at τ 5.78, due to the CH_2 protons of the corresponding *S*-sulfinate, increases upon storage of the solution, whereas that at τ 7.12, due to the alkyl, gradually disappears. It is noteworthy that for each benzyl system examined, the CH_2 resonance of the intermediate appears τ 0.62-0.74 higher than that of the *S*-sulfinate.

The reactions of the methyl compounds $Mn(CO)_5CH_3$, $Re(CO)_5CH_3$, and h^5-$C_5H_5Fe(CO)_2CH_3$ were also examined by nmr spectroscopy in liquid SO_2. Only the resonances attributable to the intermediate (h^5-C_5H_5, τ 4.75; CH_3, τ 7.85) are present when the initial spectrum of h^5-$C_5H_5Fe(CO)_2CH_3$ is recorded at −37° some 15 min after its dissolution. Storage of this solution at −30° leads to a very slow formation of the *S*-sulfinate. Accordingly, after 40 min, a very low-intensity singlet is present at τ 6.95. After 5 hr, broad resonances are observable owing to considerable decomposition; the *S*-sulfinate comprises only *ca.* 25% of the total sulfinate in solution.

The nmr spectrum of a solution of $Mn(CO)_5CH_3$ in SO_2 at −18°, recorded 45 min after its preparation, shows only 10% unreacted alkyl. Approximately 20% of the total sulfinate is the *S*-sulfinate. The corresponding spectrum of $Re(CO)_5CH_3$, also at −18°, after 20 min shows only the resonance attributable to the intermediate. Additional storage of this solution at −20° for 2 hr affords *ca.* 80% intermediate and

Table II. Proton Nmr Spectra of Metal Alkyls and Their SO_2-Insertion Products in Liquid SO_2 [a]

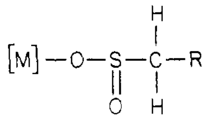
Compound	Temp, °C[c]	Chemical shift, τ[d]		
		$CH_2(CH_3)$	h^5-C_5H_5	C_6H_5
h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$	−18	7.31 s	5.20 s	2.88 s
h^5-$C_5H_5Fe(CO)_2OS(O)CH_2C_6H_5$	−18	6.57, 6.41 AB (J_{AB} = 12.6 Hz)	4.91 s	2.65 m
h^5-$C_5H_5Fe(CO)_2SO_2CH_2C_6H_5$	−18	5.79 s	4.91 s	2.53 s
h^5-$C_5H_5Mo(CO)_3CH_2C_6H_5$	−37	7.12 s	4.57 s	2.82 m
h^5-$C_5H_5Mo(CO)_3OS(O)CH_2C_6H_5$	−37	6.49, 6.31 AB (J_{AB} = 12.5 Hz)	4.29 s	2.75 m
h^5-$C_5H_5Mo(CO)_3SO_2CH_2C_6H_5$	−37	5.78 s	4.32 s	2.57 s
$Mn(CO)_5CH_2C_6H_5$	−37	7.64 s		2.83 m
$Mn(CO)_5OS(O)CH_2C_6H_5$	−37	6.41, 6.23 AB (J_{AB} = 12.5 Hz)		2.65 m
$Mn(CO)_5SO_2CH_2C_6H_5$	−37	5.70 s		2.55 s
h^5-$C_5H_5Fe(CO)_2CH_3$ [b]	−37			
h^5-$C_5H_5Fe(CO)_2OS(O)CH_3$	−37	7.85 s	4.75 s	
h^5-$C_5H_5Fe(CO)_2SO_2CH_3$	−37	6.95 s	e	
$Mn(CO)_5CH_3$	−18	10.33 s		
$Mn(CO)_5OS(O)CH_3$	−18	7.72 s		
$Mn(CO)_5SO_2CH_3$	−18	6.91 s		
$Re(CO)_5CH_3$	−18	10.20 s		
$Re(CO)_5OS(O)CH_3$	−18	7.73 s		
$Re(CO)_5SO_2CH_3$	−18	6.79 s		

[a] The intermediates are designated as the *O*-sulfinates. [b] Unable to measure owing to the rapid reaction. [c] ±7°. [d] Accurate to *ca.* 0.03 ppm. Key: s, singlet; m, multiplet; AB, AB quartet. [e] Decomposition and slow isomerization of the *O*-sulfinate precluded observation.

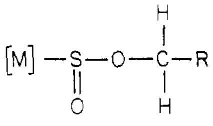
20% *S*-sulfinate. The sharp signals observed indicate considerable stability of the two rhenium carbonyl species under these conditions. Table II gives the nmr spectra of the alkyl, intermediate, and *S*-sulfinate for the six solution systems investigated. It is to be noted that the CH_3 resonance of each intermediate occurs at a higher field than that of the corresponding *S*-sulfinate.

The observed changes in the nmr spectra of SO_2 solutions of the six alkyls are consistent with the formation of a reaction intermediate (*k* step) and its subsequent conversion to the final *S*-sulfinate product (*k'* step). Differences in the behavior of these systems may be rationalized in terms of the relative rates of the *k* and *k'* processes. Qualitatively, *k'*/*k* decreases in the order h^5-$C_5H_5Mo(CO)_3CH_2C_6H_5$ > $Mn(CO)_5CH_2C_6H_5$ > h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ > $Mn(CO)_5CH_3$ > $Re(CO)_5CH_3$ ~ h^5-$C_5H_5Fe(CO)_2CH_3$. It is noteworthy that the intermediates derived from the methyl carbonyls are more stable with respect to conversion into the *S*-sulfinates than those derived from the benzyl carbonyls. This may result from a greater stabilization owing to solvation by SO_2 of the smaller, CH_3-containing species.

The appearance of the CH_2 signals as AB quartets in the nmr spectra of the benzyl intermediates points to a chiral atom therein. Since all three systems manifest this behavior and exhibit virtually identical geminal coupling constants J_{AB} (Table II) of the expected magnitude,[25] there is little doubt that the chirality is associated with the sulfur rather than, *e.g.*, the metal. In further support of this inference the infrared spectra (*vide infra*) show that the microsymmetry about the metal remains unchanged during formation of the intermediate, thus obviating the possibility of CO insertion. There are two structures that satisfy this requirement of asymmetry: I (*O*-sulfinate) and II (*S*-alkoxysulfenate) (R = C_6H_5).


$[\mathrm{M}]{-}\mathrm{O}{-}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}{-}\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}{-}\mathrm{R}$

I


$[\mathrm{M}]{-}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}{-}\mathrm{O}{-}\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}{-}\mathrm{R}$

II

[M] = h^5-$C_5H_5Fe(CO)_2$, h^5-$C_5H_5Mo(CO)_3$, $Mn(CO)_5$, $Re(CO)_5$

(ii) Electrical Conductivity. Ionic formulations, *e.g.*, $[h^5\text{-}C_5H_5Fe(CO)_2SO_2]^+C_6H_5CH_2SO_2^-$, for the intermediate are also to be dismissed on the basis of the nmr as well as the electrical conductivity data. A solution (~10^{-2} *M*) of h^5-$C_5H_5Fe(CO)_2CH_3$ in SO_2 which contains almost entirely the intermediate shows a molar conductivity of 0.24 ohm^{-1} cm^2 at −32°. The molar conductivity of *ca.* 10^{-2} *M* h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ in SO_2 at −32°, measured for 5 hr at 5-min intervals, changes from 0.11 to 0.14 ohm^{-1} cm^2, possibly owing to some decomposition. By comparison, an SO_2 solution of $[h^5\text{-}C_5H_5Fe(CO)_2P(C_6H_5)_3]^+PF_6^-$ of a similar concentration and at the same temperature shows a molar conductivity of 84 ohm^{-1} cm^2. This falls in the region expected for a 1:1 electrolyte.[26] In contrast, the intermediates derived from the two alkyls behave as virtual nonelectrolytes.

(iii) Infrared Spectra. Further support for the intermediacy of I or II in the formation of the *S*-sulfinates is furnished by examination of the infrared spectra of the alkyl solutions. The spectrum in the ν(CO) region of an SO_2 solution of h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$, recorded 3 hr after its preparation at −30°, shows two intense absorptions at 2062 and 2012 (br) cm^{-1} in addition to the weaker band at 1944 cm^{-1} of the unreacted alkyl. These frequencies are very close to, but not identical with, those (2064 and 2018 cm^{-1}) obtained for a solution of the authentic S-bonded h^5-$C_5H_5Fe(CO)_2SO_2CH_2C_6H_5$ at the same temperature in liquid SO_2. The corresponding spectrum of h^5-$C_5H_5Fe(CO)_2CH_3$, recorded after *ca.* 20-min storage of the solution at −60°, shows no ν(CO) of the alkyl. The two absorptions observed at 2061 and 2012 cm^{-1} again are very similar to those recorded for the *S*-sulfinate (2065 and 2019 cm^{-1}). On the basis of the complementary nmr data discussed earlier, they are assigned to the reaction intermediate. The molar extinction coefficients for the intermediate, ϵ of ν_s(CO) 1830 M^{-1} cm^{-1} and ϵ of ν_{as}(CO) 1740 M^{-1} cm^{-1}, are slightly lower than those for the *S*-sulfinate, ϵ of ν_s(CO) 2060 M^{-1} cm^{-1}

---

(25) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon, New York, N. Y., 1969, pp 270-279.

(26) P. J. Elving and J. M. Markowitz, *J. Chem. Educ.*, 37, 75 (1960).

Table III. Infrared CO Stretching Frequencies of the Intermediates and Final Products of the SO_2-Insertion Reaction[a]

Compound	Concn × 10^3, *M*	Reaction time, hr (temp, °C)	ν(CO),[b] cm^{-1}
h^5-$C_5H_5Fe(CO)_2OS(O)CH_2C_6H_5$	7	3 (−30)	2062, 2012
h^5-$C_5H_5Fe(CO)_2SO_2CH_2C_6H_5$	7		2064, 2018
h^5-$C_5H_5Fe(CO)_2OS(O)CH_3$	7	0.5 (−60)	2061, 2012
h^5-$C_5H_5Fe(CO)_2SO_2CH_3$	7		2065, 2019
h^5-$C_5H_5Fe(CO)_2$(*p*-$OS(O)C_6H_4CH_3$)	7	4 (−30)	2057, . . .[c]
h^5-$C_5H_5Fe(CO)_2$(*p*-$SO_2C_6H_4CH_3$)	7		2062, 2016
h^5-$C_5H_5Mo(CO)_3OS(O)CH_2C_6H_5$	5	5 (−30)	[d]
h^5-$C_5H_5Mo(CO)_3SO_2CH_2C_6H_5$	5		2062, 1991 sh, 1972 br
$Mn(CO)_5OS(O)CH_2C_6H_5$	3	3 (−30)	2147 w–m, 2098 w, 2065, . . .[c]
$Mn(CO)_5SO_2CH_2C_6H_5$	3		2147 w–m, 2098 w, 2061, 2019 w

[a] Recorded in liquid SO_2 at −60° for the isolated *S*-sulfinates. For the *O*-sulfinato intermediates ν(CO)'s were obtained on solutions of the alkyls stored at specified temperatures and for the indicated periods. [b] Very strong unless otherwise indicated. Key: m, medium; w, weak; sh, shoulder; br, broad. [c] Masked by the absorption of partially reacted alkyl. [d] Insufficient concentration for detection.

and ν_{as}(CO) 1860 M^{-1} cm^{-1}. The spectrum of h^5-$C_5H_5Fe(CO)_2$(*p*-$C_6H_4CH_3$) in SO_2 also provides evidence for the presence of the intermediate. This demonstrates a similarity in the SO_2 insertion reaction of the alkyl and aryl complexes.

The carbonyl stretching frequencies of the product of the reaction between h^5-$C_5H_5Mo(CO)_3CH_2C_6H_5$ and SO_2 observed 5 hr after preparation of the solution at −30° are identical with those of the authentic *S*-sulfinate. This fits very well with the nmr data which demonstrate a very low concentration of the intermediate at this stage of the reaction (*vide supra*). Table III presents the CO stretching frequencies of the intermediate and the isolated *S*-sulfinate for the systems examined in liquid SO_2.

It is noteworthy that the carbonyl stretching frequencies of the intermediates are not much different (lower by ⩽7 cm^{-1}) from those of the corresponding *S*-sulfinates. However, these data do not necessarily implicate metal-sulfur bonding in structure II. Several h^5-$C_5H_5Fe(CO)_2X$ complexes with X = oxygen-donor ligand show ν(CO) at wave numbers comparable to those observed here. For example, h^5-$C_5H_5Fe(CO)_2ONO_2$ absorbs at 2060 and 2007 cm^{-1} [27] and h^5-$C_5H_5Fe(CO)_2OC(O)R_F$ at 2071-2059 and 2020-2019 cm^{-1},[28] in the same regions as the iron intermediates in question (2062-2057 and 2012 cm^{-1}).

Infrared spectroscopic evidence was also obtained for the presence of the intermediate in the reaction of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ with SO_2 in organic solvents. Unlike most of the alkyls examined under comparable conditions, this complex undergoes the insertion at a conveniently measurable rate and without noticeable decomposition.

A chloroform solution containing 0.58 *M* SO_2 and *ca.* 10^{-2} *M* h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ was examined in the ν(CO) region at 2-8°. A low-frequency shoulder on the band at 2069 cm^{-1} becomes noticeable after 15 min at 8°. After 50 min, the absorptions at 2069 and 2060 cm^{-1} are approximately of equal intensity. Subsequent spectra show gradual diminution of the band at 2069 cm^{-1} and the corresponding growth of the 2060-cm^{-1} absorption. The 2060-cm^{-1} band has been shown to be due to the final *S*-sulfinate product; the band at 2069 cm^{-1} is assigned to the intermediate. The stability of this intermediate with respect to rearrangement into the *S*-sulfinate is strongly dependent on the solvent. Thus, in isopropyl alcohol the intermediate is still detectable after 2 hr. However, in nonpolar benzene only the carbonyl stretching frequencies due to the *S*-sulfinate can be discerned. Hence the intermediate is probably present in a very low concentration. These results are summarized in Table IV. Interestingly, the ν(CO) values for the intermediate are somewhat higher than those for the *S*-sulfinate, the opposite of what was observed in liquid SO_2.

A chloroform solution of SO_2 and h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ was examined also in the ν(SO) region. Such an investigation was precluded for solutions of the alkyls in liquid SO_2 because of the strong absorptions by the solvent. The spectra in the 1300-800-cm^{-1} range, recorded after a storage period of 10 and 80 min at 25°, are shown in Figure 2, and the pertinent absorptions are listed in Table IV. After about 10 min, the infrared spectrum shows bands at 1150, 1118, and 828 cm^{-1}. The 1118- and 828-cm^{-1} absorptions decrease in intensity, and new absorptions appear after 15 min at 1174, 1054, and 1034 cm^{-1}. The last three peaks are due to the isolable *S*-sulfinate, whereas the two gradually decreasing bands are assigned to the intermediate species. The absorption at 1150 cm^{-1}, due to free SO_2,[29] remains with a constant intensity throughout the reaction. After 80 min, the bands belonging to the intermediate are barely discernible. Thus, the above behavior is consistent with the previously described changes for the chloroform solutions in the ν(CO) region.

The ν(SO) region of the infrared spectrum was examined also for the intermediate in the SO_2 insertion reaction of $Re(CO)_5CH_3$. The white solid obtained by removal of SO_2 under reduced pressure at −30° from the 1 hr old solution of $Re(CO)_5CH_3$ was dissolved in 1:5 $CDCl_3$-CS_2 at −40°. The infrared spectrum showed absorptions at 1370 (s) (free SO_2), 1159 (s) (free SO_2), 1126 (s), 1106 (sh), 951 (s) (CH_3 rock), and 818 (m) cm^{-1}. Those at 1126, 1106, and 818 cm^{-1} have been assigned to the SO stretching frequencies of the intermediate. No conversion to the *S*-sulfinate was detected in this solution, even at room temperature. Apparently the presence of free sulfur dioxide stabilizes the intermediate, since passage of N_2 through the solution causes disappearance of the SO stretching absorptions and precipitation of $Re(CO)_5SO_2CH_3$. The *S*-sulfinate shows ν(SO) at 1196 and 1057 cm^{-1} and is much less soluble in CS_2 than the intermediate.

The SO stretching frequencies for the intermediates of the insertion reaction of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ and $Re(CO)_5CH_3$ compare quite well with those reported for some

---

(27) E. C. Johnson, T. J. Meyer, and N. Winterton, *Inorg. Chem.*, 10, 1673 (1971).

(28) R. B. King and R. N. Kapoor, *J. Organometal. Chem.*, 15, 457 (1968).

(29) E. C. M. Grigg and G. R. Johnston, *Aust. J. Chem.*, 19, 1147 (1966).

Table IV. Infrared CO and SO Stretching Frequencies (cm^{-1}) of the SO_2-Insertion Products of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ in Various Solvents[a]

	ν(CO)		ν(SO), ν(SOFe)	
Solvent	*O*-Sulfinate	*S*-Sulfinate[e]	*O*-Sulfinate	*S*-Sulfinate[e]
Chloroform	2069 vs, 2016 vs[b]	2060 vs, 2051 s, 2013 vs, 2003 vs	1118 s, 828 m[f]	1174 s, 1054 s, 1034 s
Isopropyl alcohol	2065 vs, 2020 vs[c]	2059 vs, 2013 vs		
Benzene	*d*	2055 vs, 2008 vs, 1999 sh		

[a] Key: vs, very strong; s, strong; m, medium; sh, shoulder. [b] Recorded using a 0.58 *M* SO_2 and ~10^{-2} *M* alkyl solution stored for 1 hr at 2°. [c] Recorded using a 1.26 *M* SO_2 and ~10^{-2} *M* alkyl solution stored for 2 hr at 26°. [d] Only ν(CO)'s of the *S*-sulfinate are discernible using a 1.08 *M* SO_2 and ~10^{-2} *M* alkyl solution. [e] Recorded using an isolated sample. [f] Recorded using a 0.56 *M* SO_2 and 3 × 10^{-2} *M* alkyl solution stored for 5 min at 25°.

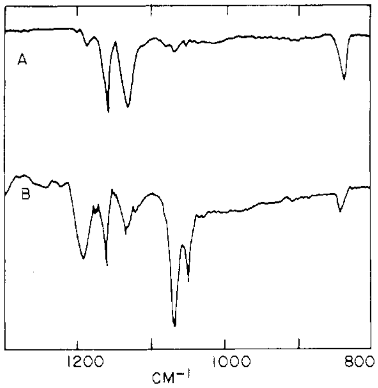


Figure 2. Infrared spectra of a solution of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ in 0.42 *M* SO_2-$CHCl_3$: A, after storage for 10 min at 25°; B, after storage for 80 min at 25°.

isolated transition metal-*O*-sulfinato complexes. For example, $Fe(p\text{-}O_2SC_6H_4CH_3)_2(bipy)_2$ exhibits ν(SO) at 1054 and ν_{as} (SOM) at 918 cm^{-1},[4] whereas *trans*-$Ir(CO)[P(C_6H_5)_3]_2(p\text{-}O_2SC_6H_4CH_3)$ shows ν(SO) at 1085 and ν_{as} (SOM) at 855, 840 cm^{-1}.[10] However, *S*-alkoxysulfenato complexes (structure II) may be expected to absorb at comparable wave numbers. Accordingly, a differentiation between structures I and II is not possible from these data.

(iv) Iodide Cleavage Reactions. In an attempt possibly to differentiate between the two structures in question we have examined reactions of the intermediates with the iodide ion. The *S*-sulfinato complexes, with the singular exception of h^5-$C_5H_5Mo(CO)_3SO_2CH_3$ (see Table I), do not react with I^-, and it was expected that the *S*-alkoxysulfenato species would behave analogously. In contrast, the *O*-sulfinato intermediates should be more amenable to such metathesis because of a polar M-OS(O)R linkage therein. Results of our studies in liquid SO_2 are summarized in Table I.

The substitution in liquid SO_2 was conducted either by adding the alkyl to the dissolved KI (or KBr) or by allowing the alkyl to react for 2-4 hr and then introducing the KI. It is to be noted that the latter procedure produces less metal carbonyl iodide than the former, no doubt by promoting conversion of the intermediate to the unreactive *S*-sulfinate before substitution. Furthermore, the amount of the metal carbonyl iodide isolated depends strongly on the nature of the alkyl; for h^5-$C_5H_5Fe(CO)_2R$, it decreases in the order $R = CH_3 > p\text{-}C_6H_4CH_3 > CH_2C_6H_5$. This order reflects the relative amounts of the three reaction intermediates present in solution, with the $R = CH_3$ system being almost entirely in the form of its intermediate species (*vide supra*).

The replacement of sulfinate with iodide can be also effected in CH_2Cl_2 or benzene. Accordingly, the reaction between h^5-$C_5H_5Fe(CO)_2CH_2Si(CH_3)_3$ and SO_2 in the presence of I^- yields 13-15% metal carbonyl iodide. Since neither the *S*-sulfinate nor the alkyl reacts with I^- under these conditions, the exchanging species must be the intermediate of the insertion reaction.

One further observation warrants discussion. Inspection of the data in Table I reveals that there is only a small increase in the amount of h^5-$C_5H_5Fe(CO)_2I$ isolated when the concentration of KI is increased by as much as 100-fold without changing the concentration of h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$. Although no attempt was made to be rigorously quantitative in these experiments, the results do indicate that the *S*-sulfinate cannot arise entirely *via* a metal carbonyl species which is also the precursor of the iodo complex. This requirement is satisfied by a scheme such as[30]

$$\begin{tikzcd}
{[M]\text{-OS(O)R}} \arrow[r, phantom, "\rightleftharpoons"] \arrow[dr] & {[M]^+RSO_2^-} \arrow[d] \arrow[dr, "I^-"] & \\
& {[M]\text{-S(O)}_2R} & {[M]\text{-I}}
\end{tikzcd}$$

$[M] = h^5$-$C_5H_5Fe(CO)_2$, etc.

From the evidence presented herein we infer that the reaction intermediate is the *O*-sulfinate ([M]-OS(O)R) rather than the isomeric *S*-alkoxysulfenate.[31] The species designated as $[M]^+RSO_2^-$, which must be invoked also for stereochemical reasons,[12] may be an ion pair whose concentration is insufficient for detection. It would be the common precursor of [M]-$S(O)_2R$ and [M]-I. However, substantial [M]-$S(O)_2R$ would have to be formed also *via* an intramolecular isomerization of [M]-OS(O)R, a process which may be analogous to the conversion of $[(NH_3)_5Co\text{-}ONO]^{2+}$ into $[(NH_3)_5Co\text{-}NO_2]^{2+}$.[32]

(30) An alternative pathway in which the *S*-sulfinate is formed directly from the alkyl, as well as from the *O*-sulfinate, also accords with the iodide cleavage experiments. However, neither the nmr nor the infrared data support such a route.

(31) Attempts have been made in our laboratory (D. W. Lichtenberg, private communication) to prepare h^5-$C_5H_5Fe(CO)_2S(O)OCH_3$ *via* reaction of $Na[h^5\text{-}C_5H_5Fe(CO)_2]$ or $[h^5\text{-}C_5H_5Fe(CO)_2]_2$ with $ClS(O)OCH_3$ but without success. We have recently learned that T. A. George and D. D. Watkins, Jr. (private communication) also have obtained only $[h^5\text{-}C_5H_5Fe(CO)_2]_2$ and/or h^5-$C_5H_5Fe(CO)_2Cl$ from the same reactions. However, these authors have synthesized $Ir(CO)[P(C_6H_5)_2CH_3]_2[S(O)OR]Cl_2$ ($R = CH_3$, C_2H_5, *i*-C_3H_7) and $Ir(CO)[P(C_6H_5)(CH_3)_2]_2[S(O)OCH_3]Cl_2$ *via* oxidative addition of ClS(O)OR to square-planar iridium(I). The nmr spectrum of $Ir(CO)[P(C_6H_5)_2CH_3]_2[S(O)OCH_3]Cl_2$ shows the OCH_3 resonance at a field lower (τ 7.08) than that for the SCH_3 protons (τ 7.82) in the corresponding *S*-sulfinate $Ir(CO)[P(C_6H_5)_2CH_3]_2(SO_2CH_3)Cl_2$. This is just the opposite of what we find here for the intermediates and the final *S*-sulfinato products of the SO_2 insertion, with the α protons of the RSO_2 absorbing at the lower fields in the latter compounds. The foregoing, as well as the observation that $Ir(CO)[P(C_6H_5)_2CH_3]_2[S(O)OR]Cl_2$ does not rearrange on heating to the corresponding *S*-sulfinates, are taken as further evidence in support of the *O*-sulfinato formulation for the intermediates in the SO_2 insertion. We thank Professor T. A. George and Mr. D. D. Watkins, Jr., for providing us with the details of their work prior to publication.

(32) R. K. Murmann and H. Taube, *J. Amer. Chem. Soc.*, 78, 4886 (1956).

Attempted Isolation of the Reaction Intermediate. As we have already mentioned, h^5-$C_5H_5Fe(CO)_2CH_3$ and $Re(CO)_5CH_3$ rapidly react with SO_2 to give the *O*-sulfinates which only slowly isomerize to the corresponding *S*-sulfinates. Therefore, these compounds presented themselves as ideal candidates for isolation and characterization of the intermediate of the insertion reaction. Unfortunately, all attempts at obtaining the *O*-sulfinates which are free of SO_2 have led to the isolation of the *S*-sulfinates instead. Removal of the last traces of SO_2 causes rapid linkage isomerization, even at −30°. The nature of this stabilization of the *O*-sulfinates by sulfur dioxide is not clear to us at present.

Conclusions

Sulfur dioxide reacts with transition metal alkyls ([M] -R) of the types h^5-$C_5H_5Fe(CO)_2R$, h^5-$C_5H_5Mo(CO)_3R$, and $M(CO)_5R$ (M = Mn, Re) either in the liquid or in solution to yield SO_2-containing species which differ from the isolable *S*-sulfinates ([M] -$S(O)_2R$). The ^1H nmr and infrared spectroscopic data, coupled with electrical conductivity measurements, identify these intermediates as either the *O*-sulfinato ([M] -OS(O)R) or the *S*-alkoxysulfenato ([M] -S(O)OR) complexes. The first formulation is supported by the relatively facile replacement of RSO_2^- in the intermediate with I^- to afford the carbonyl iodide ([M] -I). Moreover, the direction of polarization of the M-R and S-O bonds renders much more probable the formation of M-OS(O)R, known to occur with a wide variety of the main-group alkyls,[33] than of the alternative M-S(O)OR. The *O*-sulfinato intermediates undergo rearrangement in the course of attempts at their isolation to yield the stable S-bonded isomers. This behavior accords with the expected greater stability of the *S*-sulfinato than the *O*-sulfinato ligand when present in conjunction with a soft (or class "b") transition metal.

Registry No. h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$, 12093-91-3; h^5-$C_5H_5Fe(CO)_2OS(O)CH_2C_6H_5$, 36583-42-3; h^5-$C_5H_5Fe(CO)_2SO_2CH_2C_6H_5$, 12087-32-0; h^5-$C_5H_5Mo(CO)_3CH_2C_6H_5$, 12194-07-9; h^5-$C_5H_5Mo(CO)_3OS(O)CH_2C_6H_5$, 36583-43-4; h^5-$C_5H_5Mo(CO)_3SO_2CH_2C_6H_5$, 32841-90-0; $Mn(CO)_5CH_2C_6H_5$, 14049-86-6; $Mn(CO)_5OS(O)CH_2C_6H_5$, 36171-75-2; $Mn(CO)_5SO_2CH_2C_6H_5$, 20126-88-9; h^5-$C_5H_5Fe(CO)_2CH_3$, 12080-06-7; h^5-$C_5H_5Fe(CO)_2OS(O)CH_3$, 37955-99-0; h^5-$C_5H_5Fe(CO)_2SO_2CH_3$, 12080-26-1; $Mn(CO)_5CH_3$, 13601-24-6; $Mn(CO)_5OS(O)CH_3$, 37988-76-4; $Mn(CO)_5SO_2CH_3$, 19694-44-1; $Re(CO)_5CH_3$, 14524-92-6; $Re(CO)_5OS(O)CH_3$, 37988-72-0; $Re(CO)_5SO_2CH_3$, 20090-32-8; h^5-$C_5H_5Fe(CO)_2(p\text{-}OS(O)C_6H_4CH_3)$, 37955-88-7; h^5-$C_5H_5Fe(CO)_2(p\text{-}SO_2C_6H_4CH_3)$, 12087-31-9; h^5-$C_5H_5Fe(CO)_2(p\text{-}C_6H_4CH_3)$, 12093-90-2; h^5-$C_5H_5Fe(CO)_2SO_2CH(CH_3)_2$, 37955-91-2; h^5-$C_5H_5Fe(CO)_2SO_2CH_2Si(CH_3)_3$, 37955-92-3; chloroform, 67-66-3; isopropyl alcohol, 67-63-0; benzene, 71-43-2; sulfur dioxide, 7446-09-5.

Acknowledgments. This investigation has been supported by the National Science Foundation (Grant GP-22544). We thank Mr. D. L. Denton for experimental assistance.

(33) W. Kitching and C. W. Fong, *Organometal. Chem. Rev., Sect. A*, 5, 281 (1970).

Contribution from the Department of Chemistry, University
of North Carolina, Chapel Hill, North Carolina 27514

Kinetics of the Oxidation of Bis(π-cyclopentadienyldicarbonyliron) by $Ru(bipy)_2Cl_2^+$ and by $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$

JAMES N. BRADDOCK and THOMAS J. MEYER*

Received August 27, 1972

In acetonitrile bis(π-cyclopentadienyldicarbonyliron) is oxidized by $Ru(bipy)_2Cl_2^+$ (bipy is 2,2′-bipyridine) and by the tetrahedral, metal–metal bonded cluster ion $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$ according to the stoichiometry $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + 2Ox + 2CH_3CN \rightarrow 2(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+ + 2Red$, where Ox is $Ru(bipy)_2Cl_2^+$ or $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$ and Red is $Ru(bipy)_2Cl_2$ or $[(\pi\text{-}C_5H_5)Fe(CO)]_4$. For both reactions the observed rate law is $-d[(\pi\text{-}C_5H_5)_2Fe_2(CO)_4]/dt = k[(\pi\text{-}C_5H_5)_2Fe_2(CO)_4][Ox]$. The kinetics of the two reactions were measured using a stopped-flow spectrometer. For $Ru(bipy)_2Cl_2^+$ as the oxidant $k(24°) = (4.24 \pm 0.12) \times 10^4\ M^{-1}\ sec^{-1}$, $\Delta H^\ddagger = 6.2 \pm 0.5$ kcal/mol, and $\Delta S^\ddagger\ (25°) = -16.6 \pm 1.5$ eu and for $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$ as the oxidant $k(25°) = (6.12 \pm 0.21) \times 10^4\ M^{-1}\ sec^{-1}$, $\Delta H^\ddagger = 1.8 \pm 0.2$ kcal/mol, and $\Delta S^\ddagger\ (25°) = -31 \pm 3$ eu. The rate constants for both reactions were found to be somewhat sensitive to added electrolyte ($(n\text{-}C_4H_9)_4N^+PF_6^-$). The kinetic information is discussed in terms of the likely detailed mechanisms of electron transfer and also in terms of the known stereochemical properties of bis(π-cyclopentadienyldicarbonyliron) in solution.

Introduction

A common reaction of structurally simple compounds which contain strong metal–metal bonds is oxidative cleavage with halogens,[1] *e.g.*

$$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + Br_2 \xrightarrow{CH_2Cl_2} 2(\pi\text{-}C_5H_5)Fe(CO)_2Br \qquad (1)$$

The oxidation-reduction character of such reactions can be seen more clearly by using a metal ion oxidant[2]

$$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + 2Fe^{3+} + 2S \rightarrow 2(\pi\text{-}C_5H_5)Fe(CO)_2S^+ + 2Fe^{2+} \qquad (2)$$

(S = acetone or acetonitrile)

or by carrying out the net oxidation of the metal–metal bond electrochemically[3]

$$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + 2S \xrightarrow{-2e^-} 2(\pi\text{-}C_5H_5)Fe(CO)_2S^+ \qquad (3)$$

Some rate and mechanistic studies have been reported for reactions in which metal–metal bonds are oxidized by

(1) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press, New York, N. Y., 1965.

(2) E. C. Johnson, T. J. Meyer, and N. Winterton, *Inorg. Chem.*, 10, 1673 (1971).

(3) J. A. Ferguson and T. J. Meyer, *Inorg. Chem.*, 10, 1025 (1971).