Kinetics and Mechanism of Sulfur Dioxide Insertion in *Pentahapto*(substituted and unsubstituted cyclopentadienyl)alkyl(and -aryl)dicarbonyliron(II) Complexes

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Abstract: The rates of the cleavage of the iron–carbon bond in h^5-$C_5H_5Fe(CO)_2R$ and related (h^5-ring)$Fe(CO)_2R$ complexes by SO_2 have been investigated in neat sulfur dioxide. The reactions were followed by infrared spectrophotometry in the ν(CO) region over the temperature range −70 to −23°. For the h^5-$C_5H_5Fe(CO)_2R$ alkyls, the reaction velocity generally decreases with an increasing value of the Taft σ^* and with increasing ν(CO) of the reacting complex, *e.g.*, $R = CH_2CH_3 > CH_3 > CH_2OCH_3 > CH_2CN$. However, as the bulkiness of R increases, the rate of iron–carbon bond cleavage decreases, *e.g.*, $R = CH_3 > CH_2CH(CH_3)_2$ or $CH_2CH_2C(CH_3)_3 > CH_2C(CH_3)_3 > C(CH_3)_3$. For the h^5-$C_5H_5Fe(CO)_2R$ aryls, the rate constant decreases as a function of increasing σ^+, *viz.*, $R = p$-$C_6H_4OCH_3 > p$-$C_6H_4CH_3 > m$-$C_6H_4CH_3 \sim C_6H_5$, with $\rho = -4.3$. Methyl substitution on the cyclopentadienyl ring increases the rate of the insertion when $R = CH_2C_6H_5$, *viz.*, $[h^5$-$(CH_3)_5C_5]Fe(CO)_2CH_2C_6H_5 \gg (h^5$-$CH_3C_5H_4)Fe(CO)_2CH_2C_6H_5 > h^5$-$C_5H_5Fe(CO)_2CH_2C_6H_5$, but does not produce a regular trend when R is an aryl group. These insertion reactions have characteristically large and negative values of $\Delta S^{\neq}$ (−62 to −43 eu) and low values of $\Delta H^{\neq}$ (2.9–7.8 kcal/mol). The observed rate dependence on the nature of R demonstrates that the cleavage of the Fe–R bond is an electrophilic process. For the iron alkyls, the results are consistent with a backside attack of SO_2 on the α carbon which leads to the heterolysis of the Fe–R bond and formation of a contact ion pair (h^5-ring)$Fe(CO)_2{}^+O_2SR^-$. These ions appear to recombine rapidly to yield the *O*-sulfinate, (h^5-ring)$Fe(CO)_2OS(O)R$, and, more slowly, to give the *S*-sulfinate, (h^5-ring)$Fe(CO)_2S(O)_2R$. The *O*-sulfinate then isomerizes to the *S*-sulfinate, which is the final product of the insertion.

Considerable interest has been evidenced in recent years in insertion reactions involving transition metal complexes.[1,2] Although much synthetic work has been done in this context, few kinetic studies have been carried out. The insertion of carbon monoxide into transition metal–carbon bonds has been the only reaction whose mechanism has received more than cursory attention.[3]

Since its discovery in 1964[4] the sulfur dioxide insertion has been also largely dominated by synthetic considerations.[5,6] More recently, however, active interest has developed in its mechanism. Spectroscopic (infrared and ^{1}H nmr) studies have demonstrated[7] intermediacy of the oxygen-bonded sulfinates in the formation of the sulfur-bonded sulfinates from SO_2 and metal alkyls and aryls of the type h^5-$C_5H_5Fe(CO)_2R$, h^5-$C_5H_5Mo(CO)_3R$, and $M(CO)_5R$ (M = Mn or Re). Stereochemical investigations on the insertion have been also reported;[8,9] the elegant experiment of Whitesides[9] has demonstrated inversion of configuration at the α carbon in the formation of h^5-$C_5H_5Fe(CO)_2S(O)_2CHDCHDC(CH_3)_3$ from the corresponding metal alkyl and SO_2.

We now report the kinetic results of our study on the SO_2 insertion involving some h^5-$C_5H_5Fe(CO)_2R$ and other, structurally similar, iron complexes. Based on these and related previously reported results,[7-9] a plausible mechanism is suggested for the insertion. This paper deals entirely with the reactions in neat SO_2; communicated later will be our investigation on the insertion in organic solution.[10] A preliminary account of this work was published earlier.[11] Kinetic studies on insertion of SO_2 into tin–carbon bonds have been also reported.[12]

Experimental Section

General Procedures. A nitrogen atmosphere was used routinely in all preparative and kinetic aspects of this work. Ventron alumina, deactivated with distilled water (6–10%), and Florisil (60–100 mesh), from Fisher Scientific Co., were employed in chromatographic separations and purifications. Elemental analyses were performed by Dr. F. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany, and by Galbraith Laboratories, Inc., Knoxville, Tenn.

Physical Measurements. Except as noted in Table I, all infrared measurements were made with 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. Hydrogen-1 nmr spectra were obtained on a Varian Associates A-60 spectrometer using tetramethylsilane (TMS) as an internal standard. Melting points were measured either in capillaries using a mineral oil bath or with a Thomas-Hoover capillary melting point apparatus; they are uncorrected.

Materials. Anhydrous grade SO_2, from Matheson, was purified and dried as described elsewhere.[7] The compound $[N(CH_3)_4]_2S_2O_5$

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Table I. Melting Points and Infrared and ^{1}H Nmr Spectra of New (h^5-ring)Fe(CO)$_2$R Complexes

Compd			Ir, cm^{-1}		
Ring	R	Mp, °C	ν(CO)[b]	ν(SO)[c]	^{1}H nmr, τ[e]
C_5H_5	$CH_2C(CH_3)_3$	Oil	2005, 1950		CH_3, 9.04 s; CH_2, 8.24 s; C_5H_5, 5.26 s
C_5H_5	$CH_2C_6H_4OCH_3$-*p*	69–71	2007, 1955		CH_2, 7.27 s; CH_3, 6.25 s; C_5H_5, 5.27 s; C_6H_4, 3.43–3.22 m(2), 3.03–2.74 m(2)
C_5H_5	*p*-$C_6H_4OCH_3$	63–64	2027, 1971		CH_3, 6.36 s; C_5H_5, 5.30 s; C_6H_4; 3.75–3.21 m(2), 3.10–2.56 m(2)[f]
C_5H_5	*o*-$C_6H_4CH_3$	67–68	2024, 1968		CH_3, 7.62 s; C_5H_5, 5.29 s; C_6H_4, 3.47–3.01 m(3), 2.71–2.43 m(1)[f]
C_5H_5	*m*-$C_6H_4CH_3$	48–49	2027, 1970		CH_3, 7.82 s; C_5H_5, 5.58 s; C_6H_4, 3.53–2.63 m[f]
$CH_3C_5H_4$	$CH_2C_6H_5$	Oil	2007, 1956		CH_3, 8.26 s; CH_2, 7.44 s; C_5H_4, 5.70 s; C_6H_5, 3.06 s[g]
$CH_3C_5H_4$	C_6H_5	*a*	2024, 1967		CH_3, 8.29 s; C_5H_4, 5.42 m, 5.31 m; C_6H_5, 3.17–2.87 m(3), 2.67–2.37 m(2)
$CH_3C_5H_4$	*p*-$C_6H_4CH_3$	50–51	2019, 1967		C_5CH_3, 8.35 s; C_6CH_3, 7.79 s; C_5H_4, 5.49 m, 5.41 m; C_6H_4, 3.34–3.08 m(2), 2.85–2.60 m(2)
$(CH_3)_5C_5$	$CH_2C_6H_5$	91–92	1993, 1943		CH_3, 8.25 s; CH_2, 7.79 s; C_6H_5, 2.96 s
$(CH_3)_5C_5$	CH_2CN	88–89	2008, 1958		*a*
$(CH_3)_5C_5$	C_6H_5	165–166	2001, 1950		CH_3, 8.36 s; C_6H_5, 3.13–2.46 m
C_9H_7	$CH_2C_6H_5$	86–87	2008, 1957		CH_2, 7.93 s; C_5H_3, 5.39 t (J = 2.5 Hz)(1) 4.69 d (J = 2.5 Hz)(2); C_6H_4, 2.92 s; C_6H_5, 3.00–2.64 m
C_5H_5	$S(O)_2C(CH_3)_3$	*a*	2059, 2049, 2012, 2000	1178, 1033	CH_3, 8.73 s; C_5H_5, 4.79 s
C_5H_5	$S(O)_2CH_2C(CH_3)_3$	145–146	2058, 2048, 2009–2001 br	1179, 1048	CH_3, 8.83 s; CH_2, 6.87 s; C_5H_5, 4.85 s
C_5H_5	$S(O)_2CH_2CH(CH_3)_2$	103–105	2060, 2049, 2012, 2001	1181, 1172 sh, 1050	CH_3, 8.93 d (J = 6 Hz); CH, 7.9–7.2 m; CH_2, 6.97 d (J = 6 Hz); C_5H_5, 4.85 s
C_5H_5	$S(O)_2CH_2CH_2C(CH_3)_3$	185–203 dec	2059, 2050, 2014, 2005	1188, 1175 sh, 1049	CH_3, 9.07 s; CCH_2C, 8.46–8.09 m; SCH_2, 7.12–6.77 t; C_5H_5, 4.85 s
C_5H_5	$S(O)_2CH_2C_6H_4OCH_3$-*p*	167–168	2061, 2008	1206, 1046	CH_3, 6.19 s; CH_2, 5.86 s; C_5H_5, 5.07 s; C_6H_4, 3.29–2.94 m(2), 2.81–2.47 m(2)
C_5H_5	$S(O)_2CH_2OCH_3$	82.5	2060, 2013	1200, 1185 1046	CH_3, 6.21 s; CH_2, 5.80 s; C_5H_5, 4.75 s
C_5H_5	$S(O)_2CH_2SCH_3$	*a*	2062, 2021	1187, 1045	*a*
C_5H_5	$S(O)_2CH_2CH_2CN$	114–116	2067, 2027	1186, 1047	CH_2CH_2, 7.17–6.45 m; C_5H_5, 4.74 s
C_5H_5	$S(O)_2C_6H_4OCH_3$-*p*	163–164 dec	2059, 2010	1193, 1038 br	CH_3, 6.01 s; C_5H_5, 4.82 s; C_6H_4, 3.10–2.72 m, 2.30–2.06 m
C_5H_5	$S(O)_2C_6H_4CH_3$-*o*	149.5	2056, 2011	1192, 1040	CH_3, 7.19 s; C_5H_5, 4.99 s; C_6H_4, 2.87–2.56 m(3), 2.33–1.99 m(1)
C_5H_5	$S(O)_2C_6H_4CH_3$-*m*	143	2060, 2011	1191, 1046	CH_3, 7.54 s; C_5H_5, 4.94 s; C_6H_4, 2.75–2.25 m
$CH_3C_5H_4$	$S(O)_2CH_2C_6H_5$	111–112	2056, 2005	1198, 1175, 1038 br	CH_3, 8.02 s; CH_2, 5.79 m; C_5H_4, 5.25 m 5.13 m; C_6H_5, 2.57 s
$CH_3C_5H_4$	$S(O)_2C_6H_4CH_3$-*p*	137–139	2055, 2005	1192, 1038	C_5CH_3, 8.06 s; C_6CH_3, 7.59 s; C_5H_4, 5.18 m, 5.04 m; C_6H_4, 2.86–2.53 m, 2.41–2.15 m
$(CH_3)_5C_5$	$S(O)_2CH_2C_6H_5$	*a*	2028, 1980	1173, 1030	CH_3, 8.15 s; CH_2, 5.87 s; C_6H_5, 2.69 s
$(CH_3)_5C_5$	$S(O)_2C_6H_5$	188–190	2029, 1983	1179, 1041[d]	*a*
C_9H_7	$S(O)_2CH_2C_6H_5$	152 dec	2058, 2006	1199, 1053	CH_2, 5.79 s; C_5H_3, 4.63 t (J = 3 Hz)(1), 4.30 d (J = 3 Hz)(2); C_6H_4–C_6H_5, 2.80–2.34 m

[a] Not measured. [b] Cyclohexane solution of the alkyls and aryls, $CHCl_3$ solution of the *S*-sulfinates. All absorptions are very strong. [c] Recorded on a Perkin-Elmer Model 337 spectrophotometer using, except as noted, Nujol mulls. Unless otherwise indicated, all absorptions are strong. Abbreviations: br = broad, sh = shoulder. [d] $CHCl_3$ solution. [e] $CDCl_3$ solution unless otherwise noted. For groups containing nonequivalent hydrogens, the number of absorbing protons is given in parentheses. Abbreviations: s = singlet, d = doublet, t = triplet, m = complex multiplet. [f] CCl_4 solution. [g] CS_2 solution.

was prepared by the method of Jander and Hecht.[13] Other chemicals were procured in reagent grade quality and used as received. Organic solvents were purified by standard procedures.[7]

Metal Alkyls (Aryls) and *S*-Sulfinates. The melting points and infrared and ^{1}H nmr spectra of all new alkyl (aryl) and *S*-sulfinato complexes are presented in Table I. Analytical data are provided in Supplementary Table Ia.[14]

The metal carbonyl starting compounds $[(h^5\text{-}CH_3C_5H_4)Fe(CO)_2]_2$,[15] $\{[h^5\text{-}(CH_3)_5C_5]Fe(CO)_2\}_2$,[16a] and $[(h^5\text{-}C_9H_7)Fe(CO)_2]_2$[16b] ($C_9H_7$ = indenyl) were prepared by literature procedures; $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$ was purchased from Strem Chemical Co.

The majority of the alkyls h^5-$C_5H_5Fe(CO)_2R$, *viz.*, R = CH_3,[17] C_2H_5,[17] $CH(CH_3)_2$,[18] $C(CH_3)_3$,[19] $CH_2CH(CH_3)_2$,[20] $CH_2CH_2C(CH_3)_3$,[9] $CH_2C_6H_5$,[21] $CH(CH_3)C_6H_5$,[8] CH_2CN,[22] CH_2OCH_3,[23] CH_2SCH_3,[24]

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$CH_2C(O)CH_3$,[25] $CH_2Si(CH_3)_3$,[26] CH_2CH_2CN,[22] and $CH_2CH{=}CHCH_3$,[27] were synthesized by known procedures. The complexes with R = $CH_2C_6H_4OCH_3$-*p* (66% yield) and $CH_2C(CH_3)_3$ (36% yield) were prepared analogously, using $Na[(h^5\text{-}C_5H_5)Fe(CO)_2]$ in conjunction with $ClCH_2C_6H_4OCH_3$-*p* (from $HOCH_2C_6H_4OCH_3$-*p*[28]) and $BrCH_2C(CH_3)_3$, respectively. The aryliron derivatives h^5-$C_5H_5Fe(CO)_2R$ (R = C_6H_5 (19%), *p*-$C_6H_4OCH_3$ (20%), *o*- (33%), and *m*-$C_6H_4CH_3$ (39%)) were obtained in the indicated yields according to the general method of King and Bisnette,[29] as described earlier for h^5-$C_5H_5Fe(CO)_2(p\text{-}C_6H_4CH_3)$.[7]

The pentahapto-(substituted cyclopentadienyl) complexes (h^5-$CH_3C_5H_4$)$Fe(CO)_2R$ (R = $CH_2C_6H_5$ (43%), C_6H_5 (23%), and *p*-$C_6H_4CH_3$ (18%)), $[h^5\text{-}(CH_3)_5C_5]Fe(CO)_2R$ (R = $CH_2C_6H_5$ (35%), CH_2CN (16%), C_6H_5 (2%), and C_6F_5[30]), and h^5-$C_9H_7Fe(CO)_2$-$CH_2C_6H_5$ (34%) were prepared analogously to their *pentahapto*-cyclopentadienyl counterparts. The (h^5-$CH_3C_5H_4$)$Fe(CO)_2R$ derivatives are considerably less stable than the corresponding h^5-$C_5H_5Fe(CO)_2R$. During the photolysis of the (h^5-$CH_3C_5H_4$)$Fe(CO)_2C(O)R$ aroyls, some (h^5-$CH_3C_5H_4$)$_2$Fe was formed in addition to (h^5-$CH_3C_5H_4$)$Fe(CO)_2R$; the two can be readily separated by chromatography on alumina with pentane eluent. In contrast to (h^5-$CH_3C_5H_4$)$Fe(CO)_2R$, the $[h^5\text{-}(CH_3)_5C_5]Fe(CO)_2R$ derivatives appear to have higher stabilities than their h^5-$C_5H_5Fe(CO)_2R$ analogs.

The *S*-sulfinates h^5-$C_5H_5Fe(CO)_2S(O)_2R$ (R = CH_3,[21] C_2H_5,[21] $CH(CH_3)_2$,[7] $CH_2CH_2C(CH_3)_3$,[9] $CH_2C_6H_5$,[21] $CH(CH_3)C_6H_5$,[8] CH_2OCH_3,[15] $CH_2Si(CH_3)_3$,[7] $CH(CH_3)CH{=}CH_2$,[31] C_6H_5,[21] and *p*-$C_6H_4CH_3$[21]) were prepared by literature methods. All other iron *S*-sulfinates were obtained analogously by the reaction of the corresponding alkyls or aryls with neat SO_2 at reflux or at 25° in a pressure vessel.[32] Removal of SO_2 after various time intervals, dissolution of the residue in $CHCl_3$, chromatography on alumina, and crystallization from $CHCl_3$–pentane afforded the yellow crystalline *S*-sulfinates. Only h^5-$C_5H_5Fe(CO)_2C(CH_3)_3$ failed to insert cleanly giving, in addition to the *S*-sulfinate, several uncharacterized products, all in low yield. Synthetic aspects of these insertion reactions are summarized in Table II.

The alkyl complexes h^5-$C_5H_5Mo(CO)_3CH_3$[17] and $Mn(CO)_5CH_3$,[33] as well as their *S*-sulfinates,[34,35] were obtained by established procedures.

Attempted Exchange of the Alkyl Groups during the Insertion. The complexes h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ (0.21 g, 0.77 mmol) and h^5-$C_5H_5Mo(CO)_3CH_3$ (0.20 g, 0.77 mmol) were simultaneously added to 25 ml of SO_2 at reflux and allowed to react for 4 hr. Excess SO_2 was removed and the residue chromatographed on a Florisil column eluting with 1:1 acetone–dichloromethane. The nmr spectrum of the eluted band showed presence of h^5-$C_5H_5Fe(CO)_2S(O)_2CH_2C_6H_5$ and h^5-$C_5H_5Mo(CO)_3S(O)_2CH_3$ but not of the cross-products h^5-$C_5H_5Fe(CO)_2S(O)_2CH_3$ and h^5-$C_5H_5Mo(CO)_3S(O)_2$-$CH_2C_6H_5$.[34]

In another, similar experiment, h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ (0.32 g, 1.2 mmol) and $Mn(CO)_5CH_3$ (0.25 g, 1.2 mmol) were treated with 70 ml of neat SO_2 at −30° for 6 hr. Removal of the SO_2 and chromatography of the residue on alumina eluting with chloroform yielded h^5-$C_5H_5Fe(CO)_2S(O)_2R$ with R = $CH_2C_6H_5$ only. The $Mn(CO)_5S(O)_2R$ product decomposed on the column.

Kinetic Studies. The Infrared Cell. Insertion reactions in liquid SO_2 were followed by infrared spectroscopy using a Beckman Model IR-9 spectrophotometer in conjunction with a VLT-2 variable low-temperature cell unit from Research and Industrial Instruments Co., London, England (available in the U. S. from Beckman Instruments Co., Fullerton, Calif.). The unit consists of three main parts: the outer jacket, the cell holder and refrigerant vessel, and the sample cell (Model FH-01) with a thermocouple. A 0.5-mm AgCl sample cell was employed in this work.

Table II. Details of Synthesis by SO_2 Insertion of New (h^5-ring)$Fe(CO)_2R$ Complexes

Alkyl (aryl) compd Ring	Alkyl (aryl) compd R	Reaction conditions Temp, °C	Reaction conditions Time, hr	% alkyl (aryl) recovered	% *S*-sulfinate isolated
C_5H_5	$C(CH_3)_3$	−10	30	90[b]	10[b]
		25	48	0	11
C_5H_5	$CH_2C(CH_3)_3$	−10	30	51	22
C_5H_5	$CH_2CH(CH_3)_2$	−10	2	25[b]	75[b]
		−10	8	0	56
C_5H_5	$CH_2CH_2C(CH_3)_3$	−10	2	60[b]	40[b]
		−10	10	*c*	60
C_5H_5	$CH_2C_6H_4OCH_3$-*p*	−10	3	0	85
C_5H_5	CH_2OCH_3	−10	20	*c*	16
C_5H_5	CH_2SCH_3	−10	17	76	7
C_5H_5	CH_2CH_2CN	−10	50	*c*	20
C_5H_5	*p*-$C_6H_4OCH_3$	−10	5	0	90
C_5H_5	*o*-$C_6H_4CH_3$	−10	5	0	60
C_5H_5	*m*-$C_6H_4CH_3$	−10	7	0	54
C_5H_5	*p*-$C_6H_4CH_3$	−10	5	0	75
$CH_3C_5H_4$	$CH_2C_6H_5$	−10	2	0	87
$CH_3C_5H_4$	*p*-$C_6H_4CH_3$	−10	12	0	80
$(CH_3)_5C_5$	$CH_2C_6H_5$	−10	2	0	47
$(CH_3)_5C_5$	C_6H_5	−10	24	70[b]	30[b]
		25[a]	29	0	50
C_9H_7	$CH_2C_6H_5$	−10	16	0	71

[a] In addition to treatment for 24 hr at −10°. [b] Estimated from infrared spectrum of the reaction mixture. [c] Alkyl complex detected during chromatography but its recovery not attempted.

The VLT-2 unit has been described briefly elsewhere;[36] the following modifications were made for work with liquid SO_2.[37] Model LT-U Teflon leads and metal fittings (from Beckman) were used to connect the entrance and exit ports at the top of the cell to the FH-01 sample cell compartment. At the entrance port, a Tuohy Adapter A-1029 from Clay-Adams, Inc. was used to affix the Teflon tubing to the inner Luer fitting of the low-temperature syringe. Also, the original stainless steel screw fitting for the entrance port was replaced with a Teflon screw fitting. This reduced the rate of evaporation of SO_2 from the cell.

Temperature Control and Measurement. A Dry Ice–isopropyl alcohol slush was generally employed to attain the desired low temperature of the cell; Dry Ice–acetone was used when a temperature of *ca.* −70° was required. For operations above the temperature of the coolant (*i.e.*, between −65 and −23°), a disk made of a foam-like material was fitted tightly on the bottom of the dewar to provide some insulation between the refrigerant and the FH-01 sample cell. The temperature was then adjusted manually with a precision of within ±0.5° by means of two external heaters attached to the cell holder from a variable 0–12-V power unit. An iron–constantan thermocouple inserted into the front window of the FH-01 cell in conjunction with a Leeds and Northrup Co. No. 8690 millivolt potentiometer measured the temperature of the SO_2 solution. A No. 87 Wratten Gelatin Kodak Filter served to reduce the heating of the cell by the infrared beam of the spectrophotometer.

Preparation and Transfer of Solutions. Solutions of the alkyl or aryl complex in neat SO_2 (generally $\sim 7 \times 10^{-3}$ *M*) were prepared in a vessel, shown in Figure 1, which was maintained in a Dry Ice–isopropyl alcohol bath. The complexes were purified by chromatography immediately before each kinetic run. Onto the weighed amount of the complex, sulfur dioxide was added from a condenser until the desired volume of the solution had collected in the vessel. Complete dissolution was effected by rapid shaking or magnetic stirring. An aliquot of the solution was then syringed out through the side arm fitted with a serum cap. The syringe employed was enclosed in a glass jacket packed with crushed Dry Ice.

Procedure and Measurements. The cell was first evacuated to

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(32) A Model HDF4-75-304, 75-ml stainless steel sample cylinder equipped with a 16 DKM4-F4-A314 valve, from Whitey Research Tool Co., Emeryville, Calif.

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

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

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(37) We are indebted to Dr. J. P. Day of the University of Manchester for a number of very helpful suggestions.

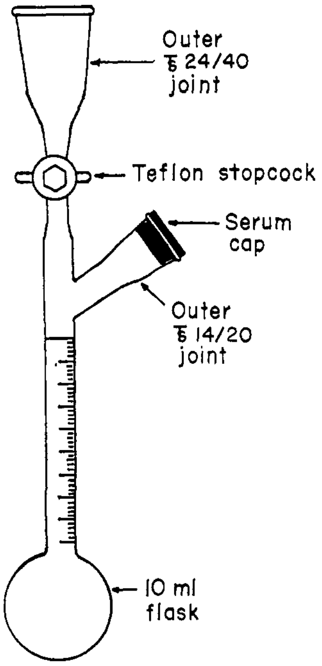

Figure 1. Vessel for preparation of solutions of metal complexes in liquid SO_2.

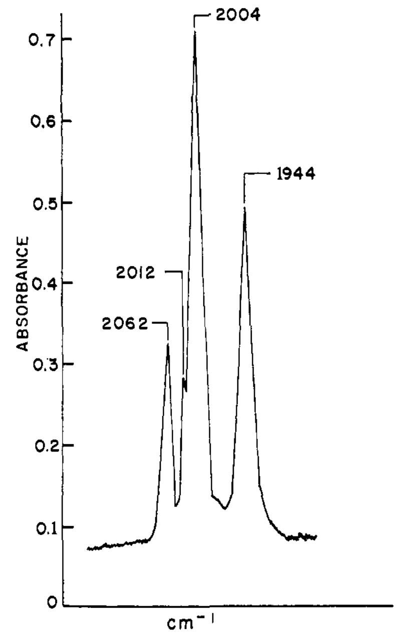

Figure 2. The infrared spectrum in the ν(CO) region of a solution of h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ (*ca.* 7 × 10^{-3} *M*) in neat SO_2 at −45° after *ca.* 50% completion of the insertion.

~0.1 Torr while the outer window was heated to prevent condensation of water. A Dry Ice–isopropyl alcohol slush was then introduced into the dewar containing the insulating disk. The variable 12-V cell heater was switched to the precalibrated reading to give the desired temperature. During the cooling operation, dry nitrogen was flushed through the apparatus to prevent water condensation on the Teflon leads and the FH-01 cell.

After the desired temperature had been attained, the SO_2 solution (~3 ml) was syringed into the cell and the Teflon leads were closed tightly with the screw clamps. *Because of the poisonous nature of SO_2, the cell was filled in a fume hood.* The first infrared measurement was made after the solution had reached thermal equilibrium in the cell (≤ 5 min).

Because of the very slow leakage of SO_2 from the cell which could not be prevented, the aforementioned procedure was applied only to the more rapidly inserting metal alkyls and aryls (generally those with $t_{1/2} < 2$ hr at −40°). Sulfur dioxide solutions of the more slowly reacting h^5-$C_5H_5Fe(CO)_2R$ complexes (R = CH_2OCH_3, C_6H_5, and *m*-$C_6H_4CH_3$) were stored in vessels immersed in appropriate organic solvent–liquid nitrogen slush baths.[38] With good stirring, these baths controlled the temperature within ±1°. Aliquots of the SO_2 solutions were periodically syringed out and introduced into the low-temperature infrared cell which was kept at the same temperature as the slush bath.

The rates of the insertion reaction were determined by observing the rate of disappearance of the lower frequency CO stretching band, ν_{as}(CO), of the alkyl (aryl) complex. In some cases, the rate of growth of the higher frequency CO stretching band, ν_s(CO), of the sulfinate was also followed for comparison. However, the latter data are of uncertain accuracy since both the *O*- and the final *S*-sulfinato products may contribute to the intensity of the observed band. For h^5-$C_5H_5Fe(CO)_2SO_2CH_3$, the molar extinction coefficients of the ν_s(CO) band of the two linkage isomers differ by 12%.[7] Therefore, results based on measurements involving the sulfinate bands, although in reasonable agreement with those involving the metal alkyl bands, are not included in this paper. Reactions run entirely in the low-temperature infrared cell were followed for 2–3 half-lives; the slush bath reactions were monitored for fewer half-lives, especially when conducted at the lower temperatures. Figure 2 shows the infrared spectrum in the ν(CO) region of a solution of h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ in neat SO_2 at −45° after approximately 50% completion of the insertion.

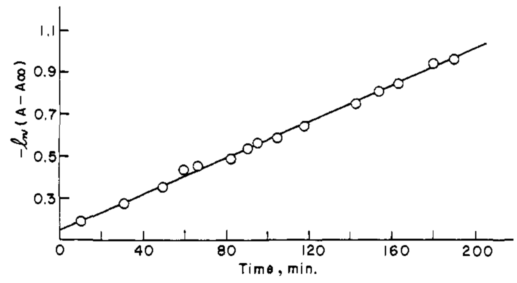

Figure 3. Sulfur dioxide insertion reaction of h^5-$C_5H_5Fe(CO)_2$-$CH_2C_6H_5$ (*ca.* 7 × 10^{-3} *M*) in neat SO_2 at −45°.

Beer's law was found to be valid for the ν_{as}(CO) absorption of h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ in the concentration range 1 × 10^{-3}–9 × 10^{-3} *M*. It was assumed also to hold for the other alkyl and aryl complexes investigated. Pseudo-first-order rate constants, k_{obsd}, were obtained by plotting $-\ln(A - A_\infty)$ *vs.* time, where *A* is the absorbance at any given time and A_∞ is the absorbance at the end of the reaction (or the base line of the band, since the insertion proceeds to completion). They are reproducible to ±10% except as noted in the appropriate tables. A plot of $-\ln(A - A_\infty)$ *vs.* time for the reaction of h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ with SO_2 at −45° is shown in Figure 3.

Results

The metal alkyls, aryls, and *S*-sulfinates employed in this study are either known compounds or close analogs thereof. All new complexes were synthesized by the appropriate adaptations of the literature methods and characterized by a combination of analytical and spectroscopic techniques. As may be seen in Table I, several newly prepared *S*-sulfinates of the type (h^5-ring)$Fe(CO)_2S(O)_2R$ show four carbonyl stretching frequencies in their infrared spectra. This phenomenon had been noted earlier[21] and is best attributed to the presence of rotamers owing to restricted rotation about the Fe–S bond.[39]

The alkyl and aryl complexes examined display a broad spectrum of reactivity toward neat SO_2. It ranges from the insertions which at −65° are too rapid

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(38) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, p 12.

(39) J. W. Faller, *Inorg. Chem.*, 8, 767 (1969).

Table III. Reactions of h^5-$C_5H_5Fe(CO)_2R$ Alkyls with Neat Sulfur Dioxide[a]

R[b]	Rate (k_{obsd}, sec^{-1})	Rel k_{obsd}	Taft σ^* [i]	ν(CO), cm^{-1} [j]
$CH_2Si(CH_3)_3$	Very fast at −65° [d]		−0.26	2012, 1961
$CH_2CH{=}CHCH_3$	Very fast at −65° [d]		+0.13	2010, 1959
CH_2CH_3	Very fast at −65° [d]		−0.10	2010, 1956 (*k*, 1937)
$CH(CH_3)_2$	Very fast at −65° [d]		−0.19	2004, 1950
CH_3	(1.1×10^{-3} at −65°)		0.00	2014, 1960 (*k*, 1940)
	(2.8×10^{-3} [e])	340		
$CH_2C_6H_4OCH_3$-*p*	(1.8×10^{-4} at −61°)			2007, 1955 (2002, 1941)
	(3.8×10^{-4} [e])	46		
$CH(CH_3)C_6H_5$	(3.4×10^{-4} at −30°)			2004, 1952 (1999, 1940)
	(2.5×10^{-4} [e])	30		
$CH_2C_6H_5$[c]	(1.6×10^{-4})	19	+0.22	2010, 1959 (2004, 1944)
CH_2OCH_3	(8.3×10^{-6} [f])	1	+0.64	2017, 1961 (2006, 1947)
$CH_2CH(CH_3)_2$	Moderate at −10° [g]			2008, 1955
$CH_2CH_2C(CH_3)_3$	Moderate at −10° [g]			2008, 1955
$CH_2C(CH_3)_3$	Slow at −10° [g]		−0.16	2005, 1950
CH_2SCH_3	Slow at 25° [g]			2026, 1970 (2021, 1964)
$C(CH_3)_3$	Slow at 25° [g]		−0.30	2003, 1948
$CH_2C(O)CH_3$	Very slow at 25° [h]		+0.60	2024, 1969 (2024, 1970)
CH_2CN	Very slow at 25° [h]		+1.30	2030, 1981 (2026, 1973)

[a] At −40° unless otherwise indicated. [b] Concentration $\sim 7 \times 10^{-3}$ *M*. [c] $\Delta H^{\ddagger} = 2.9 \pm 0.4$ kcal/mol, $\Delta S^{\ddagger} = -62 \pm 2$ eu. [d] Too rapid to be measured by this method. [e] Calculated assuming $\Delta H^{\ddagger} = 2.9$ kcal/mol. [f] Accurate to ±25% only. [g] Too slow to be conveniently measured by this method; for synthetic results see Table II. [h] No detectable product after 60 hr. [i] From J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, p 97. [j] In cyclohexane (in neat SO_2). [k] Masked.

to be followed by the infrared technique employed to those which proceed immeasurably slowly at 25°. For the iron-carbon complexes which insert SO_2 at a rate measurable by our procedure, the disappearance of the metal alkyl or aryl follows the expression

$$\text{rate} = k_{obsd}[(h^5\text{-ring})Fe(CO)_2R] \qquad (1)$$

where k_{obsd} contains an indeterminable dependence on the concentration of SO_2. Previous studies[7] have shown that the O-bonded sulfinate is the first detectable insertion product for several metal alkyls and aryls. It then isomerizes to the S-bonded sulfinate. In this investigation we measured only the rates of scission of the Fe–C σ bonds by SO_2 to yield the corresponding, detectable sulfinato products. Because all of the complexes studied here are structurally very similar to those whose *O*-sulfinates had been observed earlier, a common reaction pathway has been assumed for their SO_2 insertion.

The rate constants, k_{obsd}, for the Fe–C complexes whose reactions were investigated at several temperatures are listed in Supplementary Table IIa.[14] For reactions in which solvent appears to be involved in the transition state, it is not uncommon to compute second-order rate constants, k_2, by dividing k_{obsd} by the concentration of the solvent. However, we have refrained from doing this for reasons stated elsewhere[40] and because strong solvation of the *O*-sulfinato products[7] suggests that more than one molecule of SO_2 may be involved in the transition state. Several metal alkyls and aryls other than those listed in Supplementary Table IIa were investigated kinetically, but only at one temperature. This is because they react either too slowly at the higher temperatures or too rapidly at the lower temperatures in the experimentally accessible range of −70 to −23°. Those complexes whose insertion proceeds slowly at the above-indicated temperatures were examined under synthetic conditions at −10 or 25°. Preparative data on these latter reactions are provided in Table II. Although the data are rather qualitative because of material losses sustained on work-up, they do cast information on the relative reactivities of the more slowly inserting Fe–C complexes.

In Table III are listed the alkyls h^5-$C_5H_5Fe(CO)_2R$ in descending order of reactivity toward SO_2 at −40°. For broader comparison the complexes inserting SO_2 very rapidly at −65° or very slowly at 25° are included together with those whose k_{obsd} was determined. Also provided, for correlation purposes with the rate data, are the Taft σ^* parameters and the ν(CO) values for the metal alkyls. Activation parameters were determined for the reaction of SO_2 with h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$: $\Delta H^{\ddagger} = 2.9 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger} = -62 \pm 2$ eu. The above insertion was found to be insensitive to presence of moisture in the SO_2 at −45° or even to trace amounts of deliberately added water. This stands in sharp contrast to the reaction of SO_2 with $CH_3Co(dmgH)_2(C_5H_5N)$ (dmgH = dimethylglyoximato) which undergoes marked acceleration by water.[41] Addition of a free radical scavenger, 2,2-diphenyl-1-picrylhydrazyl (1:1 molar ratio), to a solution of h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ in SO_2 at −40° does not affect the rate of the insertion either. Likewise, the use of $S_2O_5^{2-}$ (also 1:1 molar ratio) in conjunction with the same metal alkyl in SO_2 at −52° has no apparent effect on the velocity of the reaction.

Table IV contains the aryls h^5-$C_5H_5Fe(CO)_2R$ in decreasing order of reactivity toward SO_2 at −40°. The activation parameters fall in the ranges $\Delta H^{\ddagger} = 3.4 \pm 1.1$ to 7.8 ± 0.4 kcal/mol and $\Delta S^{\ddagger} = -59 \pm 2$ to -43 ± 2 eu. The values of σ^+ and ν(CO) for the metal aryls are also provided for correlation.

Given in Table V are the rates of the reaction of SO_2 with other (h^5-ring)$Fe(CO)_2R$ alkyls and aryls at −40°. Complexes with the same R are grouped together for comparison. Some previously listed h^5-$C_5H_5Fe(CO)_2R$ compounds are included to illustrate as completely as possible variations in the rates with the nature of h^5-ring.

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(40) C. H. Langford, *J. Chem. Educ.*, **46**, 557 (1969).

(41) M. D. Johnson and G. J. Lewis, *J. Chem. Soc. A*, 2153 (1970).

Table IV. Reactions of h^5-$C_5H_5Fe(CO)_2R$ Aryls with Neat Sulfur Dioxide[a]

R^b	k_{obsd}, sec^{-1}	Rel k_{obsd}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\sigma^{+\,e}$	ν(CO), $cm^{-1\,f}$
p-$C_6H_4OCH_3$	1.4×10^{-3}	700	3.5 ± 0.5	-55 ± 2	-0.78	2027, 1971 (g, 1958)
o-$C_6H_4CH_3$	2.9×10^{-4}	150	3.4 ± 1.1	-59 ± 2		2024, 1968 (2013, 1958)
p-$C_6H_4CH_3$	6.6×10^{-5}	33	7.8 ± 0.4	-43 ± 2	-0.31	2027, 1971 (2016, 1960)
m-$C_6H_4CH_3$	$1.9 \times 10^{-5\,h}$				-0.07	2027, 1970 (2013, 1957)
	$1.4 \times 10^{-6\,c}$	~1				
C_6H_5	$2.0 \times 10^{-6\,d}$	1	7.3 ± 0.5	-52 ± 2	0.00	2023, 1972 (2018, 1960)

[a] At −40° unless otherwise indicated. [b] Concentration $\sim 7 \times 10^{-3}$ M. [c] Calculated assuming $\Delta H^{\ddagger} = 7.3$ kcal/mol. [d] Accurate to ±20% only. [e] From H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958). [f] In cyclohexane (in neat SO_2). [g] Masked. [h] At −23°.

Table V. Reactions of Various (h^5-ring)$Fe(CO)_2R$ Complexes with Neat Sulfur Dioxide[a]

Compd[b]				
Ring	R	Rate (k_{obsd}, sec^{-1})	Rel k_{obsd}[i]	ν(CO), $cm^{-1\,j}$
$(CH_3)_5C_5$	$CH_2C_6H_5$	Very fast at −60° [c]		1993, 1943
$CH_3C_5H_4$	$CH_2C_6H_5$	$(1.2 \times 10^{-3})^d$	8	2007, 1956 (2002, 1940)
C_5H_5	$CH_2C_6H_5$	(1.6×10^{-4})	1	2010, 1959 (2004, 1944)
C_9H_7	$CH_2C_6H_5$	$(1.2 \times 10^{-4})^e$	~1	2008, 1957 (2002, 1944)
$CH_3C_5H_4$	p-$C_6H_4CH_3$	$(2.8 \times 10^{-4}$ at $-47°)$	7	2019, 1967 (2012, 1955)
C_5H_5	p-$C_6H_4CH_3$	$(4.0 \times 10^{-5}$ at $-47°)$	1	2027, 1971 (2016, 1960)
$(CH_3)_5C_5$	C_6H_5	Slow at −10° [f]		2001, 1950 (1993, 1934)
$CH_3C_5H_4$	C_6H_5	Slow at −21° [g]		2024, 1967 (2015, 1958)
C_5H_5	C_6H_5	(2.0×10^{-6})		2023, 1972 (2018, 1960)
$(CH_3)_5C_5$	CH_2CN	Very slow at 25° [h]		2008, 1958
$(CH_3)_5C_5$	C_6H_5	Very slow at 25° [h]		2023, 1978

[a] At −40° unless otherwise indicated. [b] Concentration $\sim 7 \times 10^{-3}$ M. [c] Too rapid to be measured by this method. [d] $\Delta H^{\ddagger} = 5.2 \pm 0.3$ kcal/mol, $\Delta S^{\ddagger} = -52 \pm 2$ eu. [e] $\Delta H^{\ddagger} = 5.0 \pm 0.2$ kcal/mol, $\Delta S^{\ddagger} = -54 \pm 2$ eu. [f] Too slow to be conveniently measured by this method; for synthetic results see Table II. [g] Complicated by extensive decomposition. [h] No detectable product after 60 hr. [i] Calculated within each series of complexes with identical R. [j] In cyclohexane (in neat SO_2).

Discussion

Effect of R on the Reactions of h^5-$C_5H_5Fe(CO)_2R$ Alkyls. Inspection of the data in Table III reveals that when steric factors are minimized the rates of the insertion generally decrease with increasing values of (1) the Taft polar substituent constant, σ^*, of the group R or (2) the ν(CO) of the alkyl complex. The observed orders R = CH_2CH_3 > CH_3 > CH_2OCH_3 > CH_2CN and R = $CH_2C_6H_4OCH_3$-p > $CH_2C_6H_5$ are consistent with these trends. An increase in σ^* corresponds to a reduced electron-releasing ability of R.[42] Higher values of ν(CO) reflect a more positive charge at the metal and therefore are diagnostic also of decreased electron-releasing properties of R. Thus, the observed dependence of the rate on both the σ^* of R and the ν(CO) of the alkyl complex supports electrophilic scission of the Fe–R bond. The most striking exception to this behavior is provided by the complex with R = $CH_2CH{=}CHCH_3$. It reacts much more rapidly than one would predict on the basis of its positive value (+0.13) of σ^*. However, this insertion proceeds with rearrangement of the allylic moiety[31] and is thought to involve a mechanism significantly different from that operating for the metal alkyls.[43]

As the bulkiness of R increases, steric factors come into play in determining the rate of the insertion. The observed order R = CH_3 > $CH_2CH(CH_3)_2$ or $CH_2CH_2C(CH_3)_3$ > $CH_2C(CH_3)_3$ > $C(CH_3)_3$ parallels increasing crowding of the metal by the CH_3 substituents. The reactions of the metal alkyls containing R = $CH_2C(CH_3)_3$ and $C(CH_3)_3$ are much slower than one would expect from their respective negative values of σ^* (−0.16 and −0.30).

The observation that the iron alkyl with R = $CH_2C(CH_3)_3$ reacts much more slowly than that with R = CH_3 is particularly illuminating. Considering the fact that the insertion in the former complex is somewhere between 25 and 50% complete after 30 hr at −10° (*cf.* Table II), one obtains a rate constant, k_{obsd}, of 2.6×10^{-6}–6.4×10^{-6} sec^{-1}. Assuming now that the energy of activation for the insertion in h^5-$C_5H_5Fe(CO)_2CH_3$ is 2.9 kcal/mol (same as $\Delta H^{\ddagger}$ for h^5-$C_5H_5Fe(CO)_2$-$CH_2C_6H_5$ and close to $\Delta H^{\ddagger}$ for h^5-$C_5H_5Mo(CO)_3CH_3$ which is 2.7 kcal/mol[44]), one obtains $k_{obsd} = 4.7 \times 10^{-3}$ sec^{-1} at −10°. Thus at this temperature the CH_3 complex reacts about 700–1800 times faster than its $CH_2C(CH_3)_3$ counterpart. In electrophilic cleavage reactions which are accompanied by retention of configuration at the α carbon (SE2 retention), neopentyl compounds have been reported to react at about the same rate as their CH_3, CH_2CH_3, or $CH(CH_3)_2$ analogs.[45] By way of contrast, in reactions which involve inversion of configuration at the α carbon (either SN2 or SE2 inversion), the methyl group is about 2000–3,000,000 times more reactive than the neopentyl group.[46,47] Thus the relative reactivities of the h^5-$C_5H_5Fe(CO)_2R$ complexes with R = CH_3 and $CH_2C(CH_3)_3$ toward SO_2 suggest backside attack of the electrophile at the α carbon. Such a backside approach is also in harmony with the observed relatively

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[42] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

[43] R. L. Downs and A. Wojcicki, manuscript in preparation.

[44] S. E. Jacobson, Ph.D. Thesis, The Ohio State University, 1972.

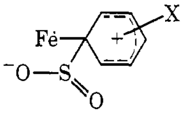
[45] E. D. Hughes and H. C. Volger, *J. Chem. Soc.*, 2359 (1961).

[46] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 13.

[47] F. R. Jensen and D. D. Davis, *J. Amer. Chem. Soc.*, **93**, 4048 (1971).

slow insertion in the iron alkyls having R = $CH_2CH(CH_3)_2$ and $CH_2CH_2C(CH_3)_3$. The recent report of inversion of configuration at the α carbon during the SO_2 insertion in *threo*-h^5-$C_5H_5Fe(CO)_2CHDCHDC(CH_3)_2$[9] significantly strengthens the above proposal of the mode of electrophilic attack.

Effect of R on the Reactions of h^5-$C_5H_5Fe(CO)_2R$ Aryls. As shown in Table IV, for the meta- and para-substituted aryl complexes, the rate constants decrease as a function of increasing σ^+. This behavior is typical of electrophilic aromatic substitution reactions.[48] A ρ value of -4.3 obtained for the insertion in question is to be compared with $\rho = -1.87$ for the SO_2 insertion in $(CH_3)_3SnR$[12a,b] and with $\rho = -2.4$ and -9.1 for the aromatic Friedel–Crafts ethylation and acetylation, respectively.[48] It appears to reflect moderate stabilization by the substituent X of the positive charge developing on the phenyl ring during the reaction. On this basis we feel that a reasonable transition state approaches structure I, which resembles the classical σ complex of electrophilic aromatic substitution reactions.[49] It is of further interest that the values of ν(CO) are virtually the same for all of the aryl complexes examined. This adds strength to the proposal that the stabilities of the transition states rather than of their respective ground states determine the relative reactivities in the insertion.



I

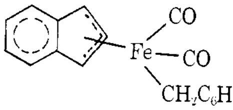
It is also noteworthy that the low $\Delta H^{\ddagger}$ (3.4 and 3.5 kcal/mol, respectively) causes the iron aryls with R = *p*-$C_6H_4OCH_3$ and *o*-$C_6H_4CH_3$ to undergo the fastest insertion (Table IV). This is in spite of their most negative $\Delta S^{\ddagger}$ which would tend to slow down these reactions. The high reactivity of the two compounds may be a consequence of the ability of their aryl groups best to stabilize the developing charges in the transition state. This would in turn lead to extensive solvation by SO_2 thus weakening the Fe–C bond and promoting its cleavage.

Effect of h^5-ring on the Reactions of (h^5-ring)$Fe(CO)_2R$. Fom the data assembled in Table V it is readily seen that when R = $CH_2C_6H_5$ the rates of the insertion increase with the increasing number of methyl substituents on the cyclopentadienyl ring. Accordingly, the reactivities vary with h^5-ring in the order $C_5H_5 < CH_3C_5H_4 \ll (CH_3)_5C_5$. The change is relatively small (eightfold) on going from h^5-C_5H_5 to h^5-$CH_3C_5H_4$ but very large from h^5-$CH_3C_5H_4$ to h^5-$(CH_3)_5C_5$. The values of ν(CO) for the three benzyl complexes decrease from h^5-C_5H_5 to h^5-$(CH_3)_5C_5$, indicating that the electron density on the iron increases as the extent of methyl substitution on the ring increases. This is not unexpected since the electron-releasing methyl groups should enhance donor strength of the *pentahapto*cyclopentadienyl ligand. An increase in the electron density on the metal in turn leads to a greater carbanionic character of R. Therefore, the observed order of reactivity toward SO_2 is entirely consistent with electrophilic cleavage of the Fe–R bond.

By contrast with the aforementioned reactivities of the benzyl complexes, metal aryls of the type (h^5-ring)$Fe(CO)_2R$ exhibit less regularity in their behavior toward SO_2. When R = *p*-$C_6H_4CH_3$, the rate of the insertion increases from h^5-ring = C_5H_5 to $CH_3C_5H_4$, as observed for the analogous R = $CH_2C_6H_5$ complexes. However, when R = C_6H_5, methyl substitution on the cyclopentadienyl ring inhibits the reaction; accordingly, h^5-ring = $C_5H_5 > (CH_3)_5C_5$. The phenyl complex (h^5-$CH_3C_5H_4$)$Fe(CO)_2C_6H_5$ also reacts more slowly than h^5-$C_5H_5Fe(CO)_2C_6H_5$, but extensive decomposition during its insertion precludes meaningful comparisons. The slow reaction of $[h^5\text{-}(CH_3)_5C_5]Fe(CO)_2C_6H_5$ compared to h^5-$C_5H_5Fe(CO)_2C_6H_5$ may be a result of the greater $Fe{=}C_6H_5$ π bonding in the former metal aryl owing to the higher electron density at its iron. Generally, inductive effects are thought to be more important than resonance effects (π bonding) in metal–aryl bonding for transition metal aryl carbonyls.[50] Nevertheless, some increase in $Fe{=}C_6H_5$ π bonding is expected on going from h^5-$C_5H_5Fe(CO)_2C_6H_5$ to $[h^5\text{-}(CH_3)_5C_5]Fe(CO)_2C_6H_5$. Such an increase, although not detectable from the positions of the ν(CO) of the two phenyl complexes, may be sufficient to strengthen substantially the latter Fe–C_6H_5 bond to electrophilic cleavage. Since the exact contributions of the σ and π components of the Fe–C_6H_5 linkages are not easy to assess and since the two effects are compensatory in controlling electron density at the α carbon, any further attempts at rationalization of the above data would be mere conjecture.

It is noteworthy that the use of the h^5-$(CH_3)_5C_5$ ring in conjunction with strong electron-withdrawing groups R, *viz.*, CH_2CN and C_6F_5, has no measurable accelerating effect on the insertion into the Fe–R bond. These complexes, like the corresponding h^5-$C_5H_5Fe(CO)_2R$, show no visible reaction with SO_2 at 25°.

Comparison of the rates of the SO_2 insertion in h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ and h^5-$C_9H_7Fe(CO)_2CH_2C_6H_5$ is of interest. In the indenyl complex a mechanism exists for the iron to vacate an orbital for attack by SO_2 through formation of an h^3-allyl structure such as that represented by II. An analogous structure is thought to be responsible for the higher reactivity (*ca.* ten- to 20-fold) of h^5-$C_9H_7Mo(CO)_3CH_3$ than of h^5-$C_5H_5Mo(CO)_3CH_3$ toward P-donor ligands in the carbon monoxide insertion.[51] However, the rates of the SO_2 insertion in the two iron complexes are almost the same at $-40°$, and their $\Delta H^{\ddagger}$ values differ only by *ca.* 2 kcal/mol. This suggests that such a vacant orbital on the iron does not play a major role in the SO_2 insertion. The above finding is therefore entirely consistent with an electrophilic attack by SO_2 on the α carbon rather than with a nucleophilic attack on the metal.



II

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[48] R. Breslow, "Organic Reaction Mechanisms," W. A. Benjamin, New York, N. Y., 1965, Chapter 5.

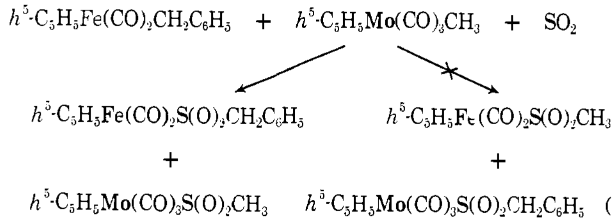
[49] C. A. Olah, *Accounts Chem. Res.*, 4, 240 (1971).

[50] (a) R. P. Stewart and P. M. Treichel, *J. Amer. Chem. Soc.*, **92**, 2710 (1970); (b) A. N. Nesmeyanov, L. G. Makarova, N. A. Ustynyuk, B. A. Kvasov, and L. V. Bogatyreva, *J. Organometal. Chem.*, **34**, 185 (1972).

[51] A. J. Hart-Davis and R. J. Mawby, *J. Chem. Soc. A*, 2403 (1969).

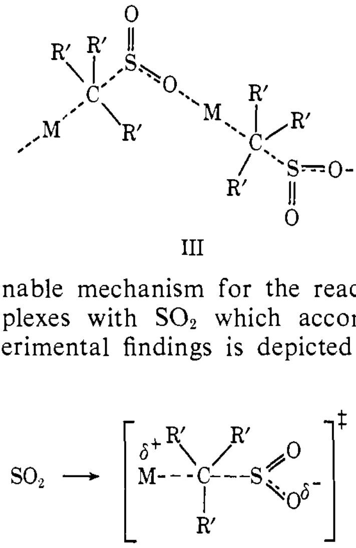
Mechanism of the Insertion Reaction. Evidence has already been presented (*vide supra*) that in the alkyl complexes investigated the electrophile attacks the α carbon of R from the backside. The attacking electrophile is almost certainly sulfur dioxide itself rather than, *e.g.*, a cationic species such as SO^{2+}.[52,53] This receives support from the virtual insensitivity of the rate of the insertion in h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ to the added $S_2O_5^{2-}$ ($SO_2 + SO_3^{2-}$ [54]). A substantial inhibition of the reaction would be expected if SO^{2+} were the reactive species.

A free radical pathway contributes little, if anything, to the insertion, since addition of the radical scavenger 2,2-diphenyl-1-picrylhydrazyl to a solution of h^5-C_5H_5-$Fe(CO)_2CH_2C_6H_5$ in SO_2 has no effect on the rate. Another experiment which bears on the mechanism of the insertion is summarized in eq 2. A similar result



(2)

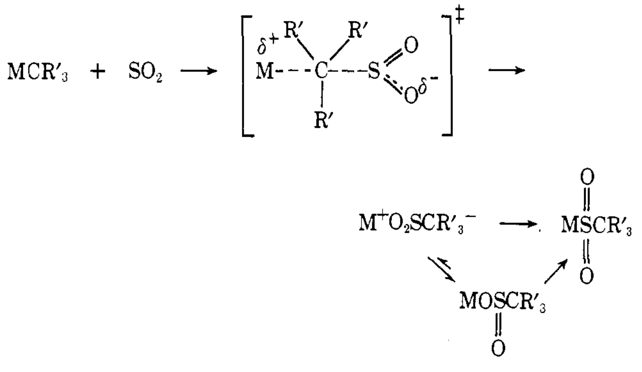
was obtained when h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ and $Mn(CO)_5CH_3$ were allowed to react together with neat SO_2. The absence of the *S*-sulfinato cross-products in these reactions precludes intermolecular interactions of the general type III or random recombination of the ions.



III

A reasonable mechanism for the reaction of metal alkyl complexes with SO_2 which accommodates the above experimental findings is depicted in Scheme I.

Scheme I



M = (h^5-ring)Fe(CO)$_2$

The large and negative values of $\Delta S^{\ddagger}$ (−62 to −52 eu) for the scission of the M–CR′$_3$ bond no doubt result from the developing charges in the transition state and, very likely, from extensive solvation by SO_2. These entropies of activation are comparable to those reported for the Menschutkin reaction, $R_3N + RX$,[55] and for the oxidative addition of RX to $Ir[P(C_6H_5)_3]_2(CO)X$,[56] where highly polar transition states have been implicated. For further comparison, $\Delta S^{\ddagger}$ for the solvent-assisted CO insertion ranges from −33 to −17 eu[3] and that for the SO_2 insertion into the Sn–$CH_2C_6H_5$ bond of $(CH_3)_3SnCH_2C_6H_5$ in methanol is −40 eu.[12c] Some support for the pronounced solvation in the SO_2 insertion comes from the observation that several *O*-sulfinato intermediates, MOS(O)CR′$_3$, are remarkably stable in neat SO_2 but undergo rapid linkage isomerization upon removal of the solvent.[7]

The activated complex depicted in Scheme I cannot, for geometric reasons, give the *O*-sulfinate directly in a concerted fashion. Thus we propose scission of the M–CR′$_3$ bond to yield $M^+R'_3CSO_2^-$ which, by rotation of the anion, gives a contact ion pair $M^+O_2SCR'_3{}^-$. The formation of $M^+O_2SCR'_3{}^-$ has to be invoked also for chemical reasons; this we have already discussed elsewhere.[7] The contact nature of the ion pair is suggested by the absence of the *S*-sulfinato cross-products when two alkyl complexes having different M and CR′$_3$ groups are allowed to react together with neat SO_2 (*vide supra*). The existence of such an ion pair in liquid SO_2 would be promoted by the low dielectric constant of the medium (15.4 at 0° [57]). Interestingly, calculations on a number of compounds of formulas MX (M = Li, Na, K; X = Cl, Br, I) and R_4NX (R = CH_3, C_2H_5; X = Cl, Br, I, ClO_4, *inter alia*) have shown that there is little or no solvent separation of paired ions in sulfur dioxide.[58] This conclusion stems from determination of the Bjerrum distances of closest approach[59] and comparison of the obtained values with the sum of the appropriate ionic radii.

The proposed ion pair $M^+O_2SCR'_3{}^-$ cannot be detected by infrared or ^1H nmr spectroscopy; therefore its concentration must be very low. As shown in Scheme I,[60] recombination of the ions is thought to result in the formation of both the *O*-sulfinate and the *S*-sulfinate. Since the *O*-sulfinate represents a readily detectable intermediate in the insertion, the former mode of recombination proceeds more rapidly than the latter. Isomerization of the *O*-sulfinate to the *S*-sulfinate appears to occur both intramolecularly and through dissociation to $M^+O_2SCR'_3{}^-$; this aspect of the insertion reaction was considered elsewhere.[7]

The insertion of SO_2 in the aryl compounds likely

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[52] Although the extent of the dissociation $2SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-}$ in neat SO_2 has been shown not to be significant,[53] we have nonetheless taken into consideration possible presence of such ions in trace amounts.

[53] T. H. Norris, *J. Phys. Chem.*, **63**, 383 (1959).

[54] J. Lauder and E. Rossiter, *Nature (London)*, **163**, 567 (1949).

[55] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 137.

[56] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3511 (1966).

[57] N. N. Lichtin and H. P. Leftin, *J. Phys. Chem.*, **60**, 160 (1956).

[58] N. N. Lichtin, *Progr. Phys. Org. Chem.*, **1**, 75 (1963).

[59] R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience, New York, N. Y., 1959, Chapter 16.

[60] In connection with this mechanism it is noteworthy that the formation of (h^5-1-CH_3-3-$C_6H_5C_5H_3$)Fe(CO)[P(C_6H_5)$_3$]S(O)$_2$CH$_3$ from (h^5-1-CH_3-$C_6H_5C_5H_3$)Fe(CO)[P(C_6H_5)$_3$]CH$_3$ in neat SO_2 at −60° proceeds with high (*ca.* 80%) stereoselectivity (presumably retention) at iron. This requires that the contact ion pair (h^5-1-CH_3-3-$C_6H_5C_5H_3$)-Fe(CO)[P(C_6H_5)$_3$]$^+$$O_2SCH_3^-$, if indeed present, possess high configurational stability. For further details see A. Wojcicki and T. G. Attig, Abstracts of Papers, 6th International Conference on Organometallic Chemistry, Amherst, Mass., Aug 1973.

proceeds through the intermediacy of a σ complex, I. This complex may then dissociate to an ion pair, $M^{+}O_2SC_6H_4X^{-}$, or form the *O*-sulfinate in a concerted fashion through simultaneous scission of the $M-C_6H_4X$ bond and formation of the M–OS(O) bond, or do both. The remaining aspects of the reaction, although not specifically elucidated, are probably similar to those for the alkyl complexes.

Before concluding we wish to address ourselves to two points which are relevant to the theme of this investigation. First, we wish to emphasize that the reaction picture presented herein may not apply to the SO_2 insertion in various coordinatively unsaturated metal alkyls and aryls. In fact, the recent isolations of $Rh[P(C_6H_5)_3]_2(CO)(SO_2)CF_2CHF_2$[61] and $Ir[P(C_6H_5)_3]_2(CO)(SO_2)C{\equiv}CR$[62] from the appropriate four-coordinate complexes and SO_2 suggest that the SO_2 insertion in $PtL_2(R)Cl$ (L = P-, As-, Se-, and Te-donor ligands) to give $PtL_2[S(O)_2R]Cl$[63] may proceed through a five-coordinate intermediate, $PtL_2(SO_2)(R)Cl$. Similarly, $(h^5\text{-}C_5H_5)_2Ti(CH_3)Cl$ may undergo the insertion[64] *via* initial coordination of SO_2 to the titanium. Our second point is that this study has revealed significant mechanistic differences between the CO insertion and the SO_2 insertion, the former having been shown earlier to involve an intramolecular transfer of R onto a coordinated CO.[3] These differences further underscore absence of mechanistic connotations in the term "insertion reaction."

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Supplementary Material Available. A listing of analytical data and rate constants will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-6962.

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[61] G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc. A*, 1392 (1970).

[62] C. K. Brown, D. Georgiou, and G. Wilkinson, *J. Chem. Soc. A*, 3120 (1971).

[63] F. Faraone, L. Silvestro, S. Sergi, and R. Pietropaolo, *J. Organometal. Chem.*, **46**, 379 (1972).

[64] P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organometal. Chem.*, **33**, 181 (1971).

Reactions of Dithiolene Complexes with Amines. II. The Formation and Properties of Mixed-Ligand Dithiolene α-Diimine Complexes of Nickel

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Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received May 15, 1973*

Abstract: A series of neutral, four-coordinate, square-planar nickel complexes composed of one dithiolene and one α-diimine ligand have been prepared by (a) substitution of bis(dithiolene) nickel complexes, (b) substitution of a bis(α-diimine) nickel complex, and (c) ligand exchange between bis(dithiolene) and bis(α-diimine) nickel complexes. The dithiolene ligands RC(S)C(S)R contain R = CN, CF_3, and Ph, and the α-diimine ligands are *o*-phenylenediimine, biacetylbisanil, 1,10-phenanthroline, and derivatives. The complexes undergo electron-transfer reactions, studied voltammetrically, and exist as members of an electron-transfer series of complexes with charges +1, 0, −1, −2. Species other than the neutral complexes have not been isolated. Spectra of the strongly colored complexes show the same pattern as the bis-ligand complexes, with the exception that the low energy (12–20 kK) intense charge-transfer absorption is negatively solvatochromic. The complexes evidently possess a substantial ground-state electric dipole which is reduced or reversed by this low-energy dithiolene to α-diimine charge-transfer transition. On the basis of the spectral and electrochemical potential data a partial molecular orbital model for the mixed-ligand complexes is proposed.

Numerous four-coordinate bis(dithiolene) nickel complexes, I, are known.[1] Analogous bis(α-diimine) complexes, II, have been described.[2] However, the literature contains but passing reference, without details, to two examples of the mixed ligand, dithiolene α-diimine type of complex, III. The compound Ni(mnt)(dipy)[3] is listed as red and diamagnetic in a review,[4] and Ni(S—S,Ph)(dipy) was prepared by reaction of Ni(S—S,Ph)($(CH_3S)_2C_2Ph_2$) with molten 2,2′-dipyridyl and "identified by its nmr spectrum."[5] We report here the

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[1] J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

[2] A. L. Balch and R. H. Holm, *J. Amer. Chem. Soc.*, **88**, 5201 (1966).

[3] The general abbreviations for dithiolene and diimine ligands are ($S—S,R_1$) and ($N—N,R_2,R_3$), respectively. Also, (S—S,CN) ≡ mnt, ($S—S,CF_3$) ≡ tfd; phen ≡ 1,10-phenanthroline, $5\text{-}NO_2$phen ≡ 5-nitro-1,10-phenanthroline, dipy ≡ 2,2′-dipyridyl, and *o*-$C_6H_4(NH)_2$ ≡ *o*-phenylenediimine.

[4] Reference 1, p 186.

[5] G. N. Schrauzer and H. N. Rabinowitz, *J. Amer. Chem. Soc.*, **90**, 4297 (1968).