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Kinetic Studies of Sulfur Dioxide Insertion Reaction of Some h^5-$C_5H_5Fe(CO)_2R$ Alkyl Complexes in Organic Solvents

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The rates of the cleavage of the iron–carbon σ bond of h^5-$C_5H_5Fe(CO)_2R$ by SO_2 in chloroform, isopropyl alcohol, and benzene have been investigated by infrared spectroscopy in the ν(CO) region over the temperature range of 2 to 39° C. The reaction of the R = $CH(CH_3)_2$ complex is first-order in each of the iron alkyl and SO_2, and proceeds with a $\Delta H^{+} = 8.7 \pm 0.6$ kcal/mol and a $\Delta S^{+} = -45 \pm 2$ e.u. in chloroform solution. At 26° C, this insertion is approximately 7–8 times faster in chloroform or in isopropyl alcohol than in benzene. The relative second-order rate constants for the reaction of h^5-$C_5H_5Fe(CO)_2R$ with SO_2 in chloroform solution at 26° C decrease with R in the order R = $CH(CH_3)_2$ (430) > $CH_2C(CH_3)_3$ (30) ≳ $CH_2Si(CH_3)_3$ (26) > CH_3 (1) ≫ $CH_2C_6H_5$, $C(CH_3)_3$; in isopropyl alcohol, also at 26° C, the order is R = $CH(CH_3)_2$ (440) > $CH_2Si(CH_3)_3$ (57) > $CH_2C(CH_3)_3$ (24) > CH_3 (15). An associative mechanism which incorporates a polar, constrained transition state is proposed; various possible structures of the transition state are considered and discussed.

Introduction

In the previous two papers of this series we reported the kinetics and mechanism of the sulfur dioxide insertion reaction of various (h^5-$C_5H_xR'_{5-x}$)$Fe(CO)_2R$ complexes[1] and the relative reactivities toward SO_2 of several alkyls and aryls of other transition metals.[2] All of these reactions were conducted in neat sulfur dioxide, and therefore the dependence of the rate on the concentration of SO_2 could not be determined.

In order to obtain this information we have now carried out a kinetic study of the reaction between some h^5-$C_5H_5Fe(CO)_2R$ alkyl complexes and sulfur dioxide in organic solutions of chloroform, isopropyl alcohol, and benzene. A further goal of this work was to compare the rate constants, the activation parameters, and the rate profile as a function of the group R for the insertion reaction of these complexes in neat SO_2 and in SO_2-containing organic solvents.

In this paper, the last of the series on kinetics and mechanism of sulfur dioxide insertion, we report results of our investigation.

Experimental

Materials

Anhydrous grade SO_2, from Matheson, was purified and dried as given elsewhere.[3] Chemicals were procured in reagent grade quality and were used as received. Organic solvents were purified by previously employed procedures.[3]

Iron–Alkyl and –S-Sulfinate Complexes

The alkyls h^5-$C_5H_5Fe(CO)_2R$ where R = CH_3,[4] CH_2CH_3,[4] $CH(CH_3)_2$,[5] $C(CH_3)_3$,[6] $CH_2C(CH_3)_3$,[1] $CH_2Si(CH_3)_3$,[7] and $CH_2C_6H_5$,[8] and the *S*-sulfinates h^5-$C_5H_5Fe(CO)_2S(O)_2R$ where R = CH_3,[8] CH_2CH_3,[8] $CH(CH_3)_2$,[3] $C(CH_3)_3$,[1] $CH_2C(CH_3)_3$,[1] $CH_2Si(CH_3)_3$,[3] and $CH_2C_6H_5$[8] were synthesized by known procedures.

Kinetic Measurements[9]

(i) The infrared cell

The insertion reactions were run in organic solvents containing SO_2, and were followed by infrared spectroscopy. A Beckman Model IR-9 spectrophotometer was employed in conjunction with a VLT-2 variable low-temperature cell unit manufactured by Research and Industrial Instruments Co., London, England (available in the U.S. from Beckman Instruments Co., Fullerton, Calif.). It incorporated a 0.5-mm AgCl sample cell. Metal screws sealed the cell so as to eliminate all dead space above the solution. A 0.5-mm reference cell was used with isopropyl alcohol and benzene solvents.

(ii) Temperature control and measurement

The temperature in the cell was maintained at 2–39° C, with ice being employed as a coolant for the lower temperatures. The temperature was adjusted manually with a precision of within ±0.5° C by means of two external heaters attached to the cell holder from a variable 0- to 12-volt power unit. An iron–constantan thermocouple in conjunction with a Leeds and Northrup Co. No. 8690 millivolt potentiometer measured the temperature of the solution as described previously.[1] The beam of the spectrophotometer heated the reaction mixture by 1.5–2.0° C during the first five minutes, but after that the temperature remained constant to ±0.5° C. This change was, of course, recorded by the potentiometer.

(iii) Preparation of solutions

The organic solvent was first saturated with nitrogen by continuous bubbling for $^1/_2$ hr. Part of this solution was then similarly treated with gaseous SO_2. Appropriate volumes of the two solutions were introduced into a volumetric flask to give approximately the desired concentration of SO_2;[10] the flask was then quickly stoppered.

Because of the general instability and air sensitivity of the iron alkyls employed in this study, these complexes were either sublimed or chromatographed before each kinetic run. The freshly purified complex was introduced into the volumetric flask containing a solution of SO_2 at the desired temperature. The resulting mixture was well shaken and an aliquot of it was syringed into the sample cell of the low-temperature unit at the preset temperature.

The concentration of SO_2 in the solution was determined by a standard titrimetric method.[11] An aliquot of the solution was pipetted into a flask containing a large volume of H_2O (*ca.* 200 ml), the flask was stoppered, and its contents were vigorously shaken to extract the SO_2 into the aqueous layer. This layer was titrated with 0.2*M* NaOH using phenophthalein as indicator. At least three titrations were made at each SO_2 concentration and were reproducible to within ±3%.

(iv) Collection and treatment of data

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 complex. The reactions of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ were followed for 2–3 half-lives; those of the other, more slowly reacting complexes were monitored for fewer half-lives because of decomposition. Pertinent information is furnished in the appropriate tables of data. Figure 1 shows the infrared spectra in the ν(CO) region of a solution of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ and SO_2 in chloroform at various time intervals.

All reactions were run under pseudo-first-order conditions, with at least a 15-fold excess of SO_2 over the iron alkyl. A concentration of the alkyl complex of 6×10^{-3} to $7 \times 10^{-3}M$ was generally employed. The pseudo-first-order rate constants, k_{obsd}, were obtained by plotting $-\ln(A-A_\infty)$ *vs* time, as described previously.[1] A plot of $-\ln(A-A_\infty)$ *vs* time for the reaction of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ with SO_2 in chloroform is shown in Figure 2. A least two kinetic runs were made at each concentration and temperature. Results are reproducible to ±7% for h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$; larger errors were found for the slower reacting alkyl complexes, as shown with the appropriate tabulated data.

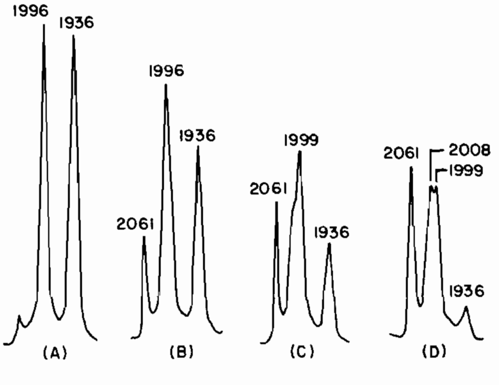


Figure 1. The infrared spectra in the ν(CO) region of a solution of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ (*ca.* $7 \times 10^{-3}M$) and SO_2 (0.28*M*) in chloroform at 26° C: (A) 5 min, (B) 70 min, (C) 140 min, and (D) 270 min from its preparation. The bands at 1996 and 1936 cm^{-1} are due to h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$, whereas the remaining bands are due to the corresponding *O*- and *S*-sulfinato products.

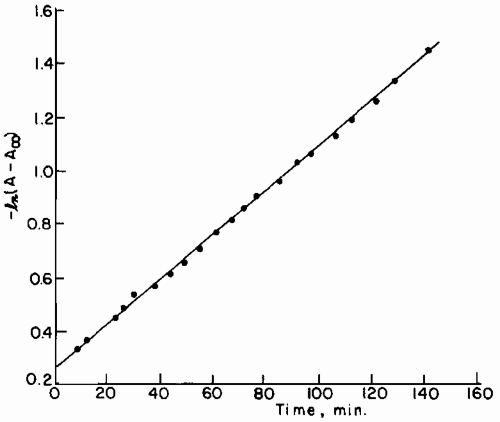


Figure 2. Plot of $-\ln(A-A_\infty)$ *vs* time for the reaction of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ (*ca.* $7 \times 10^{-3}M$) with SO_2 (0.57*M*) in chloroform at 8.8° C.

Results

Iron–alkyl complexes of the formula h^5-$C_5H_5Fe(CO)_2R$ generally react slowly with SO_2 in saturated solutions of organic solvents; this is in contrast to their much greater reactivity in neat sulfur dioxide.[8] Irrespective of the medium employed, these insertion reactions lead to the formation of h^5-$C_5H_5Fe(CO)_2S(O)_2R$ as the final, isolable product.

We have now observed that, under ambient conditions, the isopropyl complex h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ reacts with SO_2 in organic solvents at a conveniently measurable rate and, when care is exercised, without noticeable decomposition. Accordingly, most of the kinetic data reported herein were collected for h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ in the temperature range of 2–39° C.

Evidence was presented in an earlier paper[3] that the first detectable product of the reaction between h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ and SO_2 in chloroform, ispropyl alcohol, or benzene is the *O*-sulfinate, h^5-$C_5H_5Fe(CO)_2OS(O)CH(CH_3)_2$. It then rearranges to the corresponding *S*-sulfinate, h^5-$C_5H_5Fe(CO)_2S(O)_2CH(CH_3)_2$. Analogous *O*-sulfinato intermediates are assumed to be formed in the insertion of the other alkyl compounds investigated herein; in several cases, such intermediates have been actually detected in liquid SO_2.[3] In this study we measured only the rates of scission of the Fe–R σ bonds by SO_2 to yield the appropriate, detectable sulfinato products. The *O*-sulfinate to *S*-sulfinate rearrangement was not examined.

Kinetic runs were made for h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ in chloroform solution at several temperatures in the range of 2–39° C, and in isopropyl alcohol and benzene solutions at 26° C. In each experiment, a large (15- to 260-fold) excess of SO_2 over the iron complex was employed. In Table I are presented pseudo-first-order rate constants, k_{obsd}, for these runs; they increase with an increase in the concentration of SO_2. A plot of k_{obsd} *vs* $[SO_2]$, shown in Figure 3 for a run in chloroform solution at 26° C, gives a straight line and thus shows that

$$k_{obsd} = k_2[SO_2] \tag{1}$$

and hence

$$\frac{-d[h^5\text{-}C_5H_5Fe(CO)_2CH(CH_3)_2]}{dt} = k_2[h^5\text{-}C_5H_5Fe(CO)_2CH(CH_3)_2][SO_2] \tag{2}$$

where k_2 is a second-order rate constant. A similar relationship holds for the insertion reaction of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ in the solvents isopropyl alcohol and benzene. The appropriate rate constants are presented in Table II. In considering concentrations of SO_2 in benzene no allowance was made for the formation of a 1 : 1 benzene–SO_2 π-complex.[12] For the insertion in chloroform solution, $\Delta H^{+} = 8.7 \pm 0.6$ kcal/mol and $\Delta S^{+} = -45 \pm 2$ e.u.

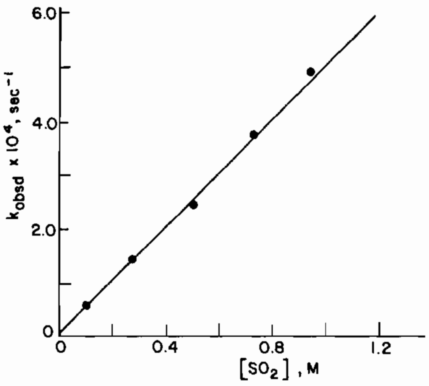


Figure 3. Plot of k_{obsd} *vs* concentration of SO_2 for the reaction of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ with SO_2 in chloroform at 26° C.

TABLE I. Pseudo-First-Order Rate Constants for Reaction of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ with Sulfur Dioxide at Various Temperatures.[a]

Solvent	Temp,° C	$[SO_2]$, *M*	$k_{obsd} \times 10^4$, sec^{-1}
Chloroform	2	0.572	0.872
	4	0.572	0.816
	14	0.572	1.50
	26	0.106	0.577
	26	0.276	1.44
	26	0.498	2.48
	26	0.572	2.92
	26	0.730	3.74
	26	0.946	4.90
	26	1.44	7.17
	37	0.572	4.98
	39	0.572	5.13
Isopropyl alcohol	26	0.191	0.988
	26	0.354	1.97
	26	0.756	4.36
	26	1.26	6.71
Benzene	26	1.07	0.759
	26	1.80	1.32

[a] $[h^5\text{-}C_5H_5Fe(CO)_2CH(CH_3)_2] = 6 \times 10^{-3}$–$7 \times 10^{-3}$ *M*.

In Table III are listed the alkyls h^5-$C_5H_5Fe(CO)_2R$ in descending order of reactivity toward SO_2 in chloroform, isopropyl alcohol, and benzene solutions at 26 °C. A second-order rate expression of the type given for h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ in equation (2) has been assumed to hold for all the other alkyl compounds, which were not studied in the same detail as the isopropyl complex because of the much slower reactions. In chloroform ($\varepsilon = 4.81$[13]) solution, the

TABLE II. Second-Order Rate Constants and Activation Parameters for Reaction of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ with Sulfur Dioxide at Various Temperatures.

Solvent	Temp,° C	$k_2 \times 10^4$, M^{-1} sec^{-1}	ΔH^{+}, kcal/mol	ΔS^{+}, e.u.
Chloroform	2	1.52	8.7 ± 0.6	−45 ± 2
	4	1.43		
	14	2.63		
	26	5.10		
	37	8.70		
	39	8.95		
Isopropyl alcohol	26	5.45		
Benzene	26	0.710		

TABLE III. Second-Order Rate Constants for Reactions of h^5-$C_5H_5Fe(CO)_2R$ with Sulfur Dioxide at 26° C.

Solvent	R	Taft σ^*	$k_2 \times 10^4$ M^{-1} sec^{-1}	Rel k_2
Chloroform	$CH(CH_3)_2$	–0.19	5.2	430
	$CH_2C(CH_3)_3$	–0.16	0.36[a]	30
	$CH_2Si(CH_3)_3$	–0.26	0.31[a]	26
	CH_3	0.00	0.012[a,b]	1
	$CH_2C_6H_5$	+0.22	v. slow[c]	
	$C(CH_3)_3$	–0.30	v. slow[c]	
Isopropyl alcohol	$CH(CH_3)_2$		5.3	440
	$CH_2Si(CH_3)_3$		0.68[a]	57
	$CH_2C(CH_3)_3$		0.29[a]	24
	CH_3		0.18[a]	15
Benzene	$CH(CH_3)_2$		0.71	59

[a] 20–25% error in reproducibility. [b] Reaction followed only to 30% completion because of slow rate. [c] Only a trace of product after one week.

rates decrease with R in the order R = $CH(CH_3)_2$ (430) > $CH_2C(CH_3)_3$ (30) $\gtrsim$ $CH_2Si(CH_3)_3$ (26) > CH_3 (1) $\gg$ $CH_2C_6H_5$, $C(CH_3)_3$ (v. slow). The ethyl complex, h^5-$C_5H_5Fe(CO)_2CH_2CH_3$, decomposed extensively during the insertion thus precluding collection of reliable data. In isopropyl alcohol (ε = 18.3[13]) solution, the rate constants are comparable to those in chloroform for every alkyl complex examined except that with R = CH_3, which reacts about 15 times more rapidly than in $CHCl_3$. The insertion in benzene (ε = 2.28[13]) proceeds significantly more slowly than in chloroform or isopropyl alcohol, and therefore was studied only for the R = $CH(CH_3)_2$ complex. A slow rate of the sulfur dioxide insertion in benzene, compared to methanol, was recently noted for $(CH_3)_3SnC_6H_5$ by Fong and Kitching.[14]

The rate of the SO_2 insertion reaction of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ in isopropyl alcohol is increased by added $LiClO_4$. Accordingly, for a solution 7 × $10^{-3}M$ in the alkyl complex, 0.35M in SO_2, and 0.70M in $LiClO_4$, a k_{obsd} of 7.25 × 10^{-4} sec^{-1} was obtained at 26° C. This is to be compared with a k_{obsd} of 1.97 × 10^{-4} sec^{-1} for a solution of comparable composition, but without $LiClO_4$, almost a 4-fold enhancement of rate. By way of contrast, addition of 2,2-diphenyl-1-picrylhydrazyl (7 × $10^{-3}M$), a free radical scavenger, to a solution of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ (7 × $10^{-3}M$) and SO_2 (0.42M) in chloroform at 26° C has no perceptible effect on the velocity of the insertion.

Discussion

The complex h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ reacts very rapidly with neat SO_2 even at –65° C;[1] in contrast, this same reaction proceeds at a moderate rate in organic solvents and can be studied kinetically at ambient temperatures. The derived rate expression, given in equation (2), indicates that one molecule of SO_2 is involved in the transition state. The same dependence on the concentration of SO_2 was obtained recently by Kitching for the monoinsertion of SO_2 in various tin complexes of general formulas $(CH_3)_3SnC_6H_4X$[14] and $(CH_3)_3SnCH_2C_6H_4X$.[15]

The enthalpy of activation of 8.7 kcal/mol for the reaction of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ with SO_2 in chloroform is higher than that reported for the insertion in various complexes (h^5-$C_5H_xR_{5-x}'$)$Fe(CO)_2R$ in liquid SO_2. Accordingly, $\Delta H^{\ddagger}$ for the SO_2 insertion in h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ is 2.9 kcal/mol, and for that in several (h^5-$C_5H_xR_{5-x}'$)$Fe(CO)_2R$ compounds examined falls in the range of 2.9–7.4 kcal/mol.[1] For the reactions of $(CH_3)_3SnC_6H_5$[14] and $(CH_3)_3SnCH_2C_6H_5$[15] with SO_2 in methanol, $\Delta H^{\ddagger}$ = 7.4 and 9.6 kcal/mol, respectively, values comparable to that obtained in our study. The entropy of activation of –45 e.u. for the reaction of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ with SO_2 in chloroform is less negative than that obtained for the reaction of (h^5-$C_5H_xR_{5-x}'$)$Fe(CO)_2R$ in neat SO_2. Thus, $\Delta S^{\ddagger}$ for the SO_2 insertion in h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ is –62 e.u., and spans the range of –62 to –43 e.u. for several (h^5-$C_5H_xR_{5-x}'$)$Fe(CO)_2R$ complexes examined.[1] In contrast, the reactions of $(CH_3)_3SnC_6H_5$[14] and $(CH_3)_3SnCH_2C_6H_5$[15] with SO_2 proceed with $\Delta S^{\ddagger}$ = –40 and –43 e.u., respectively, values which are less negative than the preceding, but similar to the result of this work. The higher $\Delta H^{\ddagger}$ and the less negative $\Delta S^{\ddagger}$ in organic solvents as compared to neat SO_2 may reflect reduced solvation by the SO_2 of the transition state in the former media. Nonetheless, a substantial loss in freedom of vibrational and translational modes still occurs for the insertion in organic solvents.

The second-order rate constants for the insertion reaction of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ in chloroform and isopropyl alcohol solvents are approximately the same, but appreciably (7–8 times) larger than that for benzene solution. The above difference likely arises from the transition state being more polar than the ground state; this inference receives further support from the value of $\Delta S^{\ddagger}$ for the SO_2 insertion in chloroform *(vide supra)*. The slowest rate of the insertion reaction in benzene may be ascribed only in part to the formation of a 1:1 benzene–SO_2 π-complex[12] which lowers the concentration of free SO_2. Thus, using the equilibrium constant, K_c = 4.71 × 10^{-2} M^{-1},[12] for the formation of this complex at 25° C, assuming that the volume of the solution is essentially that of the solvent, and taking the density of benzene to be 0.879 g/cc,[16] one obtains $[SO_2]$ = 0.70M when the concentration of total SO_2 in solution is 1.07M

(see Table I). This then raises the value of k_2 by *ca.* 50%, an increase which is clearly insufficient to change the relative order of rates for the insertion in benzene and the other two solvents.

The remaining h^5-$C_5H_5Fe(CO)_2R$ complexes whose reactions with SO_2 were investigated in more than one solvent generally underwent the insertion more rapidly in isopropyl alcohol than in chloroform. Accordingly, when R = $CH_2C(CH_3)_3$ the rates are roughly the same in the two media, but when R = $CH_2Si(CH_3)_3$ and CH_3, respectively, they are about 2 and 15 times faster in isopropyl alcohol than in $CHCl_3$.[17] This general order may be an indication of the greater stabilization of the transition state by the more polar and better coordinating solvent isopropyl alcohol. Such stabilization of positive charge on iron through solvation might be expected to contribute most when the R group is small, as for R = CH_3.[18]

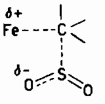
A polar nature of the transition state is further indicated by an approximately 4-fold enhancement of rate of the reaction of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ with SO_2 in isopropyl alcohol upon addition of 0.70*M* $LiClO_4$. A similar positive salt effect was recently reported for the SO_2 insertion reaction of $(CH_3)_3SnC_6H_5$ in methanol.[14] There, the acceleration is much smaller, however: 0.541*M* $LiClO_4$ increases the rate by 64%.

Turning now to a possible free radical mechanism of the insertion, we note that there is negative evidence for any significant contribution therefrom, especially in the reaction of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$. First, the reaction of this last-mentioned compound in $CHCl_3$ solvent is not affected by the addition of 2,2-diphenyl-1-picrylhydrazyl, a free radical scavenger. Second, the kinetics are well-behaved and reproducible, with no observed induction period for any of the alkyl complexes examined. Third, the reaction of h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ does not yield any detectable $[h^5$-$C_5H_5Fe(CO)_2]_2$ during the kinetic runs, and only trace amounts of it in similar, synthetic-scale experiments. A homolysis of the Fe–$CH(CH_3)_2$ bond would be expected to produce substantial $[h^5$-$C_5H_5Fe(CO)_2]_2$. Finally, the observed first-order dependence on the concentration of SO_2 and the large and negative value of $\Delta S^{\neq}$ for the insertion in h^5-$C_5H_5Fe(CO)_2CH(CH_3)_2$ argue against mechanisms which exclude significant bond-making in the transition state.

From the foregoing considerations a mechanism may be proposed which is associative in nature and which incorporates a polar, constrained transition state. Under favorable conditions, some information about the nature of the transition state for a given reaction of structurally analogous alkyl complexes may be derived by examination of the rate profile as a function of the group R.[19] However, this approach does not always yield an unequivocal answer, and therefore must be used with caution.[20]

The effect of the group R on the rates of SO_2 insertion in h^5-$C_5H_5Fe(CO)_2R$ in organic solvents is in part strictly identical with that for the insertion in neat SO_2.[1] Accordingly, the rates in all of these media vary with R in the order $CH(CH_3)_2$, $CH_2Si(CH_3)_3 >$ $CH_3 > CH_2C_6H_5$, $C(CH_3)_3$. This order is influenced by both steric (*e.g.*, $C(CH_3)_3$) and inductive properties of R. The latter are reflected in the values of the Taft polar substituent constants, σ^*,[21] given in Table III. The most striking difference between the insertion reaction in organic solvents and in liquid SO_2 is observed when R = $CH_2C(CH_3)_3$. In neat SO_2 at –10° C, the neopentyl complex is 700–1800 times less reactive than its methyl analog;[1] however, in chloroform solution at 26° C, it is 30 times as reactive, and in isopropyl alcohol at 26° C, it is about $1^1/_2$ times as reactive as the methyl derivative. This observed reversal of the relative reactivities of the neopentyl and methyl compounds on going from liquid SO_2 to organic solvents suggests that there may be a difference in mechanism in the two types of reaction media.

In general, reactions which involve a backside attack of an electrophile or a nucleophile at the α carbon of R proceed some 2000–3,000,000-fold faster for R = CH_3 complexes than for their R = $CH_2C(CH_3)_3$ counterparts.[19,22] By way of contrast, reactions which occur *via* a frontside attack at the α carbon usually have comparable rates for analogous neopentyl and methyl complexes.[23] Thus, the results of this study suggest that the reaction of SO_2 with h^5-$C_5H_5Fe(CO)_2R$ in organic solvents is a bimolecular electrophilic process of the type S_E2 retention[24] (**I**) or S_Ei[24] (**II**) rather than S_E2 inversion[24] (**III**), proposed for the insertion in liquid SO_2.[1]



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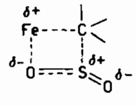

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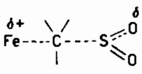

III

Whitesides[25] has recently examined the stereochemistry of the SO_2 insertion reaction of h^5-$C_5H_5Fe(CO)_2CHDCHDC(CH_3)_3$ to give h^5-$C_5H_5Fe(CO)_2S(O)_2CDHCHDC(CH_3)_3$ under a variety of experimental conditions. He finds that in pentane, chloroform, methanol, and *N,N*-dimethylformamide under a 42 psi pressure of SO_2, this reaction proceeds with complete (> 95%) inversion of configuration at the α carbon, as it also does in neat SO_2. However, the organic solutions employed in these stereochemical studies contain SO_2 in concentrations which are significantly higher than those used in our work. Approximate calculations[26] show that at 25° C and under a 42 psi pressure of SO_2, chloroform solutions are *ca.* 4.6*M* in SO_2 (or contain *ca.* 2:3 SO_2–$CHCl_3$

mol ratio), which may be compared with a concentration range of 0.106–1.44*M* (generally, 0.572*M*) used in our study (see Table I). Therefore, it cannot be dismissed that these conditions of high concentration promote a behavior which is closer to that occurring in neat SO_2 than to that in dilute solution. A similar difficulty arises in the application to this kinetic work of the stereochemical result from SO_2 insertion in optically active h^5-$C_5H_5Fe(CO)_2CH(CH_3)C_6H_5$.[27] There, it was found that the reaction in SO_2-saturated pentane yields the *S*-sulfinate with the same sign (although a lower value) of specific rotation as that of the sulfinate from the corresponding reaction in liquid SO_2.

Summarizing, although it is inviting to suggest that the SO_2 insertion reactions of h^5-$C_5H_5Fe(CO)_2R$ in dilute organic solutions proceed *via* a frontside attack of SO_2 at the α carbon, such a proposal would be in discord with the observed (albeit not unambiguously) stereochemical outcome at this carbon center. Clearly, stereochemical data are needed from experiments on less concentrated solutions of SO_2; however, this type of information may prove to be difficult to obtain because of the low reactivity under such conditions. The recent reports that h^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)C_6H_5$[27] and ($h^5$-1-$CH_3$-3-$C_6H_5C_5H_3$)$Fe(CO)[P(C_6H_5)_3]CH_3$[28] insert SO_2 with high stereospecificity (probably retention[29]) at iron both in neat sulfur dioxide and in dichloromethane solution are of interest in their own right; however, they do not help differentiate between the mechanisms of the insertion considered herein.

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