

spectrum of the complex differs from that of the diradical **3** in several striking ways: (a) the longest wavelength band is tripled in intensity and shifted 1000 Å to shorter wavelengths, (b) the first ultraviolet absorption band is narrowed and shifted somewhat to shorter wavelengths, (c) the second ultraviolet absorption band appears as a narrow intense band in place of a broad low band. A simple molecular orbital treatment permits a tentative assignment of the transitions in the  $\text{MgI}_2$  complex, and therefore of diradical **3**. The spectra of **3** and  $\text{3-MgI}_2$  are shown in Figure 1. The assignment will be discussed in detail in a full paper.

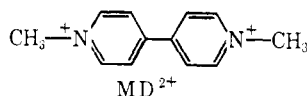
Titration of the  $\text{3-MgI}_2$  complex with excess methylviologen dichloride ( $\text{MD}^{2+}$ ) indicates that the complex has two more electrons than the precursor diiodide. The magnesium content of the solution corresponds to one atom of magnesium for each mole of diiodide, and oxidation with oxygen produces 1 mol of hydrogen peroxide and 1 mol of 1,1'-trimethylenebispyridinium ion for each mole of diiodide ( $\text{3}^{2+}$ ) originally reduced.

The diradical  $\text{3-MgI}_2$  complex exhibits a weaker epr signal than the diradical **3** itself. The stronger and sharper light absorption spectrum together with the weaker epr signal from solutions of the  $\text{3-MgI}_2$  complex suggest that the magnesium ion is coordinated to the ester groups of both pyridinyl radicals, serving to orient them and to hold them together. Thus, as expected, the magnesium iodide complex of the pentamethylene diradical ( $\text{5-MgI}_2$ ) behaves as a  $\pi$ -mer, although the diradical **5** itself shows no intramolecular complex formation.<sup>1</sup>

The  $\text{3-MgI}_2$  complex is far more reactive chemically than the diradical **3** or the corresponding monoradical. Qualitatively,  $\text{3-MgI}_2$  reacts much faster with methylviologen ( $\text{MD}^{2+}$ ) than **3** itself. Quantitatively, the rate of reaction of  $\text{3-MgI}_2$  with methyl iodide is about 100 times faster than that of the 1-ethyl-4-carbomethoxy-pyridinyl<sup>4</sup> and almost  $10^4$  faster than the reaction of diradical **3** with methyl iodide.

The calcium, zinc, and manganese complexes,  $\text{3-CaI}_2$ ,  $\text{3-ZnI}_2$ , and  $\text{3-MnI}_2$ , can be prepared from the diiodide and the metals in acetonitrile. The spectrum of the calcium complex is slightly different from that of the magnesium complex; the spectra of the other complexes differ more substantially from that of the magnesium complex.

Preliminary examination of the series in which the number of methylene groups between the pyridinyl radical moieties is varied from 3 to 10 indicates that intramolecular  $\pi$ -mer formation can be induced by magnesium iodide for a diradical containing as many as six methylene groups.



The discovery of these radical-metal ion complexes presents many new and exciting opportunities for chemical, epr, and spectroscopic studies, and clearly offers new possibilities for introducing and controlling  $\pi$ -mer interactions, in simple as well as polymeric systems.

(4) E. M. Kosower and I. Schwager, *J. Amer. Chem. Soc.*, **86**, 5528 (1964).

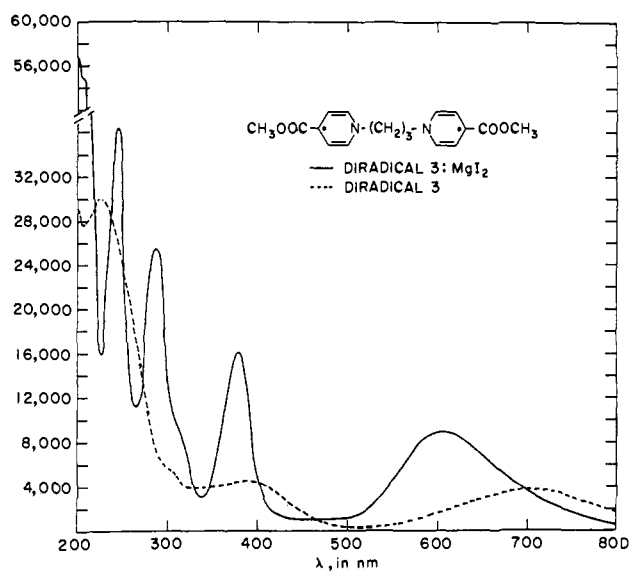


Figure 1. The spectra of diradical **3** and the  $\text{3-MgI}_2$  complex in acetonitrile at 25°. The previously reported spectrum of  $\text{3}^1$  is the same as that shown here but terminated at about 300 nm.

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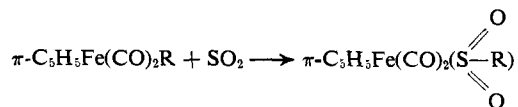
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### Electronic Effects in Sulfur Dioxide Insertion Reactions<sup>1</sup>

Sir:

Although sulfur dioxide insertion reactions of metal alkyl complexes have been studied extensively under synthetic conditions,<sup>2</sup> kinetic data on these processes are still lacking. Neither have there been any attempts at a systematic investigation of the dependence of metal alkyl reactivity on electronic and structural factors. To fill the existing void and to complement our preparative efforts we have now initiated a kinetic study on these reactions. Inasmuch as our early findings are very relevant to the rapidly developing concept of transition metal basicity,<sup>3</sup> and in view of the widespread interest in insertion reactions and related processes,<sup>4</sup> we herein report some preliminary results.

The reaction<sup>5</sup>



(1) Sulfur Dioxide Insertion. XIV. For part XIII of this series, see D. A. Ross and A. Wojcicki, *Inorg. Chim. Acta*, in press.

(2) M. Graziani and A. Wojcicki, *ibid.*, **4**, 347 (1970), and references therein.

(3) See, for example, D. F. Shriver, *Accounts Chem. Res.*, **3**, 231 (1970).

(4) See, *inter alios*, M. F. Lappert and B. Prokai, *Advan. Organometal. Chem.*, **5**, 225 (1967); J. Halpern, *Accounts Chem. Res.*, **3**, 386 (1970).

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

**Table I.** Reactions of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  Alkyls with Liquid  $\text{SO}_2$  at  $-40^\circ$ 

R <sup>a</sup>	$k_{\text{obsd}}, \text{sec}^{-1}$	Rel $k_{\text{obsd}}^b$	Taft $\sigma^*$	$\nu(\text{CO}), \text{cm}^{-1}$ ( $\text{SO}_2$ soln) <sup>c</sup>	$\nu(\text{CO}), \text{cm}^{-1}$ ( $\text{C}_6\text{H}_{12}$ soln) <sup>c</sup>
$\text{CH}_2\text{Si}(\text{CH}_3)_3$	Very fast <sup>d</sup>		-0.26		2012, 1961
$\text{CH}_2\text{CH}=\text{CHCH}_3$	Very fast <sup>d</sup>		+0.13		2010, 1959
$\text{C}_2\text{H}_5$	$1.3 \times 10^{-3}$ ( $-65^\circ$ )	1600	-0.10	<i>f</i> , 1937	2010, 1956
$\text{CH}_3$	$1.1 \times 10^{-3}$ ( $-65^\circ$ )				
	$3.2 \times 10^{-3}$ <sup>e</sup>				
	$2.7 \times 10^{-3}$ <sup>e</sup>	1400	0.00	<i>f</i> , 1940	2014, 1960
$\text{CH}_2\text{C}_6\text{H}_5$	$1.6 \times 10^{-4}$ <sup>g</sup>	80	+0.22	2004, 1944	2010, 1959
$\text{CH}_2\text{OCH}_3$	$8.3 \times 10^{-6}$	4	+0.60	2006, 1947	2017, 1961
$\text{CH}_2\text{SCH}_3$	<i>h</i>			2021, 1964	2026, 1970
$\text{CH}_2\text{CN}$	<i>i</i>		+1.30	2026, 1973	2030, 1981

<sup>a</sup> All new compounds have been characterized through elemental analyses. <sup>b</sup> Compared with  $k_{\text{obsd}}$  for  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5$  as 1. <sup>c</sup> Measured on a Beckman IR-9 spectrophotometer. <sup>d</sup> Too fast to measure by low-temperature infrared spectroscopy. <sup>e</sup> Calculated assuming  $\Delta H^\ddagger = 2.9$  kcal/mol. <sup>f</sup> Masked by  $\nu(\text{CO})$  of the corresponding sulfinate. <sup>g</sup>  $\Delta H^\ddagger = 2.9 \pm 0.4$  kcal/mol and  $\Delta S^\ddagger = -62 \pm 2$  eu. <sup>h</sup> Reaction 9% complete after 16 hr at  $25^\circ$ . <sup>i</sup> No detectable reaction after 60 hr at  $25^\circ$ .

**Table II.** Reactions of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  Aryls with Liquid  $\text{SO}_2$  at  $-40^\circ$ 

R <sup>a</sup>	$k_{\text{obsd}}, \text{sec}^{-1}$	Rel $k_{\text{obsd}}^b$	Hammett $\sigma^+$	$\nu(\text{CO}), \text{cm}^{-1}$ ( $\text{SO}_2$ soln) <sup>c</sup>	$\nu(\text{CO}), \text{cm}^{-1}$ ( $\text{C}_6\text{H}_{12}$ soln) <sup>c</sup>
<i>p</i> - $\text{C}_6\text{H}_4\text{OCH}_3$	$3.8 \times 10^{-4}$ <sup>d</sup>	720	-0.78	<i>e</i> , 1958	2027, 1971
<i>p</i> - $\text{C}_6\text{H}_4\text{CH}_3$	$6.6 \times 10^{-6}$ <sup>f</sup>	33	-0.31	2016, 1960	2027, 1971
<i>m</i> - $\text{C}_6\text{H}_4\text{CH}_3$	$1.9 \times 10^{-5}$ ( $-23^\circ$ )				
	$1.4 \times 10^{-6}$ <sup>g</sup>	$\sim 1$	-0.07	2013, 1957	2027, 1970
$\text{C}_6\text{H}_5$	$2.0 \times 10^{-6}$ <sup>h</sup>	1	0.00	2018, 1960	2023, 1972

<sup>a</sup> All new compounds have been characterized through elemental analyses. <sup>b</sup> Compared with  $k_{\text{obsd}}$  for  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5$  as 1. <sup>c</sup> Measured on a Beckman IR-9 spectrophotometer. <sup>d</sup>  $\Delta H^\ddagger = 3.5 \pm 0.5$  kcal/mol and  $\Delta S^\ddagger = -55 \pm 2$  eu. <sup>e</sup> Masked by  $\nu(\text{CO})$  of the corresponding sulfinate. <sup>f</sup>  $\Delta H^\ddagger = 7.8 \pm 0.4$  kcal/mol and  $\Delta S^\ddagger = -43 \pm 2$  eu. <sup>g</sup> Calculated assuming  $\Delta H^\ddagger = 7.3$  kcal/mol. <sup>h</sup>  $\Delta H^\ddagger = 7.3 \pm 0.5$  kcal/mol and  $\Delta S^\ddagger = -52 \pm 2$  eu.

where R = an alkyl or aryl group, was followed by infrared spectroscopy using a variable low-temperature

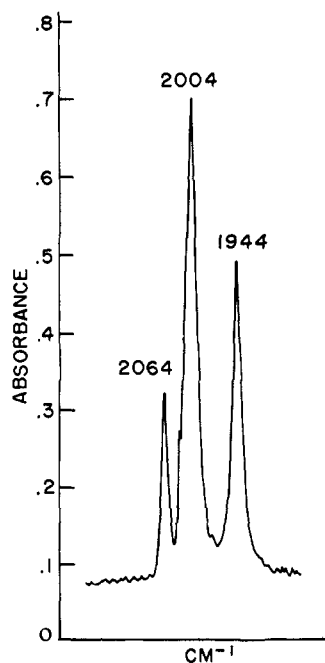


Figure 1. The infrared spectrum of an approximately 1:1 mixture of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}_6\text{H}_5$  ( $\nu(\text{CO})$  at ca. 2004 and  $1944 \text{ cm}^{-1}$ ) and  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{SO}_2\text{CH}_2\text{C}_6\text{H}_5)$  ( $\nu(\text{CO})$  at 2064 and ca.  $2004 \text{ cm}^{-1}$ ) in liquid  $\text{SO}_2$  at  $-40^\circ$ .

cell unit, obtained from Beckman Instruments, Inc., and modified as described elsewhere.<sup>6</sup> Since  $\pi\text{-C}_5\text{H}_5\text{Fe}$

(6) J. P. Day, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **90**, 6927 (1968); we are grateful to Dr. Day for supplying us with the details on the modified infrared cell.

( $\text{CO})_2\text{R}$  and  $\text{SO}_2$  react very slowly and with an accompanying decomposition in organic solvents, liquid  $\text{SO}_2$  at  $-70$  to  $-23^\circ$  was employed as the reaction medium throughout this study. Progress of the insertion was followed by measuring the intensity of the appearing  $\nu_s(\text{CO})$  of the resultant sulfinate and/or of the disappearing  $\nu_{\text{as}}(\text{CO})$  of the parent alkyl. A typical infrared spectrum in the  $2000\text{-cm}^{-1}$  region of the reaction mixture is shown in Figure 1. Average deviations for the rate constants  $k_{\text{obsd}}$  were approximately 10%. Addition of a free-radical scavenger 2,2-diphenyl-1-picrylhydrazyl or of traces of water had no effect on the rate of reaction between  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}_6\text{H}_5$  and  $\text{SO}_2$ .

The kinetic data for the alkyl and aryl complexes  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  are presented in Tables I and II, respectively. All reactions were found to obey the rate law

$$\text{rate} = k_{\text{obsd}}[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}]$$

where  $k_{\text{obsd}} = k_{x+1}[\text{SO}_2]^x$ . Of course,  $x$  is indeterminate.

The alkyls investigated are listed (Table I) in descending order of reactivity toward  $\text{SO}_2$ . The relative pseudo-first-order rate constants  $k_{\text{obsd}}$  decrease as the Taft polar substituent constant<sup>7</sup>  $\sigma^*$  for the group R becomes more positive. The only apparent exception occurs with  $\text{R} = \text{CH}_2\text{CH}=\text{CHCH}_3$ ; this is, however, due to a different mechanism of insertion which leads to rearrangement of the allylic moiety.<sup>8</sup> Approximately paralleling the increase in  $\sigma^*$  is a progressive shift to higher frequencies of  $\nu(\text{CO})$  for the parent alkyls.

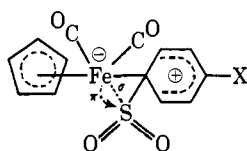
(7) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

(8) R. L. Downs, Ph.D. Thesis, The Ohio State University, 1968.

The latter trend may be ascribed to a decreasing electron density at the metal and the consequent reduction of  $M=CO \pi$  bonding.

Table II presents the corresponding data for the aryl complexes, which are also listed in decreasing order of reactivity toward  $SO_2$ . Here the relative rate constants for para- and meta-substituted phenyl complexes decrease with an increasing value of the Hammett  $\sigma^+$  parameter.<sup>9</sup>

The foregoing trends are best explicable in terms of an electrophilic interaction of  $SO_2$  with the metal-carbon bonds. For the aryl complexes, stabilization of the transition state may be achieved *via*  $M=S \pi$  bonding involving filled d orbitals of iron and empty d orbitals of sulfur, as well as through accommodation of the incipient positive charge by the aromatic ring. These interactions are represented schematically below.<sup>10</sup> The increasing reactivity of the alkyl complexes toward  $SO_2$  with accumulation of negative charge at the metal (caused inductively by R) also reflects an



electrophilic type of attack by the inserting species. However, the nature of the transition state is not clear, since in a recent study Whitesides<sup>11</sup> has demonstrated that the reaction of *threo*- $\pi$ - $C_5H_5Fe(CO)_2CHDCHDC(CH_3)_3$  with  $SO_2$  proceeds with inversion of configuration at the  $\alpha$  carbon.

Finally, it is pertinent to note that electrophilic interactions of  $SO_2$  with metal-carbon compounds may give rise to a mechanistic variation on scission of the  $M-C$  linkage when another electron-rich site is present in the organometallic molecule. Such situations have been encountered with complexes containing  $C-C$  multiple bonds, *viz.*, 2-alkenyls and 2-alkynyls, which usually react with rearrangement of the hydrocarbon moiety.<sup>8,12</sup>

**Acknowledgment.** This work has been supported by the National Science Foundation (Grants No. GP-8135 and GP-22544) and the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 2117-A3).

(9) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

(10) Alternatively, using the terminology of aromatic substitution reactions, it may be said that the transition state here resembles more a  $\pi$  complex rather than a  $\sigma$  complex, with positive charge being localized on the sulfur rather than on the aromatic ring. For a recent discussion of this aspect see, *e.g.*, G. A. Olah, M. Tashiro, and S. Kobayashi, *J. Amer. Chem. Soc.*, **92**, 6369 (1970). We make no attempt to compare the relative merits of these two descriptions.

(11) G. M. Whitesides and D. J. Boschetto, *ibid.*, **93**, 1529 (1971). We thank Professor Whitesides for sending us this information prior to publication.

(12) M. R. Churchill and J. Wormald, *ibid.*, **93**, 354 (1971); J. E. Thomasson, P. W. Robinson, D. A. Ross, and A. Wojcicki, *Inorg. Chem.*, in press.

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## Solvent Effects on Hydrogen-1, Carbon-13, and Silicon-29 Resonances in Tetramethylsilane<sup>1</sup>

Sir:

Tetramethylsilane (TMS) has been the standard species for internally referencing pmr spectra for several years. This choice was based upon (a) its chemical inertness, (b) the convenient position of its signal at the high shielding extreme of common species, and (c) early indications of only small intrinsic solvent effects on the TMS proton resonance.<sup>2</sup> More recently, with a marked upsurge in  $^{13}C$  magnetic resonance research, there has been much discussion of possible conventions for referencing  $^{13}C$  chemical shifts. The use of TMS as either a direct or indirect reference for  $^{13}C$  spectra has been under serious consideration.<sup>3</sup> In addition to bulk susceptibility effects, substantial solvent influences of different origin have been observed on the proton resonance of TMS in studies employing a variety of referencing techniques.<sup>4-8</sup> Knowledge of such effects in the  $^{13}C$  and  $^{29}Si$  resonances is also of interest.

As part of a detailed investigation into the origin and characteristics of solvent effects on  $^{13}C$  and other "less common" nuclei, we have determined resonance positions of the  $^1H$ ,  $^{13}C$ , and  $^{29}Si$  signals of TMS in 20% (by volume) solutions in nine aromatic and aliphatic solvents. Both  $^{13}C$  and  $^{29}Si$  spectra were obtained (in natural abundance) under  $^{19}F$  lock conditions on the spectrometer system described previously.<sup>9</sup> The resonances of both nuclides were measured while minimum-power, coherent proton decoupling was maintained at a fixed, predetermined frequency that was the same in all experiments. Therefore, the  $^{13}C$  and  $^{29}Si$  resonances of TMS were referenced to the  $^1H$  signal. The chemical shifts thus obtained are referred to here as "apparent"  $^{13}C$  and  $^{29}Si$  shifts,  $\Delta\sigma_C^a$  and  $\Delta\sigma_{Si}^a$ , respectively. These values are summarized in Table I, relative to the apparent  $^{13}C$  and  $^{29}Si$  chemical shifts observed for pure TMS under the same conditions.

Since the *effective* field at the TMS protons was constant for the measurements of  $\Delta\sigma_C^a$  and  $\Delta\sigma_{Si}^a$ , these values reflect solvent effects on both these two nuclei and the protons. That is, the field that was held constant was the effective field experienced by the TMS protons, rather than the applied field. If the TMS proton resonances experienced no solvent shifts, then our experimental procedure would have maintained a constant applied field, and the  $\Delta\sigma_C^a$  and  $\Delta\sigma_{Si}^a$  values would reflect influences associated only with these two nuclei.

(1) Supported by National Science Foundation Grants No. GP 8119 and GP 8518.

(2) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(3) Pacific Conference on Chemistry and Spectroscopy, Anaheim, Calif., Oct 1969.

(4) J. K. Becconsall, G. D. Daves, Jr., and W. R. Anderson, Jr., *J. Amer. Chem. Soc.*, **92**, 430 (1970).

(5) J. Homer, *Tetrahedron*, **23**, 4065 (1967).

(6) P. Laszlo, A. Speert, R. Ottinger, and J. Reisse, *J. Chem. Phys.*, **48**, 1732 (1968).

(7) E. R. Malinowski and P. H. Weiner, *J. Amer. Chem. Soc.*, **92**, 4193 (1970).

(8) J. Homer, E. J. Hartland, and C. J. Jackson, *J. Chem. Soc. A*, 931 (1970).

(9) V. J. Bartuska, T. T. Nakashima, and G. E. Maciel, *Rev. Sci. Instrum.*, **41**, 1458 (1970).