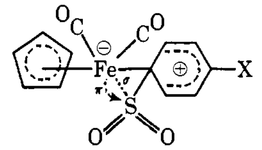
The latter trend may be ascribed to a decreasing electron density at the metal and the consequent reduction of M=CO π bonding.

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 σ^+ parameter.[9]

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 π 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.[10] 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[11] has demonstrated that the reaction of *threo*-π-$C_5H_5Fe(CO)_2CHDCHDC(CH_3)_3$ with SO_2 proceeds with inversion of configuration at the α 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.[8,12]

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[10] Alternatively, using the terminology of aromatic substitution reactions, it may be said that the transition state here resembles more a π complex rather than a σ 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.

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Solvent Effects on Hydrogen-1, Carbon-13, and Silicon-29 Resonances in Tetramethylsilane[1]

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.[2] 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.[3] 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.[4–8] 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.[9] 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.

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[1] Supported by National Science Foundation Grants No. GP 8119 and GP 8518.

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[3] Pacific Conference on Chemiistry and Spectroscopy, Anaheim, Calif., Oct 1969.

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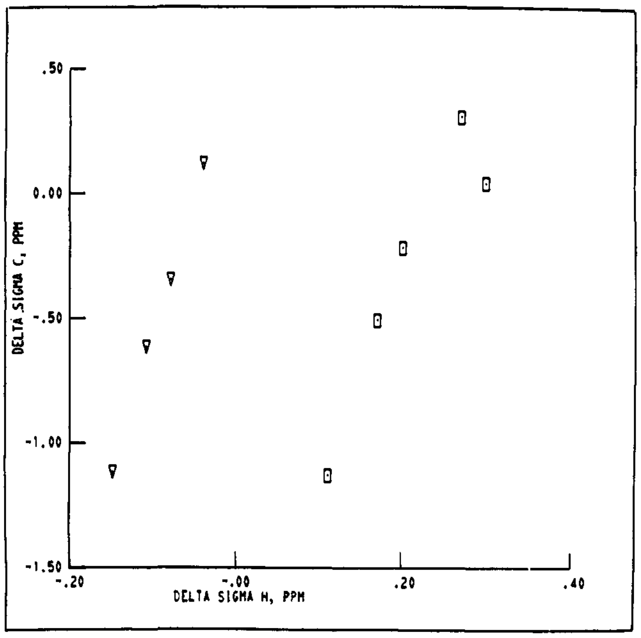

Figure 1. Plot of $\Delta\sigma_C$, the intrinsic solvent shift of the TMS carbon resonance (relative to pure TMS), *vs.* the corresponding proton solvent shift $\Delta\sigma_H$: ▽, cyclohexanes; □, benzenes.

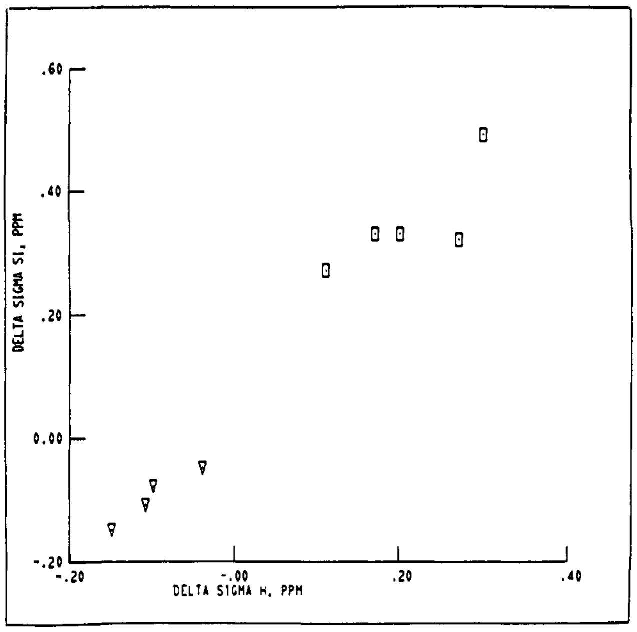

Figure 2. Plot of $\Delta\sigma_{Si}$, the intrinsic solvent shift of the TMS Si resonance (relative to pure TMS), *vs.* the corresponding proton solvent shift $\Delta\sigma_H$: ▽, cyclohexanes; □, benzenes.

In order to eliminate the uncertainties in ^{13}C and ^{29}Si solvent shifts due to solvent effects on the TMS proton resonance, it was necessary to characterize these proton solvent shifts. These are of interest in themselves, and Becconsall, Daves, and Anderson have described a highly accurate method for obtaining them.[4] This method removes uncertainties due to solvent shifts of an internal reference by employing an external reference. The method removes the need for bulk susceptibility corrections on external reference data by taking advantage of the fact that the cylindrical axis of the sample is aligned perpendicular to the field with a conventional electromagnet system, but parallel to the field if a superconducting solenoid is used. Thus, the method provides chemical shifts that one would obtain by employing external references and then applying "perfect" bulk susceptibility corrections. The ^1H shifts, obtained in this manner using pure TMS as an external reference, are referred to here as "intrinsic" proton solvent shifts $\Delta\sigma_H$. They are summarized in Table I, along with the intrinsic carbon and silicon solvent shifts, $\Delta\sigma_C$ and $\Delta\sigma_{Si}$, respectively, that are derived from the $\Delta\sigma_C{}^a$ and $\Delta\sigma_{Si}{}^a$ values by using the $\Delta\sigma_H$ values as corrections.

Table I. Solvent Effects on the ^1H, ^{13}C, and ^{29}Si Resonances of Tetramethylsilane[a]

Solvent	$\Delta\sigma_C{}^{a}$ [b]	$\Delta\sigma_{Si}{}^{a}$ [b]	$\Delta\sigma_H$ [c]	$\Delta\sigma$ [d]	$\Delta\sigma_{Si}$ [d]
C_6H_6	−0.26	0.19	0.30	0.04	0.49
C_6H_5F	0.04	0.05	0.27	0.31	0.32
C_6H_5Cl	−0.44	0.13	0.20	−0.22	0.33
C_6H_5Br	−0.68	0.16	0.17	−0.51	0.33
C_6H_5I	−1.24	0.16	0.11	−1.13	0.27
C_6H_{12}	0.16	−0.02	−0.04	0.12	−0.05
$C_6H_{11}Cl$	−0.26	−0.02	−0.08	−0.35	−0.10
$C_6H_{11}Br$	−0.51	0.00	−0.11	−0.62	−0.11
$C_6H_{11}I$	−0.97	0.00	−0.15	−1.12	−0.15

[a] Values are for 20 vol % solutions and are given in parts per million relative to pure TMS, with more positive numbers corresponding to higher shielding. [b] Values obtained as described in text with proton resonance maintained at a constant frequency. Experimental uncertainties are about ±0.02 ppm. [c] Values obtained by technique described in ref 4. Experimental uncertainties are about ±0.02 ppm. [d] Values obtained from the relation $\Delta\sigma_C = \Delta\sigma_C{}^a + \Delta\sigma_H$ or $\Delta\sigma_{Si} = \Delta\sigma_{Si}{}^a + \Delta\sigma_H$.

The apparent ^{13}C solvent shifts, $\Delta\sigma_C{}^a$, are seen from the table to parallel roughly the corresponding intrinsic values, $\Delta\sigma_C$. The parallel is by no means exact, however; the variations observed suggest that errors of 0.1–0.2 ppm would be introduced into the interpretation of ^{13}C solvent shifts referenced directly to the protons of TMS as internal standard (the procedure used to obtain $\Delta\sigma_C{}^a$, as discussed above). A similar remark applies to the ^{29}Si shifts. The ^{13}C solvent shifts cover a range of about 1.5 ppm extending over both negative and positive values with respect to pure TMS. The corresponding hydrogen solvent shifts range over about 0.5 ppm, while the silicon solvent effects span a slightly greater range, 0.65 ppm.

A plot of $\Delta\sigma_C$ *vs.* $\Delta\sigma_H$ (Figure 1) suggests two distinct, approximately linear correlations, one involving the halocyclohexane series and the other the halobenzenes (benzene itself falls significantly off this line). A comparison of this plot with that for $\Delta\sigma_{Si}$ *vs.* $\Delta\sigma_H$ (Figure 2) reveals two interesting patterns: (i) $\Delta\sigma_C$ is much more sensitive than either $\Delta\sigma_{Si}$ or $\Delta\sigma_H$ to the identity of the halogen (X) within a given solvent series, RX (*i.e.*, for a given R, C_6H_5 or C_6H_{11}) and (ii) $\Delta\sigma_C$ is far *less* sensitive than either $\Delta\sigma_{Si}$ or $\Delta\sigma_H$ to the identity of R. The pattern i seems reasonable in light of the fact that ^{13}C and ^{29}Si shieldings are far more responsive to typical variations of electronic distribution than are ^1H shieldings,[10] and the fact that silicon in TMS is more remote than carbon from the source of solvent interactions. It would be tempting

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(10) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Elmsford, N. Y., 1966.

to rationalize pattern ii, as far as ^{1}H and ^{13}C are concerned, in terms of an effect operating much more strongly in one solvent set than in the other, and manifested to a greater extent at the hydrogens than at the carbons; such an effect might be the solvent anisotropy effect which is believed to be prominent in aromatic solvents.[11] However, it seems likely (though by no means certain) that the greater sensitivity of $\Delta\sigma_{Si}$ than $\Delta\sigma_{C}$ to changing R from C_6H_{11} to C_6H_5 is due to an influence other than solvent anisotropy, perhaps dispersion effects. More detailed interpretations into the nature of these interactions will be discussed in connection with a more comprehensive experimental study.

Acknowledgment. The authors gratefully acknowledge the support of the National Science Foundation. They also thank the staff of the Molecular Biodynamics Laboratory (University of California, Berkeley) for their cooperation and use of the 220-MHz spectrometer.

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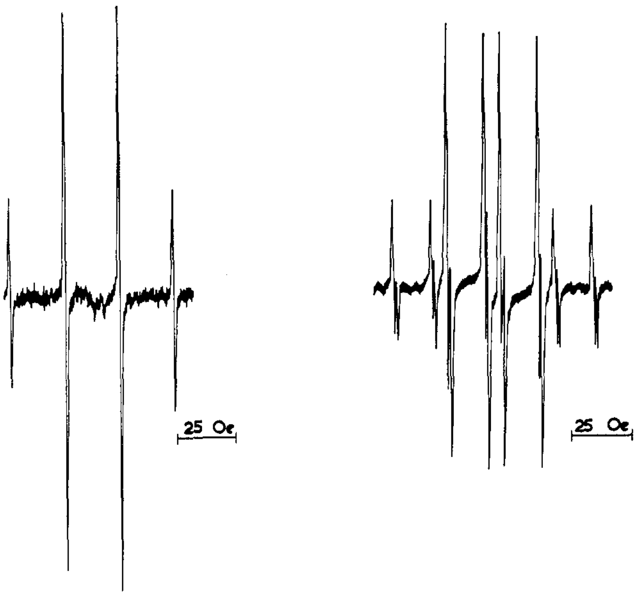
Optical and Electron Spin Resonance Detection of Radical Intermediates in the Photooxidation of Organic Molecules in Solution by Transition Metal Ions

Sir:

Although the thermal oxidations of a great many organic substrates by transition metal ions are believed to involve free-radical intermediates, the evidence for these transient species has rested chiefly on the nature of the products of reaction and on induced effects such as polymerization, sensitivity to molecular oxygen, etc.[1-3] Direct spectroscopic evidence for radicals in solution has been forthcoming only in a few specialized cases, such as the oxidation of phenols by Ce^{IV} in a flow system, which produces phenoxyl radicals detectable by electron spin resonance (esr) spectroscopy.[4] The interrelation between thermal and photochemical redox processes, which has been discussed by Kochi[3] and Adamson, *et al.*,[5] has prompted us to attempt to characterize spectroscopically radical intermediates in the photooxidations of organic molecules in solution by transition metal ions (abundant evidence for such intermediates in photooxidations of carboxylic acids having been secured by product studies[3]). Our aim has been accomplished for both alkyl and aromatic radicals in the photooxidations of simple organic substrates, such as alkanols and benzilic acid, by a number of transition metal ions including Ce^{IV}, U^{VI}, Cu^{II}, Fe^{III}, and V^{V}. The characterization is by esr for the alkyl radicals and by both optical and esr spectroscopy for the $Ph_2\dot{C}OH$ radical. Details of typical experiments are as follows.



(a) (b)

Figure 1. Esr spectra obtained by photolyzing (λ > 300 nm) solutions in ethanol at $5 \times 10^{-3} M$ concentrations of (a) ceric ammonium nitrate and (b) uranyl perchlorate.

(i) When 5×10^{-3} *M* solutions in neat degassed ethanol of, first, ceric ammonium nitrate and, secondly, uranyl perchlorate are flowed under pressure at 185°K through a flat cell cooled by cold nitrogen gas and situated in the cavity of an esr spectrometer while under filtered irradiation (λ > 300 nm) from a focused 1-kW xenon point source,[6,7] then the spectra illustrated in Figures 1a and b, respectively, are obtained. Clearly the ethanol complex of U^{VI} decomposes to give $CH_3\dot{C}HOH$ with $a_{CH} = 15.8$, $a_{OH} = 1.56$, and $a_{CH_3} = 22.9$ Oe while the Ce^{IV} complex gives $CH_3\cdot$ by a C–C cleavage mechanism ($a_H = 22.8$ Oe). Ceric perchlorate gave the same result as the ceric ammonium nitrate solution, indicating that $NO_2\cdot$ or $NO_3\cdot$ is not significantly affecting the photochemistry; the behavior of Ce^{IV} at 185°K, however, contrasts strongly with that observed at 77°K[8] when the radical produced almost exclusively is $CH_3\dot{C}HOH$. Other alcohols RCH_2OH (R = C_2H_5, *n*-C_3H_7) yield the well-resolved esr spectra of R· on photooxidation with Ce^{IV} at 185°K, although the radical at 77°K is predominantly $R\dot{C}HOH$.

(ii) When a solution in ethanol of benzilic acid (10^{-2} *M*) and ferric perchlorate (10^{-3} *M*) is photolyzed at 185°K in conjunction with the same esr technique, a complex spectrum is produced which is analyzed as that of the benzophenone ketyl radical $Ph_2\dot{C}OH$ in terms of the coupling constants $a_{2,6,2',6'} = 3.24$, $a_{3,5,3',5'} = 1.24$, $a_{4,4'} = 3.70$, $a_{OH} = 2.32$ Oe (all ±0.01 Oe); these are in good agreement with those of Wilson[9] who examined $Ph_2\dot{C}OH$ by photolyzing benzophenone in various solvents with a similar irradiation facility.

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