indicated that the instability of N_2 compounds is associated mostly with the weak σ donor properties of that ligand.

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Hyperconjugative and p–d Homoconjugative Effects of Silicon, Germanium, and Tin on Alkyl Radicals from Electron Spin Resonance Studies

Sir:

The exceptional stabilization of neighboring carbonium-ion centers by metal substituents including Si and Sn of group IVb has been ascribed to hyperconjugative electron release from the carbon–metal bonds.[1] The enhanced reactivity of allylsilanes to free-radical addition[2] can also be attributed to the stabilization of the organometallic radical. Indeed, previous studies[3] have shown that alkyl radicals with β-S, Si, Ge, and Sn substituents exist in a preferred conformational orientation in which the metal substituent (R_3M) occupies an eclipsed position relative to the half-filled carbon p orbital and optimally located to interact with it. The magnitude of this interaction can be as large as 5 kcal/mol.[4]

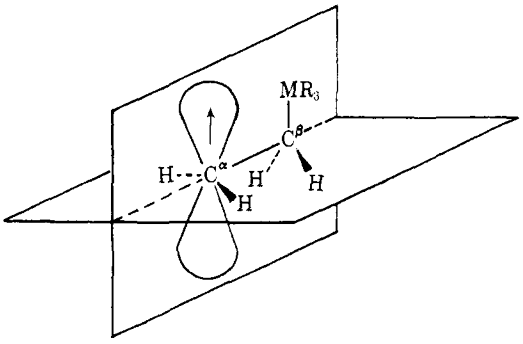

Table I. Esr Parameters of $(CH_3)_3MCH_2\dot{C}H_2$[a]

M	T, °C	$a(H_\alpha)$	$a(H_\beta)$	$a(CH_3)$	M	a(M)	$\langle g\rangle^b$ iso	$da(H_\beta)/dT$
C	−105	22.06	24.71	0.1			2.00268	0.002
Si	−112	21.05	17.68	0.10	^{29}Si	37.4[c]	2.00265	0.013
Ge	−100	20.70	16.57	0.14			2.00255	0.0075
Sn	−101	19.69	15.84	0.15	^{119}Sn	488.9[b]	2.00205	0.0067
					^{117}Sn	467.7[b]		

[a] Isotropic coupling constants in gauss. [b] Corrected to second order with respect to hyperfine interactions. [c] Value for $Et_3SiCH_2\dot{C}H_2\cdot$ at −148°.[3a]

In this report we wish to probe the mechanism of this interaction by examining the electron spin resonance (esr) parameters obtained from the spectra of the organometallic radicals listed in Table I. The radicals were generated in solution by adding the metal-centered radical [$R_3M\cdot = (CH_3)_3Si\cdot$, $(CH_3)_3Ge\cdot$, $(CH_3)_3Sn\cdot$] to ethylene[3] or by metathesis between 3,3-dimethylbutyl chloride and triethylsilyl radical.[5]

Values of the β-proton coupling constant (a_{H_β}) lower than that of the ethyl radical (26.87 G)[6] and their positive temperature dependence show that the stable conformation of the Si-, Ge-, and Sn-substituted ethyl radicals has the C_β–M bond eclipsing the p orbital on the radical center.[3b]

Two features of the esr parameters listed in Table I are noteworthy. First, the isotropic g factors of the β-metal substituted ethyl radicals decrease with increasing atomic number of M, and the drop is especially pronounced with Sn. In contrast, the g factors of the metal-centered radicals, in which the odd electron occupies mainly a valence-shell p orbital, increases as the atomic number of the metal increases: $g[CH_3\cdot] = 2.00255$,[6] $g[(CH_3)_3Si\cdot] = 2.0031$,[7] $g[H_3Si\cdot] = 2.0032$,[7] $g[(CH_3)_3Ge\cdot] = 2.01003$,[8] $g[H_3Ge\cdot] = 2.012$,[9] and $g[H_3Sn\cdot] = 2.018$.[9] Moreover, the g factors of α-metal substituted methyl radicals, in which the odd-electron orbital around the metal is mainly its valence-shell d orbital, decrease as the atomic number of the metal increases:[10] $g[(CH_3)_3CCH_2\cdot] = 2.0026$, $g[(CH_3)_3SiCH_2\cdot] = 2.0025$, $g[(CH_3)_3GeCH_2\cdot] = 2.0023$, $g[(CH_3)_3SnCH_2\cdot] = 2.0008$. The observed trend of the g factors for β-substituted ethyl radicals is, thus, consistent with the delocalization of the odd electron onto vacant d orbitals of the metal.

The second feature of these β-substituted ethyl radicals is the large hyperfine splittings by the metal. The spectrum of $(CH_3)_3SnCH_2CH_2\cdot$ in Figure 1, for example, shows the large splittings by ^{117}Sn and ^{119}Sn in natural abundance. The metal coupling constants increase with the atomic number of M and are significantly larger than those observed with the corre-

[1] (a) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 829, 7476 (1970); J. H. Jerkunica and T. G. Traylor, *ibid.*, **93**, 6278 (1971); (b) B. E. Cooper and W. J. Owen, *J. Organometal. Chem.*, **29**, 33 (1971).

[2] (a) H. Sakurai, A. Hosomi, and M. Kumada, *J. Org. Chem.*, **34**, 1764 (1969). (b) The increased reactivity of allylsilanes compared to vinylsilanes has also been noted in copolymerization studies (C. C. Price and T. Yukuta, private communication). (c) Also *cf.* R. A. Jackson, *Advan. Free-Radical Chem.*, **3**, 231 (1969).

[3] (a) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 6161 (1969); (b) *ibid.*, **93**, 846 (1971).

[4] T. Kawamura and J. K. Kochi, *J. Organometal. Chem.*, 30, C8 (1971).

[5] *Cf.* A. Hudson and R. A. Jackson, *Chem. Commun.*, 1327 (1969).

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[8] T. Kawamura and J. K. Kochi, unpublished results.

[9] R. L. Morehouse, J. J. Christiansen, and W. Gordy, *J. Chem. Phys.*, **45**, 1751 (1966).

[10] J. H. Mackey and D. E. Wood, *Mol. Phys.*, **18**, 783 (1970). In the analysis of the d-orbital contributions to the g factors these authors used the spin-orbit coupling constants of p orbitals for positive ions (Si, 190 cm^{-1}; Ge, 1200 cm^{-1}; Sn, 2800 cm^{-1}) instead of those of d orbitals (Si, 5 cm^{-1}; Ge, 60 cm^{-1}; Sn, 240 cm^{-1}): private communication. Thus the evaluated odd-electron densities on the d orbitals were underestimated about a factor of 10.

Figure 1. The central portions of the esr spectrum of $(CH_3)_3SnCH_2CH_2\cdot$ at −101° showing the high-field (a) and low-field (c) satellite lines at high gain due to ^{117}Sn and ^{119}Sn in natural abundance, together with the multiplet associated with the nonmagnetic nuclei of Sn (b) at low gain. The proton field markers are in kHz. The stick spectrum is calculated from the parameters given in Table I, including second- and fourth-order corrections.

sponding α-substituted analogs: $a[^{29}\mathrm{Si}, \mathrm{CH_3\dot{C}HSiEt_3}] = 15.2$ G[3a] and $a[^{119}\mathrm{Sn}, \cdot\mathrm{CH_2Sn(CH_3)_3}] = 137$ G.[11] The large metal coupling constants of β-metal substituted ethyl radicals,[12] therefore, cannot be explained by a long-range spin polarization or spin polarization of the σ electrons around the metal due to the odd electron density on d orbitals, and suggest that the odd electron is hyperconjugatively delocalized onto the sp^3 hybrid orbital of the metal.

An odd-electron distribution around the metal can be estimated based on the qualitative description given above. Thus, the electron density, ρ_σ, of the sp^3 hybrid orbital involved in bonding to the β-carbon atom may be evaluated directly from the metal hyperfine coupling constant a(M) as

$$\rho_\sigma = 4a(\mathrm{M})/a_0(\mathrm{M}) \tag{1}$$

where a_0(M) is the coupling constant of the metal with unit odd-electron density in its valence-shell s atomic orbital, values of which are $a_0(^{29}\mathrm{Si}) = 1640$ G and $a_0(^{119}\mathrm{Sn}) = 15{,}400$ G.[13] The values of ρ_σ obtained by this procedure are listed in Table II.

Table II. Odd-Electron Distribution around the Metal of $\dot{C}H_2CH_2M(CH_3)_3$ and $\dot{C}H_2M(CH_3)_3$

M	ρ_σ	ρ_d	$\Delta g_p \times 10^4$	$\Delta g_d \times 10^4$	ρ_d[a]
Si	0.091	0.1 ± 0.1	0.5	−0.8 ± 0.4	0.1 ∼ 0.2
Sn	0.13	0.12	15.3	−21.2 ± 0.4	0.1 ∼ 0.3

[a] The odd-electron density on the metal d orbital of $\dot{C}H_2M(CH_3)_3$.[10]

The g factor of a β-substituted ethyl radical can be given as

$$g = g_e + \Delta g_c + \Delta g_p + \Delta g_d \tag{2}$$

where g_e is the free-spin value, and Δg_c, Δg_p, and Δg_d are contributions from the odd electron distributed on the α and β carbon atoms, the odd-electron density on the valence shell p atomic orbitals of the metal, and the odd electron delocalized onto the d orbitals of the metal, respectively. The value of $g_e + g_c$ is equated to the g factor of the 3,3-dimethylbutyl radical or to that of the ethyl radical (2.00260).[6] If the odd-electron orbital of the metal-centered radical is assumed to be a pure p orbital of the metal,[14] Δg_p can be estimated from the g factor of a corresponding metal-centered species, $g(\mathrm{R_3M}\cdot)$, as[15]

$$\Delta g_p = {}^3/_4\rho_\sigma[g(\mathrm{R_3M}\cdot) - g_e] \tag{3}$$

where ${}^3/_4\rho_\sigma$ corresponds to the p orbital component of ρ_σ. Finally, Δg_d is associated with the total odd-electron density, ρ_d, on the valence-shell d orbitals[16] of the metal according to[15a]

$$\Delta g_d = 4\xi_d\rho_d/(\epsilon_0 - \epsilon_d) \tag{4}$$

where ξ_d is the one-electron spin–orbit coupling constant of the d orbital of the metal and ϵ_0 and ϵ_d are orbital energies of the odd-electron and the d orbitals, respectively. ϵ_0 (−8.4 eV)[17] may be estimated by the (negative) ionization potential of the ethyl radical and values of ϵ_d and ξ_d from atomic spectra.[18,19] Using eq 4, the values of ρ_d can be obtained from Δg_d given in Table II. The odd electron density on the metal d orbital of α-substituted methyl radicals (recomputed from the results of Mackey and Wood) are also included for comparison.[10] We suggest that the odd-electron density on the metal d orbital(s) results from p–d homoconjugation with the radical center.[20]

The values of ρ_σ and ρ_d in Table II show that the magnitudes of the p–d homoconjugative delocalization of the odd electron onto the metal d orbitals are sizable

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[11] A. Hudson and H. A. Hussain, *J. Chem. Soc. B*, 793 (1969).

[12] After completion of this work, Lyons and Symons also reported large Sn splittings in the β-substituted alkyl radicals in the solid state and ascribed the interaction to enhanced hyperconjugation [A. R. Lyons and M. C. R. Symons, *Chem. Commun.*, 1068 (1971)].

[13] These a_0(M) values are obtained according to the procedure of Mackey and Wood with a semiempirical relativistic correction: J. H. Mackey and D. E. Wood, *J. Chem. Phys.*, **52**, 4914 (1970).

[14] It is known that silyl and other radicals are pyramidal [ref 9 and P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 3939 (1969)]. However, the p nature of the odd-electron orbital is larger than that deduced directly from the metal hyperfine coupling tensors without considering spin polarization. The odd-electron orbitals of $R_3M\cdot$ were, therefore, assigned as pure p orbitals in this study. The results, however, are not greatly influenced by this assumption. For example, if the odd-electron orbital in $R_3M\cdot$ is an sp^3 hybrid orbital of the metal, the factor ${}^3/_4$ in eq 3 is replaced by 1 and results in Table II become $\rho_d(\mathrm{Si}) = 0.12$ and $\rho_d(\mathrm{Sn}) = 0.15$.

[15] (a) Based on Stone's theory of the g factor: A. J. Stone, *Proc. Roy. Soc., Ser. A*, **271**, 424 (1963); *Mol. Phys.*, **6**, 509 (1963); (b) and using a model in which the M–R σ bonds of $R_3M\cdot$ and $R_3MCH_2CH_2\cdot$ are the same, this equation is obtained.

[16] For simplification, the d orbitals are assumed to be degenerate.

[17] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. J. Herron, and K. Draxl, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," National Bureau of Standards, U. S. Government Printing Office, Washington, D. C., 1969.

[18] C. E. Moore, "Atomic Energy Levels," Circular No. 467, National Bureau of Standards, U. S. Government Printing Office, Washington, D. C.: Vol. I, 1949; Vol. III, 1958.

[19] The values are $\epsilon_d(\mathrm{Si}) = -2.0$ eV, $\epsilon_d(\mathrm{Sn}) = -1.5$ eV, $\xi_d(\mathrm{Si}) = 5$ cm^{-1}, and $\xi_d(\mathrm{Sn}) = 240$ cm^{-1}.

[20] The possibility that the odd-electron density is hyperconjugatively transferred to the metal d orbital(s) should be considered since the M–C$_\beta$ σ orbital(s) may also contain metal d orbitals. This mechanism is disfavored for two reasons: (a) Santry and Segal[21] showed by CNDO molecular orbital calculations that the hybrid orbitals of silicon in SiH_4 contain about 15% or less of silicon d orbital. If ρ_d resulted from hyperconjugation, the ratio of ρ_d/ρ_σ would be around 15:85, ∼0.2 or less, whereas the experimental ratio is about 1. (2) The odd-electron orbitals of $R_3M\cdot$ should contain the same or more contribution from d orbitals as the hybrid M–C$_\beta$ orbitals in $R_3MCH_2CH_2\cdot$; and the effects of the d character of the M–C$_\beta$ σ bond on the g factors are more or less implicitly cancelled in eq 3.

[21] D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).

and are of the same order of magnitude as the hyperconjugative delocalization of the odd electron to the C_β–M σ bond. Hyperconjugative and p-d homoconjugative interactions also both increase with increasing atomic number of the metal. Interestingly, the p-d homoconjugation between the radical center and the metal is not significantly attenuated in $R_3MCH_2\dot{C}H_2$ compared to p-d conjugation in $R_3M\dot{C}H_2$.[10] It should be borne in mind that the contributions of hyperconjugative and homoconjugative interactions do not necessarily reflect their relative importance directly in the stabilization of the radicals in the same order.

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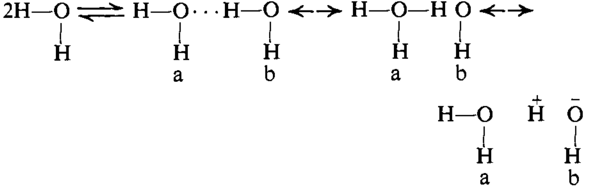
Dependence of the Acidity and Basicity of Water on the Extent of Its Hydrogen-Bonded Structure

Sir:

A pivotal idea in the flickering cluster model of liquid water is "cooperative" H bonding. Frank and Wen (FW) hypothesized that reaction 1 enhances both the



$$2\underset{\mathrm{H}}{\mathrm{H{-}O}} \rightleftharpoons \underset{\mathrm{a}}{\underset{\mathrm{H}}{\mathrm{H{-}O}}}\cdots\underset{\mathrm{b}}{\underset{\mathrm{H}}{\mathrm{H{-}O}}} \longleftrightarrow \underset{\mathrm{a}}{\underset{\mathrm{H}}{\mathrm{H{-}\overset{+}{O}}}}\mathrm{{-}H}\ \underset{\mathrm{b}}{\underset{\mathrm{H}}{\overset{-}{\mathrm{O}}}} \longleftrightarrow \underset{\mathrm{a}}{\underset{\mathrm{H}}{\mathrm{H{-}O}}}\ \ \overset{+}{\mathrm{H}}\ \ \underset{\mathrm{b}}{\underset{\mathrm{H}}{\overset{-}{\mathrm{O}}}} \qquad (1)$$

acidity of H in molecule a and the basicity of O in b.[1] This increases the equilibrium constants for formation of higher complexes by H bonding of the types $H_a\cdots OH_2$ and $O_b\cdots$H-OH.[2] Such cooperativity does not actually require both changes; diminished H_a acidity might be more than offset by sufficient increase in O_b basicity.

The predicted cooperativity is supported by *ab initio* MO-SCF calculations on linear water trimer.[3] Two calculations[3,4] estimate the altered charge distribution responsible for the dimer's enhanced H-bonding capability (Figure 1). Both show an increase (1.6–5.8%) in net negative charge on each open acceptor site (——▷), implying increased H-bonding basicity. Both show increased (2.5–5.2%) positive charge on the two unbonded H's of the proton acceptor, while the proton donor's single unbonded H becomes less positive (3.0–3.3%); in one case[3] the increase is quantitatively larger, in the other[4] case smaller. Hence the implication of increased H-bonding acidity in the dimer is less clean cut.

We now apply new and existing data to experimental tests of this corollary to the FW proposition: nonacidic, nonbasic solutes which promote water structure should alter the acidity and basicity of the medium.

We employed the ^{1}H chemical shift, δ_{CHCl_3}, of chloroform as a probe to study the H-bonding basicity of water as a function of structure-promoting additives. δ_{DMSO} was also measured in the same solutions as a potential solvent acidity probe, recognizing that the distance of these protons from the acceptor site makes DMSO an insensitive probe. Table I shows how δ varies with R in aqueous R_4NBr solutions of identical composition. The response of many water properties in such solutions to the change R = $CH_3 \rightarrow C_4H_9$ has been identified with strongly increasing water structure.[1,5–7] The δ_{CHCl_3} probe senses increasing $Cl_3CH\cdots OH_2$ H-bond strength in this series as judged from the increasing downfield shifts. This is consistent with enhanced H-bonding basicity with increasing water structure.[8] DMSO experiences very small high-field shifts not distinguishable from general medium effects.[8]

Table I. $CHCl_3$ and DMSO Chemical Shifts in Aqueous R_4NBr Solutions

R_4NBr^a	$\delta_{CHCl_3}{}^b$	$\Delta\delta_{CHCl_3}$	$\delta_{DMSO}{}^b$	$\Delta\delta_{DMSO}$
$(CH_3)_4NBr$	−347.6	0	−37.2	0
$(C_2H_5)_4NBr$	−352.1	−4.5	−35.5	1.7
$(n\text{-}C_3H_7)_4NBr$	−364.2	−16.6	−34.6	2.6
$(n\text{-}C_4H_9)_4NBr$	−374.4	−26.8	−35.3	1.9

[a] 4.990 ± 0.001 *m*. All solutions 0.124 *M* in $CHCl_3$, 0.028 *M* in DMSO, and 0.095 *M* in CH_3CN. [b] δ in Hz at 60 MHz relative to internal CH_3CN; precision ±0.05 Hz; temperature, 39°. Downfield shifts are negative.

Figure 2 shows how the probe resonances respond to increasing X_{ROH} in the system water–*tert*-butyl alcohol. The downfield movement of δ_{CHCl_3} is monotonic but bulges in the region (3–9 mol % ROH) where extrema are observed in various properties and attributed to maximum water structuring.[9–11] To separate the mass-law contributions to the shifts we combined eq 2 and 3 to yield eq 4 in which $x = X_{t\text{-BuOH}}/X_{H_2O}$.[12]

$$t\text{-BuOH} + Cl_3CH\cdots OH_2 \overset{K}{\rightleftharpoons} Cl_3CH\cdots O(H)\text{-}t\text{-Bu} + H_2O \qquad (2)$$

$$\delta^{obsd}_{CCl_3H} = \delta_{CCl_3H\cdots OH_2}N_{CCl_3H\cdots OH_2} + \delta_{CCl_3H\cdots O(H)\text{-}t\text{-Bu}}N_{CCl_3H\cdots O(H)\text{-}t\text{-Bu}} \qquad (3)$$

$$(\delta^{obsd}_{CCl_3H} - \delta_{CCl_3H\cdots OH_2})/x = K(\delta_{CCl_3H\cdots O(H)\text{-}t\text{-Bu}} - \delta^{obsd}_{CCl_3H}) \qquad (4)$$

According to eq 4 a plot like Figure 3 should be linear with slope = *K*. Figure 3 shows no linear portion

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(8) The general medium effect on δ_{CHCl_3} of the increasing volume fraction of hydrocarbon moieties in the solvent would be an increasing *high*-field shift.

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(11) E. M. Arnett in "Physico-Chemical Processes in Mixed Aqueous Solvents," F. Franks, Ed., American Elsevier, New York, N. Y., 1967, p 105.

(12) If the formation constants for the two complexes in eq 2 are similar to those known for $Cl_3CH\cdots O(C_2H_5)_2$ and $Cl_3CH\cdots O{=}C(CH_3)_2$ (K_f = 3.75 and 2 M^{-1}),[13] the fraction of unbonded $CHCl_3$ is less than 0.01 (0.05) in solution in pure water (*t*-BuOH).

(13) P. Laszlo, *Progr. Nucl. Magn. Resonance Spectrosc.*, 3, 231 (1967).