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σ^+-SUBSTITUENT CONSTANTS FOR (ORGANOMETAL)—METHYL GROUPS: A BOND POLARIZABILITY MODEL FOR HYPERCONJUGATION

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Summary

Internally consistent and properly scaled σ^+-substituent constants for (organometal)—methyl groups are derived from several photophysical data sets. These σ^+-values are well correlated by a model which considers that stabilization of an adjacent electron-deficient center is proportional to the polarizability of the carbon—metal bond as measured by bond refractions and expressed in a group polarizability function. The model also accommodates the hyperconjugative effects shown by β-deuterium substitution in solvolysis reactions and points to nonhyperconjugative effects as the basis of the Baker-Nathan order. A "best set" of σ^+-values for the $—CH_2MR_n$ substituents (M = C, Si, Ge, Sn, Pb, Hg; R = Me, Ph or X) is suggested. Seventeen other σ^+ values for organometallic substituents are presented.

Introduction

σ^+-Constants have found great utility in the study of reactions in which the substituent is directly conjugated to a cationic reactive center [1]. In our work on the elimination reactions of functionally-substituted organometallics described in the accompanying paper [2], we needed a σ^+-value for the $—CH_2SiMe_3$ group. A search of the literature revealed values that varied from —0.234 [3] to —0.87 [4] with several intermediate values [5]. The most reliable value appears to be that of Eaborn [6], —0.54, determined by the solvolysis of the *p*-substituted cumyl chloride in 90% aqueous acetone, the same method used by Brown and Okamoto [7] in their definition of the σ^+-value. Few other organometallic substituent constants have been determined in this way, most of the constants available have been derived from secondary methods, mainly Hanstein, Berwin and Traylor's [5] correlation of σ^+-values to the charge-transfer (CT) frequencies of substituted-benzene tetracyanoethylene (TCNE) molecular complexes. Of prime importance to our work [2] was a correct scaling of the organometal-

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lic substituent constants to that of the methyl group ($\sigma^+ = -0.31$) [7]. The CT-correlation results in values of -0.25 and -0.66 for methyl and $-CH_2SiMe_3$, respectively [5]. The extremely sensitive nature of the acid-catalyzed elimination reaction of $Me_3SiCH_2CR_2OH$ ($\rho^+ = -11$) could lead to differences of more than several orders of magnitude in predicted rates ratios depending on which σ^+-values are used.

By applying an additional restriction to the CT-method for the determination of σ^+-values and considering other sets of experimental data which had generally been used by the original authors to derive σ^+-constants, we have developed an internally consistent and properly scaled (to methyl) set of σ^+-constants for the organometallic substituents $-CH_2MR_3$ and $-CH_2HgX$, where M = C, Si, Ge, Sn, Pb; R = Me or Ph; and X = alkyl or halogen. In addition, σ^+-constants for several poly-metal groups are included. The magnitudes of these newly-suggested values are in excellent agreement with a model for the hyperconjugating ability of $-CH_2-G$ groups based upon the polarizability of the G group expressed in the terms of the bond refractivities of the bonds in the hyperconjugating group. This model also predicts quantitatively the direction and magnitude of β-deuterium secondary-kinetic isotope effects in solvolysis reactions.

Results

Hanstein, Berwin and Traylor [5] originally recognized two limitations on the nature of the substituents which would give a valid Hammett-type relationship between CT frequencies of TCNE—PhY complexes and σ^+-constants of $-Y$, i.e., the substituent must be electron releasing and the ionization potential of the aliphatic analog, R—Y, should be equal to or lower than that of benzene. In order to improve the accuracy of this correlation for the organometallic groups

TABLE 1

CHARGE TRANSFER FREQUENCIES OF TETRACYANOETHYLENE—PhY COMPLEXES [a] AND INITIAL ESTIMATES OF σ^+-CONSTANTS OF Y GROUPS [b]

	ν_{TCNE}(kk) [b]	σ^+(primary)	σ^+(calcd., Eq. 1)	σ^+(calcd. Eq. 2)
$-H$	25.7 [c]	0.0 [i]	-0.03	-0.07
$-CH_2Ph$	24.4 [d]	-0.17 [j]	-0.16	-0.21
$-Me$	22.8 [e]	-0.31 [i]	-0.31	-0.38
$-cC_3H_5$	21.3 [d]	-0.45 [j]	-0.45	-0.54
$-CH_2SiMe_3$	20.2 [f]	-0.54 [k]	-0.55	-0.66
$-CH_2SiPh_3$	22.2 [f]		-0.36	
$-CH_2GeMe_3$	19.6 [g]		-0.61	
$-CH_2GePh_3$	20.6 [g]		-0.52	
$-CH_2SnMe_3$	17.5 [h]		-0.82	
$-CH_2SnPh_3$	18.8 [f]		-0.69	
$-CH_2PbPh_3$	16.3 [d]		-0.92	
$-CH_2HgPh$	15.8 [h]		-0.97	
$-CH_2HgC_6H_{11}$	15.1 [h]		-1.04	
$-CH_2HgI$	21.1 [h]		-0.56	

[a] Solvent CH_2Cl_2: at 27 ± 3°C; values listed are means of reported values of the lowest energy CT band, when available; error of the mean ~±0.1 kk. [b] kk = 10^3 cm^{-1}. [c] Refs. 5, 12. [d] Ref. 5. [e] Refs. 12, 13. [f] Refs. 5, 12—14. [g] Ref. 4. [h] Ref. 15. [i] Ref. 7. [j] Ref. 16. [k] Ref. 6.

of interest here we would add the constraint that: the substituent —Y contain only σ- or π- bonding electrons.

Table 1 contains a listing of Ph—Y compounds and the long-wavelength CT-absorption frequencies of their TCNE-complexes. The first five entries have been used to derive a regression line.

$$\sigma^{+} = 9.43 \times 10^{-2}\ \nu(\text{kk}) - 2.46 \qquad (1)$$

which differs slightly from that originally proposed by Traylor [5].

$$\sigma^{+} = 10.7 \times 10^{-2}\ \nu(\text{kk}) - 2.82 \qquad (2)$$

The initial estimates of σ^{+}-values based upon ν_{TCNE} values as shown in Table 1 and calculated using eq. 1 can be used to extrapolate and interpolate values of σ^{+} for substituents based on other photophysical data such as absorption spectra of 2-substituted pyridines [8] and substituted benzenes [9]. Notably lacking in these data sets are parameters for the estimation of the σ^{+}-value of the $-CH_2PbMe_3$ group. Since even benzyltrimethyltin undergoes electron-transfer oxidation with TCNE [10], the likelyhood of obtaining reliable CT data for benzyltrimethyllead is small, however the bond polarizability-hyperconjugation model, vide infra, gives an easy means to extrapolate to the σ^{+}-constant of $-CH_2PbMe_3$, which value is in good agreement with that estimated from photoelectron spectroscopic data [11].

The difference in σ^{+}-values between the alkyl- and phenyl-substituted $-CH_2MR_n$ groups shown in Table 1 is approximately constant and appears to be an inductive effect on the C—M bonds' ability to hyperconjugate [15]. For the Group IV elements this effect can be expressed by the equation:

$$\sigma^{+} = \text{“}\sigma_R^{+}\text{”} + 0.28\ \Sigma\sigma_I \qquad (3)$$

"σ_R^{+}"(C) = —0.29; "σ_R^{+}"(Si) = —0.49; "σ_R^{+}"(Ge) = —0.59; "σ_R^{+}"(Sn) = —0.78; "σ_R^{+}(Pb) = 0.99

where $\Sigma\sigma_I$ is the sum of the inductive substituent constants for the three substituents on the metal ($\sigma_I(\text{Me}) = -0.05$ and $\sigma_I(\text{Ph}) = +0.10$) [17] and "$\sigma_R^{+}$" is a measure of the resonance or hyperconjugative interaction of the $-CH_2MR_n$ group. Because we have not accounted for the minor inductive effect of the $-CH_2MR_n$ group as a whole, we differentiate "σ_R^{+}" from the more correct σ_R^{+}.

For mercury substituents, σ^{+} can again be divided into inductive and resonance contributions and from the data in Table 3, eq. 4 can be derived for $-CH_2HgX$ substituents:

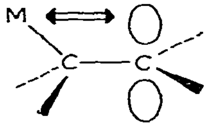
$$\sigma^{+} = \text{“}\sigma_R^{+}\text{”} + 1.07\ \sigma_I(\text{X}) \qquad (4)$$

"σ_R^{+}"(Hg) = —0.98

Similar equations for the separation of inductive and hyperconjugative effects have been proposed by Eaborn for the $-CH_2-Y$ (Y = electronegative group) groups [18] and eq. 4 is essentially a rearranged form of an earlier proposal by Traylor [15]. It should be noted that eqs. 3 and 4 treat inductive effects at the metal rather than the $-CH_2MR_n$ group as a whole. Adcock, Cox and Kitching [19] have discussed the σ_I-values of the Group IV metallo-methyl groups in detail and conclude that, at present, there is not one general scale for these values, which are usually small, ±0.05, and the derived values are both solvent and system dependent. Thus we consider σ^+ = "σ_R^+" + 0.28 $\Sigma\sigma_I$ in which the term "σ_R^+" contains the minor component of σ_I for the entire —CH_2MR_n group. This approach is justified considering the relatively small σ_I for the groups as a whole, the even smaller differences and the much larger effect that the ligand R_n on the metal has on the σ^+-value, as compared to its effect on σ_I [19].

Bond polarizability-hyperconjugation (BPH) model

In the vertical stabilization of an adjacent cationic center, the bonding interaction between the developing *p*-orbital of the cation and the hyperconjugating *β*-carbon—metal bond should be a strong function of the polarizability of the C—M bond:



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A direct dependence on the polarizability of the C—M bond would also apply to non-vertical processes such as bridging or intramolecular nucleophilic displacements [20] by σ-bonds. We limit our discussion here in terms of vertical σ—π interactions (hyperconjugation) only because of the readily available data for CT-absorptions, a vertical process. As a convenient measure of C—M bond polariz

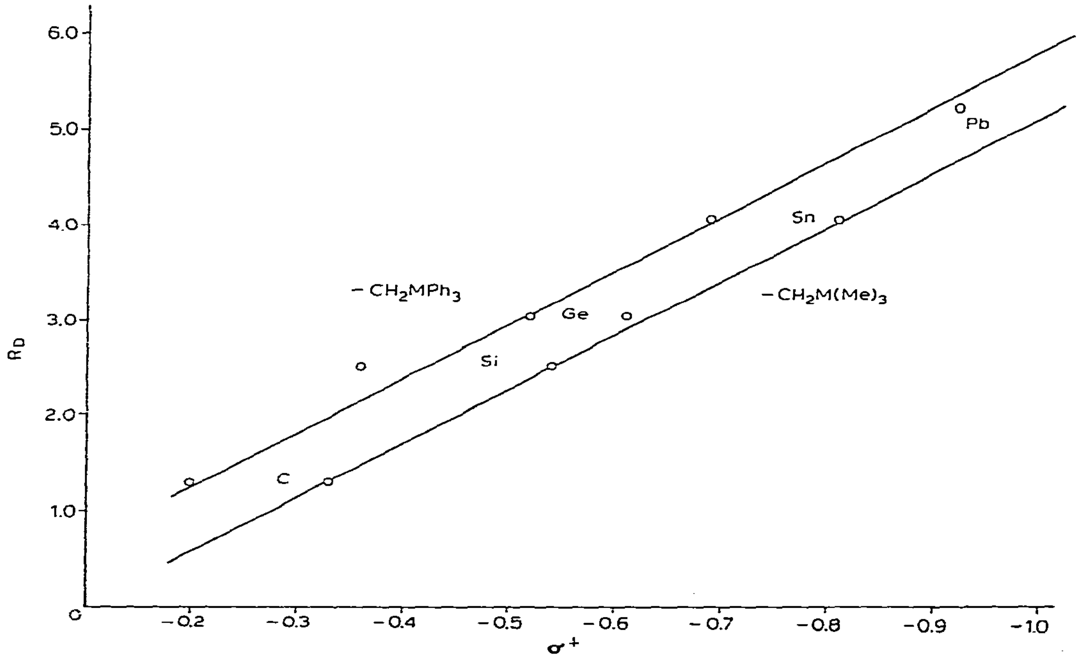

Fig. 1. Relationship between the bond refraction (R_D) of the carbon—metal bond in —CH_2—MR_3 and σ^+ constant of the —CH_2MR_3 group; for R = Me, $\sigma^+ = -0.176\,R_D - 0.097$; for R = Ph, $\sigma^+ = -0.181\,R_D + 0.055$.

TABLE 2

CORRELATION OF σ^+-VALUES WITH BOND REFRACTION OF THE CARBON—METAL BOND

Group	σ^+	Bond	R_D [a]	"σ_R^+" [g]
—CH$_2$CMe$_3$	—0.33 [b]	C—C	1.296	—0.29
—CH$_2$CPh$_3$	—0.20 [d]	C—C	1.296	
—CH$_2$SiMe$_3$	—0.54 [c]	C—Si	2.52	—0.49
—CH$_2$SiPh$_3$	—0.36 [d]	C—Si	2.52	
—CH$_2$GeMe$_3$	—0.61 [d]	C—Ge	3.05	—0.59
—CH$_2$GePh$_3$	—0.52 [d]	C—Ge	3.05	
—CH$_2$SnMe$_3$	—0.81 [d]	C—Sn	4.09	—0.78
—CH$_2$SnPh$_3$	—0.69 [d]	C—Sn	4.09	
—CH$_2$PbMe$_3$	(—1.03) [e]	C—Pb	5.26	—0.99
—CH$_2$PbPh$_3$	—0.92 [d]	C—Pb	5.26	
—CH$_2$HgC$_6$H$_{11}$	—1.04 [d, f]	C—Hg	7.21 [f]	—0.98

[a] Bond refraction at sodium-D line, Ref. 21. [b] Ref. 22. [c] Ref. 6. [d] Initial estimate taken from Table 1. [e] Extrapolated. [f] Not included in Fig. 1, vide infra. [g] Calculated from eqs. 3, 4.

ability the use of bond refraction values (R_D), as developed by Vogel and Cresswell [21], seems eminently suitable. Indeed, the correlation of σ^+-values of the —CH$_2$MR$_n$ groups with the bond refractions of the CH$_2$M bonds is excellent, as the data given in Table 2 and plotted in Figure 1 shows.

The use of bond refractions often appears to be dependent on the symmetry

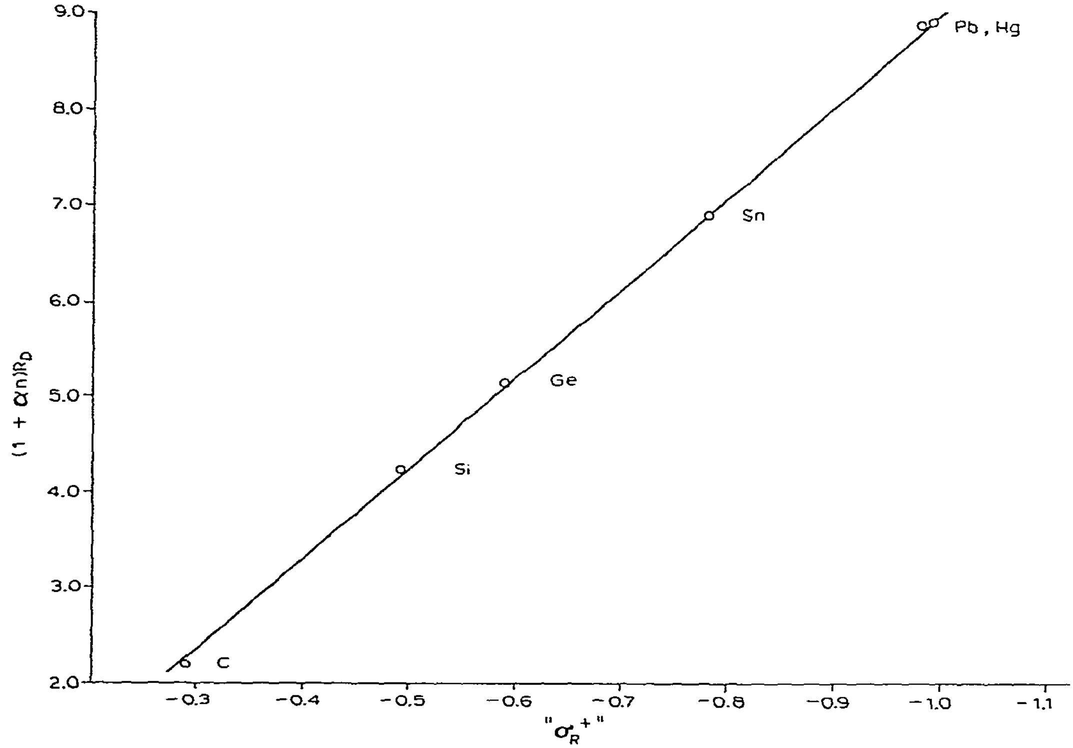

Fig. 2. Relationship between the group refractions, $(1 + \alpha n)$ R_D, of —CH$_2$MR$_m$ groups and "σ^+_R": α = 0.23.

of the substituted group and thus only tetravalent Group IV metals are shown in Fig. 1. Of great interest would be the extension of this model to the linear $-CH_2-Hg-R$ substituents, which can be accomplished by the introduction of an additional disposable parameter which accommodates remote interactions due to the multivalency of M, i.e., considers the system $-CH_2M-R_n$ where the $M-R_n$ bonds also contribute to the overall properties of the substituent. Such an effect has been noted before in the correlation of optical rotation and bond refraction for organometallic compounds [23]. If the $M-R_n$ bonds also make a contribution to the overall hyperconjugative ability of the $-CH_2-M-R_n$ substituent then for R = alkyl, with an appropriate attenuation factor, α, and inductive effects accounted for by eqs. 3 and 4, then eq. 5 is applicable, Fig. 2, in which

$$``\sigma_R^{+}" = -0.106\ R_D(1 + \alpha n) - 0.05 \qquad (5)$$

n is the number of alkyl substituents on the metal and $\alpha = 0.23$ by least squares analysis. It has not escaped our attention that the intercept of eq. 5 is approximately equal to suggested σ_I values for the isoinductive $-CH_2MR_n$ groups [19]. In view of the previous discussion on σ_I-values, however, we have chosen not to make the correction, $``\sigma_R^{+}" - \sigma_I = \sigma_R^{+}$, until a generally agreed upon set of $\sigma_I$ values is reported. Because of multivalency both Pb substituents ($n = 3$) and Hg substituents ($n = 1$) appear to possess the same hyperconjugative ability, $``\sigma_R^{+}"(-CH_2Pb) = -0.99$, $``\sigma_R^{+}"(-CH_2-Hg) = -0.98$, in spite of the larger bond refraction of a C—Hg bond.

By analogy to the ion-induced dipole interaction [24], the potential energy of the system $G-C-C_\alpha^{+}$ should be decreased by an increase in the polarizability of the C—G bond (at constant charge density on C_α) and increased with increased charge density on C_α (at constant polarizability of C—G) *. The first situation can be seen in the increase of the σ^{+}-constants along the series C—C < C—Si < C—Ge < C—Sn < C—Pb ~ C—Hg which follows the order of group refractions expressed as $(1 + 0.23\ n)\ R_D$. The effect of increasing charge density at C_α has been expressed in the Sunko-Borcic-Servis relationship [25], in which increasing charge density at C_α in solvolysis reactions, as measured by $k(CH_3/H)$, is related to increasing β-deuterium kinetic isotope effects. Since R_D C—H > R_D C—D [26] an increased rate retardation is expected for β-deuterium substitution in solvolysis reactions of high Me/H ratios, vide infra.

Suggested values of σ^{+} for CH_2-MR_n substituents

Multiple linear regression analysis of the TCNE CT data, bond refraction extrapolations, CT frequencies for dichloromaleic anhydride molecular complexes [5], absorption frequencies for 2-substituted pyridines [8] and benzyl organometallics [9] leads to a "best" set of σ^{+} values for the $-CH_2-MR_n$ substituents listed in Table 3. Reinserting these values into the original TCNE-CT data set results in eq. 6:

$$\sigma^{+} = 9.46 \times 10^{-2}\ \nu_{TCNE}(kk) - 2.466 \qquad (6)$$

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* It should be noted that the polarizability of a bond is directly related to the force-constant (see ref. 28(c), Chap. 1 and ref. 25(c), Chap. 2).

TABLE 3

"BEST" VALUES OF σ^+ FOR $-CH_2MR_n$ GROUPS

Group	$\sigma^{+\,a,b}$	Group	$\sigma^{+\,a,b}$
$-CH_2SiPh_3$	-0.38 ± 0.02	$-CH_2HgC_6H_{11}$	-1.04 ± 0.03
$-CH_2SiMe_3$	-0.54 ± 0.01	$-CH_2HgCH_2Ph$	-0.97 ± 0.02
$-CH_2GePh_3$	-0.51 ± 0.02	$-CH_2HgPh$	-0.83 ± 0.02
$-CH_2GeMe_3$	-0.63 ± 0.02	$-CH_2HgCl$	-0.47 ± 0.02
$-CH_2SnPh_3$	-0.73 ± 0.02	$-CH_2HgBr$	-0.50 ± 0.02
$-CH_2SnMe_3$	-0.81 ± 0.02	$-CH_2HgI$	-0.55 ± 0.02
$-CH_2PbPh_3$	-0.90 ± 0.02		
$-CH_2PbMe_3$	-1.03 ± 0.03		

[a] Indicated errors are errors of the mean of several correlations. [b] Refer to Ref. 5 and references therein for previous estimates.

which has been used to estimate a number of σ^+ constants for organometallic substituents based upon TCNE-CT data, Table 4.

Secondary kinetic isotope effects

β-Deuterium isotope effects on solvolysis reactions have commonly been interpreted in terms of hyperconjugative effects [28] and although the methyl group lacks the basic structural analogy to the CH_2-MR_n group and the use of eq. 5 is

TABLE 4

σ^+-VALUES FOR MISCELLANEOUS ORGANOMETALLIC GROUPS

Group	$\sigma^{+\,a}$	ν_{TCNE}	Ref.
Silicon			
$-CH_2SiBu_3$	-0.55	20.3	*b*
$-CH_2SiPrH_2$	-0.57	20.0	*b*
$-CH_2SiMe_2(CH_2Ph)$	-0.56	20.2	*b*
$-CH_2SiH(CH_2Ph)_2$	-0.45	21.3	*b*
$-CH_2CH_2SiMe_3$	-0.35	*c*	*b*
$-CH_2Si_2Me_5$	-0.62	19.6	*d, e*
$-SiMe_2SiMe_3$	-0.55	20.3	*e*
$-1\text{-}Si_3Me_7$	-0.67	19.0	*e*
$-2\text{-}Si_3Me_7$	-0.70	18.7	*e*
$-CH(SiMe_3)_2$	-0.65	19.2	*e*
$-C(SiMe_3)_3$	-0.68	18.9	*e*
Germanium			
$-CH_2GeEt_3$	-0.67	19.0	*b*
$-CH_2Ge(OEt)_3$	-0.39	22.0	*b*
$-CH_2Ge(CH_2Ph)_3$	-0.57	20.0	*b*
$-CH_2Ge(CH_2Ph)_2H$	-0.59	19.8	*b*
Tin			
$-CH(SnMe_3)_2$	-1.06	*c*	
Lead			
$-CH_2CH_2PbPh_3$	-0.08	25.2	*f*

[a] Calculated from eq. 6. [b] Ref. 4. [c] Interpolated from absorption data in 2-substituted pyridine, ref. 8. [d] Ref. 12. [e] Ref. 27. [f] Ref. 5.

probably inappropriate, the basic assumption that the hyperconjugative ability of a substituent is proportional to the bond refraction of the hyperconjugating bond allows an estimation of the ratio of "σ_R^+" values for β C—H and β C—D bonds:

$$\frac{\sigma^+(\mathrm{CH_3})}{\sigma^+(\mathrm{CH_2D})} \cong \frac{R_\mathrm{D}(\mathrm{C{-}H})}{R_\mathrm{D}(\mathrm{C{-}D})} \cong \frac{1.676}{1.650} \cong 1.0158$$

thus $\sigma^+(\mathrm{CH_2D}) = -0.31/1.0158 \cong -0.305$

The Servis-Borcic-Sunko relationship [25b]:

$$\log k(\mathrm{CH_3/CD_3}) = \frac{\Delta\sigma}{\sigma}\log(\mathrm{CH_3/H}) \qquad (6)$$

for the solvolysis of $R_2C(R_1)X$, (R_1 = CH_3, CD_3 or H) derivatives has been very successful in the analysis of secondary deuterium isotope effects and is used in the form of eq. 7 which dissects the overall kinetic isotope effect into angular and inductive components:

$$\log k(\mathrm{H/D}) = 0.66\cos^2\theta\,[0.0195 + 0.02024\log k(\mathrm{CH_3/H})] - 0.00656 \qquad (7)$$

where θ is the dihedral angle between the hyperconjugating bond and the *p*-orbital of the carbonium ion. For $\theta = 0°$, eq. 7 reduces to:

$$\log k(\mathrm{H/D}) = 1.34 \times 10^{-2}\log k(\mathrm{CH_3/H}) + 0.0064\ . \qquad (8)$$

By analogy to eq. 6 and from the σ^+-values for the $-CH_3$ and $-CH_2D$ groups:

$$\log k(\mathrm{CH_3/CH_2D}) = \frac{\Delta\sigma(\mathrm{CH_3 - CH_2D})}{\sigma(\mathrm{CH_3})}\log k(\mathrm{CH_3/H}) \qquad (9)$$

with

$$\frac{\Delta\sigma(\mathrm{CH_3 - CH_2D})}{\sigma(\mathrm{CH_3})} = 1 - 1/1.0158 = 1.55 \times 10^{-2}$$

Making a correction for the inductive effect [25b,29] of one —D gives

$$\log k(\mathrm{CH_3/CH_2D}) = 1.55 \times 10^{-2}\log k(\mathrm{CH_3/H}) - 0.00656\ . \qquad (10)$$

The BPH model gives a semi-empirical basis for estimating the slope of eq. 9 and a comparison of the secondary-isotope effects calculated from these relationships is shown in Table 5.

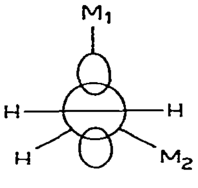
TABLE 5

SECONDARY β-DEUTERIUM ISOTOPE EFFECTS CALCULATED BY THE BPH AND SBS MODELS FOR THE SOLVOLYSIS OF $R_2(R')CX$ ($R' = CH_3$, CH_2D or H)

$\log k(\mathrm{CH_3/H})$	k(H/D) SBS	k(H/D) BPH
8	1.301	1.31
6	1.223	1.22
4	1.149	1.14
2	1.080	1.06

Poly metal-containing substituents

Both photophysical [8,27] and solvolysis [6] σ^+-values are available for several groups which contain more than one carbon—metal bond capable of hyperconjugation, for example —$CH(SiMe_3)_2$, —$CH(SnMe_3)_2$ and —$C(SiMe_3)_3$.



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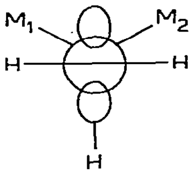

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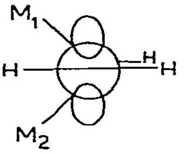

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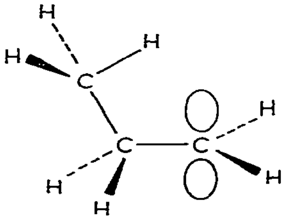
Interactions in the most reasonable conformers for the dimetal systems show the C—M bonds at different dihedral angles, θ, to the p-orbital. Using the "$\cos^2$ rule" and ignoring any differences in the inductive effects and hyperconjugation of the off-axis C—H bonds, σ^+ for —$CH_{3-m}(MR_n)_m$ should be

$$\sigma^+ \cong \cos^2\theta_1(\sigma_1^+) + \cos^2\theta_2(\sigma_2^+) + \cos^2\theta_3(\sigma_3^+)\ . \tag{11}$$

In conformation 2, $\theta_1 = 0°$, $\theta_2 = 60°$, $\theta_3 = 60°$ and thus for —$CH(MMe_3)_2$ $\sigma^+ \cong 1.25\ \sigma^+$ (—CH_2MMe_3) and σ^+ $C(MMe_3) \cong 1.5\ \sigma^+$ (—CH_2MMe_3), which gives σ^+ —$CH(SiMe_3)_2$ = —0.68 as compared to —0.65 (CT), —0.67 (pyridine) [8], —0.62 (solvolysis) [6]. For —$CH(SnMe_3)_2$, $\sigma^+ = 1.25\ \sigma^+$ (—CH_2SnMe_3) = —1.01 as compared to —1.06 as extrapolated from absorption frequencies in 2-substituted pyridines [8]. For structure 3, $\theta_1 = 60°$, $\theta_2 = 60°$, $\theta_3 = 0°$ and σ^+ $(CHM_2) \cong 0.5\ \sigma^+$ (—CH_2M). For structure 4, $\theta_1 = 30°$, $\theta_2 = 30°$, $\theta_3 = 90°$ and σ^+ $C(M_3) = \sigma^+$ $(CHM_2) = 1.5\ \sigma^+$ (CH_2M). Conformation 2 best accounts for the observed values. Major differences among the calculated (eq. 10) (—0.81), solvolytic [6] (—0.52), and CT-derived [27] value (—0.68) for the —$C(SiMe_3)_3$ group suggests that ground state and/or steric interactions may be playing an important role with this very bulky group.

The hyperconjugating ability of alkyl groups

Although the C—H bond is more polarizable (R_D = 1.676) than the C—C bond [21] (R_D = 1.296), C—C hyperconjugation is the more important since remote



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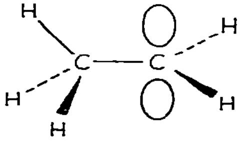
$(1 + \alpha n)R_D = 1.296 + 0.23 \times 3 \times 1.676$

$(1 + \alpha n)R_D = 2.46$



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$(1 + \alpha n)R_D = 1.676\ (n = 0)$

$(1 + \alpha n)R_D = 1.676$

contributions make the methyl group more polarizable than H, i.e., the group polarizability function, $(1 + \alpha n) R_D$, for methyl is greater than that for H. The preferred conformation for the 1-propyl cation [30] would be as shown above with the C(2)—C(3) bond eclipsing the *p*-orbital, 5. By the same argument, the purely hyperconjugative interaction of alkyl groups with an adjacent cationic center should increase with increasing group refraction, $(1 + \alpha n) R_D$, (eq. 5); $-CH_3$ (1.676), $-CH_2C(CH_3)_3$ (2.19), $-CH_2CH_3$ (2.46). When the inductive factors from eq. 3 are included however, the net effect is σ^+ (neopent) $>$ σ^+ (Et). For any general substituent then, replacement of a H by Me leads to greater hyperconjugative stabilization and since $\sigma_I(\text{Me}) < \sigma_I(\text{H})$ the inductive factor should also lead to greater stabilization of a cationic center. The Baker-Nathan order [31] is inconsistent with this prediction.

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