

gated, that it is probably the first system, investigated kinetically in which non-specifically-solvated primary carbonium ions have been formed in a solvolysis reaction, and that relative to the ground states the central carbon atoms in the transition states bear very large positive charges. Whereas the maximum differences in free energies of activation of solvolytic reactions in acetic acid previously reported for *t*-butyl and methyl compounds is approximately 8 kcal./mole, the difference for the solvolysis of *t*-butyl and methylmercuric salts is approximately 17.5 kcal./mole.

The effect of solvent on the reaction is complex. This is to be expected since some of the more ionizing solvents coordinate with mercury to a large extent. It has been found that with solvents of about the same ionizing power, the reaction occurs more slowly in the more nucleophilic solvent. The results given in Table I probably indicate that in these solvents the interaction between solvent and mercury is the most important effect, and this effect slows the reaction.

TABLE I
PARAMETERS FOR THE REACTION OF CYCLOHEXYLMERCURIC PERCHLORATE IN VARIOUS SOLVENTS AT 25°

Solvent	ΔH^* , kcal./mole	ΔS^* , e.u.	ΔF^* , kcal./ mole	$k_{rel.}$
HOAc	25.3 ± 0.4	10.9 ± 0.9	22.1	1
EtOH	30.3 ± .2	19.6 ± .6	24.5	0.017
MeOH	29.6 ± .4	18.4 ± 1.2	24.1	.030
<i>n</i> -BuOH	30.3 ± .2	19.5 ± 0.6	24.5	.0165
Dioxane	25.3 ± .3	9.9 ± .9	22.4	.60
Acetone	29.1 ± .2	20.5 ± .7	23.0	.204
H ₂ O	28.5 ± .2	17.1 ± .6	23.4	.098

If it is assumed that the degree of coordination of a solvent with mercury is approximately independent of the alkyl group attached to mercury, information regarding the nature of the transition state can be deduced from the data in Table II.

TABLE II
EFFECT OF ALKYL GROUP ON THE SOLVOLYSIS OF ALKYL MERCURIC PERCHLORATES IN WATER AND ACETIC ACID AS SOLVENTS

RHgClO ₄ R is	$\Delta H^*_{H_2O} - \Delta H^*_{HOAc}$, kcal./mole	$\Delta F^*_{H_2O} - \Delta F^*_{HOAc}$, kcal./ mole, 25°	$k_{rel. (HOAc)}$ 25°
Me	0.4	0.7	1 ^a
Et	3.0	1.6	1.19 × 10 ³
<i>n</i> -Butyl	3.4	1.8	1.7 × 10 ³
Isopropyl	...	2.0	4.1 × 10 ⁷
<i>sec</i> -Butyl	3.3	1.4	8.1 × 10 ⁷
Cyclohexyl	3.2	1.35	1.3 × 10 ⁸
<i>t</i> -Butyl	6.6 × 10 ¹²

^a $k = 3.1 \times 10^{-12}$ sec.⁻¹. Extrapolated from data at elevated temperature.

The observations that the differences in activation energies for each compound are approximately the same in solvents of widely differing ionizing power and nucleophilicity independent of the number of alkyl groups attached to the central carbon atom, and that the differences in relative rates are very large and approximately proportional to the number of alkyl groups attached to carbon indicate that in the transition states the central carbon

atoms are highly charged and that this charge is not specifically solvated. It is to be expected that solvolysis of alkylmercuric salts will be very sensitive to structural changes and that the carbonium ion intermediates will not be highly selective in their reactions.

The relative rate sequence per alkyl group on carbon is striking: $k_{i-Bu}/k_{i-Pr} = 10^{5.2}$; $k_{i-Pr}/k_{Et} = 10^{4.52}$; $k_{Et}/k_{Me} = 10^{3.07}$. For solvolysis of arylsulfonates in acetic acid (75°) the available relative rates³ are: $k_{i-Pr}/k_{Et} = 10^{1.7}$ and $k_{Et}/k_{Me} = 10^{-0.36}$. By projecting relative rates,⁴ it has been suggested that for limiting solvolysis in formic acid, $k_{i-Bu}/k_{i-Pr} \cong 10^6$. This value is not achieved in acetic acid in the present system. The change per alkyl group on carbon might be comparable. For alkylmercuric salts the ratio in formic acid is $k_{i-Pr}/k_{Et} = 10^{5.3}$. By comparison, for solvolysis of arylsulfonates³ in formic acid the ratio is $k_{i-Pr}/k_{Et} = 10^{2.3}$. Thus, solvent-on-carbon participation is exceedingly low for the production of primary (except for perhaps methyl) and secondary carbonium ions from organomercuric ions.

(3) S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952).

(4) A. Streitwieser, *Chem. Revs.*, **56**, 644 (1956).

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AN ADDITIVITY RELATION FOR C¹³-PROTON COUPLING IN NUCLEAR MAGNETIC RESONANCE

Sir:

N.m.r. C¹³-proton spin-spin coupling constants have previously been correlated with percentage *s* character of the carbon atomic orbital participating in the C-H bond^{1,2} and the C-H bond length.² For compounds of the type CH₃X, an empirical equation expressing J_{CH} in terms of the effective electronegativity of the substituent and the C-X bond length has also been proposed.² In predicting J_{CH} values of compounds involving various tetrahedral-type carbon atoms of the form CHXYZ, the above-mentioned schemes are not very practicable because, first, one seldom has detailed information concerning small deviations of the percentage *s* character of the carbon atoms and, second, bond lengths are extremely difficult to obtain. The purpose of this note is to draw immediate attention to a simple, but precise, additivity relation for predicting C¹³-proton couplings. The additivity function described here is strongly reminiscent of the well-known additivity relations of molar refractivity and parachor.

It has been found in this laboratory that C¹³-proton coupling constants, for compounds of the type CHXYZ, can be separated into three components according to the equation: $J_{CH} = \zeta_x + \zeta_y + \zeta_z$. In this equation J_{CH} is the C¹³-proton spin-spin coupling constant; components ζ_x , ζ_y and ζ_z are contributions which are associated with substituents X, Y and Z, respectively.

The coupling component for the hydrogen atom

(1) J. N. Shoolery, *J. Chem. Phys.*, **31**, 1427 (1959).

(2) N. Muller and D. E. Pritchard, *ibid.*, **31**, 768, 1471 (1959).

TABLE I
C¹³-PROTON COUPLING CONSTANTS OF METHYL PROTONS
IN CH₃X AND CALCULATED COUPLING COMPONENTS

Substituent	J _{CH} (cps.)	ζ _x (cps.) (av. value)
—H	125 ^a	41.7
—F	149 ^a	65.6
—Cl	150 ^a	68.6 ^a
—Br	152 ^a	68.6
—I	151 ^{a,4}	67.6
—OC ₆ H ₅	143 ^a	59.6
—OH	141 ¹ , 144 ¹	59.6
—S(O)CH ₃	138 ^a	54.6
—NH ₂	133 ^a	49.6
—NHCH ₃	132 ^a	48.6
—N(CH ₃) ₂	131 ^a	47.6
—CN	136 ^{a,3}	52.6
—CCl ₃	134 ^a	50.6
—CH ₂ I	132 ⁶	48.6
—C≡CH	132 ^a	48.6
—CHCl ₂	131 ⁵	47.6
—COOH	103 ^a , 131 ¹	47.1
—CH ₂ Br	128 ⁶	44.6
—CH ₂ Cl	128 ⁵	44.6
—CHO	127 ^a	43.6
—CH ₃	126 ^a	42.6
—C ₆ H ₅	126 ^a	42.6
—CHCH ₃ Br	126 ⁶	42.6
—C(O)CH ₃	126 ^a , 122 ⁸	40.6
—C(CH ₃) ₃	124 ^a , 120 ⁸	38.6

^a Based on 152 cps. instead of 150 cps. for better correspondence with data of Table II.

TABLE II
COMPARISON OF PREDICTED AND OBSERVED C¹³-PROTON
COUPLING CONSTANTS

Compound	J _{CH} (calcd.)	J _{CH} (exp.)	Diff.
C ₆ H ₅ CH ₂ C ₆ H ₅	127	127 ⁶	0
(CH ₃) ₂ CCH ₂ OH	139	132 ⁷	+7
CH ₃ CH ₂ I	152	149 ⁶	+3
CH ₃ CH ₂ Br	153	151 ⁶	+2
C ₆ H ₅ CH ₂ Cl	153	152 ⁶	+1
C ₆ H ₅ CH ₂ Br	153	153 ⁶	0
(CH ₃) ₂ CHBr	154	151 ⁶	+3
BrCH ₂ CH ₂ Br	155	157 ^{5,6}	-2
ClCH ₂ CH ₂ Cl	155	154 ^{5,6}	+1
CH ₂ ClCN	163	161 ⁶	+2
CH ₂ I ₂	177	173 ^a	+4
CH ₂ Br ₂	179	178 ⁶	+1
CH ₂ Cl ₂	179	178 ^{3,4}	+1
Cl ₂ CHCHCl ₂	185	182 ⁵	+3
CHCl ₂ CN	190	189 ⁶	+1
CHCl ₃	206	209 ^{2,4}	-3

can be evaluated from the data of methane² ($J_{CH} = 125$ cps.). According to the equation $J_{CH}(\text{CH}_4) = 3\zeta_H$; thus we find $\zeta_H = 41.7$ cps.

Zeta values for various substituents now can be calculated from C¹³-proton coupling constants of methyl protons in CH₃X type compounds, since $\zeta_x = J_{CH}(\text{CH}_3\text{X}) - 2\zeta_H$. Spectral data and the results of such calculations are presented in Table

(3) P. C. Lauterbur, *ibid.*, **26**, 217 (1957).

(4) G. V. D. Tiers, *J. Phys. Chem.*, **64**, 373 (1960).

(5) N. Sheppard and J. J. Turner, *Proc. Roy. Soc. (London)* **A252**, 506 (1959).

(6) Observed in this laboratory by Richard Magee, National Science Foundation Undergraduate Research Participant, 1961.

(7) G. J. Karabatsos, *J. Am. Chem. Soc.*, **83**, 1230 (1961).

I. The accuracy of this simple additive scheme in predicting J_{CH} values for methylene and methine protons is shown in Table II. The differences between calculated and experimental values are within the range of experimental error, that is, approximately ± 2 cps.

Upon further examination of Table I we notice that the zeta values seem to be primarily dependent upon the first atom of the substituent (the atom by which the substituent is bonded to the rest of the molecule); halogens $> O > N > C$. This variation parallels the order which these elements occupy in the Periodic Table.

Besides its utility in spectral analysis, the present scheme should have a significant bearing on general theories of nuclear spin-spin coupling. The additivity and variations of zeta values probably are the result of independent, anisotropic, electron-orbital currents localized in the substituents. Consequently, we should expect the zeta values to be angular dependent.

Further work along these lines is being conducted in this laboratory.

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SOME TRIMETHYLSILOXYTRIALKYL TIN COMPOUNDS¹

Sir:

It is worth while to add some further results of our own studies to a recent note² in the field of trimethylsiloxytrialkyltin compounds.

Trimethylsiloxytrialkyltin compounds, Me₃SiO-SnR₃, (R = *n*-Pr, and *n*-Bu) are prepared easily by cohydrolysis, as previously reported,³ of a mixture of trimethylchlorosilane (3-5 mole) and trialkyltin chloride (1 mole) in benzene solution with a slight excess of aqueous ammonia over that necessary to neutralize the mixture. The properties of the products, after rigorous fractionation, are as shown in the table.

TABLE I
PROPERTIES OF TRIMETHYLSILOXYTRIALKYL TIN COMPOUNDS:

	Me ₃ SiOSnR ₃			
	<i>n</i> -Pr		<i>n</i> -Bu	
B.p., °C. at mm.	126	20	142	2
n_D^{20}	1.4575		1.4582	
d_4^{20}	1.093		1.059	
Sn, %, calcd., found	35.21	35.29	31.30	31.28
C, %, calcd., found ^a	42.75	42.70	47.51	47.51
H, %, calcd., found ^a	8.97	8.89	9.57	9.81
Mol. wt., calcd., found ^b	337.2	336	379.2	382

^a Carbon and hydrogen analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.
^b Cryoscopic measurement in benzene.

These two transparent oils have an irritating smell and are fairly stable in a laboratory atmos-

(1) This work was presented at The Chemical Society Symposium on Inorganic Polymers at Nottingham University, England, July, 1961.

(2) H. Schmidbaur and M. Schmidt, *J. Am. Chem. Soc.*, **83**, 2963 (1961).

(3) R. Okawara, D. G. White, K. Fujitani and H. Sato, *ibid.*, **83**, 1342 (1961).