

liams,⁶ *i.e.*, M-SCN \approx M-NCS, as follows: [Pd(AsPh₃)₂(SCN)₂], 2119 cm.⁻¹; [Pd(AsPh₃)₂(NCS)₂], 2089 cm.⁻¹; [Pd(bipy)(SCN)₂], 2117 and 2108 cm.⁻¹ (doublet); [Pd(bipy)(NCS)₂], 2100 cm.⁻¹.

Conductivity measurements were made in dimethylformamide at 25° and a concentration of 10⁻³ M. The molar conductances (ohm⁻¹ cm.⁻² mole⁻¹) obtained fall within the range of conductance exhibited by non-electrolytes in DMF as found by Quagliano, *et al.*: [Pd(AsPh₃)₂(SCN)₂], 13.3; [Pd(AsPh₃)₂(NCS)₂], 13.8; [Pd(bipy)(SCN)₂], 20.3; [Pd(bipy)(NCS)₂], 20.8.

That the S-bonded 2,2'-bipyridine product is the designated isomer and not [Pd(bipy)₂][Pd(SCN)₄] was proven by preparing this pink Magnus-type salt and showing that it differs from the thiocyanato isomer. Here then is an unequivocal example of thiocyanato-isothiocyanato isomerism in metal complexes.⁸ Research will be done on the kinetics and mechanism of isomerization in these and other systems. Work is now in progress on the synthesis of the analogous linkage isomers of the type M-SeCN and M-NCSe and possibly M-NCO and M-OCN.

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(6) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

(7) J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley and S. Y. Tyree, *J. Am. Chem. Soc.*, **83**, 3770 (1961).

(8) Just as there are borderline ligands in determining the nature of thiocyanate ion bonding in metal complexes, there must also be borderline metals. Cadmium(II) is such a metal ion. In aqueous solution, the system Cd(II)-CNS⁻ shows Cd-NCS and Cd-SCN species. Under the same conditions, the other two members of this triad show only Zn-NCS and Hg(II)-SCN species, respectively. These observations were made independently by R. A. Plane, using Raman spectra, and by O. W. Howarth R. E. Richards and L. M. Venanzi, using n.m.r. (private communication).

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ADDITIVITY RELATIONSHIPS IN CARBON-13 CHEMICAL SHIFT DATA FOR THE LINEAR ALKANES¹

Sir:

Carbon-13 chemical shift data obtained in this laboratory on the linear alkanes are presented in Table I along with values obtained by Spiesscke and Schneider² for methane and ethane. The unfavorable sensitivity in detecting the carbon-13 nuclei in natural abundance (1.1%) was overcome by simultaneously irradiating the associated protons in a double resonance experiment. Spin decoupling in this manner results in a sizable signal enhancement which is due to multiplet collapse and a nuclear Overhauser effect. By accurately measuring the two irradiating frequencies when the proton decoupler has been adjusted to give a maximum signal, it is possible to determine the chemical shift with an accuracy of ± 1 c.p.s. (± 0.07 p.p.m.). All chemical shift data are given relative to benzene.

Application of the method of least squares to the data for butane through decane gave additive substituent parameters for the nine linear alkyl radicals, methyl through nonyl, and for the chemical shift of methane. The linear mathematical expression used in the treatment is

$$\delta(C_j) = \delta(\text{CH}_4) + \sum_i n_i \delta(R_i) \quad (1)$$

where $\delta(\text{CH}_4)$ and $\delta(C_j)$ are the chemical shifts of methane and of the j^{th} carbon, respectively. In

(1) Supported by the National Institutes of Health.

(2) H. Spiesscke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

addition, n_i is the number of R_i radicals attached to the j^{th} carbon, and $\delta(R_i)$ is the additive chemical shift parameter assigned to the R_i radical. The chemical shift data on methane through propane were not included in the least squares treatment because of the larger intrinsic error in the recorded values. The data in ref. 2 were reported to have an error of ± 0.3 p.p.m. and our values on propane have a similar error due to the inability to resolve the two resonance signals in the decoupling experiment. The standard deviation of the fit for the more precise data on butane through decane is 0.081 p.p.m., a value which corresponds directly with the experimental error in these data. Therefore, within experimental error all the data of Table I can be said to follow the additivity relationship proposed in Table II.

TABLE I
CARBON-13 CHEMICAL SHIFT DATA FOR THE LINEAR ALKANES

Compound		Exptl. value	Calcd. value	Deviation
Methane (ref. 2)	C ₁	130.8 \pm 0.3	131.47	+0.67
Ethane (ref. 2)	C ₁	122.8 \pm 0.3	122.37	- .43
Propane	C ₁	113.3 \pm 0.3	112.92	- .38
	C ₂	112.9 \pm 0.3	113.27	+ .37
Butane	C ₁	115.67	115.49	- .18
	C ₂	103.87	103.82	- .05
Pentane	C ₁	115.15	115.12	- .03
	C ₂	106.32	106.39	+ .07
	C ₃	94.35	94.37	+ .02
Hexane	C ₁	115.00	115.02	+ .02
	C ₂	105.97	106.02	+ .05
	C ₃	96.85	96.94	+ .09
Heptane	C ₁	114.93	114.97	+ .04
	C ₂	105.89	105.92	+ .03
	C ₃	96.49	96.57	+ .08
	C ₄	99.42	99.51	+ .09
Octane	C ₁	114.83	114.92	+ .09
	C ₂	105.86	105.87	+ .01
	C ₃	96.51	96.47	- .04
	C ₄	99.21	99.14	- .07
Nonane	C ₁	114.86	114.94	+ .08
	C ₂	105.81	105.82	+ .01
	C ₃	96.44	96.42	- .02
	C ₄	99.04	99.04	0
Decane	C ₅	98.77	98.77	0
	C ₁	114.86	114.86	0
	C ₂	105.91	105.84	- .07
	C ₃	96.46	96.37	- .09
	C ₄	99.02	98.99	- .03
C ₅	98.64	98.67	+ .03	

TABLE II
ADDITIVE CHEMICAL SHIFT PARAMETERS

Groups	Chemical shifts in p.p.m.
Methane	131.47 (rel. to C ₆ H ₆)
Radicals	
Methyl	- 9.10
Ethyl	- 18.55
Propyl	- 15.98
Butyl	- 16.35
Pentyl	- 16.45
Hexyl	- 16.50
Heptyl	- 16.55
Octyl	- 16.53
Nonyl	- 16.61

As the substituent corrections in Table II are terms which shift the resonances to lower fields, a paramagnetic shift such as proposed by McConnell³ and Pople⁴ is a possible explanation. Interactions of this type due

(3) H. M. McConnell, *ibid.*, **27**, 226 (1957).

(4) J. A. Pople, *Proc. Roy. Soc. (London)*, **A239**, 550 (1957).

to the anisotropy of carbon-carbon and carbon-hydrogen bonds can be expressed with the following approximate expression³

$$\Delta\delta = (\Delta\chi/3R^3)(1 - 3\cos^2\theta) \quad (2)$$

where the difference in the magnetic susceptibilities parallel and perpendicular to the bond axis is given by $\Delta\chi$, R is the distance to the anisotropic center, and θ is the angle between the vector describing this distance and the bond axis. The $1/R^3$ dependence of eq. 2 would seem to explain the leveling off of the substituent values for the larger radicals

The discontinuity between the ethyl value and those of the larger radicals possibly can be explained in terms of the hydrocarbon chain coiling back on itself. The angle θ in eq. 2 is such that the α,β -carbon-carbon bond makes a paramagnetic correction, while the β,γ -carbon-carbon bond gives a diamagnetic term providing the two *gauche* forms contribute to any appreciable extent. Only for substituents larger than the ethyl radical is this type of conformational coiling possible. Furthermore, for radicals larger than propyl the extension of the carbon chain is in a direction away from the substituted carbon, and a rapid leveling off in the substituent effect is expected.

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ION PAIRS IN ELIMINATION¹

Sir:

Before the distinction between ionization and dissociation was well recognized and the important role of ion pairs in carbonium ion reactions was clear, the proportions of substitution and elimination from unimolecular solvolysis were supposed to be independent of the nature of the leaving group, X, in the organic substrate, RX. Thus, in their classic work with *t*-Bu and *t*-Am systems in 80% aqueous ethanol as solvent, Hughes and Ingold² observed only minor variation of the proportions of elimination and substitution as X varied through the sequence: Cl, Br, I, ⁺SMe₂. Since rate of reaction was sensitive to leaving group, but product composition was not, this provided support for their SN1-E1 formulation. The present communication reports the striking variation of the elimination:substitution ratio in solvolysis of *t*-Bu and *t*-Am substrates with solvent and leaving group.

Using the highly dissociating solvent, water, as a point of departure, we see in Table I that the per cent olefin from *t*-BuX is small and also equal within experimental error for all four leaving groups, Cl, Br, I and ⁺SMe₂. Further, this per cent olefin is not far from the value for the carbonium ion arising from *t*-BuO⁺H₂, calculated from reported^{3a} acid-catalyzed ¹⁸O-exchange and dehydration rate constants of *t*-BuOH on the assumption that the carbonium ion loses the originally formed water molecule from its solvation shell. With *t*-AmX in water, the agreement between per cent olefin observed from *t*-AmCl and that calculated from *t*-AmO⁺H₂ is even better.

The change of solvent from water to less dissociating ethanol produces not only an increase in the fraction of elimination, but also considerable variation with leaving group. The fraction of elimination decreases in the order: Cl > Br > I > ⁺SMe₂. The further change to the still less dissociating and also less nucleophilic sol-

(1) Research supported by the National Science Foundation.

(2) E. D. Hughes, C. K. Ingold, *et al.*, *J. Chem. Soc.*, 1280, 1283 (1937); 2038 (1948).

(3) (a) I. Dostrovsky and F. S. Klein, *ibid.*, 791 (1955); (b) R. Boyd, R. Taft, Jr., A. Wolf and D. Christman, *J. Am. Chem. Soc.*, **82**, 4729 (1960).

TABLE I
MOLE PER CENT OF OLEFIN FROM SOLVOLYSIS IN SEVERAL SOLVENTS

	X	H ₂ O ^b	H ₂ O ^b	EtOH ^b	AcOH ^c
		25.0°	75.0°	75.0°	75.0°
<i>t</i> -BuX ^a	Cl	5.0 ± 1.0	7.6 ± 1.0	44.2 ± 1.0	73 ± 2 ^d
	Br	5.0 ± 1.0	6.6 ± 1.0	36.0 ± 1.0	69.5 ^d
	I	4.0 ± 1.0	6.0 ± 1.0	32.3 ± 1.0	...
	⁺ SMe ₂ ClO ₄ ⁻	...	6.5 ± 1.0	17.8 ± 1.4	11.7 ± 1.0
	⁺ OH ₂	3	4.7
<i>t</i> -AmX ^a	Cl	8.9 ± 0.4			85 ^e
	⁺ OH ₂	8.8			

^a Ca. 0.04 M. ^b 0.07-0.14 M 2,6-lutidine. ^c 0.025-0.103 M NaOAc. ^d These figures reflect a small correction for addition of acetic acid to olefin subsequent to its formation. ^e Ca. 0.1 M *t*-AmCl, 0.25 M NaOAc [see J. Takahashi, Thesis, U.C.L.A., 1960, and S. Winstein and J. Takahashi, *Tetrahedron*, **2**, 316 (1958)].

vent, acetic acid, produces a larger dependence of fraction elimination on leaving group. In this solvent, per cent olefin at 75° varies greatly, ranging from 12% with *t*-Bu⁺SMe₂ ClO₄⁻ to ca. 70% with *t*-BuBr and *t*-BuCl. Obviously, the composition of the solvolysis product from the *t*-Bu system depends markedly on the nature of the leaving group as well as the solvent.

Since there are strong arguments in favor of R-X ionization preceding both substitution and elimination in the solvents being considered, the contrast between elimination proportions from *t*-BuS⁺Me₂ and the *t*-butyl halides must be ascribed to the proximity of the counter halide ion. How much of the observed elimination involves the counter ion may be gaged roughly by using the results with *t*-BuS⁺Me₂ ClO₄⁻ as a guide to the behavior of the dissociated *t*-butyl cation.⁴ On this basis, at least 73% of the elimination from *t*-BuCl in ethanol involves the counter chloride ion, and this figure is at least 95% in acetic acid solvent.

Thus, most, or even all, of the elimination occurring in acetolysis of *t*-BuCl takes place from trimethylcarbonium chloride ion pairs. Further, it is clear that a negligible fraction of these ion pairs can become dissociated and then re-formed.⁵ This is shown⁶ by the virtual absence of radiochlorine exchange during acetolysis of 0.06 M *t*-BuCl at 50° in the presence of 0.07 M 2,6-lutidine and 0.002 M radio-labeled *n*-Bu₄NCl. Under these conditions the first-order exchange rate constant, k_e , is 3×10^{-8} sec.⁻¹, smaller than the titrimetric solvolysis rate constant,⁸ k_t , by a factor greater than 10².

The structure of the carbonium chloride ion pair giving elimination is not known in detail, so it is difficult to specify whether the proton is removed by a solvent molecule influenced by the counter chloride ion or whether it is removed by the chloride ion itself. The latter represents the simpler interpretation. However, both descriptions are consistent with the observed order of efficiency of the halide ions in this solvolytic elimination, namely: Cl > Br > I.

It would appear that elimination is another general reaction which may proceed in solvolytic and other

(4) This measure of the behavior of the dissociated carbonium ion is not ideal, since it neglects the possible effect of the departing dimethyl sulfide. Also, the sulfonate perchlorate salt very probably begins to react at least partially as associated ion pairs in the less dissociating solvents. [See, *e.g.*, J. B. Hyne and J. W. Abrell, *Can. J. Chem.*, **39**, 1657 (1961).] Therefore, some effect of the perchlorate counter ion may be present.

(5) (a) S. Winstein, *et al.*, *Chem. Ind. (London)*, 664 (1954); (b) *J. Am. Chem. Soc.*, **78**, 328 (1956).

(6) This argument presupposes that ion pair return⁵ re-forms covalent *t*-BuCl. That this does occur is indicated, *e.g.*, by the fact that kinetic control of products from the second-order reaction of isobutene with hydrogen chloride in acetic acid solvent leads to extensive formation of *t*-BuCl as well as *t*-BuOAc.⁷

(7) Y. Pocker and Y. V. S. Devi, private communication.

(8) S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, **79**, 5937 (1957).