ied as a function of irradiation time (in benzene): 15 min, 19%; 30 min, 39%; 1 hr, 52%; 3 hr, 58%; and 6 hr, 50% and solvent (for 1 hr): benzene, 52%, *tert*-butyl alcohol, 56%; cyclohexane, 21%; and toluene, 33%.

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(9) All new compounds reported in this study had ir, NMR, mass spectra, and elemental analyses in accord with assigned structures.

David S. Watt
Department of Chemistry, University of Colorado
Boulder, Colorado 80302

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Alkyl Substituent Effects in Electrophilic Substitution at Saturated Carbon. Inapplicability of Taft σ* Values

Sir:

Electrophilic displacement at saturated carbon is an important process, characteristic for organometallic intermediates. Despite extensive studies, however, there is only limited knowledge concerning the mechanism of cleavage of the alkyl-metal bond, particularly with regard to structural variations.[1-3]

We wish to report the use of alkyl substituents as sensitive probes for examining electronic effects in electrophilic cleavages. Mercury compounds are ideal models for organometals since they are substitution-inert and less subject to steric effects than other metals (due to the relatively large radius and two-coordination of mercury). Acetolysis of the dialkylmercury compounds in Table I proceeds according to eq 1 and 2,

$$\text{R-Hg-R}' + \text{HOAc} \begin{cases} \xrightarrow{k} \text{R}'\text{HgOAc} + \text{RH} & (1) \\ \xrightarrow{k'} \text{RHgOAc} + \text{R}'\text{H} & (2) \end{cases}$$

where R, R′ = Me, Et, *i*-Pr, *t*-Bu, and follows first-order kinetics to high conversions. The pseudo-first-order rate constants, k and k', are determined individually by following the rate of alkane liberation by gas chromatography and alkylmercuric acetate by its proton NMR spectrum. A large deuterium kinetic isotope effect in the range of 9–11 (in HOAc and DOAc), depending on the organomercurial, suggests that a substantial positive charge is developed on mercury in the transition state.[4]

Examination of the complete series of dialkylmercurials allows the effects of alkyl groups to be separated into two classes, namely, the cleaved alkyl group R and the departing alkyl group R′ in eq 1. The importance of steric effects is shown in Table I by the reactivity of various alkyl groups under the conditions of a *common leaving group*.[5] More importantly, when a *particular alkyl group R is cleaved*, the dependence of log k on the nature of the departing group R′Hg is in good agreement with eq 3.

$$(\log k/k_{\text{Me}}) \quad \text{Me:Et:}i\text{-Pr:}t\text{-Bu} = 0:0.76:1.31:1.44 \qquad (3)$$
$$= \mathbf{0:0.10:0.17:0.19}$$

where boldface numbers represent values after normalization of Et = 0.10 to conform to Taft σ* in eq 4. The relationship is independent of the cleaved group R as shown by

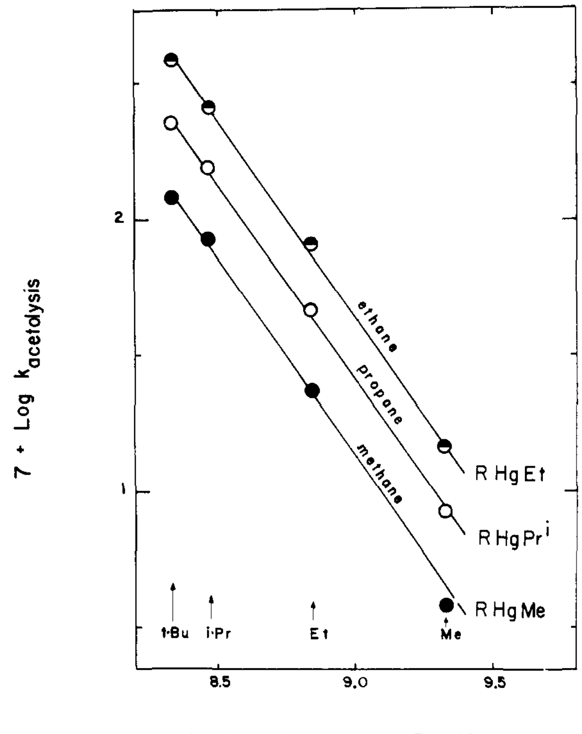

Figure 1. Correlation of the rates of acetolysis of MeHgR (●), EtHgR (◓), and *i*-PrHgR (○) with the vertical ionization potentials of RHgMe measured by He(I) photoelectron spectroscopy.

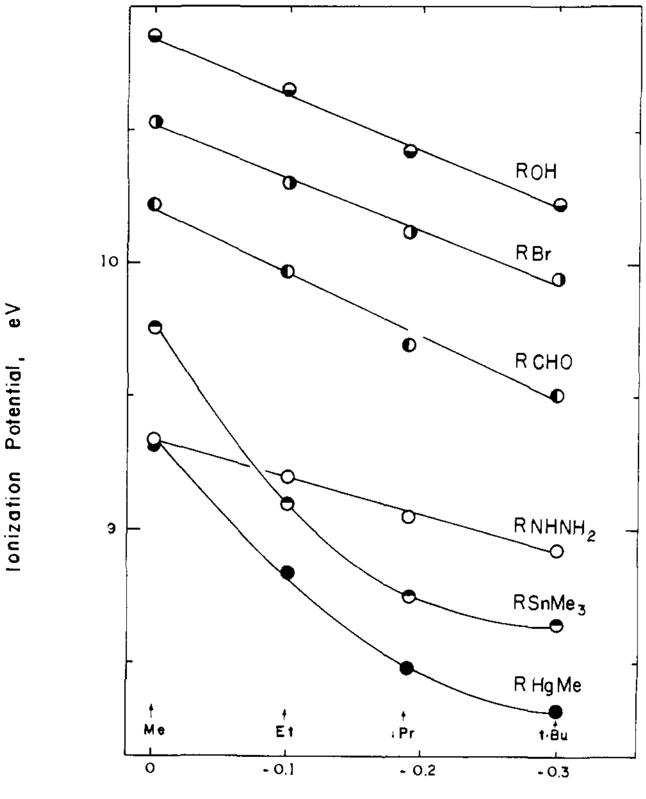

Figure 2. Comparison of the polar effects of alkyl groups using the Taft σ* values and those obtained from ionization potentials. *Additivity* effects in alkylhydrazines (○), alkyl bromides (◑), aldehydes (◐), and alcohols ( ) are from ref 8. *Saturation* effects in alkylmethylmercury (●) and alkyltrimethyltin (◓) from ref 9. (Note that linearity in the additivity effect would be further improved in every case by the use of σ* = −0.20 for *i*-Pr.)

Table I. Rates of Acetolysis of Dialkylmercurials[a]

RHgR′		$10^7 k$ (sec^{-1})	$10^7 k'$ (sec^{-1})	7 + log *k*	7 + log *k*′	IP[b] (eV)
R	R′					
Me	Me	3.90	3.90[c]	0.59	0.59	9.33
Me	Et	23.5	14.3	1.37	1.16	8.84
Me	*i*-Pr	85.8	8.45	1.93	0.93	8.47
Me	*t*-Bu	120	—[d]	2.08	—	8.32
Et	Et	81.8	81.8[c]	1.91	1.91	8.45
Et	*i*-Pr	255	47.0	2.41	1.67	8.18
Et	*t*-Bu	378	—[d]	2.58	—	8.06
i-Pr	*i*-Pr	154	154[c]	2.19	2.19	8.03
i-Pr	*t*-Bu	224	—[d]	2.35	—	7.73

[a] Pseudo-first-order rate constants in HOAc solvent at 37.5°C. [b] First vertical ionization potential by He(I) photoelectron spectroscopy; unpublished results with J. Ulman and T. P. Fehlner. [c] Rates for symmetrical mercurials are statistically corrected. [d] Rates of cleavage of *t*-Bu groups were too slow for direct measurement by this procedure.

the identical slopes of the lines in Figure 1. The nonadditivity of energies as α-hydrogens are successively replaced by methyl groups in eq 3 reflects a saturation effect.[6] This situation contrasts with the additivity requirement Taft[7] has used as a criterion to identify polar effects as denoted by the empirical substituent constants σ^*.

$$(\sigma^*) \quad \text{Me:Et:}i\text{-Pr:}t\text{-Bu} = 0{:}0.10{:}0.19{:}0.30 \qquad (4)$$

The difference between energy effects which are *saturated* and those that are *additive* provides the key, we feel, to the understanding of substituent effects in electrophilic cleavages. For example, there is a strong linear correlation in Figure 2 between σ^* values and the ionization potentials of a series of alcohols, aldehydes, alkylhydrazines, and alkyl halides represented by the process: $R{-}X \rightarrow R{-}X\cdot^+ + \epsilon$.[8] On the other hand, the ionization potentials of a series of organomercurials RHgMe also plotted against σ^* shows a saturation effect[6b] equivalent to that illustrated in Figure 1 for acetolysis. The same saturation obtains for ionization from the same series of Grignard reagents and alkyl-trimethyltin compounds $R{-}SnMe_3$ measured independently.[9] The difference can be explained by considering the highest occupied molecular orbital (HOMO) in each series. For those compounds containing nonbonding electrons, the ionization proceeds from a HOMO which is largely orthogonal to the orbital involved in the bonding of the heteroatom to carbon,[8] and its effect on the electron density in the bond is minimal.[10] In contrast, the ionization process in organometals such as Me_2Hg proceeds from a bonding molecular orbital with a node at mercury.[11] Consequently, the electron density in the bond to carbon is diminished substantially, and the cationic character of the α-carbon is accompanied by a decrease in electron repulsion which is not effectively constant as the alkyl group is systematically varied from Me to *t*-Bu.[12a] Indeed, the validity of this description is shown by values of the ionization potentials of alkyl radicals [i.e., $R\cdot \rightarrow R^+ + \epsilon$], which agree remarkably well with those obtained from SCF-MO calculations.[12,13]

Significantly, the ionization potentials of alkyl radicals[12,13] show the characteristic saturation effect described above, and they correlate well with log *k* for acetolysis and the ionization potentials of organomercurials examined in this study. The remarkable correlation of the latter in Figure 1 is perhaps best approached from the mechanistic standpoint of the Edwards oxy-base equation,[14,15] in which nucleophilicity involves both a term for basicity and one related to oxidation potential (polarizability). In the electrophilic cleavages of organometals, basicity is represented by the intercept in Figure 1, and it is controlled by the nature of the cleaved group R, i.e., by the electron density and the steric restraints surrounding the Hg-R bond. When the cleaved group is the same, contributions from polarizability are derived from the leaving group R′-Hg, and they are limited by saturation effects in R′. Thus, the reactivity of organometals as σ-donors[16] is strongly influenced by the nature of the leaving group. In protodemercurations, leaving group effects will reflect exclusively changes in polarizability produced by alkyl substituents and hence will parallel their effect on the ionization potential of the organomercurials.[17] These conclusions are noteworthy in view of the minor role generally attributed[14a] to polarizability in the nucleophilicity of π and n donors toward protonic electrophiles, and we hope that further studies will extend their generality.[18]

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(6) (a) Saturation is characterized by incremetally smaller (energy) effects resulting from the sequential replacement of α-hydrogens by methyl groups in the series: Me, Et, *i*-Pr, and *t*-Bu. For example in eq 3, the *incremental* changes in energy decrease in the order: 0.76 (Me to Et), 0.55 (Et to *i*-Pr), and 0.13 (*i*-Pr to *t*-Bu). In contrast, in the Taft relationship the effect of replacing Me with Et will be identical with the effect of replacing Et with *i*-Pr or of changing *i*-Pr to *t*-Bu. (b) Compare Figure 2 in which additivity is shown by the linear plots and saturation by the curved lines.

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(18) We wish to thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial assistance and Drs. J. Ulman and T. P. Fehlner for the photoelectron spectra.

William A. Nugent, Jay K. Kochi*

Chemistry Department, Indiana University

Bloomington, Indiana 47401

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