$$B_{12}H_{10}(CO)_2 + H_2O \rightleftharpoons H^+B_{12}H_{10}COOH \cdot CO^- \rightleftharpoons$$

$$(H^+)_2B_{12}H_{10}(COOH)_2{}^{-2} \xrightarrow{OH^-} B_{12}H_{10}(COO)_2{}^{-4}$$
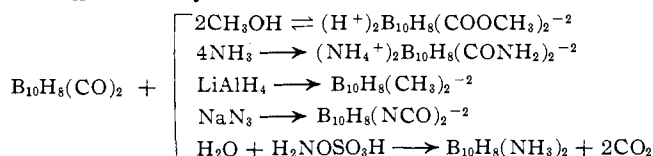
salts. Acidity function studies indicate carboxyl proton ionization constants of $\sim 10^{-9}$.

The chemistry of the dicarbonyls is of extremely broad scope. Some of their reactions are outlined below for the B_{10} system; analogous reactions occur with the B_{12} dicarbonyl.

$$B_{10}H_8(CO)_2 + \begin{bmatrix} 2CH_3OH \rightleftharpoons (H^+)_2B_{10}H_8(COOCH_3)_2{}^{-2} \\ 4NH_3 \longrightarrow (NH_4{}^+)_2B_{10}H_8(CONH_2)_2{}^{-2} \\ LiAlH_4 \longrightarrow B_{10}H_8(CH_3)_2{}^{-2} \\ NaN_3 \longrightarrow B_{10}H_8(NCO)_2{}^{-2} \\ H_2O + H_2NOSO_3H \longrightarrow B_{10}H_8(NH_3)_2 + 2CO_2 \end{bmatrix}$$

The $B_{10}H_8(NH_3)_2$ prepared in this fashion is identical with that prepared from $B_{10}H_8(N_2)_2$ and NH_3. In water the following equilibria exist.

$$B_{10}H_8(NH_3)_2 \rightleftharpoons H^+B_{10}H_8NH_2 \cdot NH_3{}^- \rightleftharpoons (H^+)_2B_{10}H_8(NH_2)_2{}^{-2}$$
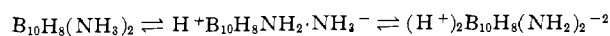
Dehydration of $Cs_2B_{10}H_8(CONH_2)_2$ is effected by heating to about $300°$. We have not encountered a

$$Cs_2B_{10}H_8(CONH_2)_2 \longrightarrow Cs_2B_{10}H_8(CN)_2$$
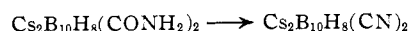
change in stereochemistry in any of the reactions of $B_{10}H_8(CO)_2$.

Halogenated carbonyls (e.g., $B_{10}Cl_8(CO)_2$, $B_{10}Br_8(CO)_2$) have been prepared by aqueous halogenation of $B_{10}H_8(CO)_2$ and $B_{12}H_{10}(CO)_2$ followed by dehydration, at elevated temperatures, of the resulting halogenated carboxylic acids. These halogenated carbonyls are even more thermally stable than the perhydro carbonyls, e.g., there was no evidence of decomposition after heating $B_{10}Cl_8(CO)_2$ at $300°$ in an evacuated sealed tube for 1 hr. A diverse chemistry based on halogenated carbonyls has been demonstrated. For example, $B_{10}Cl_8(CO)_2$ reacts with sodium borohydride to give the bishydroxymethyl species $B_{10}Cl_8(CH_2OH)_2{}^{-2}$ and couples with dimethylaniline to give $B_{10}Cl_8(COC_6H_4-NMe_2)_2{}^{-2}$. $B_{10}Cl_8(CO)_2$ is converted to $B_{10}Cl_8(NH_3)_2$ by reaction with aqueous hydroxylamine-o-sulfonic acid. Diazotization of this chlorinated diamine readily gives $B_{10}Cl_8(N_2)_2$ which, in turn, can be converted to $B_{10}Cl_8(N_3)_2{}^{-2}$ by reaction with sodium azide or to $B_{10}Cl_8(SH_2)_2$ by reaction with hydrogen sulfide.

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An Electromotive Force Cell for Carbonium Ion Stabilization Energies[1]

Sir:

Substituent effects on thermodynamic properties afford one of the principal building blocks of theoretical organic chemistry. The accepted standard, both for application of theoretical analysis and for analysis of reaction rates, is the substituent effect on the equilibrium process.[2] However, there has been an inherent dilemma in the application of such standards. For convincing tests of applications of basic theory to essentially complex organic molecules, substituent effects of substantial (optimum) magnitude are required. Variation of equilibrium constants through

(2) L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., New York, N. Y., 1940, Chapters 3, 4, 7, and 9.

many powers of ten is simply unfeasible by direct experimental determination. Resort has been made, therefore, to such devices as the use of acidity functions, for example, in proton transfer equilibria, to estimate the effects of changing acid medium. No direct experimental data have been available to test the accuracy of the acidity function method over wide ranges (corresponding to many powers of ten in equilibrium constant), and indeed recent evidence leads to certain serious questions of this usage.[3]

We report herein the determination of reversible electrode reduction potentials in acetonitrile solution at $25°$ which provide quantitative measures of the (large) substituent effects on the standard free energy change of a process[3a] which gives relative cation stabilization energies,[4] i.e.

$$R^+ + e \rightleftharpoons {}^1/_2 R\text{-}R \qquad (1)$$
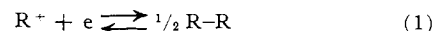
In this process, the widely delocalized charge of R^+ becomes essentially localized (for most practical purposes) in the nonpolar C–C bond. For general R^+, important steric effects on formation of R–R may be involved. In the present report, however, we have restricted R^+ to p-substituted triphenylmethyl (trityl) cations so that steric interactions in the hexaphenylethane derivatives are essentially constant.

The cell, $Pt \mid R_{2(CH_3CN)}, R^+BF_4{}^-_{(CH_3CN)} \mid Ag^+\text{-}NO_3{}^-_{(CH_3CN)} \mid Ag$, is prepared on a vacuum line with a weighed amount of $R^+BF_4{}^{-}$ [5] into which highly purified acetonitrile[6] is distilled. The e.m.f. cell contains a volumetric compartment enabling a measured volume of known concentration of the $R^+BF_4{}^-$ acetonitrile solution to be withdrawn, reduced (to the equilibrium mixture of R_2 and $R\cdot$) by metallic zinc, and titrated into the solution in contact with the Pt electrode. Contact between the two electrode compartments is obtained by use of an asbestos fiber. The e.m.f. measurements are made with an L. and N. K-3 potentiometer and are reproducible to ± 0.002 v. The e.m.f. values are stable over time intervals of a few minutes up to at least 2 hr. to the same precision. Variation of (R^+) from $0.6 \times 10^{-2} M$ to $2.6 \times 10^{-2} M$ and of (R_2) from $0.10 \times 10^{-2} M$ to $0.80 \times 10^{-2} M$ gives e.m.f. values which follow the equation

$$E = E^0 - \frac{RT}{n\mathfrak{F}} \ln \left[\frac{(R_2)^{1/2}(Ag^+)}{(R^+)} \right]$$

to a precision of ± 0.003 v.

The standard free energy change, $\Delta F_2°$, for the reaction

$$R^+ + {}^1/_2(R_0\text{-}R_0) = R_0{}^+ + {}^1/_2(R\text{-}R) \qquad (2)$$
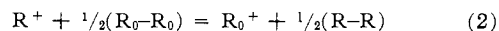
where R_0 designates unsubstituted trityl cation and R the p-substituted derivative, is obtained from E^0 corresponding to this cell reaction (which is negligibly affected by the liquid junction potential). Table I lists values of E^0, K_{equil}, and $\Delta F_2°$ for reaction 2. Also listed in Table I are $\Delta F_3°$ values for the reaction

$$R^+ + R_0\text{-}OH = R_0{}^+ + R\text{-}OH \qquad (3)$$
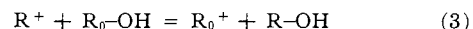
obtained through the application of the H_R acidity function.[7]

(3) E. M. Arnett, in "Progress in Physical Organic Chemistry," Vol. I, Editors, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Interscience Publishers, Inc., 1963, p. 223.

(3a) J. B. Conant, et al., J. Am. Chem. Soc., 47, 1959 (1925); 55, 3752 (1933).

(4) Cf. N. Muller and R. S. Mulliken, ibid., 80, 3489 (1958).

(5) H. J. Dauben, Jr., L. R. Honner, and K. M. Harmon, J. Org. Chem., 25, 1442 (1960).

(6) J. F. Coetzee, G. P. Cunningham, D. R. McGuire, and G. R. Padmanabhan, Anal. Chem., 34, 1139 (1962).

(7) (a) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, J. Am. Chem. Soc., 77, 3044 (1955); (b) N. C. Deno and A. Schriesheim, ibid., 77, 3051 (1955); (c) N. C. Deno and W. L. Evans, ibid., 79, 5804 (1957).

Table I shows striking agreement between our directly measured ΔF_2° values for reaction 2 in acetonitrile solution and corresponding ΔF_3° values for reaction 3 in aqueous solution. This result then offers compelling confirmation of the H_R acidity function (up to about 50 wt. % acid). The agreement further implies that the free energies to a very major extent measure internal energy effects,[8] i.e., relative cation stabilization energies. The substituent effect on the free energy of solvation of the trityl cation is apparently substantially the same in the aqueous as the non-aqueous solvent (in spite of their great difference in dielectric and other properties), a result which must be attributed to the chemical inertness of the R^+, $R-R$, and substituent toward the solvent.[3,9,10]

TABLE I

RELATIVE STABILIZATION ENERGIES OF p-SUBSTITUTED TRITYL CATIONS IN ACETONITRILE SOLUTION

p-Subst.	K_{equil}	$-E^0$, v.	ΔF_2°, kcal.	ΔF_3°, kcal.
H, H, H[a]	(1.00)	(0.000)	(0.0)	(0.0)
F, H, H[a]	0.98	.006	0.1	0.1[b]
CH$_3$, H, H[a]	3.6×10^{-2}	.086	2.0	1.9
OCH$_3$, H, H[a]	2.0×10^{-4}	.219	5.1	4.4
OCH$_3$, OCH$_3$, H[a]	3.7×10^{-8}	.381	8.8	7.4
OCH$_3$, OCH$_3$, OCH$_3$[a]	1.7×10^{-9}	.518	12.0	10.2
N(CH$_3$)$_2$, H, H[c]	6.5×10^{-12}	.660	15.2	15.5
N(CH$_3$)$_2$, N(CH$_3$)$_2$, N(CH$_3$)$_2$[c]	3.1×10^{-18}	1.037	23.9	21.8

[a] See ref. 7.   [b] Estimated from σ^+ and ρ values listed in ref. 7c. [c] R. J. Goldacre and J. N. Phillips, J. Chem. Soc., 1724 (1949).

The small differences (ΔF_2° is generally about 10% larger than ΔF_3°) may result from the fact that there is greater localization of the positive charge of R^+ in the C–C than the polar C–O bond. There are also probably some small effects on the ΔF° values due to symmetry considerations and on ΔF_3° due to solvation of the OH group.

The ionization potential of organic radicals to cations also has been a quantity of much theoretical interest.[14] The applicability of gas-phase values to chemical reactions in solution is uncertain, however, for reasons of solvation energy as well as of possible excess energy content of the gaseous ions. The great contrast between gaseous ionization potentials of the metallic elements and the corresponding aqueous e.m.f. series serves to illustrate how different in character ionization potentials in the gas and condensed phases can be. Literature values[15] for the equilibrium constants for

(8) L. G. Hepler, J. Am. Chem. Soc., **85**, 3089 (1963).

(9) (a) R. W. Taft, ibid., **82**, 2965 (1960); (b) N. C. Deno, "Equilibria in Concentrated Mineral Acid Solutions," in A. F. Scott's "Survey of Progress in Chemistry," Academic Press, New York, N. Y., 1963; (c) R. H. Boyd, J. Am. Chem. Soc., **85**, 1555 (1963); (d) E. M. Arnett and R. D. Bushick, ibid., in press.

(10) This result may be contrasted with proton transfer equilibria of m- and p-substituted benzoic acids in water[11] and with 1,3-diphenylguanidine in benzene.[12] For m-substituents there is precise fit to the Hammett $\sigma\rho$ relationship, but substituent effects are 230% greater in benzene than water. Further, for $-R$-p-substituents, enhanced resonance effects are observed in water.[13] Evidently, the nonequivalence of substituent effects is to be attributed at least in part to the chemical interactions between solvent and the CO$_2$H and CO$_2^-$ functional groups as well as to different dielectric properties of water and benzene, cf., also, C. D. Ritchie and W. F. Sager, "An Examination of Structure–Reactivity Relationships," in "Progress in Physical Organic Chemistry," 1964, in press.

(11) Ref. 2, Chapter 7.

(12) M. M. Davis and H. B. Hetzer, J. Res. Natl. Bur. Std., **60**, 569 (1958).

(13) R. W. Taft, S. Ehrenson, I. C. Lewis, and R. E. Glick, J. Am. Chem. Soc., **81**, 5352 (1959).

(14) A. Streitwieser, Jr., "Progress in Physical Organic Chemistry," ref. 3, p. 1.

(15) (a) Cf. G. W. Wheland, "Advanced Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 694; (b) J. B. Conant and N. M. Bigelow, J. Am. Chem. Soc., **53**, 676 (1931).

the reaction, $R \cdot + \frac{1}{2}(R_0-R_0) \rightarrow R_0 \cdot + \frac{1}{2}(R-R)$, in combination with E^0 values of Table I, provide for the first time quantitative measures of p-substituents on the ionization potentials of trityl radicals in acetonitrile solution. Table II lists the ionization potential data so derived. Unfortunately, gas-phase values (such as those recently reported for benzyl radicals)[16] are not presently available for comparison.

TABLE II

RELATIVE IONIZATION POTENTIALS OF p-SUBSTITUTED TRITYL RADICALS IN ACETONITRILE SOLUTION

p-Subst.	$(I - I_0)$, v.
H, H, H	(0.000)
F, H, H	$-$ .000
CH, H, H	$-$ .043
OCH$_3$, H, H	$-$ .187
N(CH$_3$)$_2$, H, H	$-$ .587

A subsequent detailed report will be made of our e.m.f. cell, as well as the results of studies of the temperature coefficients of the e.m.f. values.

(16) A. G. Harrison, P. Kebarle, and F. P. Lossing, ibid., **83**, 777 (1961).

(17) National Science Foundation Graduate Fellow, 1961–1964.

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RECEIVED OCTOBER 30, 1963

Electronic Interactions in Biradicals. II. A Singlet–Triplet Equilibrium[1,2]

Sir:

We recently reported a study of the radicals derived from 2,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)propane (I). The removal of both phenolic hydrogen atoms of I gave an equilibrium mixture of singlet (bonded) and triplet species. In this case the equilibrium favored the singlet tautomer almost completely. We have modified I in order to make formation of the internal bond more difficult, shifting the equilibrium toward the triplet state. The system we chose is formed by replacing the gem-dimethyl group in I with a 2,2'-biphenylene group, yielding II.

The ordinary (aluminum chloride–carbon disulfide) Friedel–Crafts reaction of 2,6-di-t-butylphenol with 9,9-dichlorofluorene did not appear successful. However, the addition of a solution of silver oxide in acetic acid containing excess perchloric acid to a solution of the phenol and the dichloride in acetic acid produced II in ca. 50% yield, m.p. 272–273° from benzene–hexane.

Anal. Calcd. for $C_{41}H_{50}O_2$: C, 85.66; H, 8.77. Found: C, 85.94, 85.76; H, 8.57, 8.77.

The infrared spectrum of the product was consistent with the assigned structure, λ_{max} 2.7 μ, as was the ultraviolet spectrum, $\lambda_{max}^{C_6H_{12}}$ 299 mμ (log ϵ 2.6), 310 (2.8).

An ethereal solution of the bisphenol (II) was readily oxidized by aqueous alkaline ferricyanide in the usual manner[3] and gave a dark yellow-green solution. Evaporation of the solvent with nitrogen gave a dark oil, which crystallized when treated with pentane. The infrared spectrum (carbon tetrachloride) of this product indicated that both biradical (III) and spirodienone

(1) Paper I: E. A. Chandross and R. Kreilick, J. Am. Chem. Soc., **85**, 2530 (1963).

(2) Partial support (at Washington University) of this work by the U. S. Air Force under contract, the National Science Foundation, the Petroleum Research Fund of the American Chemical Society, and an equipment loan contract with the office of Naval Research is gratefully acknowledged.

(3) E. Muller and K. Ley, Chem. Ber., **87**, 922 (1954).