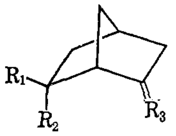
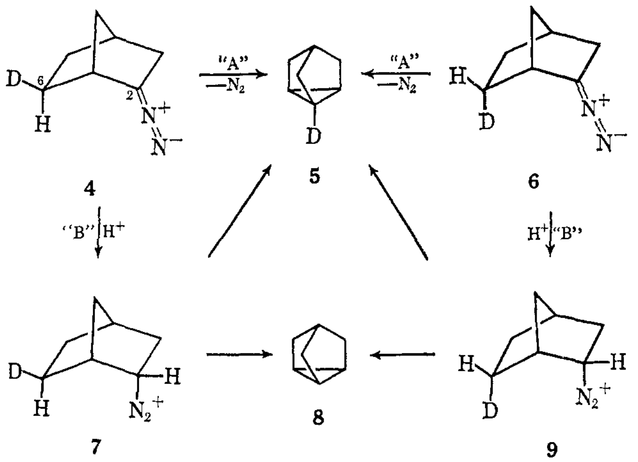
results also exclude protonation of the carbene as the sole cationic pathway, because such protonation must formally produce a norbornyl cation.

We suggest as the *simplest* interpretation that an important reactive species preceding nortricyclene is a diazonium ion or its equivalent, derived possibly by protonation of the corresponding diazohydrocarbon (path B).[18,19] Because *exo* protonation should be favored sterically,[20] the C–N bond is probably largely in the *endo* configuration (7 and 9). Unimolecular and bimolecular 1,3 elimination from 7 or 9 can lead to deuterated or nondeuterated nortricyclene (5 and 8, respectively) according to whether an *exo* or *endo* hydrogen (or deuterium) is abstracted from C-6.



a, $R_3 = O$;
b, $R_3 = NNHTs$

1, $R_1 = R_2 = H$
2, $R_1 = D$; $R_2 = H$
3, $R_1 = H$; $R_2 = D$



The greater isotope loss from presecursor 9 indicates that for the bimolecular component there is a stereoelectronic preference for cleavage of the *endo* bond at C-6 in the 1,3-elimination step.

[18] For proton transfer to diazohydrocarbons see: (a) D. Bethell and J. D. Callister, *J. Chem. Soc.*, 3801, 3808 (1963); (b) D. W. Thomas and K. Biemann, *J. Am. Chem. Soc.*, **87**, 5447 (1965); (c) G. L. Closs, R. A. Moss, and S. H. Goh, *ibid.*, **88**, 365 (1966).

[19] Intervention of hydrogen-bonded[18c] or N-protonated intermediates[10] prior to eventual C-protonation are detailed variations that can be incorporated into the interpretation.

[20] H. C. Brown and H. R. Deck, *J. Am. Chem. Soc.*, **87**, 5620 (1965).

Alex Nickon, Nick H. Werstiuk
Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218

Received February 19, 1966

Stabilization Energies of Triphenylmethyl Anions from Electromotive Force Measurements. Concerning Saturation of π Electronic Effects[1,2]

Sir:

The stabilization energies of *para*-substituted trityl (triphenylmethyl) cations relative to unsubstituted trityl cation were recently obtained from the standard free energy change of reaction 1 through the use of emf cell measurements[3]

$$R^+ + {}^1\!/_2(R_0\text{-}R_0) \rightleftharpoons R_0^+ + {}^1\!/_2(R\text{-}R) \tag{1}$$

where $R_0 \equiv$ trityl, $R \equiv$ substituted trityl, and $\Delta F°(R+) = -nFE° \equiv SE(R^+)$.

We wish to report the similar use of emf cell measurements to obtain the first measures of stabilization energies of *meta*- and *para*-substituted trityl anions, *i.e.*

$$R^- + {}^1\!/_2(R_0\text{-}R_0) \rightleftharpoons R_0^- + {}^1\!/_2(R\text{-}R) \tag{2}$$

where R_0 and R are as above and $\Delta F°(R^-) = -n\text{FE}° \equiv SE(R^-)$.

The actual observable was the reversible emf[4] for reaction 3 in purified dimethyl sulfoxide[5] (DMSO) at

$$R^-(Na^+) + Ag^+(NO_3^-) \rightleftharpoons {}^1\!/_2(R\text{-}R) + Ag \tag{3}$$

25°. The modified three-electrode emf cell[6] used to measure the potential of reaction 3 contained two platinum disk electrodes which were separated by an ultrafine glass frit. The third electrode consisted of an Ag| 0.02 *M* $AgNO_3$ (DMSO) reference electrode and was separated from the Pt electrode in the R^-|R–R compartment by an ultrafine glass frit. Tetramethylammonium tetrafluoroborate (0.20 *M*) was used as a supporting electrolyte and an atmosphere of ultrahigh-pure argon or nitrogen was maintained in the cell throughout the course of the experiment. Concentrations of R^- and R–R were varied[7] by electrolytic oxidation of the trityl anions and were followed by connecting the cell in series with a hydrogen–oxygen gas coulometer.[8] Variation of $[R^-]$ from 4.5 to 6.5 × 10^{-2} *M* and [R–R] from 1.0 × 10^{-3} to 1.0 × 10^{-2} *M* gave emf values which followed the Nernst equation to a precision of ±0.005 v.

The standard free energy change, $\Delta F°(R^-)$, was obtained from $\Delta E°$ for reaction 3 for the substituted trityl anions relative to the unsubstituted anion and is assumed to be only slightly affected by the liquid junction potential and by any small variations in ion-pair formation. Table I lists values of $E°(2)$ for reaction 2 and corresponding $\Delta F°(R^-)$ values. Also listed are values of $\delta\Delta$, the fluorine nmr shielding change on formation of 4-fluoro-4′-X-substituted trityl anion from its methane relative to the corresponding change for the unsubstituted 4-fluorotrityl system. This substituent shielding effect is expected to be a measure (1 ppm ≅ 1 kcal) of the relative stabilization

---

[1] This work was supported in part by the National Science Foundation.

[2] Taken in part from the Ph.D. Dissertation of L. D. McKeever, University of California, Irvine, 1966; work performed in part at the Pennsylvania State University.

[3] E. D. Jenson and R. W. Taft, *J. Am. Chem. Soc.*, **86**, 116 (1964).

[4] H. E. Bent and N. B. Keevil, *ibid.*, **58**, 1228 (1936), established the reversibility of cells involving the trityl anion system by measuring $E°$ for the reaction: $C(C_6H_5)_3\cdot + Na \rightleftharpoons Na^+(C_6H_5)_3C^-$.

[5] E. J. Corey and M. Chaykovski, *ibid.*, **84**, 866 (1962); **87**, 1345 (1965).

[6] The basic design of the emf cell was privately communicated by Professor Peter H. Given, Pennsylvania State University.

[7] The trityl anions were generated by treating the corresponding triarylmethane with an equimolar amount of dimsylsodium, prepared according to the technique of Corey.[5] Initial concentrations of R^- were obtained by applying the "double titration" technique of H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, **2**, 447 (1964).

[8] J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, N. Y., 1953, p 349.

energies of the anions.[9] Indeed, a satisfactory correlation exists between corresponding $\Delta F^\circ(\mathrm{R}^-)$ and $\delta\Delta$ values with slope of 1.3 kcal/ppm.

Table I. Stabilization Energies of Substituted Trityl Anions in Dimethyl Sulfoxide

Substituent	$E^\circ(2)$, v	$\Delta F^\circ(R^-)$ kcal/mole (± 0.2)	$\bar{\sigma}^-$	$\delta\Delta$, ppm
H	(0.000)	(0.0)	0.00	(0.0)
p-F	0.020[a]	−0.5	−0.03[c]	0.0
p-CH_3	0.056	−1.4	−0.17	1.6
p-CH_3O	0.209[b]	−4.8	−0.47[c]	3.3
p-$(CH_3)_2N$	0.218	−5.0	−0.52[c]	3.8
p-NO_2	−0.685	15.8	+1.63[c]	−12.1
Tris-*p*-NO_2	−0.697	18.5	+0.67[d]	....
m-NO_2	−0.291[b]	6.7	+.71	....
m-CF_3	−0.175	4.0	+.48	....

[a] Approximate value. [b] Polarographic reduction of the corresponding hexaarylethanes gave $\Delta E_{1/2}$ values agreeing within experimental error with $E^\circ(2)$ values. [c] Calculated by the procedure of Taft and Lewis, *J. Am. Chem. Soc.*, **81**, 5351 (1959). Values are the mean of those obtained from $\Delta F^\circ(\mathrm{R}^-)$ and $\delta\Delta$ values. [d] Value per NO_2 group.

Using the procedure of Taft and Lewis,[10] the $\Delta F^\circ(\mathrm{R}^-)$ values yield a ρ value for reaction 2 of −6.9 (in log K units) and the $\bar{\sigma}^-$ values listed in Table I. The magnitudes of the values of ρ and $\bar{\sigma}^-$ for *p*-NO_2 are noteworthy in that both exceed corresponding values previously reported for carbanion[11] or similar reactivities,[10] in accord with expectations for reaction 2. For *p*-F and *p*-OCH_3, $\bar{\sigma}^-$ values are more negative than normal,[12] a result in accord with Mulliken's concept of concerted inductive–mesomeric action.[10–13] The results of Table I and similar reactivities[10] in fact indicate that *the π donor destabilizing effects of p-F, p-OCH_3, p-$N(CH_3)_2$* (and probably all other UAFPD substituents[14]) *become essentially identical when substituted at electron-rich unsaturated carbon* ($\sigma^-_\mathrm{R} = -0.60 \pm 0.06$).[15] This striking result (which may be seen in terms of σ_R not σ values) can be readily accommodated by the Mulliken concept and in fact provides convincing evidence thereof.

Polar effects (field and inductive) on reactivities are known to be approximately additive.[16] We wish to emphasize in contrast the marked "saturation" of conjugative π electronic *stabilization* effects which are dramatically illustrated in Table I and by other recent results.[3,9,17] The ratio (1.17) of the stabilization energies of tris-*p*-NO_2- to mono-*p*-NO_2-trityl anions is markedly less[18] than the additive factor of 3. Similarly for trityl cations, the ratio of the stabilization energies of tris-*p*-$N(CH_3)_2$ to mono-*p*-$N(CH_3)_2$ is 1.61.[3] No additional stabilization energy has been found for the $(CH_3O)_3C^+$ cation compared to that for the $(CH_3O)_2CH^+$ cation, both relative to CH_3^+.[17] A general trend toward *increased "saturation" of multiple substitutional π electronic stabilization effects with increased magnitude of the π stabilization effect is clearly evident.*[2,3,17]

These multiple substitution effect results provide a clear negative answer to the question of whether a set of conjugation-enhanced substituent parameters (*e.g.*, σ^+, σ^-, or $\Delta\sigma_\mathrm{R}^\pm$) may be formulated which have wide general applicability.[10,19–21] Compare, for example, the markedly different effective (formal) $\bar{\sigma}^-$ values for mono-*p*-NO_2- and for tris-*p*-NO_2-trityl anions (Table I). While it must be recognized that *para*-substituent effects in trityl cations and anions are subject to steric effects of phenyl twisting at the central carbon,[22] we believe the results in these systems are of such magnitudes as to indicate that the above generalization also holds for "intrinsic" π electronic behavior in coplanar systems. This conclusion is supported by the results of model HMO calculations of the electron affinities and ionization potentials of *para*-substituted trityl radicals (relative to trityl) for both twisted and hypothetical coplanar ions.[2]

It is finally of interest to note that $\Delta F^\circ(\mathrm{R}^-) - \Delta F^\circ(\mathrm{R}^+)$ corresponds to the standard free energy change for reaction 4, which gives the substituent

$$\mathrm{R}^- + \mathrm{R}_0^+ \rightleftarrows \mathrm{R}^+ + \mathrm{R}_0^- \tag{4}$$

effect on the Mulliken electronegativity[23] ($\Delta I + \Delta A$) of trityl radicals. Since $\Delta F^\circ(\mathrm{R}^-)$ and $\Delta F^\circ(\mathrm{R}^+)$ values are not available in a common solvent, $\Delta I + \Delta A$ may only be approximated by the available data. The results conform to the $\sigma\rho$ features which have been discussed in connection with reactions 1 and 2.

---

(9) R. W. Taft and L. D. McKeever, *J. Am. Chem. Soc.*, **87**, 2489 (1965).

(10) R. W. Taft and I. C. Lewis, *ibid.*, **81**, 5351 (1959).

(11) A. Streitwieser, Jr., and H. F. Koch, *ibid.*, **86**, 404 (1964).

(12) R. W. Taft, *et al.*, *ibid.*, **81**, 5352 (1959).

(13) R. S. Mulliken, *Tetrahedron*, **5**, 253 (1959).

(14) R. W. Taft, *et al.*, *J. Am. Chem. Soc.*, **85**, 3146 (1963).

(15) Note further that this is slightly more negative than the σ^0_R value for $N(CH_3)_2$; the only deviations of consequence to this generalization appear for the *p*-NH_2 and *p*-$N(CH_3)_2$ substituents in the ionization of phenols (in contrast, in the ionization of anilinium ions the generalization holds). We propose the less negative σ^-_R values in this case result from hydrogen bonding of these substituents to water which is induced in the phenoxide ions.

(16) *Cf.* R. W. Taft in Ed., M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N.Y., 1956, Chapter 13.

(17) (a) R. H. Martin, F. W. Lampe, and R. W. Taft, *J. Am. Chem. Soc.*, **88**, 1353 (1966); (b) *cf.* also J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N.Y., 1962, p 101.

(18) A similar factor has been obtained by C. D. Ritchie and R. E. Uschold (private communication) in the ionization of the triarylmethanes in DMSO.

(19) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(20) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957).

(21) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, **32**, 971 (1959).

(22) (a) R. I. Walter, *J. Am. Chem. Soc.*, **88**, 1930 (1966); (b) F. J. Adrian, *J. Chem. Phys.*, **28**, 608 (1958).

(23) R. S. Mulliken, *ibid.*, **2**, 782 (1934); **3**, 573 (1935).

L. D. McKeever, R. W. Taft
Department of Chemistry, University of California, Irvine
Irvine, California

Received August 22, 1966

Tetracyanoethylene Complexes of Rhodium and Iridium[1]

Sir:

The fact that the nature of the transition metal–carbon σ bond is not well understood has been noted in reviews.[2] A cursory survey of the literature in-

---

(1) Paper II of the series: Metal Complexes of Cyanocarbons. Part I: W. H. Baddley and L. M. Venanzi, *Inorg. Chem.*, **5**, 33 (1966).

(2) (a) G. E. Coates and F. Glockling, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 9; (b) P. M. Trieichel and F. G. A. Stone, *Advan. Organometal Chem.*, **1**, 177 (1964).