

# STABILITIES OF SOME 2-(*PARA*-SUBSTITUTED-PHENYL)-4,4,5,5-TETRAMETHYL-1,3-DIOXOLANES RELATIVE TO THEIR CONJUGATE DIOXOLENIUM IONS, RADICALS AND CARBANIONS AS DETERMINED BY THERMODYNAMICS FOR HYDRIDE AND ELECTRON TRANSFER IN SOLUTION

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A calorimetric method is described for the determination of the hydride affinities,  $\Delta H_{\text{H}^-}(\text{R}^+)$  of seven dioxolenium ions from the title compounds and also tropylium, trityl and 9-phenyl xanthylium cations by hydride transfer to the carbocations from  $\text{BH}_3\text{CN}^-$ . Cyclic voltammetric methods yield free energies for reduction of the cations to the conjugate radicals and to the carbanions. The  $\Delta H_{\text{H}^-}(\text{R}^+)$  values correlate well with the first reduction potentials of the cations.

## INTRODUCTION

The concept of 'reactivity' so crucial to physical-organic studies of structure-energy relationships is usually expressed in terms of kinetic or thermodynamic properties for bond making or breaking. Especially important are free energies of ionization to form reactive carbenium ions or carbanions from neutral precursors by transfer of a suitable anion (e.g. halide) or cation (usually  $\text{H}^+$ ) to a Lewis acid or base. The many important free energy structure-reactivity scales, such as  $\text{p}K_{\text{R}^+}$  from the equilibration of carbenium ions with their carbinols in aqueous acid solutions,<sup>1,2</sup> or  $\text{p}K_{\text{HA}}$  for proton transfer to  $\text{K}^+\text{DMSYL}^-$  in  $\text{DMSO}^3$  have been established this way.

As an alternative approach to evaluating the effects of ring substitution on the stabilities of triphenylmethyl carbenium ions and carbanions, Taft and co-workers,<sup>4,5</sup> following Conant and co-workers' classic studies,<sup>6</sup> compared the energies for converting the ions into their conjugate radicals by electron transfer, in appropriately designed cells. Although the conditions for equilibrating the carbocations or carbanions with the radicals by electron transfer were different from those for deriving their ion stabilization energies from  $\text{p}K_{\text{R}^+}$  values and  $\sigma^-$

substituent parameters, the substituent effects on the free energy changes correlated well for the various ion  $\rightleftharpoons$  neutral processes.

In subsequent years, cyclic voltammetric methods have greatly broadened the study of electron transfer between a variety of ionic and radical species with methods that are relatively straightforward. Of particular interest is the feasibility of two-electron transfer to or from carbenium ions or carbanions at a fast enough rate so that coupling of the intermediate radical can be overridden. In such a case the stability of the cation can be established relative to its conjugate anion (or vice versa) rather than to a neutral precursor or radical. Breslow's group<sup>7</sup> developed these techniques to estimate the  $\text{p}K_{\text{HA}}$  values of very weak acids or the  $\text{p}K_{\text{R}^+}$  values of very unstable carbenium ions which were inaccessible by other methods, and several other research groups have explored two-electron redox potentials for a variety of cations<sup>8</sup> and anions.<sup>9</sup>

Such two-electron processes provide a different type of thermodynamic scale for comparing structural effects on stabilities, in terms of their influence on the carbenium ion versus that on the carbanion or radical rather than by reference to the energy required to break a bond to a leaving group in a neutral molecule.

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In a recent communication,<sup>10</sup> we proposed the term 'amphihydric' as applied to compounds, such as triphenylmethane, which carry a hydrogen as the common leaving group that may be displaced readily as a hydride ion, hydrogen atom or proton to produce reasonably stable conjugate carbenium ions, radicals or carbanions by treatment with appropriate acids, radicals or bases and may be interconverted readily by one- and two-electron transfer in solution. A complete energetic analysis of the *para*-substituted-9-phenylxanthyl system was presented which related the cations, radicals and anions to each other by electrochemistry. Reaction calorimetry related the carbocations and carbanions to their neutral 9-arylxanthene precursor, by measurement of the heats of hydride transfer from cycloheptatriene to the cation and heats of proton transfer to DMSYL<sup>-</sup> anion, respectively. Finally, the heat of heterolysis ( $\Delta H_{\text{het}}$ ) of dixanthyl was measured by reaction of xanthylum cation with xanthanide anion in sulfolane. This type of dimer is usually only accessible through radical coupling. The relevant heat of homolysis ( $\Delta H_{\text{homo}}$ ) was obtained, by combining  $\Delta H_{\text{het}}$  with redox potentials of the cation and anion.

Amphihydric compounds provide a unique opportunity to compare the energetics of formation of cognate carbocations, radicals and carbanions using hydrogen as the common leaving group provided that both the carbenium ion and carbanion are stable enough to be handled in appropriate solutions. Although hydrogen transfer has been the standard process for comparing gas-phase stabilities<sup>11</sup> for carbanions (through gas-phase acidities), radicals (through bond dissociation energies, *BDEs*)<sup>12</sup> and carbenium ions (through hydride affinity energies), only a few classes of compounds have so far

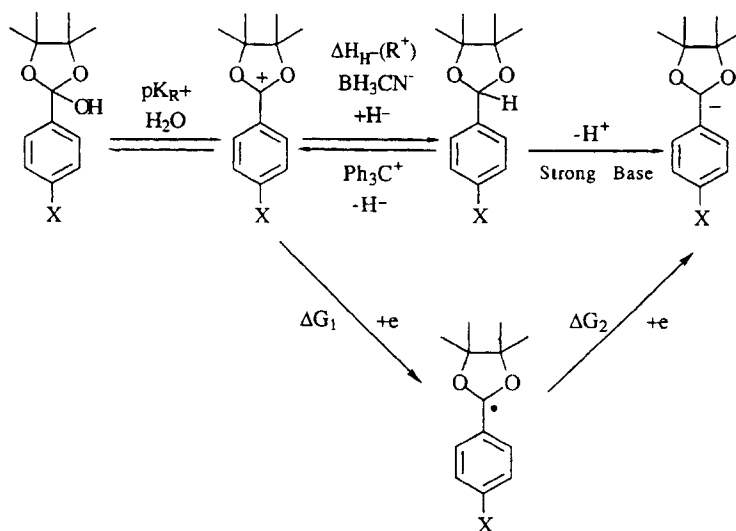
allowed such a complete treatment in solution. In general, if the carbanion is stable enough for study by deprotonation with DMSYL<sup>-</sup>-DMSO, the carbenium ion is too unstable to be produced and maintained readily in most ordinary acid solutions or vice versa.

This paper reports some results for seven 2-*para*-substituted-phenyl)-4,4,5,5-tetramethyl-1,3-dioxolanes in sulfolane solution as shown in Scheme 1. Although there is a voluminous literature<sup>13</sup> describing the properties of dioxolenium ions as highly stabilized carbenium/oxonium ions, we have found no reference to the formation of their conjugate 1,3-dioxolanate anions by treatment of the parent 1,3-dioxolanes with strong base. Although it is reasonable that a benzylic C-H bond flanked by two electronegative oxygens might be reasonably acidic, none of the dioxolanes in this study could be deprotonated cleanly in DMSYL<sup>-</sup>-DMSO. They might be acidic to stronger bases.<sup>14</sup> The analogous 2-aryl-1,3 dithianes yield stable carbenium ions in sulfolane, are deprotonated in DMSYL<sup>-</sup>-DMSO and will be reported later.<sup>15</sup>

For the six 2-substituted-tetramethyldioxolanes we present here (a) hydride affinities ( $\Delta H_{\text{H}}-\text{R}^+$ ) from reaction with NaBH<sub>3</sub>CN and (b) all one- and two-electron transfer potentials between conjugate cations, radicals and carbanions.

## EXPERIMENTAL

*Materials.* All compounds necessary for preparing the 2-aryl-4,4,5,5-tetramethyl-1,3-dioxolanes and their derived cations were available commercially (Aldrich) and were purified, if necessary, until clean as shown by <sup>1</sup>H NMR spectroscopy.



The dioxolanes were prepared by the following standard procedure.<sup>16</sup> A mixture of the substituted benzaldehyde (50 mmol), and pinacol (5.90 g, 50 mmol) was dissolved in 10 ml of benzene with a trace of *p*-toluenesulfonic acid and refluxed with water removal being effected by a Dean–Stark trap. After 1 day the reaction mixture was cooled and extracted twice with aqueous 2 M sodium hydroxide. The benzene layer was dried over magnesium sulfate and, after evaporating the benzene, the dioxolane was obtained by vacuum distillation and its structure and purity were confirmed by <sup>1</sup>H NMR spectroscopy.

Trityl tetrafluoroborate was prepared<sup>17</sup> by dissolving triphenylmethanol (13.2 g, 50 mmol) in propionic anhydride (150 ml) and cooling the solution to 10 °C. After adding 48% fluoroboric acid (4.4 g, 50 mmol), the temperature was kept between 10 and 12 °C for a few minutes. The precipitate was filtered through a cooled frit under argon and was vacuum-dried overnight. The trityl tetrafluoroborate was transferred into a dry-box.

Each dioxolenium ion was prepared by adding the parent dioxolane (14 mmol) to a stirred solution of trityl tetrafluoroborate (4.6 g, 14 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (70 ml) at room temperature under argon following Meerwein's procedure.<sup>18</sup> After completion of the addition, the mixture was stirred for 2 h. The dioxolenium salt was then precipitated by adding *n*-heptane. After filtering under argon and washing several times with dried diethyl ether, the dioxolenium salt was dried under vacuum overnight and then was transferred into a dry-box. Structure and purity were confirmed by <sup>1</sup>H NMR and elemental analysis.

*NMR and elemental analysis for dioxolenium salts.* <sup>1</sup>H NMR (CDCl<sub>3</sub>): X = F, δ 8.42–7.30 (m, 4H), 1.90 (s, 12H); X = Cl, δ 8.25–7.40 (m, 4H), 1.90 (s, 12H); X = CH<sub>3</sub>O, δ 8.28–7.15 (m, 4H), 4.01 (s, 3H), 1.82 (s, 12H); X = CN, δ 8.45–7.25 (m, 4H), 1.94 (s, 12H); X = CH<sub>3</sub>, δ 7.98–7.05 (m, 4H), 2.35 (s, 3H), 1.65 (s, 12H); X = H, δ 8.30–7.70 (m, 5H), 1.90 (s, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): X = F, δ 178.10, 169.00, 137.54, 118.11, 113.67, 103.06, 22.56; X = Cl, δ 178.63, 148.47, 135.01, 130.71, 115.71, 103.22, 22.67; X = CH<sub>3</sub>O, δ 177.46, 170.73, 137.09, 116.37, 107.95, 101.07, 22.48; X = CN, δ 207.16, 132.27, 130.02, 129.67, 127.93, 30.96, 25.26; X = CH<sub>3</sub>, δ 178.87, 154.50, 133.91, 114.09, 103.47, 22.88, 22.54; X = H, δ 179.29, 141.11, 133.67, 130.24, 117.14, 103.11, 22.52. Analysis: calculated: X = F, C 50.35, H 5.20; X = Cl, C 47.81, H 4.93; X = CH<sub>3</sub>O, C 52.20, H 5.95; X = NC, C 53.02, H 5.08; X = CH<sub>3</sub>, C 54.93, H 5.86; X = H, C 53.45, H 5.86%. Found: X = F, C 50.03, H 5.44; X = Cl, C 48.00, H 5.14; X = CH<sub>3</sub>O, C 52.30, H 6.06; X = NC, C 53.02, H 5.26; X = CH<sub>3</sub>, C 54.66, H 5.98; X = H, C 53.19, H 5.76%.

*Equipment.* A Varian XL-300 NMR spectrometer for <sup>1</sup>H and <sup>13</sup>C NMR spectra, a Vacuum Atmospheres HE-63-P Pedatrol dry-box, a BAS-100 A electrochemical analyzer and a Tronac 450 solution calorimeter were used throughout.

*Hydride affinities (ΔH<sub>H</sub><sup>-</sup>), ΔH<sub>H</sub><sup>-</sup>(R<sup>+</sup>) by hydride transfer from NaBH<sub>3</sub>CN.* Techniques for obtaining this property directly for carbenium ions in solution have not been described previously. However, Turner *et al.*<sup>19</sup> hydrogenated tropylium bromide [–89 kcal mol<sup>-1</sup> (1 kcal = 4.184 kJ)] and cycloheptatriene (–70 kcal mol<sup>-1</sup>) to cycloheptane and hydrogen bromide. Wiberg and co-workers<sup>20</sup> used lithium triethylborohydride in triglyme to measure the enthalpies of reduction of aldehydes and ketones following Davis and Carter.<sup>21</sup> We have used reaction calorimetry employing a Tronac 450 isoperibol solution calorimeter. The basic operation of the instrument has been described previously.<sup>22</sup> All hydride transfer reactions were checked for completeness by <sup>1</sup>H NMR spectroscopy.

Solutions of sodium cyanoborohydride in sulfolane–5% 3-methylsulfolane were prepared in the dry-box by dissolving an appropriate amount of the salt in sulfolane. This solution was transferred into the Dewar calorimeter vessel. A known concentration of the 2-aryltetramethyldioxolenium salt in sulfolane (*ca* 0.1 M) was prepared in the dry-box and transferred into a 2.5 ml Gilmont titration syringe. The syringe was attached to a motor-driven buret which was used to introduce precise amounts of the dioxolenium solution into a large excess of the cyanoborohydride solution (*ca* 0.9 M) at a constant rate. Each ΔH<sub>H</sub><sup>-</sup> presented here is the average of at least seven calorimetric measurements on two independently prepared solutions.

Several determinations using 18-crown-6 to sequester the sodium ion yielded only slightly more exothermic ΔH<sub>H</sub><sup>-</sup>, suggesting the influence of ion pairing. Although we may explore such effects further, we believe that the present results represent reliable evidence for the quantitative differences between the stabilities of the carbenium ions under these conditions. Like all other heats of reduction or free energies of carbocations, they should be treated as differential values, dependent on the choice of conditions.

*Electrochemistry.* All electrochemical measurements employed the BAS 100-A electrochemical analyzer using the methods and conditions described previously.<sup>23</sup>

## RESULTS AND DISCUSSION

### Dioxolenium ions

Carbocations and carbanions can enjoy considerable intramolecular stabilization by delocalization of their

charges over extended unsaturated systems (e.g. trityl), conformity to 'Hückel's rules' (e.g. tropylium cation and cyclopentadienyl anion) or transfer of electrons from an appropriately placed atom with available non-bonding electrons (e.g. N, O, S) to a cationic center. As an example of the last effect, 2-aryl-1,3-dioxolenium ions are so stable, relative to other benzyl cations, because they are primarily oxonium ions with most of the positive charge residing on the 1,3-oxygens. Nonetheless, there is enough carbenium ion character to the 2-carbon to render it highly vulnerable to attack by nucleophiles. Extensive mechanistic work by McClelland's group<sup>24</sup> has developed especially the role of dioxocarbenium ions as intermediates in the hydrolysis of tetrahedral orthoester derivatives produced by nucleophilic attack on carbonyl compounds. Stopped-flow kinetic analysis for hydrolysis in dilute aqueous acid of 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolenium tetrafluoro borate and of its unmethylated homologue showed a complex three-stage process for which all rate constants<sup>24d</sup> could be extracted and a  $pK_R^+$  of 1.4 for the tetramethyl compound determined compared with  $-0.6$  for the unmethylated compound.<sup>24g</sup> An alternative ring-opening process to ethylene glycol monobenzoate was observed in 67–77%  $H_2SO_4$ , which followed the  $H_R$  function with an intercept at  $-8.68$ .<sup>24g</sup> We have also observed formation of this type of product from the 2-aryltetramethyldioxolenium ions in intermediate acid strengths where, presumably, both types of reaction are in equilibrium.

Delocalization of charge over the dioxocarbenium triad is shown clearly by comparison of the PMR spectrum of the *p*-cyanophenyl cation with its dioxolane precursor and its cognate carbanion. In the cation the resonance for the four 4,4,5,5-methyls is a singlet at 1.94 ppm, consistent with a plane of symmetry, whereas the parent dioxolane shows a doublet 1.34–1.23 ppm, and the carbanion a doublet at 1.23–1.19 ppm,  $J = 12.3$ .

A recent x-ray study<sup>25</sup> of four dioxolan-2-ylum cations, including the 2-phenyl-1,3-dioxolane-2-ylum cation and its *p*-methoxy derivative, confirmed the planarity of these ions and provided an extensive up-to-date review of the structures and charge distributions in such ions. In conformity with the  $pK_R^+$  and ring-opening results cited above, significant charge is even transferred to the 3- and 4-carbons bearing the four methyls. In contrast to previous interpretations of NMR data,<sup>26</sup> the *p*-methoxyphenyl ion showed bonding changes in the crystal, implying some conjugative interaction of the ring and methoxy group with the cationic center.

### Hydride affinities ( $\Delta H_H^-$ )

Thermodynamic properties for hydride transfer have been the preferred means for comparing gas-phase stabilities of carbocations.<sup>11</sup> In solution several kinetic

studies of hydride transfer have been reported<sup>27,28</sup> and equilibration of systems relevant to NADH reduction.<sup>29</sup> However, more immediately, we can find no precedents for measuring  $\Delta H_H^-(R^+)$  directly in solution by reaction calorimetry other than Wiberg and co-workers' reduction of carbonyl compounds.<sup>20</sup>

Recent papers by Parker and co-workers<sup>30</sup> review the literature<sup>31</sup> on the solution thermochemistry of carbenium ions for which the leaving group has been either halide ions<sup>32</sup> in Olah-type superacids<sup>33</sup> or  $H_2O$  from protonated carbinols<sup>2</sup> from which their  $pK_R^+$  values and heats of ionization were derived. Parker and co-workers<sup>30</sup> derived both hydride and halide affinities for carbocations and radical cations by combining  $pK_R^+$  values or *BDEs* with oxidation potentials using appropriate thermodynamic cycles. We follow their convention, and that of gas-phase workers, by referring to hydride affinities for the carbocations as  $\Delta H_H^-(R^+)$ , although of course the conditions are completely different.

An elegant, but rarely cited, study by Freedman and co-workers<sup>34</sup> determined relative stabilities of a variety of carbenium ions by equilibration through transfer of hydroxy, alkoxy and halide leaving groups in acetonitrile and methylene chloride. Hydride was not included and, when we tried to employ their method, hydride exchange was prohibitively slow between the present oxycations and dioxolanes.

Since hydride abstraction by trityl cation is one of the most common techniques for preparing stable carbenium ions,<sup>35</sup> and was employed to make the dioxolenium salts discussed here, we attempted to use that reaction to determine  $\Delta H_H^-(R^+)$  values for the formation of dioxolenium cations in sulfolane in the calorimeter. However, the rates of reaction of trityl cation with the tetramethyldioxolanes were too slow for optimum reaction calorimetry and the results obtained by this approach proved to be seriously misleading. On the supposition that steric hindrance was responsible for the slow rates, we turned to hydride transfer in the reverse direction, from  $NaBH_3CN$  as a more reactive hydride donor to provide a direct measure of the hydride affinities of the cations. The results are presented in Table 1 for the seven dioxolenium ions and three other well studied carbenium ions. Reduction potentials are tabulated in order to compare the energies required to convert the various cations into their respective radicals and carbanions.

Support for our approach to determining hydride affinities is provided by several independent sources, as follows.

- Figure 1 displays an excellent linear correlation between the  $\Delta H_H^-(R^+)$  values for a variety of carbocations and their free energies of reduction to their conjugate radicals  $\Delta G_{red}^1$  in sulfolane at 25 °C. Both properties involve the conversion of the cation

Table 1. Hydride affinities,  $\Delta H_{\text{H}}^{\ominus}(\text{R}^{\ominus})$ , for hydride transfer from  $\text{NaCNBH}_3$ , free energies of reduction,  $\Delta G_{\text{red}}$ , and free energies of electron transfer,  $\Delta G_{\text{ET}}$ , for *para*-substituted-2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolanium tetrafluoroborates and reference carbocations in sulfolane (all values in kcal mol<sup>-1</sup> at 25 C)

<i>para</i> Substituent	$\Delta\Delta H_{\text{H}}^{\ominus}$	$\Delta H_{\text{H}}^{\ominus}$ ( $\text{NaCNBH}_3$ )	$\Delta G_1(E_{\text{red}})^a$	$\Delta G_2(E_{\text{red}})^b$	$\Delta G_3(E_{\text{red}})^c$	$\Delta G_{\text{ET}}$
$\text{OCH}_3$	-26.19	-27.71 ± 0.98	31.94 ± 0.02 (-1.385 ± 0.001)	63.23 ± 0.48 (-2.742 ± 0.021)	95.17 ± 0.48 (-4.127 ± 0.021)	-31.29 ± 0.48
$\text{CH}_3$	-23.77	-30.13 ± 0.57	29.49 ± 0.12 (-1.279 ± 0.005)	60.21 ± 0.14 (-2.611 ± 0.006)	89.70 ± 0.18 (-3.890 ± 0.007)	-30.72 ± 0.18
H	-22.48	-31.42 ± 0.34	29.03 ± 0.05 (-1.259 ± 0.002)	60.09 ± 0.14 (-2.606 ± 0.006)	89.12 ± 0.15 (-3.865 ± 0.007)	-31.06 ± 0.15
F	-21.25	-32.65 ± 0.63	27.07 ± 0.07 (-1.174 ± 0.003)	58.85 ± 0.12 (-2.552 ± 0.005)	85.92 ± 0.14 (-3.726 ± 0.006)	-31.78 ± 0.13
Cl	-20.15	-33.75 ± 0.98	25.37 ± 0.02 (-1.100 ± 0.001)	55.09 ± 0.12 (-2.389 ± 0.005)	80.46 ± 0.12 (-3.489 ± 0.005)	-29.72 ± 0.12
$\text{CF}_3$	-18.31	-35.59 ± 0.51	21.68 ± 0.05 (-0.940 ± 0.002)	51.95 ± 0.16 (-2.253 ± 0.007)	73.63 ± 0.17 (-3.913 ± 0.007)	-30.27 ± 0.17
CN	-14.96	-38.94 ± 0.80	19.09 ± 0.02 (-0.828 ± 0.001)	45.76 ± 0.07 (-1.984 ± 0.003)	64.85 ± 0.07 (-2.812 ± 0.003)	-26.67 ± 0.08
Tropylum	-10.61	-43.29 ± 0.98	14.34 ± 0.18 (-0.622 ± 0.008)			
9-Phenylxanthylum	-6.37	-47.53 ± 0.70	8.21 ± 0.09 (-0.356 ± 0.004)	34.71 ± 0.23 (-1.505 ± 0.010)	42.92 ± 0.25 (-1.861 ± 0.011)	-26.50 ± 0.25
Trityl	0.0	-53.90 ± 1.25	2.72 ± 0.09 (-0.118 ± 0.004)	23.29 ± 0.30 (-1.010 ± 0.013)	26.01 ± 0.32 (-1.128 ± 0.014)	-20.57 ± 0.32

<sup>a</sup>  $E_{\text{red}}^1 = \text{C}^+ + \text{e}^- \rightarrow \text{C}^{\cdot}$ 
<sup>b</sup>  $E_{\text{red}}^2 = \text{C}^+ + \text{e}^- \rightarrow \text{C}^{\cdot-}$ 
<sup>c</sup>  $E_{\text{red}}^3 = \text{C}^+ + 2\text{e}^- \rightarrow \text{C}^{2-}$

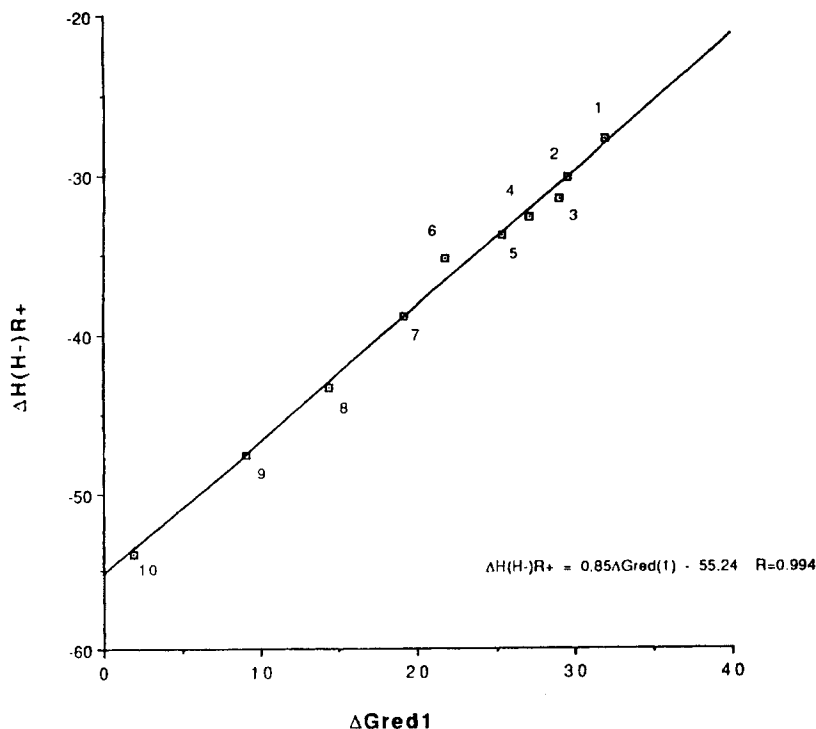


Figure 1. Heats of hydride transfer from  $\text{NaBH}_3\text{CN}$ ,  $\Delta H_{\text{H}}-(\text{R}^+)$ , to carbocations vs their first reduction potentials in sulfolane

into a neutral species, by transfer of either  $\text{H}^-$  or an electron. Several values for the putative heats of hydride transfer from the dioxolanes to trityl cation gave only scatter plots against both of these properties, indicating that this direct approach to heats of hydride transfer to this cation was not viable.

2. The standard free energy difference between trityl and 9-phenylxanthylium cation determined by Freedman and co-workers<sup>34</sup> by  $\text{OH}^-$  exchange in methylene chloride and acetonitrile is  $9.1 \text{ kcal mol}^{-1}$  compared with  $6.4 \pm 1.25 \text{ kcal mol}^{-1}$  for their difference in  $\Delta H_{\text{H}}-(\text{R}^+)$ .
3. Parker and co-workers<sup>30</sup> calculated hydride affinities of the same cations from the acidities ( $\text{p}K_{\text{HA}}$ ) of their neutral precursors in DMSO and the two-electron oxidation potentials of their carbanions. Here the difference between their estimated  $\Delta G_{\text{H}}-(\text{R}^+)$ , values is  $7 \text{ kcal mol}^{-1}$ , in excellent agreement with our value for the enthalpy difference. Their difference between trityl and tropylium is  $13 \text{ kcal mol}^{-1}$  compared with  $10.6 \text{ kcal mol}^{-1}$  in Table 1. Considering the differences between the processes and conditions used by the Freedman and Parker groups compared with our direct measurements, we believe that the general consensus is satisfactory. The contribution of entropy differences between these free

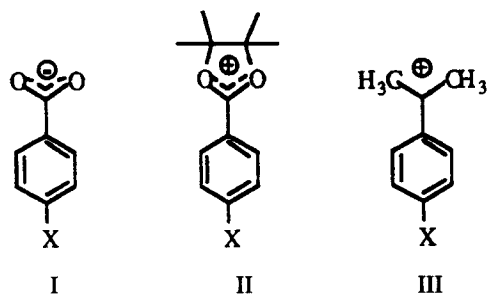
energies and our enthalpy measurements appears to be small.

4. The difference in free energies of ionization in aqueous acid ( $1.37 \times \Delta \text{p}K_{\text{R}^+}$ )<sup>1</sup> between trityl and tropylium cations is  $13 \text{ kcal mol}^{-1}$  compared with  $10.6 \text{ kcal mol}^{-1}$  in Table 1.

#### Comparisons with other ionogenic process

Physical organic chemistry has developed the use of extra-thermodynamic relationships as a powerful tool for comparing the effects of structural changes in different series of compounds on their reactivities in different processes. No one has contributed more to the rational analysis of this enormous collection of empirical structure-reactivity data than has Taft.<sup>36</sup> Although a free energy property ( $\sigma$ ) for ionization of substituted benzoic acids to benzoate anions (**I**) in water<sup>37</sup> would seem to be a far-fetched model for the heats of hydride transfer to a series of dioxolenium ions (**II**) in sulfolane a fairly good correlation ( $r = 0.974$ ) is found between the two processes. In contrast, the  $\sigma^+$  substituent constants, from rates of ionization of *para*-substituted cumyl chlorides (**III**) in 90% acetone at  $25^\circ\text{C}$ ,<sup>38</sup> yields a poorer correlation ( $r = 0.930$ ). If one considers the structures of the ionic species being compared (**I**, **II** and

III), it would be tempting to attribute the better correlation coefficient with  $\sigma$  parameters to the dioxolenium ions being more oxonium-like than carbenium-like so that relatively little demand for electrons is required from *para* substituents. However, the slopes for the two plots,  $-9.70$  ( $\sigma$ ) and  $-7.71$  ( $\sigma^+$ ), imply to us that both processes used as reference for  $\sigma$  and  $\sigma^+$  substituent constants are such poor models for the heats of hydride transfer from  $\text{BH}_3\text{CN}$  to dioxolenium ions in sulfolane that little structural insight is provided by either correlation (or many others in the literature, which use these parameters as models for drastically different processes and conditions than the model reactions).<sup>39</sup>



A more relevant model is Larsen and Ewing's heats of ionization of a series of allyl benzoates in  $\text{HSO}_3\text{F}$  to produce *para*-substituted 2-phenyl-4,4-1,3-dioxolenium ions.<sup>40</sup> Here the correlation for four points is poor ( $r=0.882$ ) but at least the slope ( $-1.23$ ) is more comparable to that for hydride transfer to these ions. Another relevant property for the formation of non-hydrogen-bonded oxonium ions from a neutral precursor in a high dielectric solvent is the heats of methylation of some substituted pyridines by Arnett and Reich in sulfolane.<sup>41</sup> Correlation of  $\Delta H_{\text{H}}-(\text{R}^+)$  with those data for four points (MeO, Me, H, CN) gives  $r=0.993$  with the slope of  $0.793$ .

As stated above, we consider the excellent correlation ( $r=0.994$ ) in Figure 1 between  $\Delta H_{\text{H}}-(\text{R}^+)$  and  $\Delta G_{\text{red}}^1$  as strong support for our approach to measurement of hydride affinities of carbenium ions. Also interesting is Figure 2, where  $\Delta H_{\text{H}}-(\text{R}^+)$  for all ten ions in Table 1 are plotted against  $\Delta G_{\text{red}}^3$ , the energy for converting each carbocation ion into its carbanion. Such a process is very endergonic. Reduction of these highly stable cations to their radicals,  $\Delta G_{\text{red}}^1$ , which are relatively much less stable, has a slope of  $0.85$  versus  $\Delta H_{\text{H}}-(\text{R}^+)$ , showing it to be dominated by the stability of the ion to about the same degree as its hydride affinity. However,

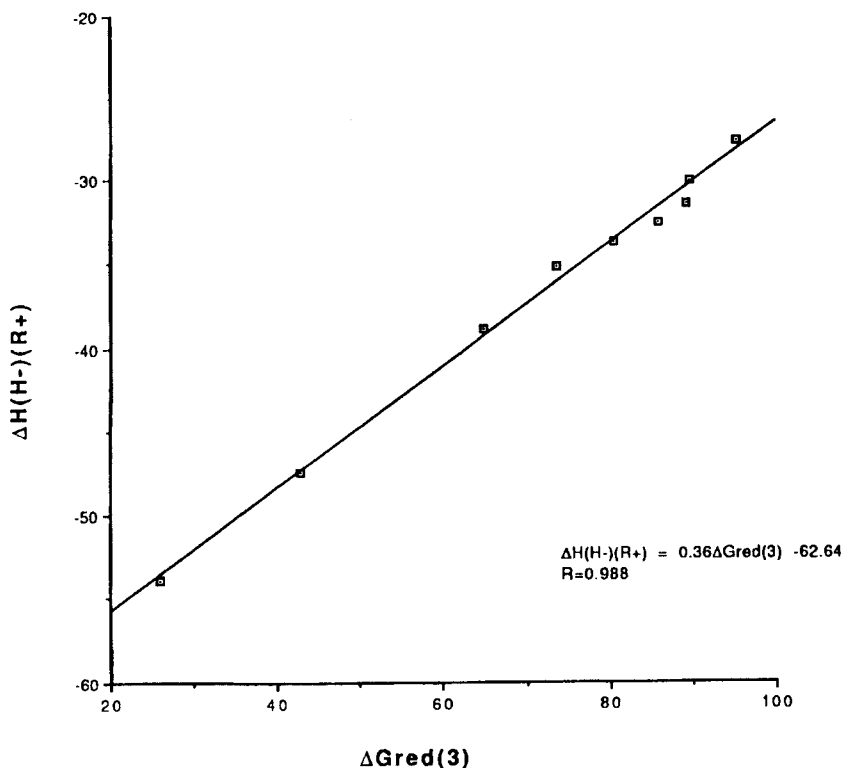


Figure 2.  $\Delta H_{\text{H}}-(\text{R}^+)$  vs  $\Delta G_{\text{red}}^3$  for ions in Table 1 in sulfolane

reduction of the radical to the anion,  $\Delta G_{\text{red}}^{\ddagger}$ , is much more endergonic and, in fact, is the term that is most responsible for the low stabilities of the anions and, therefore, the low acidities of their precursors. Whatever is the ultimate cause of the great structural sensitivity of the carbanion relative to the carbocation, it clearly is a general phenomenon for the various types of ions in Table 1 since they include some different structures from the seven dioxolenium ions. We are exploring the generality of this correlation further for a variety of other carbocations and carbanions from amphihydric precursors.

### CONCLUSION

We have reported the heats of reaction of a series of 2-aryl-4,4,5,5-tetramethyl-1,3-dioxolenium ions with sodium cyanoborohydride and their electrochemical reduction to their radicals and carbanions. The cyanoborohydride results are treated as hydride affinities of the carbocations and compared with other criteria of carbenium ion stabilities.

### ACKNOWLEDGEMENTS

E.M.A. appreciates this opportunity to acknowledge his debt to Professor Robert Taft for over 30 years of friendship and shared interest in the structure–energy relationships of the interactions of organic compounds. We are glad to acknowledge valuable measurements by Mr Chapin Rodriguez, help from Dr Richard Ludwig, sabbatical support to A.P. and a generous National Science Foundation grant CHE-9218375 to E.M.A.

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