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# Energetics of Formation for Conjugate Xanthyl Carbenium Ions, Carbanions, and Radicals by Hydride, Proton, and Electron Transfer in Solution and Their Reactions To Give Symmetrical Bixanthyls

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Gomberg's momentous discovery of persistent free radicals and their coupling reactions[1] stimulated one of the most fertile areas of organic chemistry. To this day, the presence of coupling products (R–R) is taken as very powerful evidence for the reaction of R• radicals in a system. Conversely, the thermolysis of symmetrical R–R systems is used to evaluate homolysis energies.[2]

We report here the formation of some substituted 9,9′-diarylbixanthyls *by coordination of the corresponding xanthyl cations and anions* in sulfolane solution. The calorimetric heat of reaction for this process gives directly the previously unapproachable heat of *heterolysis* ($\Delta H_{\text{coord}} = -\Delta H_{\text{het}}$) for cleavage of the symmetrically substituted bixanthyl product into its component ions. Combination of $\Delta H_{\text{het}}$ with the free energy of electron transfer from the one-electron redox potentials of these ions provides corresponding heats of homolysis ($\Delta H_{\text{homo}}$), as shown in Scheme I. Thus, we have effected a purely ionic route to the types of symmetrical compounds which usually cleave by homolysis so that $\Delta H_{\text{homo}}$ can be compared directly with $\Delta H_{\text{het}}$.

This approach has been neglected previously because of the reasonable assumption that structural factors which stabilize carbenium ions are so different from those which stabilize carbanions that the two types of species must be made under drastically incompatible conditions of acidity and basicity. Accordingly, all of our previous work has employed resonance-stabilized cations and anions of drastically different structures so that the products of their reactions were quite unsymmetrical and preferentially disposed toward heterolysis.[5] However, in the present case, the stable 9-phenylxanthyl cation ($pK_{R^+} = 1.01$)[3] and its unstable anion ($pK_{HA} = 27.9$)[4] can be handled in sulfolane solution for calorimetry and electrochemistry as we have done before for other cation–anion reactions.[5] Using correlation equations[5] which relate $\Delta H_{\text{het}}$ to ion stability factors ($pK_{HA}$, $pK_{R^+}$, $\Delta H_{\text{cmf}}$) and this value for $pK_{HA}$, one predictes $\Delta H_{\text{het}} = 42.15$ kcal/mol for 9,9′-diphenylbixanthyl, which agrees exactly with the experimental value in Table I.

We propose the term "amphihydric" for conjugate cations and anions which are generated through the removal of a hydride ion and a proton from the same C–H linkage in a given molecule, by analogy with (and in contrast to) the familiar term "amphiprotic" for protonation of a basic site which also carries an acidic hydrogen. A familiar series of amphihydric compounds is the triarylmethanes, whose radicals, cations, and anions have been studied for nearly a century and whose importance to the development of organic chemistry cannot be exaggerated. Solutions of trityl cations and anions have been subjected to a number of electrochemical studies for both one- and two-electron processes.[6] However, we know of no case where solutions of both trityl cation and anion were prepared independently in the same solvent so that the redox properties could be compared independently in both directions. It is now well known that the coupling of triphenylmethyl radicals does not produce symmetrical hexaarylethane.[7] We know of no cases where trityl cations and anions have been brought into reaction in the same solvent but hope to try a suitable example.

**Scheme I.** Relation of Properties Listed in Table I with Experimental Data for the 9-Phenylxanthyl System (X = H)

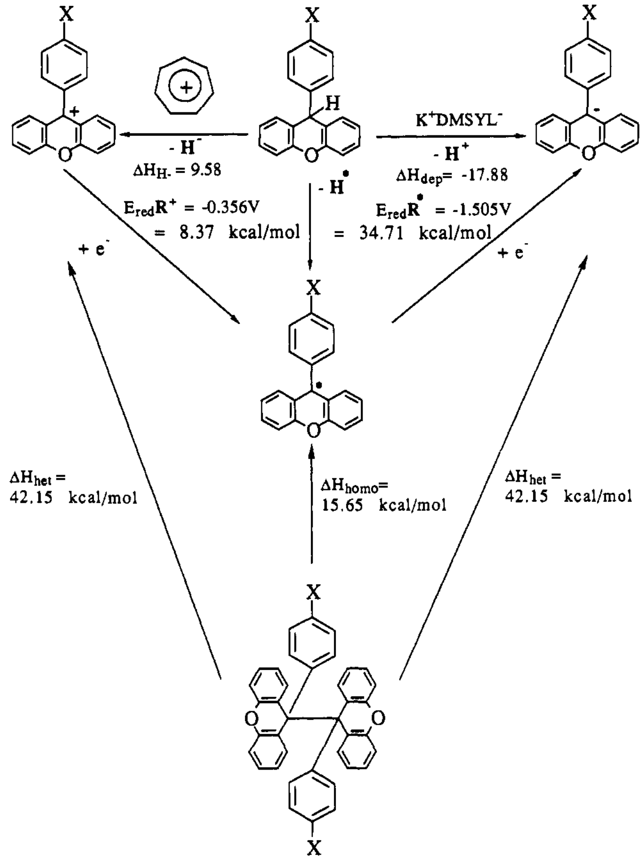

Table I lists the $\Delta H_{\text{het}}$ and $\Delta H_{\text{homo}}$ values for a series of bixanthyls and also the heats of deprotonation ($\Delta H_{\text{dep}}$) for the parent 9-arylxanthenes by K$^+$DMSYL$^-$ [8] and their heats of hydride transfer ($\Delta H_{H^-}$) from the heats of reaction of the corresponding carbenium ions with cycloheptatriene in sulfolane.[9] The bond dissociation energies (BDEs) for homolytic cleavage of the same C–H bonds were determined, as before,[5,10] by

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(1) (a) Gomberg, M. *Ber. Dtsch. Chem. Ges.* **1900,** *33,* 3150; (b) *J. Am. Chem. Soc.* **1900,** *22,* 757.

(2) (a) For a review of cleavage of symmetrically substituted C–C bonds to radicals, see: Birkhofer, H.; Beckhaus, H.-D.; Rückardt In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merenyi, D., Eds.; Reidel Pub. Co.: Dordrecht, 1986. (b) Maslak, P.; Narvaez, J. N. *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 283. (c) Maslak, P.; Guthrie, R. D. *J. Am. Chem. Soc.* **1986,** *108,* 2628; 2637.

(3) Obtained by A. Meekhof, using the excess acidity method.

(4) Bordwell, F. G. *Acc. Chem. Res.* **1988,** *21,* 456.

(5) For reviews and references to this approach, see: Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P. *Science* **1990,** *247,* 423. Arnett, E. M.; Flowers, R. A., II *Chem. Soc. Rev.* **1993,** *22,* 9. As is required, $\Delta S_{\text{redox}} \approx 0$ as shown by the negligible temperature coefficients for $E_{\text{red}}(1)$ and $E_{\text{red}}(2)$ of the *p*-Cl cation. This justifies combining enthalpy and free energy terms in this report.

(6) A partial listing of electrochemical studies on trityl cation and anions includes the following: (a) Cheng, J.-P.; Handoo, K. L.; Parker, V. D. *J. Am. Chem. Soc.* **1993,** *115,* 2655. (b) Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993,** *26,* 287. (c) Banks, S.; Ehrlich, C. L.; Zubieta, J. S. *J. Org. Chem.* **1979,** *44,* 1454. (d) Bowie, W. T.; Feldman, M. R. *J. Am. Chem. Soc.* **1977,** *99,* 4721. (e) Feldman, M. R.; Flythe, W. D. *J. Org. Chem.* **1978,** *43,* 2597. (f) Breslow, R. *Pure Appl. Chem.* **1974,** *40,* 493 and many references to prior research discussed here. (g) Breslow, R.; Chu, W. *J. Am. Chem. Soc.* **1973,** *95,* 441. This article played a seminal role in drawing attention to the use of modern electrochemical methods for physical organic problems. (h) Ritchie, C. D.; Uschold, R. F. *J. Am. Chem. Soc.* **1968,** *90,* 2821. (i) Volz, H.; Lotsch, W. *Tetrahedron Lett.* **1969,** *27,* 2275. (j) Kothe, G.; Sümmermann, W.; Baumgärtel; Zimmermann, H. *Tetrahedron Lett.* **1969,** *26,* 2185. (k) Feldman, M.; Flythe, W. C. *J. Am. Chem. Soc.* **1969,** *91,* 4577. (l) McKeever, L. D.; Taft, R. W. *J. Am. Chem. Soc.* **1966,** *88,* 4544. (m) Jenson, E. D.; Taft, R. W. *J. Am. Chem. Soc.* **1964,** *86,* 116. (n) Conant, J. B.; Chow, B. F. *J. Am. Chem. Soc.* **1933,** *55,* 3752. (o) Conant, J. B.; Small, L. F.; Taylor, B. S. *J. Am. Chem. Soc.* **1925,** *47,* 1959. (p) Bordwell, F. G.; Cheng, J.-P.; Satish, A. V.; Twyman, C. L. *J. Org. Chem.* **1992,** *57,* 6542.

(7) Lankamp, H.; Nauta, W. T.; MacLean, C. *Tetrahedron Lett.* **1968,** 249.

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**Table I.** Heats of Hydride Transfer ($\Delta H_{H^-}$), Deprotonation ($\Delta H_{dep}$), Heterolysis ($\Delta H_{het}$), and Homolysis ($\Delta H_{homo}$) for 9-Substituted Xanthenes and Derived Ions (all $\Delta H$ in kcal/mol at 25 °C)

| 9-X | $\Delta H_{H^-}$[a] ($\Delta\Delta H_{H^-}$) | $\Delta H_{dep}$[b] ($\Delta\Delta H_{dep}$) | $\Delta H_{het}$ ($\Delta\Delta H_{het}$) | $\Delta H_{homo}$ ($\Delta\Delta H_{homo}$) | BDE[c] ($\Delta$BDE) |
|---|---|---|---|---|---|
| 4-$OCH_3C_6H_4$ | 7.86 ± 0.63 (–1.72) | –17.64 ± 0.19 (0.24) | 43.44 ± 0.89 (1.29) | 16.88 ± 1.01 (1.23) | 76.2 (–0.5)[d] |
| $C_6H_5$ | 9.58 ± 0.41 (0.00) | –17.88 ± 0.59 (0.00) | 42.15 ± 1.79 (0.00) | 15.65 ± 1.81 (0.00) | 76.7 (0.0)[d] |
| 4-$CH_3C_6H_4$ | 9.32 ± 0.26 (–0.26) | –17.39 ± 0.43 (0.49) | 41.35 ± 1.51 (–0.80) | 14.16 ± 1.51 (–1.49) | 76.4 (–0.3) |
| 4-$FC_6H_4$ | 11.37 ± 0.27 (1.80) | –17.79 ± 0.28 (0.09) | 41.27 ± 1.16 (–0.88) | 14.98 ± 1.20 (–0.67) | 78.1 (1.4) |
| 4-$ClC_6H_4$ | 11.67 ± 0.73 (2.09) | –18.91 ± 1.19 (–1.03) | 40.23 ± 0.82 (–1.92) | 16.57 ± 0.83 (1.10) | 78.1 (1.4) |
| 4-$CF_3C_6H_4$ | 12.29 ± 0.17 (2.71) | | | | |
| H | 14.57 ± 0.53 (4.99) | –11.97 ± 0.58 (5.91) | 59.31 ± 1.80 (17.16) | | 60.5 (–16.2) |

[a] From the negative of heat of reaction of xanthylium tetrafluoroborate with cycloheptatriene in sulfolane. [b] Heat of reaction of xanthene with $K^+DMSYL^-$ in DMSO, all other values in sulfolane.[8] [c] Reversible potentials corrected to the standard hydrogen electrode by adding 0.75 V to the potentials for use in Bordwell's equation: BDE = $1.37pK_a + 23.06E_{ox}(C^-) + 56$.[10] At Professor Bordwell's suggestion, we have recalculated these values using the empirical constant 73.3 (instead of 56) and $E_{ox}(C^-)$ corrected to the Fc/$Fc^+$ electrode. The resulting BDEs agree exactly. [d] These values agree closely with those obtained by Bordwell's group,[6p] although their $E_{ox}(C^-)$ values were not reversible.

**Table II.** Redox Potentials and $\Delta G$ Values for 9-Substituted Xanthenes and Derived Ions ($\Delta G$ values in kcal/mol at 25 °C)

| 9-X | $\Delta G_1$[a] ($E_{red}(1)$) | $\Delta G$[a] ($E_{red}(2)$) | $\Delta G$[a] ($E_{red}(3)$) | $\Delta G_{ET}$[c] |
|---|---|---|---|---|
| 4-$OCH_3C_6H_4$ | 9.29 ± 0.07 (–0.403 ± 0.003) | 35.86 ± 0.48 (–1.555 ± 0.021) | 45.15 ± 0.49 (–1.958 ± 0.021) | –26.56 ± 0.48 |
| $C_6H_5$ | 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 |
| 4-$CH_3C_6H_4$ | 8.37 ± 0.07 (–0.363 ± 0.003) | 35.56 ± 0.07 (–1.542 ± 0.003) | 43.93 ± 0.10 (–1.905 ± 0.004) | –27.19 ± 0.09 |
| 4-$FC_6H_4$ | 7.45 ± 0.18 (–0.323 ± 0.008) | 33.74 ± 0.09 (–1.463 ± 0.004) | 41.19 ± 0.20 (–1.786 ± 0.009) | –26.29 ± 0.21 |
| 4-$ClC_6H_4$ | 7.24 ± 0.09 (–0.314 ± 0.004) | 33.16 ± 0.09 (–1.438 ± 0.004) | 40.40 ± 0.13 (–1.752 ± 0.006) | –23.66 ± 0.14 |
| 4-$CF_3C_6H_4$ | 6.76 ± 0.12 (–0.293 ± 0.005) | 30.42 ± 0.16 (–1.319 ± 0.007) | 37.18 ± 0.20 (–1.612 ± 0.009) | –23.66 ± 0.21 |
| H | 7.06 ± 0.25 (–0.306 ± 0.011)[b] | 46.67 ± 0.32 (–2.024 ± 0.014)[b] | 53.73 ± 0.80 (–2.330 ± 0.018) | –39.62 ± 0.42 |
| 4-$C_6H_5C_6H_4$ | 8.00 ± 0.07 (–0.347 ± 0.003) | 33.23 ± 0.18 (–1.441 ± 0.008) | 41.23 ± 0.19 (–1.788 ± 0.009) | –25.23 ± 0.21 |

$E_{red}(1) = C^+ + e^- \rightarrow C^\bullet$
$E_{red}(2) = C^\bullet + e^- \rightarrow C^-$
$E_{red}(3) = C^+ + 2e^- \rightarrow C^-$

[a] From 23.06 kcal/eV multiplied by the corresponding reduction potential obtained at 25 °C in sulfolane against a ferrocene/ferrocenium couple. [b] Irreversible potentials. [c] $\Delta G_{ET} = \Delta G_1 - \Delta G_2$.

combining $pK_{HA}$ with $E_{ox}$ for the carbanions. Since most of these processes are referred to different standard states, the trends should be compared by differential $\Delta H$.

A uniquely valuable feature of the electrochemistry, Table II, of the conjugate cations and anions produced from amphihydric compounds is the possibility of testing measured values for electron-transfer processes going in both directions. Thus, the two-electron reduction potential for converting the cation to the anion should exactly equal the two-electron oxidation potential for the anion. In the present case, although reduction of solutions of the relatively unstable xanthylide anions could not be carried reversibly all the way to their cations, the one- and two-electron oxidation of the very stable 9-arylxanthylium ions was reversible through both stages.[11] Thus, the *p*-fluoro anion could be oxidized reversibly to the corresponding radical at a potential that agreed exactly with the second reduction potential of its cation.

Table I provides unprecedented data for comparing experimental substituent effects on the three different modes for cleavage of the C–H bond at the 9-position of the parent xanthenes, the two modes for cleavage of the 9–9′ bond of the derived bixanthyls, and the three different electron-transfer bixanthyls processes and associating all of them energetically through a common scheme. Although we will discuss these and other properties fully in a complete paper, we draw attention to the following here.

(a) The large (~30 kcal/mol) difference between $\Delta H_{homo}$ and $\Delta H_{het}$ for the bixanthyls is mostly due to the large endergonic reduction of the radical to the unstable anion.

(b) $\Delta H_{dep}$ values for formation of the carbanions by deprotonation correlate well ($R = 0.999$) with $E_{red}(2)$ for reduction of the neutral radicals to form the carbanions. The corresponding $R$ for correlation of $\Delta H_{H^-}$ with $E_{red}(1)$ is 0.990.

(c) The measured heat of hydride transfer from cycloheptatriene to the 9-phenylxanthylium cation is –9.58 kcal/mol compared to –6 kcal/mol estimated by Cheng, Handoo and Parker[6a] from BDEs and $E_{red}(1)$ values. For comparison, the heat of hydride transfer from cycloheptatriene to the relatively unstable ($pK_{R^+} = -6.44$) trityl cation is –20.39 ± 0.48 kcal/mol.

Conant and his students investigated steric effects on the stabilities of 9-substituted xanthyl radicals, formed by the reduction of the corresponding cations with vanadous chloride, and their coupling, presumably to the symmetrical 9,9′-bixanthyls in water.[12] Similarly, we find that treatment of 9-(4-chlorophenyl)xanthylium tetraphenylboride with $SmI_2$ in THF causes an immediate change in color from the yellow of the cation to ruby red, presumably of the radical. On the standing of the solution under argon, the color is discharged and evaporation of the solvent leaves a white crystalline residue whose PMR spectrum is identical to that of the product from the cation–anion reaction and is easily interpreted as that of the 9,9′-diarylbixanthyl since its spectrum is virtually superimposable on that of the parent xanthene except for the absence of the 9-proton. Although the bixanthyl may well be formed by electron transfer between the ions followed by radical coupling, the thermochemical value does not depend on the mechanism and represents the experimental $\Delta H_{het}$ for cleavage of the bixanthyl into ions.

The results reported here provide unprecedented quantitative experimental relations between a variety of fundamental bond-breaking and bond-making processes through reaction calorimetry and electrochemistry. Scheme I may be regarded as a "Rosetta Stone" for relating carbenium ion-, radical-, and carbanion-forming processes in a common medium.

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(8) Repeated attempts to use the potassium salt of sulfolane as the deprotonating agent failed due to its precipitation in this solvent. However, the $\Delta H_{dep}$ of sulfolane by $K^+DMSYL^-$ is –2.64 ± 0.21 kcal/mol, so we include the $\Delta H_{dep}$ values of the xanthenes by this base confident that it would be almost the same in sulfolane.

(9) Hydride transfer to trityl cation is an alternative thermochemical process which we have applied to other systems, but rates were too slow in the present case to give reliable calorimetric data. Steric hindrance to attack by the trityl cation on the heavily shielded 9-position of the xanthene is an obvious explanation.

(10) Bordwell, F. G. *Acc. Chem. Res.* **1993**, *26*, 510.

(11) Breslow and Chu report problems of irreversibility for two-electron reductions of stable cations because of radical coupling or reaction of the unstable anion with excess cation, ref 6g.

(12) (a) Conant, J. B.; Sloan, A. W. *J. Am. Chem. Soc.* **1923**, *45*, 2466; (b) **1925**, *47*, 572. (c) Conant, J. B.; Small, L. F.; Sloan, A. W. *J. Am. Chem. Soc.* **1926**, *48*, 1743.