Amphielectronic† Ionization of a π-Radical, a Basis for Correlating Radical with Nucleophilic and/or Electrophilic Reactivities

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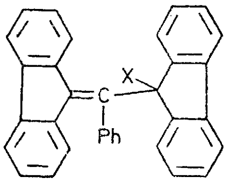
The stable free radical 9-[fluorenylidene(phenyl)methyl]fluorenyl ionizes to the corresponding cation in acidic media, whereas in basic solvents it is converted into the relevant carbanion, by accepting single electrons from various anions and from aliphatic amines. This transformation provides, in part, another example of the thermodynamic cycle recently used by Breslow and Mazur in order to correlate pK_a with pK_{R^+} values of related carbanions and carbocations. The reality of this transformation suggested a successful attempt to inter-relate kinetic and thermodynamic parameters of radicals, carbocations, and carbanions. These correlations may be thought of as corollaries of the combined Breslow–Mazur and Brønsted equations.

THERE has been a continuing interest in relating molecular parameters to processes in the gas and liquid phases.[1,2] In several cases thermodynamic parameters of free radicals have been related to parameters of the corresponding positively and/or negatively charged species, through appropriate thermodynamic cycles.[2] In a number of instances substrates have shown substituent effects in their reactions with a given radical which resemble those of ionic reactions.[2] Mackor *et al.*[4] have shown that the radical affinities of a series of aromatic hydrocarbons are related to the π-basicities of the hydrocarbons, through a Brønsted-type relation. A number of correlations of ionization potentials with the Hammett equation have been reported.[5] Of these the most interesting is the correlation between the ionization potentials of alkyl radicals with Taft's σ^* values.[6]

This paper reports a case of ready ionization of a stable free radical to both a cation and an anion, and discusses the implications of this process for some new extrathermodynamic relations which correlate the carbon acidities with the radical reactivities for hydrogen abstraction as well as the activation energies for hydrogen and proton abstraction with the ionization potentials of the free radicals.

RESULTS

We were led to attempt to correlate various kinetic and thermodynamic parameters of radicals, carbocations, and carbanions by the interesting property of the stable π-radical 9-[fluorenylidene(phenyl)methyl]fluorenyl (BDPA) (I; X = unpaired electron). This radical exhibits a pronounced tendency to form both the allylic anion BDPA$^-$ and the corresponding carbocation (BDPA$^+$) [equation (1)]. Both modes of ionization are highly solvent dependent. Ionization to BDPA$^+$ requires an acidic medium



(I)

$$\mathrm{BDPA^+} \xleftarrow[\text{media}]{\text{acidic}} \mathrm{BDPA} \xrightarrow[\text{media}]{\text{basic}} \mathrm{BDPA^-} \qquad (1)$$

with no other oxidant or electron acceptor. Although a great variety of π-electron molecules have been known [7] to ionize in acidic media to the corresponding cation radicals, to the best of our knowledge, this is the first case in which a completely dissociated (even in the solid state [8]) free radical ionizes to the corresponding diamagnetic cation.‡ Figure 1 shows the visible spectra of BDPA in a basic solvent, hexamethylphosphoramide (HMPA), and two acidic ones, concentrated sulphuric acid and trifluoroacetic acid. For the sake of comparison the spectrum of the alcohol (I; X = OH) in concentrated sulphuric

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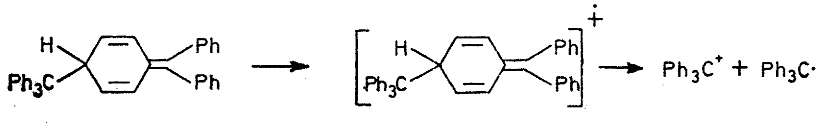
† The term amphielectronic has been used by analogy with 'amphiprotic.' The process $\mathrm{R^+} \xleftarrow{-e^-} \mathrm{R\cdot} \xrightarrow{+e^-} \mathrm{R^-}$ may be thought of as the formal analogue of the Brønsted process $\mathrm{L^-} \xleftarrow{-H^+} \mathrm{LH} \xrightarrow{+H^+} \mathrm{LH_2^+}$.

‡ The report [9] that $Ph_3C^{\cdot}$ ionizes to Ph_3C^+ in $POCl_3$ could be ambiguous. Ph_3C^+ could be derived by the alternative process (i). See ref. 7.



(i)

[1] J. E. Leffler and E. Grunwald, 'Rates and Equilibria of Organic Reactions,' Wiley, New York and London, 1963, p. 134 and references therein.

[2] See for example E. M. Arnett, *Accounts Chem. Res.*, 1973, **6**, 405; R. T. McIver, jun., and J. H. Silvers, *J. Amer. Chem. Soc.*, 1973, **95**, 8462; E. M. Arnett, F. M. Jones III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *ibid.*, 1972, **94**, 4724; D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, p. 4726; W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, jun., J. L. Beauchamp, and R. W. Taft, *ibid.*, p. 4728; J. I. Brauman and L. K. Blair, *ibid.*, 1971, **93**, 3911.

[3] W. A. Pryor, W. H. Davis, jun., and J. P. Stanley, *J. Amer. Chem. Soc.*, 1973, **95**, 4754, and references therein.

[4] E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, 1958, **54**, 66.

[5] M. Charton, *Progr. Phys. Org. Chem.*, 1973, **10**, 81 and references therein.

[6] A. Streitwieser, jun., *Progr. Phys. Org. Chem.*, 1963, **1**, 1.

[7] For a review see G. Vincow, 'Radical Ions,' eds. E. T. Kaiser and L. Kevan, Wiley–Interscience, New York and London, 1968, p. 151.

[8] R. Kuhn and F. A. Neugebauer, *Monatsh.*, 1964, **95**, 3.

[9] L. C. Anderson, *J. Amer. Chem. Soc.*, 1935, **57**, 1673.

acid is also given. Obviously BDPA undergoes ionization according to equation (2).

$$\mathrm{BDPA} \xrightarrow{\mathrm{H_2SO_4}} \mathrm{BDPA^+} + (\mathrm{H_2SO_4})^{-\cdot} \qquad (2)$$

Basic solvents are required for the conversion of BDPA into BDPA$^-$, the most effective of which are the dipolar aprotic ones dimethyl sulphoxide (DMSO), dimethylformamide (DMF), and HMPA. Various aliphatic amines as well as inorganic anions (*e.g.* CN$^-$, N$_3^-$), alkoxides, and amides such as potassium t-butoxide and lithium cyclohexylamide have been found to act as one-electron donors. The conversion of BDPA into BDPA$^-$ by the action of carbanions has been already reported.[10] The transformation can be readily followed either by observing the disappearance of the radical at its absorption maximum, 485 nm,[8] or by the BDPA$^-$ build-up at *ca.* 600 nm.[8,10]

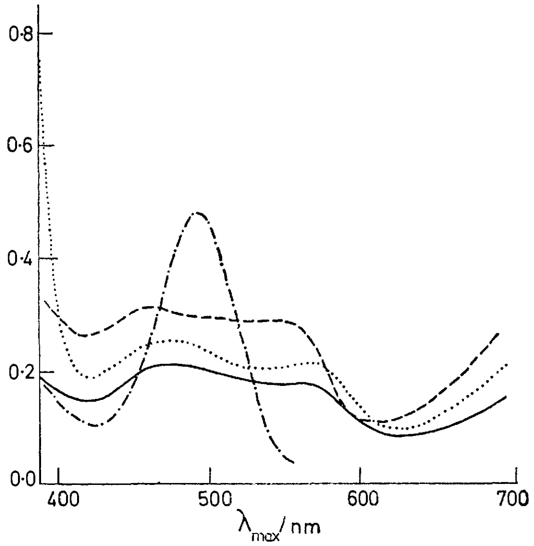


FIGURE 1 Visible spectra of BDPA in: —— H$_2$SO$_4$; ---- CF$_3$CO$_2$H; —·—·— HMPA. Visible spectrum of BDPA-OH in H$_2$SO$_4$: ····.

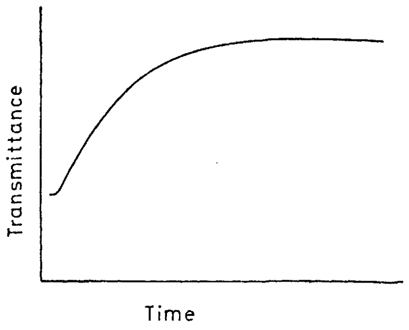


FIGURE 2 Transmittance *versus* time in the reaction between BDPA and potassium-butoxide in DMSO at 485 nm: [BDPA]$_0$ = 9 × 10^{-5}M; [Bu^{t}OK]$_0$ = 2·1 × 10^{-3}M; *T* 25 °

There is some dependence of the reaction rate on the pK_a of the conjugate acid. Anions derived from weaker acids react more readily with BDPA than those derived from stronger acids. In DMSO the observed order was CN$^-$ > AcO$^-$ > N$_3^-$ an order which parallels that of the corresponding pK_a values of HCN, AcOH, and HN$_3$,[11] referred to DMSO solvent.* The reaction of BDPA with potassium t-butoxide (t-butyl alcohol pK_a 19)[12] is so fast that it requires special techniques in order to be followed (see Figure 2). Aliphatic amines exhibit a varying reactivity toward BDPA. In DMSO the following order was observed: tetramethylethylenediamine > triethylamine, n-butylamine > t-butylamine, n-butylamine > di-n-butylamine > tri-n-butylamine.

DISCUSSION

The acceptor character of BDPA is reminiscent of the analogous behaviour of the strong π-acid tetracyanoquinodimethane (TCQD) which has been reported to accept one electron from a variety of inorganic salts and from various amines.[13] The property of BDPA to ionize by either gaining or losing an electron also bears a close analogy to the behaviour of the corresponding hydrocarbon, BDPA-H (I; X = H) which is one of the strongest carbon acids known,[14] with a pK_a value of 14, and of the alcohol BDPA-OH, which very readily ionizes to a stable allylic cation in acidic media [equations (3) and (4)]. The thermodynamic parameters pK_a and pK_{R^+} which characterize processes such as (3) and (4), have been recently correlated by Breslow and Mazur.[15] These authors employed the 'imaginary chemical cycle' (5) and derived the equation $\Delta\Delta G_f^0 = 2{\cdot}3RT\mathrm{p}K_a + FE_1 + FE_2 + 2{\cdot}3RT\mathrm{p}K_{R^+} - \Sigma\Delta G_s$ which correlates pK_a with pK_{R^+} as well as the oxidation potentials of related carbanions and radicals. The terms $\Delta\Delta G_f^0$ and $\Sigma\Delta G_s$ are the differences in free energy of formation of the alcohol and the hydrocarbon and the sum of all changes in free energy of solvation throughout the cycle, respectively. BDPA provides an example which suggests that process (5) can be of a broader scope. Furthermore one should bear in mind that thermodynamic parameters, in general, can be related to kinetic parameters through Brønsted-type relations,[16] or through an Edwards

$$\mathrm{BDPA\text{-}H(BDPA)} \xrightarrow{K_a} \mathrm{BDPA^-} \qquad (3)$$

$$\mathrm{BDPA\text{-}OH(BDPA)} \xrightarrow{K_{R^+}} \mathrm{BDPA^+} \qquad (4)$$

$$\begin{tikzcd} \mathrm{RH} \arrow[rr] \arrow[d] & & \mathrm{ROH} \\ \mathrm{R'} \arrow[r] & \mathrm{R\cdot} \arrow[r] & \mathrm{R^+} \arrow[u] \end{tikzcd} \qquad (5)$$

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* A detailed kinetic analysis will be the subject of a future publication.

[10] C. G. Screttas, *Chem. Comm.*, 1971, 406.

[11] C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, 1967, **89**, 1721.

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[13] L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, 1962, **84**, 3374.

[14] R. Kuhn and D. Rewicki, *Annalen*, 1967, **706**, 250.

[15] R. Breslow and S. Mazur, *J. Amer. Chem. Soc.*, 1973, **95**, 584; R. Breslow and W. Chu, *J. Amer. Chem. Soc.*, 1973, **95**, 411.

[16] R. F. Hudson, 'Structure and Mechanism in Organophosphorus Chemistry,' Academic Press, London, 1965, ch. 4.

equation.[17] Now in the Breslow–Mazur equation pK and/or E values can be replaced by their equivalents from the Brønsted or Edwards equations, and under certain conditions usually observed in order to have linear free energy relations, it may be expected that kinetic and/or thermodynamic data of free radicals, carbanions, and carbocations can be inter-related. Comparisons, of course, must be limited within reaction series of structurally similar compounds in which the entropy either remains constant or is linearly related to enthalpy. Another obvious condition is that the term $(\Delta\Delta G_f^0 + \Sigma\Delta G_s)$ is either constant or is ' compensated ' by other parameters in the cycle.

With all these limitations in mind, literature data were correlated for the reactions summarized in the Table, with correlation coefficients ranging between 0·95 and 0·997. Basically four types of reactions were considered. (1) Relative reactivities for liquid-phase hydrogen abstraction by a given radical from a series of acidic hydrocarbons were correlated with the pK_a values of the carbon acids. (2) Activation energies of gas-phase hydrogen abstraction from a series of hydrocarbons by a given radical were correlated with the ionization potentials of the conjugate radicals. (3) Activation energies of gas-phase hydrogen abstraction from a given substrate by a series of radicals, were correlated with the ionization potentials of the radicals. (4) Relative reactivities of organolithium compounds toward a given substrate were correlated with the ionization potentials of the radicals corresponding to the organolithium reagents. Reaction (IV) in the Table gives the most interesting correlation, because if taken in conjunction with the correlation of ionization potentials of alkyl radicals with Taft's σ^* values,[6] it can relate radical and carbocationic processes in the gas phase with parameters of ionic reactions in solution.

Some conclusions can be drawn from these correlations. There appears to be a better correlation between E_a values and ionization potentials in the case where hydrogen abstraction is referred to a common substrate, rather than to a series of similar substrates [compare reactions (II) and (IV)]. The polar radicals $CF_3^{\bullet}$ and $CH_3O^{\bullet}$ exhibit approximately the same reactivities towards the same series of substrates. In the case of reaction (VII) if the difference between the acidities of Ph_3CH and RH is the main component of the driving force for the metallation reaction, the following conclusion may be derived. The energy required for the conversion of a radical into the corresponding carbocation, in the gas phase, can be linearly related to the energy required for the conversion of the radical into the corresponding carbanion, in the liquid phase. This, of course, is expected to be true for benzyl and allyl cations and anions but only as far as the π-energy change is concerned. The soundness of this conclusion can be tested by proving that a correlation between pK_a and ionization potential exists. It must,

Correlation of kinetic and thermodynamic parameters for various reactions

Reaction	Correlation (E_a, IP/kcal mol^{-1})	Correlation coefficient	Reference
(I) $CCl_3\cdot + ArCH_3 \xrightarrow{k_r} CHCl_3 + ArCH_2$ $ArCH_3 \overset{K_a}{\rightleftharpoons} ArCH_2^- + H^+$	$\log k_r = -0{\cdot}2915\mathrm{p}K_a + 11{\cdot}0310$ $\log k_r = -0{\cdot}1145\mathrm{p}K_a + 2{\cdot}3185$	$-0{\cdot}9889$ $-0{\cdot}9947$	*a*—*c* 12, *d*, *e*
(II) $CH_3\cdot + RH \xrightarrow{E_a} CH_4 + R\cdot$ $R\cdot + e^- \xrightarrow{IP} R^+ + 2e^-$	$E_a = 0{\cdot}0036(IP) + 0{\cdot}3388$	0·9912	19, *f*, *g*
(III) $CD_3\cdot + RH \xrightarrow{E_a} CHD_3 + R\cdot$ $R\cdot + e^- \xrightarrow{IP} R^+ + 2e^-$	$E_a = 0{\cdot}0042(IP) + 0{\cdot}2133$	0·9746	19, *g*
(IV) $R\cdot + CH_4 \xrightarrow{E_a} RH + CH_3\cdot$ $R\cdot + e^- \xrightarrow{IP} R^+ + 2e^-$	$E_a = -0{\cdot}0027(IP) + 1{\cdot}7783$	$-0{\cdot}9967$	19, *g*
(V) $CH_3O\cdot + RH \xrightarrow{E_a} CH_3OH + R\cdot$ $R\cdot + e^- \xrightarrow{IP} R^+ + 2e^-$	$E_a = 0{\cdot}0071(IP) - 0{\cdot}5727$	0·9661	19, *g*
(VI) $CF_3\cdot + RH \xrightarrow{E_a} CHF_3 + R\cdot$ $R\cdot + e^- \xrightarrow{IP} R^+ + 2e^-$	$E_a = 0{\cdot}0065(IP) - 0{\cdot}4342$	0·9463	19, *g*
(VII) $RLi + Ph_3CH \xrightarrow{k_r} RH + Ph_3CLi$ $R\cdot + e^- \xrightarrow{IP} R^+ + 2e^-$	$\log k_r = -0{\cdot}0498(IP) + 11{\cdot}3875$	$-0{\cdot}9931$	19, *h*, *i*

[a] A. Streitwieser, jun., M. R. Granger, F. Mares, and R. A. Wolf, *J. Amer. Chem. Soc.*, 1973, **95**, 4257. [b] J. D. Unruh and G. J. Gleicher, *J. Amer. Chem. Soc.*, 1971, **93**, 2008. [c] H. Fischer and D. Rewicki, *Progr. Org. Chem.*, 1968, **7**, 116. [d] E. C. Kooyman, *Discuss. Faraday Soc.*, 1951, **10**, 163. [e] A. Streitwieser, jun., E. Ciuffarin, and J. H. Hammons, *J. Amer. Chem. Soc.*, 1967, **89**, 63. [f] A. A. Zavitsas, *J. Amer. Chem. Soc.*, 1972, **94**, 2779. [g] P. Gray, A. A. Herod, and A. Jones, *Chem. Rev.*, 1971, **71**, 247. [h] P. West, R. Waak, and J. I. Purmort, *J. Amer. Chem. Soc.*, 1970, **92**, 840. [i] I. P. Fisher, T. F. Palmer, and F. P. Lossing, *J. Amer. Chem. Soc.*, 1964, **86**, 2741.

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[17] J. O. Edwards, *J. Amer. Chem. Soc.*, 1954, **76**, 1540.

however, be borne in mind that the pK_a values of aliphatic and alicyclic hydrocarbons could include a considerable error. Figure 3 gives a plot of the pK_a values of a series of hydrocarbons[12,18] against the ionization potentials of the corresponding radicals.[19] A similar plot is given in Figure 4 for some acidic aromatic hydrocarbons. Both plots are only suggestive that a correlation between pK_a and ionization potential might hold, at least in a series of closely related compounds.

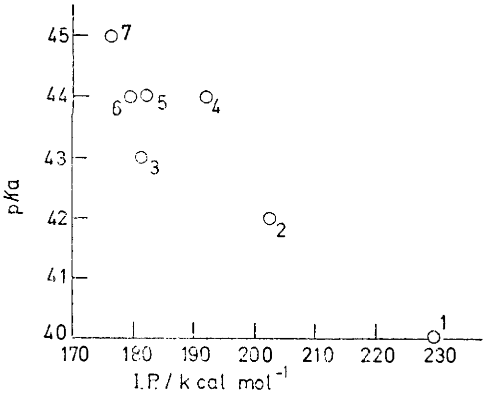

FIGURE 3 pK_a Values of aliphatic carbon acids plotted against the ionization potentials of the derived radicals: 1, methane–methyl; 2, ethane–ethyl; 3, cyclopropane–cyclopropyl; 4, neopentane–neopentyl; 5, propane–isopropyl; 6, cyclopentane–cyclopentyl; 7, cyclohexane–cyclohexyl

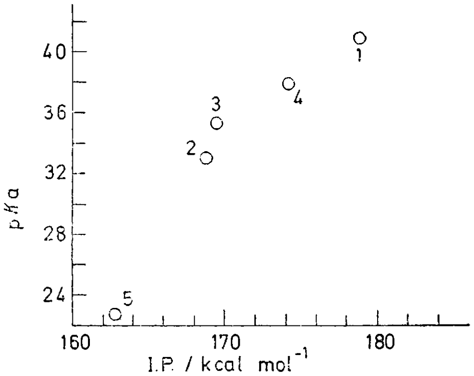

FIGURE 4 pK_a Values of aromatic carbon acids plotted against the ionization potentials of the derived radicals: 1, toluene–benzyl; 2, diphenylmethane–benzhydryl; 3, 1-methylnaphthalene-1-naphthylmethyl; 4, 2-methylnaphthalene–2-naphthylmethyl; 5, fluorene–fluoren-9-yl

Several other correlations between thermodynamic and kinetic parameters of related radicals, carbanions, and carbocations may hold. Whether all these correlations, however, can be taken to mean that in the transition state of a radical reaction there are polar contributions, or in that of an ionic reaction there are radical contributions, remains to be settled.

EXPERIMENTAL

BDPA was prepared according to the literature,[8] and was found to be >96% pure, assuming $\varepsilon_{max.}$ 28,900 (in benzene).[20] BDPA–OH was prepared as described by Nelsen and Bartlett.[21] Solvents and amines were purchased from Fluka. DMSO was distilled under vacuum from dimsylsodium, DMF was stored over molecular sieves for several weeks and used as such, HMPA was vacuum distilled from barium oxide. Tertiary amines were distilled from $LiAlH_4$, primary and secondary ones from barium oxide. Sodium cyanide, anhydrous sodium acetate, and sodium azide were Merck products. Visible spectra were recorded with a Cary 14 spectrophotometer. Reactivity orders were based on half-life measurements, under pseudo-first-order kinetics. Relaxation spectra were recorded with a Durrum stopped-flow spectrophotometer model D-110. Samples were prepared by the usual vacuum-line techniques and measurements were carried out under pure argon.

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