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TRIARYLMETHANES AND 9-ARYLXANTHENES AS PROTOTYPES AMPHIHYDRIC COMPOUNDS FOR RELATING THE STABILITIES OF CATIONS, ANIONS AND RADICALS BY C–H BOND CLEAVAGE AND ELECTRON TRANSFER

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Thermodynamic stability properties of 11 *p*-substituted trityl and seven 9-phenylxanthyl carbocations are reported in sulfolane and of their conjugate carbanions in DMSO. The cations are compared by calorimetric heats of hydride transfer from cyanoborohydride ion, their first and second reduction potentials, their pK_R^+s in aqueous sulfuric acid, ^{13}C chemical shifts and free energies of methoxy exchange. Carbanions are compared by their heats and free energies (pK_{HA}) of deprotonation and their first and second oxidation potentials. Radicals are compared by their oxidation and reduction potentials. Their bond dissociation energies are derived by alternative routes: from the carbocation and its reduction potential and from the carbanion and its oxidation potential. The various properties are correlated against each other and against appropriate Hammett-type substituent parameters. Correlations between the different measured properties reported here range from fair to excellent. Despite their importance as historic prototypes for the three trivalent oxidation states of carbon, trityl and xanthyl systems are atypical models for comparing transmission of electron demand in other series of carbocations, radicals or carbanions with significantly different structures. The 9-arylxanthyl series is especially poor because of its insensitivity to substituent effects. The effects of substituents on various properties which represent the stabilities of R$^+$s correlate surprisingly well against those for corresponding R$^-$s. Accordingly, compensating effects on the oxidation and reduction of a series of related *R*$^{\bullet}$s may lead to a nearly constant electron transfer energy and absolute hardness for the series. In contrast, the free energies for interconversion of the carbocations and carbanions which determine the gap between pK_{R^+} and pK_{HA} are very sensitive to structural change. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

Since the first year of the twentieth century the three conjugate trivalent oxidation states of carbon (henceforth R$^{+/\bullet/-}$) derived from triarylmethanes have played a leading role in the development of the theory of organic chemistry. No other class of compounds has provided such well recognized stable prototypes of radicals, carbenium ions and carbanions in solution where their structures can be demonstrated unequivocally and thus serve as *bona fide* models for the more reactive intermediates and transition structures which are now at the heart of modern mechanistic thinking and which have often required extreme conditions such as the gas phase[1] or superacid at −100 °C for their preparation and authentication.[2] Other types of compounds may form stable, isolable R$^{\bullet}$, R$^+$ or R$^-$ but the triarylmethyl systems, of which the 9-arylxanthanes are a subset, are nearly alone[3] in allowing the study of all three stable conjugates in the same types of solvent under conditions which differ only by the presence of acids or bases. Electrochemical studies of R$^{+/\bullet/-}$ show that these three species are closely interrelated,[4] although they are usually treated as belonging to three widely separated and unrelated fields.

Triarylmethyl halides were the first source of stable carbocations whose trivalent ionic structure was inferred correctly by Gomberg[5–7] only 2 years after his momentous discovery of triarylmethyl free radicals.[8] Later, the triarylcarbinols were used to establish the most commonly used free energy scale by which the stabilities of R$^+$s are expressed as the pK_{R^+}s for their equilibria with ROHs in aqueous acid.[9, 10] Triarylmethanes were identified as weak

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organic acids in 1925[11] and their conjugate bases were first named ‘carbanions’ in 1933.[12] However, the development of a reliable thermodynamic pK scale for ranking strong to weak organic Brønsted acids was delayed through the lack of appropriate media (analogous to aqueous sulfuric acid for studying carbocations) which were both highly basic, and also able to dissociate organoalkalis into various types of ion pairs[13–15] and ‘free ions’.[16]

Following Streitweiser *et al.*’s adoption of cyclohexylamine and its cesium salt as a strongly basic medium,[17] Bordwell’s group solved the problem by use of K^+ $DMSYL^-$, the potassium salt of DMSO, in this solvent. They provided the pK_{HA}s for over 2000 compounds in this medium, probably the largest database in organic chemistry from a single laboratory under identical conditions.[18] Fortunately, DMSO is a good solvent for most organic compounds, and also their potassium salts, and is well suited for UV–VIS spectrophotometry, electrochemistry and reaction calorimetry as has been used in the present study. The application of electrochemistry for interrelating triaryl $R^{+(\cdot/-}$ also has a long history.[19]

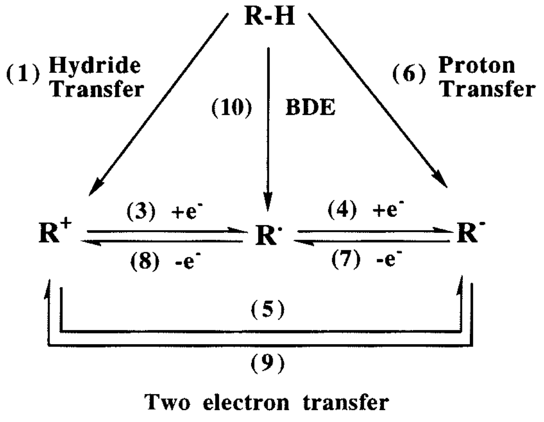
The triarylmethanes are an important class of *amphihydric* compounds,[20] for which the bond-making and -breaking energies of tetracovalent RH, ROH or RX to form the three related trivalent states can be examined under conditions which also permit their interconversion by electrochemistry.

The fact that the trivalent oxidation states of the triaylmethanes, or any other class of amphihydric compounds, can be studied in a single solvent is a fortuity. It is usually true that compounds whose R^+s are stable enough to afford pK_{R^+}s in aqueous acid will have R^-s that are too basic to allow direct determination of their pK_{HA}s with K^+DMSYL^-/DMSO. Correspondingly, RH which yield R^- that are stable in that solvent usually have R^+ that are such strong Lewis acids that they react with it. Triarylmethanes just happen to fall in the particular solvent-determined acid–base window that permits their study by both of the unrelated processes used to establish these two pK scales. Although $R^{+/\cdot/-}$ may all be stabilized by resonance-delocalization,[21, 22] it is generally true that the factors which help to stabilize R^+s (e.g. electron-releasing groups) tend to destabilize their conjugate R^-s and to have comparatively little influence on the stabilities of their conjugate $R^\cdot$s. Breslow and co-workers developed a powerful method for calculating the pK_{R^+}s of very unstable R^+s from the pK_{HA}s and the two-electron oxidation potentials of their very stable conjugate R^-s and *vice versa.*[4, 23] Amphihydric trityl compounds played an important role in authenticating this method. The free energy for *two-electron* reduction of the cation or oxidation of the carbanion is an important fundamental property since it determines the energy gap between the two conjugate ions and thus of the pK_{HA} of the carbanion and the pK_{R^+} of the carbocation.

The important differences in stability between the conjugate trivalent states $R^{+/\cdot/-}$ are determined by the (reversible) reduction potential of the cation and the oxidation potential of the anion in solution[24] or the equivalent redox potentials of the radical in solution.[25] In the gas phase the corresponding properties are I, the ionization energy, and A, the electron affinity, of the radical.[26, 27] In turn, these properties are related directly to the HOMO–LUMO gap, the electronegativity (χ), and the absolute hardness (η) of the $R^\cdot$,[28] i.e. its resistance to giving or gaining electrons. Since the stabilities of $R^{+/\cdot/-}$ are the primary determining factor for the energies required for the three modes of bond-breaking of RH, ΔG_{ET}, χ and η are the fundamental properties which drive the majority of observed structure-dependent phenomena of organic chemistry.[29]

An important feature of amphihydric compounds is that both the one- and two-electron redox potentials of both R^+ and R^- can be obtained directly under similar conditions so that electrode potentials for oxidizing and reducing $R^\cdot$ to its conjugate ions can be obtained by two independent routes and errors from irreversibility of electrode processes be assessed.[30] Correspondingly, the (homolytic) bond dissociation energy, *BDE*, of an R–H bond can be calculated[26] both from the pK_{HA} of R^- [31, 32] or from the pK_{R^+} of R^+ [30] using the appropriate redox potentials and equations thus providing another check for self-consistency.

Amphihydric compounds provide the best opportunity to establish all of these properties under similar conditions and to compare them to other familiar criteria for bond-making and -breaking energies. In principle, they also offer the unique opportunity of measuring directly the heat of heterolysis, ΔH_{het}, of the R–R bond from the calorimetric heat of reaction of R^+ with R^- in solution[20] (however, see Ref. 33 for problems in defining structures of symmetrical coupling products). This may be converted readily into the more familiar heat of homolysis, ΔH_{homo}, for such radical-coupled dimers (R–R) by combining the ΔH_{het} with the redox potentials of the conjugate ions.[24] These relationships are shown in Scheme 1 and were communicated earlier[2] as a complete analysis for a series of *p*-substituted-9-phenyl-



Scheme 1

xanthenes (Figure 1).

The appropriate equations and symbols for the measured properties depicted in Scheme 1 are as follows:

$$R^{+}+BH_3CN^{-} \rightarrow RH+BH_2CN \quad \Delta H_{H^-}(R^{+}) \tag{1}$$
$$R^{+}H_2O \rightarrow ROH+H^{+} \quad pK_{R^+} \tag{2}$$
$$R^{+}+e^{-} \rightarrow R^{\bullet} \quad \Delta G_{red}(R^{+}), E_{red}(R^{+}) \tag{3}$$
$$R^{\bullet}+e^{-} \rightarrow R^{-} \quad \Delta G_{red}(R^{\bullet}), E_{red}(R^{\bullet}) \tag{4}$$
$$R^{+}+2e^{-} \rightarrow R^{-} \quad \Delta G_{red}2(R^{+}), E_{red}2(R+) \tag{5}$$
$$RH+DMSYL^{-} \rightarrow R^{-}+DMSO \quad pK_{HA} \text{ and } \Delta H_{dep} \tag{6}$$
$$R^{-}-e^{-} \rightarrow R^{\bullet} \quad \Delta G_{ox}(R^{-}), E_{ox}(R^{-}) \tag{7}$$
$$R^{\bullet}-e^{-} \rightarrow R^{+} \quad \Delta G_{ox}(R^{\bullet}), E_{ox}(R^{\bullet}) \tag{8}$$
$$R^{-}-2e^{-} \rightarrow R^{+} \quad \Delta G_{ox}2(R^{-}), E_{ox}2(R^{-}) \tag{9}$$
$$RH \rightarrow R^{\bullet}+H^{\bullet} \quad BDE \tag{10}$$

Thus, if redox processes are reversible:

$$\Delta G_{red}(R^{+}) = -\Delta G_{ox}(R^{\bullet}) \tag{11}$$
$$\Delta G_{red}(R^{\bullet}) = \Delta G_{ox}(R^{-}) \tag{12}$$
$$\Delta G_{red}2(R^{+}) = -\Delta G_{ox}2(R^{-}) \tag{13}$$
$$BDE = 1{\cdot}37\ pK_{HA} + \Delta G_{ox}(R^{-}) + C \text{ (Ref. 31)} \tag{14}$$
$$BDE = 1{\cdot}37 pK_{R} + \Delta G_{red}(R^{+}) + C' \text{ (Ref. 30)} \tag{15}$$
$$\Delta G_{et} = \Delta G_{red}(R^{+}) - \Delta G_{red}(R^{\bullet}) \tag{16}$$
$$\eta = (I - A)/2 \approx -\Delta G_{ET}/2 \tag{17}$$

where I = ionization energy and A = electron affinity;

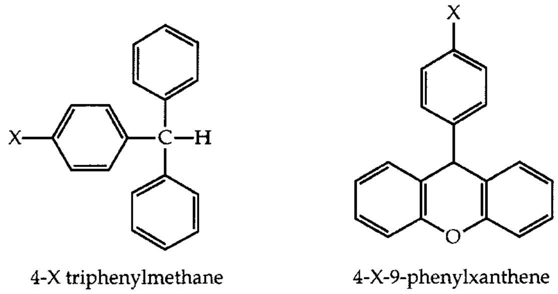
$$\chi = (i + A)/2 \tag{18}$$
$$\Delta G_{red}2(R^{+}) = \Delta G_{red}(R^{+}) + \Delta G_{red}(R^{\bullet}) \tag{19}$$
$$\Delta G_{ox}2(R^{-}) = \Delta G_{ox}(R^{-}) + \Delta G_{ox}(R^{\bullet}) \tag{20}$$

If all processes are reversible:

$$\Delta G_{red}2(R^{+}) = -\Delta G_{ox}2(R^{-}) \tag{21}$$

Scheme 1 summarizes the three processes by which $R^{+/\bullet/-}$ are formed by loss of H^{-}, $H^{\bullet}$, H^{+} from RH and their electrochemical interconversion. Scheme 1 indicates that if data are available for any of the three modes of RH bond breaking, it is possible to calculate the others by thermodynamic cycles if the appropriate reversible electron transfer properties may be obtained by electrochemistry.

Clearly, it is just as reasonable to use redox energies to relate the stabilities of the three trivalent states of carbon to each other as it is to relate them to their common tetracovalent precursor RH (effects of remote substituents on relative stabilities of ground states of triphenyl methanes should be virtually identical with those on their carbinols[4]) through the energies for the three different types of C–H bond-breaking. Indeed, because of the important relationships between the redox energies and the HOMO–LUMO gap, ΔG_{ET}, η and χ, the electrochemical data may be of more fundamental significance than the *BDE*, pK_{HA} or pK_{R^+} which are based on different processes with different standard states and can only be related to each other through the redox potentials of their trivalent states.



4-X triphenylmethane 4-X-9-phenylxanthene

Figure 1. Structures of 4-χ-triphenylmethane and 4-χ-9-phenylxanthene

Recently, we communicated a complete thermodynamic analysis, such as that in Scheme 1, for a series of *p*-substituted-9-phenylxanthenes and their cations, radicals and carbanions.[20] The present paper includes a full development of the procedures and results presented there.

Although many other types of data are available for substituted xanthylium cations, we have been unable to find a collection of pK_{R^+} values measured by the classical titration technique.[7, 9, 10] Accordingly, pK_{R^+} values in aqueous sulfuric acid are reported here for the present series of xanthylium ions. Heats of deprotonation (ΔH_{dep}) have been repeated and significantly different values found from those reported earlier.[20] All redox potentials have been remeasured and derived properties have been recalculated.

Correlations are given below for the properties reported here both against each other and also against published data from various sources. Comparisons are made of the second reduction potentials of the cations with the first oxidation potentials of their conjugate anions as tests for reversibility. *BDE*s have been estimated through the ΔH_{dep}s and ΔG_{ox} (R^{-})s and through the ΔH_{H^-}s and $\Delta G_{red}(R^{+})$s of the conjugate cations.

EXPERIMENTAL

In order to obtain a complete analysis of the type represented by Scheme 1, it is necessary to (a) have a solvent which is resistant to attack by a wide range of carbanions and carbocations, i.e. is both a relatively weak Brønsted acid and also a relatively weak Lewis base, and (b) have a small enough two-electron redox difference, $\Delta G_{red}2(R^{+})$ or $\Delta G_{ox}2(R^{-})$ between R^{+} and R^{-} so that the hydride affinity, ΔH_{H^-}, of R^{+} and the heat of deprotonation, ΔH_{dep}, of RH to form R^{-} may be measured by appropriate techniques.

Unfortunately, we have not yet found a single solvent in which we can do all of the types of experiments shown in Scheme 1. Sulfolane comes close to meeting the requirements. It is extremely resistant to attack by protonic and Lewis acids and is only slightly more acidic than dimethyl sulfoxide[18b] with which some of its important properties are compared in Table 1. However, the potassium salt of sulfolane is too insoluble to allow the preparation of a concentrated basic medium equivalent to K^{+} DMSYL^{-}. But for this shortcoming, sulfolane could be used to determine pK_{HA}s, ΔH_{dep}s and all of the other properties in Scheme 1.

Table 1. Solvent properties of sulfolane and DMSO (all ΔH values in kcal mol^{-1} at 25 °C)

Property	DMSO	Sulfolane
pK_{HA}[a]	35	31·1 (Me_2SO_2)
ΔH_{dep}[b]	0	−2·64
ΔH_{HSO3F}[c]	−26·5	−9·6
ΔH_{p}-F-$_{phenol}$[c]	−6·6	−4·25
ΔH_{SbCl_5}[d]	−29·8	−14·3
ΔH_{BF3}[e] ($CH_2Cl_2 = -10{\cdot}0$)	−105·3	−51·3
Dielectric constant[f]	46·7	43·32
Dipole moment[f]	4·81 D	3·96 D

[a] Ref. 18b.
[b] Ref. 20.
[c] Ref. 34.
[d] Ref. 35.
[e] Ref. 36.
[f] Ref. 37.

Accordingly, we have had to compromise and use sulfolane to study carbocation properties and DMSO for carbanions. The conjugate radicals can be produced in either solvent by redox of the two types of conjugate ions. Sulfolane and DMSO are closely similar in most of their important solvent properties, the principal difference being the relatively high basicity of DMSO towards both protonic and Lewis acids (Table 1).

As before,[24] we used reaction calorimetry and electrochemistry of carbocations in sulfolane (tetramethylenesulfone) containing 5% 3-methylsulfolane to lower the freezing point for operation at 25 °C [equations (1), (3) and (4)]. By analogy with Bordwell and coworkers,[31] we combined ΔH_{dep} with the first oxidation potential of R^- in DMSO [equations (6) and (15)] to give the *BDE* for C–H cleavage to give $R^{\bullet}$ and also derived *BDE*s from the corresponding $\Delta H_{H^-}(R^+)$s in sulfolane and the first reduction potential of R^+ for comparison.

Since calorimetric measurements are meaningless unless the presumed reactions are clean and complete, all of the reactants, products and processes discussed here were checked by ^1H and ^{13}C NMR spectroscopy. We recognize that these tools may not be sensitive enough to detect small quantities of reactive impurities in reactants or of side-products that would contribute to significant calorimetric errors.

Purification of solvents. All solvent batches were checked by Karl Fisher titration to ensure a water content below 50 ppm. Sulfolane (Phillips Petroleum) was distilled from butyllithium at 1 mm Hg pressure (b.p. 110–111 °C) and stored under argon. The melting point of sulfolane was lowered for work at 25 °C by addition of 3-methylsulfolane (Aldrich), which was dried by stirring overnight at room temperature with CaH_2 under an argon atmosphere followed by vacuum distillation (b.p. 101–102 °C at 1 Torr). The purified solvent was transferred to an argon-filled dry-box and a 5% (v/v) solution of 3-methylsulfolane–sulfolane was prepared. This mixture was dried further by stirring over CaH_2 overnight and was filtered before use. Potassium hydride was purified by washing an oil dispersion of potassium hydride (Aldrich) with dry hexane under an argon atmosphere to remove the mineral oil. The resulting hydride powder was dried under vacuum and sorted in an argon-filled dry-box. All solvents were checked by Karl Fisher titration for water content, which was only acceptable if <25 ppm.

General procedure for the synthesis of 9-aryl-9-xanthanols. To a solution of 2·0 g (10·2 mmol) of xanthone in THF was added dropwise 11 ml (11 mmol) of a 1·0 M solution of phenylmagnesium bromide. The solution was stirred an additional 45 min after the addition was complete and was then quenched with saturated NH_4Cl solution. The reaction mixture was diluted with diethyl ether (100 ml) and washed twice with water. The organic layer was dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure left a crude residue, which was filtered through neutral alumina to give 9-phenyl-9-xanthanol as a white solid (2·5 g; 82%). The melting points of known 9-substituted xanthanols were compared with the published values of McClelland *et al*.[38] This material was used without further purification for the preparation of 9-arylxanthyl cations and 9-arylxanthenes after examination for impurities by ^1H and ^{13}C NMR spectroscopy.

General procedure for the synthesis of triarylcarbinols. These were prepared by the reaction of aryl acid chlorides and aryl Grignard reagents.[39] For example, to a solution of 1·5 g (10·7 mmol) of benzoyl chloride in THF was added dropwise 30·0 ml (30 mmol) of a 1·0 M solution of phenylmagnesium bromide. The solution was stirred for an additional 50 min at reflux after the addition was complete and was then quenched with saturated NH_4Cl solution. The reaction mixture was diluted with diethyl ether (100 ml) and washed twice with water. The organic layer was dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure left a crude residue which was subjected to flash silica gel chromatography to give 1·1 g (40%) of triphenylmethanol. These samples were determined to be pure by ^1H and ^{13}C NMR spectroscopy.

General reduction procedure for carbinols. Both the 9-arylxanthan-9-ols and the triarylmethanols were converted to their carbon acids by heating a formic acid–Na_2CO_3 solution of the alcohol at reflux for 2–3 h[39]as in the following example. To a solution of 5·0 g (18 mmol) of 9-phenyl-9-xanthanol in 60 ml of 90% formic acid was added 10 g of sodium carbonate. The solution was refluxed for 1–1·5 h and then cooled at 5–10 °C for 4 h. The product was isolated by filtration and washed with water. The product was recrystallized from hexane to give a 95% yield of desired product, shown to be pure by ^1H and ^{13}C NMR spectroscopy.

Triarylmethyl cations. The tetrafluoroborate salts were prepared by treating the corresponding carbinol with fluoroboreic acid (48% in diethyl ether, Aldrich) in propionic anhydride as described by Dauben *et al.*[40] For example, triphenylmethanol (13·2 g, 50 mmol) was dissolved in propionic anhydride (150 ml) and cooled to 10 °C. After adding 48% fluoroboric acid (4·4 g, 50 mmol) the temperature was kept between 10 and 12 °C for 10 min. The solution was diluted with dry diethyl ether (300 ml) and the resulting precipitate was collected by filtration under argon and washed thoroughly with dry diethyl ether. The resulting solid was dried under vacuum (0·5 mmHg) overnight. The trityl tetrafluoroborate was stored in a dry-box. 4,4′,4″-Tris(*p*-chlorophenyl)methylium tetrafluoroborate salt could not be prepared using this method. The pentachloroantimonate salt was made by addition of a stoichiometric amount of antimony pentachloride to a solution of the 4,4′,4″-tris(*p*-chlorophenyl)methyl chloride in hexane as described by Freedman and co-workers.[41] These samples were determined to be pure by ^{1}H and ^{13}C NMR spectroscopy.

Equilibration measurements. pK_{HA}s of 9-arylxanthenes (HA) were determined by means of ^{1}H NMR spectroscopy instead of UV–VIS spectrophotometry as employed by Bordwell and co-workers.[18] Since the pK_{HA} of 9-phenylxanthene, HA_0, was available already[42] and each of the four species (HA, HA_0, A^- and A_0^-) had distinct and separable signals in the ^{1}H NMR spectra for the acids under study, the relative pK_{HA}s could be determined by equilibration. The difference, ΔpK_{HA}, could be derived from the response of the integrated peak areas of the four species as their stoichiometric concentrations were varied and pK_{HA} determined using a method equivalent to the methoxy exchange reaction applied by Freedman and co-workers[41] to the relative stabilities of the same series of 9-arylxanthyl carbocations in acidic solution. ΔpK_{HA} was then added or subtracted from pK_{HA_0}. The equilibrium between a substituted 9-arylxanthene (HA) and 9-phenylxanthene (HA_0) is described by the equations

$$HA + A_0^- \rightleftharpoons A^- + HA_0 \tag{19}$$

$$\Delta pK_{HA} = -\log[A-][HA_0]/[HA][A_0^-] \tag{20}$$

$$pK_{HA'} = pK_{HA_0} + \Delta pK_{HA} \tag{21}$$

where $pK_{HA'}$ refers to the compound of unknown acidity and pK_{HA_0} is that for 9-phenylxanthene. Concentrations close to 1×10^{-2} M were employed. Since threefold dilution did not affect the results, aggregation was deemed to be insignificant. The method was checked using 9-phenylxanthene and 4-methoxy-9-phenylxanthene, both of whose pK_{HA}s are known.[18c]

The determination of the pK_{HA} for 9-(*p*-methylphenyl)xanthene is given as an example of the general procedure. Equimolar quantities of 9-(*p*-methylphenyl)xanthene and 9-phenylxanthene were dissolved in DMSO-d^6 (Aldrich, distilled from KH), and the relative molar ratio of the two compounds was determined through direct integration of the ^{1}H NMR spectrum of the mixture. To this mixture was added 0·8 equiv. of KH. The ratio of the two anions and their conjugate acids was determined by direct integration of signals representative of the four species in equilibrium.

pK_{R^+} determination of xanthylium ions. Techniques for determining carbocation–carbinol equilibrium constants in aqueous acid by UV–VIS spectrophotometry are widely documented[7, 9, 10] and were followed carefully. Spectra of the cations agreed well with published spectra and gave good Beer's law plots. However, the spectra of the carbinols overlapped with the solvent in some regions, in which case the ROH concentration at equilibrium was determined from the difference between the stoichiometric concentration and that of the cation.

Relatively dilute aqueous sulfuric acid solutions covering an $H_R(10)$ range from $-1{\cdot}65$ to $1{\cdot}16$ were adequate for all pK_{R^+} measurements, which were based on linear plots of 2–6 independent measurements of $\log[R^+]/[ROH]$ vs H_R for five different acid solutions. As before,[10] the concentrations of R^+ and ROH varied in the range 10^{-6}–10^{-4} M.

Calorimetric measurements. All ΔH_{H^-} measurements reported here were made using a Tronac 450 titration calorimeter at 25 °C. In contrast to the previous[20] heats of hydride transfer, obtained with cycloheptatriene as hydride donor, the results given here used a recently published[43] procedure employing calorimetric titration of sulfolane solutions of the cation tetrafluoroboride into a 50 ml Dewar calorimeter vessel containing a large excess of 1 M sodium cyanoborohydride containing an equivalent amount of 18-crown-6 polyether to complex the sodium ion and eliminate possible small ion-pairing contributions to the measured heat of hydride transfer. A variety of reasonable hydride donors were tried before settling on this system.

In addition to titrations using a standard Tronac Model 450 calorimeter, many measurements were made with a more automated system that employed a Tronac Model 900 computer interface for collecting and analyzing the data. Each ΔH_{H^-} presented here represents an average value from at least seven calorimetric measurements on two independently prepared solutions. The relative error for reaction calorimetry with sensitive, unstable solutions such as some of these is 2–4% rather than the usual 0·5–1%. The absolute error (accuracy) is unknown and is best tested for by correlating data with a variety of other properties as reported below. This, however, provides no protection against systematic errors that persist throughout a series of related compounds.

Determination of ΔH_{dep} of triarylmethanes and 9-arylxanthenes. Heats of deprotonation are well precedented in this laboratory[44] using titration calorimetry of a molar solution of the carbon acid in DMSO into a large excess of K^+ DMSYL$^-$/DMSO. All solutions were prepared and handled in a dry-box using carefully dried DMSO whose water content was <25 ppm by Karl Fischer titration. Each ΔH_{dep} represents an average value from at least seven calorimetric measurements on two independently prepared solutions.

Electrochemistry. All electrochemical measurements employed a BAS 100-A electrochemical analyzer using cyclic voltammetry (CV) and Osteryoung square-wave voltammetry (OSWV).[45] The speed and simplicity of CV made it the first choice for characterizing redox systems. OSWV was also employed because of its ability to discriminate against charging currents and to produce a peaked curve for Faradaic processes. Computer display of the forward and reverse responses for an OSWV experiment provided a test for the reversibility of the redox processes. All measurements were made using a three-electrode arrangement consisting of a platinum disk working electrode, a platinum wire auxiliary electrode and an Ag/$AgNO_3$ reference electrode with the ferrocenium/ferrocene redox couple as the external standard. The measured values were referred to the normal hydrogen electrode by adding 0·75 V and converting to the corresponding standard free energy terms by multiplying by $-23{\cdot}06$ kcal V^{-1}. Solutions of cations and anions in 0·1 M tetrabutylammonium tetrafluoroborate supporting electrolyte were prepared under an argon atmosphere just prior to electrochemical analysis. Reduction potentials for cations were determined in 95% sulfolane–5% 3-methylsulfolane. Oxidation potentials for the anions were determined from DMSO solutions of the potassium salts of the anion using 0·1 M $TBABF_4$ as the supporting electrolyte.

RESULTS AND DISCUSSION

Cations

Carbocations have played a key role in the development of mechanistic organic chemistry. Their proposed involvement in solvolysis and electrophilic aromatic substitution demonstrated the need for reliable thermodynamic scales as a basis for structure–reactivity correlations. Especially relevant to the present discussion are Deno *et al.*'s pioneering studies of the acidity function, H_R, for determining K_R, the carbinol–cation equilibrium constants in aqueous acid,[9] Arnett and Bushick's examination[10] of the temperature coefficient of H_R and pK_Rs for a number of di- and triarylmethyl cations in aqueous H_2SO_4, Brown and co-workers' development of σ^+ substituent constants[46] and Arnett and Hofelich's measurements of the heats of formation of a corresponding series of cumyl cations from their alcohols in superacid at low temperature.[47]

More recently, Wayner and co-workers[25] have exploited a photomodulation technique to generate unstable $R^{\bullet}$s in solution and derive important thermodynamic properties for their conjugate R^+s and R^- s which are too unstable to allow direct determination of pK_{R+} or pK_{HA}s. The redox potentials of a number of highly unstable substituted benzyl, cumyl and benzhydryl radicals that were generated by photolysis of the RH precursor in acetonitrile were determined and the effects of substitution in the phenyl rings on the stabilities of the conjugate R^+ and R^- relative to their $R^{\bullet}$ were compared with each other and with published data by correlation with σ^+ and σ^- Hammett parameters.[48]

However, none of the above solution studies, except those from this laboratory,[20, 43] have combined direct measurement under comparable conditions of the stabilities of R^+ [by $\Delta H_{H^-}(R^+)$] and of R^- [by (H_{dep})] with redox potentials to provide both a complete analysis of the energetics for bond cleavage to form the $R^{+/\bullet/-}$ and also of their stabilities *relative to each other* by electron transfer, as shown in Scheme 1.

Table 2 presents a variety of experimental properties reflecting the stabilities of the trityl and xanthyl cations in sulfolane (ΔH_{H^-} and ΔG_{red}) and aqueous sulfuric acid (pK_{R^+}). In addition, hydride affinities calculated by Parker and co-worker's method[49] from the pK_{HA}s (method 1) or ΔH_{dep} (method 2) and the oxidation potential of the radical are listed. All of the data shown in Table 2 go from the least stable R^+ at the top to the most stable ones at the bottom, although the sign of the property depends on conventions for its definition.

Correlations of ΔH_{H^-} with other carbocation properties

Table 3 provides a means for comparing these properties with each other in terms of the statistics of their linear correlations rather than attempting to present the correlations graphically. In general, none of the correlations is excellent ($r>0{\cdot}99$); xanthyl and trityl are mostly differentiated with respect both to slope and *r* with correlations of the xanthyl data usually being poorer. Correlations of ΔH_{H^-} with other properties in Table 2 are mostly poorer than those for ΔH_{dep}s (see below) because of the relatively high experimental error [$\pm 0{\cdot}4$–$0{\cdot}6$ kcal mol^{-1} (1 kcal = 4·184 kJ)] of this cation property compared to the usual $\pm 0{\cdot}2$–$0{\cdot}4$ kcal mol^{-1} for reaction calorimetry.

Not surprisingly, the best correlation (3-1) for ΔH_{H^-} of the trityl cations is against their ^{13}C NMR shifts, which provide a sensitive indicator of transfer of electron demand at the cationic center to the *para* substituents.[46c] The next best correlation (3-2) is with $\Delta G_{red}(R^+)$, their free energies of reduction in sulfolane. Of particular importance is the nearly unit slope of (3-2) for all of the 40 highly diverse types of compounds for which we have measured both properties but the very low slope (3-8) and lower correlation coefficient for eight xanthylium ions compared to 11 trityl cations is noteworthy (see below).

Close correlations between C–H bond-making and -breaking processes and the redox potentials of the resulting ionic trivalent species formed are well precedented-[24d,e,h,i, 31c, 50] and might reasonably be expected since both types of process involve the difference in energy between a neutral species and an ion. However, bond-breaking processes perforce involve conversion of a tetravalent species into a trivalent one and so may be sensitive to steric effects. In contrast, redox processes involve interconversion of

Table 2. Stability data for *p*-substituted triphenylmethyl and 9-phenylxanthene cations (all ΔG and ΔH in kcal mol^{-1})

Entry No. (2-)	Series	Substituent	$-\Delta H_{H^-}$ (R$^+$)	$\Delta G_{red}(R^+)[E_{red}1(R^+)]$[a, b]	$\Delta G_{red}(R^\bullet)[E_{red}(R^\bullet)]$[a, b]	pK_{R^+}	Cation ^{13}C shift	$-\Delta G_{h^-}$[f] (R$^+$) (Parker 1)	$-\Delta H_{h^-}$ (R$^+$) (Parker 2)	ΔG_{ET}[h]	$\Delta G_{red}2(R^+)$
1	Trityl	4,4′,4″-Cl	54·4 ± 0·58	− 17·34 (0·752 ± ·009)	12·68 (− 0·550 ± ·013)	− 7·74[c]	212·7	99·94	101·18	− 30·02	− 4·65
2	Trityl	None	52·7 ± 0·23	− 12·49 (0·542 ± ·011)	16·64 (− 0·722 ± ·015)	− 6·63[c]	212·0	96·04	95·87	− 29·1	4·15
3	Trityl	4-F	52·1 ± 0·36	− 15·26 (0·662 ± ·007)	16·3 (− 0·707)	− 6·42[e]	210·0	86·74	72·81	− 31·6	1·04
4	Trityl	4-Me	51·5 ± 0·32	− 12·86 (0·558 ± ·013)	17·29 (− 0·750 ± ·011)	− 5·41[c]	209·0		97·1	− 30·2	4·43
5	Trityl	4,4′-Me	51·3 ± 0·52	− 12·33 (0·535 ± ·011)	19·32 (− 0.838 ± .010)	− 4·39[e]	208·2		94·89	− 31·6	6·99
6	Trityl	4,4′,4″-Me	49·4 ± 0·41	− 11·6 (0·503 ± ·017)	21·35 (− 0·926 ± ·009)	− 3·56[c]	206·7		93·14	− 32·9	9·75
7	Trityl	4-OMe	48·2 ± 0·37	− 11·2 (0·486 ± ·007)	18·58 (− 0·806 ± ·007)	− 3·40[c]	201·0	95·81	94·71	− 29·8	7·38
8	Trityl	4,4′4,″-tbu	48·2 ± 0·40	− 10·4 (0·451 ± ·	21·65 (− 0·939 ± ·005)	− 6·5[c]	206·0		88·27	—32·1	11·25
9	Xanthyl	9-(*p*-CF_3)Ph	48·1 ± 0·33	− 9·77 (0·424 ± ·021)	14·78 (− 0·641 ± ·017)	− 0·11[d]	174·2			− 24·6	5·01
10	Xanthyl	9-(*p*-Cl)Ph	46·7 ± 0·32	− 9·52 (0·413 ± ·010)	17·22 (− 0·747 ± ·008)	0·13	174·7	87·21	85·91	− 26·7	7·70
11	Xanthyl	9-(*p*-F)Ph	46·3 ± 0·45	− 9·17 (0·398 ± ·007)	16·83 (− 0·730 ± ·013)	− 0·64[d]	175·1	88·8	88·56	− 26·0	7·75
12	Xanthyl	None	46·1 ± 0·75	− 10·46 (0·454 ± ·017)	15·31 (− 0·664 ± 0·026)	− 0·84[c]		94·53	93·88	− 25·8	4·85
13	Thioxanthene	9-Ph	45·3 ± 0·21	− 8·69 (0·377 ± ·004)	16·55 (− 0·718 ± ·010)		172·4	87·91	87·26	− 25·2	7·86
14	Xanthyl	9-Ph	45·1 ± 0·19	− 8·57 (0·372 ± ·007)	17·82 (− 0·773 ± ·007)	0·81[d]	174·6	87·26	86·49	− 26·4	9·25
15	Trityl	4,4′-OMe	44·6 ± 0·38	− 9·63 (0·418 ± ·008)	21·00 (− 0·911 ± ·009)	− 1·24[e]	201·0		92·64	− 30·6	11·37
16	Xanthyl	9-(*p*-Me)Ph	43·9 ± 0·31	− 8·32 (0·361 ± ·011)	18·70 (− 0·811 ± ·008)	0·81[d]	172·3	86·95	87·02	− 27·0	10·38
17	Tropylium	None	43·4 ± 0·43	1·38 (− 0·060 ± ·024)	32·51 (− 1·410 ± ·024)	4·7[c]				− 33·8	31·13
18	Xanthyl	9-(*p*-OMe)Ph	43·3 ± 0·42	− 7·67 (0·333 ± ·008)	18·7 (− 0·811 ± ·007)	1·00[d]	164·8	86·17	85·55	− 26·4	11·03
19	Trityl	4,4′,4″-OMe	41·4 ± 0·18	− 5·05 (0·219 ± ·004)	24·4 (− 1·058)	0·82[e]	194·0		86·73	− 29·5	19·3
20	Cyclopropene	1,2,3-Triphenyl	38·8 ± 0·15	4·05 (− 0·176 ± ·008)	29·74 (− 1·290 ± ·012)	3·1[c]				− 33·8	33·79
21	Trityl	4,4′,4″-NMe_2	28·9 ± 0·34	8·44 (− 0·366 ± ·007)	28·54 (− 1·238 ± ·025)	9·4[e]	179·0		76·03	− 36·9	33·98

[a] In sulfolane at 25 °C.

[b] 0·1 M TBATFB, values reported are relative to the NHE.

[c] Ref. 7.

[d] This report from thesis of A.E.M. (1994).

[e] Ref. 7b.

[f] Calculated hydride affinities using Parker's method,[49] $-\Delta G_{H^-} = 1{\cdot}37\ (pK_{HA}) + \Delta G_{red}(R^+) + \Delta G_{red}(R^\bullet) + \text{constant}$.

[g] Calculated hydride affinities using a variation on Parker's method, $-\Delta H_{H^-} = -\Delta H_{dep} + \Delta G_{red}(R^+) + \Delta G_{red}(R^\bullet) + \text{constant}$.

[h] $\Delta G_{ET} = \Delta G_{red}(R^+) - \Delta G_{red}(R^\bullet)$.

Table 3. Correlations between $\Delta H_{\mathrm{H^-}}$ and other measures of carbocation stability

Entry No. (3-)	Correlation	Slope	r	n	Notes
1	Cation ^{13}C shift	1·34	0·989	11	Trityl
2	$\Delta G_{\mathrm{red}}(\mathrm{R}^+)$	− 1·04	0·923	40	[a]
3	$\Delta G_{\mathrm{red}}(\mathrm{R}^+)$	− 0·932	0·982	11	Trityl
4	$\Delta G_{\mathrm{red}}(\mathrm{R}^+)$	− 0·905	0·975	19	Xanthyl and trityl
5	ΔG (methoxy exchange)	− 0·905	0·982	11	[b]
6	1·37 p$K_{\mathrm{R^+}}$	− 0·888	0·989	10	Trityl
7	1·37 p$K_{\mathrm{R^+}}$	− 0·878	0·957	20	Trityl and xanthyl
8	$\Delta G_{\mathrm{red}}(\mathrm{R}^+)$	− 0·495	0·891	8	Xanthyl
9	1·37 p$K_{\mathrm{R^+}}$	− 0·336	0·920	7	Xanthyl
10	$\Delta G_{\mathrm{H^-}}(\mathrm{R}^+)$ (Parker 1)	0·793	0·865	5	Trityl compounds
11	$\Delta G_{\mathrm{H^-}}(\mathrm{R}^+)$ (Parker 1)	0·817	0·841	12	Trityl and xanthyl
12	$\Delta H_{\mathrm{H^-}}(\mathrm{R}^+)$ (Parker 2)	0·889	0·947	10	Trityl
13	$\Delta H_{\mathrm{tropylium}}$	0·910	0·972	6	Xanthyl
14	$\Delta H_{\mathrm{H^-}}(\mathrm{R}^+)$ (Parker 2)	0·931	0·898	17	Xanthyl and trityl
15	$\Delta H_{\mathrm{H^-}}(\mathrm{R}^+)$ (Parker 2)	1·14	0·550	7	Xanthyl
16	$\Delta G_{\mathrm{H^-}}(\mathrm{R}^+)$ (Parker 1)	1·27	0·620	7	Xanthyl

[a] All data for cations from Table 2 plus a variety of 1,3-dioxo- and 1,3-dithiocations in preparation.

[b] Ref. 41.

trivalent radicals and ions. These species may have different conformational energies, but these should be smaller than the compression changes which accompany formation or destruction of a tetracovalent species. Other significant differences between the two types of experiments are: the presence of the electrode surface and of supporting electrolyte for determination of the redox potentials. However, several $\Delta H_{\mathrm{H^-}}$ measurements were shown to be unaffected, within experimental error, by the presence of added supporting electrolyte at its working concentrations, so this factor is not significant.

Another appropriate criterion for comparing the stabilities of the trityl and xanthyl cations is the free energies for their exchange of methoxy groups at equilibrium in D_2CCl_2 and D_3CN as reported by Freedman and co-workers[41] using NMR spectroscopy. Although his conditions were different from ours, the correlation (3-5), between the heats of hydride reduction and the free energies of methoxy exchange is one of the best in Table 3. Correlation of heats of hydride transfer from cyanoborohydride ion with those from cycloheptatriene to six xanthyl cations (3-13)[20] is good, but not excellent. In view of the generally poor correlations that are found for the xanthyl cation properties (see below), it would be hard to tell whether this case reflects a difference in steric factors between the reaction of a cation with an anion vs reaction with a neutal molecule or just experimental errors due to slower reactions with this hydride source.

Parker and co-workers[49] have proposed a method for estimating the free energy hydride affinity of a carbocation, $\Delta G_{\mathrm{hydride}}(\mathrm{R}^+)$, from the measured p$K_{\mathrm{HA}}$s of the conjugate RH/R$^-$ in DMSO and the electrode potentials for oxidation of the conjugate R$^-$ and R$^\bullet$ to their conjugate R$^+$ (i.e. the two-electron process for oxidizing R$^-$ to R$^+$) in DMSO:

$$\begin{aligned}-\Delta G_{\mathrm{hydride}}(\mathrm{R}^+) = {} & 2{\cdot}303RT\,\mathrm{p}K_{\mathrm{HA}}(\mathrm{RH}) \\ & + FE^\circ_{\mathrm{NHE}}[(\mathrm{R}^\bullet/\mathrm{R}^-)+(\mathrm{R}^+/\mathrm{R})] \\ & - FE^\circ_{\mathrm{NHE}}[(\mathrm{H}^\bullet/\mathrm{H}^-)+(\mathrm{H}^+/\mathrm{H}^\bullet)] \qquad (22)\end{aligned}$$

Because of the availability of the enormous range of pK_{HA}s, BDEs and ($E_{\mathrm{ox}}\mathrm{R}^-$) data established by Bordwell's group, Parker's approach can provide estimates of $\Delta G_{\mathrm{hydride}}$ (R^+) for a much wider range of R$^+$ than the stable ones whose reactions with borohydride are presented here. The necessary data are available (Table 2 and Ref. 4a) for calculating $\Delta G_{\mathrm{hydride}}(\mathrm{R}^+)$ in DMSO for 12 of the stable R$^+$ for which we have made direct measurements of $\Delta H_{\mathrm{H^-}}$ in sulfolane, and these can at least provide a test of his estimated relative energies. The results are correlated by (3-10, 11, 16).

The estimated numerical value for $\Delta G_{\mathrm{hydride}}(\mathrm{R}^+)$ and its measured $\Delta H_{\mathrm{H^-}}(\mathrm{R}^+)$ should differ because the standard state for making the C–H bond by reaction with sodium cyanoborohydride in sulfolane is entirely different from that for C–H bond-breaking with K$^+$ DMSYL$^-$ in DMSO. Also, the assumption, which we have frequently made and justified,[24i, 51] that redox entropies of R$^\bullet$ are insignificant so that ΔHs can be interchanged with ΔGs may not hold exactly here. However, it would be reasonable to expect a rather good correlation between Parker's values and ours but only fair to poor ones are found (2-10, 11, 16) the worst, as usual, involving 9-phenylxanthylium ions.

Improvement results from using the heat of deprotonation (ΔH_{dep}) in DMSO instead of the corresponding free energy term in that solvent ($2{\cdot}303RT\mathrm{p}K_{\mathrm{HA}}$). If this substitution is made in Parker's equation, a better correlation (2-12, 14, 15) is seen. Again, the 9-phenylxanthyl cations give some of the poorest correlations of $\Delta H_{\mathrm{H^-}}(\mathrm{R^+})$ with the other properties in Table 3 (see below).

ΔG_{ET} and $\Delta G_{\mathrm{red}}2(\mathrm{R^+})$

These two properties, derived by adding or subtracting the free energies of reduction for $\mathrm{R^+}$ and $\mathrm{R^\bullet}$ or of oxidation for $\mathrm{R^-}$ and $\mathrm{R^\bullet}$ [see equations (16), (19), (20) and (21)] *are of fundamental importance to all of organic chemistry*.

ΔG_{ET} is the energy required to transfer one electron from the carbanion to the carbocation to produce a pair of radicals. It is a direct expression of the HOMO–LUMO gap and absolute hardness of $\mathrm{R^\bullet}$[26, 29] and is the necessary property from relating free energies or heats of heterolysis to those of homolysis.[24, 26, 31] In the absence of ground-state effects, stabilities of $\mathrm{R^{+/\bullet/-}}$ determine relative bond-breaking and -making energies and thus play a major role in observed rates and equilibria.

As seen in Table 2, the ΔG_{ET}s for the trityl radicals lie in a small range around -30 kcal mol^{-1} as a result of strong affinities of the cations for electrons and repulsion of electrons by their conjugate radicals leading to conflicting trends in the stabilities of $\mathrm{R^+}$ and $\mathrm{R^-}$ in response to *p*-substitution. ΔG_{ET}s of xanthyl radicals lie in a slightly lower range than trityls.

$\Delta G_{\mathrm{red}}2(\mathrm{R^+})$ or $\Delta G_{\mathrm{ox}}(\mathrm{R^-})$ are the free energies for transferring two electrons to the carbocation, that is, for interconverting the carbocation and the carbanion or removing them from the carbanion. These properties determine the gap between the $\mathrm{p}K_{\mathrm{R^+}}$ of ROH and $\mathrm{p}K_{\mathrm{HA}}$ of RH[4] and express the difference between the proclivity for trivalent R to be Lewis acid $\mathrm{R^+}$ in contrast to the strong base $\mathrm{R^-}$. Table 2 shows an enormous structure-dependent range for this property, which explains in part why so few classes of compounds can be converted readily into both their conjugate $\mathrm{R^+}$ and $\mathrm{R^-}$ in solution, i.e. are amphihydric.

Hammett-type correlations of $\mathrm{R^+}$ stability data

It has long been recognized[9, 46] that substituent effects on many processes that form/destroy carbenium ion centers are modeled better by the $\log k_{\mathrm{s}}$ for solvolysis of substituted cumenes (σ^+) in non-aqueous solvents than they are by the ionization of substituted benzoic acids in water (σ). The slopes (ρ^+) for correlations of $\mathrm{R^+}$ properties vs σ^+ can cover a wide range, which is reasonably interpretable in terms of electron demand, through one mechanism or another, from the cationic center, particular importance being given to resonance interaction with alkoxy or amino groups.

Table 4 includes correlations of results from Table 2 and other data collected by Wayner and co-workers[48] (note also 24 ρ^+s for reactions in Ref. 46a) to test the proposed relationship between ρ^+ and charge development. If, in fact, there is relatively little electron demand on ring substituents from the carbenium ion center, one might expect a better correlation with σ. Accordingly, Table 4 compares slopes and *r*s of correlations against both types of substituent constants as a measure of interaction between the carbenium center and the *p*-substituent. The electron demand at the para position should be reflected both by the slopes of correlations with σ^+ and σ and their correlation coefficients. Because substituent constants are unitless values derived from log *K*s or log *k*s, it is necessary to divide ΔHs or ΔGs

Table 4. Hammett plots for carbocation stability data[a]

Entry No. (4-)	Correlation	Slope	*r*	*n*	Notes
1	$\Delta G_{\mathrm{red}}(\mathrm{R^+})/1{\cdot}37$ vs σ^+	$-1{\cdot}16$	0·926	6	Xanthyl
2	$\mathrm{p}K_{\mathrm{R^+}}$ vs σ	$-1{\cdot}25$	0·940	5	Xanthyl
3	$\mathrm{p}K_{\mathrm{R^+}}$ vs σ^+	$-1{\cdot}57$	0·951	6	Xanthyl
4	$\mathrm{p}K_{\mathrm{R^+}}$ vs $\sigma\varkappa$	$-1{\cdot}61$	0·909	5	Xanthyl (see text)
5	$\Delta G_{\mathrm{red}}(\mathrm{R^+})/1{\cdot}37$ vs σ	$-1{\cdot}86$	0·938	6	Xanthyl
6	$\Delta H_{\mathrm{H^-}}(\mathrm{R^+})/1{\cdot}37$ vs σ^+	$-2{\cdot}70$	0·94	5	Xanthyl
7	$\mathrm{p}K_{\mathrm{R^+}}$ vs σ^+	$-3{\cdot}15$	0·999	11	Trityl
8	$\Delta G_{\mathrm{red}}(\mathrm{R^+})/1{\cdot}37$ vs σ^+	$-3{\cdot}25$	0·986	11	Trityl
9	$\Delta H_{\mathrm{H^-}}(\mathrm{R^+})/1{\cdot}364$ vs σ^+	$-3{\cdot}45$	0·995	11	Trityl
10	$\Delta G_{\mathrm{red}}(\mathrm{R^+})/1{\cdot}37$ vs σ	$-3{\cdot}50$	0·954	6	Xanthyl
11	$\Delta G_{\mathrm{red}}(\mathrm{R^+})$ vs σ°	$-3{\cdot}61$	0·954	5	Xanthyl (see text)
12	$\Delta H_{\mathrm{H^-}}(\mathrm{R^+})/1{\cdot}364$ vs σ	$-4{\cdot}43$	0·972	5	Xanthyl
13	Log k_{solv} of cumyl chlorides vs σ^+	$-4{\cdot}62$	0·980	8	Ref. 46
14	$\Delta G_{\mathrm{red}}(\mathrm{R^+})$ for DMP cations (kcal/1·37) vs σ^+	$-6{\cdot}45$	0·960	6	Ref. 48
15	$\Delta G_{\mathrm{red}}(\mathrm{R^+})$ for cumyl cations (kcal/1·37) vs σ^+	$-6{\cdot}56$	0·973	5	Ref. 48
16	$\Delta H_{\mathrm{f}}/1{\cdot}37$ of cumyl alcohols vs σ^+	$-7{\cdot}19$	0·944	8	Data from Ref. 47
17	$\Delta G_{\mathrm{red}}(\mathrm{R^+})$ for benzyl cations (kcal/1·37) vs σ^+	$-9{\cdot}3$	0·99	9	Ref. 48

[a] ΔHs and ΔGs are divided by 1·37 to make slopes unitless when plotted against substituent constants.

by 2·303*RT* to normalize them to the same scale.

Table 4 is arranged in terms of increasingly negative slope, i.e. increasing transfer of electron demand to the *para* position of the various phenyl groups. The majority of the correlations are good, with $r_s > 0{\cdot}95$ for 22 out of 36 correlations. In several cases involving xanthylium ions, correlation with σ is actually better than with σ^+ but the overall trends in Table 4 are in the direction to support strongly the notion that the magnitude of the reaction parameter is a sensitive reflection of electron demand to the *para* position and that the fewer rings share the demand, the steeper is the slope.

Use of substituent constants for trityl and xanthyl cations

The limitations of the σ^+ parameter were already well documented[52] 15 years after its successful introduction and its poor performance with reactions of 9-arylxanthylium ions has been noted more recently by several authors.[38, 53]

Freedman and co-workers[41] attempted to use σ^+ to correlate their free energies for methoxy exchange between xanthyl cations and found, as we do (Table 4, entry 11) versus (4-1 or 5), that the Taft σ° parameter[54] for systems with unconjugated charge relay gave an excellent correlation ($r^2 = 0{\cdot}995$). From this they inferred that overlap of the 9-aryl system with the adjacent xanthylium cationic center was precluded by steric hindrance between the 1 and 8 hydrogens and the *ortho*-hydrogens of the 9-phenyl ring, which restrained the two rings to a nearly perpendicular position. McClelland and co-workers[38, 53b] arrived at the same conclusion independently and found that the log *k*s for reaction of a series of xanthylium ions with various nucleophiles correlated well with σ.

An imporant factor behind the relatively poor correlations of the various data for xanthyium ions is a consequence of the feeble transmission of electron demand to their *para* positions. As a result, the range of values for all of their measured properties, as shown in Table 2, is considerably smaller relative to their experimental errors than for the trityl cations. Thus, delocalization of electron demand to the oxygen at the 4-position reduces demand at the 9-position, which in turn is relayed only weakly to the *para* position of the attached benzene ring and results in a compressed scale of observed values.

Carbanions and radicals

Table 5 presents several sets of properties for well authenticated *p*-substituted trityl and 9-phenylxanthyl carbanions in K$^+$ DMSYL$^-$–DMSO at 25 °C and Table 6 compares correlations of these data with each other and with other properties in this paper. It should also be noted that the oxidation potentials listed here for the carbanions and in Table 2 for the cations generally agree well with those of other workers[4, 19, 23, 25, 31, 42, 49, 50] for the same ions when allowance is made for differences in reference electrodes or solvent. However, we draw attention to the suspiciously discrepent value for $\Delta G_{ox}(\mathrm{R}^\bullet)$ of the 4-F-trityl anion/radical in Table 5 which is echoed to some extent by the anomolous

Table 5. Stability dta for *p*-substituted triphenylmethyl and 9-phenylxanthanyl anions (ΔH, ΔG, *BDE* in kcal mol^{-1})

Series	Substituent	ΔH_{dep}[a]	pK_{HA}[b]	$\Delta G_{ox}(\mathrm{R}^-)$ [$E_{ox}(\mathrm{R}^-)$][c]	*BDE*[e]	*BDE*$^-$[f]	*BDE*$^+$[g]
Trityl	4,4′,4″-OMe	− 3·38 ± 0·45	—	− 25·55 (1108 ± 10)	—	78·14	76·35
Trityl	4,4″-OMe	− 5·01 ± 0·34	—	− 22·81 (989 ± 12)	—	79·25	74·97
Trityl	4,4′,4″-Me	− 6·20 ± 0·37	—	− 21·91 (950 ± 14)	—	78·96	77·8
Trityl	4-OMe	− 6·93 ± 0·35	32·80	− 20·11 (872 ± 10)	80·63	80·70	77·0
Trityl	4,4′Me	− 7·15 ± 0·42	—	− 19·65 (852 ± 20)	—	80·27	79·0
Trityl	4-Me	− 7·50 ± 0·46	—	− 18·91 (820 ± 11)	—	80·66	78·64
Trityl	None	− 9·00 ± 0·25	30·60	− 19·14 (830 ± 14)	78·60	78·96	80·2
Trityl	4-F	− 9·20 ± 0·19	30·80	− 18·17 (814 ± 17)	79·24	79·13	77·2
Trityl	4,4′,4″-tBu	− 9·50 ± 0·21	—	− 23·22 (1007 ± 9)	—	74·35	77·8
Xanthene	None	− 10·30 ± 0·27	30·00	− 21·63 (938 ± 19)	75·29	75·17	77·0
Xanthene	9-(*p*-Me)Ph	− 11·63 ± 0·35	28·50	− 19·81 (859 ± 15)	75·07	75·66	75·6
Xanthene	9-(*p*-OMe)Ph	− 12·45 ± 0·38	28·40	− 20·39 (884 ± 8)	74·35	74·26	75·6
Trityl	4,4′,4″-Cl	− 12·50 ± 0·20	27·00	—	—	—	77·1
Xanthene	9-(*p*-F)Ph	− 12·81 ± 0·36	27·86	− 17·50 (759 ± 9)	76·50	76·79	77·0
Xanthene	9-Ph	− 13·29 ± 0·39	27·90	− 19·26 (835 ± 14)	74·80	74·55	73·5
Thioxanthene	9-Ph	− 13·90 ± 0·41	27·36	− 16·67 (723 ± 11)	76·65	76·53	76·6
Xanthene	9-(*p*-Cl)Ph	− 15·41 ± 0·38	26·73	− 17·76 (770 ± 12)	74·70	73·93	77·2
Xanthene	9-(*p*-CF3)Ph	—	—	− 15·31 (664 ± 15)	—	—	78·33

[a] Measured in DMSO; values are relative to 0·1 M K$^+$ DMSYL$-$ at 25 °C.
[b] Ref. 18.
[c] Relative to NHE measured in 0·1 M DMSO in TBATFB at 25 °C.
[d] Relative to NHE, measured in 0·1 M sulfolane in TBATFB at 25 C̊.
[e] $BDE = 1{\cdot}364\ \mathrm{p}K_{HA} + \Delta G_{ox}(\mathrm{R}^-) + 56.$[31c, df] $\mathrm{BDE}^- = \Delta H_{dep} + \Delta G_{ox}(\mathrm{R}^-) + 107{\cdot}1.$
[g] $BDE^+ = \Delta H_{H^-} + \Delta G_{red}(\mathrm{R}^+) + 40{\cdot}0.$

Table 6. Correlations of pK_{HA} vs other carbanion properties of *p*-substituted triphenylmethyl and 9-phenylxanthyl carbanions[a]

Entry No. (6-)	Correlation	Slope	*r*	*n*	System
1	pK_{HA} vs ΔH_{dep}	0·93	0·963	12	Triphenylmethyl and 9-Ph-xanthyl
2	pK_{HA} vs ΔH_{dep}	0·70	0·997	5	Triphenylmethyl
3	pK_{HA} vs ΔH_{dep}	1·12	0·970	7	Xanthyl
4	pK_{HA} vs $\Delta G_{ox}(R^-)$	0·956	0·965	4	Triphenylmethyl
5	pK_{HA} vs $\Delta G_{ox}(R^-)$	1·08	0·866	7	Xanthyl
6	pK_{HA} vs $\Delta G_{ox}(R^-)$	1·02	0·983	18	Triphenylmethyl[42]
7	pK_{HA} vs $\Delta G_{ox}(R^-)$	0·67	0·981	8	Xanthyl[42]
8	pK_{HA} vs $\Delta G_{red}(R^{\bullet})$	0·75	0·857	6	Triphenylmethyl and 9-Ph-xanthyl
9	pK_{HA} vs $\Delta G_{red}(R^{\bullet})$	0·91	0·996	5	Triphenylmethyl
10	pK_{HA} vs pK_{R^+}	1·42	0·966	5	Triphenylmethyl
11	ΔG_{red}(R$^{\bullet}$ vs $\Delta G_{ox}(R^-)$	1·03	0·960	16	Triphenylmethyl and 9-Ph-xanthyl

[a] All ΔH and ΔG values divided by 1·364 to make slopes unitless.

$\Delta G_{red}(R^+)$, which should correspond to the same redox process except for a slight difference in solvent and, of course, the different original source of the radical. Other measured and derived properties for the 4-F-trityl cation and anion seem to fit reasonably and solutions of the cation were well behaved. However, the solutions of this carbanion were less stable than the others and the PMR spectrum was less clean despite extra care to repeat measurements for this system.

The most reliable property for comparing the data in Tables 5 and 6 is pK_{HA}, since it is based on a very large and well tested database.[18] Also, it is derived from equilibrium constants which are inherently easier to measure precisely than are heats of reaction. Excellent correlations of ΔH_{dep} vs pK_{HA} have been reported before from this laboratory[44] and are found again in Table 6 (6-1, 2, 3) for the data in Table 5. As before, the slopes are close to unity for correlating free energies of deprotonation vs the corresponding enthalpy terms (ΔG_{dep} vs ΔH_{dep} is equivalent to pK_{HA} vs $\Delta H_{dep}/1{\cdot}37$) and the correlation coefficients are very good to excellent.

Good linear relationships between pK_{HA}s and oxidation potentials of the resulting anions have been noted frequently.[50] Correlations (6-4, 5) for the data in Tables 5 and 6 contrast sharply the trityl vs xanthyl series. Bordwell and co-workers reported a slope of 0·974 and $r=0{\cdot}994$ for 11 3- and 4-substituted trityl anions under conditions similar to those used here.

Wayner and co-workers[48] demonstrated the reversibility of electrode potentials in highly unstable benzyl and benzhydryl systems (see Table 4), by showing the equality of the reduction potential of the cation to the oxidation potential of the radical. An equivalent strategy provides a test of our assumed interconvertability of sulfolane as a medium for R^+ measurements and DMSO as a medium for study of their conjugate R^-. A small difference in solvation energies[3] for transferring the ions from DMSO to sulfolane prevents equality of electrode potentials in the two media. However, if the $\Delta G_{red}(R^{\bullet})$s for reduction of the series of $R^{\bullet}$s derived from their R^+s to their conjugate R^-s in sulfolane are really equivalent to the corresponding $\Delta G_{ox}(R^-)$s for oxidation of the same R^-s to their conjugate $R^{\bullet}$s in DMSO, then there should be good correlations between these redox free energies in the different solvents. Correlation (6-11) for 16 trityl and 9-arylxanthyl provides some strong support for this important assumption of the present study.

An alternative, but related, test is to calculate homolytic BDEs from the pK_{HA}s and $\Delta G_{ox}(R^-)$ values for carbanions in Table 4 using Bordwell's well established equation in DMSO (note, however, Ref. 32 concerning limitations due to solvent effects):

$$BDE = 1{\cdot}364\text{p}K_{HA} + \Delta G_{ox}(R^-) + 56 \qquad (23)$$

and from the heat of hydride transfer from cyanoborohydride ion to the conjugate R^+ of R^- and the first reduction potential of the cation in sulfolane by an analogous equation:

$$BDE^+ = \Delta H_{H^-} + \Delta G_{red}(R^+) + 40 \qquad (24)$$

Our value for the *BDE* of triphenylmethane agrees well with that determined by Bordwell's group,[42] who also have demonstrated[31a] that their method of combining pK_{HA}s with oxidation potentials gives reliable *BDE*s directly relatable to the gas-phase values.

The constant in equation (24) is the average of the differences between each of the 10 values in Table 5 listed under *BDE*, which were calculated by equation (23), and $\Delta H_{H^-} + \Delta G_{red}(R^+)$ from Table 2. Equation (24) was then applied to the other seven systems in Table 5 for which there were insufficient data to calculate a *BDE* using equation (23).

A similar approach was used to calculate the column in Table 5 labeled *BDE*$^-$ from data in DMSO according to equation (25) from the average difference between $\Delta H_{deps} + \Delta G_1(R^-)$ and the corresponding value for *BDE* for the same 10 compounds used to calculate the constant in equation (24) for the 'carbocation route' in sulfolane.

Table 7. Correlation of carbanion stability properties with various substituent constants[a]

Property	Substituent constant	Slope	*r*	*n*	System
$\mathrm{p}K_{\mathrm{HA}}$	σ^-	− 6·78	0·996	5	Trityl
$\Delta G_{\mathrm{ox}}(\mathrm{R}^-)/1{\cdot}37$	σ^-	− 6·17	0·942	8	Trityl
$\Delta G_{\mathrm{ox}}(\mathrm{R}^\bullet)/1{\cdot}37$	σ^-	− 6·16	0·986	7	Trityl
$\Delta H_{\mathrm{dep}}/1{\cdot}37$	σ^-	− 4·86	0·983	9	Trityl
$\Delta H_{\mathrm{dep}}/1{\cdot}37$	σ^-	− 5·37	0·890	5	Xanthyl
$\Delta G_{\mathrm{ox}}(\mathrm{R}^-)/1{\cdot}37$	σ^-	− 3·91	0·931	5	Xanthyl
$\mathrm{p}K_{\mathrm{HA}}$	σ^-	− 3·86	0·932	5	Xanthyl
$\Delta G_{\mathrm{red}}(\mathrm{R}^\bullet)$	σ^-	− 3·11	0·943	5	Xanthyl

[a] Ref. 42.

$$BDE^- = H_{\mathrm{dep}} + \Delta G_{\mathrm{ox}}(\mathrm{R}^-) + 107.1 \qquad (25)$$

Although this is not a severe test of the data because of the method of deriving both BDE^+ and BDE^- from *BDE*, the fact that the average difference between the 16 values of BDE^+ and BDE^- is only 0·22 suggests again that there are no large systematic differences between the use of enthalpy data in the two solvents and the better established free energy data in DMSO. Also, the agreement between the *BDE* values derived by the ‘cation route’ and the ‘carbanion route’ is further support for consistency and the near reversibility of the redox potentials.

Table 7 compares the power of the three types of the σ-parameter to correlate the acidic properties, $\mathrm{p}K_{\mathrm{HA}}$ and ΔH_{dep}, and the closely related redox properties for a number of substituted triphenylmethyl and 9-phenylxanthyl systems. Except for the ΔH_{dep} of the xanthyl systems, correlations of all properties can be rated from ‘excellent’ to ‘fair’ with all three types of substituent parameters with no general pattern of superiority for any one.

Correlations of energies for forming carbocations vs forming carbanions

The data available in Tables 2 and 5 provide a means for testing the reasonable notion that the effects of substitution on carbocation stability are generally in the opposite direction from those on comparable carbanions. Correlation (8-1), made by plotting $\Delta G_{\mathrm{red}}(\mathrm{R}^+)$ vs $\Delta G_{\mathrm{red}}(\mathrm{R}^\bullet)$ in the same solution under identical conditions for 16 carbocations, shows a good correlation of these apparently unrelated properties. Correlation (8-2) tests the same point.

Correlation (8-3) of bond-breaking properties $\mathrm{p}K_{\mathrm{HA}}$ vs $\mathrm{p}K_{\mathrm{R}^+}$ for five trityl cations in aqueous acid vs their conjugate anions in DMSO shows a surprisingly good correlation and correspondingly ΔH_{dep} vs ΔH_{H^-} makes the point but less forcefully. Comparison of σ^+ with σ^- (8-5) gives almost unit slope and a fair correlation coefficient.

Finally, we draw attention again to Table 2 listing ΔG_{ET}, which is the difference $[\Delta G_{\mathrm{red}}(\mathrm{R}^+) - \Delta G_{\mathrm{red}}(\mathrm{R}^\bullet)]$. If the effects of substituents on stabilizing the R^- and R^+ from a given $\mathrm{R}^\bullet$ are nearly equal and opposite, one might expect ΔG_{ET} for a given series of related radicals to remain nearly constant. In other words, the substituents should have little effect on the absolute hardness, η,[27–29] of the radicals. This is well supported by the ΔG_{ET} values in Table 2 for xanthyl and trityl radicals, all of which except 4,4′,4″-NMe_2 are distributed around an average of 30·7 kcal mol^{-1}. Since the dimethylamino group is especially effective in stabilizing the cation through resonance, it is not surprising to find it as a strong exception to the rest of the series.

CONCLUSIONS

Substituted trityl and xanthyl cations, radicals and carbanions are historically important because of their ready accessibility and stability. They provide an unusual opportunity to study a wide variety of properties for all three of these trivalent states of carbon both by bond-making and -breaking reactions and by electrochemistry and relate them

Table 8. Correlation of selected cation stability data vs anion stability data

Entry No. (8-)	Correlation	Slope	*r*	*n*	System
1	$\Delta G_{\mathrm{red}}(\mathrm{R}^+)$ vs $\Delta G_{\mathrm{red}}(\mathrm{R}^\bullet)$	0·97	0·960	16	Trityl and xanthyl
2	$\Delta G_{\mathrm{ox}}(\mathrm{R}^-)$ v s $\Delta G_{\mathrm{red}}(\mathrm{R}^+)$	1·083	0·911	9	Trityl
3	$\mathrm{p}K_{\mathrm{HA}}$ vs $\mathrm{p}K_{\mathrm{R}^+}$	1·42	0·966	5	Trityl
4	ΔH_{dep} vs ΔH_{H^-}	− 1·30	0·842	10	Trityl
5	σ^+ vs σ^-	0·99	0·930	8	

to each other quantitatively under similar conditions. Although their unusual stabilities set them apart structurally from other less stable and mechanistically more important, $R^{+/\cdot/-}$ the thermodynamic stability properties for these trityl species generally correlate well with each other and also with Hammett-type substituent parameters based on models that are structurally far removed from them.

Several tests for consistency which combine energies for forming R^+ by bond-breaking reactions with reduction potentials give good agreement with values obtained by the alternative routes from combination of energies for forming R^- with their oxidation potentials.

Studies of this type with amphihydric compounds provide a clear demonstration of the overall interrelation of carbocation, radical and carbanion chemistry, in contrast to their customary treatment as fundamentally separate fields. (Particular care is required in reaction calorimetry to confirm by suitable analysis that the course of the presumed reaction is clean and complete, otherwise the highly exothermic production of a by-product may dominate the reported value. Equilibrium free energies obtained by spectroscopy are less vulnerable to such error.)

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REFERENCES

1. (a) A. G. Harrison, P. Kebarle and F. P. Lossing, *J. Am. Chem. Soc.* **83**, 777–780 (1961); (b) M. T. Bowers, *Gas Phase Ion Chemistry*, Vol. 2. Academic Press, New York (1979); (c) S. G. Lias, J. F. Liebman and R. D. Levin, *J. Phys. Chem. Ref. Data* **13**, 695 (1984); (d) F. P. Lossing and J. L. Holmes, *J. Am. Chem. Soc.* **106**, 6917–6920 (1984); (e) J. C. Schultz, F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.* **106**, 3917–3927 (1984).
2. (a) G. A. Olah and P. von R. Schleyer, *Carbonium Ions* (4 vols). Wiley–Interscience, New York (1970); (b) G. A. Olah, G. K. S. Prakash and J. Sommer, *Superacids.* Wiley, New York (1985); (c) G. A. Olah, *Angew. Chem.* **34**, 1393–1405 (1995).
3. D. T. Stoelting, R. T. Ludwig and E. M. Arnett, *Heteroatom Chem.* **7**, 481 (1996).
4. R. Breslow, *Pure Appl. Chem.* **40**, 493–509 (1974).
5. (a) M. Gomberg, *Ber. Dtsch. Chem. Ges.* **35**, 2397 (1902); (b) P. Walden, *Ber. Dtsch. Chem. Ges.* **35**, 2018–2031 (1902).
6. C. D. Nenitzescu, in *Carbonium Ions*, edited by G. A. Olah and P. v. R. Schleyer, Vol. 1. Interscience, New York (1968).
7. (a) D. Bethell and V. Gold, *Carbonium Ions, an Introduction.* Academic Press, London (1967); (b) for an excellent review of carbocation stabilities, see also H. H. Freedman, in *Carbonium Ions*, edited by G. A. Olah and P. v. R. Schleyer, Vol. 4, Chap. 28. Wiley, New York (1975).
8. M. Gomberg, *J. Am. Chem. Soc.* **22**, 757 (1975).
9. (a) N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *J. Am. Chem. Soc.* **77**, 3044 (1955); (b) N. C. Deno and A. Schriesheim, *J. Am. Chem. Soc.* **77**, 3051 (1955); (c) N. C. Deno and W. L. Evans, *J. Am. Chem. Soc.* **79**, 5804 (1957).
10. E. M. Arnett and R. D. Bushick, *J. Am. Chem. Soc.* **86**, 1564 (1964).
11. C. A. Kraus and R. Rosen, *J. Am. Chem. Soc.* **47**, 2739–2748 (1925).
12. E. S. Wallis and F. H. Adams, *J. Am. Chem. Soc.* **55**, 3838–3851 (1933).
13. C. B. Wooster and N. W. Mitchell, *J. Am. Chem. Soc.* **52**, 688–694 (1930).
14. (a) J. B. Conant and G. W. Wheland, *J. Am. Chem. Soc.* **54**, 1212–1221 (1932); (b) W. K. McEwen, *J. Am. Chem. Soc.* **58**, 1124–1129 (1936).
15. C. R. Noller, *J. Chem. Educ.* **26**, 429–430 (1949).
16. A. A. Morton, *Chem. Rev.* **35**, 1–49 (1944).
17. (a) A. Streitwieser, Jr, E. Juaristi and L. L. Nebenzahl, in *Comprehensive Carbanion Chemistry*, edited by E. Buncel and T. Durst. Elsevier, New York (1980); for other important reviews of carbanion chemistry, see (b) D. J. Cram, in *Organic Chemistry*, edited by A. T. Blomquist, Vol. 4. Academic Press, New York (1965); (c) O. A. Reutov, I. P. Beletskaya and K. P. Butin, in *CH-Acids*, translated by T. R. Crompton. Pergamon Press, Oxford (1978).
18. (a) W. S. Mathews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Druken, Z. Margolin, R. J. McCallum and N. R. Vanier, *J. Am. Chem. Soc.* **97**, 7006 (1975); (b) F. G. Bordwell, *Acc. Chem. Res.* **21**, 456–463 (1988); (c) F. G. Bordwell, printout of pK_{HA} data, personal communication (1992).
19. (a) J. B. Conant and B. F. Chow, *J. Am. Chem. Soc.* **55**, 3752 (1933); (b) E. D. Jenson and R. W. Taft, *J. Am. Chem. Soc.* **86**, 116 (1964).
20. E. M. Arnett, R. A. Flowers, II, A. Meekhof and L. Miller, *J. Am. Chem. Soc.* **115**, 12603 (1993).
21. L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. Cornell University Press, Ithaca, NY (1960).
22. G. W. Wheland, *Resonance in Organic Chemistry.* Wiley, New York (1955).
23. R. Breslow and K. Balasubramanian, *J. Am. Chem. Soc.* **91**, 5182 (1969); (b) R. Breslow and W. Chu, *J. Am. Chem. Soc.* **95**, 411 (1973).
24. (a)E. M. Arnett, K. E. Molter, E. C. Marchot, W. H. Donovan and P. Smith, *J. Am. Chem. Soc.* **109**, 3788 (1987); (b) E. M. Arnett, L. G. Whitesell, Jr, J.-P. Cheng and E. Marchot, *Tetrahedron Lett.* **29**, 1507 (1988); (c) E. M. Arnett, N. G. Harvey, K. Amarnath and J.-P. Cheng, *J. Am. Chem. Soc.* **111**, 4143 (1989); (d) E. M. Arnett, K. Amarnath, N. G. Harvey and J.-P. Cheng, *J. Am. Chem. Soc.* **112**, 344 (1990); (e) E. M. Arnett, K. Amarnath, N. G. Harvey and S. Venimadhavan, *J. Am. Chem. Soc.* **112**, 7346 (1990); (f) E. M. Arnett, K. Amarnath, N. G. Harvey and J.-P. Cheng, *Science* **247**, 423 (1990); (g) N. J. Pienta, R. J. Kessler, K. S. Peters and E. D. O'Driscoll, *J. Am. Chem. Soc.* **113**, 3773 (1991); (h) E. M. Arnett and S. Venimadhavan, *J. Am. Chem. Soc.* **113**, 6967 (1991); (i) S. Venimadhavan, K. Amarnath, N. G. Harvey and E. M. Arnett, *J. Am. Chem. Soc.* **114**, 221 (1992); (j) E. M. Arnett, S. Venimadhavan and K. Amarnath, *J. Am. Chem. Soc.* **114**, 5598 (1992).

25. (a) D. D. M. Wayner and D. J. Griller, *J. Am. Chem. Soc.* **107**, 7764–7765 (1985); (b) D. J. Griller and D. D. M. Wayner, *Rev. Chem. Intermed.* **7**, 31–44 (1986); (c) J. A. Hawari, J. M. Kanabus-Kaminska, D. D. M. Wayner and D. J. Griller, *NATO ASI Series C*, Vol. 189, p. 91. Reidel, Dordrecht (1986); (d) T. J. Burkey, M. Majewski and D. J. Griller, *J. Am. Chem. Soc.* **108**, 2218–2221 (1986); (e) D. D. M. Wayner, D. J. McPhee and D. J. Griller, *J. Am. Chem. Soc.* **110**, 132–137 (1988); (f) D. J. Griller and J. M. Kanabus-Kaminska, *J. Mol. Struct. (Theochem 40)* **163**, 125–131 (1988); (g) D. J. Griller and D. D. M. Wayner, *Pure Appl. Chem.* **61**, 717–724 (1989); (h) D. Griller, J. A. Martinho Simoes, P. Mulder, B. A. Sim and D. D. M. Wayner, *J. Am. Chem. Soc.* **111**, 7872–7876 (1989); (i) D. D. M. Wayner and D. J. Griller, in *From Atoms to Polymers, Molecular Structure and Energetics Series*, Vol. 11, edited by J. F. Liebman and A. Greenberg, pp. 109–128. VCH, New York (1989); (j) D. D. M. Wayner and D. J. Griller, in *Advances in Free Radical Chemistry*, edited by D. D. Tanner, pp. 159–192. JAI Press, Greenwich, CT (1990); (k) P. H. Milne, D. D. M. Wayner, D. P. DeCosta and J. A. Pinock, *Can J. Chem.* **70**, 121–127 (1992).
26. J. I. Brauman, in *Frontiers of Free Radical Chemistry*, edited by W. A. Pryor, pp. 23–30. Academic Press, New York (1980).
27. (a) R. G. Pearson, *J. Org. Chem.* **52**, 2131–2136 (1987); (b) R. G. Pearson, *J. Org. Chem.* **54**, 1423 (1989); (c) R. G. Pearson, *J. Am. Chem. Soc.* **110**, 7684 (1988); (d) R. G. Pearson, *J. Mol. Struct. (Theochem)* **255**, 261–270 (1992); (e) R. G. Pearson, *Acc. Chem. Res.* **26**, 250–255 (1993).
28. (a) R. G. Parr and R. G. Pearson, *J. Am. Chem. Soc.* **105**, 7512 (1983); (b) R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules.* Oxford University Press, New York (1989); (c) P. K. Chattaraj, H. Lee and R. G. Parr, *J. Am. Chem. Soc.* **113**, 1855 (1991); (d) P. K. Chattaraj and R. G. Parr, *Struct. Bonding (Berlin)* **80**, 11–26 (1993); (e) R. G. Parr and Z. Zhou, *Acc. Chem. Res.* **26**, 256 (1993).
29. E. M. Arnett and R. T. Ludwig, *J. Am. Chem. Soc.* **117**, 6627 (1995).
30. D. D. M. Wayner and V. D. Parker, *Acc. Chem. Res.* **26**, 287–294 (1993).
31. (a) F. G. Bordwell, J.-P. Cheng, G.-Z. Ji, A. V. Satish, X. Zhang, *J. Am. Chem. Soc.* **113**, 9790–9795 (1991); (b) F. G. Bordwell, X.-M. Zhang and R. Filler, *J. Org. Chem.* **58**, 6067–6071 (1993); (c) F. G. Bordwell and X.-M. Zhang, *Acc. Chem. Res.* **26**, 510–517 (1993); (d) F. G. Bordwell, A. V. Satish, S. Zhang and X.-M. Zhang, *Pure Appl. Chem.* **67**, 735–740 (1995).
32. D. D. M. Wayner, E. Lusztyk, D. Page, K. U. Ingold, P. Mulder, L. J. J. Laarhoven and H. S. Aldrich, *J. Am. Chem. Soc.* **117**, 8737–8744 (1995).
33. (a) H. Lankamp, W. T. Nauta and C. MacLean, *Tetrahedron Lett.* **2**, 249–254 (1968); (b) H. A. Staab, K. S. Rao and H. Brunner, *Chem. Ber.* **104**, 2634–2636 (1971); (c) W. D. Hounshell, D. A. Dougherty, J. P. Hummel and K. Mislow, *J. Am. Chem. Soc.* **99**, 1916 (1977); (d) J. M. McBride, *Tetrahedron* **30**, 2009–2022 (1974) (this paper reviews the erroneous use of the symmetrical hexaphenylethane structure for trityl dimer until 1968,[33a] even though the *correct* quinoid structure had been demonstrated in 1904); (e) B. Kahr, D. Van Engen and K. Mislow, *J. Am. Chem. Soc.* **108**, 8305–8307 (1986).
34. E. M. Arnett, E. J. Mitchell and T. S. S. R. Murty, *J. Am. Chem. Soc.* **96**, 3875 (1974).
35. V. Gutmann, *Coordination Chemistry in Non-Aqueous Solutions*, p. 15. Springer, New York (1968).
36. P.-C. Maria and J.-F. Gal, *J. Phys. Chem.* **89**, 1296–1304 (1985).
37. A. K. Covington and T. Dickinson (Eds), *Physical Chemistry of Organic Solvent Systems*, p. 5. Plenum Press, London (1973).
38. R. A. McClelland, N. Banait and S. Steenken, *J. Am. Chem. Soc.* **111**, 2929–2935 (1989).
39. R. L. Shriner and C. N. Wolf, *J. Am. Chem. Soc.* **73**, 891 (1953).
40. H. J. Dauben Jr, L. R. Honnen and K. N. Harmon, *J. Org. Chem.* **25**, 1442 (1960).
41. S. V. McKinley, J. W. Rakshys Jr, A. E. Young and H. H. Freedman, *J. Am. Chem. Soc.* **93**, 4715–4724 (1971).
42. F. G. Bordwell, J.-P. Cheng, A. V. Satish and C. L. Twyman, *J. Org. Chem.* **57**, 6542–6546 (1992).
43. (a) E. M. Arnett, R. A. Flowers II, A. E. Meekof, A. Pourjavadi and S. A. Walek, *J. Phys. Org. Chem.* **7**, 663–671 (1994); (b) E. M. Arnett, R. A. Flowers II, R. T. Ludwig, A. E. Meekoff and S. A. Walek, *Pure Appl. Chem.* **67**, 729–734 (1995).
44. (a) E. M. Arnett, T. C. Moriarity, L. E. Small, J. P. Rudolph and R. P. Quirk, *J. Am. Chem. Soc.* **95**, 1492 (1973); (b) E. M. Arnett, D. E. Johnston and L. E. Small, *J. Am. Chem. Soc.* **97**, 5598 (1975); (c) E. M. Arnett and K. G. Venkatasubramaniam, *J. Org. Chem.* **48**, 1569 (1983); (d) E. M. Arnett and K. D. Moe, *J. Am. Chem. Soc.* **113**, 7068 (1991).
45. J. Osteryoung, *Acc. Chem. Res.* **26**, 77 (1993).
46. (a) Y. Okamoto and H. C. Brown, *J. Org. Chem.* **22**, 485–494 (1957); (b) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.* **79**, 1913–1917 (1957); (c) H. C. Brown, D. P. Kelly and M. Periasamy, *Proc. Natl. Acad. Sci. USA* **77**, 6956–6960 (1980).
47. E. M. Arnett and T. C. Hofelich, *J. Am. Chem. Soc.* **105**, 2889 (1983).
48. B. A. Sim, P. H. Milne, D. J. Griller and D. D. M. Wayner, *J. Am. Chem. Soc.* **112**, 6635–6638 (1990).
49. (a) V. D. Parker, *Acta Chem. Scand.* **46**, 1133–1134 (1992); (b) J.-P. Cheng, K. L. Handoo and V. D. Parker, *J. Am. Chem. Soc.* **115**, 2655–2660 (1993); (c) J.-P. Cheng, K. L. Handoo, J. Xue and V. D. Parker, *J. Org. Chem.* **58**, 5050–5054 (1993); (d) K. L. Handoo, J.-P. Cheng and V. D. Parker, *J. Am. Chem. Soc.* **115**, 5067–5072 (1993).
50. (a) See, for example, R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen and T. Chivers, *J. Am. Chem. Soc.* **88**, 460 (1996); (b) M. R. Feldman and W. C. Flythe, *J. Org. Chem.* **43**, 596 (1978); (c) Y. Okamoto, *J. Org. Chem.* **39**, 4011 (1983); (d) D. D. M. Wayner, *J. Am. Chem. Soc.* **112**, 6635 (1990); (e) E. M. Arnett and J. A. Harrelson, *Gazz. Chim. Ital.* **117**, 237 (1987); (f) V. D. Parker, *J. Org. Chem.* **58**, 5811–5815 (1993).
51. E. B. Troughton, K. E. Molter and E. M. Arnett, *J. Am. Chem. Soc.* **106**, 6726 (1984).
52. N. B. Chapman and J. Shorter (Eds), *Advances in Linear Free Energy Relationships*, p. 33. Plenum Press, London (1973).
53. (a) P. Wan, K. Yates and M. K. Boyd, *J. Org. Chem.* **50**, 2881–2886 (1985); (b) R. A. McClelland, V. M. Kanagasabapathy, N. S. Banait and S. Steenken, *J. Am. Chem. Soc.* **111**, 3966 (1989); (c) M. R. Valentino and M. K. Boyd, *J. Org. Chem.* **58**, 5826–5831 (1993); (d) R. Karaman, J.-T. L. Huang and J. L. Fry, *J. Org. Chem.* **56**, 188–195 (1991).
54. R. W. Taft Jr, *J. Phys. Chem.* **64**, 1805–1815 (1960).
55. X.-M. Zhang and F. G. Bordwell, *J. Am. Chem. Soc.* **114**, 9787–9792 (1992).

APPENDIX

Characterization data

Triphenylmethanes

Triphenylmethane, ^{1}H NMR 8·60 (2H, t, J=5·7 Hz), 8·44 (2H, d, J=7·2 Hz), 8·17 (2H, d, J=7·2 Hz), 7·99 (2H, t, J=5·7 Hz), 7·84 (3H, m), 7·72 (2H, d, J=7·2 Hz); ^{13}C NMR 174·6, 157·9, 143·9, 131·5, 130·7, 129·7, 129·0, 128·6, 123·3, 119·3, 118·7; 9-(*p*-methoxyphenyl), ^{1}H NMR 8·54 (2H, t, J=6·6 Hz), 8·36 (2H, d, J=6·9 Hz), 8·26 (2H, d, J=6·9 Hz), 7·96 (2H, t, J=6·6 Hz), 7·72 (2H, d, J=7·2 Hz), 7·39 (2H, d, J=7·2 Hz) 4·56 (3H, s); ^{13}C NMR 175·6, 164·8, 159·1, 144·8, 134·9, 132·8, 129·7, 124·2, 120·2, 118·6, 115·9, 56·7; 9-(*p*-methylphenyl), ^{1}H NMR 8·44 (2H, t, J=6·9 Hz), 8·22 (2H, d, J=7·2 hz), 8·15 (2H, d, J=7·2 Hz), 7·81 (2H, t, J=6·9 Hz), 7·52 (2H, d, J=7·2 Hz), 7·41 (2H, d, J=7·2 Hz), 2·34 (3H, s); ^{13}C NMR 172·3, 165·1, 158·1, 145·2, 133·9, 131·7, 129·2, 126·8, 121·3, 117·9, 115·8, 22·4; 9-(*p*-trifluoromethylphenyl), ^{1}H NMR 8·67 (2H, t, J=8·4 Hz), 8·50 (2H, d, J=8·7 Hz), 8·14 (4H, m), 8·03 (2H, d, J=8·4 Hz), 7·90 (2H, d, J=8·7 Hz); ^{13}C NMR 174·2, 159·7, 145·9, 132·7, 132·1, 130·3, 127·3, 126·7, 125·0, 120·5; 9-(*p*-chlorophenyl), ^{1}H NMR 8·62 (2H, t, J=5·7 Hz), 8·45 (2H, d, J=8·7 Hz), 8·17 (2H, t, J=6·0 Hz), 8·00 (2H, t, J=6·8 Hz), 7·87 (2H, d, J=8·7 Hz), 7·72 (2H, d, J=8·7 Hz); ^{13}C NMR 174·7, 159·6, 145·5, 139·1, 132·8, 132·6, 131·3, 130·5, 124·9, 120·9, 120·4; 9-(*p*-fluorophenyl), ^{1}H NMR 8·61 (2H, t, J=7·2 Hz), 8·44 (2H, d, J=8·7 Hz), 8·19 (2H, t, J=8·7 Hz), 8·00 (2H, t, J=7·2 Hz), 7·77 (2H, d, J=8·1 Hz), 7·63 (2H, d, J=8·1 Hz); ^{13}C NMR 175·1, 159·5, 146·5, 144·3, 135·4, 133·2, 131·4, 129·2, 121·8, 119·4, 116·2; 9-phenylthioixanthene, ^{1}H NMR 8·81 (2H, d, J=6·3 Hz), 8·37 (2H, t, J=6·6 Hz), 8·23 (2H, d, J=6·3 Hz), 8·02 (2H, t, J=6·9 Hz), 7·81 (2H, t, J=6·6 Hz), 7·55 (2H, d, J=6·9 Hz); ^{13}C NMR 172·4, 149·3, 138·3, 136·8, 136·1, 132·4, 131·8, 131·4, 129·53, 128·7, 128·6.

9-Arylxanthenes

9-Phenyl, ^{1}H NMR 7·23 (2H, d, J=7·2 Hz), 7·16–7·06 (11H, m), 5·40 (1H, s); ^{13}C NMR 152·7, 145·5, 137·2, 132·9, 131·9, 128·9, 128·5, 127·3, 124·9, 119·0, 117·2, 43·9; 9-(methoxyphenyl), ^{1}H NMR 7·16 (2H, d, j=7·2 Hz), 7·08–6·98 (8H, m), 6·72 (2H, d, J=7·2 Hz), 5·19 (1H, s), 3·65 (2H, s); ^{13}C NMR 151·79, 139·9, 130·6, 129·8, 129·7, 128·8, 125·9, 124·4, 124·3, 117·2, 115 ·0, 55·6, 43·9; 9-(*p*-methylphenyl), ^{1}H NMR 7·72 (2H, d, J=6·9 Hz), 7·12 (4H, m), 7·04 (6H, m), 5·32 (1H, s), 2·24 (2H, s); ^{13}C NMR 152·3, 145·1, 137·4, 132·7, 132·1, 129·1, 128·9, 127·5, 124·3, 118·5, 116·9, 43·7, 22·5; 9-(*p*-chlorophenyl), ^{1}H NMR 7·30 (2H, d, J=7·1 Hz), 7·22–7·15 (4H, m), 7·11–6·99 (6H, m), 5·39 (1H, s); ^{13}C NMR 151·7, 146·8, 132·8, 130·5, 130·4, 129·9, 129·2, 129·0, 125·1, 125·6, 117·4, 43·9; 9-(*p*-fluorophenyl), ^{1}H NMR 7·22 (2H, d, J=7·1 Hz), 7·10–7·05 (4H, m), 6·99–6·889 (6H, m), 5·42 (1H, s); ^{13}C NMR 151·7, 146·8, 132·8, 130·5, 130·4, 129·9, 129·2, 129·0, 125·1, 124·6, 117·4, 43·9; 9-phenylthioxanthene, ^{1}H NMR 7·55 (2H, d, J=7·8 Hz), 7·35 (2H, d, J=7·8 Hz), 7·25 (2H, d, J=7·8 Hz), 7·18 (3H, m), 7·09 (2H, d, J=8·4 Hz), 7·01 (2H, d, J=8·4 Hz); ^{13}C NMR 142·7, 138·1, 133·4, 130·8, 130·6, 129·1, 128·9, 128·5, 128·3, 128·1, 128·0, 53·1.

Triaryl cations

4,4′,4″-(Methoxy)triphenylmethylium tetrafluoborate, ^{1}H NMR 7·55 (6H, d, J=6·9 Hz), 7·32 (6H, d, J=6·9 Hz), 4·07 (9H, s); ^{13}C NMR 194·11. 171·23, 144·14, 133·14, 118·40, 57·74; 4,4′-(dimethoxy)triphenylmethylium tetrafluoborate, ^{1}H NMR 8·08 (1H, t, J=6·9 Hz), 7·52 (4H, d, J=6·6 Hz), 7·78 (2H, t, J=6·3 Hz), 7·67 (2H, d, j=6·3 Hz), 7·44 (4H, d, J=6·9 Hz), 4·00 (6H, s); ^{13}C NMR 201·0, 177·19, 149·20, 148·77, 140·39, 134·61, 130·53, 130·18, 119·31, 59·29; 4-(methoxy)triphenylmethylium tetrafluoborate, ^{1}H NMR 8·07 (2H, t, J=6·0 Hz), 7·87 (2H, d, J=6·0 Hz), 7·78 (4H, t, J=5·7 Hz), 7·51 (4H, d, J=6·0 Hz), 7·47 (2H, d, J=6·0 Hz), 4·11 (3H, s); ^{13}C NMR 202·02, 177·64, 149·22, 148·72, 140·37, 134·59, 130·58, 130·15, 119·14, 59·24; 4,4′,4″-(methyl)triphenylmethylium tetrafluoborate, ^{1}H NMR 7·10 (6H, d, J=7·5 Hz), 7·01 (6H, d, J=7·5 Hz), 2·25 (9H, s); ^{13}C NMR 196·37, 173·54, 147·38, 133·83, 118·12, 23·44; 4,4′-(methyl)triphenylmethylium tetrafluoborate, ^{1}H NMR 7·93 (1H, t, J=6·9 Hz), 7·64 (2H, t, J=7·5 hz), 7·45 (2H, d, J=6·0 Hz), 7·41 (4H, d, j=6·3 Hz), 7·24 (4H, d, J=6·3 Hz), 2·72 (3H, s); ^{13}C NMR 203·1, 179·91, 151·45, 149·99, 143·01, 135·22, 131·51, 130·83, 118·95, 23·53; 4-(methyl)triphenylmethylium tetrafluoborate, ^{1}H NMR 8·23 (2H, t, J=6·6 Hz), 7·86 (4H, t, J=7·2 Hz), 7·74 (2H, d, J=6·0 Hz), 7·68 (4H, d, J=6·6 Hz), 7·24 (2H, d, J=6·60 Hz), 2·72 (3H, s); ^{13}C NMR 203·3, 180·01, 151·57, 150·21, 143·40, 135·39, 131·54, 130·89, 119·03, 23·54; 4-(fluoro)triphenylmethylium tetrafluoborate, ^{1}H NMR 8·29 (2H, t, J=7·5 Hz), 7·92–7·79 (6H, m); ^{13}C NMR 210·31, 175·38, 172·11, 144·21, 141·03, 132·79, 131·33, 130·92, 119·85; 4,4′,4″-(*tert*-butyl)triphenylmethylium tetrafluororate, ^{1}H NMR 7·94 (6H, d, J=8·7 Hz), 7·60 (6H, d, j=8·7 Hz), 1·47 (27H, s); ^{13}C NMR 206·03, 169·07, 142·68, 138·55, 129·56, 37·32, 30·76; 4,4′,4″-(dimethylamino)triphenylmethylium tetrafluoroborate ^{1}H NMR 7·32 (6H, d, J=9·0 Hz), 6·96 (6H, d, J=9·0 Hz), 3·29 (18H, s); ^{13}C NMR 179·57, 156·49, 140·32, 127·07, 112·96, 40·69.