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Nuclear Magnetic Resonance Method for Determination of Aryl Carbonium Ion Stabilities ($\Delta F°_{R^+}$). Factors Which Influence Stabilities

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Abstract: A method for the quantitative determination of relative carbonium ion stabilities has been developed in which nmr is used to observe directly the equilibration between two carbonium ions and their covalent precursors (eq 4). The stabilities ($\Delta F°_{R^+}$) of meta- and para-substituted trityl, meta- and para-substituted 9-arylxanthyl, and triphenylcyclopropenium cations spanning an energy range of ~24 kcal/mol are given in Tables I and II. These data are compared with values obtained *via* two other techniques, pK_{R^+} and emf. In general, good agreement is found for the meta- and para-substituted trityls (Table I), but slightly lower values observed for the pK_{R^+} as compared to the nmr and emf methods are attributed to solvent effects. Leaving group effects on cation stability were studied. Systematic differences observed for the 9-arylxanthyl derivatives (Table II) when the leaving group is varied (–OH, –OCH$_3$, 9-arylxanthyl) are attributed to differing nonbonded steric interactions in the covalent precursors. The magnitudes of these interactions were determined by direct nmr observation of exchange between the covalent components (eq 5). Steric requirements at the cation sites were found to be in the order trityl > 9-arylxanthyl > triphenylcyclopropenyl. A general steric enhancement of stabilization energies is observed for ortho substituents (Tables V and VI) as compared to their meta- or para-substituted analogs. Because of severe conformational restraints in the 9-arylxanthyl series, electronic contributions to $\Delta F°_{R^+}$ (meta and para substituted) are minimized while steric contributions (ortho substituted) are maximized.

Since their discovery and characterization in the early part of this century,[1] the triarylmethyl cations and their analogs have served as a continuing reservoir of information concerning the role of carbonium ion intermediates in organic chemistry. The remarkable stability of these charge-delocalized ions is revealed both in their ready isolation as crystalline salts and their reversible formation from covalent precursors under suitable conditions of leaving group and solvent.[2]

The ability to generate an observable concentration of carbonium ion (R^+) in equilibrium with its progenitor (R–X) makes it possible to determine $\Delta F°$ for eq 1.

$$R\text{–}X \rightleftharpoons R^+X^- \text{ (or } R^+ + X^-) \qquad (1)$$

Quantitative evaluation of $\Delta F°_{(1)}$ under constant conditions of solvent and leaving group (X) allows the categorization of those structural features in R which favor ionization by stabilizing the resulting carbonium ion, R^+, and provides a valuable basis for the interpretation of structure–reactivity relationships involving cationic intermediates.

A variety of methods have proved useful in obtaining these stabilization energies. For those polyarylmethyl halides which are sufficiently ionized (or dissociated) in a suitable solvating medium, $\Delta F°_{(1)}$ may be evaluated by utilizing electronic spectroscopic[3] or conductometric[4] techniques suitable for measuring small concentrations of R^+. However, both of these methods are sufficiently accurate only over a limited range and in practice have yielded useful results only for those carbonium ions whose stability lies within 2–3 kcal/mol of trityl. A more versatile approach, in respect to the range of stabilities covered, involves the measurement of the reversible reduction potential of triaryl carbonium ions, as recently introduced by Jensen and Taft.[5] This emf method (eq 2) requires rather specialized apparatus

$$R^+ + e^- \rightleftharpoons {}^1\!/\!_2[R\text{–}R] \qquad (2)$$

which limits its general application.

The most widely employed method for obtaining carbonium ion stabilization energies involves the reversible ionization of arylcarbinols in an acid medium (eq 3). For carbinols which are soluble and appreciably

$$R^+ + H_2O \rightleftharpoons ROH + H^+ \qquad (3)$$

ionized in very dilute acid, determination of the pH coupled with a spectroscopic determination of [R^+] yields $\Delta F°_{(3)}$ directly. Carbinols which yield less stable carbonium ions require high acid concentrations for ionization and one must resort to acidity functions with all their attendant limitations.[6] By establishing an acidity function (H_R) scale applicable to carbinols in 0.5–98% H_2SO_4 solutions, however, Deno and coworkers[7] were able to measure the pK_{R^+} of a large number of aryl carbonium ions, spanning a wide range of stability and extending down to 10 kcal less stable than trityl.

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[1] J. F. Norris and W. W. Sanders, *J. Amer. Chem. Soc.*, **23**, 54 (1901); F. Kehrmann and F. Wentzel, *Ber.*, 34, 3815 (1901); M. Gomberg, *J. Amer. Chem. Soc.*, **23**, 328 (1901).

[2] D. Bethell and V. Gold, "Carbonium Ions, An Introduction," Academic Press, New York, N. Y., 1967, Chapters 4 and 5.

[3] A. G. Evans, A. Price, and J. H. Thomas, *Trans. Faraday Soc.*, **52**, 332 (1956), and references cited therein.

[4] N. N. Lichtin, *Progr. Phys. Org. Chem.*, **1**, 75 (1963).

[5] (a) E. D. Jensen and R. W. Taft, *J. Amer. Chem. Soc.*, **86**, 116 (1964); (b) R. W. Taft and L. D. McKeever, *ibid.*, **87**, 2489 (1965).

[6] E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

[7] (a) N. C. Deno, J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954); (b) *J. Amer. Chem. Soc.*, 77, 3044 (1955).

In studies of the effects of structure variation on the stability of carbonium ions it has been convenient[5] to use trityl cation as a reference point. This is accomplished by subtracting $\Delta F°$ for eq 2 or 3, obtained when R is trityl, from $\Delta F°$ obtained for other R. The free-energy difference obtained then refers to eq 4 where R_0^+ is the

$$R^+Y^- + R_0X \rightleftharpoons RX + R_0^+Y^- \qquad (4)$$

reference cation (*i.e.*, trityl), X is the leaving group (OH for eq 3, or $R\cdot$ for eq 2), and Y^- is the counteranion. We have suggested[8] that the term $\Delta F°_{R^+}$ be utilized to designate this free-energy comparison.[9]

When both covalent species are subject to comparable steric effects then $\Delta F°_{(4)}$ yields directly the difference in stability between the cations R^+ and R_0^+. This presupposes that contributions to $\Delta F°$ from the covalent species RX and R_0X are essentially cancelled. This is a reasonable assumption when R and R_0 are closely similar in structure (*i.e.*, differ only in the nature of substituents remote from the site of ionization), but becomes invalid when R and R_0 are grossly different. However, as is discussed in detail in a later section, it is now possible to detect and correct for such effects using the nmr method.

The general validity of both the emf and pK_{R^+} methods is indicated by the agreement between the $\Delta F°_{R^+}$ values obtained from each,[5a] despite the diverse nature of the solvents and leaving groups employed. It would be of obvious advantage, however, to have available an alternative procedure which, unlike those described above, is not limited to one particular solvent and/or leaving group, does not require unique equipment nor tedious preparation of standards, and is generally amenable to a variety of reactants and reaction conditions. The recently reported[8] nmr method is believed to have such potential.

The nmr method differs from those discussed above not only in that it takes advantage of the versatility of nmr spectroscopy to obtain K_{eq}, but also that the equilibrium in eq 4, involving two different carbonium ions and their covalent precursors, is studied directly. Inasmuch as nmr detection of an individual species in equilibrium 4 is limited to a minimum concentration of ~5%, determination of $\Delta F°_{R^+}$ by direct equilibration with trityl is limited to those cations whose stability is within ±3 kcal/mol of trityl. In practice, however, $\Delta F°_{R^+}$ values can be obtained for any carbonium ion stable enough to maintain its integrity during the time necessary for its equilibration with any other carbonium ion of comparable stability for which a $\Delta F°_{R^+}$ is known. Thus, the evaluation of a cation of completely unknown stability by the nmr method may require a trial and error approach to determine a suitable equilibrating partner. However, having established its approximate $\Delta F°_{R^+}$, the ability to use a variety of exchanging partners, and thus confirm the reliability of a particular $\Delta F°_{R^+}$ value, is a distinct advantage.

The nmr approach, though presently limited to isolatable carbonium ions, is capable of a wide degree of procedural flexibility not only in the choice of equilibrating partners but also in the choice of temperature, solvent, leaving group, direction in which equilibrium is approached, and choice of specific nmr technique used to evaluate $\Delta F°_{(4)}$. The interrelation between these factors and their role in influencing carbonium ion stabilities is discussed below.

Results

Nmr Technique for Obtaining $\Delta F°_{R^+}$. When measured quantities of a carbonium ion salt R^+Y^- and a carbonium ion precursor R_0X (where X = halogen, hydroxide, alkoxide, azide, or acetate) are dissolved in methylene chloride or acetonitrile, thermodynamic equilibrium 4 is rapidly established. In such an equilibrated mixture the relative amounts of R^+ and R_0^+ are a direct measure of their free-energy difference. Quantitative measurements of K_{eq} for eq 4 are made possible by the incorporation into R or R_0 of substituent probe groups which give single sharp nmr signals, such as methoxyl, methyl, *tert*-butyl, trifluoromethyl, and dimethylamino. Fortunately, the effect of the positive charge results in a downfield shift in the R^+ substituent probe group, generally ranging from 0.15 to 0.50 ppm, which facilitates quantitative determination of the individual species.

When X is halogen, equilibrium is reached instantaneously. This equilibrium is known to be reached *via* SN1 ionization of the halide and leads to exchange between RX and R^+Y^- and between R_0X and $R_0^+Y^-$, which is rapid on the nmr time scale.[10] The resulting spectra for R and R_0 exhibit time-averaged resonances for which the chemical shift, δ_{exch}, is proportional to the concentration of the two components of the exchanging pair as expressed by

$$\delta_{exch} = p_{RX}\delta_{RX} + p_{R^+}\delta_{R^+}$$

where p_{RX} and p_{R^+} are the mole fractions of the R-containing species and δ_{RX} and δ_{R^+} are the chemical shifts of these individual components. Equilibrium concentrations of the components can be calculated from the chemical shifts observed and used to calculate $K_{(4)}$ according to

$$K_{eq} = \frac{[R_0^+][RX]}{[R^+][R_0X]}$$

This method is most conveniently used when the initial reactants are equimolar, since then $[R_0^+]/[R_0X] = [RX]/[R^+]$. Under these conditions the probe group need not be present in both R and R_0, so that lack of a marker group in any carbonium ion need not be a deterrent to its stability measurement. It is essential, however, that chemical shifts of the marker group are known for both the covalent and cationic species. If both R and R_0 have suitable marker substituents, then time-averaged bands from both exchanging pairs can be used independently to calculate $K_{(4)}$. Details on the use of this fast-exchange technique for the equilibration between di-*p*-methyltrityl hexachloroantimonate and mono-*p*-methyltrityl chloride are described in the Experimental Section. The $\Delta F°_{R^+}$ data at 40° listed

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[8] A. E. Young, V. R. Sandel, and H. H. Freedman, *J. Amer. Chem. Soc.*, **88**, 4532(1966).

[9] As demanded by K_4, cations more stable than trityl will have a positive $\Delta F°_{R^+}$ and *vice versa.* Though this is contrary to the usual thermodynamic convention it has the psychological advantage of avoiding the assignment of a more negative value for a more stable ion. pK_{R^+} values are converted to the $\Delta F°_{R^+}$ scale most simply by the relationship

$$\Delta F°_{R^+}\text{ (kcal/mol)} = 9.0 + (1.37)pK_{R^+}$$

where pK_{R^+} of trityl cation is taken as −6.67[b] and $\Delta F°_{trityl} = 9.0$.

[10] H. H. Freedman, A. E. Young, and V. R. Sandel, *J. Amer. Chem. Soc.*, **86**, 4722 (1964).

in Table I column 1 (chloride as leaving group) as well as values in Table V for trityl derivatives have been obtained by this technique.

For carbonium ions of $pK_{R^+} > -2$ ($\Delta F°_{R^+} > 6$) the halides are significantly ionized in solvents which dissolve the carbonium ion salts and are no longer suitable for exchange 4, since the amount of carbonium ion resulting from spontaneous ionization cannot be separated from that arising from exchange. This can be circumvented by taking advantage of the fact that, unlike halogen, spontaneous ionization does not occur when the leaving group X is alkoxide, azide, acetate, or benzoate, and that therefore covalent components (RX) containing these leaving groups are equally good alternatives to halide for the determination of $\Delta F°_{R^+}$.[11] Further, we have since found that carbinols (X = OH) behave similarly, and inasmuch as carbinols are the most commonly available carbonium ion precursors, the versatility of the nmr method has now been considerably extended.[12]

With these nonhalide leaving groups, exchange reaction 4 occurs slowly on the nmr time scale, but rapidly enough to reach equilibrium in a reasonable length of time, especially when acid catalyzed. This slow exchange process presumably proceeds *via* an SE2 mechanism by analogy with the *p*-methoxybenzoate derivative for which second-order kinetics have been demonstrated.[11] Most equilibria data of this type were obtained on X = hydroxyl or methoxyl compounds and generally required a few minutes to several hours to reach equilibrium, with the exception of the *p*-dimethylamino derivatives which required several days. Although no attempts were made to obtain quantitative rate data, it appears that the nucleophilicity of the leaving group, the electrophilicity of the carbonium ion, and the presence of acidic impurities are factors which influence the rate.[13]

When R or R_0 contain suitable substituents for which individual resonances are observed for both covalent and cationic species, conventional integration techniques can be used to determine the relative concentrations of the equilibrium mixture. As indicated above, if known quantities of reactants are employed, a marker group need be present in only R or R_0 to evaluate $K_{(4)}$ and when suitable groups are present in both R and R_0 a double check is provided. Details on the use of this slow exchange technique for the equilibration of *p*-methyl-*p*′-methoxytrityl tetrafluoroborate and di-*p*-methoxytrityl alcohol are described in the Experimental Section. Attainment of equilibrium was confirmed in some cases by approaching equilibrium from both sides of eq 4, yielding $\Delta F°$ values which agreed usually to within ±0.1 kcal/mol, When equilibrium was approached from one direction only, it was monitored by repeated measurements until a constant $\Delta F°$ value was obtained. Data of Table I, column 2 (X = OH) and column 3 (X = OCH_3), Table II, columns 1 and 2, as well as data of Table III were obtained at 40° in this manner.

Table I. Relative Carbonium Ion Stabilization Energies, $\Delta F°_{R^+}$ (kcal/mol) (Meta- and Para-Substituted Trityls)

	Nmr			Emf[a]	pK_{R^+}
Trityl substituents	Cl	OH	OCH_3	·R	OH
p-Methoxybisdimethylamino		22.8			19.8[b]
Di-*p*,*p*′-dimethylamino		21.4		20.7	18.4[c]
p-Trifluoromethylbis-dimethylamino		20.0			
Di-*p*-methoxy-*p*′′-dimethylamino		18.9			
p-Methoxy-*p*′-dimethylamino		17.3			
p-Methyl-*p*′-dimethylamino		16.3			
p-Dimethylamino		15.8		15.2	15.5[c] 13.9[d] 13.8[e]
p-Trifluoromethyl-*p*′-dimethylamino		14.1			
p-Dimethylamino-*m*-methyl		12.6			
Tri-*p*-methoxy		11.4	11.3	11.9	10.2[f]
Di-*p*-methoxy		8.2	8.2	8.6	7.4[f]
Di-*p*-methyl-*p*′-methoxy		7.3			
p-Methyl-*p*′-methoxy	5.7	5.9			
Tri-*p*-methyl	4.6		4.6		4.2[f]
p-Methoxy	4.5			5.0	4.4[f]
Tri-*p*-*tert*-butyl	4.4				0.5[f]
Di-*p*-methyl	3.2	3.4		3.3	3.0[g]
m-Difluoromethyl-*p*′-methoxy		3.0			
Mono-*p*-methyl	1.6	1.8		1.8	1.9[f]
Mono-*m*-methyl	0.8	0.8		0.7	
None	[0]	[0]		[0]	
m-Methyl-*p*′-chloro	−0.2				−0.2[h]
m-Methyl-*p*′,*p*′′-chloro	−0.8				−0.7[h]

[a] Data from ref 5 and 24. ·R is triarylmethyl. [b] R. Cigen, Thesis, University of Lund, 1956. [c] R. J. Goldacre and J. N. Phillips, *J. Chem. Soc.*, 1724 (1949). [d] R. Breslow, S. Garratt, L. Kaplan, and D. LaFollette, *J. Amer. Chem. Soc.*, **90**, 4051, 4056 (1968). [e] R. Renaud, *C. R. Acad. Sci.*, **260**, 6933 (1965). [f] Calculated from reported pK_{R^+} data, taking pK_{R^+} for trityl = −6.6 at 25° (from ref 7b). [g] Calculated from reported pK_{R^+} data of ref 28. [h] Estimated from σ^+ values cited by H. C. Brown and Y. Okamoto (*J. Amer. Chem. Soc.*, **80**, 4979 (1958)) using $\rho = -4.5$.

It is important to show that identical results are obtained with both the fast exchange and slow exchange techniques. This has been demonstrated for the equilibrium between tri-*p*-*tert*-butyltrityl cation and tri-*p*-methyltrityl cation where both techniques are suitable. For fast exchange with chloride as leaving group a value of $\Delta F° = 0.2 \pm 0.1$ was obtained and for slow exchange with azide leaving group, integration gave $\Delta F° = 0.0 \pm 0.1$.

Both fast and slow exchange techniques become insensitive when the concentration of either the covalent or cationic species greatly predominates. In practice,

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[11] A. E. Young, H. H. Freedman, and V. R. Sandel, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 77S.

[12] The possibility of ether formation as a competing exchange reaction was considered, but no such products were observed.

[13] The observation that exchange rates for carbinol–carbonium ion equilibration decrease with increasing cation stability is in direct contrast to that found for the chloride–carbonium ion equilibration.[10] This is in accord with our conclusion that the halide and carbinol exchanges are, respectively, unimolecular (SN1) and bimolecular (SE2) processes. For the relatively unstable cation, trityl, a recent report (J. I. Brauman and W. L. Archie Jr., *J. Amer. Chem. Soc.*, **92**, 5981 (1970)) indicates that exchange between trityl cation and its carbinol is fast enough, in the presence of H_2O in acetonitrile at ambient temperatures, to lead to exchange broadening in its nmr spectrum. Such an exchange rate would not be unexpected for an SE2 process but would be completely contrary to that predicted for the SN1 (unimolecular) exchange. It is therefore very difficult to rationalize their conclusions that the trityl cation–carbinol exchange is zero order in carbonium ion. Inasmuch as we have found that it is not possible to obtain reproducible nmr rates (or kinetic analyses) with carbonium ions of the order of stability of trityl, presumably due to the difficulties in eliminating traces of adventitious water, it appears that these exchanges are subject to strong proton catalysis and suggests that this may be a factor in the kinetics observed by the above workers.

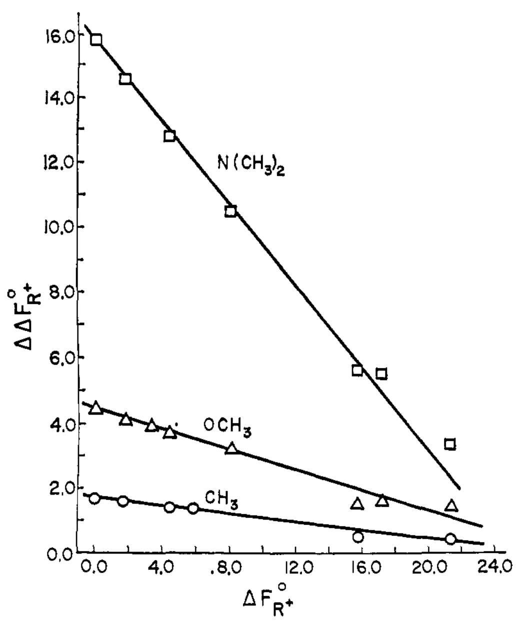


Figure 1. Plot of the stabilization energies ($\Delta F^\circ{}_{R^+}$) of trityl cations from Table I *vs.* the gain in stabilization energy ($\Delta\Delta F^\circ{}_{R^+}$) obtained by the substitution of the *p*-methyl (○), *p*-methoxy (△), or *p*-dimethylamino (□) group.

reliable data could not be obtained when the ratio of these species was greater than about 20:1, which corresponds to $|\Delta F^\circ| \sim 3$. Thus our $\Delta F^\circ{}_{R^+}$ data in Tables I and II required stepwise accumulation of equilibrium data using ΔF° increments $\gtrsim 3.5$ kcal/mol. In Table III each vertical column under ΔF° represents one or two sets of equilibrium data obtained from a reference carbonium ion, R^+Y^-, denoted by (0) for exchange reaction 4 with covalent compounds higher in stability in Table III. Table III demonstrates not only the stepwise manner in which the $\Delta F^\circ{}_{R^+}$ values in Tables I and II are obtained but also provides some indication of the errors involved in such a method. Errors are discussed in more detail below; however, it can be seen from those entries where two sets of data are available (columns 5–8) that the sum of the two adjacent diagonal numbers representing two equilibrium determinations should equal the number to their immediate upper left obtained by a third equilibrium experiment. The agreement between these two approaches has an average error of ±0.1 kcal/mol.

Table II. Relative Carbonium Ion Stabilization Energies, $\Delta F^\circ{}_{R^+}$ (kcal/mol), for Meta- and Para-Substituted Xanthyl and Other Compounds

Cation	Nmr OH	Nmr OCH$_3$	Emf[a] ·R	pK_{R^+} OH
Triphenylcyclopropenium	14.4	12.9		13.3[b]
9-(*p*-Methoxyphenyl)xanthyl	10.3	9.1	8.6	11.1[c]
9-(*p*-Methylphenyl)xanthyl		8.4		
9-(*m*-Methylphenyl)xanthyl		8.2		
9-Phenylxanthyl	9.1	8.0	7.4	10.6[c]
9-(*p*-Trifluoromethylphenyl)-xanthyl	7.2	5.9	5.5	8.5[d]
Xanthyl				7.8[e]

[a] Data from ref 24. ·R is 9-arylxanthyl. [b] R. Breslow, J. Lockhart, and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 2375 (1961). [c] R. A. Diffenbach, Thesis, The Pennsylvania State University, 1966. [d] L. R. Green, Ph.D. Dissertation, University of California, Irvine, Calif., 1970. [e] Calculated from pK_{R^+} data in ref 16a.

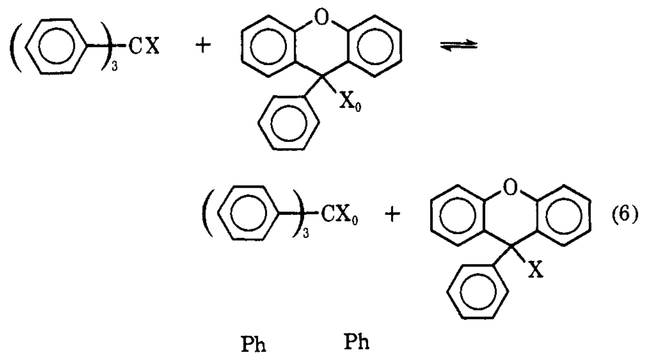
Inasmuch as the stability data are unchanged by nonnucleophilic anion (Y^-) for $SbCl_6^-$, BF_4^-, ClO_4^-, and $SbCl_5OH^-$ and identical results are obtained in acetonitrile and methylene chloride, exchange reaction 4 is both anion and solvent independent.

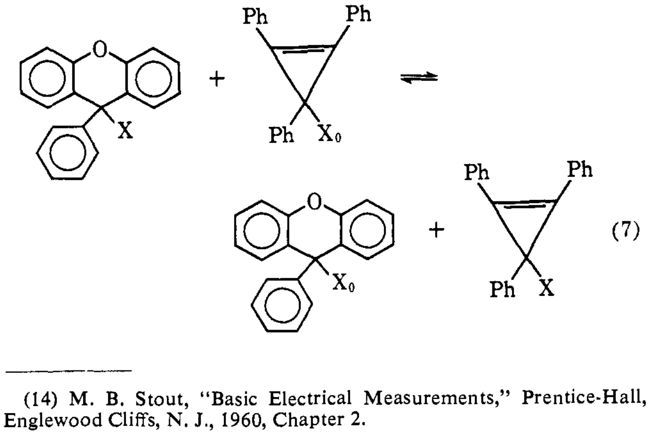
Some consideration of the uncertainty of our data is required. The reproducibility of the data for a series of measurements on the same equilibrium mixture for both a series of chemical-shift calibrations (fast exchange) and integrations (slow exchange) for a typical measurement in which the $|\Delta F^\circ|$ for eq 4 was ~2 kcal/mol was found to have a standard deivation of ±0.1 kcal/mol. This is thought to be primarily due to the limitations of accuracy on the chemical-shift calibrations for fast exchange and integrations for slow exchange; a typical series of several traces for the examples (Ia and Ib) described in the Experimental Section gave values of 1.6 ± <0.1 (standard deviation) and −2.2 ± <0.1 (standard deviation) for the fast and slow exchanges, respectively. This uncertainty should be taken as an average, since measurements of the error would be smaller when $|\Delta F^\circ| < 2$ and larger when $|\Delta F^\circ| > 2$. Since the stability tables are constructed from a stepwise series of measurements, accumulation of error is expected. It may be approximated from the usual equations[14] that the uncertainty will become no greater than ±0.3 kcal/mol for the largest values listed in Table I.

Evaluation of Leaving Group Effects. As suggested in the introduction, when R and R_0 are grossly different structures, *e.g.*, trityl and xanthyl, $\Delta F^\circ{}_{(4)}$ may be affected by the nature of X. It should be possible to obtain information on the effects of various leaving groups by studying eq 5, in which two different covalent carbonium

$$RX + R_0X_0 \rightleftharpoons RX_0 + R_0X \qquad (5)$$

ion precursors, R and R_0, containing different leaving





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[14] M. B. Stout, "Basic Electrical Measurements," Prentice-Hall, Englewood Cliffs, N. J., 1960, Chapter 2.

Table III. Stepwise Accumulation of Relative Carbonium Ion Stabilization Data, $\Delta F°_{R^+}$

Cation	$\Delta F°$									$\Delta F°_{R^+}$
Tri-*p*-methoxytrityl								2.4	1.1	11.4
9-(*p*-Methoxyphenyl)xanthyl							2.3	1.2	(0)	10.3
9-Phenylxanthyl						1.8	0.9	(0)		9.1
Di-*p*-methoxytrityl					2.2	0.9	(0)			8.2
Di-*p*-methyl-*p*′′-methoxytrityl					1.4	(0)				7.3
p-Methyl-*p*′′-methoxytrityl[a]				1.3	(0)					5.9
Tri-*p*-methyltrityl[a]			1.4	(0)						4.6
Di-*p*-methyltrityl[a]		1.6	(0)							3.2
p-Methyltrityl[a]	1.6	(0)								1.6
Trityl[a]	(0)									(0)

[a] Chlorides used as covalent precursors; all others were carbinols.

Table IV. Comparison of $\Delta F°$ for Various Leaving Groups in Equations 6 and 7

	$\Delta F°$, kcal/mol[a]	
X (X_0 = OH)	Eq 6	Eq 7
OH	[0]	[0]
OCH_3	−1.9	−0.1
OC_2H_5	−1.8	
$OCH(CH_3)_2$	−2.6	−0.9
$OC(CH_3)_3$		−2.7
N_3	0.0	
Cl	−0.3	
Br	−1.2	

[a] Identical results were obtained in both acetonitrile and methylene chloride as solvent.

groups, X and X_0, are equilibrated. It has in fact been observed that in methylene chloride containing small amounts of acidic catalysts, slow exchange does occur between pairs of covalent compounds when X and X_0 are OH, OCH_3, OC_2H_5, $OCH(CH_3)_2$, $OC(CH_3)_3$, Cl, Br, or N_3. Combinations of R and R_0 which attained equilibrium according to eq 5 in a reasonable length of time were trityl with 9-phenylxanthyl and 9-phenylxanthyl with triphenylcyclopropenyl. When either X (and/or X_0) was alkoxyl, the chemical shifts could be distinguished in the two speices RX and RX_0, and by using standard integration techniques, the equilibrium composition of the mixture and corresponding $\Delta F°_{(5)}$ could be calculated. Data of Table IV for eq 6 and 7 were obtained in this manner and for convenience are referenced to hydroxyl, the smallest leaving group, X_0 = OH.

Attainment of equilibrium (generally within ~2 weeks) was confirmed in most cases by approaching equilibrium from both directions in eq 5, and agreement in $\Delta F°$ values was usually within ±0.1 kcal/mol. When equilibrium was approached from one direction only, repetitive measurements were made until a constant $\Delta F°$ value was reached. Apparently there is no significant solvent effect since several exchanges were carried out in both CD_2Cl_2 and CD_3CN and gave identical results. As in the case of the $\Delta F°_{R^+}$ equilibrium studies, practical limitations of measuring concentration differences require $|\Delta F°| \lesssim 3$. These measurements are subject to the same types and magnitudes of errors as discussed for the slow-exchange carbonium ion covalent equilibria.

Discussion

Comparison of $\Delta F°_{R^+}$ Results Obtained by Different Methods. $\Delta F°_{R^+}$ values obtained for trityl cations are listed in Table I and compared with literature data obtained from the pK_{R^+}[7] and emf[5] techniques. Two observations can be made from this table. First, the nmr data appear to be leaving group independent; use of covalent chlorides, carbinols, or methyl ethers in the exchange reaction yields the same free-energy value. This finding is required by the original assumption that the free energy reflects only the free-energy difference of eq 4 between the cations R^+ and R_0^+ resulting from the differential stabilization of the positive charge, but has not been demonstrated previously since the emf and pK_{R^+} methods are restrained to the use of an invariant leaving group ($C(Ar)_3$ or OH, respectively). Second, results obtained by the three methods are in general similar, confirming the usefulness of each. However, closer examination reveals a systematic difference among the data sets; pK_{R^+} results are consistently smaller than emf or nmr data. The least-squares slope from a plot of pK_{R^+} data *vs.* the nmr data shows the pK_{R^+} values to be approximately 15% smaller than the nmr results. The difference between the pK_{R^+} and emf data was noted by Jenson and Taft[5a] and was attributed to a leaving group effect. However, our finding of a similar difference between the nmr and pK_{R^+} data where the same leaving group (OH) is used, in addition to the demonstration of leaving group independence for the nmr data of Table I, rules out this argument.

A possible clue to this problem is found by noting that the nmr and emf methods have in common the use of an organic, nonacidic solvent (CH_3CN or CH_2Cl_2), whereas mixtures of aqueous acid are employed in the pK_{R^+} method. It is likely, therefore, that the difference between the methods arises from small but measurable solvation effects.

In all three methods the Hammett activity coefficient postulate[15] is invoked (explicitly or implicitly) and $\Delta F°_{R^+}$ is calculated from the relative *concentrations* of the equilibrated species, even though no test of its quantitative correctness has ever been performed. If deviations from this postulate were to occur, the extent of the deviation should be solvent dependent, and consequently $\Delta F°_{R^+}$ calculated using this postulate would also be solvent dependent. As might be expected, the lower $\Delta F°_{R^+}$ values observed in aqueous acidic media (*i.e.*, pK_{R^+} data) suggest that the deviation from ideality is greater here than in organic solvents.

Substituent Effects on $\Delta F°_{R^+}$ for Trityl Derivatives. The effect of single substituents on the stabilization energies of trityl cations correlates with the parameter

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(15) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940, p 264.

σ^+ with a ρ value of -4.5.[16] This is consistent with the electronic demand at the carbonium ion center. The effects of multiple substituents are frequently not additive, however, and do not follow the same σ^+ relationship,[16c,17] the stabilization energy gained from multiple substituents often being less than the sum of the individual substituent effects. This "saturation" of electronic stabilization energies has been attributed[18] to a competition between donor substituents in the same molecule to stabilize the positive charge, so that the stabilization provided by a substituent depends on the demand placed on it by the carbonium ion system. The large amount of data reported in Table I for multiply substituted carbonium ions allows closer examination of this saturation effect. In the figure is plotted the increment of stabilization gained from substitution of *p*-methoxy, *p*-methyl, or *p*-dimethylamino groups *vs.* the stabilization energy of the cation prior to the substitution. The plot provides a striking confirmation for the concept[18] that the stabilizing effect of a substituent on a carbonium ion is not constant but dependent on the demand made upon it, and shows that this dependency is linear. The increase in the slopes from the figure (absolute values) for these groups in the order $CH_3 < OCH_3 < N(CH_3)_2$ parallels their effect on the stabilization energies, and indicates that the better stabilizing groups are more easily saturated. It should be noted that, in contrast to the saturation of stabilization energies, additive behavior is found for destabilizing groups. For example, substitution of a first, second, and third *p*-$N^+(CH_3)_3$ or NO_2 group on a trityl cation destabilizes the cation by approximately the same increment.[19]

The result for the *p*-dimethylamino-*m*-methyltrityl cation demonstrates another example of nonadditive substituent effects which, however, cannot be attributed to electronic saturation effects. Although *m*-methyl alone stabilizes the trityl cation by 0.8 kcal/mol it destabilizes the *p*-dimethylaminotrityl cation by 3.0 kcal/mol (Table I). It is likely that steric inhibition of resonance, which has been observed in similar systems,[20] is responsible for this destabilization. Because of nonbonded interactions between NCH_3 and *m*-CH_3 the coplanarity between $N(CH_3)_2$ and phenyl required for maximum delocalization of charge to N cannot be as readily attained.[18]

Leaving Group Effects. As discussed in the introduction, the results of Table I demonstrate that stabilization energies calculated by the nmr method for trityl derivatives are leaving group independent. Results in Table II show that to the contrary, $\Delta F^\circ_{\mathrm{R}^+}$ values measured for 9-arylxanthyl cations and the triphenylcyclopropenium ion with OH as leaving group are significantly larger than those measured with OCH_3 as leaving group. Further, the good agreement found in Table I between emf and nmr data is absent in Table II, the emf data being consistently and significantly smaller. The concept of nonbonded interactions in covalent cation precursors can explain these discrepancies. When R and R_0 (eq 4) are from the same family (*e.g.*, trityl) nonbonded steric interactions of X with R and R_0 are constant in the covalent species and absent in the ionic species. Hence, a variation of the leaving group size alters equally the ground-state energies of the two covalent species while the cation ground-state energies remain unchanged, and therefore, ΔF° for eq 4 is independent of leaving group effects. However, when R and R_0 are from families with different steric requirements (*e.g.*, trityl compared to 9-arylxanthyl), nonbonded steric interactions with the leaving group will differ in the two covalent species, and the difference between the interaction energies appears as a contribution to ΔF° for eq 4. The extent of this contribution depends on the size of the leaving group and inasmuch as $\Delta F^\circ_{\mathrm{R}^+}$ is always related to trityl, values obtained for other families can be leaving group dependent. Consistent with this interpretation is the fact that this leaving group dependency is no longer apparent when relative stabilization energies within the 9-arylxanthyl family are examined (*i.e.*, $\Delta\Delta F^\circ_{\mathrm{R}^+}$ for eq 4 with R_0 = 9-phenylxanthyl).

The concept of a leaving group effect was tested by determining ΔF° for the acid-catalyzed exchange reactions (eq 6 and 7) between the covalent components of eq 4 with a variety of leaving groups X. If the leaving group effect on $\Delta F^\circ_{\mathrm{R}^+}$ results from nonbonded interactions in the covalent precursors, then these interactions should also result in nonzero values for ΔF° (eq 6 and 7) and the values observed will be a quantitative measure of the leaving group effect. The results in Table IV demonstrate that indeed $\Delta F^\circ_{(6)}$ and $\Delta F^\circ_{(7)}$ are significantly dependent on the nature of X. Inasmuch as it is highly unlikely that these effects are of electronic origin, they can be attributed to nonbonded steric interactions of variable extent between the leaving groups X or X_0, and the cation precursor moieties, R or R_0. Assuming the effective size of the leaving group increases with substitution (*i.e.*, $OC_3H_7 > OCH_3 > OH$), then the results indicate that 9-phenylxanthyl in eq 6 and triphenylcyclopropheny1 in eq 7 accept X more readily when X is bulkier than OH. This establishes the relative steric requirements of these three systems in the order trityl > 9-phenylxanthyl > triphenylcyclopropenyl. The large ΔF° of 1.9 kcal/mol observed in the trityl–9-phenylxanthyl series of Table IV for X = OCH_3 decreases to 0.1 kcal/mol for the analogous 9-phenylxanthyl–triphenylcyclopropenyl series.[21] It thus appears that in the latter comparison significant steric crowding effects are not observed until leaving groups as large as isopropoxyl are introduced.[22]

It is significant that the ΔF° values in Table IV for azide and hydroxyl are identical, since these two groups have similar steric requirements but different electronic properties. These data lend further support to the hypothesis that nonbonded interactions and not elec-

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(16) (a) N. C. Deno and W. L. Evans, *J. Amer. Chem. Soc.*, **79**, 5804 (1957); (b) C. D. Ritchie, W. F. Sager, and E. S. Lewis, *ibid.*, **84**, 2349 (1962); (c) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, 1962, p 101.

(17) L. D. McKeever and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 4544 (1966).

(18) J. W. Rakshys, Jr., S. V. McKinley, and H. H. Freedman, *Chem. Commun.*, 1180 (1969), and references cited therein.

(19) H. H. Freedman, "Carbonium Ions," Vol. IV, G. A. Olah and P. von R. Schleyer, Ed., Interscience, New York, N. Y., in press.

(20) M. S. Newman, Ed., "Steric Effects in Organic Chemistry," Wiley, New York, N. Y., 1956, p 582.

(21) No exchange was observed to occur between triphenylcyclopropenyl and trityl derivatives under the conditions of eq 6 and 7. However, expected ΔF° values for this comparison can be calculated as the sum of ΔF° for eq 6 and 7 (-2.0 and -3.5 kcal/mol for OCH_3 and OC_3H_7, respectively).

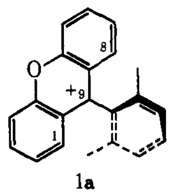
(22) ΔH° and ΔS° values for eq 6 and 7 would be of interest in this regard, but the nmr method is not sensitive enough to determine the small changes in ΔF° with temperature.

tronic effects are responsible for the observed energy differences.

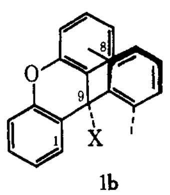
A comparison of the data in Table IV for chloride and bromide as leaving groups shows the expected order, chloride smaller than bromide, although it is somewhat surprising that OCH_3 appears to be larger than both Cl and Br. The overall apparent leaving group size trend is OH, N_3 < Cl < Br < OCH_3, OC_2H_5 < OC_3H_7 < OC_4H_9.

The origin of the leaving group effect on $\Delta F^\circ_{R^+}$ values for 9-arylxanthyl and triphenylcyclopropenium cations now becomes clear. The energy gained from the relief of steric crowding by the ionization of trityl derivatives is larger than for 9-arylxanthyl derivatives, and is increased even more by bulkier leaving groups. The smaller stabilization energies observed by the nmr method in Table I for 9-phenylxanthyl compounds when OCH_3 rather than OH is the leaving group therefore results from the enhanced steric interactions with OCH_3 in the trityl compounds. The still smaller values obtained from the emf method confirm the expectation that the triarylmethyl leaving group provides steric interactions even greater than those for OCH_3 and OH.

Substituent Effects in 9-Arylxanthyl Cations. The effects of meta and para substituents in the aryl ring of the 9-arylxanthyl cations have received little attention previously and are of unusual interest inasmuch as this system can be considered to be a trityl cation whose conformation is severely modified by the oxygen bridge. In contrast to the symmetrical trityl propeller,[23] the two bridged phenyl rings are nearly coplanar at the expense of the 9-aryl ring. Although substituent effects on $\Delta F^\circ_{R^+}$ of trityl cations correlate well with σ^+[16] a poor correlation with σ^+ is found for the 9-arylxanthyl cations. A much better correlation with $\rho = -3.8$ ($r = 0.995$) is found with σ^0,[24] the parameter defined by Taft[25] for systems where no direct conjugation occurs between the substituent and the reaction site. An electronic saturation effect resulting from charge delocalization in the planar xanthene ring will result in a smaller substituent effect for 9-arylxanthyl cations, but cannot account for the lack of correlation with σ^+. The reason for this different susceptibility to substituent effects of 9-arylxanthyl and trityl cations becomes clear from examination of a space-filling molecular model of the 9-arylxanthyl cation. Due to steric interactions between the ortho and the 1,8-hydrogens, the 9-aryl and xanthene rings are constrained to an average perpendicular conformation as in **1a**. Since the 9-aryl π system cannot interact with the xanthyl ion π system in this nearly perpendicular conformation, a σ^0 correlation with small ρ is to be expected. Significantly, a recent interpretation of esr spectra for the 9-arylxanthyl radical shows the xanthene and aryl rings are in fact out of plane.[26] Similar conclusions based on variable-temperature nmr studies on 9-arylxanthyl alcohols were arrived at recently.[27]



1a



1b

Finally, we note that lack of conjugation of the 9-phenyl with the xanthene ring suggests that the relative stabilization energy ($\Delta F^\circ_{R^+}$) of xanthyl and 9-phenylxanthyl cations should be very similar. Indeed, data in Table II show that they differ by only 2.8 kcal/mol in contrast to the ~10 kcal/mol difference found between the diphenyl and triphenyl methyl cations.[28]

Effects of Ortho Substituents. The effect of ortho substituents on carbonium ion stabilization energies has also been little studied. These effects do not follow the usual substituent parameters, and in general enhanced stabilization energies are observed. This is most strikingly demonstrated in Table V for the 9-arylxanthyl series where o-CF_3 stabilizes the cation by 3.5 kcal/mol, in contrast to the electronically similar p-CF_3 which destabilizes the cation by 2.1 kcal/mol. Thus the steric effect of o-CF_3 appears to stabilize the carbonium ion by 5.6 kcal/mol. The most reasonable explanation is that, as with the 9-arylxanthyl cations, the phenyl and xanthene rings in the covalent 9-arylxanthyl derivatives are perpendicular in their most stable conformation, as shown in **1b**.[27] Ortho substituents in this conformation are forced either into the xanthene ring or against the other 9 substituent, and such steric interactions destabilize the covalent compound. These steric interactions are relieved on ionization, however, resulting in increased stabilization as reflected by increased $\Delta F^\circ_{R^+}$ values. If the difference between $\Delta F^\circ_{R^+}$ for ortho and para substituents is taken as a measure of the ortho steric effect, the values obtained (o-CH_3, 2.5; o-C_2H_5,[29] 3.4; o-CF_3, 5.6 kcal/mol) compare favorably with the trends shown by other measures of steric effects, such as the Taft E_s parameters which have values of 0.0, −0.1, and −1.2 for these same groups.[30]

Table V. Relative Carbonium Ion Stabilization Energies, $\Delta F^\circ_{R^+}$, for Substituted Trityl and 9-Arylxanthyl Cations

Cation	$\Delta F^\circ_{R^+}$,[a] kcal/mol	$\Delta\Delta F^\circ_{R^+}$, kcal/mol
9-(2,6-Dimethylphenyl)xanthyl	>14.0	>6.0
9-(o-Ethylphenyl)xanthyl	11.8	3.8
9-(o-Trifluoromethylphenyl)xanthyl	11.5	3.5
9-(o-Methylphenyl)xanthyl	10.9	2.9
9-Phenylxanthyl	8.0	(0.0)
2,6-Xylyldiphenylmethyl	6.5	
Mono-o-ethyltrityl	1.9	
Mono-o-methyltrityl	1.8	
Mono-o-n-propyltrityl	1.5[b]	

[a] The values for the 9-arylxanthyl cations were obtained using the methyl ethers. The trityl values were obtained using chlorides. [b] Calculated from pK_{R^+} data in R. Breslow, L. Kaplan, and D. LaFollette, *J. Amer. Chem. Soc.*, **90**, 4056 (1968).

A similar trend for ortho substituents is found in the trityl compounds in Table V, but is much less pro-

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(23) J. W. Rakshys, Jr., S. V. McKinley, and H. H. Freedman, *J. Amer. Chem. Soc.*, **92**, 3518 (1970), and references therein.

(24) L. D. McKeever, Ph.D. Dissertation, University of California, Irvine, Calif., 1966.

(25) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

(26) M. D. Sevilla and G. Vincow, *ibid.*, **72**, 3641 (1968).

(27) S. V. McKinley, P. A. Grieco, A. E. Young, and H. H. Freedman, *J. Amer. Chem. Soc.*, **92**, 5900 (1970).

(28) Obtained from pK_{R^+} data taken from W. N. White and C. A. Stout, *J. Org. Chem.*, **27**, 2915 (1962).

(29) $\Delta F^\circ_{R^+}$ = 3.4 for the p-CH_3 derivative was used for comparison.

(30) Reference 20, p 598.

nounced. For these compounds also, steric interactions in both the covalent and cationic species can contribute to the observed effect. The ortho substituents will destabilize the covalent cation precursors by causing crowding about the tetrahedral carbon, but also destabilize the cation by hindering the aryl rings from approaching the coplanarity required for maximum charge delocalization. The net result of these two opposing effects cannot be predicted *a priori* without detailed knowledge of the molecular conformations, but our results suggest that some steric enhancement of the extent of ionization still occurs.

The effects of a number of ortho substituents on the stabilization energy of malachite green (**2**) can be calculated from the data of Cigen and coworkers,[31] and are listed in Table VI, along with comparative data from para substituents. The enhancement of stabilization energies for ortho substituents is obvious here also, and appears to be larger than that observed for trityl in Table V. Reasons for larger ortho effects in malachite green derivatives are not clear. One can speculate that strain energies are nearly alike in the covalent carbinols, but that there is less steric destabilization in the malachite green ions. This may be due to the fact that the unsubstituted phenyl ring in malachite green is considerably twisted out of the trigonal plane to better allow conjugation of the two *p*-dimethylaminophenyl rings, so that further twisting by an ortho substituent sacrifices little stabilization energy.

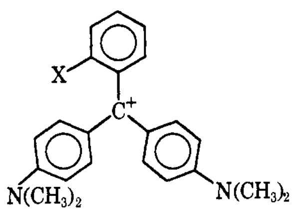

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Table VI. Relative Stabilization Energies for Malachite Green Derivatives[a]

X^b	$\Delta\Delta F^\circ_{R^+}{}^c$
o-OCH_3	1.1
p-OCH_3	1.1
o-CH_3	2.7
p-CH_3	0.4
o-F	0.0
p-F	0.0
o-Cl	1.7
p-Cl	−0.3
o-Br	1.9
p-Br	−0.3
o-I	2.7
p-I	−0.2
o-NO_2	0.5
p-NO_2	−1.4

[a] Calculated from $-\log ([K_4]/[K_6])$ from data of Cigen, *et al.*[31] [b] Substituent on ring not containing *p*-$N(CH_3)_2$. [c] Relative to malachite green, *i.e.*, $\Delta\Delta F^\circ_{R^+} \equiv 0.0$ for X = H.

Experimental Section

1. Measurement and Analysis of Nmr Spectra. The nmr measurements of eq 4–7 were obtained at 60 MHz on a Varian A56/60 spectrometer at ambient probe temperature of ~35° Accurately weighed samples of the two reactants were dissolved in CD_2Cl_2 or CD_3CN to a final concentration of ~0.1–0.3 *M*. Typical experiments illustrating both the fast- and slow-exchange techniques are described below. For the former, accurate chemical shifts were obtained by the usual side-band calibration techniques using a Hewlett-Packard audiooscillator and frequency counter, taking the average value of five or more traces. For the latter, at least five integrations were averaged. Reactants which required more than about 1 day to reach equilibrium were prepared in permanently sealed tubes.

a. Example of Fast-Exchange Process. The methyl resonances of *p*-dimethyltrityl hexachloroantimonate, *p*-dimethyltrityl chloride, *p*-methyltrityl chloride, and *p*-methyltrityl hexachloroantimonate in CD_2Cl_2 solution individually appear at 2.73, 2.31, 2.33, and 2.75 ppm. An equimolar mixture of *p*-dimethyltrityl hexachloroantimonate and *p*-methyltrityl chloride in CD_2Cl_2 gave two sharp singlets at 2.63 and 2.41 ppm with an intensity ratio of 2.00:1.00, thus identifying the lower field band as exchanging di-*p*-methyltrityl carbonium ion and chloride, and the higher field band as exchanging mono-*p*-methyltrityl carbonium ion and chloride. Using the relation between mole fraction and chemical shift (see Results), one can calculate, based on the exchange between dimethyl components, that $\Delta F^\circ = 1.67$ kcal/mol, and for exchange between monomethyl components $\Delta F^\circ = 1.56$ kcal/mol.

b. Example of Slow-Exchange Process. Equimolar quantities of *p*-methyl-*p*′-methoxytrityl hexachloroantimonate and di-*p*-methoxytrityl alcohol were dissolved in CD_2Cl_2. Nmr observations were made periodically on the methyl resonances. Initially the spectrum consisted primarily of the methyl band at 2.64 ppm of the reactant, *p*-methyl-*p*′-methoxytrityl cation. As the intensity of this band decreased with time, that of the corresponding alcohol, *p*-methyl-*p*′-methoxytrityl alcohol, appeared at 2.30 ppm. After 15 min the integrated ratio of these two bands was 0.30:1.0 and after ~1 hr the final equilibrium value of 0.176:1.00 was obtained. This corresponds to $\Delta F^\circ = -2.2$ (average deviation < 0.05) kcal/mol for five integrations.

2. Synthesis. Commercially available chemicals used in the preparation of triarylmethyl and 9-arylxanthyl alcohols were purchased from the following suppliers: *o*-, *m*-, and *p*-bromotoluene and *p*-bromoanisole (Columbia Organic Chemicals); *o*-bromoethylbenzene, 2-bromo-*m*-xylene, 4-chlorobenzophenone, 4,4′-dichlorobenzophenone, and benzanilide (Aldrich); 4-methylbenzophenone, 4,4′-dimethylbenzophenone, *p*-bromo-*N*,*N*-dimethylaniline, 4-bromo-2-methylaniline, and 4,4-bis(dimethylamino)-benzophenone (Eastman); *p*,*p*′-dimethoxybenzophenone (Chemicals Procurement Laboratories); *p*-bromobenzotrifluoride (Peninsular Chemresearch Inc.); and *p*-trifluoromethylbenzophenone (Pierce Chemical). *p*-*N*,*N*-Dimethylaminobenzophenone was prepared by the method of Hurd and Webb, mp 83–84° (lit.[32] 88–90.5°). New compounds used as reactants in the synthesis of triarylcarbinols were prepared as described in *a* and *b* below. Dow triply sublimed magnesium was used in the preparation of all Grignard reagents. Compounds synthesized gave nmr and infrared spectra consistent with the proposed structures. The melting points are uncorrected. Elementary analyses were performed by Galbraith Laboratories.

a. 4-Bromo-2-methyl-*N*,*N*-dimethylaniline. 4-Bromo-2-methylaniline was dimethylated using the procedure described by Billman, *et al.*,[33] for alkylation of amines. Yields were found sensitive to reaction temperature; insufficient heating of the amine with trimethyl phosphate resulted in no methylation or the mono-*N*-methyl compound, while overheating gave an intractable black tar. In the most successful preparations, the internal reaction temperature was held between 195 and 210° for approximately 0.5 hr followed by 1.5 hr at approximately 190°. During the heating period, the reaction turned very dark. After work-up as described in ref 33 distillation of the crude product gave a colorless oil in 68% yield, bp 84–86° (3 mm).

b. 3-(Difluoromethyl)bromobenzene. This compound was prepared in a manner similar to that described by Hasek, Smith, and Engelhardt.[34] 3-Bromobenzaldehyde (10 g) (Aldrich) (0.054 mol) was placed in a 0.6-l. monel pressure reaction cylinder under a

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(31) R. Cigen and C. G. Ekström, *Acta Chem. Scand.*, **18**, 157 (1964), and references cited therein.

(32) C. D. Hurd and C. N. Webb, "Organic Syntheses," Collect. Vol. I, H. Gilman, Ed., Wiley, New York, N. Y., 1941.

(33) J. H. Billman, A. Radike, and B. W. Mundy, *J. Amer. Chem. Soc.*, **64**, 2977 (1942).

(34) W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *ibid.*, **82**, 543 (1960).

nitrogen atmosphere. The vessel was sealed and cooled and nitrogen was removed by a vacuum pump. Using a vacuum system, approximately 0.13 mol of SF_4 (2.1 equiv) was measured by volume and condensed into the reactor cooled by liquid nitrogen. The vessel was sealed and allowed to come to room temperature and then heated to 150° for 16 hr. After reaction, the vessel was cooled to 0° and excess SF_4 as well as volatile by-products were slowly vented through a trap containing aqueous sodium hydroxide, followed by venting again at room temperature. The crude product was recovered from the reactor by dissolving in ether, and upon purification by vacuum distillation gave 8 g of a pale yellow liquid, bp 60° (5 mm). The ^{19}F and ^{1}H nmr spectra were consistent with the proposed structure ($J_{HF} = 56$ Hz).

c. **Triarylcarbinols.** These were prepared by the reaction of benzophenones and aryl Grignards in tetrahydrofuran (THF) unless otherwise specified. Crude reaction products were isolated and usually recrystallized from petroleum ether, methylene chloride–petroleum ether mixture, or alcohol–water mixture. Yields were generally 70–90%. The melting points of the following triarylcarbinols agreed with the literature: *p*-methyltriphenylmethanol,[7a,35] *m*-methyltriphenylmethanol,[36] *p,p'*-dimethyltriphenylmethanol,[37,38] tri-*p*-tolylmethanol,[39,40] *p*-methoxytriphenylmethanol,[7b] tri-*p*-*tert*-butyltriphenylmethanol,[41] *p,p'*-dimethoxytriphenylmethanol,[7b,42] tri-*p*-methoxytriphenylmethanol,[7b,43] *o*-methyltriphenylmethanol,[35,44] *o*-ethyltriphenylmethanol,[41] *p*-*N*,*N*-dimethylaminotriphenylmethanol,[45] *p,p'*-bisdimethylamino-*p''*-methoxytriphenylmethanol.[46] The physical data for other triarylcarbinols are as follows: *p,p'*-dimethyl-*p''*-methoxytriphenylmethanol, mp 80–84° (*Anal.* Calcd for $C_{22}H_{22}O_2$: C, 82.98; H, 6.96. Found: C, 82.49; H, 7.01), *p*-dimethylamino-*p'*-methyltriphenylmethanol, mp 95–98°, *p*-dimethylamino-*p'*-methoxytriphenylmethanol, mp 83–85°, *p,p'*-dimethoxy-*p''*-dimethylaminotriphenylmethanol, mp 109–111°, and *p,p'*-bisdimethylamino-*p''*-trifluoromethyltriphenylmethanol, mp 184–186° dec.

Crystalline solids were not obtained from *p*-dimethylamino-*p'*-trifluoromethyltriphenylmethanol and *p*-dimethylamino-*m*-methyltriphenylmethanol but purification by chromatography on silica gel gave oils for which the nmr spectra showed no detectable impurities.

p-Chloro-*m'*-methyltriphenylmethanol, *p,p'*-dichloro-*m''*-methyltriphenylmethanol, *p*-methoxy-*p'*-methyltriphenylmethanol, and 2,6-xylyldiphenylmethanol gave oils which were not purified but converted to the chlorides and then to the carbonium ion salts. Tri-*p*-methoxytriphenylmethanol was prepared by the addition of 3 equiv of *p*-anisyl Grignard reagent to 1 equiv of diethycarbonate in THF.

3-Difluoromethyl-4'-methoxytriphenylmethanol was prepared by treating 3-difluoromethlylbromobenzene with 1 equiv of *n*-butyllithium (Foote Mineral Co., 1.6 *N* in hexane) in THF at −60°, followed by addition of a THF solution of *p*-methoxybenzophenone. The crude product was purified by column chromatography on silica gel using petroleum ether and methylene chloride mixtures as eluents and gave a colorless oil.

d. **Triarylmethyl Chlorides.** These were prepared from the corresponding purified or crude carbinols by refluxing for approximately 30 min with a large excess of acetyl chloride in petroleum ether. After distilling off excess acetyl chloride the solid chlorides were recrystallized several times under nitrogen from benzene–petroleum ether or methylene chloride–petroleum ether mixtures containing a few drops of acetyl chloride. The chlorides were dried in a vacuum dessicator and stored in a dry atmosphere.

The melting points of the following triarylmethyl chlorides agreed with those reported in the literature: *m*-methyltrityl chloride,[36] *o*-methyltrityl chloride,[44,47] *o*-ethyltrityl chloride,[41] tri-*p*-tolylmethyl chloride,[48] di-*p*-methyltrityl chloride,[41] *p*-methoxytrityl chloride,[37] and tri-*p*-*tert*-butyltrityl chloride.[41] *p*-Chloro-*m'*-methyltriphenylmethyl chloride had mp 69–70.5° (*Anal.* Calcd for $C_{20}H_{16}Cl_2$: C, 73.40; H, 4.93. Found: C, 73.28; H, 5.02). *p,p'*-Dichloro-*m''*-methyltriphenylmethyl chloride gave a waxy low-melting solid upon standing many months. *p*-Methoxy-*p'*-methyltrityl chloride was converted to the carbonium ion salt without prior purification. Solid 2,6-xylyldiphenylmethyl chloride was isolated but decomposed upon standing and was therefore converted to its stable hexachloroantimonate salt without further purification.

e. **Triarylmethyl Ethers.** The methyl, ethyl, and isopropyl trityl ethers were prepared by method b of Arthur, *et al.*[49] Tri-*p*-methoxytrityl methyl ether was also prepared by this method and had mp 74–75°. *Anal.* Calcd for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 75.35; H, 6.70.

f. **Triphenylmethyl azide** was prepared by the method of Saunders.[50]

g. **Triarylmethyl Cations.** The tetrafluoroborate salt of *p,p'*-bisdimethylaminotrityl was prepared in a manner similar to that of Ritchie, *et al.*,[46] by treating the corresponding chloride (Eastman, Malachite Green) with aqueous $NaBF_4$. The salt obtained was recrystallized from methylene chloride and ether.

Tetrafluoroborate salts of the following alcohols were prepared by an exchange reaction of the carbinol with trityl tetrafluoroborate: *p,p'*-dimethoxy-*p''*-dimethylaminotrityl, *p*-dimethylamino-*p'*-methoxytrityl, and *p*-dimethylamino-*p'*-methyltrityl. Trityl tetrafluoroborate was dissolved in a minimal amount of methylene chloride and 1.2 equiv of the dimethylamino-substituted carbinol was added. After stirring the solution overnight there was quantitative exchange of the tetrafluoroborate anion to give the salt of the dimethylaminotrityl compound. This salt was precipitated with ether or petroleum ether while the trityl alcohol and excess unreacted dimethylaminotrityl alcohol remained in the filtrate. The salt was reprecipitated by dissolving in methylene chloride, filtering, and adding ether.

Hydroxypentachloroantimonate salts of *p*-dimethylamino-*p'*-trifluoromethyltrityl and *p*-dimethylamino-*m*-methyltrityl were formed by treatment of the corresponding carbinol with antimony pentachloride, in a manner similar to that of Pasika[51] but with methylene chloride and petroleum ether as solvents.

The tetrafluoroborate salts of trityl, di-*p*-methoxytrityl, tri-*p*-methoxytrityl, and *p*-dimethylamino-*m*-methyltrityl were prepared by treating the corresponding carbinol or chloride with fluoroboric acid in propionic anhydride as described by Dauben.[52] Tri-*p*-*tert*-butyltriphenylmethyl tetrafluoroborate was obtained from Dauben. Attempts to prepare tetrafluoroborate salts of some of the other trityl derivatives (of $\Delta F^\circ_{R^+} \gtrsim 8$ kcal/mol in Table I) using this method gave oils. However, hexachloroantimonate salts were readily prepared from the chlorides, using drybox techniques, by addition of a stoichiometric amount of antimony pentachloride dissolved in a small amount of petroleum ether to a solution of the desired triarylmethyl chloride in petroleum ether. There was immediate formation of a solid, or an oil which readily solidified. The solid was purified by dissolving in methylene chloride, filtering, and reprecipitating with petroleum ether. In some preparations carbon disulfide was substituted for petroleum ether. Hexachloroantimonate salts were prepared from trityl chloride derivatives having the following substituents: *m*-methyl-*p'*,*p''*-dichloro; *m*-methyl-*p'*-chloro; *m*-methyl; *p*-methyl; di-*p*-methyl; tri-*p*-methyl; *p*-methoxy; *p*-methoxy-*p'*-methyl; *p,p'*-dimethyl-*p''*-methoxy; *o*-methyl (*Anal.* Calcd for $C_{20}H_{17}SbCl_6$: C, 40.58; H, 2.90; Sb, 20.57; Cl, 35.95. Found: C, 40.82; H, 2.74; Sb, 20.67; Cl, 35.99); *o*-ethyl (*Anal.* Calcd for $C_{21}H_{19}SbCl_6$: C, 41.63; H, 3.16; Sb, 20.10; Cl, 35.12. Found: C, 41.54; H, 3.17; Sb, 20.76; Cl, 34.73); and 2,6-dimethyl (*Anal.* Calcd for $C_{21}H_{19}SbCl_6$: C, 41.63; H, 3.16; Sb, 20.10; Cl, 35.12. Found: C, 41.50; H, 3.38; Sb, 20.30; Cl, 34.89).

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h. 9-Arylxanthenols. These were prepared in a manner analogous to the triarylcarbinols by reaction of the appropriate aryl Grignard reagent with xanthen-9-one (Eastman, white label). Due to the low solubility of xanthenone in THF, the solid was usually added directly to the Grignard solution, and the resulting suspension was stirred overnight followed by the usual work-up procedure. Yields were generally 50–75%. The melting points of xanthenols with the following substituents agreed with those reported in the literature: 9-phenyl,[53,54] 9-*o*-tolyl,[55] 9-*m*-tolyl,[56] 9-*p*-tolyl,[57] 9-*p*-anisyl,[58] and 9-(*p*-trifluoromethyl)phenyl.[24] 9-(2,6-Dimethylphenyl)xanthenol was purified by chromatography on a silica gel column or by recrystallization from methylene chloride–petroleum ether and had mp 185–186.5° (red-brown melt). *Anal.* Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 82.92; H, 6.14. 9-(*o*-Trifluoromethylphenyl)xanthenol was not characterized but converted to the methyl ether.

i. 9-Phenylxanthyl chloride[57] was prepared by the method of Schoepfle.[59]

j. 9-Arylxanthyl Ethers. The ethers were all prepared from the 9-arylxanthenols by the following general method. To approximately 3 g of carbinol dissolved in a minimal amount of methylene chloride was added 6 ml of trifluoroacetic acid. The resulting red-brown solution of carbonium ion was added slowly to approximately 150 ml of the appropriate alcohol, and the color was discharged by neutralization with a concentrated alcoholic solution of sodium hydroxide. After 30 min the solution was poured into ice water, and the 9-arylxanthyl ethers separated either as oils or solids. Solids were recovered by filtration and recrystallized from the appropriate alcohol. Oils were extracted into diethyl ether and after removal of solvent, solids were obtained which were recrystallized from the appropriate alcohol. Melting points were in agreement with those found in the literature for methyl ethers of 9-phenyl-[54] and 9-*p*-anisylxanthenols,[58] and for 9-phenylxanthyl ethyl ether.[54] Methyl ethers of other 9-arylxanthenol derivatives had the following physical properties: 9-*o*-methyl, mp 115.5–116.5°, 9-*p*-trifluoromethyl, mp 72–73.5° (*Anal.* Calcd for $C_{21}H_{15}O_2F_3$: C, 70.78; H, 4.24; F, 16.00. Found: C, 70.02; H, 4.20; F, 15.68), and 9-*o*-trifluoromethyl, a light tan crystalline solid, mp 133–134.5° (*Anal.* Calcd for $C_{21}H_{15}O_2F_3$: C, 70.78; H, 4.24; F, 16.00. Found: C, 70.65; H, 4.41; F, 15.99). 9-Phenylxanthyl isopropyl ether had mp 101–102°.

k. 9-Arylxanthyl Cations. Tetrafluoroborate salts of all 9-arylxanthyl derivatives listed in Tables II and V were prepared and isolated by the method used for trityl fluoroborates[52] using purified carbinols or ethers as precursors. The yellow salts were reprecipitated from methylene chloride–petroleum ether mixtures.

l. Triphenylcyclopropenyl Compounds. Previously described methods were used for preparation of 1,2,3-triphenylcyclopropenium bromide,[60] *tert*-butyl ether,[60] and methyl ether.[61] 1,2,3-Triphenylcyclopropenyl isopropyl ether was prepared in a manner analogous to that of the methyl ether and was a white solid with mp 98–100°. Triphenylcyclopropenium tetrafluoroborate was prepared from the bromide. (*Anal.* Calcd for $C_{21}H_{15}BF_4$: C, 71.21; H, 4.27; F, 21.46. Found: C, 71.29; H, 4.41; F, 21.88.)

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The Basicity of Ethanol. An Acidity Function for Alcohols

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Abstract: Chemical shift data have been used to determine the basicity of ethanol in sulfuric acid solutions. This technique indicates that ethanol is one-half protonated in approximately 70% H_2SO_4 ($H_0 = -5.9$) and that the protonated species has a relatively high demand for solvation by water. Application of the Bunnett–Olsen equation gives the pK_{BH^+} to be -1.94. Since the protonation equilibrium spans a substantial range of acid concentrations it is possible to obtain an alcohol acidity function (H_{ROH}) from 33 to 94% H_2SO_4 using but a single indicator. The H_{ROH} function increases much less rapidly with increasing acid concentration than for any other known acidity function.

The basicity of aliphatic alcohols is an important topic that has been discussed in several previous papers.[1–4] A knowledge of the pK_{BH^+} values is essential to an understanding of the numerous reactions of these compounds that are subject to acid catalysis or inhibition and thus has application to both organic and biochemical processes. However, before quantitative estimates of basicity can be made, two requirements must be met: (i) it must be possible to measure the extent of protonation in solutions of varying acid concentration and (ii) a suitable function defining the acidity of the solution at each acid concentration should be available.

If these two requirements are met it is then possible to estimate pK_{BH^+} values for alcohols by use of eq 1, where H_{ROH} is an acidity function describing the protonation of alcohols.[5,6] Unfortunately, no such alcohol acidity

$$\log \{ROH_2^+\}/\{ROH\} = -H_{ROH} + pK_{BH^+} \quad (1)$$

function has previously been available. However, Yates and McClelland[7] have shown that most known

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