Thermodynamic Determination of pK_a's of Weak Hydrocarbon Acids Using Electrochemical Reduction Data. Triarylmethyl Anions, Cycloheptatrienyl Anion, and Triphenyl- and Trialkylcyclopropenyl Anions

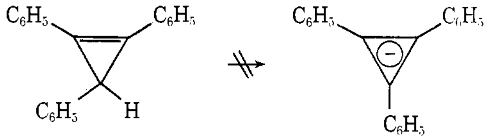
Ronald Breslow* and William Chu

Contribution from the Department of Chemistry,
Columbia University, New York, New York 10027. *Received June 21, 1972*

Abstract: A novel thermodynamic method for determining pK_a's of weak hydrocarbon acids is described. The data required include the pK_{R^+} of the corresponding cation and the two reduction potentials for conversion of the cation through the radical to the anion. These reduction potentials have been determined, using cyclic voltammetry, for a series of triarylmethyl cations, for tropylium ion, and for triphenyl-, trimethyl-, tripropyl-, and tri-*tert*-butylcyclopropenyl cations. The derived pK_a's for the triarylmethanes and for cycloheptatriene agree with values determined by direct equilibration. The pK_a's for the cyclopropenes, determined by this method, are quite high; that for triphenylcyclopropene, +50, is approximately 20 units higher than the pK_a of triphenylmethane, while the trialkylcyclopropenes have the highest pK_a's for which there is direct experimental evidence, +62, +64, and +65. These values are consistent with antiaromatic destabilization of the cyclopropenyl anion system. The effect of possible triplet ground states for the tropylium and cyclopropenyl anions on these studies is also considered.

Kinetic studies[1] on the rates of deuterium exchange of a variety of cyclopropene derivatives reveal that the conjugated cyclopropenyl anion system is difficult to form, at least as judged by kinetics. A number of kinds of evidence indicate that the low rate of base-catalyzed deuterium exchange in these compounds reflects antiaromatic[2] instability in the cyclopropenyl anion as a major contributor to the low rates of ionization. Although these kinetic indications are informative, it would clearly also be desirable to have equilibrium data on the acidities of cyclopropenes, including cyclopropenes with simple substituents such as phenyls or alkyls.

Direct equilibration of compounds such as 1,2,3-triphenylcyclopropene (I) with the triphenylcyclopropenyl anion (II) is apparently impossible. Reaction of I with strong bases has led to a number of remarkable reactions,[3] but no evidence that the proton could be removed from triphenylcyclopropene even transiently. For this reason we have been forced to develop a new method[4] to determine the pK_a of such compounds as 1,2,3-triphenylcyclopropene and 1,2,3-trimethylcyclopropene.



I

II

Several methods are available[5] for estimating the pK_a's of very weak acids, such as hydrocarbons. The ideal procedure uses equilibration[6] to construct a pK_a scale, starting with a compound whose pK_a can be determined using the glass electrode, and carrying out a series of equilibrations with compounds of decreasing acidity in order to extend the pK_a scale out of the region in which the glass electrode is usable.[7] However, extrapolation to pK_a's much above 30 is difficult. In our case the method is ruled out by the fact that simple cyclopropenes apparently cannot be converted to the corresponding 3 anions. Furthermore, in compounds such as trimethylcyclopropene it is likely that the 3 hydrogen is not the most acidic one in the molecule.

A number of attempts have been made[8] to use kinetics to determine pK_a's, based on the fact that it is possible to carry out base-catalyzed deuterium or tritium exchange even with some very nonacidic hydrocarbons. The rate of base-catalyzed exchange in such systems might be related to the equilibrium acidity by the well-known Brønsted relationship. The Brønsted coefficient α can be determined for compounds whose pK_a is also accessible by equilibration, and it can be hoped that the Brønsted coefficient would be constant into the region of higher pK_a's in which direct equilibration methods are not possible. Unfortunately, there is evidence[9] that the Brønsted coefficients are not in fact constant, and that simple kinetic methods for determining acidities may be in considerable error. In particular, it seems that the Brønsted coefficient α undergoes a large change[9] on going from delocalized anions whose pK_a's can be determined by equilibration to more localized anions such as CH_3^-. In addition to this general problem with kinetic methods, in our case they are not applicable. Triphenylcyclopropene, for instance, is kinetically inert under conditions in

---

(1) R. Breslow, J. Brown, and J. J. Gajewski, *J. Amer. Chem. Soc.*, **89**, 4383 (1967); R. Breslow and M. Douek, *ibid.*, **90**, 2698 (1968); R. Breslow, *Angew Chem., Int. Ed. Engl.*, 7, 565 (1968).

(2) R. Breslow, *Chem. Eng. News*, **43**, 90 (1965).

(3) R. Breslow and P. Dowd, *J. Amer. Chem. Soc.*, 85, 2729 (1963).

(4) For preliminary reports of this method, *cf.* (a) R. Breslow and K. Balasubramanian, *ibid.*, **91**, 5182 (1969); (b) R. Breslow and W. Chu, *ibid.*, **92**, 2165 (1970).

(5) *Cf.* D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965.

(6) W. K. McEwen, *J. Amer. Chem. Soc.*, 58, 1124 (1936); J. B. Conant and G. W. Wheland, *ibid.*, 54, 1212 (1932).

(7) C. D. Ritchie and R. F. Uschold, *ibid.*, 90, 2821 (1968), and earlier studies, sho wthat the glass electrode can be used to evaluate pK_a's up to 30, in nonaqueous solutions.

(8) (a) A. Shatenshtein, *Advan. Phys. Org. Chem.*, 1, 175 (1963); (b) A. Streitwieser, R. Caldwell, and M. Granger, *J. Amer. Chem. Soc.*, **86**, 3578 (1964).

(9) C. D. Ritchie, *ibid.*, **91**, 6749 (1969).

Table I. Thermodynamic Data

R	Anion (salt)	$E_{1/2}$ in V *vs.* sce		pK_{R^+}	pK_a calcd	pK_a by equilibration
		1st wave	2nd wave			
Triphenylmethyl	ClO_4^-	0.19 ± 0.05	-1.05 ± 0.07	-6.6	31.5	31.5
Tris(*p*-chlorophenyl)methyl	ClO_4^-	0.23 ± 0.05	-0.87 ± 0.07	-7.7	28.9 ± 2.0	30.1 ± 0.5
Dimethylaminophenyldiphenylmethyl	ClO_4^-	-0.35 ± 0.05	-1.22 ± 0.07	3.6	33.1 ± 2.0	34.8 ± 0.5
Tris(*p*-dimethylaminophenyl)methyl	Cl^-	-0.74 ± 0.05	-1.61 ± 0.07	9.4	40.3 ± 2.0	High
p-Methoxyphenyldiphenylmethyl	ClO_4^-	0.09 ± 0.05	-1.22 ± 0.07	-3.4	32.8 ± 2.0	32.5 ± 0.5
Tris(*p*-methoxyphenyl)methyl	ClO_4^-	-0.07 ± 0.05	-1.42 ± 0.07	0.8	34.6 ± 2.0	33.3 ± 0.05
7-Cycloheptatrienyl	BF_4^-	-0.23 ± 0.07	-1.51 ± 0.12	4.7	36 ± 3	36
Triphenylcyclopropenyl	ClO_4^-	-0.85 ± 0.10	-1.73 ± 0.15	3.1	50 ± 4	
Trimethylcyclopropenyl	ClO_4^-	-1.32 ± 0.15	-2.22 ± 0.15	7.4	62 ± 5	
Tripropylcyclopropenyl	BF_4^-	-1.36 ± 0.15	-2.30 ± 0.15	7.0	64 ± 5	
Tri-*tert*-butylcyclopropenyl	ClO_4^-	-1.53 ± 0.15	-2.12 ± 0.15	6.5	65 ± 5	

which triphenylmethane undergoes rapid exchange,[3] and with more vigorous conditions triphenylcyclopropene undergoes other irrelevant reactions.

Some approaches have been made to the application of electrochemistry to the determination of pK_a's.[10] Perhaps the most interesting is a study[10c] of the polarographic reduction of various dialkylmercury compounds. These undergo an irreversible reduction to generate the transient alkyl anion, and the possibility was examined that the ease of cleavage of the carbon–mercury bond, as reflected in the reduction potential, might run parallel to the pK_a of the related carbon–hydrogen bond. Since the reductions were quite irreversible electrochemically, the equilibrium acidity was plotted *vs.* $\alpha E_{1/2}$, rather than *vs.* $E_{1/2}$ itself. The reduction of a wide range of mercury derivatives was examined. The plot of $\alpha E_{1/2}$ *vs.* the "known" pK_a's defines a straight line which was used with the reduction potential for dimethylmercury to deduce a pK_a for methane of 57. Unfortunately, very few of the "known" pK_a's are reliable, and there is no theoretical value for the slope of the line from such a plot. Thus, while this polarographic method is attractive, it will require further exploration to establish whether it is reliable and to determine the best values for the electrochemical pK_a's. In any case, this technique is not available to us, since no 3-cyclopropenylmercury compounds are known.

Our Thermodynamic pK_a Method. Although simple covalent cyclopropenes cannot be in general equilibrated with cyclopropenyl anions, there is no difficulty in determining the equilibrium constant for conversion of a covalent cyclopropene to the cyclopropenyl cation.[11] Furthermore, some years ago we demonstrated[12] that it is possible to achieve the reversible reduction of triarylcyclopropenyl cations to the triarylcyclopropenyl radicals by the use of rapid-scan cyclic voltammetry, even though the resulting radicals undergo rapid irreversible dimerization. It occurred to us[4] that these facts could be combined in the construction of a thermodynamic sequence by which a covalent cyclopropene is reversibly converted to the cyclopropenyl anion, even though this cannot be achieved directly. The sequence is shown in eq 1.

$$R{-}H \rightleftarrows R{-}OH \overset{H^+}{\rightleftarrows} R^+ \overset{e}{\rightleftarrows} R\cdot \overset{e}{\rightleftarrows} R^-$$

The first step, reversible conversion of a hydrocarbon to the corresponding alcohol, is of course not a chemical process. This requires the sort of thermodynamic information available[13] from heats of formation or bond dissociation energies. Conversion of an alcohol reversibly to the carbonium ion is generally possible only for fairly stable carbonium ions such as the cyclopropenium ions,[11] the triarylmethyl cations,[14] and the tropylium ion.[15] Reversible one electron reduction of these cations to the corresponding radicals will usually require fast electrochemical techniques, such as cyclic voltammetry,[16] if a potential close to the reversible potential[17] is to be measured. Reduction of the unstable radicals to the corresponding anions is even more of a problem, since these are to be generated in a carbonium ion solution. Again with the use of fast electrochemical methods it is possible to measure a potential for this process with all the carbonium ions we have investigated, but the general irreversibility in these systems is such that this number is the least reliable one. The known pK_{R^+}'s, and our measured reduction potentials, for a series of triarylmethyl cations, for tropylium ion, and for several cyclopropenyl cations are listed in Table I.

Other studies have been done on the electrochemistry of some of these species. Thus, Bahary[12,18] has studied the cyclic voltammetry of a series of substituted triarylcyclopropenium ions, and Balasubramanian[4a] did some preliminary work on our current system. Volz and Lotsch have reported[19] reduction potentials for some triarylmethyl cations and the tropylium ion, while Feldman[20] has studied the one- and two-electron

---

[10] (a) R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen, and T. Chivers, *J. Amer. Chem. Soc.*, **88**, 460 (1966); (b) A. Streitwieser and C. Perrin, *ibid.*, **86**, 4958 (1964); (c) C. K. P. Butin, I. P. Beletskaya, A. N. Kashin, and O. A. Reutov, *J. Organometal. Chem.*, 10, 197 (1967).

[11] *E.g.*, R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 2367 (1961), for triarylcyclopropenium ions; P. Breslow, H. Hover, and H. W. Chang, *ibid.*, **84**, 3168 (1962), for trialkylcyclopropenium ions; R. Breslow and J. T. Groves, *ibid.*, **92**, 984 (1970), for the parent cyclopropenium ion.

[12] R. Breslow, W. Bahary, and W. Reinmuth, *ibid.*, **83**, 1763 (1961).

[13] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

[14] N. Deno and A. Shriesheim, *J. Amer. Chem. Soc.*, 77, 3051 (1955).

[15] W. Doering and L. Knox, *ibid.*, **76**, 3203 (1954).

[16] R. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969; L. Meites, "Polarographic Techniques, 2nd ed, Interscience, New York, N. Y., 1965.

[17] R. Nicholson, and I. Shain, *Anal. Chem.*, **36**, 706 (1964); W. Reinmuth, *ibid.*, **33**, 1793 (1961).

[18] W. Bahary, Ph.D. Thesis, Columbia University, 1961.

[19] H. Volz and W. Lotsch, *Tetrahedron Lett.*, 2275 (1969).

Table II. Cyclic Voltammetry Data for the First Reduction Wave of Triarylmethyl Cations

Compd	Frequency, V sec^{-1}	Cathodic peak potential, V	Anodic peak potential, V	i_{Cathodic}, μA	i_{Anodic}, μA
Triphenylmethyl perchlorate	0.14	+0.14	+0.26	44	29
	0.56	+0.12	+0.27	81	71
	1.12	+0.11	+0.29	111	111
	(0)	(+0.14)	(+0.25)		
Tris(*p*-chlorophenyl)methyl perchlorate	0.15	+0.11	+0.35	24.8	20.2
	0.77	+0.08	+0.40	51.8	40.5
	1.55	+0.04	+0.42	72.0	58.5
	(0)	(+0.12)	(+0.34)		
p-Methoxyphenyldiphenylmethyl perchlorate	0.24	+0.03	+0.15	8.4	7.8
	2.41	−0.02	+0.21	21.6	21.6
	6.05	−0.06	+0.25	31.8	31.8
	(0)	(+0.03)	(+0.15)		
Tris(*p*-methoxyphenyl)-methyl perchlorate	0.11	−0.17	+0.03	22.5	21.0
	0.54	−0.28	+0.14	46.5	45.0
	1.09	−0.32	+0.21	60.0	60.0
	(0)	(−0.15)	(+0.0)		
Tris(*p*-dimethylamino-phenyl)methyl chloride	1.1	−0.80	−0.68	27	27
	4.5	−0.86	−0.62	52	52
	11.2	−0.91	−0.56	77	77
	(0)	(−0.78)	(−0.70)		
p-Dimethylaminophenyl-diphenylmethyl perchlorate	0.064	−0.41	−0.29	32.4	27.0
	0.128	−0.42	−0.28	43.2	37.8
	0.640	−0.46	−0.25	91.8	86.4
	(0)	(−0.41)	(−0.30)		

reduction of a number of carbonium ions in concentrated sulfuric acid solution. Kothe, *et al.*,[21] have also done polarography on some relevant organic ions. Some of these methods have the difficulty that the resulting potentials are highly irreversible, but our data in Table I are consistent with the best of the literature values, making allowances for differences in solvent systems.

Taft has constructed[22] emf cells with which he can determine true reversible potentials for the one-electron reduction of triarylmethyl cations and the one-electron oxidation of triarylmethyl anions, although the two systems were in different solvents. The other component in each case is the equilibrium mixture of the triarylmethyl radical with its dimer. Thus the individual reduction potentials are not directly comparable to those we have reported for our reductions, which are run rapidly enough that dimerization of the radicals is suppressed. Furthermore, this type of equilibration is only possible for systems in which the dimer is in equilibrium with its radical, and this is not true of the cyclopropenyl systems. Although the individual potentials from Taft's work are thus not comparable with ours, the sum of the potentials from his processes indicates the energy change on passing from a triarylmethyl cation to triarylmethyl anion. This may be directly compared with the sum of our first and second reduction potentials, since now the question of the exact nature of the radical intermediate is irrelevant. Taft's data indicate that reduction of trianisylmethyl cations is 0.727 eV more difficult than is reduction of triphenylmethyl cation, while our data indicate 0.63 eV for this same difference. Similarly, the addition of three dimethylamino groups to the triphenylmethyl cation makes the two-electron reduction more difficult by 1.255 eV from Taft's data, while from our data the change is 1.49 eV. The agreement is fairly good, especially considering that the two emf cells examined by Taft involved different solvents.

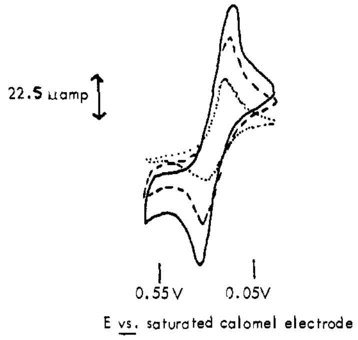


Figure 1. Cyclic voltammogram (CV) of triphenylmethyl perchlorate in dimethyl sulfoxide (DMSO) at Pt disk electrode. Triphenylmethyl perchlorate concentration 5 m*M*, 0.1 *M* tetra-*n*-butylammonium perchlorate (TBAP) support electrolyte, scan rates of 0.14, 0.56, and 1.12 V/sec.

Triarylmethyl Anions. Figure 1 is the cyclic voltammogram of triphenylmethyl perchlorate at various sweep frequencies, passing through the potential of the first reduction. These data are presented in Table II and the cathodic peak current is plotted *vs.* the square root of the frequency[23] in Figure 2. Figure 3 is a typical scan through both reduction waves of a triarylmethyl cation, indicating the poor reversibility of the second wave. Figures 4 and 5 show each of these two individual waves when they are separately scanned. For waves in which both the cathodic and the anodic component could be seen we take $E_{1/2}$ to be the mid point between these two peaks, extrapolated to zero sweep frequency. In cases where chemical irreversibility is so large that a clear anodic peak cannot be

---

(20) M. Feldman and W. Flythe, *J. Amer. Chem. Soc.*, **91**, 4577 (1969).

(21) G. Kothe, W. Sümmermann, H. Baumgärtel, and H. Zimmermann, *Tetrahedron Lett.*, **26**, 2186 (1969).

(22) E. Jenson and R. Taft, *J. Amer. Chem. Soc.*, **86**, 116 (1964); L. McKeever and R. Taft *ibid.*, **88**, 4544 (1966).

(23) This is the expected[17] relationship for a true reversible potential.

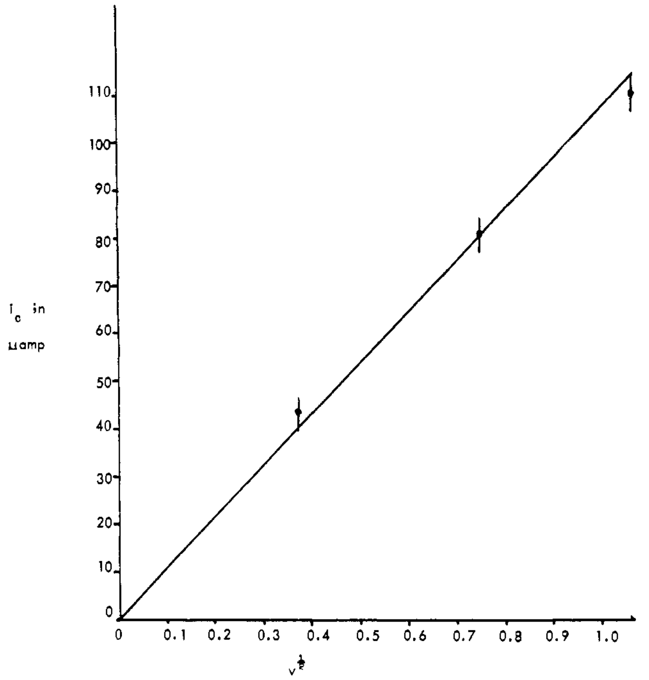


Figure 2. Plot of i_c (the cathodic peak current) *vs.* $v^{1/2}$ (square root of the frequency, which is in V/sec) for the voltammogram of 5 m*M* of triphenylmethyl perchlorate in dimethyl sulfoxide (1st wave).

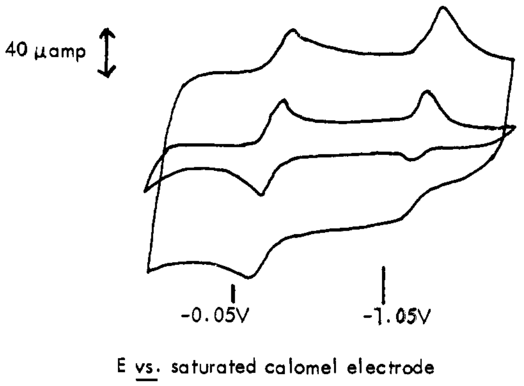


Figure 3. CV of *p*-dimethylaminophenyldiphenylmethyl perchlorate in DMSO at Pt disk electrode. Triarylmethyl perchlorate concentration 3 m*M*, 0.1 *M* TBAP, scan rates of 1.92 and 19.2 V/sec.

discerned we take $E_{1/2}$ to be at 85%[24] of the cathodic peak. These values are likely to be close to the true reversible potentials, and this is confirmed by the finding[25] that under identical conditions the two cyclic voltammetric $E_{1/2}$'s determined for triphenylmethyl cation reduction and those determined for triphenylmethyl anion oxidation in an independent experiment are identical, within close experimental error. Thus, for the triphenylmethyl series the first and second reduction potentials are reasonably well known. pK_{R^+}'s are also known for this series of cations, and these are included in Table I.

The additional piece of information required to calculate a pK_a is the energy change on conversion of a triarylmethane to the corresponding triarylcarbinol. To solve this, and a variety of related problems, we adopt triphenylmethane as our standard reference compound for which a pK_a of 31.5 is taken as known.[26] The energy change on converting other triarylmethanes to the corresponding triarylcarbinols should be identical with that for the unsubstituted case, since these energy differences do not vary widely in any case[13] and certainly would not be subject to minor substituent effects. Thus, the pK_a's of the substituted triarylmethanes can be calculated, using triphenylmethane as the standard, and these pK_a's are also listed in Table I.

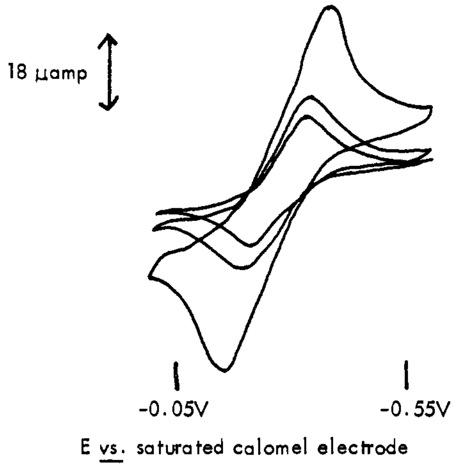


Figure 4. CV of *p*-dimethylaminophenyldiphenylmethyl perchlorate in DMSO at Pt disk electrode. Triarylmethyl perchlorate concentration 3 m*M*, 0.1 *M* TBAP supporting electrolyte, scan rates of 0.064, 0.128, and 0.640 V/sec.

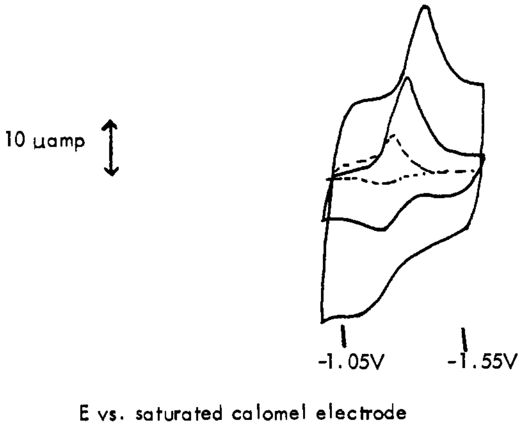


Figure 5. CV of *p*-dimethylaminophenyldiphenylmethyl perchlorate in DMSO at Pt disk electrode. Triarylmethyl perchlorate concentration 3 m*M*, 0.1 *M* TBAP supporting electrolyte, scan rates of 0.12, 1.2, and 6.2 V/sec.

As an example of such calculation, consider the pK_a of *p*-methoxyphenyldiphenylmethane. The pK_{R^+} of the corresponding cation (-3.4) is 3.2 log units more favorable than that for triphenylmethyl cation (-6.6). However, the reduction of cation to anion is 0.27 eV more difficult for the substituted case [$(0.19 - 0.09) + (-1.05 + 1.22)$]. Since at room temperature each 59 MeV corresponds to one log unit in the equilibrium constant, this 270 MeV means 4.5 log units. The

---

[24] This is the theoretical value for a reversible process, at slow scan. Increased scan frequency moves the peak to a negative potential, while irreversible chemical removal of reduction products moves it to a positive potential. Thus these effects will tend to cancel each other, and our treatment assumes that they do.

[25] Unpublished work of S. Mazur; *cf.* ref 21 for a related observation.

[26] A. Streitwieser, W. Hollyhead, G. Sonnichsen, A. Pudjaatmaka, C. Chang, and T. Kruger, *J. Amer. Chem. Soc.*, **93**, 5096 (1971).

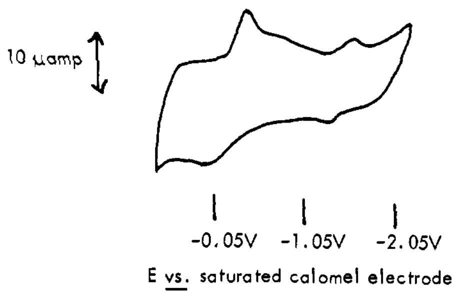


Figure 6. CV of tropylium fluoroborate in DMSO at Pt disk electrode. Tropylium fluoroborate concentration 2 mM, 0.1 M TBAP supporting electrolyte, scan rate of 22.2 V/sec.

pK_a is thus 1.3 units (4.5 − 3.2) higher than that of triphenylmethane.

Perhaps the most important result is that the pK_a's for many of these compounds are calculated to be similar, although the corresponding carbonium ions have widely different stabilities. We have directly determined the pK_a's for these substituted triarylmethanes by equilibration as a further check on our method. The results of these equilibrations are also indicated in Table I, again based on the convention that triphenylmethane has a pK_a of 31.5. The pK_a of *p*-dimethylaminophenyldiphenylmethane was determined relative to diphenylmethane, which was taken[26] to have a pK_a of 33.5. Tris(*p*-dimethylaminophenyl)methane did not afford an anion even on vigorous treatment with methyllithium, so its pK_a is simply listed as "high." It is apparent that our thermodynamic method gives good agreement with equilibration data for the series of triarylmethanes.

Cycloheptatrienyl Anion (III). In Figure 6 is the cyclic voltammogram for tropylium fluoroborate at a very high scan rate, while in Figure 7 is the cyclic voltammogram for the first reduction wave as a function of scan rate. It is apparent that both waves are chemically irreversible, and the second wave is only visible[23] at very high scan rates. Thus, $E_{1/2}$ for the first wave was taken[24] at 85% of the peak height at 7.5 V/sec sweep, while $E_{1/2}$ for the second wave was taken[24] at 85% of the cathodic peak at 32 V/sec. These values are also listed in Table I, along with the known pK_{R^+} for tropylium ion.

III

The missing leg of our thermodynamic cycle is the energy change on conversion of cycloheptatriene to cycloheptatrienol. This could again be taken as identical with the change for triphenylmethane, but thermodynamic data in the literature[13] suggest that at secondary carbons the hydrocarbon is favored over the alcohol by 2 kcal/mol more than it is at tertiary carbons, such as those of triphenylmethane. There is no evidence for major effects of phenyl substituents *per se*, since the difference in bond dissociation energies[13] for toluene *vs.* benzyl alcohol are essentially the same as those differences for other primary carbons such as ethyl or *n*-propyl. Accordingly, the pK_a calculated by our electrochemical method has been corrected by this 2 kcal/mol, although the effect of this on the calculated pK_a is small.

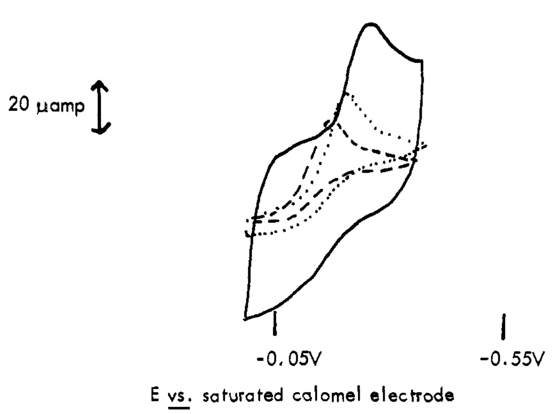


Figure 7. CV of tropylium fluoroborate in DMSO at Pt disk electrode. Tropylium fluoroborate concentration 2 mM, 0.1 M TBAP supporting electrolyte, scan rate of 0.075, 0.75, and 7.5 V/sec.

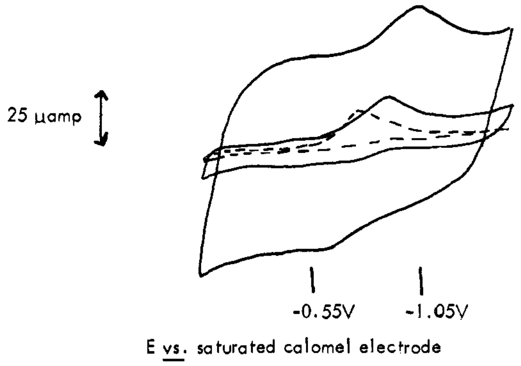


Figure 8. CV of triphenylcyclopropenium perchlorate in DMSO at Pt disk electrode. Carbonium ion concentration 2 mM, 0.1 M TBAP supporting electrolyte, scan rates of 0.29, 2.9, and 29 V/sec.

As can be seen from the table, our resulting pK_a is in excellent agreement with the value roughly determined[27] by Dauben whether this correction is made or not. This suggests that even with such poorly reversible electrochemistry as that indicated in Figures 6 and 7 there are not major errors introduced in the pK_a's.

Cyclopropenyl Anions. Figure 8 shows the cyclic voltammogram for the first reduction wave of triphenylcyclopropenium perchlorate at several sweep rates. It is apparent that this is chemically irreversible, and only at high sweep rates is it perhaps possible to distinguish both a cathodic and an anodic peak. $E_{1/2}$ for the first wave was obtained by averaging the potentials at 85% of the peak heights for sweeps at 2.9 and 29 V/sec; the value which is listed in Table I is in good agreement with that from our previous studies.[12,18] A second irreversible wave was found at −1.73 V. This was determined to be the second reduction wave of the cation because of its characteristic very large increase in intensity with increasing scan rate. This abnormal dependence of intensity on scan rate is expected from the general theory[28] of a situation in which reduction must compete with irreversible dimer-

---

(27) H. Dauben and M. Rifi, *J. Amer. Chem. Soc.*, **85**, 3041 (1963).

(28) This situation is treated in standard texts, *e.g.*, R. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969; the general problem is that material diffuses to the electrode slowly on the time scale involved, so with a slow scan all the cation is removed by one-electron reduction and dimerization before the second potential has been reached.

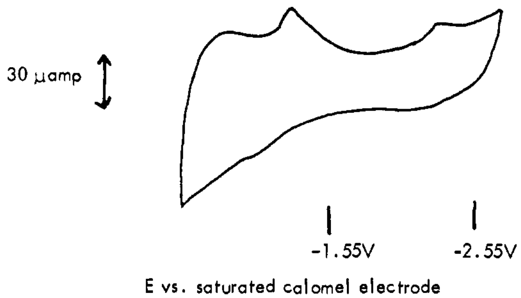
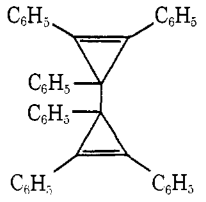


Figure 9. CV of trimethylcyclopropenium perchlorate in DMSO at Pt disk electrode. Carbonium ion concentration 3 m*M*, 0.1 *M* TBAP supporting electrolyte, scan rate of 22.2 V/sec.

ization of the triphenylcyclopropenyl radical; it is also consistent with our observations in the tropylium reductions.

Controlled potential electrolysis at either the first or second reduction potential, even in the presence of acetic acid, yielded only bistriphenylcyclopropenyl (IV)[29] as product, and no triphenylcyclopropene could be detected.[30] Apparently the triphenylcyclopropenyl anion (II) also gives dimer (IV), either by reacting with triphenylcyclopropenyl cation at the electrode or by giving up its electron in some other way and dimerizing as the radical. A similar effect is seen with cycloheptatrienyl anion, which could be trapped only to afford biscycloheptatrienyl, even in the presence of acetic acid. Failure of II or III to protonate is curious, and possibly significant. Anions II or III could be ground-state triplets,[31] a general possibility for $4n$-π-electron systems with C_3 or greater symmetry. If so, they would be formed in the triplet state, and this could raise a barrier to direct protonation to afford (singlet) triphenylcyclopropene or cycloheptatriene. Coupling of the anions with cations to form dimers might involve prior electron transfer, thus solving the multiplicity problem. However, further studies will be needed to explore this question.



IV

The two reduction potentials are listed in Table I, together with the known pK_{R^+} for triphenylcyclopropenyl cation. The missing leg of our thermodynamic cycle in this case, the energy of conversion of hydrocarbon to alcohol (relative to that for our standard compound triphenylmethane), is more of a problem. While this also involves a tertiary carbon, for which triphenylmethane might be considered a good model, the hybridization in the cyclopropene ring is such that the orbital used to bond the hydrogen or hydroxyl group should be considerably more electronegative than that of a simple open chain system.

Good data are not available which will permit us to assess the effect of this correction. One might expect that electropositive hydrogen would be better put on the electronegative orbital of a cyclopropene than would electronegative hydroxyl, all relative to the situation in open chain compounds. However, data[13] for electronegative phenyl or vinyl carbons attached to such electronegative groups as chlorine, bromine, or iodine suggest that the effects involved may amount to only a few kilocalories per mole.

In the absence of a good way of estimating this, we take the energy of conversion of triphenylcyclopropene to triphenylcyclopropenol to be identical with that for the conversion of triphenylmethane to triphenylcarbinol. The pK_a for triphenylcyclopropene listed in Table I reflects this assumption. If instead the cyclopropene carbon has an increased preference for binding hydrogen rather than hydroxyl, then we have underestimated the pK_a for triphenylcyclopropene. It would have to be raised by an amount corresponding to the energy correction, *i.e.*, by a few pK_a units. Similarly, if the high chemical irreversibility in the cyclopropenyl cyclic voltammogram has seriously perturbed our estimates of the reversible potentials, this would again lead to an underestimate of the pK_a by our method. This is because rapid chemical destruction of the product of a reduction shifts the observed peak to positive[17] potentials relative to the true $E_{1/2}$. Thus our value is a lower limit to the true pK_a of triphenylcyclopropene if electrochemical nonreversibility is a serious problem which is not balanced (or overbalanced) by iR drop.

The pK_a of triphenylcyclopropene is of the order of 20 or more units higher than that of triphenylmethane. This corresponds to a very low acidity for the cyclopropene system.[32] In the triphenylcyclopropenyl anion the phenyl groups should be more nearly coplanar with the rest of the system than they are in the triphenylmethyl anion, and this effect should have made triphenylcyclopropene more acidic than triphenylmethane. Two effects[1] which operate in the other direction are an increase in I-strain in the cyclopropene system on ionization, and the antiaromatic destabilization of the anion by interaction with the double bond in the cyclopropenyl ring. While it is difficult to make a quantitative separation of these two effects, it seems likely that both are contributing to the remarkably high pK_a of triphenylcyclopropene. It should also be noted that the triphenylcyclopropenyl anion which we are generating electrochemically has the symmetry requirements to be a ground-state triplet molecule, and if it is a triplet then the pK_a for ionization to the singlet would be even higher.

Figure 9 shows the cyclic voltammogram for trimethylcyclopropenium perchlorate[33] at a very high scan rate. Again the two waves are chemically ir-

---

[29] R. Breslow and P. Gal, *J. Amer. Chem. Soc.*, **81**, 4747 (1959).

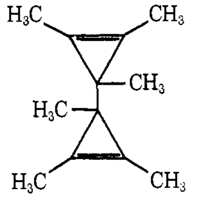
[30] This is especially curious since we had found[3], that zinc and acetic acid reduces triphenylcyclopropenyl cation to triphenylcyclopropene. Probably this latter reaction involves an organozinc, not a free carbanion.

[31] *Cf.* R. Breslow, H. W. Chang, R. Hill, and E. Wasserman, *J. Amer. Chem. Soc.*, **89**, 1112 (1967), and references.

[32] M. A. Battiste and C. T. Sprouse, Jr., *Tetrahedron Lett.*, 3165 (1969), estimate the pK_a of triphenylcyclopropene to be <37 from the fact that 1,2,3-triphenylcyclopropenyltriphenylphosphonium hydroxide cleaves to afford triphenylcyclopropene, not benzene. Cleavage in the cyclopropenyl direction can occur by allylic protonation, *e.g.*, in a cyclic six-atom transition state. Thus these kinetic observations do not necessarily furnish any information about triphenylcyclopropenyl anion, which may well not be involved in the reaction.

[33] G. L. Closs, W. A. Böll, H. Heyn, and V. Dev, *J. Amer. Chem. Soc.*, 90, 173 (1968).

reversible. The second reduction wave appears only at very high scan rates, and increases strongly in intensity as scan rates are increased. $E_{1/2}$ for the first wave was taken at 85% of the peak height at a scan rate of 11 V/sec, while $E_{1/2}$ for the second wave was taken in the same fashion at a scan rate of 45 V/sec. Similar behavior was observed for tripropylcyclopropenium fluoroborate[34] and tri-*tert*-butylcyclopropenium perchlorate.[35] In both of these cases second waves appeared only at very high frequencies, and the $E_{1/2}$'s were all determined at very high scan rates by taking a value at 85% of the cathodic peak. Controlled potential electrolysis of trimethylcyclopropenium fluoroborate at the first potential afforded hexamethylbenzene,[36] presumably *via* the biscyclopropenyl V.[37]



V

The electrochemical data are listed in Table I together with the known pK_{R^+}'s for these three cations and the calculated pK_a's from our technique. Again, there is a problem in deciding on the energy change when the hydrocarbon is converted to the alcohol, and again triphenylmethane is taken as the standard for this change in the absence of other information. Thus these may also be underestimates of the pK_a's for the three trialkylcyclopropenes, both because of this approximation and because of the high chemical irreversibility of the reductions. However, the pK_a's derived by our technique are internally consistent among the three compounds, and reasonable compared with the pK_a for the triphenylcyclopropene.

These three values are the highest pK_a's for which there is a direct experimental basis, and they exceed any experimental[38] estimates of the pK_a of simple hydrocarbons such as methane. However, it is difficult to evaluate this situation exactly, since it seems likely that the pK_a of methane has been underestimated by the experimental techniques applied to date. If the pK_a scale for very weak acids can be put on a solid experimental basis, *e.g.*, by using electrochemical techniques, the meaning of the pK_a's of these alkylcyclopropenes will become clearer.

Experimental Section

Materials. Spectroquality dimethyl sulfoxide (Matheson Coleman and Bell) was distilled over calcium hydride. Chromatoquality acetonitrile (Matheson Coleman and Bell) was distilled over P_2O_5 under N_2. Analytical grade tetrahydrofuran (Mallinckrodt) was distilled over $LiAlH_4$. Tetra-*n*-butylammonium perchlorate (Matheson Coleman and Bell) was dried under vacuum for 5 hr at 60° and stored in a desiccator. Trimethylcyclopropenium perchlorate and tri-*tert*-butylcyclopropenium perchlorate were kindly provided by Professor J. Ciabattoni. Literature procedures were used for the preparation of tripropylcyclopropenium fluoroborate, tropylium fluoroborate, 1,2,3-triphenylcyclopropene, bistriphenylcyclopropenyl, triphenylcyclopropenium perchlorate, and the various triarylcarbinols, triarylcarbenium salts, and triarylmethanes.

Cyclic Voltammetry. Carefully dried apparatus, and syringe techniques under an inert atmosphere, were used. All solutions were 0.1 *M* in tetrabutylammonium perchlorate and 2–5 m*M* in substrate, in dimethyl sulfoxide solution. A three-electrode cell utilized a Beckman platinum electrode and a platinum wire auxiliary electrode. The Ag|AgCl (in dimethyl sulfoxide saturated with KCl) reference electrode was separated from the solution through an asbestos fiber sealed in a glass probe. This reference electrode has a potential of 0.005 ± 0.01 V *vs.* the saturated calomel electrode, and the potential is stable over a period of several hours. Cyclic repetitive potential sweeps were generated by a Hewlett–Packard low frequency generator (Model 202A) in conjunction with a Princeton Applied Research Model 173 potentiostat. Sweep ranged from 0.01 to 47 V/sec. A Tektronix 5103N (D11 single beam storage display unit) oscilloscope was used as a recorder.

Controlled Potential Electrolysis. The electrolysis cell was an H-type vessel whose two compartments, 150 ml each, were separated by a fritted glass disk. One compartment contained a mercury pool cathode, a magnetic stirring bar, and a saturated calomel electrode. The other compartment contained a platinum wire auxiliary electrode. Solutions of 0.5–2.0 g of carbonium ion salts in 100 ml of 0.2 *M* tetrabutylammonium perchlorate in acetonitrile were introduced into the cathode compartment. The anode compartment contained only solvent and electrolyte. The solution was deoxygenated and kept under an argon atmosphere during electrolysis, using the Model 173 potentiostat. After the current had fallen to 5% of its peak value the electrolysis was stopped and the cathodic solution was poured into 500 ml of H_2O and 200 ml of ether. In this fashion, electrolysis of tropylium fluoroborate at −2.0 V yielded 90% of bitropyl, mp 62–63° (lit.[39] 60–61°). Electrolysis in the same fashion but with a 1:1 acetic acid–acetonitrile solvent mixture also afforded 89% of bitropyl. Electrolysis of triphenylcyclopropenium bromide in acetonitrile at −2.3 V afforded a 90% yield of bistriphenylcyclopropenyl, mp 246–247° (lit.[29] 255–256°), identical with an authentic sample. The same product was obtained when the electrolysis was performed in a 1:1 acetic acid–acetonitrile solution. Electrolysis of triphenylmethyl perchlorate in acetic acid–acetonitrile at −1.35 V afforded an 88% yield of triphenylmethane.

Equilibration Experiments. Three different procedures were tested to establish reliability. In one, 1 mmol of *p*-methoxyphenyldiphenylmethane and 1 mmol of triphenylmethane were dissolved in 5 ml of carefully dried tetrahydrofuran under nitrogen. One drop of diethylamine was added, then 1 ml of a 1.6 *M* *n*-butyllithium solution in hexane was added in 5 ml of tetrahydrofuran and the red solution was stirred at room temperature for 10 min (controls established that longer times were not needed). This was then quenched by rapid addition of 3 ml of D_2O, followed shortly thereafter by 1 ml of glacial acetic acid. The mixture of triarylmethanes was taken up in $CDCl_3$ and analyzed by integration of the appropriate nmr signals. In this run 72% of the triphenylmethane was deuterated and 22% of the *p*-methoxyphenyldiphenylmethane was deuterated, giving a pK_a value for *p*-methoxyphenyldiphenylmethane of 32.5. In another equilibration, the butyllithium and *p*-methoxyphenyldiphenylmethane were first mixed to form the anion, and the triphenylmethane was then added. After quenching and work-up, 27% of the *p*-methoxyphenyldiphenylmethane was deuterated and 79% of the triphenylmethane was deuterated, again giving a pK_a value of 32.5 for *p*-methoxyphenyldiphenylmethane. Using the alternative sequence, triphenylmethane was first allowed to react with butyllithium and the *p*-methoxyphenyldiphenylmethane was then added. In this experiment, 13% of the *p*-methoxyphenyldiphenylmethane was deuterated and 68% of the triphenylmethane was deuterated, giving *p*-methoxyphenyldiphenylmethane a pK_a value of 32.7. Since these controls and our previous studies[40] indicated that equilibration is rapid in the presence of diethylamine, the first procedure described was generally adopted for equilibrating the other compounds. In the case of *p*-dimethyl-

---

(34) R. Breslow, H. Höver, and H. W. Chang, *J. Amer. Chem. Soc.*, **84**, 3168 (1962).

(35) J. Ciabattoni and E. C. Nathan, III, *ibid.*, **90**, 4495 (1968); **91**, 4766 (1969).

(36) Unpublished work of E. C. Nathan, III, Columbia University.

(37) R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, *J. Amer. Chem. Soc.*, **87**, 5139 (1965).

(38) Estimates vary widely. Thus methane has been assigned a pK_a of 40 (ref 5) and 57 (ref 10c) on an experimental basis, and 40 (R. Pearson and R. Dillon, *J. Amer. Chem. Soc.*, **75**, 2439 (1953)), 58 (R. Bell, "The Proton in Chemistry," Methuen, London, 1959), and 84 (A. Streitwieser, W. Langworthy, and J. Brauman, *J. Amer. Chem. Soc.*, **85**, 1761 (1963), on the basis of semitheoretical arguments.

(39) W. E. Doering and L. H. Knox, *ibid.*, **79**, 352 (1957).

(40) R. Breslow and H. W. Chang, *ibid.*, **87**, 2200 (1965).

aminophenyldiphenylmethane, the compound was equilibrated with diphenylmethane and 0.2 ml of tetramethylethylenediamine was also added to the equilibration solution. Quenching and work-up in the usual way gave 29% deuteration of the triarylmethane and 45% monodeuteration of the diphenylmethane, from which the pK_a of *p*-dimethylaminophenylmethane is taken to be 33.8, assuming that diphenylmethane has a pK_a of 33.5. A solution of tris(*p*-dimethylaminophenyl)methane in tetrahydrofuran with tetramethylethylenediamine and diethylamine was heated with methyllithium at 60-65° for 30 min and quenched with D_2O. No detectable deuteration of the triarylmethane occurred, so this compound could not be equilibrated with the other anions.[41]

---

(41) Support of this work by the National Institutes of Health is gratefully acknowledged.

Medium Dependence of Acidity Functions and Activity Coefficients in Perchloric Acid

Keith Yates,* Henry Wai,[1] Graeme Welch, and Robert A. McClelland

Contribution from the Department of Chemistry, University of Toronto, Toronto 181, Ontario, Canada. *Received June 6, 1972*

Abstract: The H_A and H_0''' acidity scales have been established for 0-75% aqueous perchloric acid solutions, using pK measurements on eight substituted amides and 13 substituted tertiary amines. Activity coefficients of four typical neutral indicator bases and four typical pentacyanopropenide salts have been measured in the same acid region by the solubility technique. Acidity function differences ($H_X - H_0$), based on directly measured values of the acidity functions H_0, H_A, H_0''', H_I, and H_R', can be semiquantitatively reproduced in both $HClO_4$ and particularly H_2SO_4 using the above and other available activity coefficient data. Use of representative activity coefficient and typical acidity function data yields estimates of hydronium ion activities in 0-60% H_2SO_4 and $HClO_4$ solutions which are remarkably independent of the method used to obtain them. The utility of these data is discussed.

It is now clear that the conformity of neutral organic bases to the H_0 acidity function[2] is more the exception than the rule. The only bases that can be expected to follow H_0 closely in their protonation behavior are probably nitroanilines of the type used to make up the set of indicators on which the H_0 scale is based. Other structural classes of base are known to generate their own characteristic acidity functions, such as tertiary anilines[3a] (H_0'''), amides[3b] (H_A), and indoles[4] (H_I) for example. These, and other acidity scales, have been shown to differ considerably from H_0 and from each other in several aqueous mineral acid systems. The failure of the protonation of neutral Brønsted bases to conform to a unique acidity scale, such as H_0, has been termed by Arnett and Mach[5] "acidity function failure." This in our view is a rather misleading terminology, since what has really occurred is not the failure of acidity functions to measure some property of an acidic medium, but a breakdown of the earlier hoped for generality of the H_0 function as a unique measure of the protonating ability (or acidity) of a medium toward all neutral organic bases. What has failed in a general sense is the Hammett activity coefficient postulate,[6] namely that log ($f_{XH^+}f_Y/f_Xf_{YH^+}$) will be essentially medium independent for any pair of organic bases X and Y. It is easy to see in retrospect that such a postulate was bound to fail in the broadest sense, although it is quite probable that it holds within a reasonable degree of precision for each of a number of restricted structural classes of base. Furthermore, it is clear that any hoped for generality of H_0, or any other one acidity function, was also bound to break down in the sense that the acidity of any medium can never be defined uniquely, but only in terms of the particular bases with which it is reacting.

Hopefully, acceptance of this limitation and future measurement and analysis of acidity function behavior in different acid systems will eventually lead to a quantitative understanding of typical activity coefficient behavior of organic bases and their conjugate acids. A knowledge of typical medium variation of these activity coefficients may lead not only to more quantitatively sound measures of acid-base equilibria, but also to increased understanding of the solvent-solute interactions which cause these variations. It is not unreasonable that estimates of typical activity coefficient behavior, combined with observed rate acidity dependences, may even lead to quantitative estimates of transition-state-solvent interactions and thus to a better understanding of the mechanisms of acid-catalyzed reactions.

It is thus important to obtain more extensive data on acidity function and activity coefficient behavior, particularly in media other than aqueous sulfuric acid which has tended to be the predominantly used medium. This is important, not only for making comparisons between the strengths of various acids, but also to extend and test the generality of any conclusions regarding the factors which cause general acidity function breakdown. Apart from acidity functions which deal with

---

(1) Deceased.

(2) For a recent and complete review of acidity functions and their measurement see C. H. Rochester, "Acidity Functions," Academic Press, New York, N. Y., 1970.

(3) (a) E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, **86**, 2671 (1964); (b) K. Yates, A. R. Katritzky, and J. B. Stevens, *Can. J. Chem.*, **42**, 1957 (1964).

(4) R. L. Hinman and J. Lang, *J. Amer. Chem. Soc.*, **86**, 3796 (1964).

(5) E. M. Arnett and G. W. Mach, *ibid.*, **88**, 1177 (1966).

(6) L. P. Hammett and A. J. Deyrup, *ibid.*, **54**, 2721 (1932); see also M. Liler, "Reaction Mechanisms in Sulphuric Acid," Academic Press, New York, N. Y., 1971, Chapter 2, for a recent discussion of this postulate.