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## Stabilities of Trivalent Carbon Species. 4. Electrochemical Reduction of Carbocations in Sulfuric Acid<sup>1</sup>

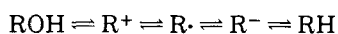
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The reduction of 11 stable carbocations in aqueous sulfuric acid was studied by rapid-scan triangular-wave cyclic voltammetry. For most cations, two one-electron waves are seen, corresponding to reduction to the radical followed by reduction to the hydrocarbon. The reduction potential of the first wave becomes more negative with increasing sulfuric acid concentration, but the second wave is independent of solvent composition. Differences between reduction potentials for different cations are constant in various solvents, implying similar solvation energies for the cations. The potential of the first reduction is used in an analysis of the ionization of alcohols. The analysis divides the ionization reaction into a bond dissociation and an electron-transfer reaction. The C-O bond dissociation energies increase in the order planar < triarylmethyl < cyclopropenyl alcohols. For planar or triarylmethyl alcohols, the free energy of ionization is independent of dissociation energy within each group and varies directly with the ionization potential of the corresponding free radical. Free energies of ionization of cyclopropenyl alcohols vary with both bond dissociation energies and radical ionization potentials. The second reduction potential measures the radical-anion energy difference and p*K*<sub>a</sub> values of hydrocarbons may be estimated thereby.

The stabilities of very reactive trivalent carbon species, such as aliphatic anions,<sup>4</sup> antiaromatic<sup>5,6</sup> and antihomoaromatic,<sup>7</sup> ions and radicals, have been determined uniquely by electrochemical measurements. Breslow and his co-workers have measured reduction potentials of several carbocations using the techniques of rapid scan triangular wave cyclic voltammetry<sup>5</sup> and second harmonic alternating current voltammetry.<sup>4,8</sup> The reduction potentials for the conversions of cations to radicals  $\epsilon_1$  and radicals to anions  $\epsilon_2$  were used in a thermodynamic cycle to obtain p*K*<sub>a</sub> values for hydrocarbons (e.g., cyclopropenes) whose corresponding anions are very unstable.



$$\Delta G \text{ related to: } pK_{R^+} \quad \epsilon_1 \quad \epsilon_2 \quad pK_a$$

Two assumptions are implicit in this calculation: (1) the free energy change for conversion of carbinols to their corresponding hydrocarbons is constant for the series of compounds studied; (2) the medium effect which arises from measuring ionization equilibria and reduction potentials in different solvents is the same for all compounds studied.

We present results of a study of reductions of carbocations in aqueous sulfuric acid, the solvent used for the determination of p*K*<sub>R+</sub> values, which support the validity of the second assumption. Patterns of stabilities of trivalent carbon species of different structural types are also reported.

Aqueous sulfuric acid is a useful solvent for polarography,<sup>9</sup> and studies on the electrochemical behavior of a few carbocations in this medium have been reported previously.<sup>6,7,10,11</sup> In general, the choice of aqueous sulfuric acid as solvent pre-

Table I. Reduction Peak Potentials,  $\epsilon$ , of Carbocations in H<sub>2</sub>SO<sub>4</sub>, 25 °C

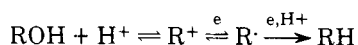
Cation	Registry no.	V <sup>a</sup>	0.09 M		3.0 M		6.0 M		10.2 M		13.8 M		17.0 M	
			I	II	I	II	I	II	I	II	I	II	I	II
1	13948-08-8	2							0.58	0.89	0.76	0.91		
		20							0.59	0.89	0.76	0.93		
		40							0.59	0.98	0.76	1.01		
		200							0.58	1.11	0.76	1.09		
2	14039-13-5	20	0.62	1.15	0.72	1.12	0.87	1.10	1.07 <sup>b</sup>		1.12 <sup>b</sup>			
		40	0.62	1.20	0.71	1.15	0.87	1.15	1.09 <sup>b</sup>		1.16 <sup>b</sup>			
		200	0.62	1.30	0.74	1.24	0.88	1.26	1.09	1.21	1.23 <sup>b</sup>			
3 <sup>c</sup>	25187-66-0	20					0.37	1.25	0.53		0.72		0.94	
		40					0.38	1.28	0.55		0.72		0.95	
		200					0.43	1.36	0.56		0.77		0.99	
4	20460-07-5	2			0.40	0.95	0.53		0.78	1.10				
		20			0.45	1.27	0.60		0.80	1.19	0.97			
		40			0.49		0.61	1.15	0.81	1.22	0.99			
		200			0.53		0.64	1.22	0.81	1.28	1.00			
5	25109-40-4	20			0.44	0.94	0.54	1.00	0.78	1.09				
		40			0.45	0.96	0.60	1.04	0.81	1.15	0.89	1.09		
		200			0.48	1.06	0.66	1.14	0.84	1.26	0.93	1.23		
6	26811-28-9	2	0.60		0.69		0.82							
		20	0.63		0.73		0.88		1.05		1.23			
		40	0.64		0.75		0.88		1.06		1.25			
		200	0.69		0.81		0.93		1.12		1.27			
7 <sup>c</sup>	33011-97-1	20					0.31	1.18	0.44	1.18	0.62		0.87	
		40					0.32	1.21	0.46	1.22	0.64		0.88	
		200					0.42	1.28	0.50	1.27	0.69		0.92	
8	25109-39-1	20							0.67	1.00				
		40							0.69	1.09	0.84	1.04		
		200							0.71	1.20	0.89	1.14		
9	20685-21-6	2									0.19	0.40		
		20									0.18	0.48	0.37	0.54
		40									0.18	0.50	0.37	0.57
		200									0.19	0.58	0.37	0.64
10	25501-79-5	20			0.51		0.70		1.06					
		40			0.65		0.82		1.11					
		200			0.91		1.05		1.29					
11	12190-17-9	20	1.25		1.31		1.49							
		40	1.26		1.33		1.51							
		200	1.31		1.42		1.60							

<sup>a</sup> Sweep rate, in V/s; concentrations listed for H<sub>2</sub>SO<sub>4</sub> in H<sub>2</sub>O; I and II correspond to potentials of first and second wave, as described in text; potentials in V referenced to Hg|Hg<sub>2</sub>SO<sub>4</sub>-17 M H<sub>2</sub>SO<sub>4</sub>. <sup>b</sup> Two-electron wave. <sup>c</sup> Potentials listed for 6.0 M H<sub>2</sub>SO<sub>4</sub> were measured in 6.8 M H<sub>2</sub>SO<sub>4</sub>.

sents three problems in the electrochemical study of carbocation reduction: (1) less stable cations cannot be generated in dilute acid; (2) in concentrated acid, solvent reduction may obscure reduction of the carbocation; and (3) reduction products (radicals, dimers, RH) are poorly solvated in H<sub>2</sub>SO<sub>4</sub>, adsorb on metal electrodes, and give rise to extraneous non-faradaic adsorption and desorption peaks.

Fortunately, cations of low stability are reduced at more positive potentials than the solvent, even at high acid concentrations, and it is possible to obtain reduction potentials for cations which have a wide range of stability by adjusting the concentration of sulfuric acid. It is not always possible, therefore, to compare directly reduction potentials for different cations in the same solvent, but, as shown below, the solvent effect on the potential may be taken into account easily.

In general, a carbocation whose stability is sufficient to ensure its complete formation in sulfuric acid may be reduced at the mercury electrode in two steps, first to the radical and then to the hydrocarbon.<sup>6</sup>



In single-sweep rapid-scan cyclic voltammetry, for most ions two waves may be seen, corresponding to these processes. The first reduction is (almost) reversible with an anodic and cathodic peak; the second reduction is irreversible and shows

only a cathodic peak. There is a medium effect on the potential of the first wave, which becomes more negative with increasing concentration of H<sub>2</sub>SO<sub>4</sub>, but the potential of the second wave is generally insensitive to the solvent composition. In some cases, at high acid concentrations, the first wave merges with the second to show a single two-electron reduction peak. A discussion of these medium effects will be presented separately.

We have examined the behavior of 11 carbocations whose stabilities vary over a range of almost 28 kcal/mol, based on  $\text{p}K_{\text{R}^+}$  values: triphenylmethyl (1), tri-*p*-anisylmethyl (2), xanthy (3), 9-phenylxanthy (4), 9-phenylthioxanthy (5), tropylium (6), dibenzo[*a,d*]tropylium (7), 5-phenyldibenzo[*a,d*]tropylium (8), 9-phenylfluorenyl (9), sesquixanthryl (10), and triphenylcyclopropenyl (11).

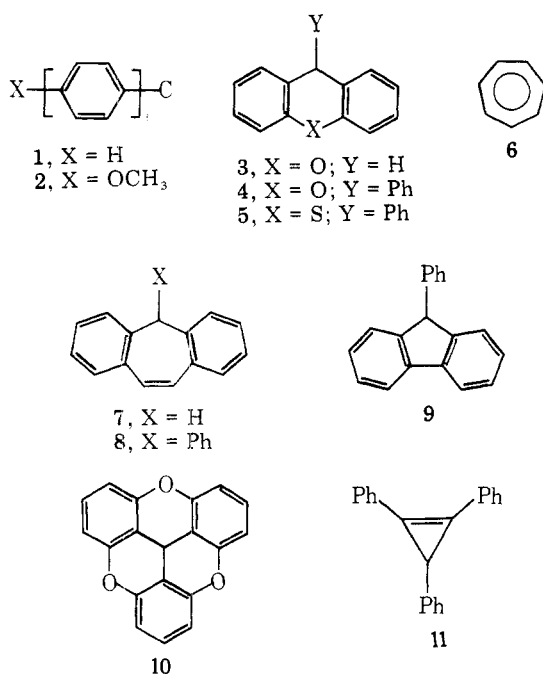
## Results

The reduction peak potentials for the carbocations which were measured in 0.09–17.0 M H<sub>2</sub>SO<sub>4</sub> are presented in Table I. None of the cations could be observed in the entire range of H<sub>2</sub>SO<sub>4</sub> concentrations. The absence of data at low acid concentrations indicates that the cation is not formed; the absence of data at high acid concentrations indicates that the cation reduction is obscured by solvent reduction. The second wave is not seen at all for several cations of interest, such as tropylium 6 and triphenylcyclopropenyl 11. The approach to elec-

Table II. Solvent Effects on  $\Delta\epsilon_1^a$ 

Solvent	1	2	11
CH <sub>3</sub> CN <sup>b</sup>	0.44, 0.46 (0.44)	-0.03	-0.60 (-0.56)
(CH <sub>3</sub> ) <sub>2</sub> SO <sup>b</sup>	0.42	0.16	-0.62
H <sub>2</sub> SO <sub>4</sub>			
0.9 M		0.03	-0.61
3.0 M		0.07	-0.61
6.0 M		0.05	-0.67
10.2 M	0.54	0.04	
13.8 M	0.51	0.04	
70% ethanol, 2 N HClO <sub>4</sub>		0.02	

<sup>a</sup> Difference in reduction potential for first wave between indicated cation and tropylium. <sup>b</sup> Taken from ref 5 and 8. Values in brackets from second harmonic AC voltammetry, all others from triangular wave cyclic voltammetry.



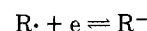
trochemical reversibility is denoted by a potential which remains constant as the sweep frequency is changed. The shift of potentials for the first peak to more negative values as the sweep frequency increases, which is displayed by several cations, arises from the rapid dimerization of the radicals near the electrode.<sup>5</sup> Reversible potentials are not obtained for cations which show this behavior. We have taken the peak potentials at the fastest sweep frequency, 200 V/s, to compare cations whose reductions may or may not be reversible. Breslow has shown that results obtained in this manner are in substantial agreement with true reversible potentials obtained by the second harmonic AC technique.<sup>8</sup> Detailed descriptions of the electrochemical behavior of each cation, including voltammograms and *i-t* curves, are given in ref 3.

### Discussion

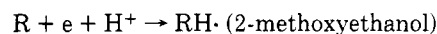
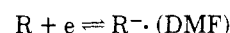
**Solvation Effects.** A comparison of the reduction potentials for the first wave in several solvents is presented in Table II. Potentials relative to tropylium as a standard are listed for triphenylmethyl 1, tri-*p*-anisylmethyl 2, and triphenylcyclopropenyl 11 cations. Satisfactory agreement is noted in all cases (except for 2 in Me<sub>2</sub>SO), which confirms that the solvation energies are similar for the ions in question and the assumption made for the first reduction in Breslow's thermodynamic cycle is valid. The similarity in solvation energies of carbocations of reasonably similar structure has been noted

recently in studies of gas phase and solution reactions of these species.<sup>12,13</sup>

The second wave arises from an irreversible reduction to form a hydrocarbon. However, the potential may be taken to measure, approximately, the free-energy difference between the radical and its corresponding anion.



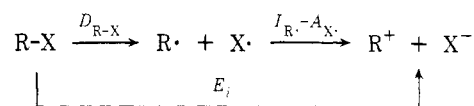
For a related case Streitwieser and Schwager<sup>14</sup> found that reduction potentials of aromatic hydrocarbons in dimethylformamide correlate linearly with reduction potentials in 2-methoxyethanol, with unit slope,



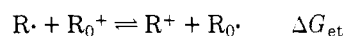
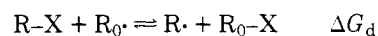
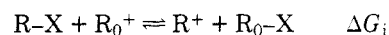
indicating that either potential measured the solution electron affinity of the hydrocarbon.

Of the various radicals which display the second wave, only the potential for 9-phenylfluorenyl 9 is significantly different from the others. We can compare the difference in potential for the second wave between triphenylmethyl 1 and 9 in 13.8 M H<sub>2</sub>SO<sub>4</sub>, 0.51 V, with the difference in oxidation potential of the corresponding anions in 1,2-dimethoxyethane, 0.45 V, reported by Breslow and Mazur.<sup>15</sup> The difference between the two values is within experimental uncertainty and suggests that the irreversible potentials which we measure may be used as the reversible radical-anion potentials and that the medium effect is negligible for anions as well as cations. Although the concept of solvation of carbanions in concentrated H<sub>2</sub>SO<sub>4</sub> is amusing, the results suggest that Breslow's assumption is also valid for the last part of the cycle. The similarity of solvation of hydrocarbon anions was previously discussed by Ritchie and Uschold to explain the constancy of differences in p*K*<sub>a</sub> values for hydrocarbons in different solvents.<sup>16</sup>

**Stabilities of Trivalent Carbon Species.** We have previously used the reduction potentials of carbocations in sulfuric acid to obtain information about the stabilities of free radicals and carbanions.<sup>6</sup> It is useful to consider heterolysis as the sum of two reactions, bond dissociation and electron transfer:

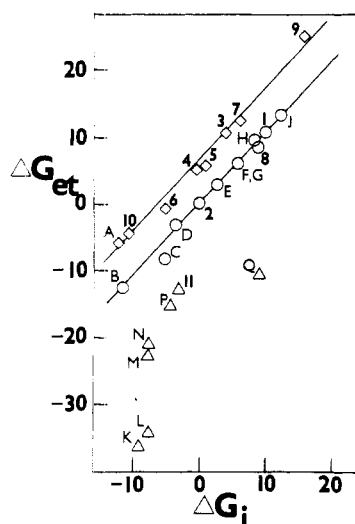


For gas-phase reactions of several relatively simple R-X compounds, all the energies in the cycle (bond dissociation *D*, ionization potential *I*, electron affinity *A*, and heterolysis energy *E<sub>i</sub>*) have been estimated.<sup>17</sup> However, if X is held constant, relative values of ionization potentials of radicals and bond dissociation energies may be obtained from measurements in solution for complex structures, such as 1-11. Consider the following equilibria:



$$\Delta G_i = \Delta G_d + \Delta G_{et}$$

Free energies of ionization,  $\Delta G_i$ , may be derived from p*K*<sub>R+</sub> values,<sup>18</sup> where X is OH. Free energies for the electron-transfer reaction,  $\Delta G_{et}$ , are obtained from reduction potentials, and free energies for the radical-exchange reaction,  $\Delta G_d$ , are obtained by difference. Differences in reduction potentials between a given cation and 2 in the various solvent systems were calculated from Table I and from the literature,<sup>19</sup> and the mean value was used to obtain  $\Delta G_{et}$ . We have used tri-*p*-anisylmethyl 2 as our standard R<sub>0</sub> because its reduction



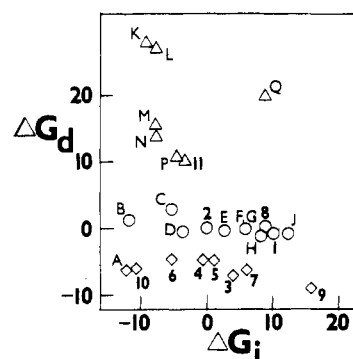
**Figure 1.** Comparison of  $\Delta G_i$  and  $\Delta G_{et}$ , kcal/mol: planar groups,  $\diamond$ ; triarylmethyl groups,  $\circ$ ; cyclopropenyl groups,  $\Delta$ . Numbers for points correspond to structures in text. Additional points as follows: A, *N*-methylacridinium. Triphenylmethyl groups substituted in *para* positions: B, tris(dimethylamino); C, bis(dimethylamino); D, dimethylamino; E, dimethoxy; F, methoxy; G, trimethyl; H, methyl; J, trichloro. Trisubstituted cyclopropenyl groups: K, trimethyl; L, tritert-butyl; M, dipropylphenyl; N, tri-*p*-anisyl; P, diphenyl-*p*-anisyl; Q, unsubstituted.

potential has been measured in a wide range of solvents in several laboratories. In an equivalent treatment, Breslow used triphenylmethyl 1.<sup>8</sup> It is difficult to estimate the probable errors, but a given  $\Delta G_d$  or  $\Delta G_{et}$  may be associated with an error of 1–2 kcal/mol or more in some cases.

The results of the calculations are presented graphically in Figure 1, where  $\Delta G_{et}$  is compared with  $\Delta G_i$ , and Figure 2, where  $\Delta G_d$  is compared with  $\Delta G_i$ . It can be seen that certain patterns emerge from the calculations. Triarylmethyl groups and groups with significant planar portions show linear relationships between  $\Delta G_i$  and  $\Delta G_{et}$  (slope 1.1),<sup>20</sup> but  $\Delta G_i$  is independent of  $\Delta G_d$ . Dissociation energies of alcohols with planar R groups are about  $6 \pm 2$  kcal/mol less than triarylcarbinols, but within each group, dissociation energies are comparable. The differences in free energies of ionization within the planar or triarylmethyl series are entirely due to differences in ionization potentials of the corresponding radicals.<sup>21</sup>

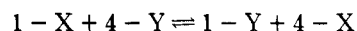
From Figure 2 one could conclude that all triarylmethyl radicals are formed with equal ease from their corresponding carbinols. This contrasts with the extensive data on triarylmethyl radical stability based on measurements of the dissociation of "hexaarylethanes", which are now known to be erroneous.<sup>22</sup> However, the apparent equality of dissociation energies for triarylcarbinols may be due to the insensitivity of the dissociation energies of alcohols in general to alkyl group structure. For example, the bond dissociation energies of methyl, ethyl, isopropyl, and *tert*-butyl alcohols are 91.1, 90.9, 91.9, and 91.2 kcal/mol, respectively,<sup>17</sup> while the bond dissociation energies for C–H bonds in methane and isobutane differ by 12 kcal/mol. If  $\Delta G_i$  were measured with other X groups, the conclusion about isoenergetic free radicals could be tested.<sup>23</sup>

The difference in dissociation energies, measured by  $\Delta G_d$ , between triarylmethyl and planar compounds is noteworthy. The interpretation of the difference is open to discussion. If one assumes that the corresponding alcohols are isoenergetic, then one concludes that planar radicals are more stable than triarylmethyl radicals. On the other extreme, the radicals may be isoenergetic and triarylcarbinols are more stable than



**Figure 2.** Comparison of  $\Delta G_i$  and  $\Delta G_d$ , kcal/mol. Points as listed in Figure 1.

planar alcohols. The second argument appears to be refuted by experiments by Freedman and co-workers,<sup>24</sup> who examined equilibria between covalent derivatives of triphenylmethyl 1 and 9-phenylxanthyl 4.



Freedman found that the larger X or Y preferred to be bonded to 4 rather than 1 and concluded that relief of steric compression which occurs in ionization was more important for 1 than for 4. This may be restated as triphenylcarbinol has a higher energy than 9-phenylxanthyl, which is contrary to the conclusion derived from the isoenergetic radical hypothesis. A *minimum* value for the stabilization of planar radicals, relative to triarylmethyl radicals, is given by  $\Delta G_d$ , since the corresponding alcohols are not, in fact, isoenergetic.

The dissection of  $\Delta G_i$  into  $\Delta G_d$  and  $\Delta G_{et}$  is particularly instructive when comparing triarylmethyl systems with planar systems. The analysis indicates that both dissociation energies and electron-transfer energies are responsible for differences in free energies of ionization between the two systems. Two cogent examples may be cited. First, tropylium 6 and tri-*p*-anisylmethyl 2 cations differ in  $pK_{R^+}$  by 3.9 units, but their reduction potentials are nearly identical. This means that virtually all of the difference in free energy of ionization of these substrates can be accounted for by differences in bond dissociation energies.

The second example compares 9-phenylxanthyl 4 and tri-*p*-anisylmethyl 2, cations which have about the same  $pK_{R^+}$  values. This occurs because of a balance between the two processes: bond dissociation energies  $\Delta G_d$  favor 4 and electron-transfer energies  $\Delta G_{et}$  favor 2. These two examples illustrate the danger in rationalizing differences in  $pK_{R^+}$  values for cations of different gross structures. Occasional warnings<sup>25</sup> have been given previously, but the data provided here confirm the necessity for caution in the interpretation of  $pK_{R^+}$  values solely in terms of carbocation stability.

The behavior of 5-phenyldibenzo[*a,d*]tropylium (8) is, at first consideration, unexpected. The structural resemblance to tropylium 6 and dibenzo[*a,d*]tropylium 7 implies that this group should behave like planar systems, rather than triarylmethyl. However, Drieding models suggest that a boat-type seven-membered ring might be easily accommodated and would remove crowding between the phenyl ring and neighboring hydrogens in positions 4 and 6 in a planar seven-membered ring. If ion 8 is a triarylmethyl ion, its stability is easily understood; its  $pK_{R^+}$  of  $-5.7$ <sup>26</sup> shows that it is slightly more stable than triphenylmethyl cation ( $pK_{R^+} = -6.6$ ).<sup>18</sup> On the other hand, ad hoc explanations must be offered to accommodate the reduction of stability of cation 8 compared to cation 7,  $pK_{R^+} = -3.7$ ,<sup>26</sup> because phenyl substitution stabilizes planar cations, e.g., xanthyl and fluorenyl.<sup>27</sup>

In contrast to the behavior of planar and triarylmethyl

species, cyclopropenyl systems are characterized by  $\Delta G_{et}$  values which are large and negative and  $\Delta G_d$  values which are large and positive, both of which may be accounted for by destabilized cyclopropenyl radicals. The limited data suggest different behavior for aryl- and alkyl-substituted cyclopropenyl systems. The apparent high C–O dissociation energies for cyclopropenyl alcohols and the destabilizing effect of alkyl groups on cyclopropenyl radicals has been discussed by Breslow.<sup>8</sup>

Other experiments indicate the difference in behavior of planar and cyclopropenyl systems, with respect to cation and radical stabilities, which parallel our results. Okamoto and co-workers<sup>28</sup> found that when the rate constants for reduction of cations to radicals by chromous ion (as  $\log k$ ) were compared with energies of charge-transfer absorption of complexes of the cations with pyrene, a single correlation fit data both for aryl-substituted tropylium and cyclopropenyl cations. However, a plot of  $\log k$  vs.  $pK_{R^+}$  gives two nearly parallel lines, one for each type of cation. These results may be interpreted in terms of our data, where  $\Delta G_i$  shows different correlations with  $\Delta G_{et}$  for the two types of compounds.

The electrochemical behavior of the ions in sulfuric acid precludes using a similar analysis for anions as for radicals. The data may be used qualitatively, however, in a useful way. For example, the reduction of 9-phenylxanthyl 4 radical (a planar radical) to its anion requires about the same energy as the reduction of triphenylmethyl radical to its anion. Because the planar radical is more stable, its anion is consequently more stable than triphenylmethyl anion, or 9-phenylxanthene should be more acidic than triphenylmethane. This is in fact the case.<sup>29</sup> The increased acidity of 9-phenylfluorene relative to triphenylmethane is in part due to the planarity of the fluorenyl anion and in part to the special anion-stabilizing effect (aromaticity) of the cyclopentadienide system. The ionization of 9-phenylfluorene is 16.9 kcal/mol more favorable than triphenylmethane ( $\text{Me}_2\text{SO}$  solvent,  $\Delta pK_a = 12.4$  at 25 °C),<sup>16</sup> of which 10–12 kcal may be attributed to charging the radicals and 5–7 kcal to breaking the C–H bonds.

### Experimental Section

**Cyclic Voltammetry.** A three-electrode, single-sweep polarographic system (SSP-2) manufactured by Chemtrix, Inc., of Beaverton, Oregon was used. This apparatus consists of an amplifier unit and a time-base unit built into a Tektronix 564 storage oscilloscope. The potential ranges are 0.5, 1.0, and 2.0 V and scan rates from 0.05 to 200 V/s can be obtained. This apparatus can be used for triangular-wave cyclic voltammetry (TWCV) with triggering to start the potential at a specific time after the beginning of the drop growth. In this study, a drop time of 3 s elapsed before the circuit was triggered. TWCV in the single- and multi-sweep modes were used.

This system can compensate for cell circuit resistance up to  $1 \times 10^7 \Omega$  by providing feedback from a third cell electrode (counter). This counter electrode is a piece of platinum wire wrapped around the DME; the DME has a drop time of 7.96 s and a  $m^{2/3} t^{1/6}$  value of 1.09  $\text{mg}^{2/3} \text{s}^{-1/2}$  in 3 M acid (open circuit). The reference electrode is a mercurous sulfate electrode containing 17 M sulfuric acid as an electrolyte. The electrode serves as a perfectly nonpolarizable electrode. A potential of 0.256 V vs. SCE was determined previously from the electrocapillary curve and by graphical elimination of the liquid junction potential between diluted and concentrated sulfuric acid.<sup>9</sup> A value of 0.246 V vs. SCE was obtained in this laboratory by determining the reduction potential of  $\text{Cd}^{2+}$  vs. both SCE and the mercurous sulfate electrode.

A jacketed H cell with the compartments separated by a stopcock and fritted disk was used. Because of IR compensation, the stopcock could be partially closed to prevent contamination of the reference electrode. The 17 M acid in the reference electrode compartment was changed for each compound studied. No appreciable change in the peak potentials of the compounds, remaining in the sample com-

partment for 40 min, was observed. A Teflon-covered stopper with two holes drilled through it for the electrodes and nitrogen tube covered the sample compartment. Deaeration was continued for 10 min and nitrogen was continuously passed over the solution during the recording of the voltammograms.

**Materials.** The compounds were dissolved in various concentrations of sulfuric acid to form the respective cations. Stock solutions (5 mM) of the cations were diluted to 0.191, 0.445, and 0.80 mM.

Cations **6** and **11** were used as fluoroborate salts. Tropylium fluoroborate was prepared according to Conrow.<sup>30</sup> Triphenylcyclopropenyl bromide was kindly provided by Professor M. A. Battiste. It was converted to the fluoroborate by reduction to triphenylcyclopropene followed by reaction with trityl fluoroborate. The other cations were generated from their corresponding alcohols, which were commercially available or prepared by standard methods. Sesquioxanthrol, precursor of cation **10**, was kindly provided by Professor J. C. Martin. The mp of all salts and alcohols agreed with literature values.

**Registry No.**— $\text{H}_2\text{SO}_4$ , 7664-93-9.

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