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THE STRUCTURE OF ARYLCARBONIUM IONS[1]

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Of the many structures proposed for the triphenylcarbonium ion, only two remain to merit consideration. In model A, the ion is propellor shaped with all three rings equivalent in the resonance hybrid (1). In model B, the positive charge is delocalized into only one or two of the rings (2). Although the three rings in model B are not equivalent in the resonance hybrid, they become so over a time average by a true process of isomerization.

To provide further evidence on this problem, the relative free energies of formation and the absorption spectra have been determined for a series of mono-, di-, and tri-arylcarbonium ions.

FREE ENERGIES OF FORMATION FOR ARYLCARBONIUM IONS

Determination of pK_{R^+}. Relative stabilities of arylcarbonium ions have been studied by three methods. Baeyer (3) used a qualitative colorimetric method which was extended by several other investigators (4, 5). A second method utilized the conductivity of the carbinyl chlorides in sulfur dioxide and nitromethane (6, 7). This method has been limited to triarylcarbinyl chlorides.

The third method and the one used in this investigation is based upon the concept of acidity functions introduced by Hammett (8). Gold and Hawes (9) defined the J_0 acidity function by equation 2 analogous to the definition of H_0, equation 1. Hammett has shown that this definition of H_0 is equivalent to equation 3 and analogously Gold and Hawes showed that the definition of J_0 is equivalent to equation 4, where "f" stands for the activity coefficient based on water as the standard state.

1. $$H_0 = (pK_{BH^+}) - \log \frac{c_{BH^+}}{c_B}; \qquad pK_{BH^+} = -\log \frac{a_B\, a_{H^+}}{a_{BH^+}}$$

2. $$J_0 = (pK_{R^+}) - \log \frac{c_{R^+}}{c_{ROH}}; \qquad pK_{R^+} = -\log \frac{a_{ROH}\, a_{H^+}}{a_{R^+}\, a_{H_2O}}$$

3. $$H_0 = -(\log a_{H^+}) - \log \frac{f_B}{f_{BH^+}}$$

4. $$J_0 = -(\log a_{H^+}) - \log \frac{f_{ROH}}{f_{R^+}} + \log a_{H_2O}$$

The relation between H_0 and J_0 is thus equation 5.

5. $$J_0 = H_0 + \log a_{H_2O} + \log \frac{f_B\, f_{R^+}}{f_{BH^+}\, f_{ROH}}$$

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Gold and Hawes (9) calculated J_0 for the water-sulfuric acid system on the basis of equation 6, which assumes that the term involving activity coefficients in equation 5 reduces to zero for this solvent system.

6. $$J_0 = H_0 + \log a_{H_2O}$$

The justification for this assumption was that J_0 values computed from equation 6 were identical to those measured by the definition, equation 2, using *triphenylcarbinol and its 4,4′,4″-trinitro derivative as the indicators.* The wide variety of carbinols used in the present work support this conclusion and provide an extensive test of equation 6 for the water-sulfuric acid system.

A result is that the J_0 values from equation 6 can be used to determine the thermodynamic pK_{R^+} values for carbinols from equation 2. In effect the change in activity coefficients that occur in going from water to the sulfuric acid concentration where the measurements are conducted is exactly counterbalanced by the same change in activity coefficients of the indicators used to set up the H_0 scale. The values of pK_{R^+} given in the Tables are thus thermodynamic pK values for equation 7 based on water as the standard state.

7. $$R^+ + H_2O = ROH + H^+$$

Relation of pK_{R^+} *to Hammett sigma values.* In Table I are listed the values of pK_{R^+} for a series of triarylcarbinols in which all three rings had identical substituents. The substituents were chosen to cover a wide range of Hammett *sigma* values (10). These carbinols group themselves into three categories. Group A contains those whose points lie on a linear curve in a plot of pK_{R^+} against the *sigma* (σ) value for the substituent. Equation 8 represents this linear curve. The deviations in pK_{R^+} from this linear curve are listed in column 3 of Table I. In group B are carbinols 8 and 11 and in group C are carbinols 1, 2, 3, and 10 in Table I.

8. $$(pK_{R^+}) + 9.2\sigma + 4.2 = 0$$

The fact that the carbinols in group A fall on a linear curve in a plot of pK_{R^+} against *sigma* values implies that the differences in entropy change ($\Delta\Delta S$) for the ionization of the carbinols (equation 7) are either zero or proportional to the polar parameter *sigma.* This is reasonable because these carbonium ions have similar spectra (Table I) indicating that electron distribution and charge distribution in the aryl rings are similar. This would indicate similar bonding within the molecule and lead to similar interaction between ion and solvent. Thus the relative entropies of ionization ($\Delta\Delta S$) are expected to be small and approximately proportional to *sigma.*

Noteworthy is the large value of *rho,* 9.2, for the above correlation.[2] This value is considerably larger than any previously reported.

Group B, carbinols 8 and 11, were unexpected deviations in the pK_{R^+} *vs sigma*

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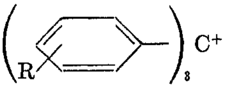
[2] If the data in ref. (6) for triphenylcarbinol and the only trisubstituted derivative studied, 4,4′,4″-tri-*tert*-butyl, are plotted pK_{R^+} *vs sigma,* the value of *rho* is 8.7.

TABLE I

STABILITY AND SPECTRA OF TRIARYLCARBONIUM IONS CONTAINING IDENTICALLY SUBSTITUTED RINGS

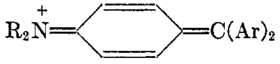


R =	pK_{R^+}[a]	[b]	Dev. in.[c] pK_{R^+}	SPECTRA		
				λ_{max} (mμ)	Log ε	Ref.[d]
1. 4-Dimethylamino	+9.36	−.205	+11.7	590	4.95	A, B, C
2. 4-Amino	+7.57	−.660	+5.7	539		A, B
3. 4-Methoxy	−0.8	−.268	+0.9	483	5.02	D, C
4. 2-Methoxy				550	4.15[e]	D, C
				415	4.12[e]	
5. 2-Methyl	−1.96			454	4.46	
6. 4-Methyl	−2.47	−.170	+0.1	452	5.03	
7. 3-Methyl	−3.78	−.069	−0.2	414	4.54	
8. 4-Isopropyl	−3.94	−.151	−1.1	456	4.88	
9. Unsubstituted	−4.18	0.0	0.0	431	4.60	E
				404	4.60	
10. 4-Chloro	−4.79	+.227	+1.5	465	4.97	
11. 4-*tert*-Butyl	−4.86	−.197	−2.5	458	4.92	
12. 3-Chloro	−7.32	+.373	+0.3	412	4.47	
13. 4-Trimethylammonium	−10.15					F
14. 4-Nitro	−11.4	+.778	0.0	450	4.46	E
				415	4.65	

[a] $pK_{R^+} = -\log \frac{a_{ROH}\, a_{H^+}}{a_{R^+}\, a_{H_2O}}$. [b] Hammett's *sigma* value, *cf.* ref. 10 in text. [c] This is the deviation in pK_{R^+} from a linear curve drawn through selected points in a plot of pK_{R^+} against *sigma*, equation 9. [d] These letters refer to the following references. When two or more references are given the first one refers to the determination of the pK_{R^+}. (A): Goldacre and Phillips, *J. Chem. Soc.*, 1724 (1949). (B): Holmes, *Ind. Eng. Chem.*, **16,** 35 (1924). (C) Brand, *J. prakt. Chem.*, **109,** 14 (1925). (D): ref. 4 in text. (E): ref. 9 in text. (F): Murray and Williams, *J. Chem. Soc.*, 3322 (1950). [e] It was not certain that the carbinol was completely ionized so that the log ε values may be too low.

plot. The similarity in spectra to those carbonium ions of group A indicates similar electron and charge distribution in the ring, so that the deviation must arise from another source. We interpret this source to be the large steric size of the *tert*-butyl group in carbinol 11 and to a lesser extent the isopropyl group in carbinol 8 which inhibit contact of the solvent with the ring. Carbonium ions, like all other ions, owe their existence to large solvation energies so that their relative free energies will be sensitive to this factor. A factor inhibiting this solvation will decrease the stability of the ion so that in this case the *p-tert*-butyl substituent actually decreases the stability of the carbonium ion relative to the triphenylcarbonium ion. In solvents of lesser solvating power for positive ions, this effect should not be so pronounced. Thus Bartlett and Lichtin (6, 7) found in contrast to our results that *p-tert*-butyl groups increased the stability of the triphenylcarbonium ion as measured by the extent of ionization of the carbinyl chlorides in liquid sulfur dioxide and nitromethane.

Two carbinols, 1 and 2 in Table I, in group C have very large deviations in pK_{R^+} from the linear curve. In conjunction with this effect, these two carbonium ions also possess very different absorption spectra compared to the carbonium ions in groups A or B. It is probable that in these two cases the substituent, *p*-dimethylamino and *p*-amino, carries a major portion of the positive charge as represented in the contributing resonance structure I.



I

This charge distribution would thus differ markedly from that of the carbonium ions in groups A and B in which we believe the positive charge is principally on the *ortho* and *para* positions of the ring or rings. In effect these two ions belong to a different series structurally and might better be considered as a special type of ammonium ion. It is thus not surprising that the Hammett *sigma-rho* treatment (10) fails.

The situation with carbinols 3 and 10 is similar but the effect is much smaller.

In these cases where a *para* substituent shares a large part of the charge of the ion, a special *sigma* value, σ_{res}, has been employed (10, 11). Since the amount of charge held by the substituent will vary in different reaction series, we question whether these σ_{res} values will have any general application to other reaction series. For example, the σ_{res} values for the *p*-methyl and *p*-methoxy groups (11), -0.63 and -2.5 respectively, fail to improve the fit in our plot of pK_{R^+} *vs sigma* and in fact lead to much greater deviations in pK_{R^+} from the linear curve than when the usual *sigma* values (10) were employed.

Effect of ortho substituents. A completely coplanar model for the triphenylcarbonium ion with C—C distances of 1.39 Å in the benzene rings and a C—C distance from central carbon to ring of 1.42 Å [one-third double bond character (12)] would force the nuclei of the *ortho*-hydrogen to within 0.58 A of each other. If the C—C distance between central carbon and ring is increased to the normal single bond distance of 1.54 Å, and the rings are rotated until the nuclei of the *ortho*-hydrogen are 2.0 Å from each other [twice the minimum van der Waals radius for hydrogen (12)], the angle between planes of the benzene rings is 47°.[3]

Another estimate of this angle can be made on the basis of the known distance (3.1 Å) between the *ortho* carbons in the *cis*-azobenzene structure (13). If this distance is assumed to be that between the *ortho* carbons in the triphenylcarbonium ion, the angle between planes of the phenyl rings is 54°. Some reduction in this angle may be possible by bending the C—H bond angles and penetrating within the van der Waals radius, but it does not seem possible that the angle could be much reduced.

[3] On a similar basis M. Szwarc [Discussions of the Faraday Society No. 2, 42 (1947)] computed a minimum angle of 30° between planes of the phenyl rings in the triphenylmethyl free radical.

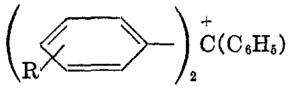
With angles of this order of magnitude, replacement of the *ortho*-hydrogen by bulkier groups in the propellor model of Lewis (1), model A, should markedly reduce the resonance energy of the resulting ion. However, the 2,2′,2″-trimethylcarbonium ion is actually more stable relative to its carbinol ($pK_{R^+} = -1.96$) than the 4,4′,4″-isomer ($pK_{R^+} = -2.47$).

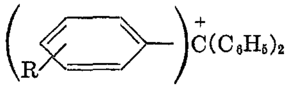
This increased stability is probably due to the relatively greater decrease in steric strain for the 2,2′,2″-isomer in going from the tetrahedral central carbon in the carbinol to the trigonal carbon in the carbonium ion. The fact that this effect outweighs any difference in resonance energy suggests that the difference in resonance energy is small. This result is more in harmony with model B than model A.

Lund (4) found that 2,2′,2″,4-tetramethoxytriphenylcarbonium ion was slightly more stable relative to the carbinol than the 4,4′,4″-trimethoxytriphenylcarbonium ion. Although this is not a direct comparison of *ortho vs para* substituted triarylcarbonium ions, the result suggests that in this case as with the methyl substituents, the *ortho* substituted triarylcarbonium ion and its *para* substituted isomer have comparable stabilities.

TABLE II

STABILITY AND SPECTRA OF TRIARYLCARBONIUM IONS



R =	pK_{R^+}	SPECTRA		
		λ_{max} (mμ)	Log ε	Ref.[a]
1. 4-Dimethylamino	+6.90	620	5.00	A, C, G
2. 4-Amino	+5.38	570		A, H
3. 4-Methoxy		500	4.82[b]	C
4. 2-Methoxy		577	3.87[b]	C
		495	3.99[b]	
5. 4-Trimethylammonium	−7.52			F
				
6. 4-Dimethylamino	+4.75	490	4.05[b]	A, C
7. 4-Amino	+4.6	477		A, G, H
8. 4-Methoxy		470	4.67[b]	C
9. 2-Methoxy		550	3.40[b]	C
10. 4-Methyl	−3.04	450	4.66	
11. 4-Nitro	−5.54	454	4.48	
		388	4.45	

[a] The same code letters are used for the references as in Table I with the following additions. (G): Kehrmann, Goldstein, and von Salis, *Helv. Chim. Acta*, **10**, 33 (1927). (H): Kehrmann and Sandoz, *Ber.*, **51**, 915 (1918).

[b] Same as footnote (*e*) in Table I.

Kolthoff (14) also found that *o*-methoxytriphenylcarbonium ions were very stable: 2,2′,2″,4,4′,4″,6-heptamethoxy-; 2,2′,2″,4,4′,4″-hexamethoxy-; and 2,2′,2″,4,4′-pentamethoxy triphenylcarbinols had pK_{R^+} of 5.85, 3.29, and 1.82 respectively.

Successive substitution in the aryl rings. In Table II are summarized some results of our own as well as others on the effect of successively substituting the phenyl ring in the triphenylcarbonium ion. The interpretation of these pK_{R^+} values will be reserved until more data are available.

Diarylcarbonium ions. All diarylcarbonium ions are less stable than the correspondingly substituted triarylcarbonium ions. In a later section it will be shown that this difference is primarily due to a relatively smaller decrease in steric strain.

Dimesitylcarbinol merits particular mention. The evidence that it ionizes to the carbonium ion in 60–100% sulfuric acid seems adequate despite the unusual properties of the ion. Thus cryoscopic data in 100% sulfuric acid showed an i-factor of 4 (2), and the absorption spectra in the visible is unchanged from 97% sulfuric acid down to the region in which the colored form is in equilibrium with the carbinol. In addition the pK_{R^+} as determined by equation 3 was constant with an average deviation of 0.10 from 53–60% sulfuric acid.

A model of the dimesitylcarbonium ion in which the C—C distance from central carbon to ring is 1.54 Å and in which the rings are at right angles to each other, gives a distance of only 3.75 Å between *ortho* carbons which is not quite twice the van der Waals radius (2 × 2.0 Å) for the methyl group (12), indicating that in this ion the two rings must be nearly at right angles to each other. Despite this presumably complete absence of coplanarity between the two rings, the ion is exceptionally stable ($pK_{R^+} = -4.19$) relative to its carbinol.

Monoarylcarbonium ions. Difficulties have arisen in studying monoarylcarbonium ions, not because of their thermodynamic stability as much as from

TABLE III

STABILITY AND SPECTRA OF DIARYLCARBONIUM IONS

CARBINOL FROM WHICH ION WAS DERIVED	pK_{R^+}	SPECTRA		
		λ_{max} (mμ)	Log ε	Ref.[a]
1. Bis-4-dimethylaminophenyl	+5.61	610		A, I
2. Bis-2,4,6-trimethylphenyl	−4.19	525	4.53	
3. Diphenyl	−8.30	440	4.64	
4. Diphenylmethyl	−8.6[b]	429	4.46	
5. Bis-4-chlorophenyl	−8.97	483	5.14	
6. Methyl bis-4-chlorophenyl	−9.5[b]	464	4.83	
7. 9-Fluorenol	−8.91	655	3.08	
		484	2.90	
8. 9-Methyl-9-fluorenol	−11.5[b]	488	4.14	

[a] The same code letters are used as for the references in Table I with the addition, (I): Dewar, *J. Chem. Soc.*, 2330 (1950). [b] Some olefin may be present which would cause these values to be too small.

TABLE IV

Stability and Spectra of Monoarylcarbonium Ions

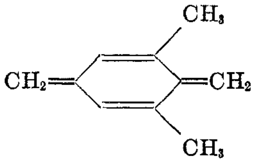
SUBSTITUTED BENZYL ALCOHOL FROM WHICH ION WAS DERIVED	pK_{R^+}	SPECTRA		
		λ_{max}	($m\mu$)	Log ϵ
1. 2,4,6-Trimethyl (mesitylcarbinol)	−12.45	470		3.39
2. α,α,2,4,6-Pentamethyl	~−13	360		4.32
3. α,α,2,3,4,5,6-Heptamethyl	~−12	380		4.00
4. α,α-Dimethyl		400		

their reactivity (2). By freezing point measurements α,α,2,4,6-pentamethylbenzyl alcohol and α,α,2,3,4,5,6-heptamethylbenzyl alcohol have been shown to ionize to carbonium ions of moderate stability in 100% sulfuric acid (2).

A third monoarylcarbinol, mesitylcarbinol (2,4,6-trimethylbenzyl alcohol), has now been shown to ionize to a carbonium ion. The ion was too unstable in 100% sulfuric acid for i-factor measurements (2), however, ionization to the carbonium ion could be demonstrated in the following way.

Mesitylcarbinol forms increasing amounts of a strongly colored species from 85–97% sulfuric acid. If this were the carbonium ion formed by the reverse of equation 7, the term ($J_0 + \log c_{R^+}/c_{ROH}$), pK_{R^+}, would be constant. Alternatively, if the colored species had a structure such as II formed by equation 9, the term ($\log a_{H_2O} + \log a_{R'}/a_{ROH}$) would be constant. Deno and Taft (16) have shown

9. $ROH = R' + H_2O;$



II

that in this region of sulfuric acid activities can be replaced by concentrations so that the term reduces to ($\log a_{H_2O} + \log c_{R'}/c_{ROH}$), which should be constant if equation 9 obtained. The data in Table V tests these two possibilities and

TABLE V

Constancy of pK_{R^+} for the Mesitylcarbonium Ion

H_2SO_4 (wt. %)	Log c_{R^+}/c_{ROH} Plus	
	J_0 (pK_{R^+})	Log a_{H_2O} (Log K_{eq} for eq. 8)
95.94	−12.44	−3.52
93.88	−12.39	−3.76
93.01	−12.41	−3.89
91.74	−12.42	−4.05
90.72	−12.52	−4.24
89.70	−12.50	−4.35

demonstrate that it is the carbonium ion which forms. This ion can be looked upon as the protonated form of structure II.

Pentamethylphenylcarbinol exhibits a complicated behavior in 80–100% sulfuric acid. At least two spectroscopically distinguishable species are present, one absorbing at 470 mμ and the other at 520 mμ. The latter is more stable at the higher concentrations of sulfuric acid. One of the species is probably the carbonium ion, and the other may be a structure analogous to II.

The colored species, λ_{max} at 400 mμ, formed by dissolving α,α-dimethylstyrene in 97% sulfuric acid is also probably a monoarylcarbonium ion.

Relative free energies of mono-, di-, and tri-arylcarbonium ions. Using equation 10, the pK_{R^+} values in Tables I–IV can be converted to relative free energies, ΔF, for reaction 7.

10. $$\Delta F = 2.3 \times RT(pK_{R^+})$$

An initial purpose of this work was to determine the difference in ΔF for the phenylcarbinols in which successive phenyl groups are introduced. This purpose has been only partially achieved. Accurate values of ΔF for diphenyl- and triphenyl-carbinols have been obtained (Table VI), but the ΔF for phenylcarbinol (benzyl alcohol) can only be estimated. The assumption that the difference in pK_{R^+} between phenylcarbinol and diphenylcarbinol is the same as that between mesitylcarbinol and dimesitylcarbinol ($\Delta\ pK_{R^+} = 7.26$) leads to an approximate value of -15.5 for the pK_{R^+} of phenylcarbinol.

An order of magnitude can be estimated for $pK_{CH_3^+}$. The ionization of methyl chloride in water has been estimated to be endothermic by about 60 kcal/mole (17). Neglecting the difference between ΔH and ΔF and recognizing that the methyl chloride-methanol equilibrium and hydrogen chloride ionization will have little total effect, $pK_{CH_3^+}$ + at 25° will be in the neighborhood of -44 and ΔF about 60 kcal/mole.

The difference in ΔF in Table VI between CH_3^+ and $C_6H_5CH_2^+$ is large (39 kcal.) and is presumably due to the increase in resonance energy.

The difference in ΔF between $(C_6H_5)_3C^+$ and $(C_6H_5)_2CH^+$, 5.6 kcal/mole, is interpreted to be due to a steric strain factor and not to a difference in resonance energy. This steric strain factor arises because in the conversion of a tetrahedral di- or tri-arylcarbinol to the trigonal carbonium ion, there will be a decrease in repulsive forces (steric strain) about the central carbon which will favor ionization. This factor will be larger in the triaryl series than in the diarylcarbinols.

TABLE VI

RELATIVE FREE ENERGIES FOR REACTION 7 AT 25° C.

CARBINOL	pK_{R^+}	ΔF (kcal/mole)	DIFF.
CH_3OH	-44	~60	39
$(C_6H_5)CH_2OH$	-15.5	~21	10
$(C_6H_5)_2CHOH$	-8.30	11.3	5.6
$(C_6H_5)_3COH$	-4.18	5.7	

The following argument supports the above interpretation and in addition supports model B for the triarylcarbonium ions.

The most important factors affecting ΔF will be resonance energy (Res), solvation energy of the positive ion (Solv), entropy of the solvent due to interaction with the ion (S), and steric strain in going from carbinol to carbonium ion (Steric). Schematically, ΔF = Res + Solv + S + Steric. In comparing a triarylcarbonium ion (Ar_3C^+) with a diarylcarbonium ion (Ar_2CH^+) containing identical aryl rings, model A and model B give very different expectations. In the extreme form of model B the positive charge is delocalized into only one ring in both the Ar_3C^+ and Ar_2CH^+ so that "Res, Sol, and S" will be relatively unchanged. There will remain a difference in "Steric", but this difference will be independent of the nature of the *meta* or *para* (but not *ortho*) substituent since these groups do not directly affect the neighborhood of the central carbon. In equation form, this principle is: $(\Delta F_{Ar_3C^+}) - (\Delta F_{Ar_2CH^+}) =$ constant. This constant is about 5.6 kcal/mole as indicated in the column labelled "Diff." in the following diagram.

SUBSTITUENT	ΔF at 25°		
	Ar_3C^+	Ar_2CH^+	Diff.
p-Dimethylamino	+12.72	+7.62	5.10
H	−5.68	−11.28	5.60
p-Chloro	−6.51	−12.19	5.68

We wish to emphasize the approximate nature of the above treatment and recognize that only first order effects are under consideration. For example the polar effect of replacing Ar by H is neglected. Nevertheless, model A leads to no such simple correlation with experiment. "Res" would differ since one less ring would be involved in resonance interaction. "Sol" and "S" would also change since the size of the ion and its charge intensity would be expected to change on the basis of model A.

It is of interest that the ΔF due to steric strain, 5.6 kcal., is the same as the ΔF due to steric strain that Taft (15) found in the hydrolysis of strongly hindered esters, in which reaction a similar change of trigonal to tetrahedral carbon occurs.

The difference in ΔF between the mono- and di-phenylcarbonium ion is 10 kcal., but this value is uncertain because of the uncertainty in the pK_{R^+} of the monophenylcarbonium ion. It is probable that this difference is due to difference in resonance energy and/or steric strain.

SPECTRA OF ARYLCARBONIUM IONS

The principal facts about the spectra of the arylcarbonium ions are as follows. (a): Substituents such as *p*-dimethylamino, *p*-amino, *p*-methoxy, and *p*-chloro cause an increase in λ_{max} and log ϵ relative to the triphenylcarbonium ion. These substituents were also those that gave a positive deviation in the plot of pK_{R^+} against *sigma* (Table I). These effects are related to the ability of these substituents to share the positive charge of the ion. (b): If each of the three rings in the triphenylcarbonium ion is successively substituted by one of

TABLE VII

ABSORPTION SPECTRA OF CARBONIUM IONS

λ (mμ)	Log ε	λ (mμ)	Log ε
Ion from mesitylcarbinol		Ion from dimesitylcarbinol	
330	3.64	330	3.83
340 max.	3.68	370 min.	2.39
420 min.	3.16	400	2.95
470 max.	3.39	450	3.81
500	3.22	525 max.	4.53
550	3.04	560	4.26
590	2.85	600 min.	3.49
		620	3.22
Ion from 9-fluorenol		Ion from 9-methyl-9-fluorenol	
330	3.62	330	3.71
420 min.	2.32	390 min.	2.66
484 max.	2.90	430	3.28
520 min.	2.53	460 max.	3.81
600	2.92	466 min.	3.78
655 max.	3.08	488 max.	4.17
700	2.97	500	3.70
750	2.68	520	2.51
800	2.57	560–700	<2

the above groups, the changes in the spectra are not continuous. The pattern of changes is the same in each series, λ_{max} and log ε increase from unsubstituted through mono- to the di-substituted triphenylcarbonium ion. However, the triply substituted ion has a slightly reduced λ_{max} and log ε relative to the di-substituted ion. This pattern is repeated when *p*-phenyl groups are successively introduced (18) and when crystal violet is successively protonated (19). Related to this effect is the close similarity in spectra between crystal violet (4,4′,4″-tris-dimethylaminotriphenylcarbonium ion) and its 3,5-dimethyl derivative (20) in which one of the *p*-dimethylamino groups is sterically inhibited from participating in resonance interaction. (c): Diarylcarbonium ions absorb at slightly higher λ_{max} and log ε than the similarly substituted triarylcarbonium ions. (d): The absorption spectra of the series Ar_2C^+(phenyl), Ar_2CH^+, Ar_3C^+, and $Ar_2C^+(CH_3)$, where Ar = an aryl ring, closely resemble each other, the first pair and the second pair bearing the closest resemblance.

Interpretation of the spectra is difficult due to the fact that increasing the length of a conjugated system may increase or decrease λ_{max} and log ε as demonstrated by the Pullmanns (21). For this reason we are not presenting our absorption spectra in detail until a consistent picture can be constructed. Likewise we defer for future consideration the conclusions of Lewis and Calvin (18) which were based on spectra.

Typical of the observations that we are unable to correlate are the following. The rings in the dimesitylcarbonium ion must be nearly at right angles to each other, or conceivably parallel (*i.e.* rotated 180° from coplanarity). Thus the absorption spectrum would be expected to closely resemble that of the monomesitylcarbonium ion. However, this is not the case, the λ_{max} differ, 525 and 470 mμ respectively, and a very large difference exists between the values of log ϵ, 4.53 and 3.39 respectively at the corresponding λ_{max}. Another remarkable difference exists between the absorption spectra of the carbonium ions derived from 9-fluorenol and 9-methyl-9-fluorenol (Table VII).

TRIARYLMETHYL FREE RADICALS

The development of theories regarding the structure of the triarylmethyl free radicals has paralleled in many ways that of the triarylcarbonium ions. With the advent of resonance theory, a structure was presented containing three equivalent rings contributing to the resonance hybrid. This was modified by the realization that steric strain was an important factor, as illustrated by the fact that *sym*-tetraphenyl-bis-triphenylmethyl (22) and *sym*-tetrabiphenylyl-bis-*tert*-butylethanes (23) were dissociated into free radicals to an extent comparable to the corresponding hexaarylethanes despite the fact that two less phenyl rings were available for resonance interaction. Finally Szwarc (*cf.* footnote 3) suggested that the benzyl free radical had as much resonance energy as the triphenylmethyl free radical, but this conclusion has been disputed (24).

EXPERIMENTAL

The concentration of carbonium ion was measured spectrophotometrically with a Beckmann model DU spectrophotometer. The temperature was maintained at 25 ± 2°.

The spectroscopic data measures the concentration of the carbonium ion (R^+). It has been tacitly assumed in calculating pK_{R^+} that the remainder of the added carbinol exists as the free carbinol (ROH) and that the amount of any other species, such as the protonated carbinol (ROH_2^+), was negligible. The best evidence for this assumption is the constancy of pK_{R^+} when computed by equation 2. However, this evidence is not completely convincing and we recognize that values of pK_{R^+} that are small may be seriously in error because of the presence of a third species, the protonated alcohol. If the carbinols had the same basicity as water (16), values of pK_{R^+} smaller than about -8.5 would be in error and the error would increase as the apparent value of pK_{R^+} decreased. No more definite statement can be made at present.

In a typical experiment the carbinol was dissolved in 95% ethanol to give a concentration of about 1 mg./ml. This stock solution was added to a glass-stoppered flask by means of a micropipette of 0.0581 ml. capacity. Then 10 ml. of sulfuric acid of the desired concentration was added. The flask was shaken and the solution measured immediately in the spectrophotometer. Some of the solutions changed optical density slowly with time, but in no case was this fast enough to introduce significant errors except with the monoarylcarbonium ions. In some cases, carbinols 5, 6, 8, 9, 11, and 12, there was no measurable change after 24 hours.

Generally the pK_{R^+} values were computed from measurements taken at five different sulfuric acid concentrations in which the ionization of the carbinol ranged from 10–90%. In the plots of J_0 against log c_{R^+}/c_{ROH}, the average deviation from a linear curve of unit slope ranged from 0.05 to 0.10. No trends were observed in the deviations except in the case of 9-fluorenol and 2,2′,2″-trimethyltriphenylcarbinol. In the first case the solution became cloudy when less than 70% was ionized. This cloudiness caused considerable light scattering which affected the 484 mμ band measurements more than those of the 655 mμ

band. The pK_{R^+} value listed in Table II is an average of data taken at 655 mμ and above 60% ionized, in which region the plot of J_0 against log c_{R^+}/c_{ROH} was linear with unit slope. Although there was no visible cloudiness, the same situation probably obtained with the 2,2′,2″-trimethyltriphenylcarbinol, because the J_0 *vs* log $c_{R^+}\lambda c_{ROH}$ plot was linear with unit slope only down to 50% ionized.

The preparation of most of the compounds has been previously described (2). The following additional compounds were used.

4,4′,4″-Tri-tert-butyltriphenylcarbinol. This compound was prepared by the method of Marvel and Kaplan (25). Forcing conditions such as described by Bachmann and Kloetzel were employed (26).

4,4′,4″-Triisopropyltriphenylcarbinol. This compound has not been previously reported. The method used was analogous to that employed for the *tert*-butyl analog. The yield of carbinol based on 4-bromoisopropylbenzene (diethyl carbonate was the other reactant) was 44%. The white prisms crystallized from dioxane with one molecule of dioxane per molecule of carbinol, m.p. 78.5–80°. The dioxane was quantitatively removed at 110°.

Anal. Calc'd for per cent dioxane: 18.56. Found: 18.01.

The solvent-free crystals prepared in this manner melted at 92–94°.

Anal. Calc'd for $C_{28}H_{34}O$: C, 87.05; H, 8.81.
Found: C, 86.74; H, 9.00.

The ether of this carbinol was obtained by evaporative distillation at 1 mm. The white crystals melted at 95–96° after recrystallization from alkanes and methanol.

Anal. Calc'd for $C_{56}H_{66}O$: C, 88.83; H, 9.05.
Found: C, 89.15; H, 9.08.

4-Methyltriphenylcarbinol. This was prepared by the method of Acree (27).

3,3′,3″-Trichlorotriphenylcarbinol. This was prepared by an adaptation of the method of Marvel, *et al.* (28).

4-Nitrotriphenylcarbinol. 4-Nitrotoluene was oxidized to 4-nitrobenzoic acid (29). The acid was converted to the acid chloride with thionyl chloride and condensed with benzene by the method of Schroeter (30). The ketone was converted to the dichloride with phosphorus pentachloride (31) and condensed with benzene (32). The crude carbinyl chloride was converted to the carbinol and purified (31). By the use of Norit, pure white crystals were obtained, m.p. 95.5–97°. The yield of pure material based on 4-nitrotoluene was 3.5%.

SUMMARY

Thermodynamic equilibrium constants for the reaction, $R^+ + H_2O = ROH + H^+$, have been measured for 20 mono-, di-, and tri-arylcarbinols. Water was chosen as the standard state. These results are tabulated with the values for 11 additional arylcarbinols measured by other workers. The λ_{max} and log ϵ for the absorption spectra in the visible region are also tabulated.

The results are interpreted as supporting a resonance hybrid structure for the triarylcarbonium ions in which the positive charge is delocalized into only one or possibly two of the aryl rings. This model leads to the relation: $(\Delta F_{Ar_3C^+}) - (\Delta F_{Ar_2CH^+}) \cong$ a constant which is a function of differences in steric strain terms. "Ar" is an *m*- or *p*-substituted phenyl ring. This relationship is experimentally observed.

Several of the pK_{R^+} values for the triarylcarbinols with similarly substituted rings give a linear curve when plotted against Hammett *sigma* values for the substituents. Two classes of deviations from this curve are discussed.

The utility of the J_0 acidity function is further demonstrated.

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