Solvent Effects in Organic Chemistry. III. Solvation of Stable Carbonium and Ammonium Ions in Water. The Temperature Coefficient of the H_R Acidity Scale[1,2]

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Apparent thermodynamic equilibrium constants in pure water as standard state have been determined for a series of triarylcarbinol–carbonium ion systems by means of measurements in aqueous sulfuric acid. This has been done carefully at four temperatures from 0 to 45° so that enthalpies and entropies of ionization may be obtained, and also the temperature coefficient of the H_R scale. Very large differences are found between the apparent thermodynamic properties of the most and least stable carbonium ions; the entropy changes especially are enormous. Most of the results are in rough agreement with a simple electrostatic treatment suggesting that stable carbonium ions do not have specific points of solvation to the aqueous medium. Because the entropy changes are proportional to the free energies of ionization of the carbinols, the often noted correlations between delocalization energy and pK_R are preserved in practice although they are wrong in principle. Very different results were obtained by Russian workers for the apparent thermodynamic properties of ionization for nitrated primary aniline Hammett indicators. It is suggested that the large entropies of ionization associated with nitrated anilines and carbinols may be artifacts. An interpretation is presented which explains the differences for carbonium and ammonium ions in terms of generalized dielectric solvation for the former and specific solvation through hydrogen bonds for the latter. Quantitative as well as qualitative support for the theory is cited which explains several other observations such as the difference between the H_R and H_0 acidity functions.

Introduction

The most important intermediates in acid-catalyzed reactions are electron deficient carbonium ions, and onium ions formed through coordination of the acidic system with one of the basic atoms of group V, VI, or VII. In order to provide a common basis for comparison of these ions in a widely used medium of good ionizing power, the equilibria involving them and their parent molecules are usually referred to a standard state of infinite dilution in water. However, all save the most stable carbonium or 'onium ions are so unstable (*i.e.*, so strongly acidic) in water that their concentrations cannot be observed directly in that medium. For the less stable ions thermodynamic equilibrium constants are therefore determined by the measurement of concentration equilibrium constants in a more acidic medium, where they can be observed directly, and are corrected back to the standard state through the overlap method invented by Hammett[3] and later applied to carbonium ion equilibria by Murray and Williams[4] and Deno.[5]

The overlap principle stands or falls on the strength of the assumption that the activity coefficients of similar ions and molecules will change in the same way through a given range of acid variation. Although this is only moderately successful for most kinds of weak organic bases and their 'onium ions,[6] it seems to hold well for di- and triarylcarbinols and the carbonium ions that are generated from them in aqueous acidic media as is evident from Deno's work[5] and that to be described below. It should be clear that if there were an analytical method which would permit the study of weak bases directly in water this would be

universally employed to give the standard thermodynamic properties. It is only because we have no means for accurately measuring say 10^{-11} mole per liter of a given carbonium ion in the presence of 10^{-5} mole per liter of its parent carbinol that we are forced to study the equilibrium in strong aqueous sulfuric acid and make correction to what it would be in water by means of the overlap principle with appropriate activity coefficients.

There is by now a wealth of data for the equilibrium constants of 'onium ion–molecule reactions[6] in aqueous acid. However, there are relatively few published values for the corresponding standard enthalpy and entropy changes, which are apt to be more revealing of solvation effects. All such free energies, enthalpies, and entropies can only be referred to the standard state if the overlap principle holds rigorously. A few values for the acid–base equilibria of strong bases have been collected recently.[7,8a,b] However, to our knowledge there is only one report of such properties for the equilibria of weak base 'onium ions ostensibly referred to water as standard state: that of Gelbstein, Shcheglova, and Temkin[9] for a series of primary aniline Hammett indicators in aqueous sulfuric acid. Their study also provides the temperature coefficient of the H_0 acidity scale.

In the investigation to be reported here, we have measured thermodynamic equilibrium constants for a series of Deno's arylcarbinols at several temperatures in aqueous sulfuric acid, the formal reaction being written in the direction

$$R^{\oplus} + HOH \rightleftharpoons ROH + H^{\oplus} \qquad (1)$$
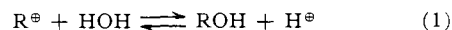
where ROH is the carbinol and R^+ is the carbonium ion. This may provide estimates of the standard thermodynamic properties for these equilibria which will allow comparison of the behavior of stabilized carbonium ions and ammonium ions in aqueous solu-

(1) From the Doctoral thesis of R. D. Bushick, University of Pittsburgh, 1961.

(2) We gratefully acknowledge the support of this work by the National Science Foundation, Grant G-14583. This manuscript was prepared in part while E. M. A. was a Visiting Lecturer at the University of Illinois. He is grateful for facilities which were made available to him there.

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(7) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959.

(8) (a) A. Albert and E. P. Sergeant, "Ionization Constants of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1962; (b) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 371.

(9) A. I. Gelbstein, G. Shcheglova, and M. I. Temkin, *Zh. Neorgan. Khim.*, **1**, 506 (1956).

tion, and also the temperature coefficient of the H_R scale.

To our knowledge, there are only three other reports of enthalpy and entropy measurements of carbonium ion equilibria. Evans and his co-workers[10] studied triarylmethyl chlorides in nitroalkane media, and Lichtin and Bartlett[11] examined two such compounds in liquid sulfur dioxide. After our measurements were complete Epple, Odintsova, and Entelis[12] presented thermodynamic properties for two triarylcarbinols in aqueous solution.

The thermodynamic properties for ions and molecules in varying acidic media refer, of course, to different standard states from that considered here and require other techniques for their measurement. We shall consider this related question in subsequent articles.

Experimental

Compounds.—Professor Norman C. Deno of Pennsylvania State University generously donated samples of the compounds: 4-methoxy-, 4,4'-dimethoxy-, and 4,4',4''-trimethoxytriphenylcarbinol; 4,4'-dinitrotriphenylchloromethane; 4,4',4''-trichlorotriphenylcarbinol; and $\alpha,\alpha,2,4,6$-pentamethylbenzyl alcohol. Xanthydrol, 9-fluorenol, and 4,4'-dimethoxybenzhydrol were prepared by the method of Bachmann[13] employing sodium amalgam reduction of the corresponding ketones which were Eastman White Label products.

4,4',4''-Trinitrotriphenylcarbinol was prepared using Montagne's[14] method for oxidation of 4,4',4''-trinitrotriphenylmethane which in turn was made from the trinitration of triphenylmethane (Eastman) with fuming nitric acid (Fisher Scientific Co.) following the method of Schwarz.[15] The melting points of the carbinol and methane were 189° (lit.[14] 189°) and 201–203° (lit.[15] 206°), respectively.

4-Nitrotriphenylmethane was prepared following Baeyer and Löhr[16] and then oxidized by Montagne's method.[14] The melting point of the methane was 89° (lit.[17] 93°) and of the carbinol was 135° (lit.[16] 136°).

4-Methyltriphenylcarbinol was made by the reaction of phenylmagnesium bromide and 4-methylbenzophenone using the procedure described by Vogel.[18] It melted at 72–73° (lit.[17] 73–74°). Triphenylcarbinol and hexamethylbenzene were Eastman White Label compounds.

Many of these compounds are difficult to prepare and maintain in pure form because of a strong tendency to revert to the bis-triarylcarbinyl ether. In every case the identity and purity were confirmed just prior to use by melting point determination and infrared spectrum. The visible or ultraviolet bands used for the indicator study also were checked against literature values for position and intensity.

Sulfuric Acid Solutions.—A large series of aqueous sulfuric acid solutions was prepared from Baker and Adamson C.P. grade concentrated sulfuric acid and distilled water. Their strengths were usually determined by density and indicator measurements as described by Arnett and Wu.[19] Concentrations of the acid solutions remained constant over several years. Whenever a solution gave evidence of contamination it was discarded.

Optical Density Measurements.—A Cary Model-14 spectrophotometer was used throughout the study and matched 10-cm. silica cells were employed to permit a low concentration of carbinol and also to provide maximum area of contact between the cells and the thermostated jackets that held them. The latter were made of brass tubing with inlet and outlet tubes placed as

far apart as possible so that good circulation of coolant would occur. Conditions and solutions in the sample and reference cells were identical in every respect except for the presence of the compound under study. The temperature in the jackets was maintained at 0, 15, 30, or 45° by means of reservoirs held at those temperatures with an ice slurry, a thermostated refrigerator, and conventional constant temperature baths, respectively. Heavily insulated hoses and a good circulating pump prevented the temperature gradient between reservoir and cell from exceeding 0.60°. Within the cell, temperatures did not vary more than ±0.01° as was shown by careful measurements using a dummy cell placed inside a model of the cell chamber.

Stock solutions were prepared just prior to use by dissolving the pure carbinol in 25 ml. of Spectrograde anhydrous methanol or glacial acetic acid. The concentration of the stock was chosen so that dilution of 0.1 ml. with 50 ml. of aqueous acid would result in an optical density of about 0.50 using the 10-cm. cell. Because of the high absorbance of these carbonium ions, their concentrations could be maintained between 10^{-4} and 10^{-6} mole per liter. Details of preparing the sample solutions are essentially those described by Arnett and Wu.[19]

Checks for precipitation and decomposition were performed on each compound[6,19] and also Beer's law plots.

Results

Calculations and Errors.—Concentration units for indicator and acid were moles per liter. Volume changes over our temperature range were estimated to cause variation of only 0.001 molarity unit which was ignored.

The standard state for all of the thermodynamic properties described here is ostensibly dilute solution in pure water. In order to tie our acidity scale to aqueous solution, the pK_{R^+} for the most basic carbinol, 4,4',4''-trimethoxytriphenylcarbinol was estimated through a linear extrapolation of $\log \left(\dfrac{C_{R^\oplus}}{C_{ROH}} - C_{H^\oplus} \right)$ $vs.$ $C_{H_2SO_4}$ to water following the procedure described by Paul and Long.[20] Deno[21] has already suggested that this is a somewhat extravagant precaution. The values for H_R of the various solutions and pK_{R^+} of the carbinols were then obtained through the overlap method.[3,5,6,20] Good overlap was uniformly observed in the sense that similar values of d $(\log Q)/$d % H_2SO_4 (where Q is the indicator ratio) were found for adjacent indicators at the same acid strengths. This is illustrated in Fig. 1 which shows the results at zero degrees where solubility problems are worst and accordingly the most serious disagreements might be expected. In Tables I–IV the values for H_R at the four temperatures of our study are presented for sulfuric acid solutions in terms of weight per cent.

Values for pK_{R^+} at 25° can be read from the plot of pK_{R^+} $vs.$ $1/T$ which was prepared for each indicator. In each case our result was very close to that obtained by Deno and his co-workers.[5] There are several ways of estimating the precision of our pK_{R^+} values. In one complete replica run for p-methoxytriphenylcarbinol there was over-all agreement within ±0.03 pK unit which matches well the standard deviation of ±0.02 pK found by us in another study[22] for repeated measurements of pK_a using the same equipment as that used in the current work. It is also possible to estimate the error from deviation of the pK_{R^+} values obtained analytically from indicator measurements

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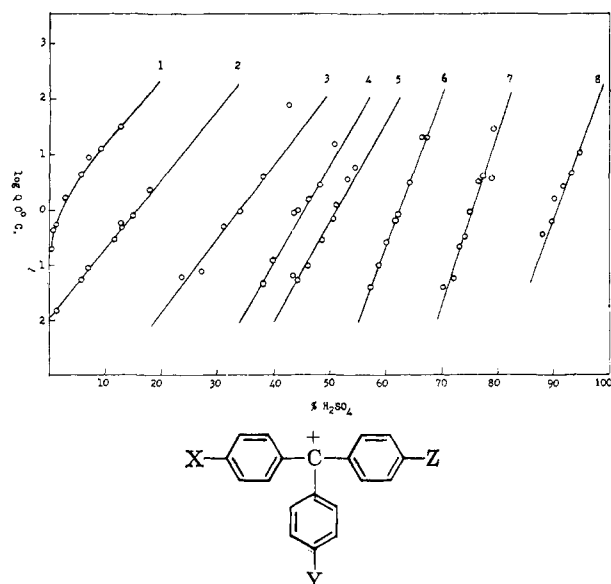(22) E. M. Arnett, T. Cohen, A. A. Bothner-By, R. D. Bushick, and G. Sowinski, *Chem. Ind.* (London), 473 (1961).

Fig. 1.—Indicator ratios of triarylcarbonium ions as a function of per cent sulfuric acid at 0°: 1, X = Y = Z = OCH₃; 2, X = Y = OCH₃, Z = H; 3, X = OCH₃, Y = Z = H; 4, X = CH₃, Y = Z = H; 5, X = Y = Z = H; 6, X = NO₂, Y = Z = H; 7, X = Y = NO₂, Z = H; 8, X = Y = Z = NO₂.

at each acidity through the relationship

$$pK_{R^+} = H_R + \log Q \qquad (2)$$

where $Q = C_{R^+}/C_{ROH}$. This is a harsher and less realistic method since it does not average small errors, as does the usual linear plot of the above equation. It gives entirely too much weight to the points that are far removed from the pK region. Nonetheless, this method of estimating the error leads to a standard deviation of about ±0.10 as an average figure for the carbinols studied.

TABLE I

H_R Values at 0° from the Smoothed Curve of H_R vs. % H₂SO₄

% H₂SO₄	H_R	% H₂SO₄	H_R	% H₂SO₄	H_R
0.75	+1.07	30.00	−3.09	66.00	−10.14
1.00	+0.94	32.00	−3.40	68.00	−10.71
1.50	+ .80	34.00	−3.71	70.00	−11.30
2.00	+ .69	36.00	−4.03	72.00	−11.95
4.00	+ .30	38.00	−4.38	74.00	−12.56
5.00	+ .14	40.00	−4.71	76.00	−13.14
6.00	− .02	42.00	−5.07	78.00	−13.71
8.00	− .28	44.00	−5.42	80.00	−14.28
10.00	− .49	46.00	−5.78	82.00	−14.81
12.00	− .70	48.00	−6.15	84.00	−15.33
14.00	− .91	50.00	−6.51	86.00	−15.88
16.00	−1.16	52.00	−6.90	88.00	−16.38
18.00	−1.40	54.00	−7.28	90.00	−16.85
20.00	−1.69	56.00	−7.68	92.00	−17.32
22.00	−1.93	58.00	−8.10	94.00	−17.80
24.00	−2.20	60.00	−8.56	96.00	−18.20
26.00	−2.50	62.00	−9.06	98.00	−18.63
28.00	−2.80	64.00	−9.60		

A third approach, which is probably most realistic, is to consider the standard deviation of points from the pK_{R^+} vs. $1/T$ plots for each compound. These are good straight lines and deviations for them represent the effective scatter to be considered in estimates of the $\Delta H°$ and $\Delta S°$ for the series. By this method the average standard deviation for pK_{R^+} is ±0.03

TABLE II

H_R Values at 15° from the Smoothed Curve of H_R vs. % H₂SO₄

% H₂SO₄	H_R	% H₂SO₄	H_R	% H₂SO₄	H_R
0.75	+1.12	30.00	−2.84	66.00	−10.40
1.00	+0.99	32.00	−3.14	68.00	−10.98
1.50	+ .83	34.00	−3.45	70.00	−11.55
2.00	+ .70	36.00	−3.78	72.00	−12.16
4.00	+ .30	38.00	−4.10	74.00	−12.79
5.00	+ .12	40.00	−4.45	76.00	−13.45
6.00	− .06	42.00	−4.80	78.00	−14.12
8.00	− .35	44.00	−5.20	80.00	−14.81
10.00	− .62	46.00	−5.59	82.00	−15.55
12.00	− .84	48.00	−6.01	84.00	−16.24
14.00	−1.09	50.00	−6.47	86.00	−16.86
16.00	−1.32	52.00	−6.92	88.00	−17.46
18.00	−1.51	54.00	−7.36	90.00	−18.04
20.00	−1.70	56.00	−7.82	92.00	−18.56
22.00	−1.91	58.00	−8.30	94.00	−19.08
24.00	−2.11	60.00	−8.80	96.00	−19.53
26.00	−2.32	62.00	−9.30	98.00	−20.00
28.00	−2.58	64.00	−9.83		

TABLE III

H_R Values at 30° from the Smoothed Curve of H_R vs. % H₂SO₄

% H₂SO₄	H_R	% H₂SO₄	H_R	% H₂SO₄	H_R
0.75	+1.16	30.00	−2.78	66.00	−10.37
1.00	+1.05	32.00	−3.10	68.00	−11.00
1.50	+0.95	34.00	−3.42	70.00	−11.67
2.00	+ .84	36.00	−3.79	72.00	−12.40
4.00	+ .50	38.00	−4.14	74.00	−13.15
5.00	+ .37	40.00	−4.50	76.00	−13.89
6.00	+ .23	42.00	−4.87	78.00	−14.60
8.00	− .01	44.00	−5.23	80.00	−15.28
10.00	− .20	46.00	−5.60	82.00	−15.94
12.00	− .40	48.00	−6.00	84.00	−16.58
14.00	− .61	50.00	−6.40	86.00	−17.21
16.00	− .82	52.00	−6.81	88.00	−17.82
18.00	−1.08	54.00	−7.23	90.00	−18.42
20.00	−1.33	56.00	−7.67	92.00	−18.99
22.00	−1.60	58.00	−8.09	94.00	−19.53
24.00	−1.89	60.00	−8.61	96.00	−20.07
26.00	−2.17	62.00	−9.17	98.00	−20.57
28.00	−2.49	64.00	−9.76		

TABLE IV

H_R Values at 45° from the Smoothed Curve of H_R vs. % H₂SO₄

% H₂SO₄	H_R	% H₂SO₄	H_R	% H₂SO₄	H_R
0.75	+1.10	30.00	−2.80	66.00	−10.70
1.00	+1.10	32.00	−3.08	68.00	−11.36
1.50	+0.88	34.00	−3.40	70.00	−12.01
2.00	+ .72	36.00	−3.70	72.00	−12.72
4.00	+ .40	38.00	−4.00	74.00	−13.46
5.00	+ .25	40.00	−4.35	76.00	−14.20
6.00	− .16	42.00	−4.69	78.00	−14.98
8.00	− .08	44.00	−5.03	80.00	−15.80
10.00	− .29	46.00	−5.41	82.00	−16.70
12.00	− .51	48.00	−5.80	84.00	−17.54
14.00	− .76	50.00	−6.23	86.00	−18.22
16.00	−1.00	52.00	−6.71	88.00	−18.84
18.00	−1.23	54.00	−7.28	90.00	−19.43
20.00	−1.49	56.00	−7.78	92.00	−19.98
22.00	−1.73	58.00	−8.31	94.00	−20.47
24.00	−2.00	60.00	−8.88	96.00	−20.96
26.00	−2.25	62.00	−9.46	98.00	−21.43
28.00	−2.52	64.00	−10.08		

and it is considerably better than this for many of the compounds.

Free energies of ionization were estimated from the expression

$$\Delta F^\circ = 2.303RT\mathrm{p}K_{\mathrm{R^+}} \qquad (3)$$

An error of ± 0.03 for $\mathrm{p}K_{\mathrm{R^+}}$ leads to an error of ± 288 cal. for ΔF°.

Enthalpies of ionization were obtained from the slope of a plot of $\mathrm{p}K_{\mathrm{R^+}}$ vs. $1/T$ following the vant Hoff equation which may be written for our purposes as

$$\mathrm{p}K_{\mathrm{R^+}} = \frac{\Delta H^\circ}{2.303RT} - \frac{\Delta S^\circ}{2.303R} \qquad (4)$$

The necessary assumption that ΔH° is constant over our temperature range within experimental error is supported by the clean straight lines which were obtained for every carbinol (see Fig. 2). This is in sharp contrast to what may be seen for ionogenic reactions such as the dissociation of molecular acids.[23] From eq. 4 one may easily estimate that the standard deviation in ΔH° is ± 271 cal./mole.

Entropy of ionization figures may be obtained from the other two properties through the definition

$$\Delta S^\circ = (\Delta H^\circ - \Delta F^\circ)/T \qquad (5)$$

Accordingly, the standard deviation of our ΔS° figures is ± 1.9 e.u.

The errors considered above are random errors but there are also important systematic errors which might spoil the accuracy of our results due to the cumulative failure of the overlap principle. Although changes in d log $Q/$d $\%$ H_2SO_4 are small as we go from each indicator to its nearest neighbor, Fig. 1 shows clearly that there is a progressive increase in this differential as we go to steadily stronger acid. This means than the operational acidity of the H_R scale increases much more steeply in strong acid solutions than in the weaker ones for each increment of added acid. Insofar as there are cumulative errors due to overlap failure, they will result in errors of accuracy for all the standard thermodynamic properties. The question of over-all accuracy and reasonableness of the results will be considered in the Discussion. If there were important differences in the response of d log $Q/$d $\%$ H_2SO_4 to changes of temperature, this would have serious effects on the estimated values of ΔH° since the $\mathrm{p}K_a$'s of the different indicators would be influenced not only by the changes to be expected if perfect overlap obtained, but also by the influence of temperature on whatever factors may prevent the overlap principle from working for these indicators. A careful examination of the effect of temperature on d log $Q/$d $\%$ H_2SO_4 as presented in Table V shows that such changes are small and random except for compounds 7 and 8 which bear two and three nitro groups, respectively. We shall consider the implications of this behavior later.

In Table VI are presented the $\mathrm{p}K_{\mathrm{R^+}}$ values obtained for each of the compounds we have studied referred at each temperature to the standard state. Also shown is the wave length used for optical density measurements of each carbonium ion. In general the absorption peaks were large and broad and showed little or no medium effects.

(23) G. N. Lewis and M. Randall, "Thermodynamics," 2nd Ed., revised by K. S. Pitzer and L. Brewer, McGraw–Hill Book Co., Inc., New York, N. Y., 1961, p. 305.
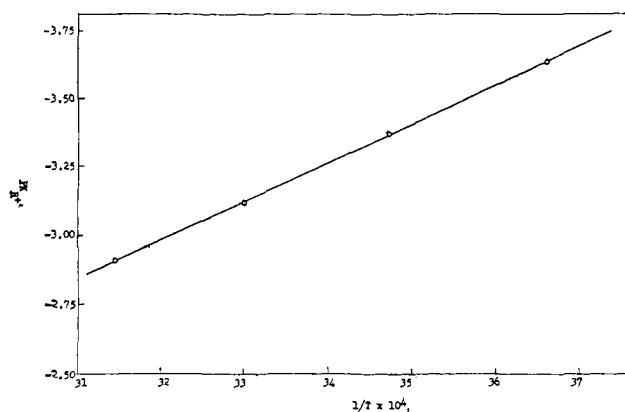

Fig. 2.—The $\mathrm{p}K_R{}^+$ of 4,4'-dimethoxytriphenylcarbinol in sulfuric acid as a function of $1/T \times 10^4$.

In Table VII are listed the standard thermodynamic properties for ionization of the triarylcarbinols investigated in this study and several relevant related compounds.

TABLE V

A TABULATION OF d LOG $Q/$d $\%$ H_2SO_4 VALUES AT 0, 15, 30, AND 45° FOR SOME TRIARYLCARBINOLS

No.	Substituent	$\%$ H_2SO_4	0°	15°	30°	45°
1	4,4',4''-Trimethoxy-	8.0	0.13	0.13	0.12	0.11
2	4,4'-Dimethoxy-	14.0	.13	.12	.12	.12
3	4-Methoxy-	30.0	.14	.13	.15	.15
4	4-Methyl-	48.0	.19	.21	.20	.20
5	Unsubstituted	58.0	.20	.22	.22	.22
6	4-Nitro-	70.0	.32	.26	.29	.29
7	4,4'-Dinitro-	81.0	.30	.33	.34	.41
8	4,4',4''-Trinitro-	83.0	.23	.29	.32	.33
		93.0	.24	.29	.33	.33

Discussion

The most striking feature of the results presented in Table VII is the extraordinarily large change in entropy of ionization observed over this series of carbonium ions. This raises a number of questions which shall be dealt with below: (1) Are the results presented in Table VII accurate? Is there any precedent for them? (2) If the results for the carbonium ions are correct, how do they compare with those found by Gelbstein, et al.[9] (3) If there are large differences between the behavior of carbonium and ammonium ions (and it will be seen that there are), what are the reasons for these differences?

1. **Validity of the Results.**—Support for our results is mustered from several sources. The only really comparable study is that of Epple, et al.,[12] for two triarylcarbinols which were studied at several temperatures in aqueous hydrochloric acid solution. If their measurements and ours are indeed referred to the same standard state, it should not matter what the actual experimental medium is as long as the overlap principle applies. It is gratifying to find that their values for 4,4'-dimethoxytriphenylcarbinol are $\Delta H^\circ = 5.72 \pm 0.03$ kcal./mole and $\Delta S^\circ = 13.49 \pm 0.04$ e.u.[24] in good agreement with ours. Lichtin and Bartlett[11] found the following values for the ionization of two triphenylcarbinyl chlorides in liquid sulfur dioxide: for unsubstituted trityl chloride, $\Delta F^\circ = +5.49$,

(24) It is not clear from this paper how the authors obtain the extraordinarily high precision in measuring entropy of ionization which they claim.

Table VI

Tabulation of Spectral and Basicity Data for Ionization of Triarylcarbinols and Related Compounds in Aqueous Sulfuric Acid Solutions

	Compound	mμ	pK 0°	15°	30°	45°
1	4,4',4''-Trimethoxytriphenylcarbinol	482	+0.65	+0.75	+0.84	+0.93
2	4,4'-Dimethoxytriphenylcarbinol	495	−1.20	−1.18	−0.69	−0.69
3	4-Methoxytriphenylcarbinol	472.5	−3.63	−3.37	−3.12	−2.91
4	4-Methyltriphenylcarbinol	450	−5.52	−5.34	−5.14	−5.08
5	Triphenylcarbinol	432	−6.71	−6.55	−6.39	−6.36
6	4-Nitrotriphenylcarbinol	452	−9.38	−9.44	−9.39	−9.48
7	4,4'-Dinitrotriphenylchloromethane	498	−13.10	−13.22	−13.46	−13.80
8	4,4',4''-Trinitrotriphenylcarbinol	420	−16.93	−17.81	−18.31	−18.84
9	4,4',4''-Trichlorotriphenylcarbinol	458	−7.60	. . .	. . .	−7.32
10	4,4'-Dimethoxybenzhydrol	503	−5.87	−5.69	−5.62	−5.36
11	Xanthydrol	372	−0.36	−0.34	−0.06	−0.04
12	4,4'-Dimethoxybenzophenone[c]	403	. . .	−4.37	−4.34[a]	−4.31
13	Xanthone[c]	333	. . .	−4.85	−4.81	−4.78
14	N-Methyl-2-nitro-4-chloroaniline[c]	455	. . .	−1.21	. . .	−1.20
15	N,N-Dimethyl-2,4,6-trinitroaniline[c]	385	−4.75	−4.71	. . .	−4.54
16	Hexamethylbenzene[c]	395	. . .	−8.41	. . .	−8.15
			. . .	−17.90[b]	. . .	−19.25[b]
17	9-Fluorenone[d]					
18	9-Fluorenol[d]					
19	α,α,2,4,6-Pentamethylbenzyl alcohol[d]					
20	3,5-Dimethyl-4-methoxybenzhydrol[d]					

[a] pK determined at 35°.   [b] pK based on the H_R acidity function.   [c] The pK's for these compounds were based on the H_0 acidity function whereas the pK's for all carbinols were based on the H_R acidity function.   [d] Could not be studied because of either solubility or decomposition.

Table VII

Tabulation of Apparent Standard Thermodynamic Quantities for Ionization of Triarylcarbinols and Some Related Compounds

$$R^\oplus + H_2O \rightleftharpoons ROH + H^\oplus$$

Compound	pK$_{R+}$ or pK$_a$, 25°	ΔF°, 25°, kcal./mole	ΔH°, 25°, kcal./mole	ΔS°, 25°, cal./mole deg.	TΔS, kcal./mole
4,4',4''-Trimethoxytriphenylcarbinol[a]	+0.82	+1.11	−2.49	−12.10	−3.61
4,4'-Dimethoxytriphenylcarbinol[a]	−0.89	−1.22	−5.68	−14.95	−4.46
4-Methoxytriphenylcarbinol[a]	−3.20	−4.37	−6.48	−7.10	−2.12
4-Methyltriphenylcarbinol[a]	−5.25	−7.16	−3.86	+11.08	+3.30
Triphenylcarbinol[a]	−6.44	−8.78	−3.41	+18.02	+5.37
4,4',4''-Trichlorotriphenylcarbinol[a]	−7.43	−10.13	−2.49	+25.64	+7.64
4-Nitrotriphenylcarbinol[a]	−9.44	−12.88	+0.87	+46.12	+13.74
4,4'-Dinitrotriphenylchloromethane[a]	−13.45	−18.35	+6.06	+81.90	+24.41
4,4',4''-Trinitrotriphenylcarbinol[a]	−18.08	−24.66	+16.80	+139.13	+41.46
4,4'-Dimethoxybenzhydrol[a]	−5.60	−7.64	−4.10	+11.87	+3.54
Xanthydrol[a]	−0.17	−0.23	−3.86	−12.19	−3.63
N-Methyl-2-nitro-4-chloroaniline[b]	−1.21	−1.65	−0.14	+5.05	+1.50
N,N-Dimethyl-2,4,6-trinitroaniline[b]	−4.65	−6.35	−2.39	+13.28	+3.96
Hexamethylbenzene	−18.37[a]	−25.06	+19.06[a]	+148.05[a]	+44.12[a]
	−8.32	−11.34	−3.66	+25.77	+7.68
4,4'-Dimethoxybenzophenone	−4.35	−5.94	−7.96	−6.80	−2.03
Xanthone	−4.83	−6.59	−9.84	−10.92	−3.25

[a] Values based on the H_R scale.   [b] These compounds were studied at two temperatures and in some cases three temperatures; therefore, there will be larger error for these values than for those based on four temperatures.

ΔH° = −8.9, and ΔS° = −1.8, while for the 4,4',4''-tri-t-butyl compound they obtained ΔF° = +2.62, ΔH° = −1.8, and ΔS° = −17. To compare their results with ours it is necessary to change the signs since they report the results for ionization rather than the reaction of carbonium ion with base as we do. It will be noted that a rather large entropy difference is found between these two compounds even though the structural change is modest.

Turning now to Fig. 3, a linear relationship between ΔF° and ΔS° is to be expected for a series of closely related compounds undergoing ionization if the only factor determining the stabilities of the ions is the work of charging them in a continuous dielectric medium.[25,26]

It is then easily shown that

$$\Delta S° = \Delta F°(d \ln D/dt)$$

where D is the dielectric constant of the medium. This expression predicts here a ΔS° vs. ΔF° slope of −4.63 × 10⁻³ (d ln D/dt for water)[27] and that the correlation line should pass through the origin. The best straight line (solid) through all of the' points in Fig. 3 has a slope of −6.3 × 10⁻³. However, this line gives heavy

(25) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book, Co., Inc., New York, N. Y., 1940.

(26) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., Inc., New York, N. Y., 1953.

(27) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 141.

weight to points 6, 7, and 8 for nitrated carbinols. Hammett and Chapman[28] observed that nitrated aromatics exhibit sharp increases of solubility in strong aqueous acid compared to many other organic solutes, and Boyd[29] has recently shown how this activity coefficient behavior can influence acidity functions. In Table V it was seen that d log Q/d % H_2SO_4 is relatively invariant with temperature for all indicators except 7 and 8. It is therefore worth considering the result of excluding the nitrated indicators from the correlation in Fig. 3 since the very high entropies associated with them may be an artifact resulting from specific solvation of the nitro groups.[30] The dashed line has been drawn with the electrostatic slope of -4.6×10^{-3}. It accommodates fairly well the rest of the compounds. Although the fit is rough, it is in general conformity with the notion that ordinary triarylcarbonium ions approach electrostatic behavior in aqueous solution. A similar plot from the data of Evans and co-workers[10] for the ionization of seventeen triarylmethyl chlorides in nitromethane has a slope of -1.8×10^{-3} although d ln D/dt may be estimated[31] as -4.3×10^{-3}. In that solvent there is much ion aggregation so that thermodynamic properties are a composite of the effects of ionization and dissociation and the situation cannot be directly compared with that in a good ionizing medium.

A number of authors have correlated quantum mechanical delocalization energies of carbonium ions with pK_a's of carbinol indicators. This, of course, is based on the assumption that the calculated energies correspond to those which would apply to the ion under vacuum at absolute zero and that the entropy change involved in transferring them from these conditions to aqueous solution at room temperature should be zero or constant. The results cited above show that such an assumption is erroneous but that the frequently observed correlations will not be damaged by the error. If the carbonium ions follow the electrostatic law, the entropy of ionization is proportional to the free energy of ionization and the parallel between delocalization energy and free energy is preserved. Indeed, linear correlations of free energy and entropy are quite common even for systems that are not governed by purely electrostatic factors.[8a] The enthalpies of ionization in Table VII combine internal and solvation energies so that they too may be a poor guide to pure potential energy factors.

2. Comparison of Carbonium and Ammonium Ion Equilibria.

—Deno,[21] Taft,[32] and Boyd[29] have presented good evidence that there is considerable difference in solvation between triarylcarbonium ions and 'onium ions of Hammett bases in aqueous solution. Since solvation changes are usually most clearly displayed by enthalpy and entropy factors, we may now consider what differences exist between our results and those of Gelbstein and his co-workers[9] who studied
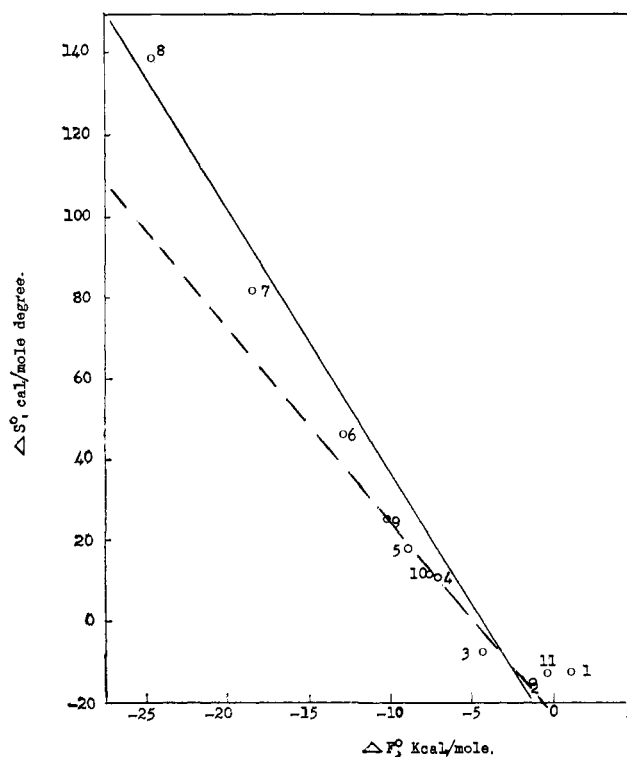
(28) L. P. Hammett and R. P. Chapman, J. Am. Chem. Soc., **56**, 1282 (1934).

(29) R. H. Boyd, ibid., **85**, 1555 (1963).

(30) This limitation on the results cited here has been added since E. M. A. discussed them at the Symposium on Reactions in Strong Acids at the American Chemical Society Meeting in New York, September 11, 1963. It will not change the validity of most of the material presented by him there.

(31) F. Buchley and A. A. Maryott, J. Research Natl. Bur. Standards, **53**, 229 (1954).

(32) R. W. Taft, Jr., J. Am. Chem. Soc., **82**, 2965 (1960).

Fig. 3.—The apparent standard change in entropy as a function of the standard change of free energy for carbinol indicators: 1, X = Y = Z = OCH_3; 2, X = Y = OCH_3, Z = H; 3, X = OCH_3, Y = Z = H; 4, X = CH_3, Y = Z = H; 5, X = Y = Z = H; 6, X = NO_2, Y = Z = H; 7, X = Y = NO_2, Z = H; 8, X = Y = Z = NO_2; 9, X = Y = Z = Cl; 10, 4,4'-dimethoxybenzhydrol; 11, xanthydrol; solid line is best line through all points; dashed line is that required by electrostatic theory.

primary aniline Hammett indicators at a series of temperatures in aqueous sulfuric acid.

From Table VIII, which presents their data, it is clear that there is a large increase in the apparent entropy of ionization between the most and least basic of their compounds. Furthermore, this entropy increase is linearly related to the changes in free energy and enthalpy. However, the slope for the ΔF° vs. the ΔS° plot in this case is -1.5×10^{-3} showing that the anilinium ions do not conform to the simple electrostatic theory.

TABLE VIII

TABULATION OF THERMODYNAMIC DATA FOR SUBSTITUTED ANILINES AT 25°

Compound, aniline	pK_a[a]	ΔH°,[b] kcal./ mole	ΔF°,[a] kcal./ mole	ΔS°,[b] cal./ mole deg.	$T\Delta S^\circ$, cal./ mole
p-Nitro-	+0.99	+4.60	+1.52	+10.5	+3.08
o-Nitro-	−0.29	+3.36	−0.64	+12.1	+3.60
p-Chloro-o-nitro-	−1.03	+3.08	−1.19	+14.5	+4.32
2,4-Dichloro-6-nitro-	−3.32	+1.68	−4.01	+19.2	+5.61
2,4-Dinitro-	−4.53	+0.42	−5.99	+21.5	+6.40
6-Bromo-2,4-dinitro-	−6.71	0	−9.00	+30.14	+8.97
2,4,6-Trinitro-	−9.41	−3.10	−12.67	+31.7	+9.45

[a] Reference 20.   [b] Reference 9.

All of the compounds studied by the Russians carry nitro groups, as indeed do most of the weakly basic indicators used for the construction of all present acidity functions. We have just suggested above that the very large free energies and entropies associated with the least basic carbinols may be artifacts resulting from the presence of nitro groups: the same challenge

may be addressed *a fortiori* to the aniline indicators. For them, however, there is an independent (but presently inconclusive) test since nonnitrated anilines are strong enough bases to be studied directly in dilute acid approximating the standard medium. A plot of presently available[8a] $\Delta F°$ *vs.* $\Delta S°$ data for nine methyl substituted anilines and one chloroaniline produces a random scatter pattern even when those with *ortho* groups are omitted. Taken at face value, this clearly implies that no simple relationship between free energy and entropy of ionization is actually to be expected in the standard medium for anilines and therefore the correlation which we have found for them is probably an artifact introduced by variations in specific solvation of the nitro groups with changing temperature and acidity. Unfortunately, most of the thermodynamic data for ionization of anilines in water are presently under a cloud of suspicion.[8a] At this point it seems wise to consider that the thermodynamic data for all nitrated indicators, both carbinols and anilines, are not truly referrable to an aqueous standard state. It remains to be seen whether the values presented for the other carbinols are really standard values.

3. Reasons for the Differences between the Behavior of Carbonium Ions and Ammonium Ions in Solution.—If it is true that carbonium ions follow the predictions of simple electrostatic theory in contrast to the anilinium ions, it is implied that the interaction of the latter with the medium is through more specific chemical mechanisms such as hydrogen bonding.

These results bear out suggestions of Taft and Deno regarding differences in solvation of carbonium and other kinds of 'onium ions. The conjugate acid of a primary aniline carries three acidic hydrogens for hydrogen bonding to the solvent. The positive charge is centered on the nitrogen atom and can be reduced

<pre>
      H–O–H
        |
      H ⊕   H
             /
   Ar–N–H···O
        | \
        H   H
        |
        O
       / \
      H   H
</pre>
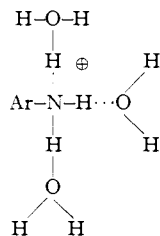
through delocalization into the medium through solvation. Specific hydrogen bonding apparently provides a more effective means for lowering the energy of this kind of ion in water than does the generalized readjustment of solvent dipoles around a small and somewhat crowded center. As the ammonium ion becomes more acidic through accumulation of electron-attracting groups, the hydrogen bonds to the surrounding water become increasingly acidic and the delocalization of charge into the solvent requires the involvement of larger numbers of water molecules held by stronger interactions.

Carbonium ions differ sharply from protonated onium ions in that they carry no acidic hydrogens for direct solvation. Since they carry a positive charge, they cannot be hydrogen bond acceptors in the way that anions can. Their only means of direct chemical solvation is through interaction of their open orbitals with the unshared pairs of surrounding water molecules. However, this type of Lewis acid-base

interaction must result in collapse of the solvate to give the carbinol; it is probably the main kind of solvation of unstable carbonium ions during solvolysis. Unlike 'onium ions the charge in carbonium ions is delocalized over most or all of the ion which is sufficiently large compared to the surrounding water molecules so that it probably "sees" relatively little fine structure in the solvent. Ordinary triarylcarbonium ions therefore may interact with the solvent through general reorientation of solvent dipoles around their peripheries. The only alternative means for reducing the energy of such an ion are pairing with its counterion (as may happen in very nonpolar solvents) or delocalization of charge into electronically adaptable groups. The stablest carbonium ions are obviously those which carry substituents suitable for delocalization of the charge. The difference between solvation of ammonium ions and carbonium ions then lies in the means that the former has for fitting into the existing structure of water through hydrogen bonding so that a smaller number of water molecules are reoriented in the process of solvation.

It is well known that the H_R function changes much more rapidly as acidity is increased than does H_0. The two functions may be written in terms of activities as

$$H_R = -\log \frac{a_{H^-} f_{ROH}}{a_{H_2O} f_{R^-}}$$

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

so that

$$H_R - H_0 - \log a_{H_2O} = \log f_{BH^-}/f_{R^-}$$

if the usual assumption is made that the activity coefficients for B and ROH respond in a similar manner to changes in acidity.[5,33] This is probably safe except for B and ROH bearing different numbers of hydrogen-bonding groups in strong acid. The ratio f_{BH^-}/f_{R^+} changes considerably with increasing acid strength and is the main factor in deciding the difference between the two acidity functions.[5] Since an activity coefficient represents the work required to transfer the entity under consideration from the standard state to the solution in question, the fact that $\log f_{BH^-}/f_{R^-}$ becomes increasing large and positive indicates that the solubilities of carbonium ions increase rapidly relative to ammonium ions as one goes from water toward strong acid. Boyd's[29] recent elegant study of the solubility of appropriate ammonium and carbonium ion salts supports this completely. In brief, his results show a steady increase in solubility (decrease in *f*) for all types of these ions as acidity is increased. However, the solubilities of primary anilinium ions increase least rapidly while those of secondary and tertiary ones rise more rapidly in that order. Large spherical cations with no acidic protons, such as tetraalkylammonium ions or 4,4',4''-trimethoxytriphenylcarbonium ion, increase most rapidly of all. It is clear, therefore, that the main difference between the H_R and H_0 acidity functions (after the formal differences involving $\log a_{H_2O}$ has been disposed of) lies in the two

(33) N. C. Deno and C. Perizzolo, *J. Am. Chem. Soc.*, **79**, 1345 (1957).

different modes of solvation open to the two series of ions used to develop these functions.

Sulfuric acid has often been recognized as a nearly ideal electrolytic solvent. At 20°, its low frequency dielectric constant is 110,[34] a good 30 units greater than water. It is naturally an extraordinarily poor hydrogen bond acceptor. Accordingly, the behavior observed by Boyd is exactly what would be expected from the picture we have outlined: large spherical ions have considerable incentive to reduce their energies through transfer from water to sulfuric acid, while small polybasic acidic ions must sacrifice specific solvation to water in order to enjoy the greater non-specific solvation in sulfuric acid.

Boyd's results show clearly that anilinium ions are appreciably solvated and that their solvation differs with the degree of the aniline base. In agreement with this observation, independent measurements[35] in the writer's laboratory show clearly that there is a considerably different H_0 acidity function for a series of tertiary amine indicators than that published recently for primary ones[36]; furthermore, the function for the tertiary ones falls part way between that for the primaries and the H_R function for carbonium ions in conformity with the above discussion. This observation has two other important implications. Firstly, it shows clearly the severe limitations of the activity coefficient postulate[3,6,20] upon which the exact use of the

H_0 function for Brönsted bases is hinged. Secondly, it indicates that the widely quoted calculation of the H_0 acidity function by Bascombe and Bell[37] purely from the concentration of tetrahydrated hydrogen ions and the activity of water is fortuitous. Those authors make clear that their treatment assumes negligible hydration of the indicator and its cation, a requirement which is no longer supportable as Taft has already suggested.[32]

Effect of Temperature on the H_R Acidity Scale.— Gelbstein, et al.,[9] found that the H_0 scale does not change much with temperature and that the direction of change depends upon the strength of acid. The H_R scale behaves the same way becoming steadily more negative with increasing temperature for solutions above 65% and behaving erratically in lower concentrations. The H_0 function is determined by three activity terms and the H_R function by four. We feel that an analysis of the effects of temperature on these different components would be an unwarranted and fruitless speculation at this time.[38]

Acknowledgment.—In the development of this work the authors have had many useful discussions with various colleagues. We are particularly indebted to the help of Professors N. C. Deno, H. Frank, E. Grunwald, L. P. Hammett, and R. W. Taft, Jr.

(34) J. C. D. Brand, J. C. James, and A. Rutherford, *J. Chem. Soc.*, 2447 (1953).

(35) G. Mach and E. M. Arnett, unpublished results.

(36) M. J. Jorgenson and D. R. Hartter, *J. Am. Chem. Soc.*, **85**, 878 (1963).

(37) R. P. Bell and K. N. Bascombe, *Discussions Faraday Soc.*, **24**, 158 (1957).

(38) Professor Hammett suggests that the small temperature coefficients of the H_0 and H_R acidity scales implies that the heat of transfer of a proton from aqueous solution to the medium in question is nearly equal to the difference between the heats of transfer of the ammonium or carbonium ion and its corresponding base to the same solution. This is supported by the fact that $\Delta H°$ values in both series are of comparable magnitude over most of the acidity range.

The Solvation of Polar Groups. III. Conformational and Chemical Effects of the Solvation of Polar Groups[1]

BY C. D. RITCHIE AND A. L. PRATT[2]

RECEIVED AUGUST 7, 1963

Dissociation constants for the 1:1 complexes of acetonitrile and of *p*-anisonitrile with dimethyl sulfoxide are found to be essentially the same as those previously found for a series of substituted benzonitriles. The importance of this type of specific solvation on the equilibrium of *cis*- and *trans*-4-*t*-butylcyclohexylcarbonitrile and on the relative rates of borohydride reduction of cyclohexanone and dihydroisophorone is illustrated, and the generality of the effects is discussed.

In earlier work,[1] we have shown that the cyano group and the carbonyl group of solutes in dimethyl sulfoxide or dimethylformamide solvents form 1:1 complexes with the solvent in which the solvent attachment is to the polar group rather than to the entire molecule. The implications of this discovery are manifold, and the phenomenon is almost certainly a general one for many polar groups and polar solvents.

In the present paper, we report results which further indicate the insensitivity of stability of the complexes to electronic features of the moiety of the solute not directly involved in the complex formation. In order

to observe the sensitivity of the complex formation to steric effects, and at the same time illustrate the importance of specific solvation on the chemical and physical properties of solutes, we have studied the solvent effects on the equilibrium constant for the conversion of *cis*- to *trans*-4-*t*-butylcyclohexylcarbonitrile, and on the relative rates of borohydride reduction of cyclohexanone and 3,3,5-trimethylcyclohexanone (dihydroisophorone).

Methods and Results

Solvent Effects on the Intensities of Infrared Nitrile Bands.—The solvent effects on the infrared intensities of the nitrile bands of acetonitrile and of *p*-anisonitrile in binary mixtures of carbon tetrachloride and dimethyl sulfoxide were studied by the previously developed methods.[1] The data obtained for acetonitrile