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Temperature Variation of the H_R Acidity Function in Aqueous Sulfuric Acid[1]

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Abstract: The variation of the H_R acidity function with temperature has been defined by the extent of ionization of triarylcarbinol indicators at temperatures of 25, 40, 60, 80, and 90°. The correlation of H_R and temperature is expressed by an empirical equation which should have important applications in mechanistic investigation. A linear relationship is found between the pK_{R^+} values at 25° and ΔH_{25}.

Previously, we have reported investigations on the variation of H_0 in aqueous sulfuric acid with temperature[2] and the correlation of the pK_a values of the nitroaniline indicators with ΔH_{25} in a linear free energy-enthalpy correlation.[3] In continuation of these studies, we have now obtained data on the temperature dependency of the H_R scale in aqueous sulfuric acid. This variation had previously been investigated by Arnett and Bushick;[4] however, their results extended only to 45°. They concluded that the H_R scale becomes steadily more negative with increasing temperature for solutions above 65% but that it behaved erratically and discontinuously in lower concentrations. For example H_R for 20% H_2SO_4 was reported as -1.69 (0°), -1.70 (15°), -1.33 (30°), and -1.49 (45°). These conclusions appeared suspect for at least two reasons: (i) there is no analogy with the temperature variation of the H_0 scale,[2] the work of Gel'bshtein[5] being incorrect, and (ii), although the erratic behavior made it difficult to interpolate for 25°, if this is done approximately then significant discrepancies are found with the results reported by Deno[6] for the single temperature of 25°. Values of H_R at elevated temperatures would be most useful for the elucidation of carbonium ion type reactions carried out in aqueous sulfuric acid above room temperature. We ourselves are particularly interested in the variation of nitronium ion concentration with temperature, for more explicit elucidation of nitration studies in heteroaromatic compounds,[7] following Moodie and Schofield's demonstration[8] that the acidity variation of the rate constants for such nitrations are given by eq 1. Unfortunately,

$$\log k_2 = -(H_R + \log a_{H_2O}) + \text{constant} \qquad (1)$$

extrapolation of Arnett's H_R scale to higher temperatures is impossible because of the discontinuous variation reported (see figure quoted above for 20% H_2SO_4). It was therefore essential to reinvestigate the temperature variation of H_R. Our studies have now shown that the earlier conclusions[4] are incorrect; the H_R scale is proved to be a well-behaved continuous function of temperature and does indeed show considerable analogy to the temperature dependence of the H_0 scale.

Throughout these investigations, the experimental techniques and methods of calculation outlined in the previous paper[2] were employed. No modification or extension was required. Random checks on instrument reproducibility using the results of the initial paper entirely confirmed their accuracy.

Errors. Correlation coefficients and standard deviations shown in the tables were calculated by standard formulas.[9,10]

Experimental Section

Materials. Sulfuric and hydrochloric acids were Analar grade reagents. Water was purified as previously.[2]

The triphenylmethanol indicators used for the determination were 4,4′,4″-trimethoxy, 4,4′-dimethoxy (as chloride) (solutions made up with the chloride), 4-methoxy-4′-methyl, 4-methoxy (as chloride), 4,4′,4″-trimethyl, 4-methyl, unsubstituted, 4,4′,4″-trichloro, 4-nitro, 3,3′,3″-trichloro (as chloride), 4,4′-dinitro (as chloride), 4,4′,4″-tris(trimethylammonium) (as perchlorate), and 4,4′,4″-trinitro. These were prepared and purified by standard procedures. Their analyses corresponded with their molecular formulas and their melting points agreed with previous workers.[9] Synthetic difficulties often encountered in this field were found here—intractable gum and tar formation from which products crystallized reluctantly in low yield. It has been suggested[9a] that the trinitrocarbinol is unstable; our observations confirmed this and showed that it is also light sensitive. Stock solutions of this compound were therefore kept in the dark at −80°. The measurements on the indicator showed that the results were accurate up to and at 60°, but above this, at 80°, they were less reliable and impossible to obtain at 90°, because decomposition had become so rapid. Extensive checks on all the other indicators showed them to be stable in all strengths of sulfuric acid at 90°.

Methods. The preparation of solutions and their spectrophotometric determination were carried out precisely as described previously.[2,9] Medium effects on uv spectral characteristics were in all cases negligible.

Results. The pK_{R^+} values for the anchoring indicator, 4,4′,4″-trimethoxytriphenylcarbinol were measured in aqueous HCl. They are recorded in Table I. Table II gives indicator data. Measurements of I ($[R^+]/[ROH]$) were made for the whole indicator series, in aqueous sulfuric acid, at temperatures of 25, 40, 60, 80, and 90°. Readings for each indicator were made at two or three different wavelengths, and each set of determinations was duplicated. The averaged values of log I were then plotted on large scale graph paper and values read off at close intervals of acidity as given in Table III, which also contains the complete set of data for the first two indicators of the series, from which the accuracy and repro-

Table I. pK_{R^+} Determinations of 4,4′,4′′-Trimethoxytriphenylcarbinol in Aqueous Hydrochloric Acid[a]

Molal concn, pcH[b]	pK_{R^+} (apparent) 25°	40°	60°	80°	90°
0.052	0.840	0.894	0.980	1.065	1.117
0.084	0.842	0.903	0.990	1.082	1.130
0.100	0.847	0.907	0.998	1.095	1.139
0.131	0.862	0.917	1.011	1.103	1.153
0.143	0.871	0.924	1.018	1.115	1.166
0.160	0.873	0.927	1.029	1.129	1.178
0.195	0.888	0.937	1.038	1.134	1.189
0.243	0.906	0.960	1.059	1.166	1.219
0.320	0.939	0.973	1.093	1.206	1.267

pK_{R^+}[c]	Temp (°C)	Correlation coefficient
0.817 ± 0.002	25	0.989
0.874 ± 0.002	40	0.985
0.959 ± 0.002	60	0.995
1.044 ± 0.002	80	0.994
1.089 ± 0.002	95	0.994

[a] Absorbance measured at 482, 486, and 488 nm; the ionization ratios are calculated, and then averaged. [b] pcH = −log [H$^+$], see ref 2. [c] Averaged from three reading collections, of which the results above are one.

ducibility of the readings may be judged. Table III may be found in the microfilm edition of this volume. See paragraph at end of paper regarding supplementary material. Table IV gives pK_{R^+} values at the various temperatures, and the regions of overlap available for calculation of ΔpK_{R^+} and Figure 1 shows the plots of log I *vs.* % H_2SO_4 at the temperature extremes. The "parallelism" of such plots is best judged by the correlation between one set of log I values and the next in the overlapping region. Such a process may be computerized[2] and the relevant figures are given in Table V. It can be seen that the degree of parallelism is poor in several cases, notably the overlap between indicators 9 and 10 and 10 and 11. This stems from the very high slope of the log I/per cent H_2SO_4 plots which would necessitate the preparation of an inordinately large number of indicators for experimental observation of overlap in regions where log I values are most accurate, which must be considered in conjunction with synthetic difficulties. In this context the σ^+ correlations reported in the discussion section can be taken as an important verification of the validity of our results, but we are not unaware that we have previously[2] criticized other workers with regard to inadequate overlap.

Table VI gives the temperature variation of the H_R scale. Table VII gives a direct comparison of our H_R values with those of Arnett[4] and of Deno.[6] Whereas the agreement with Deno is satisfactory, there is significant disagreement with the other data.[4]

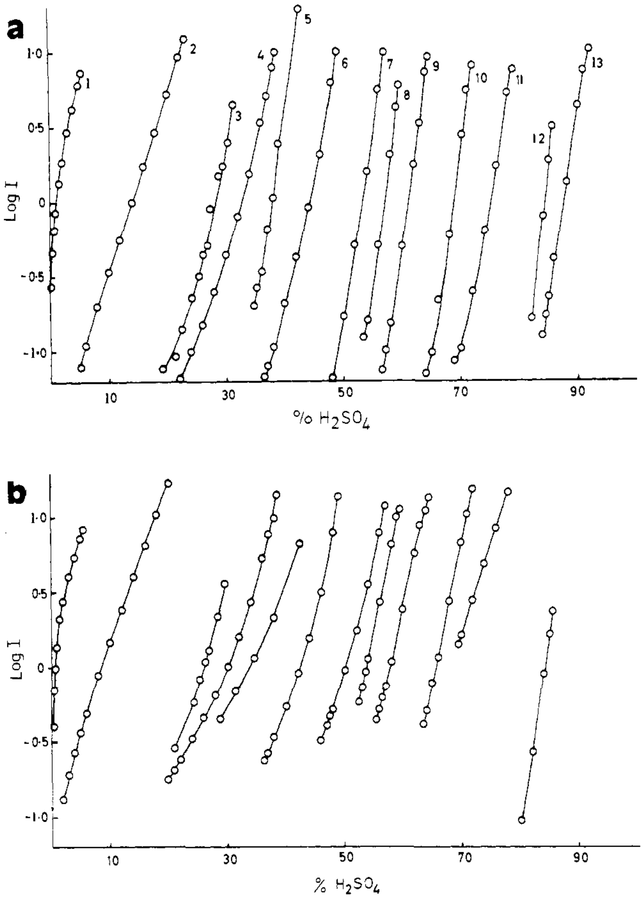

Figure 1. Logarithm of the ionization ratios of triarylcarbinols *vs.* % sulfuric acid at: (a) 25°, (b) 90°.

H_R was found to be proportional to $1/T$ (degrees absolute), so that previously discussed methods[2] were used to calculate figures for A and B, given in Table VIII, from eq 2. Figure 2 shows the H_R scale and its temperature variation diagrammatically.

$$H_R = A/T + B \qquad (2)$$

Discussion

Our values for H_R yield excellent straight lines, all of correlation coefficient better than 0.995, when plotted

Table II. Indicator Data

Compound no.	Triphenylmethanol	Mp, °C	Lit. mp, °C	Ref
1	4,4′,4′′-Trimethoxy	82.5–83.5	83.5–84	*a*
2	4,4′-Dimethoxy (as the chloride)	113–114	114–115	*b*
3	4-Methoxy-4′-methyl	Analysis obtained of oil which could not be crystallized		*c*
4	4-Methoxy (as the chloride)	118–121	124	*b*
5	4,4′,4′′-Trimethyl	92.5–93	94	*d*
6	4-Methyl	73–74	73–74	*e*
7	Unsubstituted	162–163	164.2	*f*
8	4,4′,4′′-Trichloro	92.5–93.5	98	*g*
9	4-Nitro		97–98	*h*
10	3,3′,3′′-Trichloro (as the chloride)	89–91	90–92	*i*
11	4,4′-Dinitro (as the chloride)	138–139.5	141	*j*
12	4,4′,4′′-Tris(trimethylammonium)	293–294 dec	296 dec	*k*
13	4,4′,4′′-Trinitro	188–189	189	*l*

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Table IV. pK_R - Values of Triarylcarbinols

Compd no.	pK_R 25°	40°	60°	80°	90°
1	0.82 ± 0.00	0.87 ± 0.00	0.96 ± 0.00	1.04 ± 0.00	1.09 ± 0.00
2	−1.02 ± 0.043	−0.88 ± 0.034	−0.60 ± 0.006	−0.36 ± 0.038	−0.21 ± 0.015
3	−2.84 ± 0.057	−2.62 ± 0.006	−2.44 ± 0.012	−2.04 ± 0.053	−1.93 ± 0.054
4	−3.51 ± 0.272	−3.35 ± 0.211	−2.97 ± 0.154	−2.27 ± 0.010	−2.22 ± 0.164
5	−4.46 ± 0.101	−4.06 ± 0.048	−3.43 ± 0.010	−2.57 ± 0.102	−2.53 ± 0.153
6	−5.70 ± 0.207	−5.24 ± 0.153	−4.59 ± 0.083	−3.57 ± 0.014	−3.37 ± 0.016
7	−7.66 ± 0.050	−7.02 ± 0.090	−5.87 ± 0.151	−4.59 ± 0.093	−4.42 ± 0.122
8	−8.64 ± 0.038	−7.95 ± 0.021	−6.59 ± 0.072	−5.17 ± 0.053	−4.92 ± 0.03
9	−9.76 ± 0.107	−9.01 ± 0.117	−7.58 ± 0.048	−6.15 ± 0.021	−5.59 ± 0.04
10	−11.77 ± 0.163	−10.84 ± 0.083	−9.14 ± 0.028	−7.60 ± 0.021	−6.94 ± 0.00
11	−13.06 ± 0.300	−12.16 ± 0.157	−10.21 ± 0.107	−8.38 ± 0.101	−7.46 ± 0.093
12	−15.77 ± 0.097	−14.40 ± 0.040	−12.60 ± 0.064	−10.84 ± 0.092	−9.90 ± 0.03
13	−16.68 ± 0.148	−14.96 ± 0.247	−13.06 ± 0.191	−11.14 ± 0.095	

Table V. Values of Slope in Region of Overlap

Overlap	Slope	Overlap	Slope
1-2	0.759	7-8	1.074
2-3	1.412	8-9	1.340
3-4	1.629	9-10	3.091
4-5	0.749	10-11	2.108
5-6	1.877	11-12	0.682
6-7	1.244	12-13	1.705

Table VI. H_R Values at Different Temperatures

Wt % H_2SO_4	25°	40°	60°	80°	90°
6	−0.08	−0.08	0.05	0.09	0.12
8	−0.03	−0.03	−0.02	−0.02	−0.02
10	−0.55	−0.54	−0.44	−0.40	−0.36
12	−0.78	−0.75	−0.65	−0.63	−0.60
14	−1.02	−1.00	−0.90	−0.85	−0.80
16	−1.25	−1.23	−1.15	−1.05	−0.95
18	−1.50	−1.45	−1.38	−1.25	−1.15
20	−1.75	−1.70	−1.60	−1.40	−1.35
22	−2.05	−1.95	−1.86	−1.60	−1.50
24	−2.23	−2.20	−2.15	−1.75	−1.66
26	−2.55	−2.50	−2.36	−1.90	−1.85
28	−2.85	−2.80	−2.60	−2.10	−2.01
30	−3.15	−3.10	−2.85	−2.30	−2.12
32	−3.45	−3.35	−3.10	−2.50	−2.34
34	−3.75	−3.60	−3.35	−2.65	−2.55
36	−4.15	−3.95	−3.60	−2.85	−2.75
38	−4.60	−4.28	−3.90	−3.05	−2.90
40	−5.00	−4.65	−4.15	−3.25	−3.10
42	−5.35	−5.05	−4.45	−3.50	−3.35
44	−5.80	−5.40	−4.75	−3.75	−3.60
46	−6.20	−5.75	−5.05	−4.00	−3.85
48	−6.60	−6.10	−5.35	−4.25	−4.10
50	−7.05	−6.50	−5.70	−4.55	−4.40
52	−7.45	−6.90	−6.05	−4.80	−4.70
56	−8.40	−7.85	−6.80	−5.50	−5.25
58	−9.00	−8.30	−7.20	−5.80	−5.55
60	−9.50	−8.85	−7.70	−6.20	−5.85
62	−10.00	−9.40	−8.15	−6.65	−6.25
64	−10.50	−9.95	−8.60	−7.05	−6.65
66	−11.00	−10.40	−9.05	−7.45	−7.05
68	−11.55	−10.85	−9.40	−7.80	−7.35
70	−12.05	−11.25	−9.80	−8.25	−8.15
72	−12.55	−11.75	−10.15	−8.70	−7.90
74	−13.05	−12.20	−10.50	−9.10	−8.20
76	−13.50	−12.65	−10.95	−9.40	−8.45
78	−13.95	−13.05	−11.35	−9.75	−8.70
80	−14.34	−13.50	−11.75	−10.10	−8.95
82	−14.80	−13.90	−12.15	−10.50	−9.25
84	−15.30	−14.35	−12.60	−10.85	−9.60
86	−15.80	−14.75	−13.00	−11.30	−9.90
88	−16.15	−15.20	−13.45	−11.65	−10.25
90	−16.75	−15.60	−13.85	−12.05	−10.60

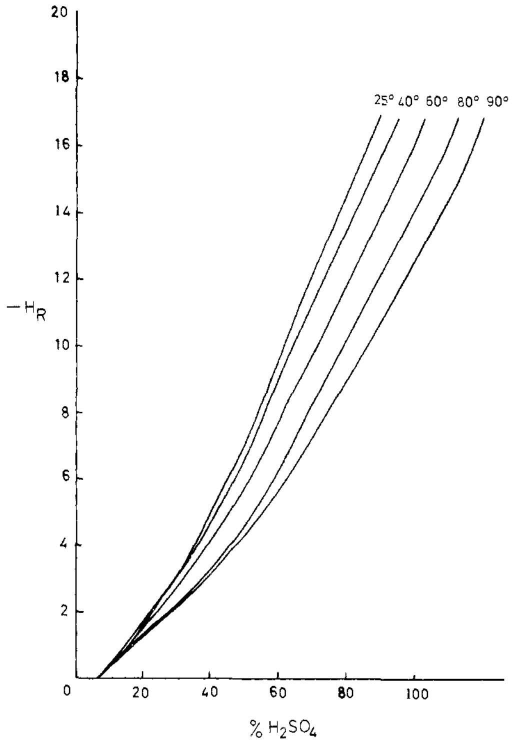

Figure 2. H_R *vs.* % sulfuric acid.

against H_0 at the same temperature. The slopes are 1.923, 1.764, 1.751, 1.572, and 1.476 with intercepts −0.165, −0.400, −0.167, −0.061, and −0.101 at 25, 40, 60, 80, 90° respectively. The small but significant variation in these slopes suggests that the relationship between acidity functions varies slightly with temperature.

Our work on the nitroaniline bases[2] showed that the stronger bases of the series decreased in basicity as temperature was increased, and the reverse was true for the weaker bases. The transition came with 2-chloro-6-nitroaniline, whose pK_a remained constant at *ca.* −2.40. The variation of pK_{R^+} with temperature (Table IV) shows an increase in the stability of the carbonium ions, uniformly over the whole acidity range.

It is of interest to utilize these pK_{R^+} values in a Hammett equation treatment. Previous results have already been investigated using the Yukawa–Tsuno equation (3).[11] However, the use of this equation and the value of r derived have been interpreted in terms of the difference between the extent of carbonium ion formation in the reaction under consideration and the reaction defining σ^+ constants, the ionization of phenyldimethylcarbinyl chlorides.[12] In the case under study here, deviations from σ^+ could arise not only from this cause but also because of the inability of the rings

$$\log K/K_0 = \rho[\sigma + r(\sigma^+ - \sigma)] \quad (3)$$

Table VII. Comparison of H_R Values

% H_2SO_4	This work 25°	Deno[6] 25°	Arnett[4] 30°	This work 40°	Arnett[4] 45°
10	−0.55	−0.72	−0.20	−0.54	−0.29
20	−1.75	−1.92	−1.33	−1.70	−1.49
30	−3.15	−3.22	−2.78	−3.10	−2.80
40	−5.00	−4.80	−4.50	−4.65	−4.35
50	−7.05	−6.60	−6.40	−6.50	−6.23
60	−9.50	−8.92	−8.61	−8.85	−8.88
70	−12.05	−11.52	−11.67	−11.25	−12.01
80	−14.34	−14.12	−15.28	−13.50	−15.80
90	−16.75	−16.72	−18.42	−15.60	−19.43

Table VIII. Values of the Constants A and B in the Expression $H_R(T) = A/T + B$

Wt % acid	$-(A \times 10^{-3})$	B	Wt % acid	$-(A \times 10^{-3})$	B
6	0.358	1.118	50	4.534	8.235
8	0.021	0.040	52	4.765	8.616
10	0.317	0.514	54	4.910	8.726
12	0.315	0.270	56	5.329	9.585
14	0.355	0.177	58	5.883	10.820
16	0.419	0.180	60	6.115	11.137
18	0.496	0.192	62	6.272	11.166
20	0.638	0.421	64	6.476	11.354
22	0.826	0.765	66	6.640	11.408
24	0.827	0.628	68	7.059	12.246
26	1.123	1.295	70	6.950	11.298
28	1.337	1.719	72	7.534	12.831
30	1.574	2.234	74	7.819	13.273
32	1.727	2.445	76	8.078	13.733
34	1.932	2.837	78	8.302	14.052
36	2.311	3.699	80	8.440	14.155
38	2.769	4.791	82	8.605	14.254
40	3.156	5.679	84	8.846	14.575
42	3.359	6.018	86	9.034	14.704
44	3.719	6.762	88	9.012	14.315
46	3.990	7.270	90	9.392	14.969
48	4.262	7.778			

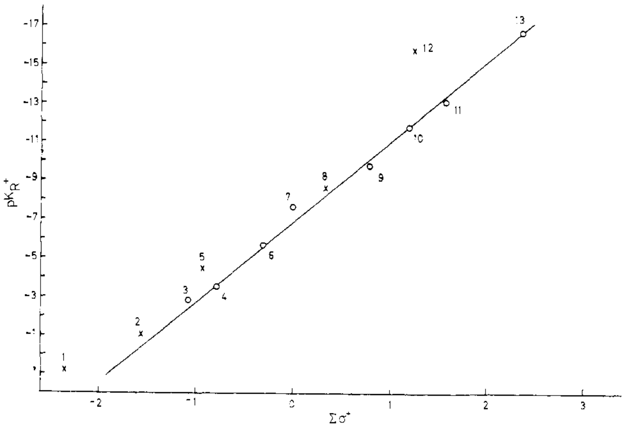

Figure 3. pK_a values *vs.* $\Sigma\sigma^+$ for triarylcarbinols at 25°.

to become mutually coplanar. A plot of $\Sigma\sigma^+$ *vs.* pK_{R^+} (Figure 3) at 25° yields a good straight line. Significant deviations are found only for the 4,4′-dimethoxy, the 4,4′,4″-trimethoxy, and the 4,4′,4″-trimethyl derivatives, suggesting that r in the Yukawa-Tsuno equation is unity and that deviations are due to restriction of mesomerism in the carbonium ion arising from noncoplanarity.

The effective $\Sigma\sigma^+$ value for 4,4′,4″-tris(trimethylammonium perchlorate)triphenylmethanol is 2.20; this gives a value of σ_p^+ of 0.75 for $N^+(CH_3)_3$, much nearer to its σ_p value (0.88) than its reported σ_p^+ value (0.40). This confirms the result, predicted by the σ^+ correlation of the trimethylanilinium ion on nitration,[13] that the value of 0.40 originating from the *tert*-cumyl chloride hydrolysis is in error, although it should be noted that $N^+(CH_3)_3$ can function as a resonance donor with a contribution of −0.15 to its σ_p^0 constant,[14] a value which could well be even more negative in its σ_p^+ constant. As in the case of the pK_a-temperature variation of H_0 indicators,[3] ΔG_{25} was found to correlate with ΔH_{25} to reveal a linear free energy-enthalpy relationship. The thermodynamic parameters are given in Table IX, and the plot is shown in Figure 4, for which the best straight line is given by eq 4. Also plotted on Figure 4 are

$$\Delta G^0 = 0.470\Delta H_{25} + 1186 \qquad (4)$$

Arnett's[4] results; the true magnitude of the discrepancies between these and those of the present work is apparent.

Table IX. Thermodynamic Parameters of Triarylcarbinols

Compd no.	ΔG°, cal mol^{-1}	ΔH°, cal mol^{-1}	ΔS^0, esu
1	1,118 ± 30	−2,137 ± 89	10.87 ± 0.31
2	−1,391 ± 58	−6,215 ± 193	16.01 ± 0.815
3	−3,873 ± 78	−6,970 ± 202	10.24 ± 0.605
4	−4,787 ± 371	−10,713 ± 1193	19.34 ± 3.14
5	−6,083 ± 138	−15,766 ± 886	32.13 ± 2.78
6	−7,774 ± 282	−18,485 ± 1636	35.40 ± 4.521
7	−10,447 ± 68	−26,219 ± 88	52.35 ± 0.445
8	−11,783 ± 52	−30,040 ± 587	60.66 ± 1.79
9	−13,311 ± 145	−32,685 ± 487	64.12 ± 1.727
10	−16,052 ± 222	−37,679 ± 1301	74.74 ± 3.719
11	−17,811 ± 409	−43,582 ± 729	87.06 ± 1.870
12	−21,507 ± 131	−44,548 ± 165	76.78 ± 0.283
13	−22,748 ± 209	−48,104 ± 563	85.08 ± 1.121

Table X. pK_R–$\Sigma\sigma^+$ Correlations at Elevated Temperatures

Temp, °C		Correlation coefficient
25	−3.983	0.9973
40	−3.597	0.9981
60	−3.046	0.9977
80	−2.623	0.9954
90	−2.154	0.9951

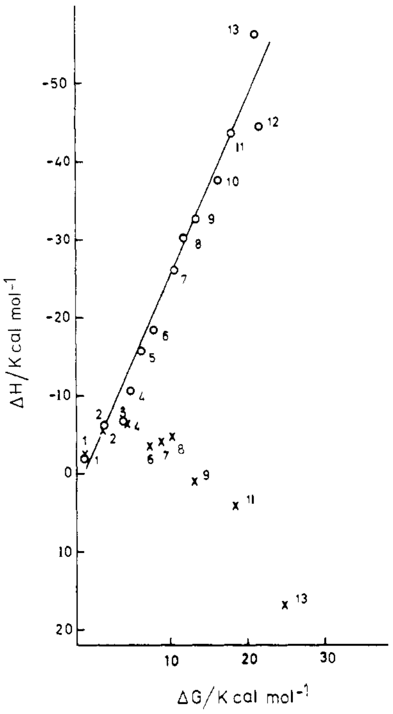

Figure 4. Free energy–enthalpy correlation for triarylcarbinols at 25°: O, our data; X, data of Arnett.[4]

It is of interest to note that Hepler[15] has demonstrated that only for a reaction series entailing a linear $\Delta G-\Delta H$ relationship can a Hammett type correlation be followed precisely at more than one temperature, although this is difficult to check experimentally.[13] Table X shows the ρ values obtained for plots of the form of Figure 3, using the results at temperatures 25, 40, 60, 80, and 90°, and omitting in the determinations of 4,4′,4″-trimethoxy-, 4,4′-dimethoxy-, 4,4′,4″-trimethyl-, 4,4′,4″-trichloro-, and 4,4′,4″-tris(trimethylammonium perchlorate)triphenylmethanols.

The existence of correlations between pK_a values derived from the acidity function approach, and other physicochemical parameters not depending on acidity function theory for their definition, is of vital importance in establishing the thermodynamic validity of such pK_a values. Such correlations have been reported for the H_0 scale;[3,16] the σ^+ correlations and the linear free energy-enthalpy relationship discussed above in the present study testify to the authenticity of the pK_{R^+} and hence H_R values obtained. These pK_{R^+} values (eq 5) are thus thermodynamic quantities accurately

$$pK_{R^+} = 0.00034\Delta H_{25} + 0.86919 \qquad (5)$$

related to the standard state of pure water. The H_R values may be utilized with some confidence for the correlation of rates for appropriate acid catalyzed reactions at elevated temperatures; in this context work is currently in hand[17] to utilize these data in the interpretation of nitration studies[7] as detailed initially.

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Supplementary Material Available. Data supplementary to this article will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, refering to code number JACS-75-760.

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A Secondary Effect on Barriers to Rotation in Substituted Ethanes

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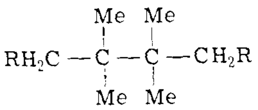
Abstract: The temperature-dependent nmr spectra for a number of closely related substituted ethanes have been studied by full line shape analysis to give barriers to rotation. These range from 10.4 to 13.8 kcal mol^{-1}. The variation in barriers cannot be explained satisfactorily by primary steric effects alone. The data are best rationalized on the basis of a compression effect operating in the eclipsed transition state.[1]

When rotation of a *tert*-butyl group attached to an sp^3 hybridized carbon atom is slow on the nmr time scale, it is usually possible to obtain activation parameters for the rotation by examining the temperature dependence of the nmr spectrum.[2] Bulky substituents, such as alkyl groups[3] or halogen atoms[4] raise the barrier to rotation due to increased steric interactions along the *t*-Bu–C(sp^3) bond in an eclipsed transition state. However, substituent effects on barrier heights cannot always be explained by such primary steric effects along the ethane bond and more subtle secondary effects need to be considered. We now describe one of these, that of bulky groups not directly attached to the ethane bond, but separated from it by one atom, *i.e.*, β-substituents, which give rise to unusually high barriers to rotation. For example, while the barrier in hexamethylethane (**1**) may be reasonably estimated to be between 9.6[5] and 10.0[6] kcal mol^{-1}, we have found that introduction of two *tert*-butyl substituents in a β position giving 2,2,4,4,5,5,7,7-octamethyloctane (**2**) leads to a barrier of 13.8 kcal mol^{-1}. An interpretation of this and other observations is presented in this paper.



$$RH_2C-\underset{Me}{\overset{Me}{C}}-\underset{Me}{\overset{Me}{C}}-CH_2R$$

1, R = H
2, R = *t*-Bu