A Redetermination and Extension of the H_0 Scale of Acidity in Aqueous Perchloric Acid

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Using the uniform set of primary aniline indicators established by Jorgenson and Hartter, we have re-examined and extended the H_0 scale in aqueous perchloric acid to cover the entire range of values accessible to measurement at 25°. The H_0 scale in this acid decreases more rapidly than in aqueous sulfuric acid, 79% perchloric acid having an indicator acidity equivalent to that of 98% sulfuric acid.

Introduction

In applying the acidity function approach to the study of equilibria of weak organic bases, the most commonly used medium has been aqueous sulfuric acid. Values of the H_0 function,[1,2] defined as in eq. 1, are available for this acid over the entire concentration

$$H_0 = -\log a_{H^+} f_B/f_{BH^+} =$$
$$pK_{BH^+} - \log [BH^+]/[B] \quad (1)$$

range 0–100% acid. This provides a very wide range of experimentally accessible indicator acidities. However, for certain types of base, notably hydroxy- and alkoxybenzene derivatives, the use of sulfuric acid can lead to considerable difficulties arising from sulfonation of the bases. Therefore, apart from the obvious desirability of having more extensive acidity function data for other media, we have considered it of interest to reinvestigate and extend the H_0 scale for as wide a range of concentrations of aqueous perchloric acid as possible. The H_0 function for perchloric acid has been investigated previously. Hammett and Deyrup[3] in their pioneering studies of acidity functions obtained values for 0–64% acid, but without benefit of modern spectrophotometric techniques. Bonner and Lockhart[4] subsequently extended these measurements to 71% perchloric acid. However, in both cases a reliable set of structurally uniform indicators was not used to establish the scale. Jorgenson and Hartter[2] have recently reinvestigated the H_0 scale in aqueous sulfuric acid using solely primary anilines as indicators and have shown that their newly established values are progressively more negative than the original H_0 values in this acid.

In order to establish a set of reasonably valid indicator pK values, and hence a valid H_0 scale, it is necessary that such a structurally uniform set of indicators be employed. Only in this way can the Hammett activity coefficient postulate[5] be expected to be closely obeyed. Thus the relationship between any two indicators

$$pK_{CH^+} - pK_{BH^+} = \log [CH^+]/[C] -$$
$$\log [BH^+]/[B] - \log f_C f_{BH^+}/f_{CH^+} f_B \quad (2)$$

can be reduced to the simpler relationship

$$pK_{CH^-} - pK_{BH^-} = \log [CH^+]/[C] -$$
$$\log [BH^+]/[B] \quad (3)$$

for use in the standard stepwise procedure for determining pK and H_0 values. We have therefore used the Jorgenson and Hartter set of indicators to reinvestigate and extend the H_0 scale over the entire range of perchloric acid which is accessible to measurement at or near room temperature, namely 0–80% acid. It was hoped that this scale would provide a suitable alternative to that in sulfuric acid which would extend over an equally wide range of acidity values.

It should be stressed, however, that the validity of such a scale, and the corresponding scale in sulfuric acid, is limited to bases (and substrates in the case of rate–acidity correlations) of the same structural type as the indicators employed, unless it can be demonstrated experimentally that bases of other structural types follow the scale with reasonable precision. The limited applicability of acidity scales of the H_0 type has been clearly demonstrated by recent work, using in the one instance tertiary amines[6] and in the other primary amides[7] as indicators. Each of the H_0-type scales obtained were found to be considerably different numerically from that based on primary anilines.

Experimental

Indicators.—The following compounds were obtained from the Aldrich Chemical Co. as part of a standard set of Hammett indicators and were used without further purification: 2-nitroaniline, 4-chloro-2-nitroaniline, 2,4-dinitroaniline, and 2-bromo-4,6-dinitroaniline. Commercially available (Aldrich and Eastman) samples of the following compounds were recrystallized from ethanol to constant melting point: 2,5-dichloro-4-nitroaniline, m.p. 154–155.5° (lit.[8] 157°); 2,6-dinitroaniline, m.p. 141–142° (lit.[9] 139–140°); 2,6-dichloro-4-nitroaniline, m.p. 194.5–195.5° (lit.[10] 195°); and 4-chloro-2,6-dinitroaniline, m.p. 144–145° (lit.[11] 144–145°). 3-Methyl-2,4,6-trinitroaniline was prepared by the method of Jorgenson and Hartter,[2] m.p. 138.5–139.5° (lit.[2] 138–138.5°). *Anal.* Calcd. for $C_7H_6N_4O_6$: C, 34.89; H, 2.71; N, 23.00. Found: C, 34.7; H, 2.5; N, 23.1. We are very grateful to Dr. M. J. Jorgenson for supplying us with samples of 2-chloro-6-nitroaniline and 3-bromo-2,4,6-trinitroaniline. All melting points were obtained on a Gallenkamp melting point apparatus and are uncorrected.

Perchloric Acids.—Perchloric acid solutions below 60% by weight were prepared by diluting Baker and Adamson reagent perchloric acid (60%) with doubly distilled water. Those from 60–70% were prepared by mixing this acid with Baker and Adamson 70–72% perchloric acid. Solutions more concentrated than 70% were obtained by dissolving perchloric acid monohydrate (84.8% by weight) supplied by the G. Frederick Smith Chemical Co. in the more dilute acids. Concentrations were determined by titrating weighed samples with standard sodium hydroxide. Restandardization at the conclusion of the work showed there were no significant changes in acid concentration with time.

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TABLE I

ULTRAVIOLET ABSORPTION AND pK VALUES OF INDICATORS IN PERCHLORIC ACID AT 25°

Indicator (aniline)	$\lambda_{max}{}^a$ of aniline (B), mμ	$\epsilon_B{}^a$	ϵ^b of anilinium ion (BH$^+$)	Medium shift,^{c} mμ	Measured p$K_{BH^+}{}^d$ ± mean dev.	pK_{BH^+} values in H$_2$SO$_4{}^e$
2-Nitro-	413	4,440	. . .	. .	-0.29^f	-0.29^f
4-Chloro-2-nitro-	424	4,550	. . .	. .	-1.07 ± 0.01	-1.03
2,5-Dichloro-4-nitro-	370	9,810	144	. .	-1.79 ± 0.02	-1.78
2-Chloro-6-nitro-	408	4,730	. . .	1	-2.41 ± 0.02	-2.43
2,6-Dichloro-4-nitro-	366	11,600	. . .	. .	-3.20 ± 0.10	-3.27
2,4-Dinitro-	349	5,600	120	1	-4.26 ± 0.02	-4.53
2,6-Dinitro-	446	9,600	. . .	4	-5.25 ± 0.02	-5.54
4-Chloro-2,6-dinitro-	455	8,620	. . .	5	-6.12 ± 0.02	-6.14
2-Bromo-4,6-dinitro-	350	12,600	361	. .	-6.69 ± 0.01	-6.68
3-Methyl-2,4,6-trinitro-	370^g	6,920	534	. .	-8.56 ± 0.04	-8.22
3-Bromo-2,4,6-trinitro-	380^g	6,930	609^h	. .	-9.77 ± 0.04	-9.46

^{a} Measured in acid concentrations of about 2 H_0 units greater than pK. ^{b} Measured in acid concentrations of about 2 H_0 units less than pK. ^{c} Observed shift of λ_{max} over range of acids corresponding to approximately 10–90% protonation. ^{d} Obtained by direct stepwise comparison in this work. ^{e} Taken from ref. 2. ^{f} "Best" value of Long and Paul.[1] ^{g} Wave lengths used for measurement approximately at the center of a broad shoulder. ^{h} Obtained by the method of Arnett and Wu.[12]

Spectrophotometric Measurement of Ionization Ratios.— Stock solutions of each indicator were prepared by dissolving a weighed sample of the indicator in reagent grade chloroform. Suitable aliquots were transferred to 10-ml. volumetric flasks using a Hamilton syringe and Chaney adaptor. The chloroform was then evaporated under vacuum and the sample dissolved in perchloric acid of the desired strength. On very few occasions heating was required to effect solution. This is not recommended with the more concentrated acids unless absolutely necessary. Solution can usually be achieved in the cold quite readily with shaking. Spectra of these solutions were measured with a Bausch and Lomb Spectronic 505 recording spectrophotometer using 1-cm. silica cells and a thermostatically controlled cell block at 25 ± 0.05°. Concentrations were adjusted so that all solutions used gave optical densities in the range 0.2–1.3. Ionization ratios were obtained from the expression $I = [BH^+]/[B] = \epsilon_B - \epsilon/\epsilon - \epsilon_{BH}{}^+$, where ϵ_B and $\epsilon_{BH}{}^-$ are the extinction coefficients of the unprotonated and fully protonated base, respectively, and ϵ is the measured extinction of a test solution in which both forms are present. All measurements were carried out in duplicate, and acids of approximately 2 H_0 units on either side of the pK value were used to obtain ϵ_B and $\epsilon_{BH}{}^-$ values. Spectra were frequently repeated with time but no evidence of decomposition was found within the time required to complete the measurements.

In the case of 3-bromo-2,4,6-trinitroaniline no perchloric acid was available which was strong enough to ensure complete protonation of the base. The $\epsilon_{BH}{}^+$ value for this indicator was obtained by the method of Arnett and Wu[12] using a first approximate pK of -9.8. This estimate was based on our own value for the next strongest indicator and the appropriate pK values of Jorgenson and Hartter[2] in sulfuric acid. The $\epsilon_{BH}{}^+$ value thus obtained was then used to obtain values of $[BH^-]/[B]$ and hence a second value for pK. The whole calculation was recycled until no further change in either $\epsilon_{BH}{}^+$ or pK was found.

Results and Discussion

Measurement of Ionization Ratios.— Ionization ratios of the eleven substituted anilines investigated were obtained by the standard spectrophotometric technique, essentially as described by Jorgenson and Hartter.[2] All indicators showed strong ultraviolet absorption in the 350–450-mμ region. The λ_{max} values for individual compounds are given in Table I. It can be seen that these are very similar to those observed in aqueous sulfuric acid. Medium shifts of the absorption peaks over the range of acid concentrations necessary to convert the bases to their conjugate acids were very small, as shown in Table I. These small medium effects were corrected for by taking ϵ values at the wave length of maximal absorption in each solution regardless of where it occurred, rather than by selecting some fixed λ_ϵ for all solutions of a particular indicator. Noyce and

Jorgenson[13] have shown that this treatment is in effect the well-known isosbestic point method of correcting for medium effects. In the case of 3-methyl-2,4,6-trinitroaniline and 3-bromo-2,4,6-trinitroaniline, the absorption bands appearing as shoulders in the 370-mμ region were used to obtain values of $[BH^+]/[B]$. Several wave lengths in the region of the shoulders were used to calculate ionization ratios. The results obtained at different wave lengths were in excellent agreement for each indicator and those wave lengths were chosen which gave the highest precision. These shoulders appear on the side of more intense maxima occurring near 340 mμ. The latter absorption bands were found to be relatively insensitive to medium composition and hence unsuitable for determination of $[BH^+]/[B]$, and are presumably due to the presence of the nitro groups which undergo less drastic changes with medium composition than the amino group.

The ionization ratios were calculated for each indicator based on the ϵ_B and $\epsilon_{BH}{}^-$ values given in Table I and are listed in Table II.

Determination of Indicator pK Values.— The values of $\log [BH^+]/[B]$ for each indicator are plotted as a function of per cent perchloric acid as shown in Fig. 1, and the best smooth curves drawn through the experimental points. These curves are not in general linear, nor would linearity be predicted, since weight per cent of acid would hardly be expected to reflect the proton-donating ability of the medium in a precisely linear fashion, nor in fact would any other conventional measure of acid concentration. The ionization curves for successive indicators show the expected progressive increase in slope, especially at the higher acidities. The overlap is extensive and the parallelism between successive curves is very good and demonstrates that the Hammett activity coefficient postulate[5] is justified for this set of indicators (*i.e.*, $\log f_{CH}{}\text{-}f_B/f_C f_{BH}{}^- \simeq 0$ for two indicators in the same acid solution). Hence eq. 3 can be used to determine a set of reliable pK values by the standard stepwise method of comparison. The pK of the first indicator, 2-nitroaniline, was taken as -0.29, the "best" value given by Long and Paul[1] which had been obtained in dilute solutions of several different acids. Thus all pK values are ultimately referred back to this value and are based on dilute aqueous solution as standard state. The pK values

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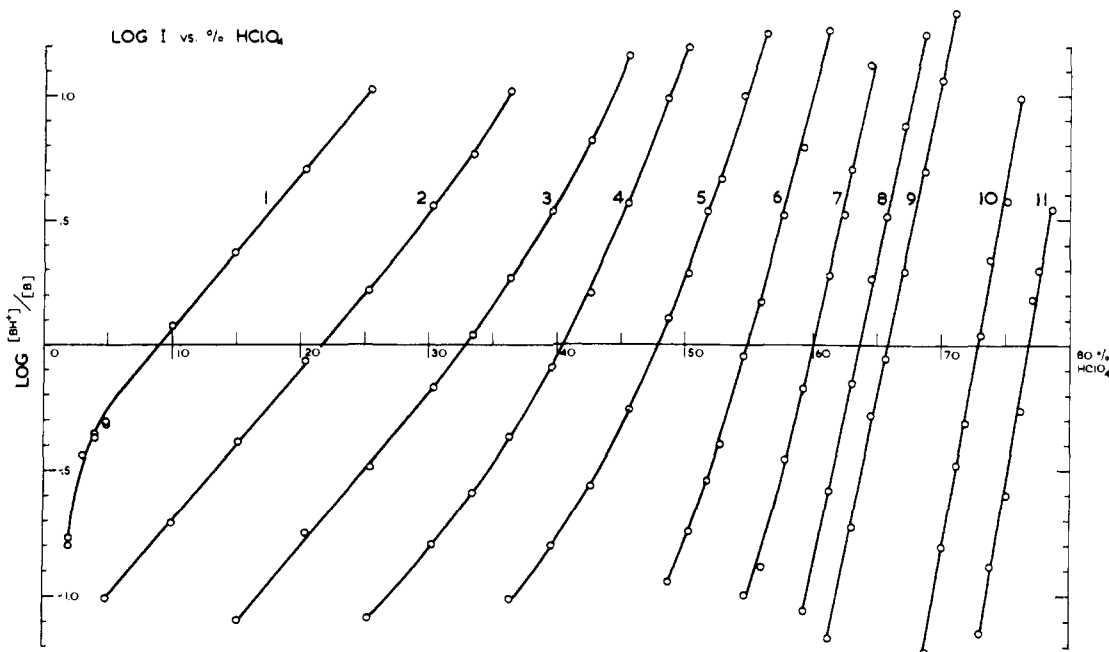
Fig. 1.—Logarithm of ionization ratio against per cent perchloric acid for primary aniline indicators: 1, 2-nitroaniline; 2, 4-chloro-2-nitroaniline; 3, 2,5-dichloro-4-nitroaniline; 4, 2-chloro-6-nitroaniline; 5, 2,6-dichloro-4-nitroaniline; 6, 2,4-dinitroaniline; 7, 2,6-dinitroaniline; 8, 4-chloro-2,6-dinitroaniline; 9, 2-bromo-4,6-dinitroaniline; 10, 3-methyl-2,4,6-trinitroaniline; 11, 3-bromo-2,4,6-trinitroaniline.

were calculated from eq. 3 and the previously described ionization ratios, using only values of log $[BH^+]/$ $[B]$ in the range ± 1.2 (corresponding to 6–94% protonation). Values corresponding to very high and very low degrees of protonation are extremely sensitive to small errors in the reference data, as pointed out previously by other workers,[2,14] and were not considered reliable. Several pK values were obtained in this way for each indicator, depending on the number of overlapping points on the ionization curves. These were averaged and are listed in Table I. The agreement between the values obtained for each indicator was very good, as shown by the mean deviations. No significant drift of pK was observed in any case.

If these pK values are compared with the corresponding values in sulfuric acid, reported by Jorgenson and Hartter,[2] six are identical in both acids within the usual experimental uncertainty, as they should be if they are to be considered as valid thermodynamic pK values. However, four of the values obtained in the present work differ by 0.3 pK unit from those in sulfuric acid. In the case of the two 3-substituted trinitroanilines, this discrepancy is not considered too serious and can be attributed partly to the fact that both are extremely weak bases and that both are highly nitro substituted. Since errors are cumulative in the stepwise method, it is doubtful whether pK values obtained in very concentrated acids can ever be considered accurate to better than ± 0.2 pK unit. In addition it is quite possible that differences in specific solvation of the three nitro groups in perchloric and sulfuric acids are appreciable in acids where the amount of available water is drastically reduced. However, the discrepancy of 0.3 unit between the values for 2,4-dinitro- and 2,6-dinitroanilines in the two media cannot be dismissed as easily. Jorgenson and Hartter[2] did not actually measure the value of -4.53 reported

for 2,4-dinitroaniline but based their value on the original data of Hammett and Deyrup[3] and the overlap between this and their own data for the next stronger base, 2,6-dichloro-4-nitroaniline. Since the old colorimetric data cannot be considered as precise as modern spectrophotometric data, and since the overlap obtained for these two ionization curves in sulfuric acid was very limited, it is quite possible that this pK is in error by several tenths of a pK unit. In the present work it was considered advisable not to use any of the old colorimetric data or pK values based on this, with the exception of the "best" value for 2-nitroaniline. This is a much more reliable starting point since it is an average of five closely-spaced independent values obtained in several different media.[1] Thus all pK values in Table I are based almost entirely on new spectrophotometric data, with good overlap of ionization curves being achieved in every case.[15] We therefore consider that our values of -4.26 for 2,4-dinitroaniline and -5.25 for 2,6-dinitroaniline are at least as reliable as previously reported values. The pK value of -4.36 (corrected as in Long and Paul's compilation[1] to -4.48) reported[4] for 2,4-dinitroaniline in perchloric acid is also based heavily on the original colorimetric data of Hammett and Deyrup.[3]

Determination of the H_0 Scale in Perchloric Acid.— Using the pK values and ionization ratios previously described, values of H_0 were determined for the range 5–79% perchloric acid. The H_0 value for each of the 36 acid concentrations studied was obtained from all indicators which were measurably ionized in that acid, with the limitation that only values of log $[BH^+]/$ $[B]$ within the range ± 1.0 were used. The average values obtained for each acid are listed in Table III, along with the mean deviations. The agreement be-

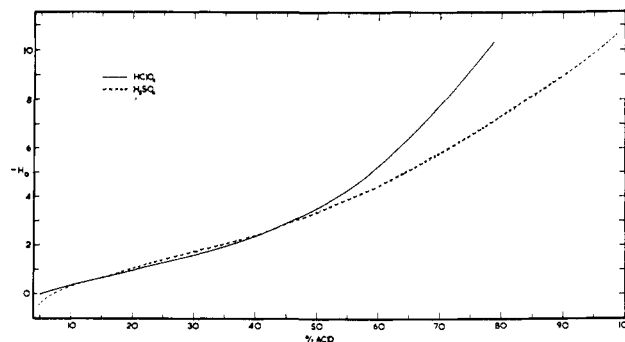(14) W. M. Schubert and R. H. Quacchia, *J. Am. Chem. Soc.*, **84**, 3778 (1962).

(15) Attempts to improve the overlap by insertion of another indicator of pK between -6.7 and -8.2 were unsuccessful. 2-Chloro-4,6-dinitro aniline was found to have an ionization curve almost identical with that of 2-bromo-4,6-dinitroaniline, and 2,4,5-trinitroaniline was too unstable in acid solution to be of any use.

TABLE II

IONIZATION RATIOS OF SUBSTITUTED ANILINE INDICATORS

% HClO₄	Log I	% HClO₄	Log I	% HClO₄	Log I
2-Nitroaniline		4-Chloro-2-nitroaniline		2,5-Dichloro-4-nitroaniline	
4.92	−0.312	4.92	−1.098	15.13	−1.099
10.06	0.075	10.06	−0.710	20.36	−0.765
15.13	0.373	15.13	−0.390	25.37	−0.483
20.36	0.703	20.36	−0.068	30.38	−0.172
25.37	1.026	25.37	0.221	33.43	0.040
		30.38	0.559	36.34	0.268
		33.43	0.766	39.58	0.535
		36.34	1.019	42.55	0.819
				45.59	1.157
2-Chloro-6-nitroaniline		2,6-Dichloro-4-nitroaniline		2,4-Dinitroaniline	
25.37	−1.084	36.34	−1.022	48.67	−0.950
30.38	−0.802	39.58	−0.798	50.30	−0.750
33.43	−0.598	42.55	−0.564	51.74	−0.543
36.34	−0.368	45.59	−0.264	52.81	−0.404
39.58	−0.089	48.67	0.105	54.58	−0.045
42.55	0.207	50.30	0.280	55.90	0.173
45.59	0.566	51.74	0.532	57.70	0.516
48.67	0.991	52.81	0.666	59.21	0.790
50.30	1.193	54.58	1.002	61.21	1.260
2,6-Dinitroaniline		4-Chloro-2,6-dinitroaniline		2-Bromo-4,6-dinitroaniline	
54.58	−1.005	59.21	−1.078	61.21	−1.165
55.90	−0.884	61.21	−0.571	63.00	−0.727
57.70	−0.463	63.00	−0.156	64.49	−0.278
59.21	−0.172	64.49	0.261	65.66	−0.051
61.21	0.278	65.66	0.514	67.10	0.292
62.40	0.522	67.10	0.875	68.69	0.695
63.00	0.702			69.98	1.062
64.49	1.123			71.08	1.344
2-Methyl-2,4,6-trinitroaniline		3-Bromo-2,4,6-trinitroaniline			
68.69	−1.237	72.93	−1.153		
69.98	−0.803	73.73	−0.883		
71.08	−0.483	74.96	−0.602		
71.85	−0.309	76.08	−0.253		
72.93	0.040	77.03	0.186		
73.73	0.341	77.68	0.299		
74.96	0.574	78.60	0.536		
76.08	0.985				

Fig. 2.—Plot of revised and new H_0 values in perchloric acid; data for sulfuric acid taken from ref. 1 and 2.

for 98% sulfuric acid. Thus a perchloric acid solution of high concentration is a much more effective protonating medium than sulfuric acid of the same concentration, at least towards primary anilines. The possible reasons for this difference in the two acids will be discussed in a later section.

TABLE III

REVISED AND NEWLY DETERMINED H_0 VALUES FOR PERCHLORIC ACID

% HClO₄	H_0	Mean dev. (±)[a]	% HClO₄	H_0	Mean dev. (±)[a]
4.9	+0.02[b]	0.03	59.2	−5.06[g,h]	0.01
10.1	−0.36[b,c]	0.002	61.2	−5.54[h,e]	0.01
15.1	−0.67[b,c]	0.01	62.4	−5.77[h]	...
20.4	−1.01[b-d]	0.01	63.0	−5.97[h-j]	0.005
25.4	−1.30[c,d]	0.01	64.5	−6.39[i,j]	0.02
30.4	−1.62[c-e]	0.01	65.7	−6.63[i,j]	0.005
33.4	−1.83[c-e]	0.01	67.1	−6.99[i,j]	0.01
36.3	−2.05[d,e]	0.01	68.7	−7.35[i,j]	0.03
39.6	−2.35[d-f]	0.04	70.0	−7.75[j,k]	0.005
42.6	−2.62[d-f]	0.01	71.1	−8.08[k]	...
45.6	−2.96[e,f]	0.02	71.9	−8.25[k]	...
48.7	−3.34[e-g]	0.04	72.9	−8.60[k]	...
50.3	−3.50[f,g]	0.01	73.7	−8.90[k,l]	0.01
51.7	−3.73[f,g]	0.01	75.0	−9.15[k,l]	0.02
52.8	−3.86[f,g]	0.01	76.1	−9.53[k,l]	0.01
54.6	−4.22[f-h]	0.01	77.0	−9.96[l]	...
55.9	−4.40[g,h]	0.03	77.7	−10.07[l]	...
57.7	−4.78[g,h]	0.005	78.6	−10.31[l]	...

[a] Mean deviation of H_0 values obtained from different indicators. H_0 values determined from the following substituted aniline indicators. [b] 2-Nitroaniline. [c] 4-Chloro-2-nitroaniline. [d] 2,5-Dichloro-4-nitroaniline. [e] 2-Chloro-6-nitroaniline. [f] 2,6-Dichloro-4-nitroaniline. [g] 2,4-Dinitroaniline. [h] 2,6-Dinitroaniline. [i] 4-Chloro-2,6-dinitroaniline. [j] 2-Bromo-4,6-dinitroaniline. [k] 3-Methyl-2,4,6-trinitroaniline. [l] 3-Bromo-2,4,6-trinitroaniline.

tween H_0 values based on different indicators can be seen to be very good. All H_0 values fall well on a smooth curve when plotted against per cent perchloric acid. This curve is shown in Fig. 2 with the corresponding curve for sulfuric acid for comparison. It can be seen that the perchloric acid curve increases (in a negative sense) much more steeply above 50% acid. Since aqueous perchloric acid is only completely liquid at 25° in the concentration ranges 0–79% and 94–100%,[16] the curve in Fig. 2 represents the entire range of H_0 values accessible to measurement near room temperature. In order to investigate its acidity function behavior over the complete range 0–100% as has been done for sulfuric acid, it would be necessary to study indicator behavior at 50° or above, where the acid remains liquid over the whole concentration range. However, comparison of the H_0 curves for the two acids shows that for most purposes the present range of H_0 values in perchloric acid is quite adequate. The value for 79% perchloric is less than −10.3, compared with the value of −10.41 reported[2]

It is interesting to speculate on what acidity values might be attained by perchloric acids greater than 80%, i.e., whether the curve at 50° would continue to increase roughly as steeply as that at 25° or whether a discontinuity would occur at or above the monohydrate region (84.8%). If the former occurred, then in view of the demonstrated insensitivity of acidity functions to changes in temperature,[17] one could estimate conservatively that H_0 values of about −16 would be reached near the 100% acid, even if no sharp increase in acidity were to occur in this region, as is found for sulfuric acid. It seems more likely, however, that the acidity function behavior would not be as simple as this, since it is known that the chemical

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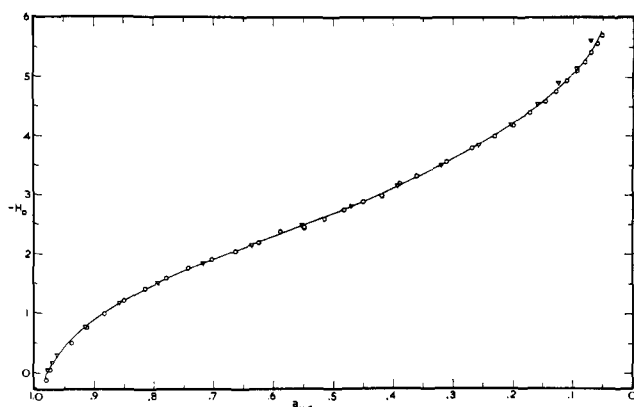
Fig. 3.—Plot of H_0 against a_{H_2O} for perchloric and sulfuric acids[1,2]; water activity data taken from ref. 22 and 23 (triangles, perchloric acid; circles, sulfuric acid).

composition of 80–100% perchloric acid is quite complex[16] and contains no well-defined chemical species except $HClO_4 \cdot H_2O$ and Cl_2O_7. This might well lead to an irregularly shaped H_0 profile in this concentration region.

Comparison of Present H_0 Values with Previous Data in Perchloric Acid.—The H_0 values obtained in the present work agree reasonably well with those of Hammett and Deyrup[3] as listed by Long and Paul.[1] Over most of the range studied by the earlier worker (5–64%), the agreement is within ±0.15 H_0 unit. Some divergence is apparent above 55% acid when the present scale tends to more negative values, the difference becoming 0.35 unit at 64%. This is similar qualitatively to the difference observed by Jorgenson and Hartter[2] when they re-evaluated the H_0 scale in sulfuric acid in the more concentrated region, using the same uniform set of indicators. The data of Bonner and Lockhart[4] who measured H_0 for the 50–71% acid range show similar agreement with the present data, except for the last two values reported (for 70.3 and 71.3% acid). However, these were obtained from log [BH+]/[B] values of −1.58 and −2.09, respectively. Unlike the previous data, the present re-evaluated H_0 values are based completely on structurally uniform indicators and spectrophotometric measurements. They also follow a much smoother function of acid concentration than the earlier data and should be regarded as superseding this.

The Difference in the H_0 Scale in Perchloric and Sulfuric Acids.—The H_0 functions in perchloric and sulfuric acids are compared numerically in Table IV in which H_0 and $dH_0/d\%$ acid have been taken from best smooth curves of the available experimental data. It can be seen that there is little difference in the two H_0 scales up to about 50% acid. However, above this concentration the perchloric acid scale starts to decrease more sharply, to the extent that by 75% acid $dH_0/d\%$ $HClO_4$ is twice as great numerically as $dH_0/d\%$ H_2SO_4, and the absolute difference in H_0 approaches 3 log units. Similar differences have been observed in the behavior of other acidity functions. The H_R function in perchloric acid[18] also decreases more steeply than the same function in sulfuric acid. For example, at the highest concentration (60% acid) for which data are presently available for both acids,[18,19] $dH_R/$

(18) N. C. Deno, H. E. Berkheimer, W. L. Evans, and H. J. Peterson, J. Am. Chem. Soc., **81**, 2344 (1959).

$d\%$ $HClO_4$ has a value of −0.42, while $dH_R/d\%$ H_2SO_4 is only −0.26. Thus dH_R/dH_0 is roughly comparable in each of the two acids. Therefore the greater acidity observed for perchloric over sulfuric acid does not seem to depend very strongly on the type of indicators used to establish acidity.

TABLE IV

COMPARISON OF THE H_0 FUNCTIONS FOR AQUEOUS PERCHLORIC AND SULFURIC ACIDS AT 25°

Acid concn., % w./w.	$-H_0$ (HClO$_4$)	$-dH_0/d\%$ HClO$_4$	$-H_0^a$ (H$_2$SO$_4$)	$-dH_0/d\%$ H$_2$SO$_4$	H_0^b
10	0.35	0.07	0.31	0.05	−0.04
20	0.98	0.06	1.01	0.07	+0.03
30	1.60	0.07	1.72	0.07	+0.12
40	2.40	0.09	2.41	0.08	+0.01
50	3.48	0.13	3.38	0.11	−0.10
55	4.23	0.18	3.91	0.11	−0.32
60	5.27	0.22	4.46	0.12	−0.81
65	6.45	0.25	5.08	0.13	−1.37
70	7.75	0.28	5.80	0.15	−1.95
75	9.21	0.30	6.56	0.15	−2.65
80	10.75^c	..	7.34	..	−3.41

^{a} Data up to 60% acid taken from ref. 1 and for higher concentrations from ref. 2. ^{b} $H_0 = H_0 (HClO_4) - H_0 (H_2SO_4)$. ^{c} Obtained by a short extrapolation of data obtained in present work.

The possible factors contributing to this difference in acidity can be considered by expressing the H_0 function as in $H_0 = -\log C_{H^-} - \log f_{H^+} - \log f_B/f_{BH^+}$. It is not likely that the log C_{H^+} term is ever sufficiently different for the two strong acids to account quantitatively for observed differences in indicator acidity; thus the explanation must be sought in the activity coefficient behavior of the various species involved in the indicator equilibrium. The similarity in the behavior of the H_0 and H_R functions would seem to suggest that the activity coefficient variation of the indicators is less important than that of the hydrated protons. However, the relative importance of the log f_{H^-} term and the log f_H/f_{BH^+} term cannot be decided at present in view of the paucity of the data available on activity coefficient behavior. Boyd's recent valuable study[20] of the activity coefficient behavior of typical indicators throws much light on the variation of log f_B/f_{BH^-} in sulfuric acid. Unfortunately no comparable data are available for perchloric acid solutions.

The importance of these activity coefficient terms and their relationship to the hydration requirements of the various species involved can be seen in the dependence of H_0 on the water activity of perchloric and sulfuric acids. Wyatt[21] has already pointed out that H_0 is a unique function of the water activity for several strong acids. Using the present H_0 data in perchloric acid and the re-evaluated H_0 data for sulfuric acid, the relationship found by Wyatt is even more closely obeyed. Figure 3 shows a plot of H_0 vs. a_{H_2O} for both perchloric and sulfuric acid up to the highest concentrations where water activity data[22,23] are

(19) N. C. Deno, J. J. Jaruszelski, and A. Schriesheim, ibid., **77**, 3044 (1955).
(20) R. H. Boyd, ibid., **85**, 1555 (1963).
(21) P. A. H. Wyatt, Discussions Faraday Soc., **24**, 162 (1957).
(22) J. N. Pearce and A. F. Nelson, J. Am. Chem. Soc., **55**, 3075 (1933); R. A. Robinson and O. J. Baker, Trans. Roy. Soc. New Zealand, **76**, 256 (1946).
(23) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth and Co., Ltd., London, 1959, Appendix 8.4.

available for both. The similarity of the H_0 dependence on water activity for the two acids is truly remarkable, both sets of data following one curve to well within the experimental uncertainty in H_0 over most of the range. Thus the observed more rapid increase in the acidity of perchloric acid is reflected precisely in a correspondingly more rapid decrease in the water activity of this acid, as compared to sulfuric acid.

Mononegative Molecular Ions of Aromatic Hydrocarbons in γ-Irradiated Organic Glasses

By N. Christodouleas and W. H. Hamill

The electronic spectra of the mononegative molecular anions of biphenyl, anthracene, phenanthrene, 1,2-benzanthracene, triphenylene, o-terphenyl, pyrene, triphenylethylene, tetraphenylethylene, cycloheptatriene, and hexamethylbenzene produced in γ-irradiated organic glasses at 77°K. have been investigated. Relative anion formation efficiencies have been determined. The spectrum of γ-irradiated perylene has been investigated and attributed to the perylene monopositive ion.

Introduction

The mononegative molecular ions of some aromatic hydrocarbons (naphthalene, phenanthrene, etc.) have been prepared chemically[2-5] by the interaction of alkali metals with aromatic hydrocarbons in suitable solvents, and their qualitative interpretation has been made with the aid of the LCAO–MO method including configuration interaction.[6]

A general method has been developed recently for the spectrophotometric observation of intermediates produced and trapped in γ-irradiated media at 77°K. which has provided information about electron solvation, simple and dissociative electron attachment, and photodetachment.[7] It is the purpose of this work to examine anion formation by γ-irradiation by extending this method to a series of aromatic compounds in which chemical methods have been previously employed and to determine the relative electron attachment efficiencies of these aromatic hydrocarbons.

Experimental

Solvents.—Of primary consideration in the selection of 2-methyltetrahydrofuran (MTHF) as a solvent was the fact that it forms clear glasses transparent from the near-ultraviolet to the far-infrared, dissolves the aromatic hydrocarbons under investigation relatively well, and is chemically similar to the solvents used in chemical preparation. It was purified by passing through a column containing basic alumina (Woelm). Phillips pure grade 3-methylpentane (3MP) and 2-methylpentene-1 (2MP-1), which were used as solvents to a small extent, were also purified by passing through a column of silica gel.

Solutes.—The following materials were used as received: biphenyl, Monsanto (recrystallized from ethanol); anthracene, phenanthrene, o-terphenyl, triphenylethylene, and pyrene, East-

man White Label products; 1,2-benzanthracene, triphenylene, perylene, triphenylethylene, and tetraphenylethylene, Aldrich Chemical products.

The methods of γ-irradiation, dosimetry, and absorption spectrophotometry relevant to this work have been described elsewhere.[7] Unless otherwise indicated, the doses were approximately 0.75×10^{18} e.v./ml.

Results and Discussion

γ-Irradiation of organic glasses ejects electrons from the solvent and these appear to become attached through diffusion to solute or solvent molecules or else to recombine with positive ions. In pure MTHF at 77°K. a broad absorption appears extending from approximately 9000 to 16,000 Å. and with maxima at ~12,100 and 13,700 Å. This absorption can be bleached by infrared light and is attributed to solvated electrons. In the presence of a small amount of biphenyl the anion absorption of biphenyl appears with a concomitant decrease of the solvated electron absorption. With concentrations of biphenyl as large as 0.15 mole % and at doses approximating 0.75×10^{18} e.v./ml. the solvated electron absorption disappears, while the biphenyl anion band acquires its limiting intensity (O.D. = 0.76 at 4100 Å.). The process is competitive in the sense that the ejected electrons divide themselves between solute and solvent molecules according to the efficiency of the solute for electron attachment and its concentration, and depending upon the positive hole mobility of the solvent.[7] In the presence of two different solutes X and Y the number N of anions X⁻ and Y⁻ formed is given by

$$N_{X^-}/N_{Y^-} = \sigma_X C_X / \sigma_Y C_Y \qquad (1)$$

where σ_X, σ_Y are electron-attachment cross sections of solute X and Y, respectively, and C_X, C_Y are the corresponding concentrations. Since the optical density of absorption of a certain anion species is proportional to the number of anion species (N), eq. 1 is easily transformed[7b,d] into

$$1/D_{Y^-} = 1/D_{Y^-}^0 + \sigma_X C_X / \sigma_Y D_e^0 C_Y \qquad (2)$$

where D_{Y^-} is the O.D. of the anion of the reference solute (biphenyl, for example), and D_Y^0 is the limiting O.D. of this anion.

(1) The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is document COO-38-339.

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