The D_0 Acidity Function for Perchloric Acid

By **Robin A. Cox,* Sai-On Lam, Robert A. McClelland,** and **Thomas T. Tidwell,*** Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

The D_0 acidity function, densities, and excess acidities for 0—56% w/w (0—9M) $DClO_4$–D_2O mixtures are reported. Differences between the H_0 and D_0 functions for perchloric acid arise from density differences, so that these functions are essentially identical when compared at the same molarity.

STUDIES of organic reactions in solutions of moderately to highly concentrated aqueous acids have most commonly been carried out using sulphuric acid. The acidity function behaviour of this medium has been frequently reviewed.[1] Because of the valuable mechanistic information which is available from solvent isotope effect measurements the acidity function D_0 for D_2SO_4 solutions in D_2O has also been determined.[2] It has been found for sulphuric acid solutions of the same weight percent that the magnitude of D_0 exceeds that of H_0 by a roughly constant factor of 0.3 units except above 97% acid. This difference evidently is a manifestation of the fact that the density of D_2O (1.104 4 at 25 °C) [3] exceeds that of H_2O, as confirmed by the finding that the acidity functions are almost identical when the comparison is made at equal molarities.[2]

Although perchloric acid has not been as widely used as a reaction medium as has sulphuric acid, its acidity function behaviour has also been widely studied.[4] The fact that perchloric acid is monobasic and is much more completely dissociated than sulphuric acid in concentrated solutions renders it an attractive medium for mechanistic studies.

There have been relatively few studies of solvent isotope effects in $DClO_4$. One major cause of this has been the relative inaccessibility of the material. One reported preparation of $DClO_4$ involved treatment of $HClO_4$ by ' slow simultaneous continuous addition of D_2O below the surface and distillation of water ',[5a] and another distillation from $NaClO_4$ and D_2SO_4.[5b] In view of the known explosive properties of perchlorates [6] these methods are not attractive. More recently $DClO_4$ reagent has become commercially available,† and its use may be anticipated to become more common.

Many solvent isotope effects in perchloric acid have been reported [7-18] but scrutiny of these data reveals several seemingly anomalous results. For example, solvent isotope effects for protonation of substituted styrenes show significant variations with perchloric acid concentration. Thus for styrene k_{H^+}/k_{D^+} is 2.27 for 4.91M-$HClO_4$ and 3.33 for 6.79M-acid.[5a] There are also inconsistencies in the isotope effects for different acids. Thus for cyclohexa-1,3-diene k_{H^+}/k_{D^+} was reported as 2.1 for sulphuric acid [8] and 1.2 for perchloric acid,[9] in 1.05M-solutions in both cases. For cyclohexene k_{H^+}/k_{D^+} was found to be 1.06 and independent of concentration for sulphuric acid, whereas for perchloric acid, values were reported of 1.82, 1.34, and 0.87, for 5.55, 7.20, and 8.15M-solutions, respectively.[10]

TABLE 1

pK(BD^+) Values of aniline indicators in $DClO_4$

Indicator[a]	pK_{BD^+}[b]	Slope *vs* D_0	pK_{BH^+}[c]	Δ[d]
4-NO_2 (1)	1.57 ± 0.01	0.98 ± 0.03	1.00	0.57
2-NO_2 (2)	0.18 ± 0.05	1.01 ± 0.01	-0.29	0.47
4-Cl-2-NO_2 (3)	-0.55 ± 0.06	0.98 ± 0.01	-1.03	0.48
2,5-Cl_2-4-NO_2 (4)	-1.41 ± 0.08	1.02 ± 0.01	-1.79	0.38
2,6-Cl_2-4-NO_2 (5)	-3.06 ± 0.08	0.99 ± 0.02	-3.27	0.21
2,4-$(NO_2)_2$ (6)	-4.13 ± 0.14	1.02 ± 0.02	-4.26	0.13
2,6-$(NO_2)_2$ (7)	-5.08 ± 0.14	1.02 ± 0.03	-5.24	0.16

[a] Substituted aniline. [b] This work, given with propagated error. [c] In $HClO_4$; see refs. 4*a,d*. [d] $pK_{BD^+} - pK_{BH^+}$.

It was possible that some of these seemingly anomalous results might arise from the acidity function behaviour of $DClO_4$. In any case the increasing popularity of this medium for mechanistic studies made a determination of its acidity behaviour highly desirable and we have accordingly carried out such an investigation.

EXPERIMENTAL

The $DClO_4$ used was 99 atom % D, 70% in D_2O, supplied by Merck, Sharp and Dohme, Canada Ltd. The Hammett indicators 4-nitroaniline, 2-nitroaniline, 4-chloro-2-nitroaniline, 2,5-dichloro-4-nitroaniline, 2,6-dichloro-4-nitroaniline, 2,4-dinitroaniline, and 2,6-dinitroaniline (1)—(7), all available from previous work,[4a] were recrystallized before use, and stock solutions in methanol prepared. Spectra were recorded at ambient temperature (22—23 °C) using a Cary 14 u.v.-visible spectrophotometer and 5-mm cells.

A successive dilution technique was employed in obtaining ionisation ratios. A solution of the indicator in the strongest acid used was progressively diluted with D_2O, using calibrated syringes and adding sufficient indicator to restore its concentration each time. At each dilution the spectrum was recorded, and the solution analysed by titrating a weighed portion with NaOH of appropriate molarity, giving the composition of wt % directly. This was repeated until spectra characteristic of the unprotonated indicator were obtained. The technique was tested using $HClO_4$–H_2O mixtures; results in good agreement with those of Yates and Wai [4a] and Attiga and Rochester [4d] were obtained, showing the method to be reliable.

Ionisation ratios (I) were calculated from the absorbance (A) measurements at fixed wavelengths,[4a] using $I = (A_B - A)/(A - A_{BH^+})$. Absorbance values for the unprotonated (A_B) and protonated (A_{BH^+}) indicators were obtained from the most dilute and concentrated solutions used, if possible as averages of several measurements.

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† From Merck, Sharpe and Dohme, Ltd. and Aldrich Chemical Co.

Values at constant composition, obtained from these by linear interpolation, were used to derive the acidity function.

Densities of $DClO_4$–D_2O mixtures at 25 °C, needed to convert from wt % to molarity, were measured using an Anton Paar model DMAO2C digital precision density meter, calibrated against air and water. The most concentrated solution was measured, diluted, and re-measured as before; the molarity was determined at each dilution by triplicate or quadruplicate titrations of 50 μl portions.

RESULTS

The indicator pK_{BD^+} values in $DClO_4$ were determined using a method based on that of Yates and Wai [4a] for $HClO_4$, modified so as to permit the use of small acid volumes. The log ionisation ratios, $\log I = \log (C_{BD^+}/C_B)$, were measured over a range of acid concentrations for 7 primary aniline indicators. The pK_{BD^+} of 4-nitroaniline was obtained in the normal way; [1a] a plot of the equilibrium quotient ($\log I - \log C_{D^+}$) against C_{D^+}, which was linear, was extrapolated to zero concentration, giving pK_{BD^+} as the intercept. For the other compounds, pK_{BD^+} values were obtained using the normal overlap procedure [4a] of

$$pK_{AD^+} - pK_{BD^+} = \log I_A - \log I_B \qquad (1)$$

equation (1) for successive indicators A and B. The results are given in Table 1, together with the propagated error resulting from this type of overlap procedure,[19] and other relevant information. In all cases comparisons were available with previous determinations using D_2SO_4 or DCl; [2] agreement was within experimental error.

TABLE 2

D_o Values and excess acidities for $DClO_4$–D_2O mixtures

$\%DClO_4$ (w/w)	$-D_o$	$-(D_o + \log C_{D^+}) \simeq X$
0	—	0
0.5	−1.28	−0.02
1	−0.96	0.00
1.5	−0.73	0.05
2	−0.54	0.12
3	−0.26	0.22
4	−0.14	0.21
5	−0.02	0.23
6	0.10	0.27
8	0.26	0.30
10	0.42	0.36
12	0.53	0.39
14	0.68	0.46
16	0.79	0.51
18	0.91	0.58
20	1.03	0.65
22	1.17	0.74
24	1.30	0.83
26	1.44	0.93
28	1.60	1.05
30	1.76	1.17
32	1.92	1.30
34	2.08	1.43
36	2.26	1.58
38	2.44	1.73
40	2.67	1.93
42	2.92	2.15
44	3.16	2.36
46	3.44	2.62
48	3.76	2.91
50	4.06	3.19
52	4.38	3.49
54	4.70	3.78
56	5.17	4.23

The values of D_o, obtained using equation (2), are listed in Table 2. Also given there are the excess acidities X, which

$$D_o = pK_{BD^+} - \log I \qquad (2)$$

are the differences between the observed acidities and those which the system would have if it were ideal.[20] In terms of the amine activity coefficients involved, these are given by equation (3). Figure 1 illustrates the behaviour of D_o, H_o,[4a] and X with increasing wt % acid. The experimental error in D_o, best estimated from X (which is a difference), is about ±0.02 units.

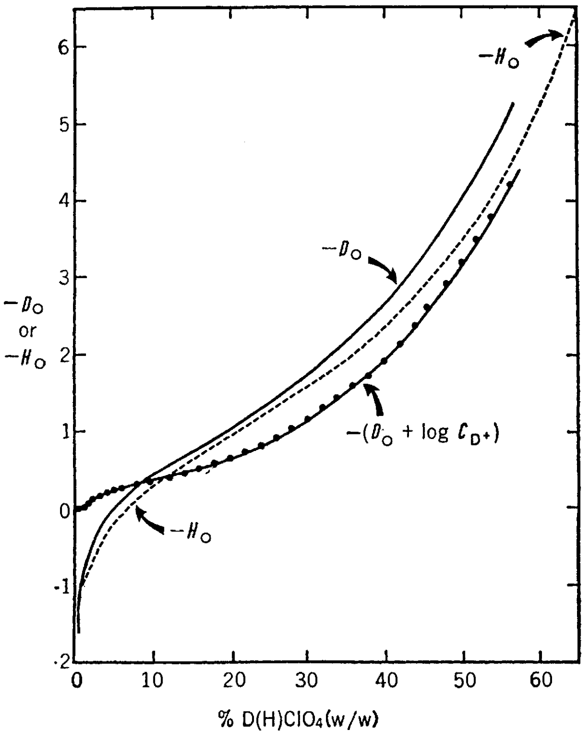

FIGURE 1 D_o, H_o, and excess acidity for perchloric acid as a function of weight percent acid

$$X \simeq \log (f_{Am}f_{D^+}/f_{AmD^+}) = -(D_o + \log C_{D^+}) \qquad (3)$$

In order to facilitate concentration unit interconversions, the densities of $DClO_4$–D_2O mixtures at 25 °C, which have not been previously reported, were determined; the results are in Table 3. Equation (4) relates the densities (ρ) of $DClO_4$ and $HClO_4$ [21] solutions of equal molarities

$$\rho(DClO_4/D_2O) = \rho(HClO_4/H_2O) + 0.107\,4 \text{ g cm}^{-3} \qquad (4)$$

within our experimental error, where 0.107 4 g cm^{-3} is the density difference between H_2O and D_2O.[3] Subsequent

TABLE 3

Densities of $DClO_4$ solutions

$DClO_4$ (M)	Density (25°) (g cm^{-3})
0	1.1046
2.40 ± 0.04	1.2372
3.89 ± 0.24	1.3301
4.43 ± 0.29	1.3891
5.18 ± 0.41	1.4439
7.66 ± 0.36	1.5530
10.29 ± 0.43	1.6966
11.35 ± 0.08	1.7492

concentration unit conversions were performed using this equation. In Table 4 are listed D_0 values and weight percent acid at fixed molarities. Figure 2 compares the behaviour of D_0, H_0,[4a] and log C_{D^+} or log C_{H^+}, as a function of acid molarity.

TABLE 4

D_0 values for $DClO_4$ solutions

$DClO_4$ (M)	% $DClO_4$ (w/w)	$-D_0$
0	0	—
0.05	0.46	−1.30
0.10	0.91	−1.00
0.15	1.37	−0.79
0.20	1.82	−0.61
0.30	2.72	−0.34
0.40	3.60	−0.19
0.50	4.48	−0.08
0.60	5.35	0.02
0.70	6.21	0.12
0.80	7.06	0.19
1.00	8.74	0.32
1.25	10.80	0.46
1.50	12.80	0.59
1.75	14.76	0.72
2.0	16.68	0.83
2.5	20.37	1.06
3.0	23.90	1.29
3.5	27.26	1.54
4.0	30.48	1.80
4.5	33.56	2.04
5.0	36.50	2.30
5.5	39.31	2.59
6.0	42.01	2.92
6.5	44.59	3.24
7.0	47.07	3.61
7.5	49.45	3.98
8.0	51.75	4.34
8.5	53.93	4.69
9.0	56.07	5.19

DISCUSSION

A comparison of the D_0 and H_0 acidity functions for perchloric acid is shown as a function of weight per cent acid in Figure 1 and as a function of acid molarity in Figure 2. As can be seen the magnitude of D_0 exceeds that of H_0 at the same weight per cent acid, but when comparisons are made at the same molarity the functions are almost identical. This is the same behaviour found for sulphuric acid, as noted in the introduction.

The fact that the D_0 scale is essentially the same as H_0 for both sulphuric and perchloric acids at most molarities is reassuring and indicates that unusual behaviour due to self association and incomplete dissociation phenomena is not apparent. Only above 90% sulphuric acid is there any significant deviation.

The results also indicate that the inconsistencies noted previously in the solvent isotope data for certain reactions in perchloric acid do not arise from diverging behaviour of the H_0 and D_0 functions at different concentrations. The causes of the unusual isotope effects will have to be sought elsewhere; perhaps in the experimental methods used for the determinations or in the reaction mechanisms of the particular substrates involved.

Thermodynamic basicities for compounds which do not follow D_0 can be approximated by making use of the excess acidity, X.[20] Since only primary amine data were available, it was not thought worthwhile to derive a rigorous X-function [20] for this medium. Values of pK_{BD^+} for non-D_0 compounds may be obtained using either the Bunnett–Olsen [22] equation (5), or the X-function (Marziano–Cimino–Passerini [23]) equation (6),[20] which will give identical results for this medium [see equation (3)].

$$\log I + D_0 = \phi(D_0 + \log C_{D^+}) + pK_{BD^+} \quad (5)$$

$$\log I - \log C_{D^+} = m^* X + pK_{BD^+} \quad (6)$$

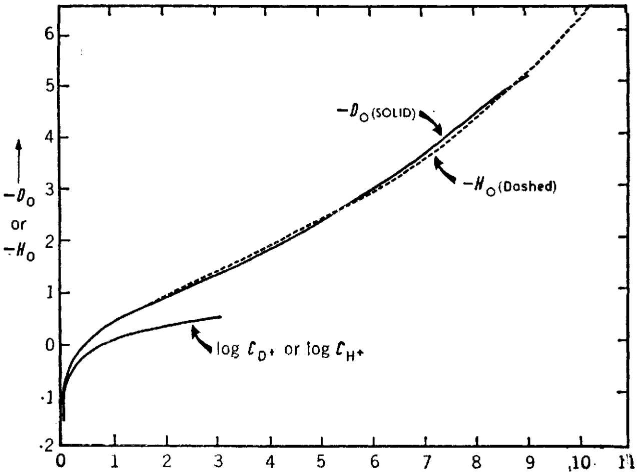

FIGURE 2 Comparison of D_0 and H_0 for perchloric acid as a function of acid molarity

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