652. *Mechanism of the Benzidine and Semidine Rearrangements. Part VIII.*[1] *Some Acidity Functions in Aqueous Dioxan. Kinetics of Rearrangement of Hydrazobenzene at High Acidities.*

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Previous work on the acidity function H_0 of perchloric acid, as sole electrolyte, in " 60% " aqueous dioxan is supplemented and extended to lower acidities. Acidity functions of perchloric acid in the same solvent at constant total electrolyte, made up with lithium perchlorate, are developed.

The linear plot of the logarithm of the specific rate of rearrangement of hydrazobenzene in " 60% " aqueous dioxan in the presence of perchloric acid in concentrations up to 1N against H_0 for perchloric acid as sole electrolyte has a slope of 2·35. But a part of this gradient arises from an ionic-strength effect, and, when the rate at constant total electrolyte concentration made up with lithium perchlorate is similarly correlated with H_0 for perchloric acid in identical salt-conditions, the slope becomes 2·1. This is in agreement, to within the uncontrolled errors of method, with the slope, 2·0, resulting at low acidities from the analogous correlation of rate with acid concentration. Previous conclusions to the effect that the rearrangement is specific hydrogen-ion, rather than general acid, catalysed with respect to both of the kinetically implicated protons are thus confirmed.

BUNTON, LEY, RHIND-TUTT, and VERNON described[2] the acidity function H_0 of some strong acids in certain organic solvents, thus extending the usefulness of the Hammett

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[1] Parts I—VII, *J.*, 1962, 2386, 2402, 2407, 2413, 2418, 2429, 2436.

[2] Bunton, Ley, Rhind-Tutt, and Vernon, *J.*, 1957, 2327.

function in the treatment of acid catalysis in organic reactions, in which the reactants are often insufficiently soluble for kinetic studies in water. One of the acid–solvent systems for which they established the existence of the function was that of perchloric acid in "60%" aqueous dioxan.

Early use was made of this function in the study of the acid catalysis of the rearrangement of hydrazobenzene in that system at high acidities. Bunton, Ingold, and Mhala found[3] that, whilst the plot of the logarithm of the specific rate of rearrangement against the logarithm of the concentration of acid gave a straight line of slope 2·0 from low acidities up to about 0·25N, from that acidity upwards the plot ran away on a rapidly steepening curve. However, they found that the plot of the logarithm of the specific rate against H_0 was linear as far as it could be followed, *viz.*, from 0·2N- to 1·0N-acid. Nevertheless, a puzzling anomaly appeared, in that the slope of the line was 2·6 rather than the expected 2·0. Discrepancies of such a magnitude in the slopes of Hammett plots are not otherwise unknown. But we set ourselves to track down the cause of this one, and thus became led into the present work on acidity functions of perchloric acid, work which was eventually developed with the idea of increasing further the general kinetic usefulness of such functions.

(1) *Acidity Functions of Perchloric Acid in "60%" Aqueous Dioxan.*—The first difficulty we had with the H_0 scale of Bunton, Ley, Rhind-Tutt, and Vernon was that their measurements became scanty and then ceased altogether around and below 0·25N-acid, *i.e.*, just where we would like to see what happens to the H_0 plot in the region of overlap with the linear log [H^+] plot for the rearrangement of hydrazobenzene. We have therefore filled out and extended those authors' scale in the region from 0·5N- down to 0·1N-acid, as shown in Table 1, and in the uppermost curve of Fig. 1. There are many acid-catalysed organic reactions for the kinetic investigation of which this will be a useful range of acid-concentration over which to know the H_0 function. This range has been used already in Parts V—VII of this series.[1]

The second difficulty was that the acid rearrangement of hydrazobenzene is subject to a general kinetic salt-effect; wherefore, in order to isolate the specific effect of a strong acid, one should build up the ionic strength with an added salt to a standard value while the concentration of the acid is being varied. In our kinetic experiments we have done this, adding lithium perchlorate along with the perchloric acid in order to standardise the concentration of total electrolyte in runs to be compared with respect to the effect of acidity on rate. But Bunton, Ingold, and Mhala could not do it, because the only H_0 function available to them was for perchloric acid as the only electrolyte, not for perchloric acid at constant total electrolyte; and hence they must have included an unwanted general ionic-strength along with the sought specific effect of acid. Thus the need arose for an H_0 function which would express the acidity of perchloric acid, not when alone in the solvent, but when present with salt to a standard concentration of total electrolyte. It is obvious that, for most kinetic purposes, this type of acidity function will be more appropriate than the hitherto used functions at unadjusted ionic strengths. The unadjusted and the adjusted function must be expected to differ, because of the effect of the electrolyte in reducing the activity of the solvent, and hence reducing its solvating power for hydrogen ions and for ionic conjugate acids. As is recorded in Table 1, we have determined two salt-adjusted functions for perchloric acid. In one, the total electrolyte is built up with lithium perchlorate to 0·5M; and in the other it is similarly built up to 1·0M. These functions show in Fig. 1 as the branch-curves which join the uppermost curve at the acid concentrations mentioned. One of these functions has already been used in Parts V and VII of this series.[1] The other is used in Section 2 below.

(2) *Rearrangement of Hydrazobenzene: Dependence of the Rate on Hammett Acidity.*—When the logarithms of Bunton, Ingold, and Mhala's specific rates, obtained in the absence

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[3] Bunton, Ingold, and Mhala, *J.*, 1957, 1906.

TABLE 1.

Acidity functions H_0 of perchloric acid in " 60% " aqueous dioxan without other electrolyte and with lithium perchlorate added to make constant total electrolyte at 20°.

No salt; μ variable		$\mu = [HClO_4] + [LiClO_4] = 0·5M$		$\mu = [HClO_4] + [LiClO_4] = 1M$	
$[HClO_4]$	H_0	$[HClO_4]$	H_0	$[HClO_4]$	H_0
0·100	2·38	0·098	2·03	0·133	1·74
0·12	2·29	0·13	1·90	0·199	1·55
0·13	2·25	0·16	1·80	0·264	1·42
0·16	2·12	0·20	1·74	0·297	1·35
0·20	2·05	0·23	1·72	0·332	1·30
0·23	1·91	0·30	1·60	0·397	1·23
0·30	1·81	0·33	1·57	0·531	1·08
0·37	1·65	0·37	1·52	0·664	0·97
0·40	1·55	0·40	1·47	0·796	0·87
0·50	1·39	0·47	1·38	0·929	0·80
0·995	0·75	0·500	1·39	0·995	0·75

of added salts, were plotted against H_0 values, taken from the now extended scale of acidities of perchloric acid as sole electrolyte in " 60% " aqueous dioxan, a straight line of slope 2·35 was obtained. Evidently some of the original anomaly was due to imperfect knowledge of H_0 values over the relevant acidity range. We do not here reproduce this plot, because it becomes further corrected in the sequel.

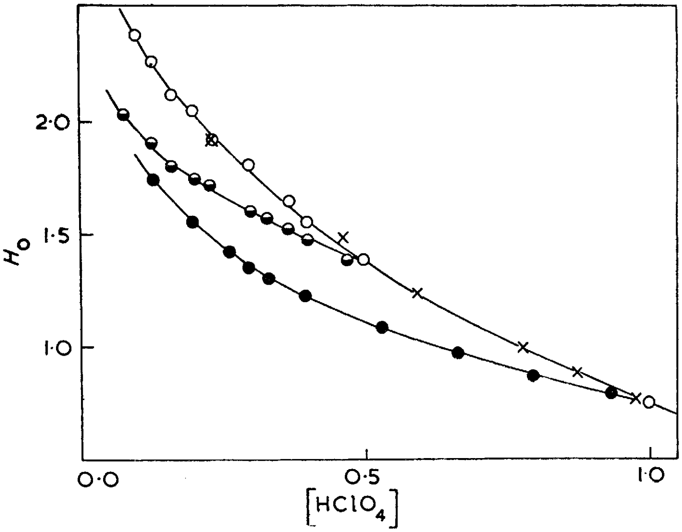

FIG. 1. Hammett functions H_0 for perchloric acid in aqueous dioxan at 20°.
Without other electrolyte: (○) this investigation; (×) Bunton, Ley, Rhind-Tutt, and Vernon.[2] Lithium perchlorate added to constant total electrolyte: (◒) 0·5M; (●) 1·0M.

Since general salt effects in hydrazo-rearrangements are large and positive, an apparent order in acid given by a set of rates, so determined that when the acidity is raised the ionic strength is raised with it, must be fictitiously augmented. We therefore determined the specific rates of rearrangement of hydrazobenzene in " 60% " aqueous dioxan, under catalysis by perchloric acid in concentrations from 0·2N to 1·0N, and in the presence of enough lithium perchlorate to make up the total electrolyte to 1·0M throughout the series of experiments. The results are in Table 2.

These specific rates are suitable for correlation with the H_0 function recorded above for perchloric acid with lithium perchlorate added to make up the total electrolyte concentration to 1·0M. The result of such a correlation should be to give a kinetic order in acid which is not spuriously raised by general salt effects. When the logarithms of the specific rates were plotted against these H_0 values, the points obtained defined a straight line, except that, as Fig. 2 shows, the three highest rates were too high by more than the casual experimental errors. We have convinced ourselves that a systematic experimental error is present here, and that it is thermal.

TABLE 2.

Specific rates, k_1 in sec.$^{-1}$, of rearrangement of hydrazobenzene, initially about 0·004M in 60% aqueous dioxan at 0·0° in the presence of perchloric acid and of lithium perchlorate added to make the total electrolyte 1·0M throughout.

$[HClO_4]$	0·198	0·297	0·343	0·435	0·540	0·640	0·765	0·877	1·000
10^3k_1	1·14	3·10	4·75	6·70	11·9	22·0	42 *	68 *	130 *

* Rate raised by thermal error (see text).

All the runs were started by mixing a solution of hydrazobenzene in aqueous dioxan containing less than the ultimate proportion of water with a solution in water of more than the ultimate concentration of perchloric acid. In order to start the strongly acid runs, the original aqueous perchloric acid had to be 2—3N. There was a heat of mixing, and, when the acidity was maximal, the heat was maximal, and the time available to get rid of the heat, before kinetic readings had to be taken, was minimal. In the three most acidic runs the times of half-change were 5, 10, and 16 sec., and, even working with small volumes in thin-walled tubes, the heat developed in starting these runs could not be dissipated quickly enough. In somewhat slower runs, the same thermal effect could be seen, though now only as an initial disturbance, to be succeeded by a series of valid kinetic readings. In still slower runs, the thermal disturbance could not be seen at all.

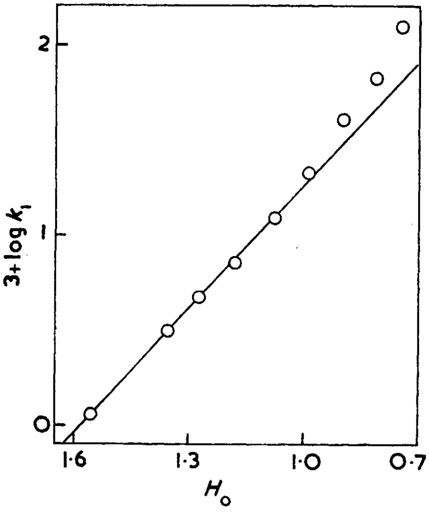

FIG. 2. Plot of the logarithm of the specific rate of rearrangement of hydrazobenzene against the acidity function H_0 of the perchloric acid catalyst in " 60% " aqueous dioxan containing 1·0M-total electrolyte made up with lithium perchlorate. (The straight line has the slope 2·1.)

If we accept this explanation of the high values of the highest rates, the line drawn in Fig. 2 is the correct line to take as indicating the specific dependence of rate on acidity. The slope of the line is 2·1, and is thus quite close to that of the plot of the logarithm of the specific rate against the logarithm of the acid concentration at low acidities, *viz.*, 2·0.

There are other possible causes of error in the slope of 2·1, including two, capable of being experimentally investigated, which we have not investigated. First, the logarithm of the rate of a reaction involving a double proton transfer should be plotted against $H_0 + H_+$, rather than against $2H_0$. This would involve a determination of the function H_+ for the acid in the solvent at the relevant levels of total electrolyte, *i.e.*, a repetition for H_+ of what has already been done for H_0. In the one system for which H_0 and H_+ have as yet been compared, *viz.*, for sulphuric acid in water, they have been found to be parallel functions,[4] so that linear plots of any independent variable against $H_0 + H_+$, and against $2H_0$, would have the same slope. We cannot expect such parallelism to be universal and exact; [5] but we do hope for approximate parallelism in our case.

Secondly, it would be desirable to eliminate the difference between the customary temperature, 20°, to which we have adhered, of the indicator-equilibrium measurements on which the acidity functions are based, and the temperature, 0°, of the kinetic measurements correlated with the acidity functions. It has been found for the inversion of sucrose that a larger temperature interval than this does affect the slope of the Hammett plot.[6] Yet a survey of many Hammett plots [7] does not disclose an association of outstanding discrepancies of slope with large temperature differences (up to 70°). So again, we hope that our temperature interval of 20° is not a cause of serious error in the slope that we record.

We did not evaluate these essentially corrigible but probably small errors, because, were they corrected, an ineradicable uncertainty would still remain as to how accurate is the basic assumption of the Hammett method, that the activity-coefficient ratio, $(f_B/f_{BH^+})/(f_S/f_{\neq})$, is independent of acidity. Again we hope for no more than a small error here, because our indicator base, *p*-nitroaniline, was structurally about as like as we could make it to each protonated aniline residue of the hydrazobenzene molecule. Therefore we temporarily rest satisfied with the approximate agreement demonstrated between the slope of the H_0 plot at higher acidities and that of the log $[H^+]$ plot at lower ones.

Bunton, Ingold, and Mhala set up two supports for the concept of specific hydrogen-ion, rather than general acid, catalysis in respect of both the protons kinetically involved in the rearrangement of hydrazobenzene.* One was that the rate correlates with Hammett acidity, rather than with stoicheiometric acidity, in the range over which these functions diverge. The other was that the rate is not retarded, but is accelerated, and, indeed, undergoes a four-fold, and not a two-fold, increase, when the water of the solvent is replaced by deuterium oxide. The present work removes a numerical anomaly that might have been held to weaken the first of these supports. The second has already been further strengthened in the work described in Parts I, VI, and VII on solvent isotope effects.[1]

Cohen and Hammond claim to have shown general acid catalysis by weak acids in aqueous ethanol.[8] They criticise Hughes and Ingold for having interpreted the previous kinetic evidence otherwise. However, their demonstration is weakened, first, because their " catalytic constants " do not obey the Brönsted relation, and secondly, because they put so much of the catalysing acids into their experiments as effectively to change the solvent. It should be appreciated that our evidence for specific hydrogen-ion catalysis in respect of both proton transfers applied only to the range of acidities, and to the partly aqueous solvents, that we used. While questioning general acid catalysis in Cohen and Hammond's conditions, we do not in principle exclude it towards low enough acidities, or in non-aqueous solvents.

* Semantic differences seem to have caused some confusion, to avoid which we would explain that, by " specific hydrogen-ion catalysis," we mean the concept that the proton is passed over from its acid to the transition state *practically completely*. The two points to be noted are that our criterion is the completeness, rather than the rate, of proton transfer; and that it is based on practical tests, rather than indirect argument. Thus we would not seek to put into a different category processes in which the transfer is at least arguably incomplete in principle, but is agreed to be indistinguishably different from complete by the available practical tests.

[4] Bonner and Lockhart, *J.*, 1957, **364**.

[5] M. W. Fuller, in a forthcoming paper, shows this for H_0 and H_-.

[6] Leininger and Kilpatrick, *J. Amer. Chem. Soc.*, 1938, **60**, 2891.

[7] Long and Paul, *Chem. Rev.*, 1957, **57**, 935.

[8] Cohen and Hammond, *J. Amer. Chem. Soc.*, 1953, **75**, 880.

EXPERIMENTAL

Materials.—The hydrazobenzene, prepared by Cohen's method,[9] and crystallised from ethanol, had m. p. 128°. The *p*-nitroaniline, crystallised from water, had m. p. 147°. The dioxan was freed from peroxides, degassed, and kept under nitrogen.*

Indicator Equilibria.—The indicator was *p*-nitroaniline ($\text{p}K_{\text{B}} = 0{\cdot}99$). The indicator ratios were measured spectrophotometrically at 20° over the broad absorption maximum at 381 mμ of the unprotonated base. The data recorded are means of several determinations, usually 5 or 6 near the lower end of the acidity range. Here, the indicator is not much protonated, and hence the photometric accuracy is lower; but we did not change to a more strongly basic indicator, because Bunton, Ley, Rhind-Tutt, and Vernon had shown that the H_0 scales of different indicators do not always overlap perfectly, and we thought that the uncertainty thus created by changing the indicator might neutralise the benefits of easier measurement.

Kinetics.—The runs were conducted by the inverted-Y-tube technique. They were quenched with Bindschedler's Green, excess of which was titrated to visual end-points with titanous chloride. Near the end-points, the solutions were warmed to 50° in order to hasten attainment of the end-points.

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* For checking the presence or absence of peroxides in dioxan, we have been using a test, which arose out of the work of Part I,[1] and is much more sensitive than the usual ferrous thiocyanate method. Freshly crystallised, colourless, 1,1'-hydrazonaphthalene (0·1 g.) was dissolved in the dioxan (10 ml.), and the solution was maintained at 20° for 3 min. A red colour of 1,1'-azonaphthalene indicates the presence of peroxides. The nitrogen under which we stored our dioxan could not have been absolutely free from oxygen, because this test, applied to purified and stored samples, remained negative only for about one week, and shortly thereafter became clearly positive.

[9] J. B. Cohen, " Practical Organic Chemistry," Macmillan, London, 1949, p. 162.