Kinetic Acidity Function $H_C^\ddagger$. Part 3.[1] Applicability to Hydration of Styrenes

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Variation of rate of hydration of substituted styrenes with acidity has been measured in aqueous sulphuric acid solutions. This reaction proceeds through a rate-limiting carbon protonation step. Linear Pfluger plots of unit slope result from the data. These appear to validate the applicability of an acidity function to the results; possible sources of error in this and related conclusions are carefully discussed.

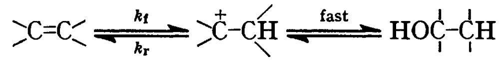
WE advanced the idea of a kinetic acidity function governing the rate of protonation of carbon bases,[1-3] defined by equation (1). The validity of the function relies on

$$H_C^\ddagger = -\log a_{H^+}f_B/f_\ddagger \qquad (1)$$

constant selectivity of the solvated proton to nucleophilic carbon centres whatever their reactivity, thus requiring constancy of the $f_B/f_\ddagger$ ratios for carbon bases at given acidities.

The question arises, how accurate is such a concept? In particular, and in contrast to our deductions, Scorrano and his co-workers have postulated variable slopes against acidity for hydration of olefins. They discussed the attendant variations in $f_B/f_\ddagger$ ratios in terms of changes in transition state solvation.[4,5]

Hydration of styrenes in aqueous acid proceeds *via* rate-determining carbon protonation[6] [equation (2)]. Studies of the rates were made in both aqueous perchloric acid[7] and sulphuric acid.[8]



$$>C=C< \underset{k_r}{\overset{k_f}{\rightleftharpoons}} >\overset{+}{C}-CH< \xrightarrow{\text{fast}} HOC-CH \qquad (2)$$

$$k_{obs} = k_f + k_r \qquad (3)$$

The reaction is of known mechanism and measurements of rate are readily carried out by u.v. analysis.[7,8] We therefore extended previous studies to obtain maximum overlap between one 'kinetic acidity function indicator' and the next, and thence constructed Pfluger plots[9] of the data.

We emphasise that our investigations did not arise from doubt about the accuracy of previous French work.[8] Indeed, the results matched quite closely, and we note that the French workers proposed the notion of a kinetic acidity function[10] well before us.

Pfluger plots are a good way of demonstrating parallelism of rate–acidity profiles and thus our purpose was to extend regions of overlap to maximum range. We also extended the acid range of measured rates of hydration of phenylacetylene, previously examined with great care,[4,11] to include an example of rate-determining proton transfer to a triple carbon–carbon bond within our Pfluger analysis.

EXPERIMENTAL

The olefins and phenylacetylene were available commercially or prepared and purified by standard means.[12] Rate measurements were carried out as previously indicated,[8,11,12] at 25 °C, using a Pye–Unicam SP8-200 u.v.–visible spectrophotometer.

As other workers have found,[4,8,11] amounts of alcohol are sometimes necessary to achieve solution of this type of base in aqueous sulphuric acid. We found generally 5% v/v of the final solution was sufficient: this was the case for *p*-methoxy-, *p*-methyl-, and *m*-methyl-styrene, styrene itself, and phenylacetylene. However, for solubility and manipulative reasons, particularly necessitated in the faster reaction, a 10% v/v solution in ethanol were used for 2-vinylnaphthalene and *m*-chloro-, *p*-chloro-, and *m*-nitrostyrene. This is a potential source of error which must be taken into account when comparing rates measured in different concentrations of ethanol. Nevertheless, experiments using variable amounts of ethanol between 5 and 10% for styrene, phenylacetylene, and *m*-methylstyrene produced no discernable changes in rate for a given acidity.

Styrenes exist in aqueous acid in equilibrium with carbinols; the rate constant for the forward reaction k_f may readily be evaluated[8,12] [equation (3)].

Difficulties in the measurement of rates for *m*-nitrostyrene, due to significant u.v. absorption of both styrene and alcohol at the wavelength for measurement, were found as recorded previously.[8,12] In all cases plots of $1 + \log (A - A_\infty)$, where A is absorbance, *versus* time were linear to 95% reaction at least. For very slow reactions with half-lives of several days, however, the reaction was only followed to *ca.* 40% extent. Correlation coefficients were always greater than 0.999 and usually greater than 0.9999, and standard deviations in the rate constants ± 0.0001 or less.

RESULTS

Table 1 gives the rate results obtained for *p*-methoxystyrene. Figure 1 compares our value for k_f for styrenes with those of previous workers,[4] and Figure 2 compares the values for phenylacetylene hydration. Figure 3 gives the Pfluger plot for *p*-methoxystyrene and *p*-methylstyrene, and Table 2 the slopes for all such plots. The rates required for these plots were either obtained by direct measurement at the same acidity for each of the two carbon bases, or by interpolation. No extrapolations were involved. The difference between log k_{obs} and log k_f for each styrene was acid invariant, within the limits of accuracy of the experiments (see Table 1), and very small, so log k_{obs} was used for the Pfluger plots.

TABLE 1

Rate constants for hydration of *p*-methoxystyrene (measurements at λ 258 nm)

H_2SO_4–H_2O (% w/w)	$10^5\,k_t$/ s^{-1}	$-\log k_t$	$10^5\,k_{obs}$/ s^{-1}	$-\log k_{obs}$	A_∞
5.00	5.07	4.30	5.47	4.26	0.059
	4.94	4.31	5.44	4.26	0.067
	4.79	4.32	5.19	4.29	0.045
5.25	5.89	4.23	6.24	4.21	0.040
8.00	11.3	3.95	12.2	3.91	0.061
	11.9	3.92	12.9	3.89	0.055
9.75	15.5	3.81	19.3	3.71	0.114
	15.8	3.80	17.0	3.77	0.030
14.50	50.9	3.29	54.7	3.26	0.063
	41.8	3.38	47.0	3.33	0.058
15.88	58.0	3.24	63.8	3.20	0.064
	58.3	3.23	61.9	3.21	0.065
19.50	111	2.96	121	2.92	0.048
	107	2.97	117	2.93	0.048
20.63	146	2.83	157	2.80	0.021
	147	2.83	158	2.80	0.022
24.25	268	2.57	298	2.53	0.060
	278	2.56	329	2.48	0.073
29.06	716	2.15	836	2.08	0.093
	710	2.15	815	2.09	0.070
32.31	1 210	1.92	1 380	1.86	0.063
	1 300	1.89	1 530	1.82	0.054

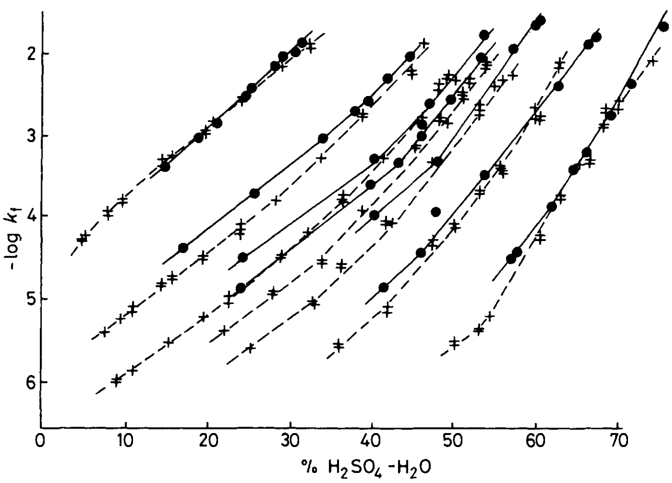


FIGURE 1 Plots of log k_t *versus* % H_2SO_4–H_2O (w/w) for hydration of styrenes: +, present data; ●, data from ref. 8. The substituted styrene plots are from left to right: *p*-OCH_3, *p*-CH_3, *m*-CH_3, styrene, *p*-Cl, *m*-Cl, *m*-NO_2

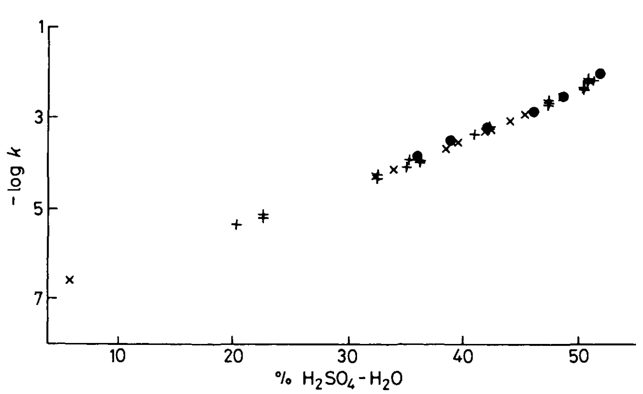


FIGURE 2 Plot of log *k versus* % H_2SO_4–H_2O (w/w) for hydration of phenylacetylene: +, present data, solutions contained 5 or 10% ethanol (see Experimental section); ●, data from ref. 4, solutions contained no ethanol; ×, data from ref. 11, solutions contained 5% ethanol

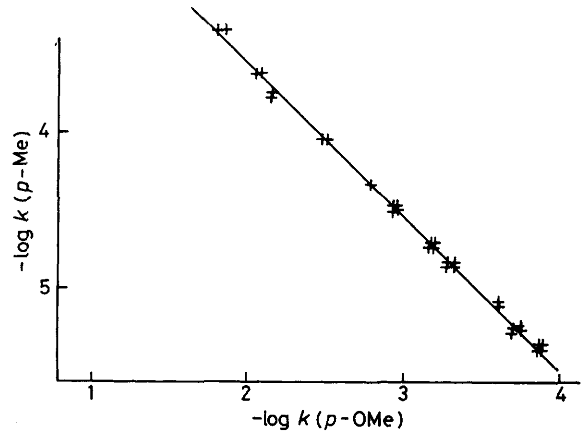


FIGURE 3 Plot of log k_{obs} for *p*-methoxystyrene against log k_{obs} for *p*-methylstyrene

TABLE 2

Pfluger analysis

Pfluger pair [a]	Slope [b]	Acid range (%)
p-CH_3, *p*-OCH_3	0.997 (0.9979, ±0.011)	8.0—32.3
2-Vinylnaphthalene, *p*-CH_3 [c]	0.984 (0.9994, ±0.007)	10.6—46.0
m-CH_3, *p*-CH_3	0.967 (0.9996, ±0.005)	9.5—46.0
Styrene, *p*-CH_3	0.994 (0.9989, ±0.011)	22.3—46.1
m-CH_3, 2-vinylnaphthalene [c]	0.991 (0.9998, ±0.004)	10.6—50.4
Styrene, *m*-CH_3	0.989 (0.9992, ±0.009)	22.3—49.3
Styrene, phenylacetylene	1.002 (0.9997, ±0.006)	22.3—51.3
p-Cl, styrene [c]	1.044 (0.9994, ±0.008)	25.5—54.1
m-Cl, styrene [c]	1.018 (0.9981, ±0.016)	36.3—54.1
m-Cl, *p*-Cl	0.983 (0.9989, ±0.011)	36.3—57.0
m-NO_2, *m*-Cl	0.872 (0.9965, ±0.016)	50.4—62.8

[a] Substituted styrenes: other olefins named in full. [b] Correlation coefficient, standard deviation of slope given in parentheses. [c] 5% v/v difference in alcohol content of acid solution used for measurement of rates (see Experimental section).

DISCUSSION

The Pfluger plots (Table 2) show no evidence of systematic and only very small random deviations from slopes of unity. Similar plots for overlapping log ionisation ratios of aniline bases defining the H_0 extrathermodynamic acidity function display much greater deviations from unity.[13] This constancy of $f_B/f_\ddagger$ terms represent a partial resurrection of the Zucker–Hammett hypothesis (which has suffered a good deal of criticism) in that its basic contentions included constancy of such terms.[6] The only deviation in slope from unity is that for *m*-chlorostyrene and *m*-nitrostyrene. We believe that arises from short overlap between the two and inaccuracies in the measurement of *m*-nitrostyrene hydration rates (see Experimental section) rather than any selectivity effect, although the latter possibility cannot be ruled out.

We are surprised that the hydration rates of phenylacetylene closely parallel those of styrenes. Some deviation expressing the different characteristics of solvation of a vinyl *sp* carbenium ion compared with an sp^2

carbenium ion, relative to their respective unprotonated ground state solvation, had been expected.

The parallelism of the styrene plots gives rise to a ρ value of −3.55 using σ^+ values at 35% acid (correlation coefficient 0.998) which remains constant as the acidity is varied, although acid dependent values have previously been suggested.[4,5] This constancy of ρ value as acidity and thus rate is varied may further validate the concept of immutable σ^+ values independent of reaction rate. We have argued this before;[14] on the other hand, the idea of immutable σ^+ values has been stringently criticised,[15] both from the viewpoint of the concept itself, and also in terms of its statistical basis.

Conclusions.—The linear Pfluger plots point to the validity of the kinetic acidity function concept, and thus to invariant Hammett ρ values, for substituted styrenes and related compounds. This conclusion must be tempered with consideration of potential experimental discrepancies arising from the use of variable amounts of ethanol in the aqueous acid solutions, from other difficulties in the measurements for *p*-nitrostyrene, and from possible statistical errors in the definition of ρ values. The significance of such sources of error have been discussed rigorously above or previously.

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