The Kinetics and Mechanism of the Electrophilic Substitution of Hetero-aromatic Compounds. Part XXXIII.[1] Hammett Treatment for Hydrogen Exchange of Monosubstituted Benzenes in Sulphuric Acid under Standard Conditions

By **Sergio Clementi** and **Alan R. Katritzky**,* School of Chemical Sciences, University of East Anglia, Norwich NOR 88C

Available kinetic data for the acid-catalysed hydrogen exchange of monosubstituted benzenes are extrapolated to give k_0 values relating to $H_0 = 0$ and $T = 100°$. These k_0 values yield ρ -7.5 for the exchange reaction in aqueous sulphuric acid: rates in other acids are also discussed.

AN important aim of structure–reactivity relationships is the evaluation of reaction constants ρ. Although these are well known for many electrophilic substitutions of monosubstituted benzenes, two typical aromatic substitutions, hydrogen exchange and nitration, are notable exceptions with ρ constants not precisely defined because of variations in the acidic media used. Following our suggested procedure for obtaining rate constants for hydrogen exchange in sulphuric acid at standard conditions (pH = 0 and $T = 100\ °C$),[2] we now apply the Hammett treatment to calculate a precise ρ value, which is needed in the treatment of heterocyclic derivatives. The results are compared with earlier work and the different sensitivity to structural changes in different acidic media is discussed.

RESULTS AND DISCUSSION

Stock and Brown[3] reported ρ -8.2 for detritiation but, as the authors pointed out, even the fair correlation found was surprising, since reactivities determined under widely different conditions had been used. Available literature data for hydrogen exchange in aqueous sulphuric acid are collected in Table 1; standardised rates (k_0) were calculated as previously described.[2] Only monosubstituted benzenes together with xylenes, furan, and thiophen are considered, because of possible breakdown of the additivity principle in polysubstituted (other than polyalkyl) derivatives.[4]

The results for individual compounds show very large differences, and the reliability of many of the k_0 values obtained is suspect. Thus, most of the slopes for the

[1] Part XXXII, A. El-Anani, S. Clementi, A. R. Katritzky, and L. Yakhontov, preceding paper.
[2] A. El-Anani, J. Banger, G. Bianchi, S. Clementi, C. D. Johnson, and A. R. Katritzky, *J.C.S. Perkin II*, 1973, 1065.

[3] L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**. 96.
[4] M. Godfrey, *J. Chem. Soc. (B)*, 1971, 1545.

Olsson [5-8] work are drawn through a very few points and the Gold and Satchell [9-11] acidity determinations have been criticised by Taylor.[12] The data of Eaborn and Taylor [13-15] follow a curved acidity dependence with the Paul and Long [16] H_0 scale, although fairly good straight lines are obtained for these compounds using the Shapiro [17] H_0 scale. As an approximation, we applied the Hammett treatment using the average values for each of the compounds of Table 1, together

Despite the unreliability of many of the individual k_0 values, Figure 1 discloses a good correlation ($r = 0.958$) with ρ -7.11. Taking all the individual k_0 values of Table 1 yields (Figure 2) a poor correlation ($r = 0.920$), with a slightly different ρ (-7.95). The three bold points of Figures 1 and 2, depicting k_0 values determined in our laboratories, lie on a good line ($r = 0.999$), with ρ -7.53; the average of the previous figures. We therefore consider ρ -7.5 as the most reliable estimate.

TABLE 1

Kinetic data for hydrogen exchange in H_2SO_4 of monosubstituted benzenes and related compounds

No.	Compound	Ref.	Reaction	$T/°C$	Position(s)	Range $-H_0$	No. of points	Slope	$-\log k$(stoich) at $H_0 = 0$	$-\log k_0$
1	Benzene	a	H/D	25	1	5·6—8·1	6	1·23	13·57	9·15
2	Benzene	b	H/T	25	1	6·7—8·3	7	1·74	17·64	12·96
3	Benzene	c	H/D [d]	25	1	7·8—8·7	3	1·96	19·22	14·80
4	Toluene	e	H/D	25	4	3·9—6·7	5	1·23	11·67	7·25
5	Toluene	b	H/T	25	4	5·9—7·0	5	1·39	12·79	8·11
6	Toluene	f	H/T	25	4	5·3—7·0	5	1·31	12·34	7·41
7	Toluene	g	H/D [d]	25	4	7·3—7·8	2	1·58	13·87	9·45
8	Toluene	f	H/T	25	2	5·3—6·9	5	1·29	12·23	7·55
9	Toluene	b	H/T	25	3	6·7—7·9	5	1·62	16·10	11·42
10	t-Butylbenzene	f, h	H/T	25	4	6·4—6·4	2	1·31 [i]	12·45	7·77
11	Anisole	j	H/D	25	4	1·8—3·8	5	1·19	8·67	4·25
12	Anisole	k	H/D [d]	25	4	4·3—5·4	2	1·02	8·04	3·62
13	Anisole	j	H/D	25	2	2·7—4·0	5	1·21	9·06	4·64
14	Bromobenzene	l	H/D [d]	25	4	8·7—9·4	2	1·46	16·00	11·58
15	m-Xylene	g	H/D [d]	25	2	5·4—6·2	2	1·21	9·23	4·81
16	p-Xylene	g	H/D [d]	25	2	6·2—7·3	3	1·53	12·86	8·44
17	NN-Dimethylaniline	m	T/H	65	2, 4, 6		1	0·00 [n]	6·21 [o]	−0·08 [p]
18	Thiophen	q	H/D [r]	20	2	1·2—4·2	3	1·13	7·75	2·96
19	Thiophen	s	H/T	25	2	0·9—3·3	5	1·04	6·50	1·82
20	Thiophen	q	H/D [r]	20	3	4·2—7·4	2	1·31	11·83	7·04
21	Thiophen	s	H/T	25	3	4·0—5·6	4	1·14	9·64	4·96
22	Furan	q	H/D [r]	20	2	1·2—4·2	3	1·00	7·55	2·76

[a] Ref. 9.   [b] Ref. 13.   [c] Ref. 5.   [d] Both H/D and H/T are carried out leading to very similar results: the average is reported.   [e] Ref. 10.   [f] Ref. 14.   [g] Ref. 6.   [h] Ref. 15.   [i] Since the points are too close for an accurate evaluation of the slope, it was taken equal to that of toluene, which reactivity is very similar, reported in the same paper, ref. 14.   [j] Ref. 11.   [k] Ref. 7.   [l] Ref. 8.   [m] Ref. 22.   [n] Slope taken 0·00 since free base reaction.   [o] Reactivity at one position only, owing to the kinetic procedure.   [p] log k(stoich) ($H_0 = 0, T = 100°$) + pK_a (100°).   [q] K. Schwetlick, K. Unverferth, and R. Mayer, Z. Chem., 1967, **7**, 58.   [r] Reaction in the presence of MeOH.   [s] A. R. Butler and J. B. Hendry, J. Chem. Soc. (B), 1970, 852.

with values for benzene,[18] aniline,[19] and phenol [2] determined in this laboratory (Table 2). Throughout we have considered rates as equal at the ortho- and para-positions (i.e. $\sigma_o^+ = \sigma_p^+$); the reaction has low steric requirements,[20,21] and reactivities at these positions are experimentally very close (ref. 2 and Table 1). Rates reported in Tables 1 and 2 concern reactivities at one position only, so that no correction for statistical factors is needed. Phenol, aniline, and NN-dimethylaniline underwent deuteriation or tritiation at all reactive positions, but the kinetic procedures used in determining k values already account for the statistical correction.[2,22]

Knowledge of ρ enables us to calculate the σ_p^+ constant for the negatively charged substituent O^- as -1.6 from the log k_0 for the phenolate anion of 0·95.[2] The activating effect of O^- is close to that of an NR_2 group ($\sigma_p^+ -1.7$).

Substituent Effects in Anhydrous Trifluoroacetic Acid and Related Media.—Detritiations in anhydrous trifluoroacetic acid, reported by Eaborn and co-workers [23,24] represent the most comprehensive set for the hydrogen exchange of monosubstituted benzenes under identical

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[6] S. Olsson, Arkiv Kemi, 1970, **32**, 89.
[7] M. Russell and S. Olsson, Arkiv Kemi, 1970, **31**, 455.
[8] S. Olsson, Arkiv. Kemi, 1970, **32**, 105.
[9] V. Gold and D. P. N. Satchell, J. Chem. Soc., 1955, 3619.
[10] V. Gold and D. P. N. Satchell, J. Chem. Soc., 1956, 2743.
[11] D. P. N. Satchell, J. Chem. Soc., 1956, 3911.
[12] R. Taylor, ' Kinetics of Electrophilic Aromatic Substitution,' in ' Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1972, vol. 13, p. 199.
[13] C. Eaborn and R. Taylor, J. Chem. Soc., 1960, 3301.
[14] R. Baker, C. Eaborn, and R. Taylor, J. Chem. Soc., 1961, 4927.

[15] C. Eaborn and R. Taylor, J. Chem. Soc., 1961, 247.
[16] M. A. Paul and F. A. Long, Chem. Rev., 1957, **57**, 1.
[17] C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, J. Amer. Chem. Soc., 1969, **91**, 6654.
[18] J. Banger, C. D. Johnson, A. R. Katritzky, and B. R. O'Neill, work in progress.
[19] S. Clementi, C. D. Johnson, and A. R. Katritzky, in preparation.
[20] R. Taylor, Chimia (Switz.), 1968, **22**, 1.
[21] H. V. Ansell, R. B. Clegg, and R. Taylor, J.C.S. Perkin II, 1972, 766.
[22] B. B. P. Tice, I. Lee, and F. H. Kendall, J. Amer. Chem. Soc., 1963, **85**, 329.
[23] R. Baker, C. Eaborn, and R. Taylor, J.C.S. Perkin II, 1972, 97.
[24] Ref. 12, p. 244.

TABLE 2

Reactivity data used in the Hammett treatment

No.	Compound	Ref.	Position	$-\log k_0$ [a]	σ^+ [b]
14	Bromobenzene	c	4	11·58	0·15
23	Benzene	d	1	11·00	0·00
9	Toluene	c	3	11·42	−0·07
10	t-Butylbenzene	c	4	7·77	−0·26
24	Toluene	e	2, 4	7·95	−0·31
16	p-Xylene	c	2	8·44	−0·38 [f]
25	Thiophen	e	3	6·00	−0·52 [g]
15	m-Xylene	c	2	4·81	−0·62 [f]
26	Anisole	e	2, 4	4·17	−0·78
27	Thiophen	e	2	2·39	−0·79 [g]
28	Phenol	h	2, 4, 6	4·00	−0·92
22	Furan	c	2	2·76	−0·93 [i]
29	Aniline	j	2, 4, 6	1·24	−1·30
17	NN-Dimethylaniline	c	2, 4, 6	−0·08	−1·70
30	Benzene	k	1	11·98	0·00

[a] Reactivities always refer to one position only. [b] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979, unless otherwise stated. [c] Table 1. [d] Ref. 18. [e] Average from data in Table 1. [f] Assuming additivity. [g] S. Clementi, P. Linda, and G. Marino, *J. Chem. Soc.* (B), 1970, 1153. [h] Ref. 2. [i] S. Clementi, P. Linda, and G. Marino, *Tetrahedron Letters*, 1970, 1389. [j] Ref. 19. [k] For a comparison only: average from data in Table 1 and compound 23.
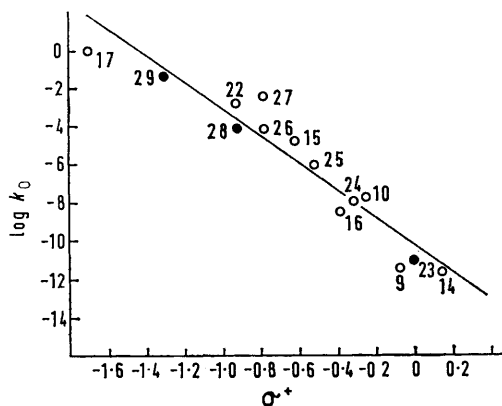

FIGURE 1 Hammett plot for hydrogen exchange of mono-substituted benzenes in H_2SO_4 at pH = 0 and T = 100 °C. Numbers denote compounds as in Table 2
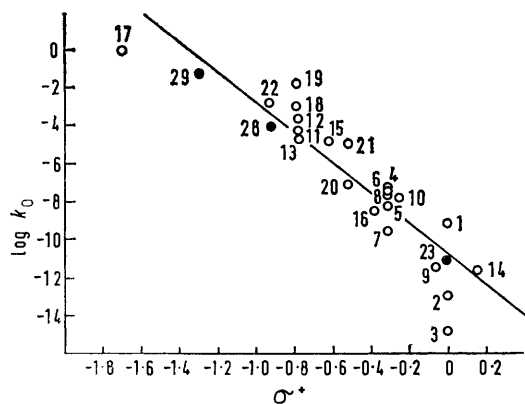

FIGURE 2 Hammett plot for hydrogen exchange of mono-substituted benzenes in H_2SO_4 at pH = 0 and T = 100 °C. Numbers denote compounds as in Tables 1 and 2. The bold points refer to reactivities determined in our laboratories

conditions. The same authors also reported detritiations in mixed media containing trifluoroacetic or acetic acid. The sensitivities to substituent effects in these media are compared in Table 3 with aqueous sulphuric acid. The ρ values are 6·11—8·80,† the increasing spread in reactivity being attributed to the solvating power of different media.[15] This topic has recently been discussed by Taylor.[25]

TABLE 3

ρ Values for hydrogen exchange of monosubstituted benzenes in some acidic media

Acid	Mol %	T/°C	ρ	Ref.
H_2SO_4–H_2O		100	−7·53	a
CH_3CO_2H–H_2O–H_2SO_4	26 : 34 : 40	25	−7·82	b
CH_3CO_2H–H_2O–$HClO_4$	98·1 : 1·8 : 0·1	66	−8·38	c
CF_3CO_2H–H_2O–H_2SO_4	95·3 : 2·2 : 2·5	25	−8·68	b, d
	83·4 : 2·0 : 14·6	25	−6·86	e, f
CF_3CO_2H–H_2O–$HClO_4$	92·0 : 5·5 : 2·5	25	−6·46	b, d
	89·5 : 4·5 : 6·0	55	−7·23	e
	96·8 : 0·8 : 2·4	55	−6·11	e
CF_3CO_2H–H_2O	82 : 16	70	−8·80	g
CF_3CO_2H [h]		70	−8·52	i

[a] This work. [b] Ref. 15. [c] Ref. 12, p. 257. [d] C. Eaborn and R. Taylor, *J. Chem. Soc.*, 1961, 1012. [e] C. Eaborn and R. Taylor, *J. Chem. Soc.*, 1961, 2388. [f] Ref. 12, p. 256. [g] W. M. Lauer, G. W. Matson, and G. Stedman, *J. Amer. Chem. Soc.*, 1958, **80**, 6433. [h] Anhydrous. [i] Ref. 23.

Knowledge of ρ constants for different media enables the reactivity in one of them to be calculated from reactivity measured in the other, by the equation
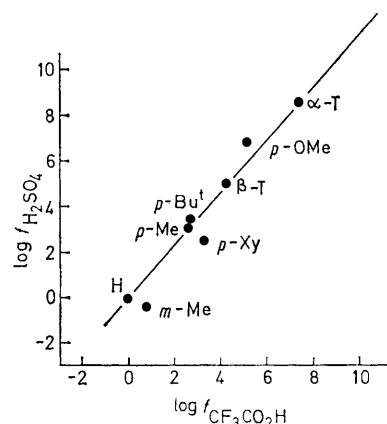

FIGURE 3 A comparison of substituent effects in H_2SO_4 and CF_3CO_2H. Plot of log f values in these media

$\log f_S = (\rho_S/\rho_T)\log f_T$, where the subscripts S and T indicate sulphuric and trifluoroacetic acid respectively. Plotting $\log f_S$ *versus* $\log f_T$ as in Figure 3 (the slope, 1·15, is coincidental with the ratio of the ρ constants), yields the same result but use of the ρ values requires less points common to both media. Data are not available for either CF_3CO_2H and H_2SO_4 to check this approach for polysubstituted compounds, in particular

† The ρ value for reaction in anhydrous trifluoroacetic acid was reported as −8·75,[23] but this included some fused-ring compounds exclusion of which gives −8·52.

[25] Ref. 12, p. 243.

whether the breakdown of the additivity principle varies.

Mineral Acids.—Few kinetic data are available for hydrogen exchange of monosubstituted benzenes in HCl, HClO$_4$, and H$_3$PO$_4$; they are seldom directly comparable with reactivities in H$_2$SO$_4$. To estimate the reactivity for compounds not studied in H$_2$SO$_4$ requires

temperature dependence of H_0 in these acids limits tests to data at 25°: available only for *p*-cresol (in HCl),[27,28] *p*-chlorophenol (in H$_3$PO$_4$),[27] and benzene (in HClO$_4$).[11] The results obtained by the standard extrapolation procedure (Table 4) encourage its application to different acids, provided that the behaviour of H_0 is known in these media. Furthermore, since standardised rates do

TABLE 4

Standardised rates in different mineral acids: a comparison with values in H$_2$SO$_4$

Compound	Reaction	Acid	Ref.	Range $-H_0$	Slope	$-\log k$(stoich) $H_0 = 0, T = 25$	$-\log k_0$	$-\log k_0$ (H$_2$SO$_4$)	Slope (H$_2$SO$_4$)	Ref. (H$_2$SO$_4$)
Benzene	H/D	HClO$_4$	a	6·6—7·8	1·45	15·1	10·7	11·0	1·62	b
p-Cresol	H/D	HCl	c	0·7—2·3	1·15	7·2	2·8	3·2	1·01	d
p-Cresol	H/T	HCl	e	1·2—2·4	1·28	7·6	3·2	3·2	1·01	d
p-Chlorophenol	H/D	H$_3$PO$_4$	c	1·8—3·0	0·90	8·5	4·1	4·8	0·86	d

a Ref. 11. *b* Ref. 18. *c* Ref. 27. *d* Ref. 19. *e* Ref. 28.

knowledge of the compatibility of the 'standard procedure' towards results for these media. We thus need kinetic data on the acidity dependence for compounds both in H$_2$SO$_4$ and another acid, to check the identity of the extrapolated rates. The acidity function H_0 is known for each medium,[26] and one shou.d find different slopes but the same intercept as in H$_2$SO$_4$, since all acidity functions merge when $H_0 = 0$. The unknown

not depend significantly on the acid in which measurements are carried out, such data should be sound estimates of reactivity in hydrogen exchange.

[26] For a comprehensive review see C. H. Rochester, ' Acidity Functions,' Academic Press, London, 1970, ch. 2.

[27] V. Gold and D. P. N. Satchell, *J. Chem. Soc.,* 1955, 3622.
[28] V. Gold, R. W. Lambert, and D. P. N. Satchell, *J. Chem. Soc.,* 1960, 2461.