# The Kinetics and Mechanism of the Electrophilic Substitution of Hetero-aromatic Compounds. Part XXXVII.[1] The Acid Catalysed Detritiation of Benzene and Naphthalene

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The exchange rates of protium for tritium in [³H]benzene, [1-³H]naphthalene, and [2-³H]naphthalene have been found over a wide range of concentrations of aqueous sulphuric acid. The results are compared with those of other workers. The rate–acidity profiles are analysed in terms of current theories regarding the $A–S_E2$ mechanism of hydrogen exchange. Correcting the activation parameters for the effect of temperature on $H_0$ values affords more acceptable values than those obtained without this correction.

PREVIOUS work on electrophilic substitution in aromatic and heteroaromatic molecules from this laboratory has included extensive studies of protium–deuterium exchange in $D_2O–D_2SO_4$ in the pyridine, azine, quinoline, and isoquinoline series. For comparative purposes, we required equivalent data for the carbocyclic aromatic molecules benzene and naphthalene. However, the limited solubility of these substrates in sulphuric acid–water mixtures obviated the use of deuterium exchange followed by the n.m.r. technique; consequently we turned to tritium–protium exchange, which can be studied with a much smaller substrate concentration. Rate profiles in aqueous sulphuric acid have previously been determined for [²H]benzene,[2] [³H]benzene,[3,4] and several substituted benzenes and toluenes,[5] but in most cases the ranges of acidity covered were limited for a very wide variety of acid concentrations. Similar data for naphthalene appears to be absent for sulphuric acid (although extensive for other media, e.g. trifluoroacetic acid).[6]

## EXPERIMENTAL

*Materials.*—Commercial AnalaR sulphuric acid, toluene, and butyl-2-phenyl-5-(4-biphenylyl)-1,3,4-oxadiazole (butyl-PBD) were used without further purification. Tritiated

water of nominal activity 100 mCi ml⁻¹ was kindly donated by Dr. P. Ballance. [³H]Benzene, [1-³H]naphthalene, and [2-³H]naphthalene were prepared from the appropriate bromo-compounds by formation of the Grignard reagent and decomposition in tritiated water.[7] Pure benzene was obtained by fractional distillation, and the pure naphthalenes by successive sublimations.

*Kinetic Procedures.*—Measurements were carried out in sulphuric acid solutions prepared by weight at ca. 2% intervals. The scintillator mixture used was butyl-PBD in toluene (5 g l⁻¹). Counting vials were straight sided, clear glass cylindrical tubes (capacity 20 ml) with screw top stoppers, containing a relatively low percentage of the ⁴⁰K isotope.

*Exchange in Benzene.*—Sulphuric acid (30 ml) of the required concentration was added to a weighed amount of [³H]benzene (15—20 mg) and the mixture shaken vigorously for 5 min in a tightly stoppered conical flask (50 ml) to ensure complete dissolution. Equal volumes (2 ml) of the solution were then syringed out into ampoules (2 × 10 ml) and the ampoules sealed, and placed in a thermo-statted bath at the appropriate temperature which was maintained to within ±0·1°. Ampoules were removed at suitable time intervals, washed with acetone and then water, and broken under 3% sodium hydroxide solution (100 ml). Scintillator solution (20 ml) was added to each quenched

[1] Part XXXVI, A. G. Burton, A. R. Katritzky, M. Konya, and H. O. Tarhan, preceding paper.
[2] V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 1955, 3619.
[3] C. Eaborn and R. Taylor, *J. Chem. Soc.*, 1960, 3301.
[4] S. Olsson and M. Russell, *Arkiv. Kemi*, 1969, **31**, 439.

[5] V. Gold in ' Friedel-Crafts and Related Reactions,' ed. G. A. Olah, Interscience, New York, vol. II, part 2, 1964, p. 1253.
[6] C. Eaborn, P. Golborn, R. E. Spillett, and R. Taylor, *J. Chem. Soc. (B)*, 1968, 1112.
[7] Full details are given in the Ph.D. Thesis of J. Banger, University of East Anglia, Norwich, 1971, and the Ph.D. Thesis of B. R. O'Neill, University of East Anglia, Norwich, 1973.

sample, and the mixture shaken mechanically for 10—15 min. The upper organic layer was separated, washed with water (2 × 50 ml), dried (MgSO$_4$), and this solution (10 ml) counted. When the reaction was carried out in stoppered flasks and aliquot portions pipetted into the sodium hydroxide solution, erroneous and inconsistent results were obtained, particularly at the lower acidities.

*Exchange in Naphthalene.*—The procedure was identical for that with benzene, with the exception that the required amount of [$^3$H]naphthalene was difficult to dissolve in 50 ml of sulphuric acid. The naphthalene (0·2—0·3 mg) was therefore dissolved in trifluoroacetic acid (*ca.* 0·1 ml) to which was then added sulphuric acid (40—50 ml). This quantity of trifluoroacetic acid has negligible effect on both the $H_0$ value of the solution and rate of exchange.[7]

*Analytical Procedures.*[7]—The benzene solutions were counted on an Intertechnique automatic liquid scintillation spectrometer, model SL 30. On the slower runs, each observed count $c'$ was converted to a corrected count $c$ allowing for tritium decay ($t_{\frac{1}{2}}$ 12·26 years)[8] by equation (1).

$$c = c'e^{(-1·79 \times 10^{-10})t} \quad (t \text{ in s}) \qquad (1)$$

Since the exchange experiments were carried out under pseudo-first-order conditions (acid in large excess over substrate) a plot of $\log_{10}(c - c_\infty)$ against time should be linear, of slope $-k/2·303$. The background (infinity) count $c_\infty$ was taken as that given by 10 ml of scintillator solution. The rate constant $k$ was evaluated by a computer program[7] which rejected points whose error was greater than two standard deviations.

A typical rate measurement is presented in Table 1.

## TABLE 1

### A typical rate measurement $^a$

|   | Time (s) | $c$ (10 min) |
|---|---|---|
| 1 | 1200 | 116,033 |
| 2 | 60,000 | 100,445 |
| 3 | 148,000 | 86,495 |
| 4 | 228,600 | 74,578 |
| 5 | 330,600 | 57,803 |
| 6 | 414,000 | 51,644 |
| 7 | 503,100 | 46,203 |
| 8 | 580,500 | 38,739 |
| 9 | 655,800 | 32,971 |
| 10 | 701,000 | 30,121 |

$^a$ $k = 1·88 \pm 0·04 \times 10^{-6}$ s$^{-1}$. Error = 2·17%.

*Determination of Acidity.*—From the wt. % of the acid solutions, $H_0(25°)$ was found,[9] and for runs at other than 25°, $H_0(T)$ was calculated using equation (2),[9] where $K$ is a constant for a given acidity.

$$H_0(T) = H_0(25°) + K(298·15 - T)/298·15 \, T \qquad (2)$$

*Corrections for Sulphonation.*—Several groups of workers have reported rate measurements of the sulphonation of benzene. Gold and Satchell's data[10] have been questioned,[11] while Eaborn's and Cerfontain's results for the same conditions lead to a correction of *ca.* 3% or less at the highest acidity, not distinguishable from the error in

[8] 'Handbook of Chemistry and Physics,' Chemical Rubber Co., Cleveland, 51st edn., 1970, p. B-247.

[9] C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J Amer. Chem. Soc.*, 1969, **91**, 6654.

[10] V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 1956, 1635.

[11] A. W. Kaandorp, H. Cerfontain, and F. L. J. Sixma, *Rec. Trav. chim.*, 1962, **81**, 969.

[12] H. Cerfontain and A. Telder, *Rec. Trav. chim.*, 1967, **86**, 527.

rate constant measurement. The latter worker[12] also reports studies on the sulphonation of naphthalene which

## TABLE 2

### (i) Tritium–protium exchange of [$^3$H]benzene

| Wt. % acid | $T/°C$ | $-H_0(25°)$ | $-H_0(T)$ | $k_{obs}$ s$^{-1}$ |
|---|---|---|---|---|
| 83·71 | 25 | 8·08 | 8·08 | $(4·17 \pm 0·07) \times 10^{-4}$ |
| 81·50 | 25 | 7·73 | 7·73 | $(1·07 \pm 0·01) \times 10^{-4}$ |
| 79·45 | 25 | 7·38 | 7·38 | $(3·31 \pm 0·04) \times 10^{-5}$ |
| 74·31 | 25 | 6·52 | 6·52 | $(1·07 \pm 0·04) \times 10^{-6}$ |
| 70·84 | 25 | 5·96 | 5·96 | $(1·53 \pm 0·32) \times 10^{-7}$ |
| 68·09 | 25 | 5·54 | 5·54 | $(3·14 \pm 1·13) \times 10^{-8}$ |
| 81·79 | 35 | 7·78 | 7·54 | $(4·56 \pm 0·34) \times 10^{-4}$ |
| 81·79 | 35 | 7·78 | 7·54 | $(4·72 \pm 0·16) \times 10^{-4}$ |
| 77·90 | 35 | 7·12 | 6·91 | $(4·86 \pm 0·09) \times 10^{-5}$ |
| 74·31 | 35 | 6·52 | 6·32 | $(3·53 \pm 0·25) \times 10^{-6}$ |
| 70·84 | 35 | 5·96 | 5·79 | $(5·60 \pm 0·36) \times 10^{-7}$ |
| 70·78 | 35 | 5·95 | 5·78 | $(5·28 \pm 0·16) \times 10^{-7}$ |
| 68·35 | 35 | 5·56 | 5·40 | $(1·16 \pm 0·14) \times 10^{-7}$ |
| 68·09 | 35 | 5·54 | 5·38 | $(1·88 \pm 0·40) \times 10^{-7}$ |
| 81·33 | 45 | 7·71 | 7·26 | $(1·18 \pm 0·04) \times 10^{-3}$ |
| 77·90 | 45 | 7·12 | 6·70 | $(1·57 \pm 0·03) \times 10^{-4}$ |
| 73·79 | 45 | 6·43 | 6·06 | $(1·82 \pm 0·03) \times 10^{-5}$ |
| 70·78 | 45 | 5·95 | 5·61 | $(1·88 \pm 0·04) \times 10^{-6}$ |
| 68·35 | 45 | 5·56 | 5·26 | $(5·88 \pm 0·26) \times 13^{-7}$ |
| 65·90 | 45 | 5·20 | 4·93 | $(2·50 \pm 0·13) \times 10^{-7}$ |
| 64·65 | 45 | 5·02 | 4·76 | $(1·07 \pm 0·11) \times 10^{-7}$ |
| 81·33 | 55 | 7·71 | 7·05 | $(3·02 \pm 0·08) \times 10^{-3}$ |
| 77·90 | 55 | 7·12 | 6·51 | $(3·76 \pm 0·19) \times 10^{-4}$ |
| 74·25 | 55 | 6·50 | 5·96 | $(3·13 \pm 0·10) \times 10^{-5}$ |
| 70·78 | 55 | 5·95 | 5·47 | $(5·76 \pm 0·27) \times 10^{-6}$ |
| 65·90 | 55 | 5·20 | 4·80 | $(6·38 \pm 0·41) \times 10^{-7}$ |
| 64·65 | 55 | 5·02 | 4·65 | $(1·49 \pm 0·42) \times 10^{-7}$ |
| 63·65 | 55 | 4·85 | 4·49 | $(3·35 \pm 0·16) \times 10^{-7}$ |

### (ii) Tritium–protium exchange of [1-$^3$H]naphthalene

| Wt. % acid | $T/°C$ | $-H_0(25°)$ | $-H_0(T)$ | $k_{obs}$ s$^{-1}$ |
|---|---|---|---|---|
| 68·50 | 25 | 5·59 | 5·59 | $(1·77 \pm 0·08) \times 10^{-5}$ |
| 66·61 | 25 | 5·30 | 5·30 | $(9·66 \pm 0·02) \times 10^{-6}$ |
| 64·98 | 25 | 5·07 | 5·07 | $(3·52 \pm 0·10) \times 10^{-6}$ |
| 63·85 | 25 | 4·89 | 4·89 | $(3·23 \pm 0·07) \times 10^{-6}$ |
| 60·27 | 25 | 4·40 | 4·40 | $(5·16 \pm 0·55) \times 10^{-7}$ |
| 66·90 | 35 | 5·35 | 5·20 | $(3·30 \pm 0·07) \times 10^{-5}$ |
| 64·15 | 35 | 4·95 | 4·81 | $(8·88 \pm 1·32) \times 10^{-6}$ |
| 60·30 | 35 | 4·41 | 4·30 | $(2·65 \pm 0·08) \times 10^{-6}$ |
| 55·64 | 35 | 3·85 | 3·76 | $(6·30 \pm 0·20) \times 10^{-7}$ |
| 52·10 | 35 | 3·48 | 3·40 | $(2·05 \pm 0·55) \times 10^{-7}$ |
| 66·90 | 45 | 5·35 | 5·06 | $(1·06 \pm 0·02) \times 10^{-4}$ |
| 60·30 | 45 | 4·41 | 4·20 | $(9·37 \pm 0·21) \times 10^{-6}$ |
| 59·86 | 45 | 4·36 | 4·14 | $(6·00 \pm 0·19) \times 10^{-6}$ |
| 55·64 | 45 | 3·85 | 3·68 | $(2·04 \pm 0·04) \times 10^{-6}$ |
| 52·10 | 45 | 3·48 | 3·33 | $(7·12 \pm 0·13) \times 10^{-7}$ |
| 66·90 | 55 | 5·35 | 4·93 | $(2·29 \pm 0·22) \times 10^{-4}$ |
| 60·30 | 55 | 4·41 | 4·10 | $(2·36 \pm 0·06) \times 10^{-5}$ |
| 55·64 | 55 | 3·85 | 3·60 | $(5·96 \pm 0·24) \times 10^{-6}$ |
| 52·10 | 55 | 3·48 | 3·21 | $(2·01 \pm 0·03) \times 10^{-6}$ |
| 49·60 | 55 | 3·23 | 3·03 | $(1·22 \pm 0·05) \times 10^{-6}$ |

### (iii) Tritium–protium exchange of [2-$^3$H]naphthalene

| Wt. % acid | $T/°C$ | $-H_0(25°)$ | $-H_0(T)$ | $k_{obs}$ s$^{-1}$ |
|---|---|---|---|---|
| 71·98 | 25 | 6·12 | 6·12 | $(4·55 \pm 0·09) \times 10^{-6}$ |
| 71·13 | 25 | 6·02 | 6·02 | $(4·21 \pm 0·14) \times 10^{-6}$ |
| 69·04 | 25 | 5·67 | 5·67 | $(1·18 \pm 0·06) \times 10^{-6}$ |
| 67·90 | 25 | 5·50 | 5·50 | $(9·58 \pm 0·33) \times 10^{-7}$ |
| 65·80 | 25 | 5·18 | 5·18 | $(6·30 \pm 0·26) \times 10^{-7}$ |
| 65·77 | 25 | 5·18 | 5·18 | $(6·04 \pm 0·25) \times 10^{-7}$ |
| 63·62 | 25 | 4·86 | 4·86 | $(2·46 \pm 0·13) \times 10^{-7}$ |
| 63·55 | 25 | 4·85 | 4·85 | $(2·41 \pm 0·15) \times 10^{-7}$ |
| 61·83 | 25 | 4·60 | 4·60 | $(1·16 \pm 0·14) \times 10^{-7}$ |
| 67·90 | 35 | 5·50 | 5·34 | $(4·27 \pm 0·08) \times 10^{-6}$ |
| 65·80 | 35 | 5·18 | 5·04 | $(2·71 \pm 0·12) \times 10^{-6}$ |
| 63·55 | 35 | 4·85 | 4·72 | $(1·02 \pm 0·04) \times 10^{-6}$ |
| 61·83 | 35 | 4·60 | 4·48 | $(5·12 \pm 0·11) \times 10^{-7}$ |
| 59·90 | 35 | 4·35 | 4·24 | $(2·27 \pm 0·18) \times 10^{-7}$ |
| 65·90 | 45 | 5·19 | 4·91 | $(9·30 \pm 0·57) \times 10^{-6}$ |
| 63·60 | 45 | 4·87 | 4·62 | $(5·83 \pm 1·5) \times 10^{-6}$ |
| 60·17 | 45 | 4·38 | 4·17 | $(1·30 \pm 0·18) \times 10^{-6}$ |
| 63·60 | 55 | 4·87 | 4·51 | $(1·26 \pm 0·02) \times 10^{-5}$ |
| 62·25 | 55 | 4·66 | 4·32 | $(5·28 \pm 0·17) \times 10^{-6}$ |
| 60·17 | 55 | 4·38 | 4·07 | $(2·40 \pm 0·17) \times 10^{-6}$ |
| 57·80 | 55 | 4·11 | 3·83 | $(2·21 \pm 0·10) \times 10^{-6}$ |
| 56·70 | 55 | 3·96 | 3·69 | $(1·06 \pm 0·03) \times 10^{-6}$ |

show that in our work the appropriate correction will be much smaller than experimental error even at the highest acidities. Studies at variable temperatures have not been reported. No sulphonation correction is therefore needed for any of the present results for either benzene or naphthalene.
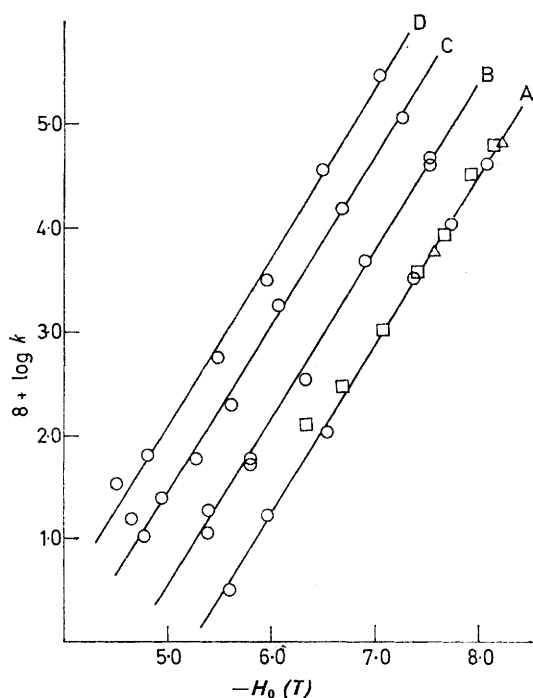


FIGURE 1 Rate–acidity profiles for tritium–protium exchange in [³H]benzene in aqueous sulphuric acid: ○ present work; □ ref. 3; △ ref. 4: A, 25°; B, 35°; C, 45°; D, 55°
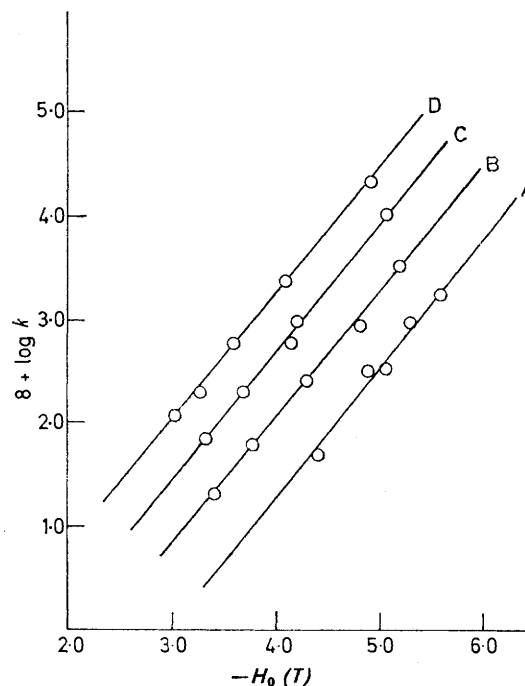


FIGURE 2 Rate–acidity profiles for tritium–protium exchange in [1-³H]naphthalene in aqueous sulphuric acid: A, 25°; B, 35°; C, 45°; D, 55°

## RESULTS

[³H]*Benzene*.—The observed first-order rate constants for tritium–protium exchange in [³H]benzene are recorded in Table 2, and the rate acidity profiles constructed in Figure 1, together with relevant results of Eaborn and Taylor [3] and

### TABLE 3
Arrhenius activation parameters

| [³H]Benzene | | | | | | $\Delta S^{\ddagger}$/cal mol$^{-1}$ | |
|---|---|---|---|---|---|---|---|
| (i) Uncorrected | Wt. % acid | $-H_0$ | $E_A$/kcal mol$^{-1}$ | log $(A/\text{s}^{-1})$ | $\Delta H^{\ddagger}$/kcal mol$^{-1}$ | K$^{-1}$ | $\Delta G^{\ddagger}$/kcal mol$^{-1}$ |
| | 65·90 | | | | 18·41 | −30·8 | 27·60 |
| | 68·09 | | | | 23·04 | 13·6 | 27·66 |
| | 70·84 | | | | 24·63 | −7·20 | 26·74 |
| | 74·31 | | | | 21·30 | −14·6 | 25·60 |
| (ii) Corrected [b] | 5·0 | | 36·7 | 18·51 | 36·1 | 24·1 | |
| | 6·0 | | 36·9 | 20·3 | 36·2 | 32·1 | |
| | 7·0 | | 37·0 | 22·0 | 36·4 | 40·1 | |
| | 7·5 | | 37·2 | 23·7 | 36·6 | 44·3 | |
| | 0 [a] | | 35·2 | 9·32 | 34·6 | −18·0 | |
| [1-³H]Naphthalene | | | | | | | |
| (i) Uncorrected | 52·10 | | 22·95 | 9·59 | 22·32 | −16·74 | |
| | 55·64 | | 22·55 | 9·80 | 21·92 | −15·78 | |
| | 60·30 | | 29·52 | 15·41 | 28·90 | 9·89 | |
| | 66·90 | | 19·25 | 9·16 | 18·63 | −18·72 | |
| (ii) Corrected [b] | 3·0 | | 30·5 | 14·32 | 29·9 | 4·9 | |
| | 4·0 | | 29·6 | 14·90 | 29·0 | 7·9 | |
| | 5·0 | | 28·8 | 15·61 | 28·1 | 10·8 | |
| | 6·0 | | 27·9 | 16·25 | 27·3 | 13·8 | |
| | 0 [a] | | 33·0 | 12·3 | 32·4 | −4·4 | |
| [2-³H]Naphthalene | | | | | | | |
| (i) Uncorrected | 56·70 | | 42·45 | 3·15 | 36·05 | −75·06 | 25·97 |
| | 63·60 | | 25·01 | 11·72 | 24·39 | −7·04 | 26·49 |
| | 65·90 | | 25·56 | 12·54 | 24·95 | −3·19 | 25·90 |
| (ii) Corrected [b] | 3·5 | | 29·77 | 13·63 | 29·15 | 1·72 | 28·64 |
| | 4·0 | | 29·73 | 14·19 | 29·10 | 4·26 | 27·84 |
| | 5·0 | | 29·65 | 15·30 | 29·02 | 9·34 | 26·38 |
| | 6·0 | | 29·56 | 16·41 | 28·94 | 14·4 | 24·64 |
| | 0 [a] | | 30·0 | 9·7 | 29·4 | −16·3 | 34·24 |

[a] Obtained by extrapolation.   [b] Correct for change of the acidity function $H_0$ with temperature as described in ref. 16.

Olsson and Russell.[4]   The Arrhenius activation parameters are given in Table 3; those in section (ii) were calculated from rate constants read off the rate profiles at different temperatures for a single $H_0$ value.
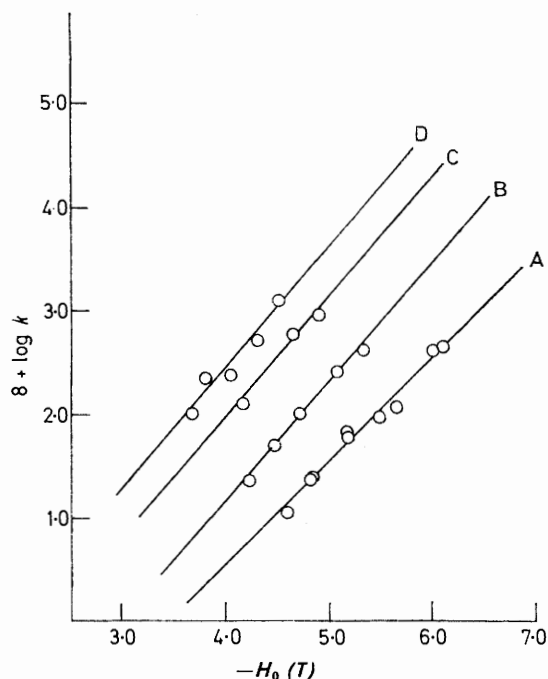


FIGURE 3   Rate–acidity profiles for tritium–protium exchange in [2-³H]naphthalene in aqueous sulphuric acid: A, 25°; B, 35°; C, 45°; D, 55°

[1-³H]- and [2-³H]-Naphthalene.—The observed rate constants are collected in Table 2, and the rate profiles shown in Figure 2 for [1-³H]naphthalene and Figure 3 for [2-³H]naphthalene.   Table 3 gives the Arrhenius parameters.

DISCUSSION

In the correlation of the rates of acid catalysed hydrogen exchange of aromatic molecules with acidity functions, a basic problem is the extent to which the rate constant for proton transfer from an acidic medium (i.e. the kinetic acidity) parallels thermodynamic acidity, as measured by the degree of protonation of a suitable basic indicator.   As Adsetts and Gold have indicated,[13] optimum correspondence should be obtained when the indicators defining the acidity function closely resemble the aromatic substrate, and when the transition state occurs late on the reaction co-ordinate so that it resembles the conjugate acid.   Such a situation does not generally occur; wide variations exist, both between the slope for equilibrium and kinetic protonation for a given

[13]   J. R. Adsetts and V. Gold, J. Chem. Soc. (B), 1969, 950.
[14]   M. T. Reagan, J. Amer. Chem. Soc., 1969, 91, 5506.
[15]   A. J. Kresge, H. J. Chen, L. E. Hakka, and J. E. Kouba, J. Amer. Chem. Soc., 1971, 93, 6174; A. J. Kresge, S. G. Mylonakis, Y. Sato, and V. P. Vitullo, ibid., p. 6181.
[16]   A. El-Anani, J. Banger, G. Bianchi, S. Clementi, C. D. Johnson, and A. R. Katritzky, J.C.S. Perkin II, 1973, 1065.
[17]   M. Liler, ' Reaction Mechanisms in Sulphuric Acid and other Strong Acid Solutions,' Academic Press, London, 1971, p. 266.

substrate [14,15] and between the slopes for the kinetic protonation of one substrate and another.[16,17]

For the compounds now studied, the graphs of log $k$ (exchange) vs. $H_0$ have slopes precisely linear.   This enables accurate extrapolation of our data to the standard state of pH 0, at 100 °C.[16]

$$\log k = -H_0 + \frac{\log f_{BH^+} \cdot f_{\ddagger}}{f_B \cdot f_{ArH}} + \text{constant} \qquad (3)$$

$$\log f = K[\text{electrolyte}] \qquad (4)$$

$$\log k + H_0 = K M_{acid} + \text{constant} \qquad (5)$$

A more adequate expression for the rate variation is (3) where $f_{ArH}$, $f_B$, $f_{BH^+}$, and $f_{\ddagger}$ refer to the substrate undergoing acid catalysed reaction, the base and conjugate acid form of a Hammett indicator, and the transition state for the reaction, respectively.   If the activity coefficient term in (3) follows the Setschenow equation (4), then (5) follows, where M is the molarity of the acid and $K$ is the combined Setschenow product for the medium effect of $f_{ArH}$, $f_B$, $f_{BH^+}$, and $f^{\ddagger}$.   Equation (5) has been successfully applied to hydrogen exchange [13] and other acid catalysed reactions.[18]   Figure 4 shows that it produces a good straight line correlation for [³H]-benzene at 25°, of slope −0·4, but in the case of the exchange in the two positions of naphthalene, the equivalent plots showed much scatter.[7]   Scatter was found for all three sets of data when $H_c$ was utilised in place of $H_0$ in this treatment.[15]

An alternative approach to the correlation of rate and medium acidity has been developed by Bunnett [19] and modified by Yates et al.[20,21]   The modified equation is (6)
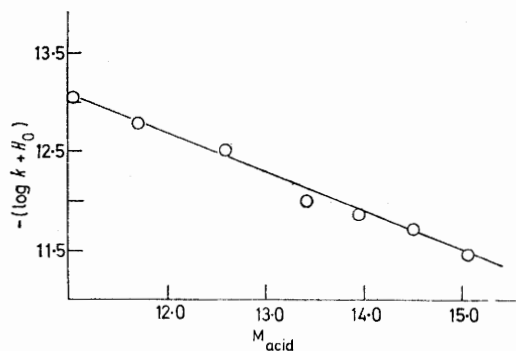


FIGURE 4   Plot of −(log $k$ + $H_0$) against M$_{acid}$ for [³H]benzene at 25°

where $H_x$ is the thermodynamic acidity function most appropriate for the substrate investigated, and $r$ is the increase in number of water molecules involved in the transition state over the number involved in solvation of the conjugate acid, in this case the Wheland intermediate.   $H_c$ Is probably the correct scale to utilize for

[18]   E. M. Arnett and G. W. Mach, J. Amer. Chem. Soc., 1966, 88, 1177.
[19]   J. F. Bunnett, J. Amer. Chem. Soc., 1961, 83, 4956, 4968, 4973, 4978.
[20]   K. Yates and J. B. Stevens, Canad. J. Chem., 1965, 43, 529; K. Yates and J. C. Riordan, ibid., p. 2328.
[21]   K. Yates and R. A. McClelland, J. Amer. Chem. Soc., 1967, 89, 2686; K. Yates, Accounts Chem. Res., 1971, 4, 136.

$H_x$, because it is derived from equilibrium carbon protonations of aromatic molecules.[14] Whether $H_0$ or $H_c$ was used in this treatment, approximately straight lines were obtained although there was again scatter,

$$\log k + H_x = r \log a_{H_2O} + \text{constant} \quad (6)$$

particularly in the case of the naphthalene compounds.[7] Melander and Myrhe [22] and Gold [23] have postulated a changeover from the $A-S_E2$ to the $A1$ mechanism at high acidities in which the rate-determining step is the rearrangement of a $\pi$ to a $\sigma$ complex, but the linearity of our plots implied the absence of such a mechanistic changeover in the acidity regions studied.

TABLE 4

Rate–acidity profile data

| | d log $k$/d $H_0$ | $-\log k$(pH = 0) |
|---|---|---|
| (i) At 25° | | |
| [³H]Benzene | 1·62 | 16·49 |
| [1-³H]Naphthalene | 1·29 | 11·91 |
| [2-³H]Naphthalene | 1·01 | 11·54 |
| (ii) At 35° | | |
| [³H]Benzene | 1·64 | 15·70 |
| [1-³H]Naphthalene | 1·19 | 10·72 |
| [2-³H]Naphthalene | 1·18 | 11·58 |
| (iii) At 45° | | |
| [³H]Benzene | 1·62 | 14·68 |
| [1-³H]Naphthalene | 1·25 | 10·32 |
| [2-³H]Naphthalene | 1·19 | 10·83 |
| (iv) At 55° | | |
| [³H]Benzene | 1·64 | 14·14 |
| [1-³H]Naphthalene | 1·21 | 9·59 |
| [2-³H]Naphthalene | 1·18 | 10·29 |

Table 3 shows the uncorrected and corrected [16] Arrhenius activation parameters for exchange in benzene and the 1- and 2-positions of naphthalene, the latter set of values apparently representing much the more systematic and rational of the two sets.

The slopes of log $k$ *vs.* $H_0$ are included in Table 4, and compared diagramatically at 55° in Figure 5. These slopes are consistently higher for benzene than for the naphthalene reactions, the slopes for the latter being the same within experimental error, with the exception of the 25° measurements. Thus, in the extrapolations to pH 0 at 25°, also recorded in Table 4, the reactivity difference between [1-³H]- and [2-³H]-naphthalene becomes reversed, although the higher temperature measurements are all in the predicted order. The

validity of the lowest temperature measurement is also brought into question by a comparison with that at 35°, where the reactivity of the 2-naphthalene position appears to fall with increasing temperature. The results at 25° for this reaction were carefully checked, and found to be experimentally reproducible; the apparent
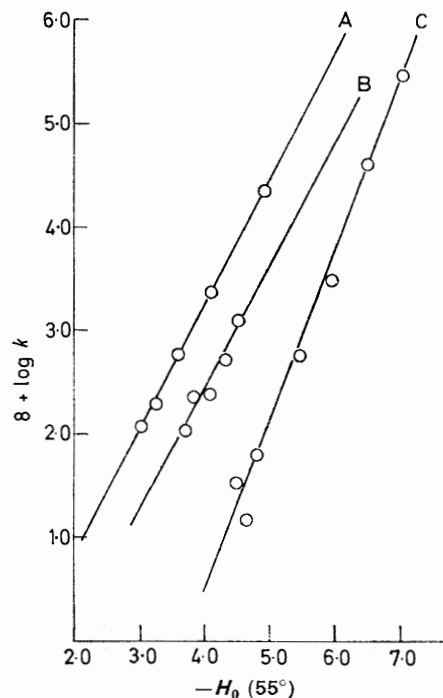


FIGURE 5 Collected rate profiles at 55°: A, 1-naphthalene; B, 2-naphthalene; C, benzene

anomaly illustrates the error which can be introduced by these lengthy extrapolations.

The data from Table 4, taken with the $\Delta H^{\ddagger}$ values from Table 3, enable calculation of the rates at pH 0 and 100°. These are as follows; [³H]benzene, log $k =$ $-11·25$; [1-³H]naphthalene, $-7·00$; [2-³H]naphthalene, $-8·37$. We intend to use these results in subsequent structure–reactivity correlations in heteroaromatic hydrogen exchange.

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[23] V. Gold, *Proc. Chem. Soc.*, 1961, 453.