Reactions in Strongly Basic Media. Part III.[1] Kinetic Acidity-dependences in Methanolic Solutions of Sodium Methoxide

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Kinetic measurements for nine reactions in concentrated solutions of sodium methoxide provide no example of a direct correlation between reaction rate and either the H_- function or stoicheiometric base concentration. No relation between kinetic acidity-dependence and mechanism is found among examples of $E2$ and $E1$cB β-eliminations, S_N2 and S_N1cB substitutions, and mechanisms of base-catalysed hydrogen exchange; reactions with the same mechanism show different acidity-dependences and reactions with different mechanisms show the same acidity-dependence. It is shown that the acidity-dependences can be expressed as free-energy relationships by plotting log k_2 against $H_- - pK_{MeOH} - \log (c_{MeO^-}/c_{MeOH})$. The plots so obtained show satisfactory linearity and their slopes may be related semiquantitatively or qualitatively to the transition-state structures for the reactions. The possibility that diffusion-controlled reactions display a unique acidity-dependence is noted.

THE role of acidity functions in the interpretation of kinetic behaviour has been much discussed.[2,3] This paper sets out to compare the effectiveness of various approaches [4-9] to the interpretation of data for some reactions occurring in strongly basic solutions of methanolic sodium methoxide, with special emphasis on the linear free-energy treatment developed by Bunnett and Olsen.[5,10] The results are presented in the following steps: (*a*) a correlation is sought between acidity-dependence and reaction mechanism; (*b*) free-energy plots are prepared and tested for linearity; and (*c*) the value of a free-energy formulation as a framework for interpreting kinetic acidity dependences is examined.

RESULTS

Rate measurements have been made for the following reactions: $E2$ eliminations of β-phenethyl halides (I; X = Br, I, or F) to form styrene [reaction (1)]; $E2$ elimination and S_N2 substitution [reactions (1) and (2) of β-phenethyl toluene-*p*-sulphonate (I; X = OTs)]; $E1$cB elimination of 9-fluorenylmethanol (II; L = H) to form dibenzofulvene [reaction (3)]; and radioactive hydrogen exchange of [9-$^3H_1$]9-fluorenylmethanol (II; L = T), of [9-$^3H_1$]-fluorene, and of 1,2,3,5-tetrafluorobenzene (III) [reaction (4)]. The paper also considers results for the S_N1cB hydrolysis of chloroform and $E2$ elimination of β-phenethyl chloride (I; X = Cl) reported previously.[2] Second-order rate constants for the reactions are listed as functions of the sodium methoxide concentration in Tables 1 and 2. The kinetics were measured by previously used standard methods which are referred to in the Experimental section.

DISCUSSION

The acidity-dependence of reaction rates and equilibria have commonly been expressed by correlation with an appropriate acidity function, and in solutions of sodium methoxide this has normally been the H_- function. In the customary notation,[2] H_- for solutions of sodium methoxide may be expressed in the equivalent forms:

$$H_- = -\log \frac{a_{H^+}f_{B^-}}{f_{BH}} = pK_a + \log \frac{c_{B^-}}{c_{BH}}$$

$$= pK_{MeOH} + \log \frac{a_{MeO^-}f_{BH}}{a_{MeOH}f_{B^-}}$$

where $K_{MeOH} = 10^{-16 \cdot 92}$ is the autoprotolysis constant of methanol [2,11] and the standard state for ionisation of the indicator acid BH is pure methanol. Measurements of H_- in methanol,[12-14] the most recent and extensive of which have been made by Terrier,[14] have used nitroaniline derivatives as indicators.

Acidity-dependence and Reaction Mechanism.—The acidity-dependence of a selection of reactions from Tables 1 and 2 are shown in Figure 1 as plots of $k_2/k_2°$ against c_{MeO^-}; k_2 is the second-order rate constant at a sodium methoxide concentration c_{MeO^-} and $k_2°$ is its value extrapolated to infinite dilution; the division by $k_2°$ brings the measurements on to a common scale.

It has long been thought that acidity-dependences may show a correlation with reaction mechanism.[4] For reactions in sodium methoxide an extreme expression of this view leads to the expectation that straight lines of unit slope should be obtained from plots of log k_1 (where $k_1 = k_2c_{MeO^-}$) against either H_- or log c_{MeO^-}. In terms of the co-ordinates of Figure 1 such behaviour

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† *Present address:* University College, Belfield, Dublin 4, Republic of Ireland.

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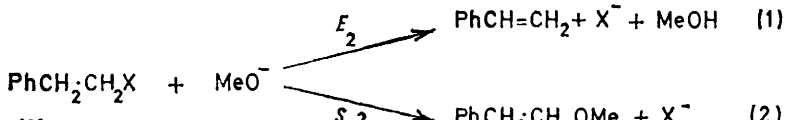
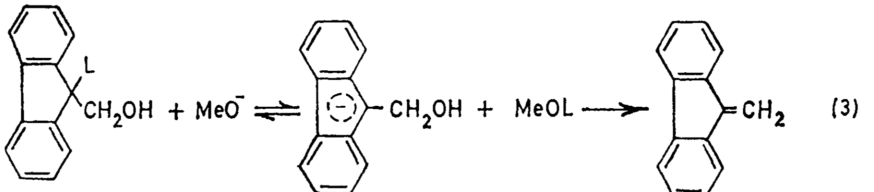
[14] F. Terrier, *Ann. Chim.* (*France*), 1969, **4**, 153.

would be represented by the dashed line $K_{\mathrm{MeOH}}/h_{-}c_{\mathrm{MeO}}$ (where h_{-} = antilog $-H_{-}$) or the abscissa of the plot respectively, and it is at once apparent that of the seven reactions shown not one conforms to the predicted pattern. Indeed the E1cB elimination of 9-fluorenylmethanol, which involves a proton transfer in a pre-equilibrium step[15] and fulfils precisely the conditions originally expected to lead to a correlation of log k_1 with H_{-}, is among reactions showing the closest approach to dependence on log $c_{\mathrm{MeO^-}}$ (line A of Figure 1).



(I)



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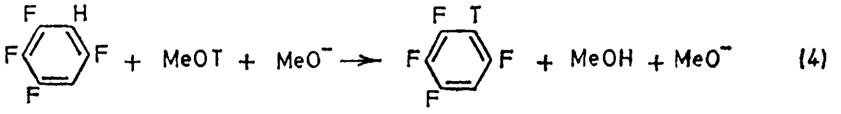

(III)

TABLE 1

The dependence of second-order rate constants[a] upon [NaOMe] for $E2$ elimination of phenethyl derivatives, $PhCH_2{\cdot}CH_2X$; temperatures ±0·05 °C

X = I [NaOMe]/M	t = 25 °C 10^5k_2 / l mol^{-1} s^{-1}	X = Br [NaOMe]/M	t = 25 °C 10^5k_2 / l mol^{-1} s^{-1}	X = OTs [NaOMe]/M	t = 25 °C 10^5k_2 / l mol^{-1} s^{-1}	X = F [NaOMe]/M	t = 89·5 °C 10^5k_2 / l mol^{-1} s^{-1}
0·31	20·5	0·49	3·45	0·65	2·03	0·52	2·06
0·92	26·5	0·94	4·07	1·27	3·40	0·96	2·58
1·57	35·9	1·58	5·95	1·74	4·85	1·44	3·65
2·17	47·9	2·25	8·35	2·30	8·41	1·89	5·36
2·86	73·5	2·84	11·8	2·92	13·8	2·40	8·08
3·45	109·0	3·47	15·7	3·29	19·4	2·70	11·2
3·92	143·0	3·93	19·4	3·82	32·0	3·30	17·7
		4·68	25·9	4·20	42·6	4·24	35·3
				4·80	71·4		

TABLE 2

The dependence of second-order rate constants[a] upon [NaOMe]; temperatures ±0·05 °C

9-Fluorenylmethanol E1cB elimination t = 25 °C		[9-$^3H_1$]-9-Fluorenylmethanol tritium exchange t = 25 °C		[9-$^3H_1$]Fluorene tritium exchange t = 25 °C		1,2,3,5-Tetrafluorobenzene exchange with MeOT t = 0 °C		β-Phenethyl toluene-p-sulphonate S_N2 substitution t = 25 °C	
[NaOMe]/M	10^5k_2 / l mol^{-1} s^{-1}	[NaOMe]/M	10^5k_2 / l mol^{-1} s^{-1}	[NaOMe]/M	10^5k_2 / l mol^{-1} s^{-1}	[NaOMe]/M	10^5k_2 / l mol^{-1} s^{-1}	[NaOMe]/M	10^5k_2 / l mol^{-1} s^{-1}
0·485	3·93	0·39	17·2	0·33	3·82	0·71	0·364	0·65	10·8
0·81	4·85	0·97	22·1	0·83	5·03	1·22	0·559	1·27	19·1
1·77	6·61	1·94	31·8	1·65	8·57	1·78	1·10	1·74	25·3
1·90	8·09	2·92	52·3	2·48	14·8	2·38	2·43	2·30	42·9
2·50	9·37	3·89	92·3	3·80	37·0	2·81	4·66	2·92	63·6
2·87	12·8	4·86	146·1			3·59	12·90	3·29	79·6
3·50	17·4					4·04	25·60	3·82	123·3
4·20	22·1							4·20	156·4
4·69	52·0							4·80	237·1

Further inspection of Figure 1 reveals no evidence of an alternative connection between acidity-dependence

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[15] R. A. More O'Ferrall and S. Slae, *J. Chem. Soc.* (*B*), 1970, 260; R. A. More O'Ferrall, *ibid.*, p. 268.

and mechanism. Despite a grouping of reactions about common correlation lines it is apparent (*a*) that reactions with different mechanisms show the same acidity-dependence and (*b*) that reactions with the same mechanism show different acidity-dependences. Thus line A of Figure 1 represents examples of base-catalysed hydrogen exchange as well as of *E*2 and *E*1cB elimination, while both lines A and B represent examples of base-catalysed hydrogen exchange, and lines A and C represent examples of the formally comparable mechanisms *E*1cB and S_N1cB. The diffusion-controlled hydrogen exchange of tetrafluorobenzene [16] (line D) may stand out mechanistically (see below), but as an isolated example it offers no basis for a wider correlation of acidity dependence with mechanism.

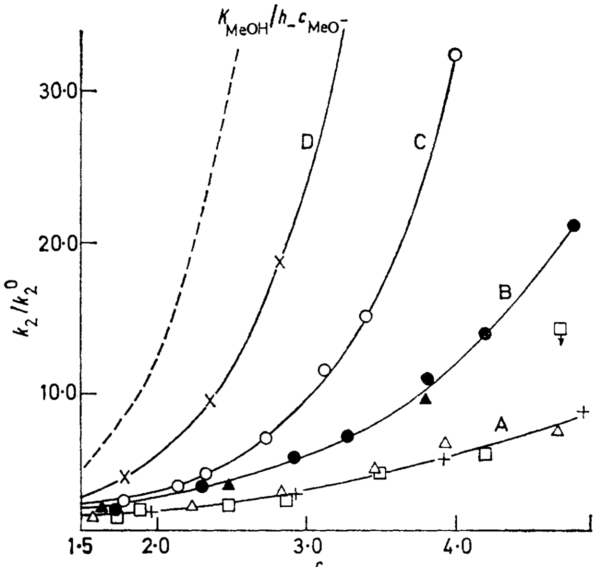

FIGURE 1 Plots of $k_2/k_2°$ against [NaOMe]: ×, tritium-exchange of tetrafluorobenzene; ○, hydrolysis of chloroform; ●, S_N2 substitution of phenethyl toluene-*p*-sulphonate; ▲, tritium-exchange of fluorene; +, tritium-exchange of 9-fluorenylmethanol; □, *E*1cB elimination of 9-fluorenylmethanol; △, *E*2 elimination of phenethyl bromide; – – – –, $K_{MeOH}/h_{-}c_{MeO^-}$ where h_{-} = antilog $-H_{-}$

Acidity-dependences as Linear Free-energy Relations.—Bunnett and Olsen have shown that by relating acidity-dependences for different reactions through plots of log k_2, for reaction rates, and of log K_c or of $-H_x$ − log c_{H^+} for equilibria, it is possible to set up correlations with the normal form of linear free-energy relationships.[5,10] This has the useful consequence that it places acidity-dependences in a well understood context and allows a range of existing chemical experience to be brought to bear in their interpretation. Thus, from the well known fact that the parameters ρ and α defined by the Hammett and Brønsted relationships vary widely between reactions of the same mechanism it follows at once that similar behaviour for kinetic acidity-dependences should cause no surprise.

In practical terms it is not expected that a free-energy relationship should always be linear but, to be useful, linearity should be the norm. In acidic solutions it has been found[5,10] that plots of log k_2 or log K_c against $-H_0$ − log c_{H^+} show as good or better linearity than the more conventional plots of log k_1 against $-H_0$ or log c_{H^+}, and, as with other free-energy relationships, correlations are improved by restricting them to structurally or mechanistically related reactions.[7,17] Formulated in the above manner, it is notable that the correlations involve only one variable: the slope of the plot. This suggests that the acidity-dependences are dominated by a single factor,[18] and many authors have pointed to the importance of solvation energies,[2,3,5,10,17,19] of the transition state for reaction rates, and of the protonated base for equilibria. Other factors, such as activity-coefficient changes of substrate or base and variations in ionic strength, can be of importance[19,20] but outside the extremes of dilute or concentrated acidic solutions they appear normally to be sufficiently small, compensating, or closely parallel to the over-riding effect not seriously to disturb the correlations. In the discussion that follows, solvation changes will be used as an approximate basis for interpreting acidity-dependences.

The advantages of Bunnett and Olsen's approach suggest that it should be tried for basic media. For methanolic sodium methoxide, acidity functions may be adapted to a linear free-energy formulation by considering the effect of a medium change from pure methanol to a solution of sodium methoxide upon $\Delta\bar{G}$, the free energy of ionisation of 1 mol of a weak acid, BH, present at infinitely low concentration. This may be expressed in terms of the activity coefficient quotient or K_c, the concentration equilibrium 'constant', for the equilibrium:

$$\mathrm{BH + MeO^- \rightleftharpoons B^- + MeOH}$$

$$i.e., \quad \frac{\delta_M \Delta\bar{G}}{2{\cdot}303RT} = \log\frac{f_{B^-} f_{MeOH}}{f_{BH} f_{MeO^-}} = \log\frac{K}{K_c}$$

where δ_M denotes the medium change in question.[18] If a linear free-energy relationship between medium effects on different equilibria exists, the following relations will hold:

$$\delta_M \Delta\bar{G} \propto \delta_M \Delta\bar{G}' \text{ and } \delta_M \log K_c \propto \delta_M \log K_c'$$

These differ from the earlier formulations of Leffler and Grunwald[18] only in avoiding the inconsistency of separating K_c and c_{MeO^-} (or, for acid solutions, c_{H^+}).

Equilibria for which values of $\delta_M\Delta\bar{G}$ are identical

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[16] A. Streitwieser, jun., J. A. Hudson, and F. Mares, *J. Amer. Chem. Soc.*, 1968, **90**, 648.

[17] A. J. Kresge, H. J. Chen, L. E. Hakka, and J. E. Kouba, *J. Amer. Chem. Soc.*, 1971, **93**, 6174.

[18] J. Leffler and E. Grunwald, 'Rates and Equilibria of Organic Reactions,' Wiley, New York, 1963.

[19] R. H. Boyd in 'Solute-Solvent Interactions,' eds. J. F. Coetzee and C. D. Ritchie, Dekker, New York, 1969.

[20] E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, 1966, **88**, 1177.

may be used to define an acidity function, in terms of which $\delta_M\Delta\tilde{G}$ may also be expressed. For the family of nitroaniline derivatives on which H_- is based:

$$\frac{\delta_M\Delta\tilde{G}}{2{\cdot}303RT} = H_- - \mathrm{p}K_{\mathrm{MeOH}} - \log\frac{c_{\mathrm{MeO^-}}}{c_{\mathrm{MeOH}}}$$

If the H_- equilibria are taken as a reference, the existence and scope of linear free-energy relationships can be tested by plotting log K_c for an isolated equilibrium,

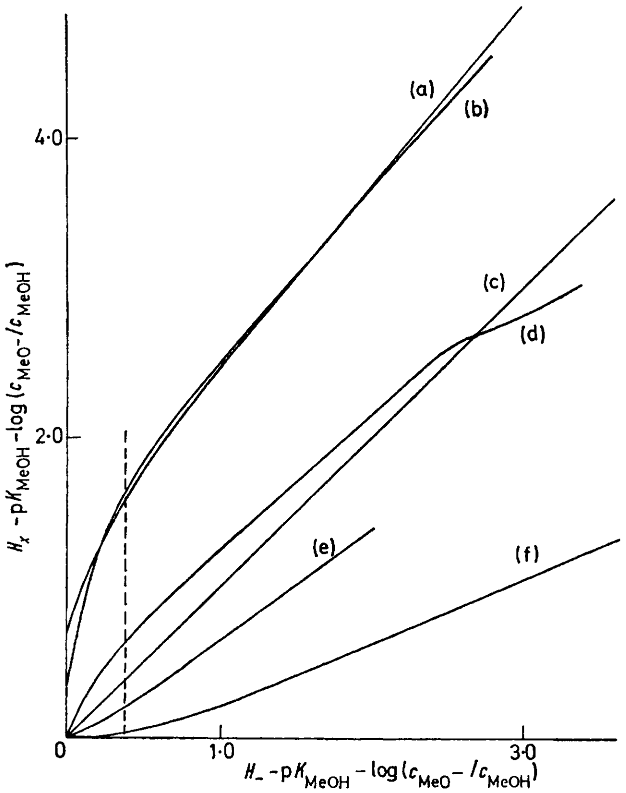

FIGURE 2 Plots of $H_x - \mathrm{p}K_{\mathrm{MeOH}} - \log c_{\mathrm{MeO^-}}/c_{\mathrm{MeOH}}$ against $H_- - \mathrm{p}K_{\mathrm{MeOH}} - \log c_{\mathrm{MeO^-}}/c_{\mathrm{MeOH}}$ for nitroanilines (ref. 14): (a) $H_x = J_- - \log a_{\mathrm{MeOH}}$ (ref. 14); (b) $H_x = H_=$ for the second ionisation of aminobenzene carboxylic acids (ref. 21); (c) $H_x = H_-$; (d) $H_x = H_{\mathrm{R^-}} + \log a_{\mathrm{MeOH}}$ (ref. 22); (e) $H_x = H_-$ for 2,6-di-t-butylphenols (ref. 23); (f) $H_x = H_-$ for indoles (ref. 24). The broken line corresponds to $c_{\mathrm{MeO^-}} = 1\textsc{m}$

$H_x - \mathrm{p}K_{\mathrm{MeOH}} - \log(c_{\mathrm{MeO^-}}/c_{\mathrm{MeOH}})$ for an acidity function, or (by a small extension) log k_2 for a reaction rate, against $H_- - \mathrm{p}K_{\mathrm{MeOH}} - \log(c_{\mathrm{MeO^-}}/c_{\mathrm{MeOH}})$.

Such plots for acidity functions measured in sodium methoxide are shown in Figure 2, with the functions listed in the caption.[21-24] Values of J_- and $H_{\mathrm{R^-}}$, shown as lines (a) and (d), which are based on the addition of methoxide ion to nitrobenzenes [14] and α-cyanostilbenes [22] respectively, are made formally compatible with functions based on the ionisation of Brønsted acids by addition of the activity of methanol.[25] A $J_=$ function measured by Rochester [26] for solutions of sodium methoxide greater than 1M and reported to parallel J_- is not shown. The value of c_{MeOH} was taken as the molar concentration of methanol divided by the molar concentration in the pure solvent (*cf.* ref. 27) and was calculated from the density data of Freeguard *et al.*[28] Its variation is so small that it could sensibly have been neglected.

In Figure 2 the plots are not linear. However, closer inspection reveals that the main curvature is confined to dilute solutions, where specific ionic effects are expected to be important (indeed more so in methanol than in water), and at higher base concentrations, above *ca.* 1M-sodium methoxide, a reasonable approach to linearity is achieved. The behaviour of Stewart and Kroeger's $H_{\mathrm{R^-}}$ function [22] represented by line (d) is exceptional, but this may be due to the difficulty of determining extinction coefficients for indicators ionising in concentrated solutions; for all other functions extending to high base concentrations an approximation devised by Terrier and Schaal [29] was used to extrapolate exteme acidity values. The broad range of reaction types included being considered, the results do not discourage the use of a free-energy approach outside the dilute range, and the slopes of the plots appear to correlate qualitatively with the expected solvation requirements of the indicator anions.

Figure 2 may be compared with Figure 3 in which plots of log k_2 against $H_- - \mathrm{p}K_{\mathrm{MeOH}} - \log c_{\mathrm{MeO^-}}/c_{\mathrm{MeOH}}$ for the reactions of Tables 1 and 2 are shown. Although deviations in dilute solutions are again evident a very good overall linearity is observed, as indicated by Table 3 in which the slopes and the standard deviations of experimental points from their regression lines (σ_y) are given. The median value of σ_y for the 11 reactions of Table 3 together with seven other reactions for which data have been reported [30,31] is 0·035. This compares with median values of $\sigma_y = 0{\cdot}08$ for the corresponding plots of log k_1 against H_- and $\sigma_y = 0{\cdot}03$ found by Bunnett and Olsen from plots of log k_2 against $-H_0 - \log c_{\mathrm{H^+}}$ for 160 acid-catalysed reactions.[5] Again in view of their wide scope the correlations appear quite good enough to justify use as a basis for interpreting kinetic acidity-dependences.

Kinetic Acidity-dependences and Transition-state Structure; Base-catalysed Hydrogen Exchange.—An important application of linear free-energy relationships has been the elucidation of transition-state structure, in at least a

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[21] F. Terrier, *Bull. Soc. chim. France*, 1969, 1894.

[22] D. J. Kroeger and R. Stewart, *Canad. J. Chem.*, 1967, **45**, 2163.

[23] C. H. Rochester, *J. Chem. Soc.* (*B*), 1966, 121.

[24] F. Terrier, F. Millot, and R. Schaal, *Bull. Soc. chim. France*, 1969, 3002.

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[26] C. H. Rochester, *J. Chem. Soc.*, 1965, 2404.

[27] K. N. Bascombe and R. P. Bell, *Discuss. Faraday Soc.*, 1957, **24**, 158.

[28] G. F. Freeguard, R. B. Moodie, and D. J. G. Smith, *J. Appl. Chem.*, 1965, **15**, 179.

[29] F. Terrier and R. Schaal, *Compt. rend.*, 1965, **260**, 5567.

[30] F. Terrier and R. Schaal, *Compt. rend.*, 1967, **264**, 465; F. Terrier, *ibid.*, 1965, **261**, 1001; R. Schaal and J-C. Latour, *Bull. Soc. chim. France*, 1964, 2177; R. Schaal and F. Peuré, *ibid.*, 1963, 2638.

[31] D. V. Banthorpe, S. Doonan, R. A. More O'Ferrall, and J. H. Ridd, unpublished results.

qualitative sense, through comparisons of kinetic and equilibrium behaviour.[18] The procedure has become familiar for reactions subject to general acid- or base-catalysis where the exponents α and β for the Brønsted relation have been interpreted as measures of the extent of proton transfer in the transition state.[18] Recently it has been shown that for aromatic hydrogen exchange in strongly acidic solutions a parameter ' α ' analogous to that of the Brønsted relation can be obtained from a comparison of kinetic and equilibrium acidity-dependences.[6] It follows that a suitable comparison between rates of base-catalysed hydrogen exchange and the equilibrium ionisations of weak acids, as expressed in the H_- function, should yield a comparable parameter ' β ' appropriate to basic media.

TABLE 3

Dependence of log k_2 upon $H_- - \mathrm{p}K_{\mathrm{MeOH}} - \log(c_{\mathrm{MeO^-}}/c_{\mathrm{MeOH}})$

Substrate	Reaction mechanism	t/°C	$10^5 k_2^{\circ}$ [a] / l mol^{-1} s^{-1}	Slope	σ_y
β-Phenethyl iodide	$E2$	25	20·2	0·32	0·013
β-Phenethyl bromide	$E2$	25	3·50	0·27	0·039
β-Phenethyl toluene-*p*-sulphonate	$E2$	25	1·88	0·47	0·034
β-Phenethyl chloride	$E2$	59·7	3·11	0·26	0·008
β-Phenethyl fluoride	$E2$	89·5	1·89	0·44	0·033
9-Fluorenylmethanol	E1cB	25	3·66	0·31	0·066
9-Fluorenylmethanol	T exch.	25	16·8	0·27	0·014
[9-^{3}H$_1$]Fluorene	T exch.	25	3·86	0·39	0·035
Tetrafluorobenzene	T exch.	0	0·250	0·72	0·013
β-Phenethyl toluene-*p*-sulphonate	S_N2	25	11·2	0·40	0·050
Chloroform	S_N1cB	45·1	1·93	0·56	0·023

[a] k_2° is the second-order rate constant extrapolated to infinite dilution, *i.e.*, $H_- - \mathrm{p}K_{\mathrm{MeOH}} - \log(c_{\mathrm{MeO^-}}/c_{\mathrm{MeOH}}) = 0$.

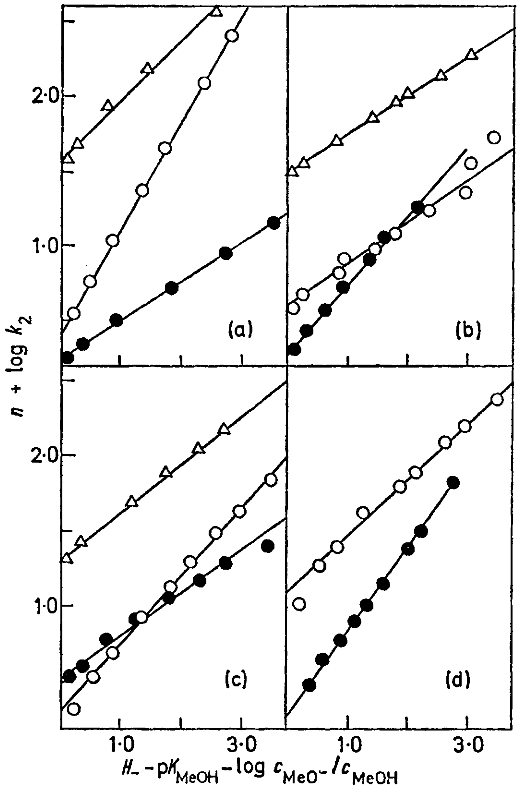

FIGURE 3 Plots of $\log k_2 + n$ against $H_- - \mathrm{p}K_{\mathrm{MeOH}} - \log c_{\mathrm{MeO^-}}/c_{\mathrm{MeOH}}$. (a) Tritium exchange: △, [9-^{3}H$_1$]fluorene, $n = 6$; ○, 1,2,3,5-tetrafluorobenzene, $n = 6$; ●, [9-^{3}H$_1$]-fluorenylmethanol, $n = 4$; (b) β-elimination: △, 9-fluorenylmethanol, $n = 6$; ●, phenethyl fluoride, $n = 5$; ○, phenethyl chloride, $n = 5$; (c) β-elimination; △, phenethyl iodide, $n = 5$; ○, phenethyl toluene-*p*-sulphonate, $n = 5$; ●, phenethyl bromide, $n = 5$; (d) substitution: ○, phenethyl toluene-*p*-sulphonate (S_N2), $n = 5$; ●, chloroform (S_N1cB), $n = 5$

How such a parameter can be related to transition-state structure can best be seen by writing an acid–base equilibrium in three stages, with the reaction in each direction proceeding *via* an encounter complex formed in a pre-equilibrium step; *i.e.*,

$$\mathrm{BH} + \mathrm{MeO^-} \rightleftharpoons \mathrm{BH{,}MeO^-} \longrightarrow [\mathrm{T.S}]^{\ddagger} \longrightarrow \mathrm{B^-{,}MeOH} \rightleftharpoons \mathrm{B^-} + \mathrm{MeOH}$$

If it is assumed that the encounter complexes represent limiting structures for the transition state and that activity coefficients for species in the complexes do not differ from their values in the bulk solution, limiting kinetic acidity-dependences can be derived by substitution of appropriate values for the activity coefficient of the transition state, $f_{\ddagger}$, into the familiar Brønsted rate expression:

$$k_2 = \left(\frac{f_{\mathrm{BH}} f_{\mathrm{MeO^-}}}{f_{\ddagger}}\right) k_2^{\circ}$$

Thus for a reactant-like transition state $f_{\ddagger} = f_{\mathrm{MeO^-}} f_{\mathrm{BH}}$, so that:

$$k_2 = \left(\frac{f_{\mathrm{BH}} f_{\mathrm{MeO^-}}}{f_{\mathrm{BH}} f_{\mathrm{MeO^-}}}\right) k_2^{\circ} = k_2^{\circ}$$

and $\log k_2$ = constant, while for a product-like transition state, $f_{\ddagger} = f_{\mathrm{B^-}} f_{\mathrm{MeOH}}$

$$k_2 = \left(\frac{f_{\mathrm{BH}} f_{\mathrm{MeO^-}}}{f_{\mathrm{B^-}} f_{\mathrm{MeOH}}}\right) k_2^{\circ}$$

and $\log k_2 = H_- + \log K_{\mathrm{MeOH}} - \log \dfrac{c_{\mathrm{MeO^-}}}{c_{\mathrm{MeOH}}} + \log k_2^{\circ}$

Formulation of the general case in relation to these limits leads to the following natural definition of β:

$$f_{\ddagger} = (f_{\mathrm{MeO^-}} f_{\mathrm{BH}})^{1-\beta} (f_{\mathrm{MeOH}} f_{\mathrm{B^-}})^{\beta}$$

Clearly β has the limits 0 and 1 and provided that the kinetic and equilibrium measurements apply to the same or similar reactions it measures the degree to which the transition state resembles reactants or products. Substitution of $f_{\ddagger}$ in the Brønsted expression gives:

$$\log k_2 = \beta[H_- - \mathrm{p}K_{\mathrm{MeOH}} - \log(c_{\mathrm{MeO^-}}/c_{\mathrm{MeOH}})] + \log k_2^{\circ}$$

so that β can be obtained from the slope of plots of $\log k_2$ against $H_- - \mathrm{p}K_{\mathrm{MeOH}} - \log(c_{\mathrm{MeO^-}}/c_{\mathrm{MeOH}})$. (From the same plots values of k_2°, the second-order rate constant at infinite dilution, can be obtained from the intercepts.)

Measurements of β for the three hydrogen-exchange reactions listed in Table **3** range from 0·27 to 0·72 and thus fall within the expected limits. For exchange of tetrafluorobenzene, however, it is believed[16] that the rate-determining step involves separation of the anion–solvent complex by diffusion and a value of $\beta = 1{\cdot}0$ might have been expected. It seems unlikely that the lower value, $\beta = 0{\cdot}72$, could be due to the difference in substrates used in the rate and equilibrium measurements, because the intuitive expectation of a lower solvation energy for the tetrafluorophenyl carbanion than for the nitroaniline anions formed from ionisation of H_- indicators suggests a difference in the opposite direction; it might be due to the inability of methanol bound in the diffusion complex to play a normal solvation role, leading to a difference in activity coefficient behaviour from that of methanol in the bulk solvent. The point is of interest in that a diffusion-controlled reaction is subject to no variation in transition-state structure in the normal sense, and it seemed possible that, provided the appropriate acidity function was used, its acidity-dependence might be genuinely diagnostic of mechanism. The few results at present available[32] are not inconsistent with this view.

As judged by measurements of hydrogen isotope effects[15] and the positive values of $\Delta\bar{b}^{\circ}$, values of $\beta = 0{\cdot}27$ and 0·39 for ionisation of fluorene and 9-fluorenylmethanol are again low. They are, on the other hand, within range of the Brønsted exponents of 0·4—0·5 derived from comparisons of kinetic and equilibrium acidities of 2- and 9-substituted fluorenes.[33]

Elimination Reactions.—In cases where direct comparisons of rates and equilibria are not possible acidity-dependences may still be related to transition-state structure, although in a more qualitative manner. Limits to the acidity-dependence are set by the acidity functions governing the equilibria between the reactants proper and the immediate reactants and products of the rate-determining step. For *E*2 eliminations [reaction (1)] the first and only step of the reaction is rate-determining and in the reactant-like limit of the transition state log k_2 should, as for hydrogen exchange, approach independence of base concentration. In the product-like limit the acidity dependence will be controlled by the equilibrium:

$$RCH_2{\cdot}CH_2X + MeO^- \rightleftharpoons RCH{=}CH_2 + MeOH + X^-$$

and can be expected to be particularly sensitive to the solvation energy of X^-, the leaving group anion. This means that the interpretation of acidity correlations for β-eliminations will be complicated by their dependence not only upon the structure of the transition state but also upon the nature of the leaving group.

A further complication arises in that transition states for *E*2 eliminations do not fall squarely in structure between reactants and products, but can involve varying degrees of imbalance of C–H and C–X bond-breaking[34] which also can influence the acidity-dependence. In Figure 3 and Table 3 acidity-dependences for *E*2 eliminations of phenethyl toluene-*p*-sulphonate and four phenethyl halides are shown. The slopes of the plots cover a reasonable range, from 0·25 to 0·46,* but in the event it is perhaps not surprising that no detailed interpretation of their relative magnitudes (or indeed of their variation between different solvent systems[35]) can be given. The modest acidity-dependences observed for reactions with transition states possessing important carbanion character,[34] such as β-phenethyl chloride, do suggest, however, that in the transition state the effect of solvation of the leaving group may largely compensate the partial neutralisation (with consequent desolvation) of the methoxide ion. In this context the small slope of 0·31 for *E*1cB elimination of 9-fluorenylmethanol, for which proton transfer is completed before the rate-determining step,[15] may reasonably be ascribed to the high solvation energy of the incipient hydroxide ion present in the transition state.

Aliphatic Substitutions.—As for β-eliminations the acidity-dependence of substitution reactions is probably largely determined by the degree of desolvation of the methoxide ion occurring in the transition state, and the extent to which this is balanced by solvation of the leaving group. As seen in Figure 3 $S_{\mathrm{N}}2$ substitution of β-phenethyl toluene-*p*-sulphonate shows an acidity-dependence similar to that for *E*2 elimination of the same substrate.

The S_{N}1cB hydrolysis of chloroform is hardly a typical substitution. Here, as in the *E*1cB elimination of 9-fluorenylmethanol, a carbanion is formed before formation of the transition state. The weaker solvation of the chloride leaving group than hydroxide is probably responsible for the steeper acidity-dependence in this case.

Addition Reactions.—For additions of the methoxide ion semiquantitative kinetic–equilibrium correlations analogous to those for hydrogen exchange are again possible provided that the acidity function used is J_- or H_{R^-} rather than H_-. No such reaction was studied here but Stewart and Kroeger[8] have compared kinetic and equilibrium acidity-dependences for the addition of hydroxide ion to cyanostilbenes in dimethyl sulphoxide–water mixtures and have defined a parameter γ similar to the β used above and α defined by Kresge *et al.*[6]

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* For trimethyl-β-phenethylammonium bromide[31] the slope for reaction at 45 °C is 0·53.

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EXPERIMENTAL

Materials.—Commercial samples of β-phenethyl bromide and iodide were distilled; β-phenethyl toluene-*p*-sulphonate was prepared from the corresponding alcohol in the usual way,[36] and β-phenethyl fluoride was obtained from the toluene-*p*-sulphonate by use of the procedure of De Puy and Bishop.[37] 1,2,3,5-Tetrafluorobenzene was obtained from the Pierce Chemical Co. and separated from a 5% impurity by preparative g.l.c. The preparation of 9-fluorenylmethanol and its 9-tritiated derivative and also of [9-$^3H_1$]fluorene have been described.[15] Tritiated methanol was prepared by adding a small amount of tritiated water to MeOH and drying (including distillation from magnesium methoxide). The preparation of sodium methoxide has been described.[13] The identity and purity of materials were checked by n.m.r., g.l.c., and m.p. or b.p. as appropriate.

Kinetics.—The kinetics of hydrogen exchange were measured by liquid scintillation counting,[15] and of elimination by following the increase in u.v. absorption due to formation of styrene [1] or dibenzofulvene [15] on Cary 14 spectrophotometers. The rate constant for substitution of β-phenethyl toluene-*p*-sulphonate was obtained by combining the rate constant for *E*2 elimination with a product analysis. The concentration of styrene in the products was determined spectrophotometrically and it was assumed that the only other product was the substitution product methyl β-phenethyl ether; this was confirmed by g.l.c. Rate constants measured at temperatures other than 25 °C were corrected for the thermal expansion of methanol.

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