968. *Reactions in Strongly Basic Media. Part I. The H_- function in Methanol containing Sodium Methoxide.*

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Equilibrium constants are reported for the ionisation of a number of acidic indicators in methanol containing sodium methoxide, and details are given of the spectra of the conjugate bases. These spectra are largely independent of the solvent, except for *p*-nitrobenzyl cyanide where the ionisation in methanolic sodium methoxide appears to give a different product from that in aqueous alkali. The depence of the ionisation of the different indicators on the concentration of sodium methoxide is described in terms of an H_- acidity function defined with respect to a standard state in methanol. This function deviates markedly from ideal behaviour.

The work described in this and the following paper had its origin in an attempt to use acidity functions as a mechanistic criterion in the study of base catalysis.[1,2] When this work started, acidity functions had already been measured with respect to a number of basic media, including aqueous hydrazine [3] and aqueous ethylene diamine; [4] some indirect measurements of the H_- function were also available for aqueous solutions of the alkali hydroxides.[5] However, for various reasons these media are unsuitable for the mechanistic application of the H_- function: the low solubility of most substrates precludes the use of aqueous alkali, and the presence of at least two strong bases in the other media cited introduces mechanistic complications. A solution of sodium methoxide in methanol should be one of the simplest systems combining adequate solvent properties with a high dielectric constant and the presence of a single strong base. This paper is therefore concerned with the H_- function in this medium. Other workers have recently reported [6] the values of the H_- function in the related system sodium methoxide–methanol–dimethyl sulphoxide, with a constant concentration of sodium methoxide.

Determination of the Equilibrium Constants.—The indicators used were substituted anilines and diphenylamines containing at least one nitro-group. In methanolic sodium methoxide, these compounds take part in a reversible equilibrium leading to a highly coloured product; at the higher concentrations of methoxide ion, this equilibrium is followed by an irreversible decomposition. In other basic media, this initial equilibrium is usually taken to involve proton loss from the indicator and to check this interpretation we have studied the spectra of the ionised form of the indicator in several media including water and other alcohols. With the exception of the indicator 4-nitrobenzyl cyanide (discussed separately below), the spectra in different media are very similar; this is illustrated by the figures below for the main absorption maxima of ionised 4-nitrodiphenylamine. This similarity is consistent with the small medium effects expected on the spectrum of the conjugate base.

Medium (ROH)	MeOH	EtOH	Bu^{t}OH	H_2O
$[OR^-]$ (M)	3	2	0·1	2
$\lambda_{max.}$ (Å)	4800	4850	4750	4730—4900 *

* In tetramethylammonium hydroxide. This value is a little difficult to determine because of the low percentage of ionisation.

The complete ionisation of the indicator in solutions of sodium methoxide is complicated by the decomposition referred to above. For indicators with two nitro-groups, complete

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[1] Ridd, *Chem. and Ind.*, 1957, 1268.

[2] Allison, Bamford, and Ridd, *Chem. and Ind.*, 1958, 718.

[3] Deno, *J. Amer. Chem. Soc.*, 1952, **74**, 2039.

[4] Schaal, *J. Chim. phys.*, 1955, **52**, 784, 796.

[5] Schwarzenbach and Sulzberger, *Helv. Chim. Acta*, 1944, **27**, 348.

[6] Stewart, O'Donnell, Cram, and Rickborn, *Tetrahedron*, 1962, **18**, 917.

ionisation was attained without significant decomposition by using solutions of sodium isopropoxide in isopropyl alcohol; for indicators with one nitro-group, solutions of sodium t-butoxide in t-butyl alcohol were used instead. The corresponding extinction coefficients at the absorption maxima were then used to calculate the ionisation ratio ($R = c_{S^-}/c_{SH}$) for the indicator in methanol. Since medium effects on the position of the absorption maximum are small, this is probably also true for medium effects on the maximum extinction coefficients. The consistency of the results given below supports this assumption.

The dissociation constants of the more acidic indicators were calculated from the indicator ratio by extrapolation to infinitely dilute solutions. For the ionisation of a neutral base (SH), the equilibrium constant

$$K_B = a_{SH}a_{OMe^-}/a_{S^-} \,.\, a_{MeOH}$$

is related to the indicator ratio (R) and to the concentration of sodium methoxide by equation (1):

$$\mathrm{p}K_b = \log R - \log c_{OMe^-} + \log \frac{f_{S^-} \,.\, a_{MeOH}}{f_{SH}f_{OMe^-}} \,. \qquad (1)$$

When the activity of pure methanol is taken as unity, the last term of equation (1) becomes equal to zero in infinitely dilute solution: a plot of ($\log R - \log c_{OMe^-}$) against c_{OMe^-} therefore leads to the value of pK_b by extrapolation. As shown in Fig. 1, this extrapolation is facilitated by the linearity of the graph at low concentrations of methoxide ion.

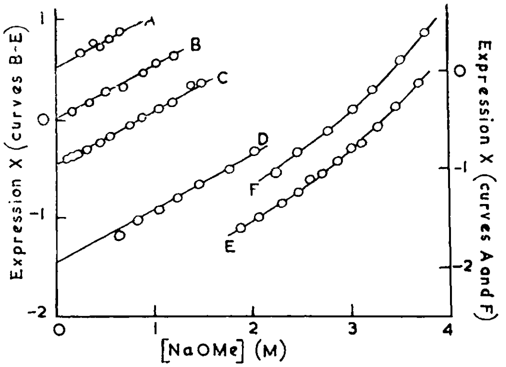

FIG. 1. Plots to determine the values of pK_b for the ionisation of the indicators. The lettering corresponds to that in Table 1. Expression X = $\log R - \log$ [NaOMe].

At a given concentration of methoxide ion, the slopes of the graphs for different indicators in Fig. 1 are approximately equal; the pK_b values of the less acidic indicators can therefore be obtained by the usual method of stepwise comparison. The results are collected in Table 1, together with the corresponding pK_a values obtained by taking the ionic product of methanol[7] (K_{MeOH}) to be $10^{-16\cdot7}$ and the pK_b values[8] for the same equilibria in water.

The Ionisation of 4-*Nitrobenzyl Cyanide*.—The reactions of this indicator have been studied as described above; the absorption spectrum of the ionised form (Fig. 2) was found to be the same in several alcoholic media and the plot to obtain the pK_b in methanol is included in Fig. 1. The indicator was also studied in solution in aqueous sodium hydroxide and could be completely ionised in this medium. The pK_b obtained is similar to that reported by earlier workers[3,4,9] and the value of ΔpK_b (Table 1) accords with those of the other indicators. However, as shown in Fig. 2, the spectrum of the ionised form in aqueous alkali is quite different from that in alcoholic media, both in the position and in

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[7] Bell, " The Proton in Chemistry," Methuen, London, 1959, Chap. 4.

[8] Stewart and O'Donnell, *J. Amer. Chem. Soc.*, 1962, **84**, 493.

[9] Stearns and Wheland, *J. Amer. Chem. Soc.*, 1947, **69**, 2025.

TABLE 1.

Acid–base constants in methanol and water.

Indicator	pK_a	pK_b MeOH	pK_b H_2O	ΔpK_b ($pK_b^{MeOH} - pK_b^{H_2O}$)
(A) 4-Nitrobenzyl cyanide	16·67	0·03	(0·65) *	(−0·62) *
(B) 6-Bromo-2,4-dinitroaniline	16·72	−0·02	+0·37	−0·39
(C) 2,4-Dinitrophenylamine	17·17	−0·47	+0·16	−0·63
(D) 2,4-Dinitroaniline	18·18	−1·48	−1·00	−0·48
(E) 4-Nitrodiphenylamine	18·83	−2·13	−1·90	−0·23
(F) 2,4-Dichloro-6-nitroaniline	18·93	−2·23	—	—
			Mean	−0·43

* Not used because the pK_b's in water and methanol appear to refer to different equilibria; see text.

the number of the absorption maxima. The differences are sufficient to show that different products are formed in the two media.

The dependence of the two equilibria on the concentration of lyate ion shows that both reactions involve one lyate ion. A recent kinetic study[10] at low temperatures suggests that the reaction in alcoholic solvents involves proton loss. The reaction in aqueous media has generally been taken to involve proton loss[3,4,9] but, if so, the conjugate base of 4-nitrobenzyl cyanide must be capable of existing in two isomeric forms depending on the medium. It is also possible that the reaction in aqueous solution involves the addition of a hydroxide ion.

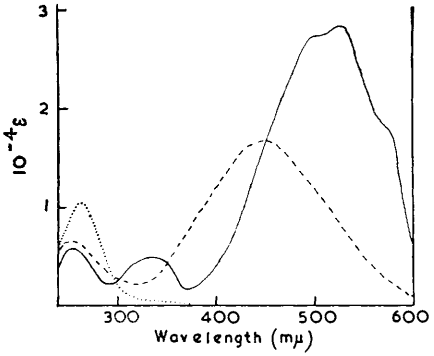

FIG. 2. The absorption spectrum of 4-nitrobenzyl cyanide as the neutral molecule in methanol (· · ·), as the ionised form in aqueous sodium hydroxide (– – –), and as the ionised form in methanolic sodium methoxide (——).

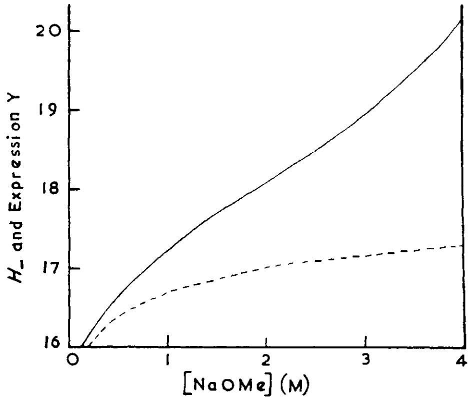

FIG. 3. The deviation of the H_- function (——) from the corresponding expression (Y = log [NaOMe] + pK_{MeOH}) for ideal behaviour (– – –). The values of the H_- function are based on pK_a's in methanol (see text).

A recent communication[8] refers to the ionisation of 4-nitrobenzyl cyanide as "anomalous," and two spectra similar in form to those in Fig. 2 have been reported[4] for the ionisation of 4-nitrobenzyl cyanide in different concentrations of aqueous ethylene diamine; this change in the spectrum is ascribed[4] to the successive loss of one and two protons from the indicator. Our results make it more probable that the change of spectrum is a consequence of the change of solvent as ethylenediamine replaces water. We have observed a similar effect on the spectrum in media of much lower basicity by the addition of tetramethylammonium compounds to a solution of the indicator in aqueous sodium hydroxide.

[10] Caldin and Harbron, *J.*, 1962, 2314.

The H_- Function in Methanol.—The fact that the slopes of the plots in Fig. 1 depend on the concentration of methoxide ion but not on the nature of the indicator suggests that the validity of the H_- function in these solutions should be similar to that of the H_0 function in aqueous media. However, the differences in the ΔpK_b values in Table 1 show that the basicity of solutions of sodium methoxide in methanol cannot be related to the basicity of aqueous media without reference to the indicator concerned. This does not prevent the calculation of the H_- function in methanol, providing the function is defined with respect to methanol as the standard state and therefore calculated from the pK_a's appropriate to methanol.

The H_- function has been calculated in this way from equation (2) by using the pK_a's listed in Table 1.

$$H_- = pK_a + \log R. \qquad (2)$$

The variation of H_- with the concentration of methoxide ion is shown in Fig. 3 and values of this function at selected molarities of sodium methoxide are listed in Table 2. The best approximation to the corresponding values on the " aqueous " scale are obtained by subtracting 3·13 from the values in Table 2; this allows for the mean difference in the pK_a's in the two media.

TABLE 2.

Dependence of the H_- function on the concentration (M) of sodium methoxide. The corresponding standard state is defined with respect to methanol as solvent.

[NaOMe]	H_-	[NaOMe]	H_-	[NaOMe]	H_-	[NaOMe]	H_-
0·25	16·26	1·25	17·49	2·25	18·30	3·25	19·24
0·50	16·66	1·50	17·71	2·50	18·52	3·50	19·53
0·75	16·97	1·75	17·90	2·75	18·74	3·75	19·85
1·00	17·23	2·00	18·10	3·00	18·98	4·00	20·20 *

* Based on a slight extrapolation.

The relationship of the H_- function to the concentration of sodium methoxide is given by equation (3):

$$H_- = \log c_{\mathrm{OMe^-}} + pK_{\mathrm{MeOH}} + \log \frac{f_{\mathrm{SH}} f_{\mathrm{OMe^-}}}{f_{\mathrm{S^-}} \cdot a_{\mathrm{MeOH}}}. \qquad (3)$$

This is derived from equations (1) and (2) and the relationship $pK_a + pK_b = pK_{\mathrm{MeOH}}$. A plot of ($\log c_{\mathrm{OMe^-}} + pK_{\mathrm{MeOH}}$) is included in Fig. 3; the difference between the two functions indicates the importance of the final term in equation (3). Since this term smoothly approaches zero as the concentration of methoxide ion is decreased [cf. Fig. 1 and equation (1)], the H_- function becomes identical with ($\log c_{\mathrm{OMe^-}} + pK_{\mathrm{MeOH}}$) at very low concentrations of methoxide ion.* However, at concentrations of methoxide ion above M, the deviation of the H_- function from ideality is very marked and considerably exceeds the analogous deviation in aqueous alkali.[12] The results in methanol accord with, and extend, the work reported in preliminary communications [1,13] involving fewer indicators and a narrower range of basicity.

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* This result does not imply that the H_- function is simply related to $-\log c_{\mathrm{H^+}}$ at low concentrations of methoxide ion. The H_- function and $\log c_{\mathrm{H^+}}$ are related by the equation:

$$H_- = -\log c_{\mathrm{H^+}} - \log \frac{f_{\mathrm{H^+}} \cdot f_{\mathrm{S^-}}}{f_{\mathrm{SH}}}.$$

In this equation [unlike equation (3)], the last term is very sensitive to the composition of the medium at low ionic strengths. This point has been discussed recently by Fuller [11] with respect to the H_- function in acidic media. From the definition of the acidity functions, the relation between H_0 and $-\log c_{\mathrm{H^+}}$ is paralleled by that between H_- and ($\log c_{\mathrm{OR^-}} + pK_{\mathrm{ROH}}$).

[11] Fuller, Ph.D. Thesis, London, 1961.

[12] Edward and Wang, *Canad. J. Chem.*, 1962, **40**, 399.

[13] Lambert and Schaal, *Compt. rend.*, 1962, **255**, 2256.

The reason for these deviations is of considerable interest because, as outlined in the following paper, they provide a potential mechanistic criterion. The deviation in aqueous solution has been attributed in part to the greater solvation of the hydroxide ion over that of the indicator base;[12] the ionisation of the indicator, therefore, sets free a number of solvent molecules as shown in equation (4):

$$\mathrm{SH} + \mathrm{OR}^- \rightleftharpoons \mathrm{S}^- + (n + 1)\mathrm{ROH} \qquad (4)$$

In this equation, the symbols SH, OR^-, and S^- denote the solvated species, so that the excess solvation of $\mathrm{SH} + \mathrm{OR}^-$ over S^- is equivalent to n solvent molecules. On one simple approximation,[14] the classical equilibrium constant, $K_c = c_{\mathrm{SH}}c_{\mathrm{OR}^-}/c_{\mathrm{S}^-}$, should then be proportional to the concentration of free solvent molecules raised to the power $(n + 1)$.

The extent to which these arguments can be applied to solutions in methanol is uncertain, but this approach provides a possible explanation of the greater deviation of H_- from ideality in methanolic than in aqueous solutions. The difference could be a consequence of the difference in the number of moles of methanol per l. compared to that for water; the concentration of "free" methanol and hence the classical equilibrium constant K_c should then be more sensitive to the number of moles of solvent involved in solvating the alkoxide ions. We have found that the values of the H_- function in methanol can be fitted by the method of Bascombe and Bell[14] by putting $n = 4$ in equation (4); however, we do not stress this agreement because of the approximations involved. Unfortunately, little is known concerning the activity of either solutes or solvent in methanolic sodium methoxide.

EXPERIMENTAL

Reagents.—The alcohols used as solvents were purified by standard methods.[15,16] The sodium was melted and filtered through glass wool under nitrogen (B.O.C., oxygen-free grade). This method of purification was found to be necessary to obtain clear, concentrated solutions of sodium methoxide; full details are available elsewhere.[15] The subsequent reactions of the alcohols with sodium were also carried out under nitrogen. The stability of the alcoholic solutions of the sodium alkoxides varied considerably; sodium methoxide appeared perfectly stable, sodium isopropoxide, and sodium t-butoxide were stable for several weeks, but sodium ethoxide, at concentrations exceeding 1M, became discoloured after 24 hr.

Tetramethylammonium hydroxide was purified by passage through an ion-exchange column to remove chloride ions.[17] 6-Bromo-2,4-dinitroaniline was obtained pure from Aldrich Chem. Co.; the other indicators were purified by repeated recrystallisation.

Measurement of Indicator Equilibria.—A stock solution of the indicator in one of the alcoholic solvents was diluted by a factor of ten with an alcoholic solution of the corresponding alkoxide. A portion of this solution was transferred to a stoppered silica cell, and a matched cell was filled with a solution of the sodium alkoxide of equal strength. These operations were carried out under an atmosphere of nitrogen in a dry-box. The cells were then removed from the dry-box and the optical density was measured in a Unicam S.P. 500 spectrophotometer.

The measurements in aqueous solutions of sodium hydroxide and tetramethylammonium hydroxide were carried out by introducing a small amount of an alcoholic indicator solution into 10 ml. of the aqueous base by a micrometer syringe. The syringe was found to deliver 0·05 ml. with an accuracy of $\pm 2\%$. The aqueous media therefore contained 0·5% of methanol, but it was assumed that this small amount had no effect on the spectra obtained.

The instability of solutions of 4-nitrobenzyl cyanide, 4-nitrodiphenylamine, and 2,4-dichloro-6-nitroaniline in dilute basic media was overcome by plotting the optical density as a function of time and extrapolating back to the time of making up the solution. The rate of decomposition of 4-nitrobenzyl cyanide in methanolic sodium methoxide has a maximum value at about M-sodium methoxide and the reaction is then too fast to be followed in this way. At much higher concentrations of sodium methoxide the indicator is again stable.

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[14] Bascombe and Bell, *Discuss. Faraday Soc.*, 1957, **24**, 158.

[15] More O'Ferrall, Ph.D. Thesis, London, 1962.

[16] Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1948.

[17] Cundiff and Markunas, *Analyt. Chem.*, 1958, **30**, 1450.

TABLE 3.

The change in the absorption spectrum of the indicators as a result of proton loss.

		Neutral molecule		Conjugate base	
Indicator	Medium	$\lambda_{\text{max.}}$ (Å)	$10^{-4}\varepsilon$	$\lambda_{\text{max.}}$ (Å)	$10^{-4}\varepsilon$
4-Nitrobenzyl cyanide	MeOH	2620°	1·05	5280	2·87
6-Bromo-2,4-dinitroaniline	$\mathrm{Pr^iOH}$	3360	1·35	5120	1·28
2,4-Dinitrodiphenylamine	,,	3380	1·71	5000	1·49
2,4-Dinitroaniline	,,	3350	1·54	5130	1·30
4-Nitrodiphenylamine	$\mathrm{Bu^tOH}$	3930	2·22	4750	2·84
2,4-Dichloro-6-nitroaniline	,,	4120	0·530	5000	0·868

Details of the relevant absorption maxima of the conjugate bases of the indicators are given in Table 3, together with the details of the nearest absorption band of the neutral indicators. Fortunately, the absorption of the neutral indicators is not significant at the absorption maxima of the conjugate bases. Medium effects on the calculated indicator ratios were allowed for by comparing optical densities in different alcohols at the absorption maxima of the conjugate base, not at a fixed wavelength; for most indicators, this correction is very small. The measurements involving t-butyl alcohol were carried out at 26—30°; all other measurements refer to room temperature (20° ± 3°).

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