A Nuclear Magnetic Resonance Study of the Addition of Methanol and Methoxide Ions to Substituted Benzaldehydes, and Corresponding J_M Acidity Function Values

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Values of the equilibrium constants, K_S, for the addition of methanol, and K_{OR}, for the addition of methoxide ions at the carbonyl group of a series of eleven substituted benzaldehydes have been determined by using an n.m.r. method. The results lead to the determination of a new J_M acidity scale for methanolic sodium methoxide solutions which is compared with existing functions.

ALTHOUGH many studies have been made of the covalent addition of water or alcohols to aliphatic carbonyl compounds [1,2] little quantitative information is available regarding additions to aromatic aldehydes. One reason for this is that the extent of solvent addition is usually small and hence difficult to determine by the usual u.v. spectroscopic methods. However, decreases in the u.v. absorption of substituted benzaldehydes occurring in aqueous base have been attributed to hydroxide ion addition at the carbonyl group and have been used to determine equilibrium constants for adduct formation.[3,4]

N.m.r. spectroscopy has previously been used to study the formation of solvates from a number of aliphatic aldehydes.[1,2] Separate bands may be observable due to the unchanged parent and to solvate so that integration yields equilibrium constants. Our interest in this subject was aroused when a study of the reaction of methanolic sodium methoxide with 4-methoxy-3,5-dinitrobenzaldehyde revealed competition between base

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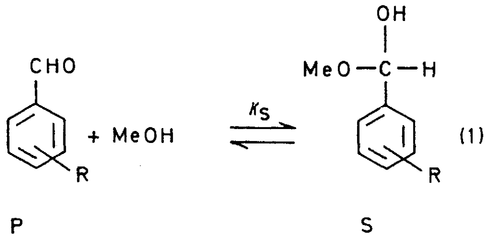
[1] R. P. Bell, *Adv. Phys. Org. Chem.*, 1966, **4**, 1.

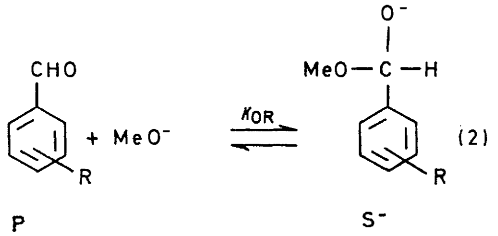
[2] Y. Ogata and A. Kawasaki, 'The Chemistry of the Carbonyl Group,' Interscience, New York, 1970, vol. 2, p. 1.

[3] P. Greenzaid, *J. Org. Chem.*, 1973, **38**, 3164.

[4] W. J. Bover and P. Zuman, *J.C.S. Perkin II*, 1973, 786; *J. Amer. Chem. Soc.*, 1973, **95**, 2531.

addition at a ring carbon atom, to give a Meisenheimer complex, and addition at the carbonyl group.[5] It was noted that, in the presence of base, fast exchange, on the n.m.r. time-scale, occurs between the parent, its hemiacetal, and hemiacetal anion. These measurements have now been extended to a series of eleven monosubstituted benzaldehydes where Meisenheimer complex formation does not occur. They allow the accurate determination of the values of the equilibrium constants, K_S, for the addition of methanol at the carbonyl group [equation (1)] and also the values, K_{OR}, for methoxide ion addition [equation (2)]. The results are of particular interest in that they allow the determination of a new J_M acidity scale[6] for methanolic sodium methoxide solutions.





EXPERIMENTAL

AnalaR methanol was used without purification. Sodium methoxide solutions were prepared by the reaction of clean sodium with methanol under nitrogen. Concentrations were determined by titration with standard acid.

^{1}H N.m.r. measurements were made at 25 ± 1 °C with a Varian A56/60 instrument (tetramethylsilane as internal reference). Solutions containing the required concentrations of reagents were prepared immediately before measurement.

RESULTS

^{1}H N.m.r. spectra of the benzaldehydes, stoicheiometric concentration 0·20M, were recorded in methanol and in solutions containing known concentrations of sodium methoxide.

Spectra in Methanol.—For those benzaldehydes containing electron-withdrawing groups distinct bands were observed[5] in methanol due to unchanged parent and to solvate, S. The aldehydic protons in the parent molecules had chemical shifts of δ *ca.* 10·0, similar to the values previously measured in carbon tetrachloride.[7] The corresponding CH protons in the hemiacetals, S, gave bands at δ *ca.* 5·5. Chemical shifts are collected in Table 1. Comparison of the areas under these peaks yielded values of K_S (= [S]/[P]) directly. Distinct bands were also observed due to the ring protons in parent benzaldehyde and hemiacetal. The equilibrium position was reached within about 2 min of dissolution of the aldehyde.

For other substituents values of K_S were too small to allow accurate determination by integration of peak areas.

Spectra in Methanolic Sodium Methoxide.—In the presence of sodium methoxide the spectra indicate the formation of methoxide adduct, S⁻, in addition to solvate, S, and parent, P. Interconversion of these species is sufficiently fast for combined n.m.r. bands to be observed. Thus as the concentration of base was increased the combined band due to aldehydic protons and extracyclic CH protons in the adducts moved to high field. In the case of *p*-NO_2, *m*-NO_2, *m*-Br, and *m*-Cl substituents a limiting position was reached at sufficiently high base corresponding to virtually complete conversion of substrate into S⁻. For all the compounds studied the spectra were consistent only with addition at the carbonyl group. Only small shifts of *ca.* 0·2—0·3 p.p.m. to high field occurred in the positions of ring-proton resonances, showing the absence of attack at ring positions.

Treatment of Data.—In order to determine values of K_S and K_{OR} we made use of the large shift (>4 p.p.m.) in the position of the aldehydic proton resonance occurring on adduct formation. The analysis required values for the chemical shifts of species P, S, and S⁻. The data in Table 1 indicate that these values do not vary greatly with substituent. Hence in those cases where direct determination was not possible differences in chemical shift between P and S of *ca.* 4·5 p.p.m. and between S⁻ and S of *ca.* 0·2 p.p.m. were assumed.

The resonance frequency, ν_x, in Hz from tetramethylsilane, was measured as a function of sodium methoxide concentration for each substituted benzaldehyde. A graph of ν_x *vs.* the stoicheiometric base concentration, $[NaOMe]_{stoich}$, was then extrapolated to zero base concentration to give a value $(\nu_x)_0$. Since in the absence of base only P and S will be present the value of K_S is found from equation (3), where ν_P and ν_S are the known values corresponding to parent and solvate. A representative plot for *m*-methoxybenzaldehyde is shown in Figure 1. The

$$K_S = \frac{[S]}{[P]} = \frac{\nu_P - (\nu_x)_0}{(\nu_x)_0 - \nu_S} \qquad (3)$$

TABLE 1

Chemical shift data for substituted benzaldehydes and their adducts,[a] and values of K_S at 25°

Substituent	P δ_{CHO}	S $\delta_{CH(OH)(OMe)}$	S⁻ $\delta_{CH(O^-)(OMe)}$	K_S
p-OMe	9·87	(5·40)	(5·60)	
p-Me	9·97	(5·45)	(5·60)	
m-Me	9·97	(5·45)	(5·60)	
H	10·04	5·50	(5·67)	
m-OMe	9·97	(5·50)	(5·67)	
p-Cl	9·98	5·53	(5·70)	
p-Br	10·00	5·52	(5·70)	
m-Cl	9·99	5·52	5·70	0·45 ± 0·06
m-Br	9·97	5·50	5·70	0·40 ± 0·05
m-NO_2	10·13	5·62	5·80	2·1 ± 0·2
p-NO_2	10·13	5·60	5·80	3·0 ± 0·4

[a] Values in parentheses were not determined directly, but by interpolation from the data for other substituents.

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[5] M. R. Crampton, M. A. El Ghariani, and M. J. Willison, *J.C.S. Perkin II*, 1974, 441.

[6] C. H. Rochester, 'Acidity Functions,' Academic Press, London, 1970.

[7] R. E. Klinck and J. B. Stothers, *Canad. J. Chem.*, 1962, **40**, 1071.

extrapolation is nearly linear at low base concentration giving a value of $(\nu_x)_0 = 576 \pm 1$ Hz. In combination with the values $\nu_P = 598{\cdot}5$ and $\nu_S = 330$ Hz this gives a value for K_S of 0·090 ± 0·005. This method of determination of K_S worked well with the other substituted benzaldehydes, being best for values of K_S between 0·05 and 0·20.

Values of the term $(\nu_P - \nu_x)/(\nu_x - \nu_{S,S^-})$ were then calculated for various stoicheiometric sodium methoxide concentrations. Here ν_{S,S^-} is a weighted average of the resonance positions of S and S^-. These species have similar but not identical chemical shifts so that the exact value depends on the proportion of each present. This allowed the determination of values of the ratio $[S^-]/[P]$ *via* equations (4) and (5).

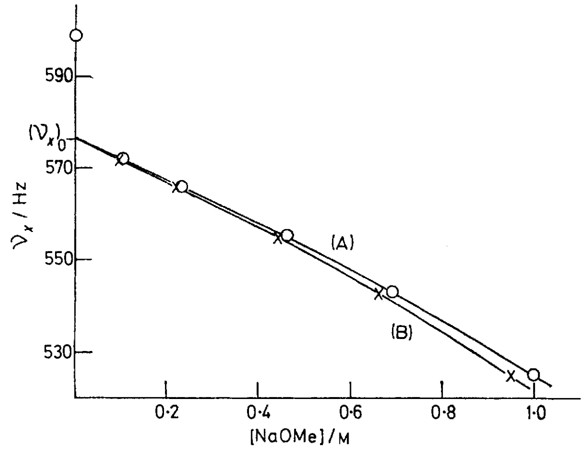

FIGURE 1 Graph to determine the value of K_S for *m*-methoxybenzaldehyde; plots of ν_x *vs.* (A) $[\mathrm{NaOMe}]_{\mathrm{stoich}}$ and (B) $[\mathrm{NaOMe}]_{\mathrm{free}}$

$$(\nu_P - \nu_x)/(\nu_x - \nu_{S\,S^-}) = ([S] + [S^-])/[P] \qquad (4)$$

$$= K_S + [S^-]/[P] \qquad (5)$$

This treatment is inadequate as it stands in that the relatively high concentrations (0·2M) of the benzaldehydes required resulted in depletions of sodium methoxide. However, from approximate values of K_S and $[S^-]/[P]$, values of the free sodium methoxide concentration could be found from $[\mathrm{NaOMe}]_{\mathrm{free}} = [\mathrm{NaOMe}]_{\mathrm{stoich}} - [S^-]$. A graph of ν_x *vs.* $[\mathrm{NaOMe}]_{\mathrm{free}}$ was then plotted giving a better value for K_S, and new values of the ratio $[S^-]/[P]$ were determined. Little improvement was found on making more than one iteration. Experimental results and calculated values of $[S^-]/[P]$ after one iteration, are in Table 2. All measurements were made at 25 °C. Tests were made to find whether the presence of small concentrations of water in the solvent would affect the results. It was found that the addition of up to 0·5M-water had no effect, within experimental error, on values of ν_x.

Calculation of Values of K_{OR} *and* J_M.—The extent of conversion of P into S^- will be expected to show an acidity function dependence rather than a dependence on the concentration of sodium methoxide. Since methoxide ion addition at the carbonyl group occurs, the J_M function is appropriate.[6]

$$J_M = \mathrm{p}(K_{OR}K_{MeOH}) + \log_{10}[S^-]/[P] \qquad (6)$$

The value of $\mathrm{p}K_{MeOH}$ is 16·92 and K_{OR} is the thermodynamic equilibrium constant for methoxide ion addition referred to pure methanol as standard state. For all compounds except the *p*-OMe and *p*-Me derivatives significant conversion of P into S^- occurred at relatively low base concentrations so that values of K_{OR} were obtained in the usual manner[6] by extrapolation to zero base concentration of plots of $\log_{10}([S^-]/[P]) - \log_{10}[\mathrm{NaOMe}]_{\mathrm{free}}$ *vs.* $[\mathrm{NaOMe}]_{\mathrm{free}}$. Values of J_M at higher base concentrations could then be determined and are given in Table 2. The known values of J_M were then applied to, the other two benzaldehydes to yield values of K_{OR}.

DISCUSSION

The n.m.r. spectra for solutions in neutral methanol indicate the formation of solvate S. For *m*-nitro-, *p*-nitro-, *m*-chloro-, and *m*-bromo-substituted compounds direct integration of peak areas allowed the determination of values of K_S. For benzaldehydes containing less strongly electron-withdrawing groups accurate

TABLE 2

Results and calculated parameters

$[\mathrm{NaOMe}]_{\mathrm{stoich}}$ /M	$[\mathrm{NaOMe}]_{\mathrm{free}}$ /M	ν_x	ν_{S,S^-}	$\dfrac{\nu_P - \nu_x}{\nu_x - \nu_{S,S^-}}$	$\dfrac{[S^-]}{[P]}$	J_M
m-Methoxybenzaldehyde, K_S = 0·090						
0	0	598·5				
0·10	0·096	572	332	0·110		
0·23	0·22	566	333	0·139	0·049	16·31
0·46	0·44	555	335	0·198	0·108	16·65
0·69	0·66	543	336	0·268	0·178	16·87
1·00	0·95	525	337	0·390	0·30	17·10
1·50	1·42	491	338	0·70	0·61	17·41
2·00	1·90	457	339	1·20	1·11	17·67
2·80	2·66	411	339	2·60	2·51	18·02
3·40	3·24	389·5	340	4·23	4·14	18·24
3·90	3·73	371	340	7·35		
m-Methylbenzaldehyde, K_S = 0·070						
0	0	598·5				
0·10	0·098	578·5	329	0·080		
0·23	0·225	576	330	0·091		
0·46	0·45	569·5	331	0·121	0·051	16·65
0·69	0·68	561·5	332	0·161	0·091	16·90
1·00	0·97	549·5	333	0·226	0·156	17·13
1·50	1·45	522	334	0·406	0·336	17·47
2·00	1·92	491	335	0·69	0·62	17·73
2·50	2·40	458·5	336	1·14	1·07	17·97
3·20	3·06	421	336	2·10	2·03	18·25
3·90	3·74	385	337	4·45	4·38	18·58
Benzaldehyde, K_S = 0·090						
0	0	602·5				
0·098	0·096	575·5	331	0·110		
0·20	0·195	572·5	332	0·125	0·035	
0·40	0·39	565	333	0·162	0·072	16·62
0·60	0·58	556	335	0·21	0·12	16·84
0·80	0·78	546	336	0·27	0·18	17·02
1·00	0·96	535	337	0·34	0·25	17·16
1·50	1·44	503	338	0·60	0·51	17·47
1·96	1·87	473·5	339	0·96	0·87	17·70
2·00	1·91	470	339	1·01	0·92	17·72
3·25	3·10	402	340	3·23	3·14	18·26
p-Methoxybenzaldehyde, K_S = 0·012						
0	0	591·8				
0·10	0·10	588·5	325			
0·23	0·23	588	326			
0·46	0·46	587·5	328			
1·00	1·00	585	330			
1·96	1·95	574	333	0·074	0·062	17·73
2·50	2·48	563	334	0·126	0·114	18·00
2·80	2·78	558	334	0·151	0·14	18·09
3·00	2·97	552	334	0·182	0·17	18·17
3·50	3·46	534	335	0·29	0·28	18·39
3·82	3·76	515	335	0·425	0·41	18·55
3·92	3·86	511	335	0·46	0·45	18·59

TABLE 2 (*Continued*)

$[\text{NaOMe}]_{\text{stoich}}$ /M	$[\text{NaOMe}]_{\text{free}}$ /M	ν_x	$\nu_{\text{S,S}^-}$	$\frac{\nu_p - \nu_x}{\nu_x - \nu_{\text{S,S}^-}}$	$\frac{[\text{S}^-]}{[\text{P}]}$	J_M
p-Methylbenzaldehyde, K_S = 0·034						
0	0	598				
0·10	0·10	587·5	328			
0·20	0·198	586	330			
0·50	0·49	581	332	0·068	0·034	16·85
1·00	0·98	571	334	0·114	0·080	17·22
1·50	1·47	554	335	0·201	0·167	17·54
1·96	1·92	534·5	336	0·27	0·24	17·70 [a]
2·50	2·44	508	336	0·52	0·49	18·01
3·92	3·80	426	337	1·93	1·9	18·60
p-Chlorobenzaldehyde, K_S = 0·24						
0	0	599				
0·20	0·18	530	336	0·355	0·115	
0·40	0·36	506	338	0·55	0·31	16·51
0·60	0·53	483	340	0·81	0·57	16·78
1·20	1·10	436	340	1·7	1·46	17·18
1·60	1·46	408	341	2·9	2·65	17·44
2·80	2·62	365	341			
3·90	3·7	350	342			
p-Bromobenzaldehyde, K_S = 0·27						
0	0	600				
0·20	0·18	517	335	0·455	0·185	16·22
0·40	0·36	493	337	0·685	0·415	16·57
0·60	0·54	474	339	0·935	0·665	16·77
1·00	0·90	438	340	1·65	1·38	1·709
1·50	1·36	406	341	2·98	2·71	17·38
2·40	2·23	369	341	8·35	8·08	17·86
2·80	2·62	362	342			
3·90	3·70	349	342			
m-Bromobenzaldehyde, K_S = 0·45						
0	0	598				
0·20	0·15	473	335	0·90	0·45	16·12
0·40	0·32	443	337	1·46	1·01	16·47
0·60	0·49	421	338	2·14	1·69	16·70
1·00	0·86	392	339	3·9	3·45	17·01
2·8	2·61	346	340			
3·9	3·7	342	340			
m-Chlorobenzaldehyde, K_S = 0·45 (from Table 1)						
0	0	599·5				
0·23	0·18	475	336	0·90	0·45	16·23
0·46	0·38	442	338	1·51	1·06	16·61
0·69	0·58	419	339	2·26	1·81	16·84
1·00	0·86	396	340	3·64	3·19	17·08
2·8	2·6	349	341			
3·4	3·2	345	341			
3·9	3·7	343	341			
m-Nitrobenzaldehyde, K_S = 2·1 (from Table 1)						
0	0	608				
0·20	0·105	388	344	5·0	2·9	16·02
0·40	0·27	372	345	8·7	6·6	16·38
0·60	0·44	364	346	13·5	11·4	16·62
2·8	2·6	348				
3·9	3·7	348				
p-Nitrobenzaldehyde, K_S = 3·0 (from Table 1)						
0	0	608				
0·05	0·005	393	338	3·9	0·9	
0·20	0·08	371	342	8·2	5·2	
0·40	0·25	361	343	13·7	10·7	
0·60	0·42	354	344	25·4	22·4	
2·9	2·7	346	346			

[a] This J_M value was calculated by using data from the other substituted benzaldehydes and was used as the anchor point for this compound.

values of K_S were found *via* extrapolation to zero base concentration of the frequency of the combined aldehydic-extracyclic CH resonance. Values are in Table 3. These results are broadly similar to those obtained by Fuchs, Young, and Rodewald [8] using the enthalpies of transfer of benzaldehydes from methanol to dimethylformamide. There are however notable differences: for example with benzaldehyde itself, for which our value is considerably greater. We consider our values to be the more reliable since the previous measurements depend on a value (—0·8 kcal) for transfer of the aldehyde group which was determined by using *para*-substituents capable of resonance interaction with the aldehyde function.

TABLE 3

Values for the equilibrium constants for addition of methanol, K_S, and methoxide ions, K_{OR}, to substituted benzaldehydes at 25°

No.	Substituent	K_S	K_{OR}/l mol^{-1}
1	*p*-OMe	0·012 ± 0·003	$(9·5 \pm 1·0) \times 10^{-3}$
2	*p*-Me	0·034 ± 0·004	$(4·0 \pm 0·5) \times 10^{-2}$
3	*m*-Me	0·070 ± 0·005	$(9·5 \pm 1·0) \times 10^{-2}$
4	H	0·090 ± 0·005	0·14 ± 0·01
5	*m*-OMe	0·090 ± 0·005	0·20 ± 0·005
6	*p*-Cl	0·24 ± 0·02	0·80 ± 0·10
7	*p*-Br	0·27 ± 0·03	0·93 ± 0·07
8	*m*-Cl	0·45 ± 0·06	2·2 ± 0·3
9	*m*-Br	0·43 ± 0·05	2·8 ± 0·2
10	*m*-NO_2	2·1 ± 0·2	23 ± 4
11	*p*-NO_2	3·0 ± 0·4	50 ± 10

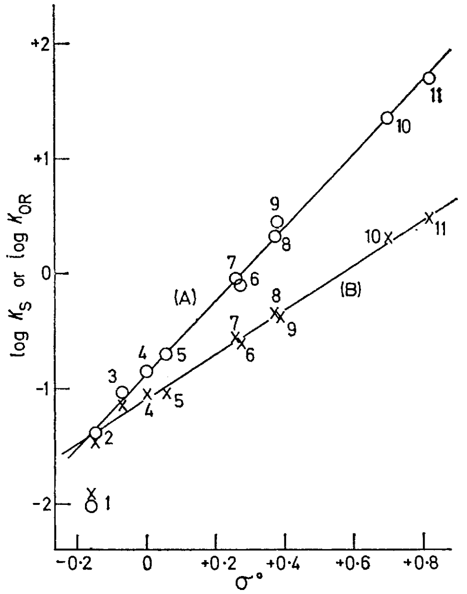

FIGURE 2 Hammett plots for the addition of (A) methoxide ions and (B) methanol to substituted benzaldehydes (numbering as in Table 3)

In the presence of base, n.m.r. spectra indicate the presence of methoxide adduct, S^-, as well as S and P. Measurements were made within 5 min of dissolution of the benzaldehydes. In this time no appreciable decomposition by deformylation [9,10] or the Cannizzaro reaction [11] occurred. The formation of acetals, rather

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[8] R. Fuchs, T. M. Young, and R. F. Rodewald, *Canad. J. Chem.*, 1973, **51**, 4122.

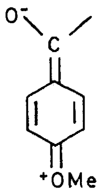
[9] J. F. Bunnett, J. H. Miles, and K. V. Nahabedian, *J. Amer. Chem. Soc.*, 1961, **83**, 2512.

[10] E. J. Forbes and M. J. Gregory, *J. Chem. Soc.* (*B*), 1968, 205.

[11] T. A. Geissman, *Org. Reactions*, 1944, **2**, 94.

than hemiacetals, is known to occur in acidic solutions but not in neutral or basic media.[12]

Values of the equilibrium constants for methoxide ion addition, K_{OR}, are in Table 3. Graphs of $\log_{10} K_S$ and $\log_{10} K_{OR}$ *vs.* Taft's σ^0 values [13] are shown in Figure 2. Excellent straight lines with slopes, ρ, of $2{\cdot}0 \pm 0{\cdot}1$ and $3{\cdot}2 \pm 0{\cdot}1$, respectively, are obtained except for the *p*-methoxy-substituted compound. The smaller propensity of this compound for adduct formation is no doubt due to stabilisation of the parent aldehyde by resonance interaction of the form (I). The positive ρ values show that, as expected, the presence of electron-withdrawing groups in the ring favours nucleophilic attack at the carbonyl group. For comparison, ρ values of 2·76 (ref. 4) and 2·24 (ref. 5) have been found for hydroxide ion addition to substituted benzaldehydes in water. From the values of K_S and K_{OR} it is of course possible to calculate values for the acid dissociation constants in methanol, K_a, of the methanol adducts, S, of the substituted benzaldehydes [equation (7)]. A Hammett plot for the dissociation constants, K_a, gives a ρ value of $1{\cdot}2 \pm 0{\cdot}1$, similar to that for the dissociation of substituted benzoic acids.


(I)

$$K_a = [S^-][H^+]/[S] = K_{OR}K_{MeOH}/K_S \qquad (7)$$

Measurements in basic solution of values of the ratio $[S^-]/[P]$ lead to the determination of a new J_M acidity scale [6] for methanolic sodium methoxide (Table 4). The agreement between the individual substituted benzaldehydes was excellent. These values of J_M can be compared with those from previous determinations relating to methoxide ion additions to polynitrobenzenes [14,15] or to α-cyanostilbenes.[16] The present scale increases much less steeply with base concentration than do the other scales. For example at 3·8M-sodium methoxide values are 18·59 (present scale); 21·8 (ref. 14) or 22·3 (ref. 15) (polynitrobenzenes); 20·6 (α-cyanostilbenes [16]); and 20·2 (H_M scale for anilines [6]).

TABLE 4

J_M Values determined from methoxide addition to substituted benzaldehydes

[NaOMe]/ M	J_M	[NaOMe]/ M	J_M
0·4	16·60 ± 0·03	2·0	17·75
0·6	16·82	2·5	18·01
0·8	17·01	3·0	18·20
1·0	17·15	3·5	18·41
1·5	17·50	3·8	18·59

These differences show that no single J_M scale applies to methanolic sodium methoxide solutions. A major factor contributing to these deviations is likely to be the variation with structure of the solvation requirements of the various indicator molecules and their adducts.[17] Thus the J_M acidity function may be written [6,17] as in equation (8) where n is the difference in solvation between P plus MeO^- and S^-. A plot of

$$J_M = pK_{MeOH} + \log_{10}[NaOMe] - n\log_{10}(a_{MeOH}) - \log_{10}\left(\frac{f_{S^-}}{f_P f_{OMe^-}}\right) \qquad (8)$$

$J_M - \log_{10}[NaOMe]$ against $-\log_{10} a_{MeOH}$ had a slope of 4. This figure probably has little significance in terms of actual numbers of methanol molecules involved.[17,18] Nevertheless this approach does illustrate how differences in solvation may affect J_M values. It would be expected that the benzaldehyde adducts, S^-, where the negative charge is localised on an oxygen atom, would be well solvated by methanol, leading to a small value of n. In the case of methoxide adducts of polynitrobenzenes, where the negative charge is more delocalised, higher values of n might be expected. This may in part account for the differences in observed J_M values. It is unlikely, however, to be the only factor involved. For example in the case of polynitrobenzene derivatives, stabilising interactions between the adducts and the cations present have been postulated.[5,19]

[4/1717 *Received*, 15*th August*, 1974]

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[13] R. W. Taft, *J. Phys. Chem.*, 1960, **64**, 1805.

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

[15] F. Terrier, *Ann. chim.* (*France*), 1969, 153.

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

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[19] M. R. Crampton and H. A. Khan, *J.C.S. Perkin II*, 1972, 1173, 2286; 1973, 110.