442. *Acidity Functions in Strongly Basic Media. Part II.*[1] *The Reactions of Four Aromatic Nitro-compounds in Methanolic Sodium Methoxide*

By C. H. ROCHESTER

2,4-Dinitroaniline and 2,4-dinitroanisole interact with methoxide ions to form the amine anion RNH⁻ and a 1 : 1 addition complex, respectively. The species thus formed in each case react further probably by addition of another methoxide ion. The ionisation of the amine to RNH⁻ parallels the H_- function for NaOMe–MeOH solutions but the reversible equilibria involving methoxide addition are consistent with the definition of a J_- acidity function.

The picrate anion and also the Meisenheimer addition complex derived from 2,4,6-trinitroanisole each undergo two further consecutive equilibria in NaOMe–MeOH solutions. The first equilibrium in each parallels the J_- acidity function and the second equilibrium parallels H_-.

RECENT measurements have shown that solution of aromatic nitro-compounds in concentrated aqueous sodium hydroxide or methanolic sodium methoxide solutions results in interactions which often involve a series of concurrent and consecutive equilibria followed

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[1] Part I, C. H. Rochester, *J.*, 1965, 676.

by a slow irreversible reaction.[2,3] Spectrophotometric studies of the equilibria have suggested that the extent of interaction between aromatic substrate and base to form a given complex is probably dependent on an appropriate acidity function for the basic solution.[2,3] Indicator ratios for eight such equilibria in methanolic sodium methoxide solutions have been measured by us, the results being consistent with the definition of a J_- acidity function.[3a,4]

EXPERIMENTAL

Picric acid (m. p. 122°), 2,4-dinitroaniline (m. p. 177°), and 2,4-dinitroanisole (m. p. 89°) were recrystallised from aqueous ethanol and dried in a vacuum desiccator. 2,4,6-Trinitro-anisole (m. p. 68°) was prepared from picryl chloride and sodium methoxide in methanol, the resulting deep red solution being poured on to ice. Stock solutions containing known concentrations of the nitro-compounds in methanol were prepared. The purification of methanol and preparation of sodium methoxide solutions was as before.[1]

Reaction solutions were prepared by weight from stock indicator and sodium methoxide solutions, and kept in the dark because of their known light sensitivity. Complete spectra were recorded with a Unicam S.P. 800 spectrophotometer and optical densities at individual wavelengths were measured using a Unicam S.P. 500 spectrophotometer with a thermostat-controlled (25°c) cell compartment. Matched 1 cm. silica stoppered cells were used. Where reaction solutions were unstable readings were taken for sufficient time to allow accurate extrapolation of the required zero time values.

RESULTS

2,4-Dinitroanisole.—In methanol 2,4-dinitroanisole has a spectral maximum at 292 mμ ($\varepsilon = 10,900$). With increasing sodium methoxide concentration in the range $0 < [NaOMe] < 2\cdot8M$ the intensity of this maximum decreases and new bands at 500 and ~345 mμ appear, a series of spectra showing an isosbestic point ($\varepsilon = 6700$) at 316 mμ (Figure 1). In the further concentration range $2\cdot8M < [NaOMe] < 3\cdot6M$ the isosbestic point is absent. Above $3\cdot6M$ a series of spectra show a new isosbestic point ($\varepsilon = 9150$) at 329 mμ and the intensity of the 500 mμ maximum decreases with increasing NaOMe concentration until in $[NaOMe] = 4\cdot8M$ the dinitroanisole is nearly completely converted into a species with an absorption maximum ($\varepsilon = 19,900$) at 302 mμ (Figure 1).

The spectra indicate that interaction between sodium methoxide and 2,4-dinitroanisole (D_1) results in two consecutive equilibria to, at low concentrations of base, a species A_1 ($\lambda_{max.} = 500$ mμ) and, at higher concentrations of base, a species B_1 ($\lambda_{max.} = 302$ mμ). The concentrations of the three species D_1, A_1, and B_1 in a given reaction solution were calculated from optical-density values D_0 at 316 and 500 mμ (Table 1) as follows.

At 316 mμ, since $\varepsilon_{D_1} = \varepsilon_{A_1}$ it follows that

$$D_0 = \varepsilon_{D_1}([A_1] + [D_1]) + \varepsilon_{B_1}[B_1], \tag{1}$$

which combined with the material balance

$$[A_1] + [B_1] + [D_1] = [D_1]_{stoich} \tag{2}$$

permits the calculation of $[B_1]$ from

$$[B_1] = (D_0 - \varepsilon_{D_1}[D_1]_{stoich})/(\varepsilon_{B_1} - \varepsilon_{D_1}) \tag{3}$$

A small extrapolation of the measured D_0 values was necessary to establish $\varepsilon_{D_1} = 18,080$. Above $[NaOMe] = 3\cdot6M$ presence of the isosbestic point at 329 mμ in reaction spectra indicates that $[D_1] = 0$, and therefore $[A_1]$ was calculable from equation (2). As D_1 and B_1 both show negligible absorption at 500 mμ, D_0 (500 mμ) $= \varepsilon_{A_1} [A_1]$. A plot of D_0 (500 mμ) against $[A_1]$ calculated as above was linear with slope ε_{A_1} (500) $= 21,500$. Concentrations of A_1 in reaction solutions were finally calculated by using $[A_1] = D_0$ (500 mμ)/21,500 this giving more reliable values, particularly at the higher base concentrations studied, than is obtained by using equations

[2] V. Gold and C. H. Rochester, *J.*, 1964, (a) 1687; (b) 1692, 1697, 1704, 1710, 1717, 1722, 1727.
[3] C. H. Rochester, *Trans. Faraday Soc.*, 1962, **59**, (a) 2820; (b) 2829.
[4] V. Gold and B. W. V. Hawes, *J.*, 1951, 2102.

(2) and (3). For [NaOMe] $<$ 3·6M, [B$_1$] was calculated from equation (3) and [D$_1$] from equation (2). Above [NaOMe] $=$ 3·6M, [B$_1$] was calculated from [B$_1$] $=$ ([D$_1$]$_{stoich}$ $-$ [A$_1$]). A summary of the concentrations of each species is given in Table 1.

TABLE 1

Summary of data for 2,4-dinitroanisole

$$[D_1]_{stoich} = 4·70 \times 10^{-5}M$$

[NaOMe] (M)	D_0 (500 mµ)	D_0 (316 mµ)	$10^5[D_1]$ (M)	$10^5[A_1]$ (M)	$10^5[B_1]$ (M)	Acidity functions * θ_1	θ_2
1·50	0·010	0·315	4·65	0·04$_6$		18·23	
2·09	0·091		4·28	0·42		19·23	
2·45	0·228	0·315	3·64	1·06		19·70	
2·82	0·453		2·59	2·11		20·15	
2·90	0·519	0·326	2·18	2·42	0·09$_7$	20·29	20·26
3·08	0·638	0·344	1·48	2·97	0·25	20·54	20·59
3·32	0·700	0·393	0·75	3·26	0·69	20·88	20·99
3·51	0·682	0·443	0·40	3·18	1·12	21·14	21·21
3·68	0·595	0·535		2·76	1·94		21·51
3·74	0·527	0·569		2·45	2·25		21·62
3·86	0·424	0·622		1·97	2·73		21·80
4·03	0·303	0·690		1·41	3·29		22·03
4·25	0·180	0·738		0·84	3·86		22·32
4·58	0·094	0·809		0·44	4·26		22·65
4·70	0·067	0·821		0·31	4·39		22·81
4·80	0·057	0·818		0·27	4·43		22·87

* $\theta_1 = 20·24 + \log_{10}([A_1]/[D_1])$; $\theta_2 = 21·66 + \log_{10}([B_1]/[A_1])$.

2,4-Dinitroaniline.—In methanol 2,4-dinitroaniline has absorption maxima at 336 ($\varepsilon =$ 14,600) and 258 mµ ($\varepsilon =$ 9400). Addition of sodium methoxide results in new maxima at 515 and 383 mµ, a series of spectra for [NaOMe] $<$ 2M showing an isosbestic point ($\varepsilon =$ 3570) at 299 mµ (Figure 2). In the further range 2M $<$[NaOMe]$<$ 3·6M the isosbestic point is absent
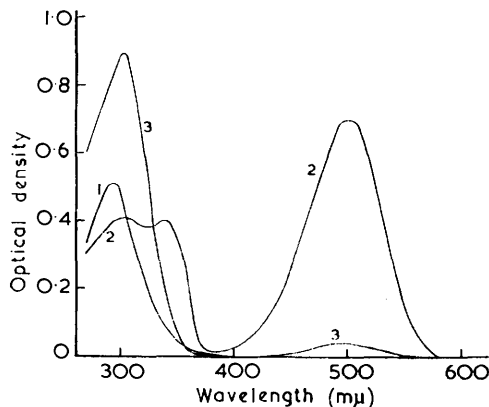

FIGURE 1. Absorption spectra of 2,4-dinitro-anisole (4·70 $\times$ 10^{-5}M) in methanolic sodium methoxide
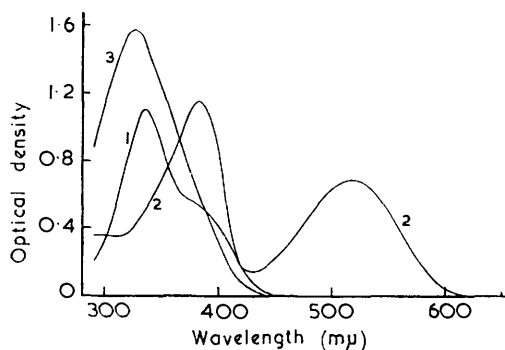
[NaOMe]: 1, 0; 2, 3·22M; 3, 4·70M

FIGURE 2. Absorption spectra of 2,4-dinitro-aniline (7·62 $\times$ 10^{-5}M) in methanolic sodium methoxide

[NaOMe]: 1, 0; 2, 3·04M; 3, 4·84M

and above 3M the bands at 383 and 515 mµ begin to decrease in intensity. Above 3·6M a new isosbestic point ($\varepsilon =$ 13,100) appears at 365 and the 383 and 515 mµ bands continue to decrease until above 4·8M the 2,4-dinitroaniline is completely converted into a species with a broad absorption maximum ($\varepsilon =$ 21,700) at 326 mµ (Figure 2).

The situation here is therefore very similar to that for 2,4-dinitroanisole. Optical densities at 299 and 510 mµ were measured (Table 2) and hence concentrations of unchanged 2,4-dinitro-aniline D$_2$ and the species A$_2$ ($\lambda_{max.} =$ 515, 383 mµ) and B$_2$ ($\lambda_{max.} =$ 326 mµ) were calculated by an identical procedure to the above. These are summarised in Table 2.

TABLE 2

Summary of data for 2,4-dinitroaniline

$[D_2]_{stoich} = 7.62 \times 10^{-5}$M

[NaOMe] (M)	D_0 (510 mμ)	D_0 (299 mμ)	$10^5[D_2]$ (M)	$10^5[A_2]$ (M)	$10^5[B_2]$ (M)	Acidity functions * θ_3	θ_4
0·52	0·029		7·36	0·26		16·70	
0·56	0·042	0·273	7·25	0·37		16·86	
0·75	0·053		7·15	0·47		16·97	
1·04	0·110	0·272	6·65	0·97		17·31	
1·16	0·113		6·62	1·00		17·33	
1·50	0·206	0·272	5·80	1·82		17·65	
1·53	0·242		5·48	2·14		17·74	
1·82	0·336		4·65	2·97		17·96	
1·97	0·383		4·23	3·39		18·05	
2·01	0·434	0·284	3·67	3·84	0·11	18·17	19·52
2·44	0·625	0·305	1·80	5·53	0·29	18·64	19·78
2·51	0·617	0·306	1·86	5·46	0·30	18·62	19·80
2·72	0·680	0·336	1·05	6·01	0·56	19·91	20·03
3·04	0·673	0·396	0·59	5·95	1·09	19·15	20·32
3·22	0·599	0·499	0·32	5·30	2·00	19·37	20·64
3·36	0·503	0·650		4·45	3·17		20·91
3·38	0·473	0·671		4·18	3·44		20·98
3·48	0·430			3·81	3·81		21·06
3·53	0·393			3·48	4·14		21·14
3·53	0·361	0·768		3·20	4·42		21·20
3·61	0·300	0·834		2·65	4·97		21·33
3·71	0·207	0·920		1·83	5·79		21·56
4·00	0·119	0·990		1·05	6·57		21·86
4·22	0·057	1·060		0·50	7·12		22·22
4·69	0·013	1·127		0·11$_5$	7·50		22·87
4·77	0·011	1·121		0·09$_7$	7·52		22·95

* $\theta_3 = 18.15 + \log_{10}([A_2]/[D_2])$; $\theta_4 = 21.06 + \log_{10}([B_2]/[A_2])$.

TABLE 3

Summary of data for picric acid

$[pic]_{stoich} = 7.51 \times 10^{-5}$M

[NaOMe] (M)	D_0 (480 mμ)	D_0 (394 mμ)	$10^5[A_3]$ (M)	$10^5[B_3]$ (M)	$10^5[C_3]$ (M)	Acidity functions * θ_5	θ_6
0·94	0·015	0·764	7·48	0·03$_2$		17·85	
1·41	0·036	0·764	7·43	0·07$_8$		18·27	
1·87	0·119	0·843	6·73	0·26	0·52	18·84	18·00
2·05	0·186	0·940	5·94	0·40	1·17	19·08	18·16
2·21	0·271	1·098	4·71	0·58	2·22	19·34	18·27
2·36	0·325	1·300	3·25	0·70	3·56	19·58	18·40
2·54	0·368	1·549	1·54	0·79	5·18	19·96	18·51
2·69	0·329	1·717	0·48	0·71	6·32	20·42	18·64
2·80	0·246	1·800	0·11	0·53	6·87		18·90
3·28	0·065	1·875		0·14	7·37		19·41
3·76	0·015	1·881		0·03	7·40		—
4·22	0	1·897			7·51		

* $\theta_5 = 20.25 + \log_{10}([B_3]/[A_3])$; $\theta_6 = 17.69 \pm \log_{10}([C_3]/[B_3])$.

Picric Acid.—In dilute sodium methoxide solution picric acid (*ca.* 10^{-4}M) exists entirely as the picrate anion A_3 ($\lambda_{max.} = 355$ mμ).[5] At higher concentrations of methoxide two consecutive equilibria are apparent and give rise to complexes B_3 ($\lambda_{max.} \sim 470$ mμ) and C_3 ($\lambda_{max.} = 394$ mμ, $\varepsilon = 25,300$) (Figure 3). Spectra of solutions containing only A_3 and B_3 showed an isosbestic point ($\varepsilon = 10,000$) at 394 mμ whereas for solutions containing only B_3 and C_3 isosbestic points at 408, 343, and 292 mμ were present. Since A_3 and C_3 had negligible absorption at 480 mμ measurement of optical densities at this wavelength and 394 mμ (Table 3) enabled a complete analysis for $[A_3]$, $[B_3]$, and $[C_3]$ (Table 3) to be carried out by a similar method to that used for 2,4-dinitroanisole.

2,4,6-Trinitroanisole.—Conversion of 2,4,6-trinitroanisole into a 1 : 1 addition complex A_4 ($\lambda_{max.} = 410$, 480 mμ) is complete in 0·1M-sodium methoxide solutions.[2a] At higher methoxide

[5] N. A. Izmailov and E. L. Gurevich, *Optics and Spectroscopy,* 1961, **10**, 9.

concentrations the 410 mμ absorption becomes weaker and the 480 mμ absorption stronger indicating further equilibrium to a complex B_4 ($\lambda_{max.} = 480$ mμ), a series of spectra for the range 1M $<$[NaOMe]$<$ 2·4M showing an isosbestic point ($\varepsilon = 12,700$) at 431 mμ. Spectra relating to these equilibria have been recorded elsewhere.[2a] Above [NaOMe] $= 3$M the intensity of the
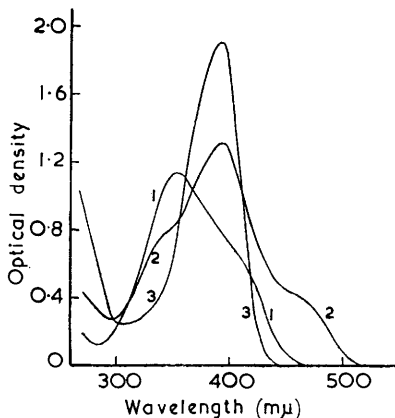

FIGURE 3. Absorption spectra of picric acid ($7·51 \times 10^{-5}$M) in methanolic sodium methoxide

[NaOMe]: 1, 0; 2, 2·36M; 3, 4·22M

480 mμ absorption decreases until in 4·4M-sodium methoxide the 2,4,6-trinitroanisole is mostly converted into a colourless complex C_4 ($\lambda_{max.} = 299$ mμ).

By using a similar expression to equation (3), concentrations of C_4 in reaction solutions were calculated from optical-density measurements at 431 mμ (Table 4). Measurements at 410 mμ

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TABLE 4

Summary of data for 2,4,6-trinitroanisole

$[TNA]_{stoich} = 3·45 \times 10^{-5}$M

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[NaOMe] (M)	D_0 (431 mμ)	D_0 (410 mμ)	$10^5[A_4]$ (M)	$10^5[B_4]$ (M)	$10^5[C_4]$ (M)	Acidity functions * θ_7	θ_8
0·94	0·442	0·858	3·43	0·02$_0$		17·58	
1·24	0·441	0·851	3·39	0·06$_1$		18·06	
1·42	0·440	0·841	3·32	0·12$_2$		18·38	
1·79	0·439	0·803	3·09	0·36		18·87	
1·89	0·441	0·785	3·00	0·45		18·98	
2·21	0·440	0·730	2·68	0·77		19·27	
2·34	0·438	0·667	2·29	1·16		19·51	
2·82	0·417	0·432	1·00	2·27	0·18	20·17	18·70
3·03	0·380	0·324	0·51	2·47	0·47	20·50	19·08
3·29	0·341	0·231	0·24	2·48	0·77	20·82	19·29
3·40	0·301	0·199	0·07	2·29	1·09		19·48
3·73	0·208	0·131	0·01	1·62	1·82		19·85
3·97	0·146	0·091		1·15	2·30		20·10
4·10	0·120	0·075		0·94	2·51		20·22
4·35	0·080	0·051		0·63	2·82		20·47

* $\theta_7 = 19·81 + \log_{10}([B_4]/[A_4])$; $\theta_8 = 19·80 + \log_{10}([C_4]/[B_4])$.

were used to evaluate $[A_4]$ and $[B_4]$ as follows. From the material balance $[A_4] + [B_4] (= [TNA]_{stoich} - [C_4])$ was calculated and divided into the optical densities at 410 mμ to give a series of numbers which tended to a constant (7970) at high sodium methoxide concentrations. As ε_{D_4} (410) is negligible this must be the extinction coefficient of B_4 at 410 mμ, since at high concentrations $[A_4]$ will be negligible and therefore

$$D_0/([A_4] + [B_4]) = D_0/[B_4] = \varepsilon_{B_4}.$$

Hence knowledge of the extinction coefficient of A_4 from the spectrum of 2,4,6-trinitroanisole in 0·1M-sodium methoxide and combination of the material balance with the equation (relating to 410 mμ)

$$\varepsilon_{A_4}[A_4] + \varepsilon_{B_4}[B_4] = D_0$$

permitted the evaluation of $[A_4]$ and $[B_4]$ (Table 4).

DISCUSSION

Measurement of the ionisation ratios ([S$^-$]/[SH]) for an equilibrium

$$SH + OMe^- \rightleftharpoons S^- + nMeOH$$

in methanolic sodium methoxide solutions allows definition of the H_- acidity function [6] according to the equations

$$H_- = pK_{SH} + \log_{10} ([S^-]/[SH]) \tag{4}$$

$$= pK_{MeOH} + \log_{10} [OMe^-] - n \log_{10} a_{MeOH} + \log_{10} (f_{OMe}-f_{SH}/f_{S}-) \tag{5}[1]$$

Similarly the definition of the J_- acidity function [3a,4] according to

$$J_- = pK + \log_{10} ([SH \cdot OMe^-]/[SH]) \tag{6}$$

$$= pK_{MeOH} + \log_{10} [OMe^-] - m \log_{10} a_{MeOH} + \log_{10} (f_{OMe}-f_{SH}/f_{SH \cdot OMe^-}) \tag{7}$$

where K is the equilibrium constant for

$$SH + MeOH \rightleftharpoons SH \cdot OMe^- + H^+,$$

follows from measurement of ionisation ratios [SH·OMe$^-$]/[SH] for the reversible equilibrium

$$SH + OMe^- \rightleftharpoons SH \cdot OMe^- + mMeOH.$$

Of the eight sets of ionisation ratios ([A$_1$]/[D$_1$], [B$_1$]/[A$_1$], [A$_2$]/[D$_2$], etc.) measured in the present work two refer to equilibria in which SH is a neutral substrate, four describe equilibria involving SH$^-$, and two involving SH^{2-}.

The variation of the ionisation ratios with sodium methoxide concentration suggests the equilibria as falling into two groups. The constant pK in the acidity function equation was evaluated for one equilibrium in each group from the intercept at [NaOMe] = 0 of a plot of $\{\log_{10} \text{(ratio)} - \log_{10} \text{[NaOMe]}\}$ against [NaOMe].[7] Values of pK (Table 5) for the other equilibria were deduced by the usual stepwise procedure.[8] An acidity function pertaining to each equilibrium was thence deduced (Tables 1—4). The acidity functions

TABLE 5

Summary of pK values

Relevant ionisation ratios	[A]/[D]	[B]/[A]	[C]/[B]
2,4-Dinitroaniline	18·15	21·06	
2,4-Dinitroanisole	20·24	21·66	
Picric acid		20·25	17·69
2,4,6-Trinitroanisole		19·81	19·80

are compared in Figure 4. The lower group of three parallel More O'Ferrall and Ridd's H_- scale whereas the upper five change more rapidly with increasing stoicheiometric sodium methoxide concentration but agree excellently with each other. In Figure 5 the acidity function thus defined is compared in relation to the ideal function ($pK_{MeOH} + \log_{10}$ [NaOMe]) with the H_- scales defined by the ionisation of amines [7] and phenols [1] in methanolic sodium methoxide.

Only two of the equilibria studied involve interactions between a neutral substrate SH and sodium methoxide. 2,4-Dinitroaniline probably ionises by loss of an amino-proton and on this assumption has been used for measurement of the H_- acidity function.[7,9] However, the further interaction of the amine anion with sodium methoxide above [NaOMe] = 2M leads to small errors in any acidity function deduced on the assumption

[6] M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1.
[7] R. A. More O'Ferrall and J. H. Ridd, *J.*, 1963, 5030.
[8] L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721.
[9] R. Schaal and G. Lambert, *J. Chim. phys.*, 1962, 1164.

that only undissociated amine and amine anion RNH^- exist in the solution.   2,4-Dinitro-
anisole on the other hand probably forms a Meisenheimer [10] type complex by addition of
methoxide ions to the neutral molecule.   The acidity function deduced from this equi-
librium would therefore be consistent with a J_- acidity function as defined by equation 6.
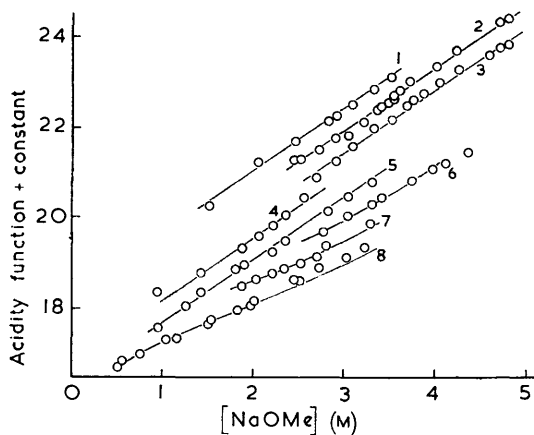The large deviation between J_- and H_- in these solutions (Figure 5) may arise from

FIGURE 4.   Acidity functions from Tables
  1—4 as a function of sodium methoxide
  concentration.   Functions are staggered
  by 0·5 unit amounts for clarity

  1, θ_1; 2, θ_4; 3, θ_2; 4, θ_5; 5, θ_7; 6, θ_8;
           7, θ_6; 8, θ_3

Lower three lines represent More O'Ferrall
  and Ridd's H_- scale whereas upper five
  are linear and staggered by 0·5 unit
 amounts

FIGURE 5.   Comparison of acidity func-
  tions for methanolic sodium methoxide
  solutions

1, $J_- = J_{2-}$ (present work); 2, H_- (sub-
  stituted amines); 3, H_- (substituted
  phenols);   4, $pK_{MeOH} + \log_{10}$ [NaOMe]
  (ideal expression)
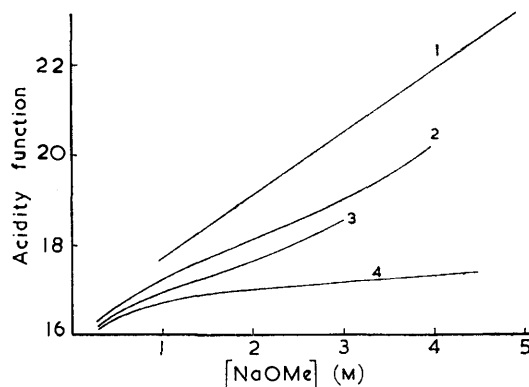
differences in the solvation factors n and m (equations 5 and 7), a similar explanation having
been proposed to explain deviations between J_0 and H_0 in aqueous acid solutions.[11]
    The four reactions which involve interaction between a singly negative charged sub-
strate SH^- and methoxide are all consistent with the J_- function above (Figure 4).   It
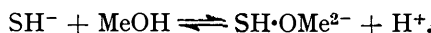being assumed that all four relate to addition of methoxide ions to SH^- according to

$$SH^- + OMe^- \rightleftharpoons SH \cdot OMe^{2-} + qMeOH$$
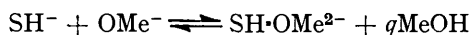
the relevant acidity function to be considered is J_{2-} where

$$J_{2-} = pK' + \log_{10} ([SH \cdot OMe^{2-}]/[SH^-]) \qquad (8)$$

$$= pK_{MeOH} + \log_{10} [OMe^-] - q \log_{10} a_{MeOH} + \log_{10} (f_{OMe^-}f_{SH^-}/f_{SH \cdot OMe^{2-}}) \qquad (9)$$

and K' is the equilibrium constant for

$$SH^- + MeOH \rightleftharpoons SH \cdot OMe^{2-} + H^+.$$

[10] J. Meisenheimer, *Annalen*, 1902, **323**, 205.
[11] R. W. Taft, jun., *J. Amer. Chem. Soc.*, 1960, **82**, 2965.

The agreement between the J_2- function relevant to these equilibria and the J_- function for the 2,4-dinitroanisole $+$ methoxide reaction suggests by comparison of equations 7 and 9 that in these cases the solvation factors m and q are identical. If this were a general result for any organic substrate adding to methoxide then the J_- function defined could provide a useful criterion of mechanism in concentrated sodium methoxide solutions particularly in view of its large deviation from H_-. However, a study of the ionisation of hindered phenols in sodium methoxide solutions suggests that the H_- function is not independent of the class of indicator used to measure it,[1] and if this is so the use of acidity functions as a criterion of mechanism will be limited.

The two remaining equilibria which involve interaction between SH^{2-} and sodium methoxide provide acidity functions which closely agree with the H_- scale (Figure 4). However, whether these reactions relate to methoxide addition to SH^{2-} (appropriate acidity function J_3-) or proton abstraction from SH^{2-} (appropriate function H_3-) must be in doubt.

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