Meisenheimer Adduct Formation between 2,4-Dinitrophenetole and Ethanolic Alkali Ethoxide Solutions: the Course of the Acidity Function J_E and Thermodynamic Solvent Isotope Effects

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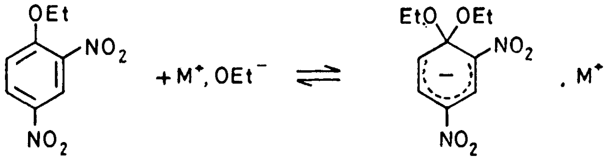
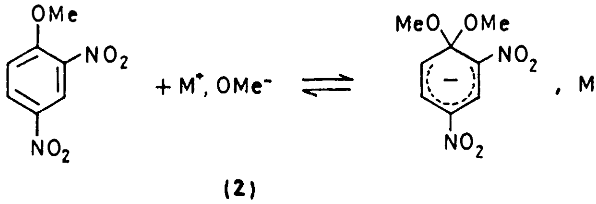
Spectrophotometric measurements of the equilibrium constant (K_{app}) for formation of a Meisenheimer adduct from 2,4-dinitroanisole and ethanolic sodium and potassium ethoxide have been used to define an acidity function J_E for alkoxide solutions in ethanol (analogous to the functions J_M for methanol). Sodium and potassium ethoxide behave identically up to a concentration of *ca.* 0.3 mol dm^{-3}; above this value solutions of sodium ethoxide are slightly less basic. The dependence of K_{app} on base concentration is interpreted in terms of ion-pairing effects. The formation of a 1 : 2 adduct becomes significant at high base concentrations, and appears to involve cation-specific ion-pairing effects. The limiting value of log K_{app} at low concentrations is −3.1. In EtOD solutions of the same alkoxide concentration, the equilibrium constant is greater than that in EtOH solutions by a factor of 2.5. This result and measurements in mixtures of EtOH and EtOD are consistent with the formulation of the ethoxide ion as an entity containing three hydrogen-bonded solvent molecules, and a deuterium fractionation factor of *ca.* 0.72—0.73 for the hydrogen-bonded positions.

By comparison with the large amount of reliable information available about the basicity of solutions of alkali hydroxides in water and also of alkali methoxide solutions in methanol[1,2] there are relatively few published quantitative data on the behaviour of alkali ethoxides in ethanol.[3] It is generally known that such solutions are more basic than methoxide solutions of the same concentration,[4,5] and also that organic substances are commonly more soluble in ethanol. For these reasons, ethanolic sodium or potassium ethoxide is often employed as a medium for base-catalysed organic reactions. The present paper provides information on two aspects of this solvent system, complementing a recent paper by Crampton.[4]

First, we have studied equilibrium (1) for M = Na and K, covering a wide concentration range of alkoxide, from *ca.* 3×10^{-3} to 2.4M (2.6M for sodium ethoxide). The dependence of the equilibrium constant for formation of the Meisenheimer adduct from 2,4-dinitrophenetole (DNP) on the nature of the cation has been examined, and the measurements are compared with analogous data[5,6] on the reaction (2) of methanolic sodium methoxide with 2,4-dinitroanisole (DNA). Indicator measurements on the latter system have been used to define an acidity function[6,7] J_M. Correspondingly, our data on reaction (1) with DNP can be expressed in terms of an analogous acidity function J_E for ethanol.



(1)



(2)

Secondly, we report determinations of the solvent isotope effects K_D/K_H and K_n/K_H between normal ethanol (C_2H_5OH), deuteriated ethanol (C_2H_5OD), and partially deuteriated ethanol (deuterium atom fraction *n* in the hydroxy group), where the subscripted *K* is the apparent equilibrium constant of reaction (1). As in corresponding studies on aqueous and methanolic systems,[8] these results have been examined in terms of the solvation of the alkoxide ion.

EXPERIMENTAL

Reagents.—Ethanol (AnalaR) was kept overnight over CaO and distilled after decantation. The distillate was kept over molecular sieve in a dry atmosphere.

Ethanolic solutions of sodium and potassium ethoxide were prepared in an inert atmosphere and with cooling by the addition of small pieces of metal which had been washed in light petroleum and dried in a stream of nitrogen. The solutions were centrifuged in closed tubes, protected from the atmosphere, and were always maintained under strict exclusion of atmosphere.

Anhydrous ethan[^{2}H]ol (99% minimum; Merck, Sharp and Dohme) was used without further purification. Different mixtures of EtOH–EtOD were prepared by weight and the corresponding solutions of sodium ethoxide were prepared from these mixtures.

2,4-Dinitrophenetole was prepared by a modification of a literature method[9] from 1-chloro-2,4-dinitrobenzene (10 g) suspended in ethanol (50 cm^3) by treatment with 6 cm^3 of an aqueous solution of 30% sodium hydroxide. The yellow precipitate formed was filtered off, washed (water and 0.1M aqueous sodium hydroxide), crystallised (fine needles) three times from dry ethanol, and dried under reduced pressure, first at room temperature and then at 90 °C (above the m.p.). The solidified melt was ground up, m.p. (block) 85.5 °C (lit.,[10] 85.5 °C).

Equilibrium Measurements.—Spectroscopic measurements were made at 25 °C either on a Unicam SP 800 or (for weak absorbances) on a Cary 16 spectrophotometer. Three different procedures were used, depending on the concentration of the base.

For intermediate concentrations of ethoxide (0.2—1.5 mol dm^{-3}), different mixtures were prepared in the quartz spectrophotometer cells by the addition of a volume V_1 of a stock solution of ethoxide and of a volume V_2 of ethanol. The cuvettes were maintained at 25 °C in a thermostat bath together with a stock solution of DNP. After several minutes a volume V_3 of the stock solution of DNP was added to the cell, so that the total volume $(V_1 + V_2 + V_3)$ was equal to 2 ml. Identical ethoxide solutions were taken as reference.

For more concentrated solutions of base the technique of measurement was slightly different, owing to the difficulty of obtaining sufficiently concentrated ethoxide solutions. The concentrated solution of ethoxide (2 ml) was introduced into a cell at 25 °C. Measured amounts of a concentrated solution of DNP, amounting to a few microlitres, were then added. The absorbance before the introduction of DNP was measured at a fixed wavelength (496 nm for sodium ethoxide or 498 nm for potassium ethoxide). For the most concentrated solutions of ethoxide the absorbance at the absorption maximum decreases slowly with time after the mixture is prepared. In these cases readings were taken over a period of time and extrapolated to zero time.

For low concentrations of ethoxide the measurements were carried out on the more sensitive Cary 16 spectrophotometer, with a double-walled thermostatted cell into which 2 ml of a concentrated solution of DNP were introduced. After equilibration a few microlitres of a concentrated solution of ethoxide (drawn from a screw-cap system vial to exclude carbon dioxide) were added to the cell. The reference cell contained ethanol. The concentration of ethoxide was calculated from the concentration of the stock solution and the volume used on the assumption of additivity of volumes. By this method it was possible to measure absorbances down to 0.01.

For ethoxide concentration lower than 1.5M the spectra did not show a significant change with time. On the other hand, when ethanol of AnalaR quality was used without prior distillation from CaO, there was a fairly rapid decrease of the band characteristic of the complex, corresponding to the disappearance of the red colour and the development of a yellow colour. This points to the requirement of using a dried sample of ethanol.

Solutions of ethoxide were titrated with HCl (0.1 or 1M) using both Bromothymol Blue and phenolphthalein in order to detect a possible contamination of the solutions by carbon dioxide. In no case was there a discrepancy between the two titres.

RESULTS

Absorption Spectra.—Solutions of DNP exhibited two new absorption bands in the presence of alkali ethoxide (at 496 and near 340 nm for sodium ethoxide, and at 498 and near 340 nm for potassium ethoxide). These bands correspond closely to those observed for 2,4-dinitroanisole in methanolic sodium methoxide solutions and are attributed to a 1 : 1 Meisenheimer adduct. The intensity of these bands rose rapidly with increasing concentration of ethoxide up to a concentration of 2 mol dm^{-3} approximately, with an accompanying decrease of the absorption band characteristic of DNP, $\lambda_{max.}$ 293 nm ($\varepsilon_{max.}$ 11 900). Up to that concentration both ethoxides show qualitatively the same behaviour. Beyond 2 mol dm^{-3} the two systems diverge. The apparent molar extinction coefficient at 498 nm in potassium ethoxide solutions tends towards a limiting value, suggesting that, for solutions of *ca.* 2.5 mol dm^{-3}, formation of the 1 : 1 adduct according to equation (1) is virtually complete. The limiting absorption corresponds to a value $\varepsilon_{498}^{1:1} = 25\,000$ for the molar extinction coefficient of the 1 : 1 adduct at 498 nm (*cf.* reported values of 25 800 [6] and 22 500 [5] at 500 nm for the 1 : 1 adduct of DNA and potassium methoxide in methanol). For solutions of sodium ethoxide the absorption intensities at 496 and 340 nm each pass through a maximum at a concentration of *ca.* 2.15 mol dm^{-3} and progressively decrease at higher base concentrations. Such a decrease in absorptions has also been observed in methoxide solutions of DNA and is attributed to the formation of a 1 : 2 adduct.[5,6] These changes in absorption intensity are quantitatively expressed in Table 1; the dependence of the absorption intensity on the logarithm of the ethoxide concentration is sketched in Figure 1. The limits of observation (4.28 × 10^{-3}—2.56 for sodium ethoxide and 3.3 × 10^{-3}—2.38 mol dm^{-3} for potassium ethoxide solutions) were set by the lowest measurable apparent molar extinction coefficient at low ethoxide concentrations and by the solubility of the ethoxides at high concentrations.

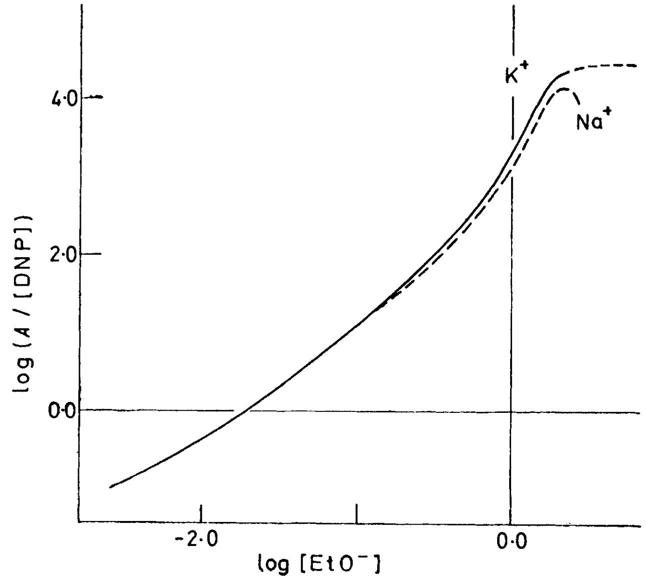


FIGURE 1 Dependence of apparent molar absorption coefficient on concentration of base

The absorbance of DNP is negligible near 500 nm. Since the presence of 1 : 2 adduct is not noticeable except at very high concentrations, equation (3) relates the absorbances (A) at 293 and 498 nm. The subscript st denotes a stoicheiometric concentration. Using equation (3), the following molar extinction coefficients were graphically deduced from the results for potassium ethoxide solutions: $\varepsilon_{293}^{1:1} =$ 4 500, $\varepsilon_{498}^{1:1} = 25\,000$, $\varepsilon_{293}^{DNP} = 11\,900$ dm^3 mol^{-1} cm^{-1}. The value of ε_{293}^{DNP} was independently checked by measurements in neutral methanol.

$$\frac{A_{293}}{[\mathrm{DNP}]_{st}} = \frac{A_{498}}{[\mathrm{DNP}]_{st}} \frac{\varepsilon_{293}^{1:1} - \varepsilon_{293}^{\mathrm{DNP}}}{\varepsilon_{498}^{1:1}} + \varepsilon_{293}^{\mathrm{DNP}} \qquad (3)$$

Terrier has reported a small difference between the molar absorption coefficients of the sodium (ε 25 200) and potassium methoxide (ε 25 800) Meisenheimer adducts of DNA.[6] As the value of $\varepsilon_{496}^{1:1}$ for DNP cannot be obtained as an

TABLE 1

Results of measurements in OEt^-–EtOH solutions

$[OEt^-]$/M	$10^3[DNP]_{st}$/M	A_{496}	($\log K_{app}$)
(a) NaOEt			
0.004 28	84.1	0.0147	−2.778
0.006 80	83.5	0.0280	−2.695
0.008 46	83.1	0.0300	−2.757
0.0100	66.5	0.0275	−2.771
0.0124	81.6	0.0477	−2.714
0.0124	66.0	0.0347	−2.760
0.0125	82.1	0.0495	−2.704
0.0165	81.1	0.0720	−2.656
0.0195	64.5	0.0700	−2.642
0.0240	79.0	0.1105	−2.621
0.0240	63.7	0.0830	−2.653
0.0262	84.0	0.160	−2.527
0.0262	83.5	0.155	−2.536
0.0348	83.0	0.221	−2.504
0.0348	83.5	0.227	−2.494
0.0433	83.0	0.320	−2.438
0.0517	82.0	0.380	−2.435
0.0641	82.0	0.535	−2.380
0.0680	81.4	0.562	−2.381
0.0680	65.5	0.455	−2.378
0.0845	65.0	0.615	−2.338
0.0845	65.0	0.600	−2.349
0.0845	81.1	0.790	−2.326
0.0845	81.1	0.775	−2.337
0.119	19.9	0.348	−2.220
0.1315	78.5	1.345	−2.272
0.161	62.0	1.48	−2.215
0.161	77.0	1.90	−2.203
0.168	18.8	0.520	−2.170
0.210	18.8	0.770	−2.096
0.232	9.4	0.420	−2.104
0.252	18.8	1.025	−2.051
0.252	9.4	0.495	−2.067
0.294	9.4	0.666	−2.004
0.294	18.8	1.33	−2.005
0.310	9.4	0.71	−1.999
0.317	11.0	0.90	−1.974
0.317	20.0	1.615	−1.980
0.336	18.8	1.67	−1.962
0.336	9.4	0.865	−1.948
0.348	9.4	0.87	−1.961
0.378	9.4	1.08	−1.902
0.387	9.4	1.09	−1.908
0.420	9.4	1.32	−1.862
0.426	3.74	0.502	−1.887
0.426	9.4	1.32	−2.778
0.464	4.71	0.76	−1.844
0.473	4.15	0.683	−1.842
0.503	4.71	0.90	−1.805
0.511	2.99	0.610	−1.783
0.532	3.74	0.815	−1.771
0.541	1.42	0.344	−1.732
0.542	4.71	1.050	−1.769
0.580	4.71	1.23	−1.730
0.603	3.95	1.18	−1.687
0.649	1.42	0.510	−1.638
0.745	3.74	1.78	−1.573
0.757	1.42	0.79	−1.511
0.852	1.87	1.31	−1.460
0.865	1.42	1.105	−1.419
0.904	0.395	0.315	−1.428
0.959	0.374	0.360	−1.386
0.988	0.902	1.04	−1.300
1.065	0.374	0.495	−1.270
1.10	0.902	1.48	−1.184
1.19	0.288	0.57	−1.130
1.30	0.288	0.805	−1.002
1.41	0.288	1.09	−0.886
1.51	0.288	1.34	−0.807
1.53	0.112	0.600	
1.66	0.109	0.81	
1.76	0.182	1.53	
1.87	0.075	0.89	
1.91	0.111	1.29	
2.00	0.092	1.15	
2.04	0.108	1.45	
(a) NaOEt (*Continued*)			
$[OEt^-]$/M	$10[DNP]/_{st}$M	A_{496}	($\log K_{app}$)
2.12	0.074	1.01	
2.17	0.1105	1.57	
2.17	0.1115	1.50	
2.25	0.073	1.01	
2.31	0.109	1.52	
2.37	0.076	1.00	
2.42	0.110	1.43	
2.50	0.074	0.75	
2.50	0.075	0.85	
2.56	0.109	1.21	
(b) KOEt			
0.0033	84.4	0.0110	−2.800
0.0075	83.5	0.0230	−2.833
0.0075	83.5	0.0247	−2.802
0.0107	83.0	0.0382	−2.764
0.0158	82.0	0.063	−2.710
0.208	81.0	0.087	−2.684
0.208	81.0	0.087	−2.684
0.0305	79.0	0.148	−2.610
0.0327	83.5	0.200	−2.534
0.0398	77.3	0.210	−2.563
0.0433	83.3	0.295	−2.485
0.0539	82.9	0.395	−2.452
0.075	82.0	0.610	−2.400
0.085	82.0	0.768	−2.355
0.105	80.9	1.02	−2.319
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0.118	20.6	0.330	−2.265
0.125	80.2	1.30	−2.285
0.148	20.6	0.48	−2.200
0.154	79.1	1.87	−2.212
0.175	15.4	0.47	−2.156
0.188	19.3	0.67	−2.131
0.200	15.4	0.60	−2.107
0.207	20.4	0.87	−2.084
0.219	14.2	0.66	−2.070
0.225	15.4	0.73	−2.082
0.251	19.3	1.11	−2.037
0.253	15.4	0.90	−2.040
0.282	14.2	1.06	−1.973
0.313	19.3	1.80	−1.922
0.366	8.75	1.10	−1.860
0.412	8.75	1.49	−1.779
0.470	1.75	0.38	−1.730
0.522	1.75	0.465	−1.686
0.547	1.75	0.51	−1.666
0.575	1.75	0.60	−1.616
0.595	1.75	0.66	−1.568
0.640	1.47	0.65	−1.553
0.650	1.75	0.84	−1.521
0.700	1.75	1.03	−1.462
0.720	1.46	0.94	−1.438
0.750	1.75	1.29	−1.393
0.765	1.35	1.08	−1.364
0.800	1.47	1.35	−1.320
0.815	1.35	1.28	−1.314
0.860	1.35	1.38	−1.306
0.895	0.93	1.15	−1.234
0.970	0.855	1.48	−1.115
0.980	0.930	1.56	−1.133
1.07	0.560	1.29	−1.024
1.12	0.292	0.78	−0.972
1.20	0.295	1.00	−0.884
1.28	0.290	1.24	−0.792
1.38	0.184	1.03	−0.680
1.40	0.109	0.62	−0.677
1.465	0.179	1.23	−0.587
1.48	0.110	0.80	−0.557
1.56	0.109	0.94	−0.473
1.56	0.112	0.995	−0.452
1.64	0.110	1.16	−0.350
1.64	0.111	1.17	−0.352
1.64	0.111	1.15	−0.365
1.88	0.109	1.63	−0.102
2.13	0.075	1.48	0.259
2.38	0.055	1.20	0.478

asymptotic limit from measurements at high concentrations of sodium ethoxide, we have assumed a similar small difference to apply between sodium and potassium ethoxide adducts of DNP, and accordingly estimate $\varepsilon_{496}^{1:1} = 24\,400$ for the adduct with sodium ethoxide.

The apparent equilibrium constant for reaction (1), defined in equation (4), can be expressed by equation (5)

$$K_{\mathrm{app}} = [1:1]/([\mathrm{OEt}^-][\mathrm{DNP}]) \qquad (4)$$

$$K_{\mathrm{app}} = \left(\frac{A/[\mathrm{DNP}]_{\mathrm{st}}}{\varepsilon - A/[\mathrm{DNP}]_{\mathrm{st}}}\right)/[\mathrm{OEt}^-] \qquad (5)$$

where ε is the molar extinction coefficient at the absorption maximum of the 1 : 1 adduct near 500 nm and A is the measured absorbance at the same wavelength.

Analogous measurements were carried out with sodium ethoxide in ethan[^{2}H]ol (EtOD) and in five mixtures of EtOH and EtOD. In the calculation of the apparent equilibrium constants [defined according to equation (4) but here designated by subscripted symbols K_{H}, K_{D}, or K_{n}] it was assumed that the molar extinction coefficient at the absorption maximum of the adduct has the same value in isotopically different solvents. In order to minimise the consequences of an error caused by this assumption in the determination of the isotope effect, the study was restricted to relatively low ethoxide concentrations for which the concentration of 1 : 1 adduct was always small relative to the stoicheiometric concentration of DNP (Table 4). The calculated atom fractions of deuterium in mixtures were based on the stated deuterium content of the commercial sample (99%).

The variation of log K_{app} with concentration of sodium ethoxide in different isotopic solvent mixtures and in EtOH and EtOD is represented in Figure 2. The values of K_{app} at rounded concentrations of 0.2, 0.3, and 0.4 mol dm^{-3} (Table 5) were obtained by interpolation. The corresponding ratios $K_{\mathrm{n}}/K_{\mathrm{H}}$ show no significant dependence on ethoxide concentration (Table 5).

TABLE 2

Test of equation (9) (see text for values of parameters)

[OEt⁻]	$y_\pm$	α	(log K_{app}) [equation (6)]	(log K_{app})calc [equation (6)]
(a) NaOEt				
0.001	0.845	0.936	−2.95	−2.97
0.002	0.804	0.895	−2.90	−2.90
0.005	0.744	0.813	−2.80	−2.78
0.010	0.698	0.733	−2.72	−2.68
0.020	0.653	0.641	−2.62	−2.60
0.050	0.600	0.514	−2.46	−2.48
0.100	0.566	0.421	−2.32	−2.36
0.200	0.536	0.337	−2.14	−2.24
(b) KOEt				
0.001	0.844	0.943	−2.99	−3.01
0.002	0.803	0.905	−2.93	−2.93
0.005	0.742	0.829	−2.84	−2.81
0.010	0.695	0.753	−2.75	−2.70
0.020	0.650	0.664	−2.64	−2.62
0.050	0.597	0.537	−2.48	−2.48
0.200	0.532	0.355	−2.12	−2.20

TABLE 3

Comparison of J_{E} and J_{M} scales

[OR⁻]/M	$J_{\mathrm{E}}(\mathrm{K}^+)$	$J_{\mathrm{M}}(\mathrm{K}^+)$	Diff	$J_{\mathrm{E}}(\mathrm{Na}^+)$	$J_{\mathrm{M}}(\mathrm{Na}^+)$	Diff
0.001	16.06	13.92	2.14	16.06	13.92	2.14
0.010	17.30	15.10	2.20	17.29	15.10	2.19
0.100	18.73	16.50	2.17	18.69	16.45	2.24
0.500	20.05	17.87	2.18	19.92	17.75	2.17
1.000	20.96	18.75	2.21	20.70	18.58	2.22
2.000	22.39	20.15	2.24			
2.500	23.04	20.86	2.18			

TABLE 4

Equilibrium constants in EtOH–EtOD mixtures as a function of concentration of OEt⁻

$n = 0.99$		$n = 0.79$		$n = 0.50$	
[OEt⁻]/M	−log K_{app}	[OEt⁻]/M	−log K_{app}	[OEt⁻]/M	−log K_{app}
0.146	1.805	0.107	1.935	0.117	2.079
0.1755	1.761	0.128	1.919	0.146	2.029
0.205	1.728	0.171	1.848	0.175	1.966
0.233	1.670	0.214	1.782	0.184	1.945
0.234	1.686	0.257	1.735	0.205	1.929
0.263	1.664	0.300	1.704	0.221	1.899
0.280	1.665	0.300	1.704	0.234	1.890
0.292	1.619	0.342	1.632	0.258	1.853
0.292	1.612	0.385	1.592	0.263	1.862
0.332	1.573	0.428	1.560	0.293	1.829
0.326	1.562			0.293	1.825
0.351	1.548			0.295	1.818
0.372	1.522			0.322	0.793
0.380	1.501			0.332	1.780
0.409	1.492			0.351	1.747
0.420	1.475			0.351	1.758
0.439	1.476			0.369	1.745
0.466	1.443			0.380	1.726
0.512	1.400			0.405	1.706
0.622	1.296			0.410	1.704
				0.442	1.679
				0.479	1.640

$n = 0.60$		$n = 0.40$		$n = 0.20$	
[OEt⁻]/M	−log K_{app}	[OEt⁻]/M	−log K_{app}	[OEt⁻]/M	−log K_{app}
0.154	1.931	0.176	2.005	0.232	1.993
0.193	1.875	0.211	1.947	0.290	1.918
0.243	1.835	0.246	1.905	0.348	1.875
0.257	1.799	0.282	1.856	0.348	1.867
0.308	1.721	0.317	1.833	0.406	1.803
0.349	1.712	0.352	1.788	0.464	1.743
0.385	1.662	0.387	1.749	0.522	1.708
0.423	1.631	0.422	1.712		
0.462	1.603	0.458	1.692		

TABLE 5

Solvent isotope effects on K_{app} at rounded interpolated concentrations of base [a]

	[OEt⁻] = 0.2M		[OEt⁻] = 0.3M		[OEt⁻] = 0.4M	
n	10^2K_{app}	$K_{\mathrm{n}}/K_{\mathrm{H}}$	10^2K_{app}	$K_{\mathrm{n}}/K_{\mathrm{H}}$	10^2K_{app}	$K_{\mathrm{n}}/K_{\mathrm{H}}$
0	0.758		1.00		1.294	
0.20			1.202	1.20	1.545	1.19
0.40	1.086	1.43	1.422	1.42	1.824	1.41
0.50	1.186	1.56	1.538	1.54	1.950	1.51
0.60	1.349	1.78	1.762	1.76	2.250	1.73
0.79	1.542	2.03	2.04	2.04	2.63	2.03
0.99	1.870	2.46	2.48	2.48	3.205	2.48

[a] $K_{\mathrm{n}}/K_{\mathrm{H}} = (K_{\mathrm{app}})_{\mathrm{n}}/(K_{\mathrm{app}})_{\mathrm{H}}$.

DISCUSSION

Dependence of K$_{\mathrm{app}}$ *on Ethoxide Concentration.*—It has previously been noted that the value of K_{app} corresponding to reaction (2), defined and evaluated by exact analogy with equations (4) and (5), varies with the concentration of alkali methoxide.[6,7] Linear extrapolations of plots of log K_{app} against either [OMe⁻] or [OMe⁻]$^{1/2}$ to zero concentration have been employed in attempts to obtain a thermodynamic value of K at infinite dilution.[6,7] Our measurements with ethoxides show a similar pattern, in that log K_{app} is an approximately linear function of $[OEt^-]$ above *ca.* 0.5 mol dm^{-3}, but this does not hold at lower concentrations, and an extrapolation of the linear portion of the curve does not give a correct intercept, as previously noted for the methoxide results.[11] (The present measurements extend to lower alkoxide concentrations than the results for methoxide and therefore afford a more demanding test of the behaviour at low concentrations.) The alternative procedure of plotting log K_{app} against $[OEt^-]^{1/2}$ again yields a linear graph over only a limited concentration range and fails to give a satisfactory extrapolation.

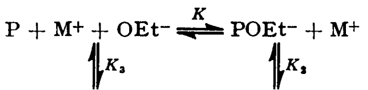
We find that an empirical representation of the results is provided by equation (6). A good fit of the data, according to the least-squares criterion, is provided by

$$\log K_{app} = \log K + a[OEt^-]^{1/2}/(1 + b[OEt^-]^{1/2}) + d[OEt^-] \quad (6)$$

this equation with the parameters log $K = -3.11$, $a = 5.77$, $b = 5$, $d = 0.844$ in the case of sodium ethoxide (standard deviation 0.026), and log $K = -3.15$, $a = 5.87$, $b = 5$, $d = 1.081$ for potassium ethoxide (standard deviation 0.029). In this curve-fitting the choice of b is not very critical. The mean value p$K = 3.13$ should be compared with p$K = 4.30$ for the reaction of DNA with methoxide in methanol. The difference probably reflects the greater Lewis basicity of the ethanolic ethoxide ion but may also be partly due to the change of substrate.

Crampton and Khan have suggested that the variation of K_{app} with methoxide concentration for reaction (2) is due to ion association, and that this is more marked between the cation and the anionic Meisenheimer adduct than between the cation and methoxide ion.[12] Because of the lower dielectric constant (relative permittivity) of the solvent one would expect such an effect to become more pronounced in ethanol solution. We have accordingly applied this model to our data, as has Crampton [4] for similar experiments on this system. Since our measurements go down to quite low ionic strengths, Crampton's treatment has been extended by the inclusion of an ionic strength effect according to a Debye–Hückel approximation.

Equilibrium (1) is accordingly represented by the



$$\begin{tikzcd} P + M^+ + OEt^- \arrow[r, shift left, "K"] \arrow[d, shift left, "K_3"] & POEt^- + M^+ \arrow[l, shift left] \arrow[d, shift left, "K_2"] \\ P + \{M^+, OEt^-\} \arrow[u, shift left] & \{POEt^-, M^+\} \arrow[u, shift left] \end{tikzcd}$$

SCHEME

Scheme, in which K_2 and K_3 represent the ion-pair association constants, as defined by Crampton and Khan.[12] The spectrophotometric determination is assumed to measure the sum of the concentrations of free and associated adduct, *i.e.* $POEt^-$ and $\{POEt^-, M^+\}$.

If it is assumed, as is usually done, that the activity coefficient for the ion pair $\{EtO^-, M^+\}$ is equal to unity, the degree of dissociation (α) of metal ethoxide ion pairs is given by equation (7) where y is the mean activity

$$K_3 = (1 - \alpha)/(\alpha^2 y^2[OEt^-]) \quad (7)$$

coefficient for free ions[13] of the two electrolytes appearing in the Scheme. The value of y is related to the overall concentration of ethoxide ($[OEt^-]$) by a modified

$$-\log y = A(\alpha[OEt^-])^{\frac{1}{2}}/\{1 + Bq(\alpha[OEt^-])^{\frac{1}{2}}\} \quad (8)$$

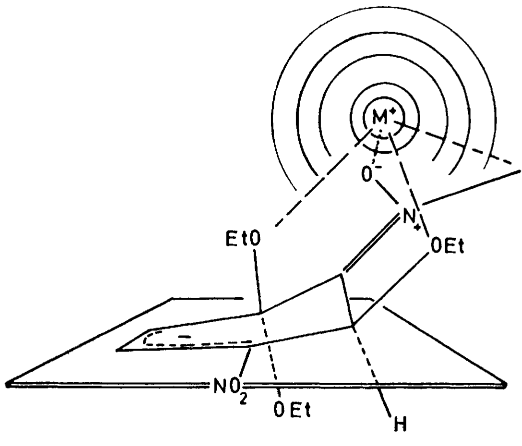
Debye–Hückel equation (8) in which $A = 2.391$, $B = 5.907$ mol^{-1} dm^3 nm^{-1} (the Debye–Hückel parameters for ethanol at 25°) and q is the Bjerrum critical distance ($e^2/2DkT$) which has the value 1.153 nm in this system.[14] The Bjerrum distance is used in equation (8) because interactions within this distance between ions have already explicitly been taken into account by the introduction of ion-pair association [equation (7)]. The two unknowns α and y were evaluated from equations (7) and (8) by iteration, on the assumption of Barthel's revised values[14] of K_3, deduced from conductivity measurements ($K_3 = 102 \pm 8$ mol^{-1} dm^3 for sodium ethoxide, 90 ± 4 mol^{-1} dm^3 for potassium ethoxide).

Restricting the treatment to the case $[OEt^-] \gg [POEt^-]_{total}$, the apparent and thermodynamic equilibrium constants for reaction (1) are then related by expression (9) given by Crampton and Khan,[12] where

$$K_{app} = K(1 + K_2\beta)/(1 + K_3\beta) \quad (9)$$

$\beta = \alpha y^2[OEt^-]$ and in which the activity coefficient of the ion pair $\{POEt^-, M^+\}$, as well as that of $\{EtO^-, M^+\}$, is assumed to be unity. By insertion of the calculated values of α and y and a range of trial values of K_2 it is found that equation (9) satisfactorily accounts for the variation of K_{app} with concentration up to nearly 0.1M-ethoxide if $K_2 \simeq 700$ mol^{-1} dm^3 (see Table 2). As expected this value is much larger than that (K_2 25—90 mol^{-1} dm^3) deduced for methoxide systems.[12] (Using Barthel's older value[15] of $K_3 = 50$ mol^{-1} dm^3 for sodium ethoxide, Crampton[4] derived a value of 200 mol^{-1} dm^3 for K_2.)

The difference between the values of K_3 for sodium and potassium ethoxide is hardly outside the limits of experimental error, and similarly the same value of K_2 satisfies the results for both sodium and potassium Meisenheimer adducts. By contrast, sodium and potassium ethoxide systems behave quite differently at high concentrations, with a 1 : 2 adduct apparently being formed much more readily in the former case. It seems likely that this divergence is caused by a larger ion-pair association constant of the dianion (1) with sodium ions than with potassium ions. This difference may possibly be due to clathrate-like binding of a cation of suitable size within the cradle of oxygen atoms present in the dianion, as schematically indicated in the formula. Preliminary (unpublished) measurements (by J. T.) indicate that the decrease in intensity of the absorption at 500 nm is much more pronounced at high concentrations of lithium ethoxide than at corresponding concentrations of sodium ethoxide, and is evident even at moderate concentrations. This adds support to our interpretation that the effect is due to 1 : 2 adduct formation and that this, in turn, is profoundly influenced by size-dependent cation binding.



(1)

Whatever the precise causes of the non-ideal concentration dependence of the basicity of alcoholic alkoxide solutions, it ought not to escape notice that there is a close parallelism between the ethoxide and methoxide media. It is possible to use our experimental data to evaluate the acidity function J_E [formally defined according to equation (10) where K_E is the autoprotolysis constant of ethanol]. When these values are plotted against Terrier's values [6] of J_M at the same concentration of base, one obtains an exact straight line of slope 1.01, and the points for both sodium and potassium alkoxides fall on the same line. At the same concentration of base, the J_E values of solutions of ethoxide are greater, by *ca.* 2.1—2.2 units, than the corresponding J_M values (see Table 3).

$$J_E = pK + pK_E + \log ([POEt^-, M^+]/[DNP]) \quad (10)$$

Solvent Isotope Effect.—The ratio of K_{app} in ethan[^{2}H]ol solution to the corresponding value at the same base concentration in ethanol (K_D/K_H) has the extrapolated value of 2.53. This result is very close to that of Bernasconi's analogous measurements on DNA in methanolic methoxide media (K_D/K_H 2.6).[11] The parallelism extends further, and it is possible to account for this result and for our measurements of K_n/K_H (relating to partially deuteriated ethanol solutions) in a more quantitative fashion by applying the solvent isotope theory, originally developed for methanol,[8] also to ethanol, as follows.

In order to recognise explicitly the involvement of exchangeable hydrogen atoms in equilibrium (1), we write this reaction according to equation (11). The solvent isotope effect is then given by equations (12) and (13) where n denotes the atom fraction of hydroxylic deuterium in the solvent and the subscripts σ, S, and OEt refer to the hydrogen-bonded hydroxylic hydrogen atoms in POEt⁻, P, and OEt⁻, respectively. The fractionation factors ϕ express the ratio of the abundance of deuterium, in the positions indicated, to the abundance of deuterium in bulk ethanol. As in the case of the corresponding solvent isotope effect for the reaction between 2,4-dinitroanisole and methanolic sodium methoxide,[11] the observed value of K_D/K_H is consistent with equation (12) if one assumes that $\phi_\sigma{}^p/\phi_S{}^s$ does not significantly differ from unity, and that the value of m is 3. (The former assumption is justifiable on the ground that the hydrogen bonds of ethanol bonded to POEt⁻ and P are expected to be much weaker than those to OEt⁻.) Equation (14) then follows.

$$\begin{aligned} &P, s\mathrm{EtOH} + \mathrm{OEt}^-, m\mathrm{EtOH} \rightleftharpoons \\ &\qquad \mathrm{POEt}^-, p\mathrm{EtOH} + (m + s - p)\mathrm{EtOH} \quad (11) \end{aligned}$$

$$K_D/K_H = \phi_\sigma{}^p/\phi_S{}^s\phi^m{}_{OEt} \quad (12)$$

$$\frac{K_n}{K_H} = \frac{(1 - n + n\phi_\sigma)^p}{(1 - n + n\phi_S)^s(1 - n + n\phi_{OEt})^m} \quad (13)$$

$$K_D/K_H = \phi^{-3}{}_{OEt} \quad (14)$$

The requisite value of ϕ_{OEt} has been measured by the n.m.r. method in two laboratories. Beltrame *et al.*[16] reported a value of 0.72 at a temperature of 42 °C (recalculated [17] 0.71), and measurements in our laboratory [17] (at 34.8 °C) gave a value of 0.72. Both results are uncorrected for counterion effects which, by analogy with the analysis given for methanol,[8] may raise these values by *ca.* 0.01, and there may be a further slight correction to obtain from these results the value applicable at 25 °C, the temperature to which our spectrophotometric measurements relate. The value of ϕ_{OEt} required to

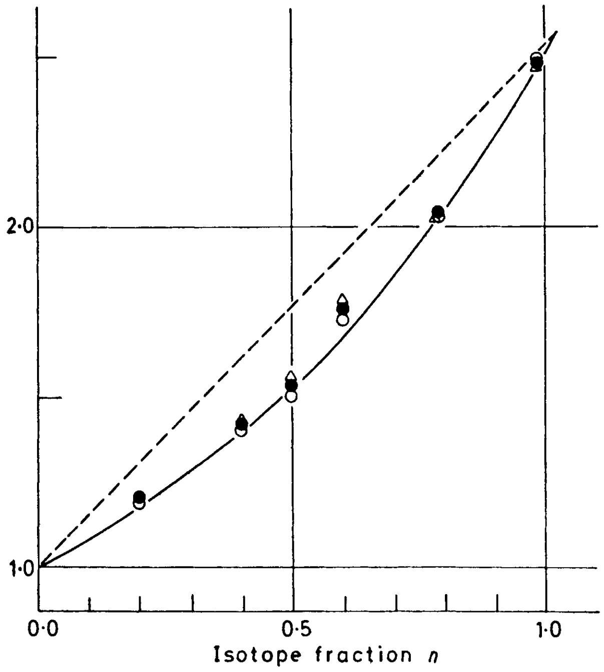


FIGURE 2 Variation of K_n/K_H with n. (triangles, [NaOEt] =0.2M; filled circles, [NaOEt] = 0.3M; open circles, [NaOEt] =0.4M). The curve is calculated from equation (13), with $\phi_\sigma = \phi_S = 1$, $\phi_{OEt} = 0.734$, $m = 3$

satisfy the experimental result for K_D/K_H (2.53) according to equation (14) is 0.734.

Figure 2 shows the curve of K_n/K_H calculated from equation (13) with $m = 3$; $\phi = 0.734$, $\phi_\sigma = \phi_S = 1$, together with the experimental points, confirming the adequacy of the foregoing analysis.

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REFERENCES

[1] C. H. Rochester, 'Acidity Functions,' Academic Press, New York, 1970, ch. 7.

[2] F. Coussemant, M. Hellin, and B. Torck, ' Les fonctions d'acidité et leurs utilisations en catalyse acido-basique,' Gordon and Breach, Paris, 1969.

[3] R. S. Stearns and G. W. Wheland, *J. Amer. Chem. Soc.*, 1947, **69**, 2025; R. Schaal and C. Gadet, *Bull. Soc. chim. France*, 1961, 2154.

[4] M. R. Crampton, *J.C.S. Perkin II*, 1977, 1442.

[5] K. Bowden, *Canad. J. Chem.*, 1965, **43**, 2624; *Chem. Rev.*, 1966, **66**, 119.

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

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

[8] V. Gold and S. Grist, *J. Chem. Soc.* (*B*), 1971, 1665, 2272, 2282.

[9] M. Marqueyrol and A. Scohy, *Bull. Soc. chim. France*, 1930, **27**, 105.

[10] L. Kofler and A. Kofler, ' Thermo-Mikro-Methoden,' Verlag Chemie, Weinheim, 1954, vol. 3, p. 422.

[11] C. F. Bernasconi, *J. Amer. Chem. Soc.*, 1968, **90**, 4982.

[12] M. R. Crampton and H. A. Khan, *J.C.S. Perkin II*, 1972, 1175; 1973, 1103.

[13] See for example, R. A. Robinson and R. H. Stokes, ' Electrolyte Solutions,' Butterworth, London, 1955.

[14] J. Barthel, J. C. Justice, and R. Wachter, *Z. phys. Chem.* (*Frankfurt*), 1973, **84**, 113.

[15] J. Barthel, G. Schwitzgebel, and R. Wachter, *Z. phys. Chem.* (*Frankfurt*), 1967, **55**, 33.

[16] P. Beltrame, A. M. Bianchi, and M. G. Cattania, *Gazzetta*, 1972, **102**, 456.

[17] K. P. Morris, Ph.D. Thesis, London, 1977.