Addition of alkoxide ions to alkenes. The $H_{\mathrm{R^-}}$ scale[1]

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By using α-cyanostilbenes as Lewis acids, Lewis acidity scales have been established in ethanolic and methanolic dimethyl sulfoxide containing the appropriate 0.01 M sodium alkoxide and in the system sodium methoxide – methanol. This scale, designated $H_{\mathrm{R^-}}$, describes the ability of the solvent to add an alkoxide ion to an alkene. The $H_{\mathrm{R^-}}$ values range from 11.73 in methanol to 21.74 in 93.27 mole % dimethyl sulfoxide in ethanol.

The most acidic indicator used to establish the scale was α-cyano-2,4-dinitrostilbene, with a pK_{A} of 12.73 in dimethyl sulfoxide – methanol. The least acidic was α-cyano-3-trifluoromethylstilbene, with a pK_{A} of 21.98 in dimethyl sulfoxide – ethanol.

The increase in the system's ability to add alkoxide ion to the cyanostilbenes as the dimethyl sulfoxide concentration rises is ascribed chiefly to its effect on the activity of the alkoxide ion. The functions H_- and $H_{\mathrm{R^-}}$, unlike their analogues in acid systems (H_0 and H_{R}), do not diverge greatly as the concentration of the hydroxylic solvent component is decreased.

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INTRODUCTION

We have previously constructed H_- scales for strongly basic solutions by making use of the greatly enhanced basicity of systems containing hydroxide or alkoxide ions in polar aprotic solvents such as dimethyl sulfoxide (DMSO) (1–4). The acidities, relative to water as the standard state, of acids as weak as aniline can be determined by this technique. The relation between H_- and pK_{HA} is

$$H_- = \mathrm{p}K_{\mathrm{HA}} + \log \frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$

for the ionization of the weak acid HA.

$$\mathrm{HA} + \mathrm{OH^-} \rightleftarrows \mathrm{A^-} + \mathrm{H_2O}$$

$$\text{or}\quad \mathrm{HA} + \mathrm{OR^-} \rightleftarrows \mathrm{A^-} + \mathrm{ROH}$$

The role of the polar aprotic solvent in pushing this equilibrium to the right is believed to result mainly from its low solvating powers for anions (5, 6). The activities of small localized ions such as $\mathrm{OH^-}$ or $\mathrm{OR^-}$ are raised by the replacement of water or alcohol with DMSO to a much greater degree than those of the large, delocalized anions that are the usual products of the ionization of weak carbon and nitrogen acids.

In the present work we have examined the effect of DMSO on a related equilibrium, the addition of alkoxide ion to unsaturated systems (eq. [1]). The ion $\mathrm{OR^-}$ is

$$[1]\qquad \mathrm{A} + \mathrm{OR^-} \rightleftarrows \mathrm{AOR^-}$$

a nucleophile, or Lewis base, rather than a Brönsted–Lowry base. Gold *et al.* (7) and Rochester (8) have previously studied the addition of alkoxide ions to polynitro aromatic compounds in alcohol solution.

One can express the addition reaction shown in eq. [1] in terms of the equilibrium shown in eq. [2]. This equation differs from

$$[2]\qquad \mathrm{A} + \mathrm{ROH} \rightleftharpoons \mathrm{AOR^-} + \mathrm{H^+}$$

eq. [1] by the addition of $\mathrm{H^+}$ to both sides of the equation. An acidity function that is analogous to the well-established functions H_0, H_-, and H_{R} (or J_0) can then be derived from this reaction. The equilibrium constant for the reaction shown in eq. [2] is as follows, where a means activity and concentrations are expressed in terms of moles per liter.

$$K_{\mathrm{A}} = \frac{a_{\mathrm{AOR^-}}a_{\mathrm{H^+}}}{a_{\mathrm{A}}a_{\mathrm{ROH}}}$$

$$= \frac{[\mathrm{AOR^-}]}{[\mathrm{A}]} \times \frac{a_{\mathrm{H^+}}f_{\mathrm{AOR^-}}}{a_{\mathrm{ROH}}f_{\mathrm{A}}}$$

$$= \frac{[\mathrm{AOR^-}]}{[\mathrm{A}]} \times h_{\mathrm{R^-}},$$

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[1] Taken in part from the Ph.D. thesis of D. J. Kroeger, University of British Columbia, Vancouver, 1966.

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where

$$h_{\mathrm{R}^-} \equiv \frac{a_{\mathrm{H}^+} f_{\mathrm{AOR}^-}}{a_{\mathrm{ROH}} f_{\mathrm{A}}}$$

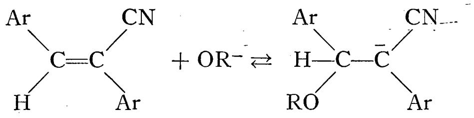
Taking negative logarithms gives

$$[3] \qquad H_{\mathrm{R}^-} = -\log h_{\mathrm{R}^-}$$

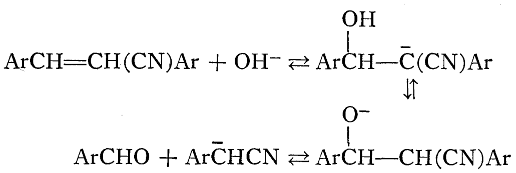
$$= \mathrm{p}K_{\mathrm{HA}} + \log \frac{[\mathrm{AOR}^-]}{[\mathrm{A}]} .$$

An equation similar to eq. [3] was derived by Rochester (8), who designated the function as J_- because of its relationship to the acidity function which governs the formation of carbonium ions from alcohols ($\mathrm{A}^+ + \mathrm{H_2O} \rightleftarrows \mathrm{AOH} + \mathrm{H}^+$). This function is designated J_0 by some, and H_{R} by others. The background of this disagreement about which symbol should be used will not be recounted (9). It is sufficient to say that the symbol H_{R} seems now to have wider usage than J_0, and that this is the basis for our selection of the symbol H_{R^-} for the function which governs the equilibrium shown in eq. [2].

The J_- scale derived by Rochester was applied to the addition of methoxide ion to polynitro aromatic compounds in methanol. We have chosen α-cyanostilbenes as our Lewis acids and have examined the position of the following equilibrium.



By substitution in the aromatic rings the Lewis acidity of these compounds can be varied, and an acidity scale can be constructed by using the conventional Hammett technique of overlapping indicators (11). These compounds have some advantages over polynitrobenzenes as substrates, since with the latter there is the possibility of more than one place of attack within the molecule, the possibility of nitrite displacement, and the probability of proton loss if polynitrated anilines are used. On the other hand, the cyanostilbenes can be used only in anhydrous systems, since cleavage occurs in the presence of labile protons (10).



$$\mathrm{ArCH{=}CH(CN)Ar} + \mathrm{OH^-} \rightleftarrows \mathrm{Ar\overset{\overset{OH}{|}}{C}H{-}\bar{C}(CN)Ar}$$

$$\downarrow\uparrow$$

$$\mathrm{ArCHO} + \mathrm{Ar\bar{C}HCN} \rightleftarrows \mathrm{Ar\overset{\overset{O^-}{|}}{C}H{-}CH(CN)Ar}$$

EXPERIMENTAL

Solvent Systems

DMSO was dried over calcium hydride and distilled under nitrogen at reduced pressure. Ethanol and methanol were purified in the usual way. Sodium methoxide and sodium ethoxide solutions were prepared by dissolving weighed amounts of solid sodium in the dry alcohols. The DMSO–alcohol stock solutions were prepared and stored as previously described (2).

Calculations

In all cases the anion absorbed in the visible part of the spectrum, and in many cases the absorption of the molecule was negligible at this wavelength (Table I). The indicator ratio of ion to molecule ($I = [\mathrm{AOR}^-]/[\mathrm{A}]$) was measured at 25° essentially as previously described (2).

After log I, for each indicator, was plotted as a function of the solvent composition (in mole percentage DMSO), a smooth curve was drawn through the points for which log I was between 1 and -1. This corresponded to using only that part of the ionization curve for which the indicator was between 10 and 90% ionized. The plots of log I for the various indicators used versus the solvent composition gave, in most cases, closely parallel slopes at any given composition. By using Hammett's method (11), pK values were then obtained by a graphical technique. For any two indicators (i and j) which ionize to an appreciable extent in a given solvent, the $\Delta\mathrm{p}K_{\mathrm{A}}$ value is given by eq. [4], where I_i and I_j refer to the

$$[4] \qquad \Delta\mathrm{p}K_{\mathrm{A}} = \log I_i - \log I_j$$

ionization ratios of the two indicators in a solvent of one particular composition. By interpolating log I values for indicators i and j at regular intervals of solvent composition, a number of $\Delta\mathrm{p}K_{\mathrm{A}}$ values were obtained by using eq. [4]. These were then averaged to obtain the $\Delta\mathrm{p}K_{\mathrm{A}}$ value between indicators i and j.

Since α-cyanostilbenes are readily hydrolyzed in basic aqueous solutions, the $\mathrm{p}K_{\mathrm{A}}$ values of the indicators could not be determined in aqueous buffer solutions. Because of this difficulty, an arbitrary $\mathrm{p}K_{\mathrm{A}}$ value of 14.42 was given to the indicator α-cyano-4,4′-dinitrostilbene, which was then used as the standard to which all other $\mathrm{p}K_{\mathrm{A}}$ values were referred. The value of 14.42 was arrived at by assuming an H_{R^-} value of 14.0 for a 0.01 M sodium ethoxide solution in ethanol, which is the same as the H_- value reported by Bowden and Stewart (4) when carbon acids were used as indicators, since H_{R^-} and H_- values should be very close in dilute basic solutions. The quantities h_- and h_{R^-} are defined as follows.

$$h_{-} \equiv \frac{a_{H^+} f_{A^-}}{f_{HA}}$$

$$h_{R^-} \equiv \frac{a_{H^+} f_{AOR^-}}{a_{ROH} f_A}$$

If the activity coefficient ratios f_{A^-}/f_{HA} and f_{AOR^-}/f_A are identical, and if the activity of the alcohol is unity, then h_- and h_{R^-} become identical. (In alcohol solution these conditions are probably nearly met.) By inserting the experimental value of -0.42 for log I for α-cyano-4,4′-dinitrostilbene in the above solution into eq. [3], the pK_A value of 14.42 was obtained.

The pK_A values of a number of substituted α-cyanostilbenes were measured relative to the arbitrary standard. The values obtained in DMSO–ethanol and DMSO–methanol are listed in Table II.

TABLE I

Cyanostilbenes and their ethoxy ion adducts in DMSO–ethanol*

Substituent	Neutral compound		Anion	
	λ_{max}	ϵ	λ_{max}	ϵ
2,4-Dinitro			480	27 100
4,4′-Dinitro†	336	32 500	553	42 100
3′-Chloro-4-nitro‡	332	28 000	547	43 700
4-Nitro§	336	27 600	547	42 600
4′-Methyl-4-nitro‖	350	28 600	547	42 800
4′-Methoxy-4-nitro¶	372	29 800	547	42 500
4-Cyano-4′-nitro	336	30 100	393	44 000
4′-Dimethylamino-4-nitro**	456	38 400	552	43 300
4-Cyano-3′-chloro	321	29 500	402	47 200
4-Cyano††	326	30 000	402	47 400
2-Nitro‡‡			603	7 630
3-Cyano-4-chloro	318	26 000	374	33 600
3-Cyano	315	23 000	363	28 800
3-Trifluoromethyl	316	22 400	353	23 700
2-Chloro-4-nitro			550	40 500
1,1-Bis(4-nitrophenyl)ethene§§			710	25 700

*The spectra in DMSO–ethanol and DMSO–methanol were almost identical.
†Melts at 214–215° (lit. m.p. 211–212° (15)).
‡Melts at 168–168.5° (lit. m.p. 161.5° (32)).
§Melts at 176–176.5° (lit. m.p. 175.6° (16)).
‖Melts at 146–147° (lit. m.p. 146–147° (33)).
¶Melts at 162–163° (lit. m.p. 165° (33)).
**Melts at 244.5–245.5° (lit. m.p. 244–246° (15)).
††Melts at 144.5–145.5° (lit. m.p. 145° (34)).
‡‡Melts at 114–145.5° (lit. m.p. 115° (35)).
§§Melts at 174–175° (lit. m.p. 175–176.5° (36)).

TABLE II

pK_A values of α-cyanostilbenes

Substituent	pK_A in DMSO–ethanol	pK_A in DMSO–methanol	pK_A in sodium methoxide – methanol
2,4-Dinitro		12.73	12.96
4,4′-Dinitro	14.42	14.42	14.42
3′-Chloro-4-nitro	15.20	15.08	15.06
4-Nitro	15.95	15.81	15.73
4′-Methyl-4-nitro	16.31	16.17	16.10
4′-Methoxyl-4-nitro	16.74	16.59	16.52
4-Cyano-4′-nitro	17.38	17.38	
4′-Dimethylamino-4-nitro	18.07	17.97	17.76
4-Cyano-3′-chloro	18.23	18.13	
4-Cyano	19.20	19.08	
2-Nitro	20.11	20.02	
3-Cyano-4-chloro	20.34	20.23	
3-Cyano	21.44	21.20	
3-Trifluoromethyl	21.98	21.54	
2-Chloro-4-nitro	16.1*		
1,1-Bis(4-nitrophenyl)ethene	19.1*		

*These compounds were not used in the establishment of the scale. The listed pK_A values are taken as the H_{R^-} of half-ionization.

TABLE III

$H_{\mathrm{R}-}$ values for DMSO–alcohol containing 0.01 M sodium alkoxide and for methanol – sodium methoxide

mole % DMSO in DMSO–ethanol	$H_{\mathrm{R}-}$	mole % DMSO in DMSO–methanol	$H_{\mathrm{R}-}$	Sodium methoxide concentration (M)	$H_{\mathrm{R}-}$
0.98	14.00	0.00	11.73	0.01	12.12
1.99	14.05	0.68	11.83	0.0562	12.87
3.51	14.21	2.32	12.03	0.115	13.23
5.63	14.38	5.39	12.37	0.229	13.59
10.82	14.78	8.75	12.72	0.464	14.06
15.54	15.13	15.30	13.38	0.697	14.36
20.09	15.45	20.60	13.87	0.952	14.64
25.09	15.79	25.54	14.29	1.19	14.91
30.09	16.14	30.47	14.72	1.48	15.23
35.07	16.48	35.14	15.12	1.78	15.53
40.16	16.84	39.88	15.53	2.07	15.83
45.22	17.20	44.05	15.89	2.36	16.13
50.27	17.57	49.95	16.40	2.65	16.44
55.03	17.92	54.79	16.82	2.93	16.75
59.62	18.29	59.61	17.25	3.24	17.12
64.59	18.68	64.32	17.63	3.51	17.43
69.26	19.06	69.63	18.14	3.82	17.60
74.15	19.50	74.26	18.59	4.08	17.88
79.11	20.01	78.52	19.05	4.73	18.37
84.12	20.52	83.52	19.61		
89.17	21.12	88.24	20.17		
93.27	21.74	93.98	21.14		
		97.61	21.65		

By substituting the pK_{A} values from Table II and the experimental log I values into eq. [3], the $H_{\mathrm{R}-}$ values were calculated for the various DMSO–ethanol and DMSO–methanol solutions. Because of the overlapping of the ionization curves of indicators, several $H_{\mathrm{R}-}$ values were often obtained for a solvent of a particular composition. The averaged $H_{\mathrm{R}-}$ values are listed in Table III. The graphical representations of how the $H_{\mathrm{R}-}$ values vary with the solvent compositions are given in Fig. 1 for DMSO–ethanol and DMSO–methanol.

The pK_{A} values of two indicators which were not used to establish the $H_{\mathrm{R}-}$ scale were also measured in the DMSO–ethanol system, and were estimated to be equal to the values of $H_{\mathrm{R}-}$ for the solutions in which the indicators were half-ionized. Because a plot of log I versus $H_{\mathrm{R}-}$ for the indicator α-cyano-2-chloro-4-nitrostilbene did not give a line of unit slope, this indicator was not used to establish the $H_{\mathrm{R}-}$ scale. In the case of 1,1-bis(4-nitrophenyl)-ethene, a plot of log I versus $H_{\mathrm{R}-}$ gave a fairly good straight line of near unit slope. This indicator was not used in establishing the $H_{\mathrm{R}-}$ scale because it was desirable to keep the indicators that were used to set up the scale as structurally similar as possible. The pK_{A} values for these two indicators are also listed in Table I.

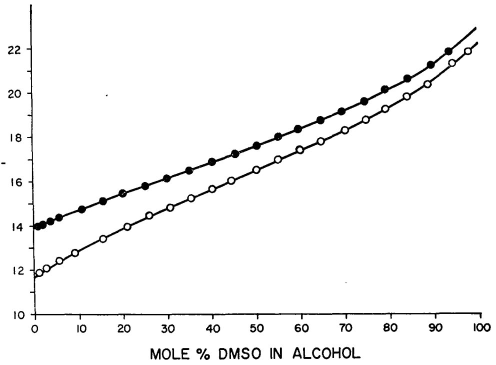


FIG. 1. $H_{\mathrm{R}-}$ as a function of the solvent composition for DMSO–alcohol solutions containing 0.01 M sodium alkoxide. LEGEND: ●, ethanol; ○, methanol.

The use of the Hammett postulate (11) to establish the acidity scale by using a series of structurally similar indicators seems to be justified. This postulate stipulates that the value of $\log I_i - \log I_j$ be constant for two overlapping indicators when measured in the same solution. This implies that the activity coefficient ratio is independent of the indicator. A close parallelism between lines for overlapping indicators was found when log I was plotted against the solvent composition; this conforms to the basic Hammett postulate.

The Hammett postulate also implies that the pK_{A} values should be independent of the solvent system. In cases where a Lewis base is involved this must be restricted to the same base in different solvent systems (12). That this holds fairly well for DMSO–methanol and sodium methoxide – methanol solutions can be seen from Table III. A closer inspection of the pK_{A} values in DMSO–methanol and sodium methoxide – methanol shows that, apart from indicators 1 and 8, the other indicators differ, at the most, by 0.08 pK unit in the two solvent systems, a good indication that the pK values for the equilibrium addition of methoxide ion to α-cyanostilbenes are independent of the solvent in which they are measured. This, as well as the parallelism of the ionization ratios for overlapping indicators, probably results from the fact that the indicators used are so similar in structure. Whether the function H_{R-} determined herein governs the addition of alkoxide ions to other kinds of Lewis acids remains to be seen. It will probably be most successful in those cases where the negative charge is greatly dispersed by resonance.

The difference in the measured pK_A values for α-cyano-4′-dimethylamino-4-nitrostilbene in DMSO–methanol and sodium methoxide – methanol is 0.20 unit. This indicator was the last one used in the sodium methoxide – methanol system. Because of this there was doubt about whether the indicator was completely ionized in the most basic solution used; thus the difference in the pK_A values for this indicator in the two solvent systems is likely an experimental error.

The difference in the pK_A values for α-cyano-2,4-dinitrostilbene of 0.23 unit in the two solvent systems is more serious. Since the pK value of α-cyano-4,4′-dinitrostilbene was taken as an arbitrary starting point in all solutions, the difference in the ΔpK_A values between these two indicators as a result of solvent change is a direct reflection on the reliability of the experimental measurements. It should first of all be noted that the ΔpK_A value between the two indicators was found to be 1.69 in DMSO–methanol, and that this is near the limit for effective overlap. As the amount of overlapping in the ionization curves of two indicators decreases, the error in the pK values increases because there is a smaller number of experimental points over which the pK values can be averaged. Furthermore, the most accurate spectral measurements are possible when the indicator is between 10 and 90% ionized. As these limits are reached, the errors in individual spectral measurements increase and are reflected in the error of the ΔpK measurements. Associated with these two causes is the rapid rise in H_{R-} at low concentrations of sodium methoxide in methanol. We feel that these causes of error are enough to explain the difference of 0.23 unit in the pK_A values for indicator 1 in the two solvent systems.

Preparation of Compounds

A number of the cyanostilbenes have not previously been prepared. The details of their preparation are given below. The melting points and literature references of those compounds previously known are given in the footnotes to Table I.

α-Cyano-2,4-dinitrostilbene

To a solution of 0.7 g of 2,4-dinitrobenzyl cyanide, prepared according to Fairbourne and Fawson (13), and 0.4 g of benzaldehyde in 20 ml of ethanol was added 4 drops of piperidine, and the mixture was refluxed for 16 h. The solution was cooled, some of the ethanol was evaporated, and the dark-colored solid was removed by filtration to yield 0.6 g (60%) of crude material. This was recrystallized from acetic acid to a constant melting point of 160–161°.

Anal. Calcd. for $C_{15}H_9N_3O_4$: C, 61.02; H, 3.07; N, 14.23. Found: C, 60.93; H, 3.24; N, 14.17.

α,4-Dicyano-4′-nitrostilbene

4-Cyanobenzyl cyanide was prepared in a low yield from 4-cyanobenzyl bromide and potassium cyanide in aqueous ethanol by the method of Gabriel and Otto (14). It was condensed with 4-nitrobenzaldehyde in ethanol, using piperidine as catalyst, according to the method of Merckx (15), to give a 56% yield of α,4-dicyano-4′-nitrostilbene. This was recrystallized from acetic acid as fine yellow needles, m.p. 212°.

Anal. Calcd. for $C_{16}H_9N_3O_2$: C, 69.81; H, 3.30; N, 15.27. Found: C, 69.58; H, 3.98; N, 15.14.

α,4-Dicyano-3′-chlorostilbene

4-Cyanobenzyl cyanide, prepared as described above, was condensed with 3-chlorobenzaldehyde in ethanolic sodium ethoxide at 40° according to the method of Schonne *et al.* (16). The product, collected in a 63% yield, was recrystallized from ethanol and acetic acid to a constant melting point of 195–195.5°.

Anal. Calcd. for $C_{16}H_9N_2Cl$: C, 72.60; H, 3.43; N, 10.58. Found: C, 72.76; H, 3.55; N, 10.62.

α,3-Dicyanostilbene

The condensation of 3-cyanobenzyl cyanide, which was prepared in the manner described by Ipatieff *et al.* (17), with benzaldehyde in ethanolic sodium ethoxide yielded α,3-dicyanostilbene in a 95% yield. The product was recrystallized from ethanol as colorless crystals melting at 148–149°.

Anal. Calcd. for $C_{16}H_{10}N_2$: C, 83.46; H, 4.38; N, 12.17. Found: C, 83.72; H, 4.22; N, 12.04.

α,3-Dicyano-4-chlorostilbene

3-Cyano-4-chlorotoluene was prepared from 3-amino-4-chlorotoluene by the Sandmeyer reaction according to the method described by Vogel (18). 3-Cyano-4-chlorobenzyl bromide was prepared by brominating 6.4 g of 3-cyano-4-chlorotoluene with 9 g of *N*-bromosuccinimide in 125 ml of carbon tetrachloride under reflux for 3.5 h, using benzoyl peroxide as catalyst. After the carbon tetrachloride was removed, the crude product was dissolved in 100 ml of ethanol and reacted with 2.6 g of potassium cyanide in 20 ml of water. After the mixture was refluxed for 45 min, the ethanol was evaporated, the resulting oil was extracted with ether, and the ether was evaporated. The oil solidified and was recrystallized from water; 0.3 g of material was obtained. This was condensed with 0.1 g of benzaldehyde in 5 ml of ethanol and a few drops of a 1 *N* ethanolic sodium ethoxide solution at 40° to give a 78% yield of α,3-dicyano-4-chlorostilbene, which was recrystallized from ethanol to a constant melting point of 156–157°.

Anal. Calcd. for $C_{16}H_9N_2Cl$: C, 72.60; H, 3.43; N, 10.58. Found: C, 73.83; H, 4.06; N, 10.30.

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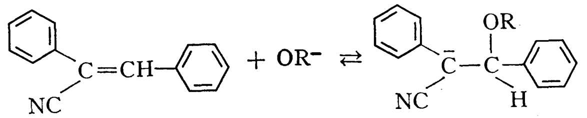

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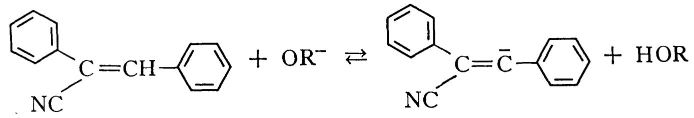

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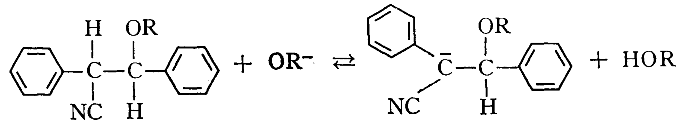


α-Cyano-2-chloro-4-nitrostilbene

This indicator was prepared by the method of Meerwein *et al.* (19). To a filtered solution of the diazonium salt of 2-chloro-4-nitroaniline, prepared according to the method described by Vogel (18), was added 3.5 g of sodium acetate, 2.1 g of cinnamonitrile in 19 ml of acetone, and 0.68 g of cupric chloride in 2 ml of water. The aqueous solution in the distillation flask was decanted, and the residue was dissolved in acetone and passed through an alumina column, with benzene as eluent. The resulting dark-colored product, left after the benzene was evaporated, was recrystallized from acetic acid, with charcoal to decolorize it, to give a small amount of yellow crystals melting at 174–175°.

Anal. Calcd. for $C_{15}H_9N_2O_2Cl$: C, 63.28; H, 3.19; N, 9.84. Found: C, 63.61; H, 3.65; N, 10.01.

α-Cyano-3-trifluoromethylstilbene

3-Trifluoromethylbenzyl cyanide was prepared in a 78% yield from 3-trifluoromethylbenzyl chloride and potassium cyanide in an ethanol–water solution according to the method of Rosenkrantz *et al.* (20). It was condensed with benzaldehyde in an ethanolic sodium ethoxide solution at 55° according to the method described by Schonne *et al.* (16) to give a 70% yield of the corresponding α-cyanostilbene. The product was recrystallized once from ethanol and twice from methanol to give colorless crystals melting at 80–81°.

Anal. Calcd. for $C_{16}H_{10}NF_3$: C, 70.33; H, 3.69; N, 5.13. Found: C, 70.54; H, 3.68; N, 5.02.

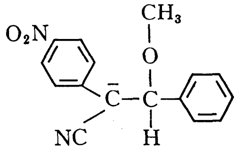
DISCUSSION

The Validity of the H_R- Function

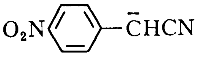
The H_R- function describes the basicity of a solution in which the base adds to an unsaturated system to form the negatively charged species. With α-cyanostilbene indicators, the equilibrium is given by eq. [5].

It seems clear that the equilibrium studied was indeed that described in eq. [5], although other modes of ionization are possible. Instead of ionization by an equilibrium addition of the Lewis base, a proton might be abstracted by the base, giving rise to an H_- function (eq. [6]). That such an ionization is possible in the case of stilbenes was shown by Hunter and Cram (21) by deuterium exchange studies. Using potassium *t*-butoxide in *t*-butanol, they found that the half-life for the deuterium exchange at 116° was approximately 100 h. This shows that the deuterium exchange is very slow and that the equilibrium, as expressed in eq. [6], must be far to the left. In addition, Zinn *et al.* (22) were able to show that, whereas ethyl cinnamate, ethyl β-phenylcinnamate, chalcone, and *trans*-cinnamonitrile underwent deuterium exchange at the α position in deuterioethanol with catalytic amounts of sodium ethoxide, ethyl α-phenylcinnamate did not undergo any deuterium exchange at all. These two pieces of evidence strongly suggest that the ionization does not involve the removal of the proton from the β carbon to a significant extent.

The spectral evidence also supports the ionization shown in eq. [5] rather than that shown in eq. [6]. It would be expected that the electronic spectra of anions II and III would be very similar. In fact, the electronic



II



III

spectrum of II has a maximum at 548 mμ in DMSO–methanol, and that of III has a maximum at 540 mμ in 95 mole % sulfolane in water (23), the general shape of both spectra being similar. Such a close similarity would not be expected for the electronic spectra of ions I and III. The effect of substituents on the equilibrium (37) also strongly supports alkoxide addition rather than proton removal.

An equilibrium which certainly is operative in these basic solutions is that shown in eq. [7], involving the alcohol adduct. However, its importance depends on the relative pK values for equilibria [5] and [7]. If 4-nitrobenzyl cyanide can be taken as a model compound for the reaction shown in eq. [7], then we can obtain some idea about the relative pK values for the two processes. The pK_{HA} value most often quoted for 4-nitrobenzyl cyanide is 13.45 (24, 25). This value can be taken as a rough estimate even if the ionization behavior of 4-nitrobenzyl cyanide is in doubt (23). The estimated pK_A value for the addition of ethoxide ion to α-cyano-4-nitrostilbene is 15.95 in DMSO–ethanol. At an H_{R^-} value of 14.95, the ratio of the ionized to un-ionized forms of α-cyano-4-nitrostilbene would be 0.10. This is approximately the lower limit of possible measurements. If the H_{R^-} and H_- values are approximately equivalent in this region, 4-nitrobenzyl cyanide would be 97% ionized. This indicates that only a small amount of the alcohol adduct was present at any time and that the equilibrium which was measured was really that shown in eq. [5].

The spectral evidence also supports the above argument. The alcohol adduct should not absorb to any appreciable extent in the region where the α-cyanostilbene absorbs. The fact that a reasonable isosbestic point was obtained again indicates that the reaction shown in eq. [7] does not contribute appreciably to the overall equilibrium.

Interpretation of the Lewis Basicity of the Solutions

The addition of DMSO to ethanol or methanol containing 0.01 M sodium alkoxide was found to have a profound effect on the ability of the alkoxide ion to act as a Lewis base. The H_{R^-} values were found to increase from 14.00 in 0.98 mole % DMSO in ethanol to 21.74 in 93.27 mole % DMSO in ethanol, and from 11.73 in methanol to 21.65 in 97.61 mole % DMSO in methanol. In the first case the Lewis basicity of the ethoxide ion increases by approximately 7 powers of 10, and in the second case the Lewis basicity of the methoxide ion increases by about 10 powers of 10. This shows the substantial effect of DMSO on the Lewis basicity of the alkoxide ions, as expressed by the H_{R^-} function (eq. [8]).

$$[8] \qquad H_{R^-} = -\log \frac{a_{H^+} f_{AOR^-}}{a_{ROH} f_A}$$

This can be rewritten as shown in eq. [9],

$$[9] \qquad H_{R^-} = -\log \frac{K_{ROH} f_{AOR^-}}{a_{RO^-} f_A}$$

where $K_{ROH} = a_{H^+}a_{RO^-}/a_{ROH}$. The sharp increase in H_{R^-} is probably due chiefly to an increase in the activity of the alkoxide ion. The activity coefficients of the charge-delocalized ion (AOR⁻) and the indicator molecule (A) are probably affected to a much smaller extent (5, 6).

The inferior solvating ability of DMSO towards hydroxyl and alkoxyl ions is well known. This may be augmented by a breakdown of the methanol structure as the DMSO composition is increased (26).

Comparison of the H_{R^-} and H_- Scales

The acidity function (H_-) which governs the ionization of a neutral acid (HA) is given by the following expression.

$$H_- = -\log \frac{a_{H^+} f_{A^-}}{f_{HA}}$$

It differs from the H_{R^-} function (eq. [8]) only by lacking a term for the activity of the solvent and by having a somewhat different set of activity coefficients.

$$H_{R^-} - H_- = \log a_{ROH} - \log \frac{f_{AOR^-} f_{HA}}{f_A f_{A^-}}$$

There is a similar difference between the functions H_0 and H_R, which govern the formation of ammonium and carbonium ions, respectively, in acid systems (11).

$$\mathrm{B} + \mathrm{H}^+ \rightleftarrows \mathrm{BH}^+$$

$$H_0 = -\log \frac{a_{\mathrm{H}^+} f_{\mathrm{B}}}{f_{\mathrm{BH}^+}}$$

$$\mathrm{ROH} + \mathrm{H}^+ \rightleftarrows \mathrm{R}^+ + \mathrm{H_2O}$$

$$H_{\mathrm{R}} = -\log \frac{a_{\mathrm{H}^+} f_{\mathrm{ROH}}}{a_{\mathrm{H_2O}} f_{\mathrm{R}^+}}$$

$$H_{\mathrm{R}} - H_0 = \log a_{\mathrm{H_2O}} - \log \frac{f_{\mathrm{ROH}} f_{\mathrm{BH}^+}}{f_{\mathrm{R}^+} f_{\mathrm{B}}}$$

It is known that a large difference develops between H_0 and H_{R} as sulfuric acid solutions are made more concentrated, and that this difference is much larger than that caused by the lowered activity of water (27). The difference, amounting to over 7 units in 80% sulfuric acid, can be traced chiefly to the activity coefficient terms, in particular to the differing degrees of solvation of the two cations: the ammonium ion (BH^+) and the carbonium ion (R^+) (28–30). The activity of the former rises enormously as the water content decreases, partly, at least, because of the lowered potential for hydrogen bonding ($\mathrm{BH}^+ \text{- - - -} \mathrm{OH_2}$).

In the case of the functions H_- and $H_{\mathrm{R}-}$, no such large divergence occurs. It is difficult to make a direct comparison because the published values for methoxide–methanol–DMSO are for nitrogen acids (3). (The H_- values for ethoxide–ethanol–DMSO, using carbon acids, are less firmly established than the scale for nitrogen acids (2). This is due, at least in part, to spectral shifts in the carbanions. Indeed, in attempting to set up an H_- scale for direct comparison with $H_{\mathrm{R}-}$, we found cases where distinctly nonparallel ionization slopes occurred; this points to the necessity of redetermining the H_- scale for carbon acids in mixed solvents.) However, a rough comparison can be made between $H_{\mathrm{R}-}$ and H_- by using the H_- values for carbon and nitrogen acids in alkoxide–alcohol–DMSO and methoxide–methanol solutions; it is clear that no great divergence occurs. For example, 60 mole % DMSO in methanolic DMSO containing 0.025 *M* sodium methoxide has an H_- value of 16.2 (3), and the same solution containing 0.01 *M* sodium methoxide has an $H_{\mathrm{R}-}$ value of 17.3. A solution that is 60 mole % DMSO in ethanol and 0.01 *M* in sodium ethoxide has an H_- value of 17.8 (4) and an $H_{\mathrm{R}-}$ value of 18.3. A 3.0 *M* solution of sodium methoxide in methanol has reported values of 17.2 (31) or 15.8 (5) for H_-, and an $H_{\mathrm{R}-}$ value of 16.8.

The lack of sharp divergence in the H_- and $H_{\mathrm{R}-}$ scales is not surprising in view of the similarity in the structures of the anions A^- and AOR^-. Both are carbanions with extensive change delocalization. The activity of neither should be altered drastically by changes in the medium.

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