aromatic cyclobutenes and the corresponding quinododimethides. The energies of the former compounds were assumed equal to the parent aromatics. As this approach neglects changes in the σ system and as the determination of absolute energy differences is beyond π-energy calculations, it is the relative energies which are most revealing. Not surprisingly, SCF modifications predict that those *o*-quinododimethides which are predicted to be least stable (**5**, **8**, **21**, and **31**) should not be readily formed in ring-opening reactions. For these systems any aromatic character in the cyclobutene will be lost in the quinododimethide which can maintain no benzenoid structural units. As is to be expected in cases involving only changes in π-bonding energy, the CBL and VBL methods differ slightly. Very similar results are also obtained from HMO calculations.

The data in Table VI may also be applied to the question of relative rates of ring opening if it is of course assumed that the transition state for the reaction strongly resembles the quinonoid system. The possibility of nonconcerted ring opening through a triplet diradical state can also be treated by the present approach. The relative calculated energies of quinododimethides and the corresponding triplets have already been shown to vary greatly with structure. In Table VII are presented the calculated differences in π-binding energy between aromatic cyclobutenes and the corresponding triplet diradicals as determined by the SCF CBL approach. The differences with the results in Table VI are of interest. The completely quinonoid structures associated with compounds **5**, **8**, **21**, and **31** are not maintained in the corresponding diradical, and these latter systems may achieve large resonance stabilization of the radical centers. Conversely, systems such as **14** should be far more stable in closed-shell configuration and opening to a diradical will not be favored. The concertedness of ring opening in the above systems could be decided not only on the basis of stereochemical findings, but upon the relative rate of reaction. Interestingly, HMO calculations predict that all the diradical structures should be formed more readily than the *o*-xylylyl diradical.

Table VII. Calculated SCF π-Binding Energy Differences between Aromatic Cyclobutene and the Corresponding Diradicals[a]

System[b]	$-E_{\Pi_b}$	$-E_{\Pi_b}$[c]	$-\Delta E_{\Pi_b}$	$-\Delta\Delta E_{\Pi_b}$[d]
1	9.064	7.825	1.239	0.000
3	14.708	13.462	1.246	0.007
5	14.871		1.409	0.170
7	20.344	18.924	1.420	0.181
8	20.475		1.551	0.312
11	20.529	19.296	1.333	0.094
12	20.612		1.316	0.077
13	20.503		1.207	−0.032
14	20.487		1.191	−0.048
18	23.849	22.336	1.513	0.274
19	23.531		1.195	−0.044
20	25.659	24.332	1.327	0.088
21	25.936		1.603	0.364
25	26.318	25.056	1.262	0.023
26	26.289		1.233	−0.006
29	26.390	25.262	1.128	−0.111
30	31.193	29.718	1.475	0.236
31	31.352		1.634	0.395

[a] In electron volts. [b] Systems correspond to triplet forms of quinododimethides in Figure 1. [c] Energy of parent arene. [d] Relative to benzocyclobutene → *o*-xylylyl diradical.

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J_- Acidity Scale Based on Addition of Hydroxyl Ions to Substituted Benzaldehydes[1]

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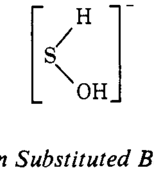
Abstract: Whereas at lower pH values benzaldehydes exist predominantly in nonhydrated form, in sodium hydroxide solutions changes in uv spectra indicate reversible addition of hydroxyl ions following reaction 6. Determination of the equilibrium constant of this reaction made it possible to evaluate the acidity function J_-. This has been found practically identical with the acidity function J_-(k) obtained from kinetic data; the latter is, nevertheless, available only over a limited range of sodium hydroxide concentrations. Up to 10 *M* sodium hydroxide, the J_- scale also followed closely the H_- scale, but has shown deviations at higher concentrations.

Whereas a rather detailed investigation has been carried out on acidity functions for various types of acid-base systems in strongly acidic media,[3] much less attention has been paid to the scales expressing acidity in strongly alkaline media. Two types of reactions are considered for the acid-base equilibria in aqueous alkaline solutions: hydrogen ion abstraction (1) and addition of a hydroxyl ion (2). The addition of water (or another hydroxylic solvent molecule),

$$\mathrm{SH} + \mathrm{OH}^- \rightleftharpoons \mathrm{S}^- + \mathrm{H_2O} \quad (1)$$

$$\mathrm{SH} + \mathrm{OH}^- \rightleftharpoons$$  (2)

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(1) Partly presented at the Third Northeast Regional Meeting of the American Chemical Society, Oct 11, 1971.

(2) (a) Edward Western Fellow of the Electrochemical Society, 1972; (b) Western Publishing Company Fellow of the Educational Council of the Graphic Arts, 1972–1973; (c) in partial fulfillment of the Ph.D. Thesis.

(3) C. H. Rochester, "Acidity Functions," Academic Press, New York, N. Y., 1970.

which is a much weaker nucleophile, can usually be neglected at pH >10. Here the symbol SH represents the compound studied (indicator), which is considered to be a very weakly acidic molecule bearing no unit charge.

Acidity scales H_- for the proton abstraction reaction 1 in strongly alkaline media are reasonably well established.[4,5] The question as to whether an acidity scale based on one type of indicator can be rigorously applied to acid–base equilibria involving structurally different acidic groups cannot be, for the reactions in strongly alkaline media, presently answered because of the lack of experimental data. The good agreement of the scales based on indigo[5a] and indole[5b] derivatives is perhaps understandable, as the structure of the conjugate acids of the two groups of compounds are similar. For substituted anilines,[6] behavior both parallel[7] and nonparallel[8] to the H_- scale based on indole derivatives has been reported. The limited solubility of anilines in aqueous solutions of alkali metal hydroxides, reactions of the aniline derivative with more than one hydroxyl ion, irreversible substitution reactions,[9a] and possibility of hydroxyl ion addition rather than proton abstraction (in particular for nitro derivatives[9b]) complicate interpretation of experimental data.

Even when the scope of applicability of the function H_- to very weak acids of varying structure has yet to be determined, it seems, based on linear plots of log C_{S^-}/C_{SH} against H_- for indicators differing in structure,[7] that acidity functions for concentrated solutions of alkali metal hydroxides are less sensitive to variations in the structure of the indicator than the acidity functions for concentrated acid solutions.[3] For the time being, the acidity function H_- might be used as a first approximation even for indicators of different structure than those for which the scale was developed.

For addition of hydroxyl ions (eq 2), the acidity function J_- has been defined[8,9a,10] as (3), where a_i are activities, c_i concentrations, y_i activity coefficients, and index w corresponds to water. If the difference in hydration of SH and SHOH$^-$ is neglected, the relationship between H_- and J_- can be expressed as (4), where

$$J_- = -\log (a_{H^+}y_{SHOH^-}/y_{SH}a_w) = pK_2 + pK_w + \log C_{SHOH^-}/C_{SH} \quad (3)$$

$$J_- = H_- + \log a_w + \log (y_{SH}y'_{S^-}/y'_{SH}y_{SHOH}) \quad (4)$$

the primed values correspond to indicators used for establishing the H_- scale.

Previous attempts[8,9,10b,11] to develop the J_- acidity function scale based on equilibrium measurements have been unsuccessful. Most frequently studied addition reactions of hydroxyl ions are those involving nitroaromatic compounds (formation of Meisenheimer complexes). Measurements of equilibria of type 2 involving nitro compounds were found complicated by consecutive reactions,[8,9] by uptake of a second hydroxyl ion,[11a] or by complicated changes in absorption spectra.[11]

In the absence of equilibrium measurements, attempts have been made to establish the J_- scale based on kinetic data. The attempt[12a] to approximate eq 4 by $J_- = H_- + \log a_w$ was only partly successful. Recently, a kinetic scale J_-(k) based on the Zucker–Hammett hypothesis[13] has been proposed by Rochester[12b] relating kinetic and acidity data by expression 5

$$J_-(\mathrm{k}) = \log k - \log (k_0K_w) = -\log (a_{H^+}y^{\mp}/a_wy_{SH}) \quad (5)$$

where k is the rate constant at a given sodium hydroxide concentration, k_0 at [NaOH] = 0, and $y^{\mp}$ the activity coefficient of the transition state in the rate limiting step of the particular reaction used to measure J_-(k). The aromatic SN2 reactions between hydroxide ions and 2,4-dinitroanisole, 2,4-dinitrophenetole, and 1-chloro-2,4-dinitrobenzene gave the same acidity function J_-(k) for concentrations of sodium hydroxide up to 5 M. A comparison with the rate constants of chloramine and carbon disulfide SN2 hydrolyses indicates the need for a separate J_- acidity function. An analogous function denoted as H_{R^-} has been derived for the addition of methoxide and ethoxide ions to α-cyanostilbenes in dimethyl sulfoxide–methanol (and ethanol) mixtures.[14] Nevertheless, due to retroaldolization fission, it was not possible to use this reaction for determination of acidity function in aqueous media.

In the course of polarographic and spectrophotometric investigations of isomeric phthalaldehydes,[15] it has been observed that substituted benzaldehydes undergo addition of hydroxyl ions in a reversible reaction 6. Equilibrium constants of reaction 6 have been measured for a series of substituted benzaldehydes and the data used for a definition of a J_- acidity scale based on equilibrium measurements are presented in this publication.

$$\mathrm{ArCHO} + \mathrm{OH}^- \underset{K_2}{\rightleftharpoons} \mathrm{ArCH(OH)O}^- \quad (6)$$

Experimental Section

Materials and Solutions. Most of the aldehydes employed were supplied by Aldrich Chemical Co. (Milwaukee). Purity was checked by measurement of their melting or boiling points (Table I) and by recording a gas–liquid chromatogram of an ether solution of the aldehydes. The few benzaldehydes the purity of which proved to be unsatisfactory were recrystallized from ether or ethanol solutions.

The 0.01 M stock solutions of aldehydes in absolute ethanol or water were prepared fresh every day and kept in dark at 4°. Ethanol was preferred as a solvent for preparation of the stock solution, with respect to the solubility. For benzaldehydes (p-CH_3, p-OCH_3, and m-OH, derivatives) where it was necessary to carry out experiments at concentrations of sodium hydroxide higher than 8 M, aqueous stock solutions of the benzaldehydes were prepared, because of the limited miscibility of ethanol in such solutions.

Spectrophotometric experiments were carried out by addition of 0.1 ml of the stock solution (delivered by a 100-μl pipet) to 9.9 ml of the buffer or sodium hydroxide solution. The resulting solution was 1×10^{-4} M in benzaldehyde and contained 99% water and 1% ethanol. For p-CH_3, p-OCH_3, and m-OH derivatives where aqueous

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(4) C. H. Rochester, *Quart. Rev. Chem. Soc.*, 20, 511 (1966).

(5) (a) G. Schwarzenbach and R. Sulzberger, *Helv. Chim. Acta*, **27**, 348 (1944); (b) G. Yagil, *J. Phys. Chem.*, 71, 1034 (1967).

(6) (a) R. Stewart and J. P. O'Donnell, *Can. J. Chem.*, **42**, 1694 (1964); (b) R. Stewart and D. Dolman, *ibid.*, **45**, 925 (1967).

(7) R. Stewart and J. P. O'Donnell, *ibid.*, **42**, 1681 (1964).

(8) C. H. Rochester, *Trans. Faraday Soc.*, **59**, 2820 (1963).

(9) (a) C. H. Rochester, *ibid.*, **59**, 2829 (1963); (b) V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1727 (1964).

(10) (a) V. Gold and B. W. V. Haves, *ibid.*, 2102 (1951); (b) V. Gold and C. H. Rochester, *ibid.*, 1722 (1964).

(11) (a) R. Schaal, *C. R. Acad. Sci.*, **239**, 1036 (1954); (b) V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1710 (1964); (c) *ibid.*, 1717 (1964).

(12) (a) C. H. Rochester, *Trans. Faraday Soc.*, **59**, 2826 (1963); (b) C. H. Rochester, *J. Chem. Soc. B*, 1076 (1967).

(13) L. Zucker and L. P. Hammett, *J. Amer. Chem. Soc.*, **61**, 2791 (1939).

(14) D. J. Kroeger and R. Stewart, *Can. J. Chem.*, **45**, 2163 (1967).

(15) W. J. Bover and P. Zuman, unpublished results.

Table I. Physical and Optical Properties of Benzaldehydes Studied

		SH[b]		SHOH^{-}[c]		
Aldehyde	Bp, °C (mm)	λ_{max}, nm (B) (ϵ)	λ_{max}, nm (E) (ϵ)	λ_{max}, nm (B) (ϵ)	λ_{iso},[d] nm	λ_{calcd},[e] nm
p-Nitrobenzaldehyde	105–108[a]	268 (14,000)	200 (16,000)	285 (8500)	284	260
m-Nitrobenzaldehyde	56–57[a]	270 (2800)	235 (19,000)	273 (7300)	263	238
m-Cyanobenzaldehyde	70–74[a]	245 (8000)	217 (17,000)	225[f] (15,000)	234 265 285	245
p-Cyanobenzaldehyde	133 (12)	254 (19,000)	200 (18,000)	235 (13,000)	239	258
m-Chlorobenzaldehyde	213–214	249 (10,000)	210 (20,000)[f]	250 (1000)		250
p-Chlorobenzaldehyde	42–44[a]	260 (16,000)	210 (11,000)	225 (10,000)[f]	235	260
m-Hydroxybenzaldehyde	100–102[a]	266 (6000)	238 (23,000)[f]	290 (3000) 239 (9500)	283	265
m-Tolualdehyde	199	254 (13,800)	208 (20,000)	255 (1000)		255
p-Tolualdehyde	204–205	261 (17,000)	205 (14,000)	265 (400)		263
m-Anisaldehyde	143 (50)	225 (9000)	219 (19,000)	272 (1400)		250
p-Anisaldehyde	248	(280)[f] (16,000)	221 (10,600)	275 (1000)		280
Benzaldehyde	177	250 (12,800)	205 (19,000)	260 (100)		250

[a] Melting point. [b] Wavelengths of absorption maxima and molar extinction coefficients (l./(mol cm)) for the B and K bands (B) and E bands (E) of the aldehydic form (SH). [c] Wavelengths of absorption maxima and molar extinction coefficients for the B and K bands of the anion of the geminal diol (SHOH$^-$). [d] Wavelength of the isosbestic point. [e] Wavelengths used in the calculation of C_{SHOH^-}/C_{SH}. [f] Estimated values.

stock solutions were used, it has been proved that spectra obtained at concentrations of sodium hydroxide lower than 8 *M* in the presence of 1% ethanol were practically identical with spectra obtained in purely aqueous solutions.

A preliminary spectrophotometric investigation of all of the benzaldehydes studied had been performed prior to the detailed study of the alkaline solution. To cover the entire aqueous pH range, 0.1 *N* H_2SO_4, 0.1 *N* NaOH, and the following buffers were used: acetate buffer, pH 4.7; phosphate buffer, pH 6.8; and borate buffer, pH 9.3. All these solutions were prepared from Baker Analytical Grade reagents and freshly distilled water.

Sodium hydroxide solutions for the definite studies were prepared from 0.1 *N* and 1.0 *N* Baker Reagent grade Dilut-it standardized solutions and from 50% Baker Analyzed sodium hydroxide (0.03% carbonate) which were diluted with freshly boiled out distilled water cooled in a stream of nitrogen. The 50% hydroxide solution was standardized against potassium acid phthalate and found to be 18.86 *M*. From this solution, 11, 12, and 13 *M* solutions of sodium hydroxide were prepared by dilution with distilled carbonate free water, as well as 10 and 5 *M* stock solutions of sodium hydroxide, and then standardized against potassium acid phthalate. From the latter two, stock solutions 1-9 *M* solutions were prepared by dilution. The transfer of 50%, 10 and 5 *M* solutions for dilution was carried out in a nitrogen atmosphere. The 0.1–1.0 *M* sodium hydroxide solutions were prepared by dilution of the 1.0 *M* Dilut-it standard solution, those 0.01–0.1 *M* in sodium hydroxide by dilution of 0.1 *M* Dilut-it standard.

Equipment. A Unicam SP-800-A (Pye-Unicam, Cambridge, England) recording spectrophotometer was employed for all measurements of the uv absorption spectrum. Matched fused quartz cells (10-mm sample path) were placed in a thermostated compartment through which water was circulated by means of thermostat Mark FJ (Haake, Berlin) so that the temperature of the solution in the cell was kept 25 ± 0.1°. The cells were cleaned with a diluted aqueous solution (1:5) of nitric acid, followed by repeated rinsing with distilled water and drying with acetone.

A Sargent Model DR pH-meter with a combination glass–calomel electrode was employed for pH measurement of buffers used in the preliminary experiments. A Varian Aerograph series 1200 Chromatograph with a flame ionization detector and Sargent Model SR recorder was employed in the analysis of the purity of the commercial aldehyde samples. The 5 ft × $^1/_8$ in. stainless steel column used was packed with 3% SE-30 on 100–120 Varaport No. 30. Least-squares calculations were performed on a modified PDP-8 computer (Digital Equipment Corp., Maynard, Mass.).

Results

To calculate values of acidity function J_- by means of eq 3 at varying sodium hydroxide concentrations, the value of log C_{SHOH^-}/C_{SH} was determined from spectrophotometric measurements. This was made possible by the difference in the absorption of the aldehyde (SH) and the anionic adduct (SHOH$^-$).

Benzaldehydes generally show three main absorption bands in the uv region, *viz.* an n → π* carbonyl absorption band (R band) of low intensity at about 300 nm, a medium intensity absorption band at 250–280 nm (B and K bands), corresponding to electronic transitions involving the aromatic ring conjugated with the carbonyl group, and a strong absorption band at about 210 nm, corresponding to π → π* transitions (E band). Since at higher sodium hydroxide concentrations the cutoff due to the OH$^-$ absorption shifted to about 230 nm, measurements of the 210 nm band were impractical. The forbidden transition band at 300 nm was in a region where most anions SHOH$^-$ do not show measurable absorption, but because of low sensitivity due to the low extinction coefficient, measurement of this band had been made use of only in some few instances where further confirmation was necessary.

Since the anion SHOH$^-$ is, in the majority of the cases, transparent in the region of benzenoid absorption, the region 250–280 nm has been in most cases used for determination of the ratio C_{SHOH^-}/C_{SH}. The molar absorptivity (extinction) coefficient of this absorption band for the various benzaldehydes (SH) generally ranged from 7000 to 19,000 l. mol^{-1} cm^{-1} (Table I). These values were obtained at pH <12 where the formation of the anion can be neglected. The residual absorption in solutions in which the conjugate base (SHOH$^-$) predominates was negligible when compared with that of the aldehyde and had an extinction from 100 to 1000 units.

For benzaldehydes bearing as a substituent a chromophoric group (like NO_2 or CN), the wavelengths of the absorption maxima of the anionic form SHOH$^-$ differed sufficiently from at least one of the bands of the corresponding benzaldehyde SH (Table I). In such cases, well-defined isosbestic points were observed (Figure 1). No measurable solvent shifts have been observed for sodium hydroxide concentrations below 10 *M*. At higher concentrations, corrections for the solvent shifts observed were applied to measurements of absorbancies.

Dependence of the absorbance at a chosen wave-

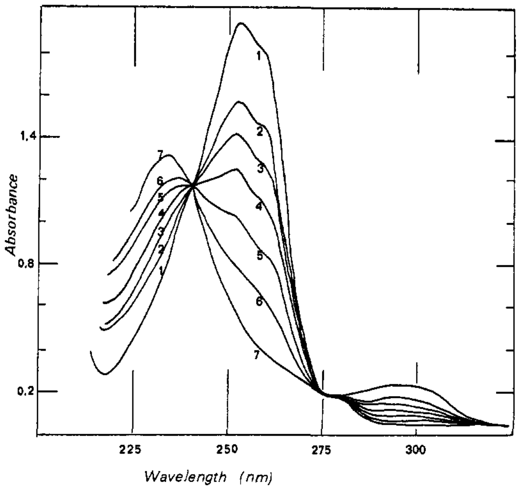

Figure 1. The uv absorption spectra of *p*-cyanobenzaldehyde in aqueous (1% ethanol) sodium hydroxide solutions of the following molar concentrations: (2) 0.04, (3) 0.06, (4) 0.10, (5) 0.20, (6) 0.40, and (7) 2.50. The first curve was in phosphate buffer, pH 10.03. The solutions were 1.0×10^{-4} *M* in aldehyde, at 25°.

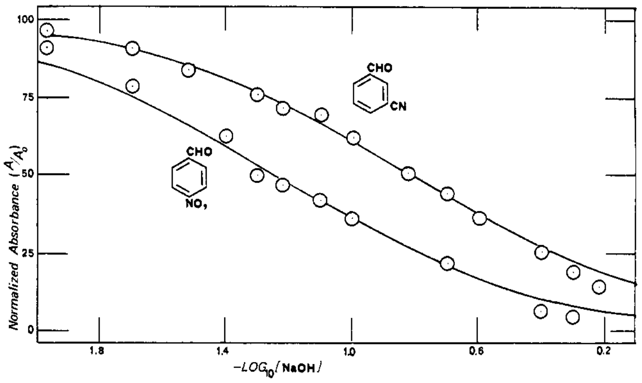

Figure 2. The plot of absorbance (normalized) against $-\log C_{\text{NaOH}}$ for *m*-cyano- and *p*-nitrobenzaldehyde. The circles are experimental points, while the curve was calculated for the addition of one hydroxide ion to the indicator molecule.

length in the 250–280-nm range on log [OH$^-$] for the more reactive derivatives (*e.g.*, *p*-nitro- and *m*-cyanobenzaldehydes) has a shape approximating a dissociation curve (Figure 2), corresponding to the transfer of one hydroxyl ion. This was considered as a contribution to the proof for reaction 6. The reversibility of the process was confirmed after dilution or acidification of the sodium hydroxide solution.

The wavelength at which the absorbance *A* was measured was generally chosen so as to correspond to the wavelength of the absorption maximum of the benzenoid absorption band (Table I).

The absorbance at a selected wavelength for a given sodium hydroxide concentration was used for calculation of the ratio $C_{\text{SHOH}^-}/C_{\text{SH}}$ to be used in connection with eq 3 by means of expression 7

$$C_{\text{SHOH}^-}/C_{\text{SH}} = [(A_0 - A_{\text{R}}) - (A - A_{\text{R}})]/(A - A_{\text{R}}) = (A_0 - A)/(A - A_{\text{R}}) \quad (7)$$

where A_0 is the absorbance of the aldehyde at lower pH or in a more dilute sodium hydroxide solution (at $J_- < \text{p}K - 2$), A_{R} is the residual absorbance in the most concentrated sodium hydroxide solutions (at $J_- > \text{p}K + 2$), and *A* is the absorbance at the given sodium hydroxide concentration. For compounds with p*K* values above 15, the determination of A_{R} in this way was not practical and extrapolation of the measured values of *A* with increasing hydroxide concentration against tabulated values of H_- was used to obtain approximate values of A_{R}. In 8 and 9 *M* sodium hydroxide, where presence of 1% ethanol caused turbidity, the spectra were zeroed to the base line at a wavelength where both species were transparent.

The values of $C_{\text{SHOH}^-}/C_{\text{SH}}$ were determined at 10–15 different sodium hydroxide concentrations chosen so that the acidity range investigated was centered around the p*K* value of the aldehyde, if possible from 97% of C_{SHOH^-} to 97% of C_{SH}.

p*K* Values of Indicators. After the value of $C_{\text{SHOH}^-}/C_{\text{SH}}$ has been found, the value of pK_2 for individual indicators must be calculated in order to determine values of the J_- acidity functions. An overlap procedure was used, which required determination of the thermodynamic values of equilibrium constants $K_2 = (C_{\text{SHOH}^-}/C_{\text{SH}}C_{\text{OH}^-})(y_{\text{SHOH}^-}/y_{\text{SH}}y_{\text{OH}^-})$. Such values can be obtained for the strongest acids in the studied reaction series.

Preliminary experiments and the plotting of log $C_{\text{SHOH}^-}/C_{\text{SH}}$ against both pH and tabulated data on H_- indicated that *p*-nitro-, *m*-nitro-, *m*-cyano-, and *p*-cyanobenzaldehydes show p*K'* (where $K' = K_2K_{\text{w}} = (C_{\text{SHOH}^-}C_{\text{H}^+}/C_{\text{SH}})(y_{\text{SHOH}^-}y_{\text{H}^+}/y_{\text{SH}})$) smaller than 13.5.

The thermodynamic value (pK_2^{T}) for such compounds can be obtained in dilute solutions of sodium hydroxide by means of (8). The values of log $C_{\text{SHOH}^-}/C_{\text{SH}}$ were

$$\text{p}K_2 = \log C_{\text{OH}^-} - \log (C_{\text{SHOH}^-}/C_{\text{SH}}) - \log (y_{\text{SHOH}^-}/y_{\text{SH}}y_{\text{OH}^-}) \quad (8)$$

determined at several concentrations of sodium hydroxide and log ($C_{\text{SHOH}^-}/C_{\text{SH}}$) − log C_{OH^-} were plotted against C_{OH^-}. The resulting curves are linear (Figure 3) and the intercept of the extrapolated lines of C_{OH^-} (*i.e.*, at $\mu = 0$) is then equal to the thermodynamic value pK_2^{T}. Intercepts were found by a least-squares computer program. For the sake of comparison with p*K'* values, the values of pK_2^{T} obtained were transformed to pK = pK_2^{T} + pK_{w} (Table II).

p*K* values of other indicators were then determined

Table II. Concentrations of Sodium Hydroxide ($C_{1/2}$) at Which Concentrations of the Aldehyde and of the Anion of the Geminal Diol Are Equal and Corresponding p*K* Values for the Reaction of Substituted Aldehydes with Hydroxyl Ions (25°)

Aldehyde	$C_{1/2}$	pK_2[a]	pK'[b]	pK[c]
p-Nitrobenzaldehyde	0.06	−1.21	12.79	12.79
m-Nitrobenzaldehyde	0.10	−0.96	13.04	13.08
m-Cyanobenzaldehyde	0.15	−0.74	13.26	13.24
p-Cyanobenzaldehyde	0.10	−0.94	13.06	13.03
m-Chlorobenzaldehyde	0.65	−0.08	13.92	
p-Chlorobenzaldehyde	1.75	0.44	14.44	
m-Anisaldehyde	2.30	0.61	14.61	
Benzaldehyde	3.40	0.90	14.90	
m-Tolualdehyde	3.80	1.00	15.00	
p-Tolualdehyde	5.55	1.39	15.39	
p-Anisaldehyde	8.35	1.96	15.96	
m-Hydroxybenzaldehyde	7.60	1.81	15.81	

[a] $K_2 = (C_{\text{SHOH}^-}/C_{\text{SH}}C_{\text{OH}^-})(y_{\text{SHOH}^-}/y_{\text{SH}}y_{\text{OH}^-})$. [b] $K' = K_2K_{\text{w}} = (C_{\text{SHOH}^-}C_{\text{H}^+}/C_{\text{SH}})y_{\text{SHOH}^-}y_{\text{H}^+}/y_{\text{SH}}$ obtained from overlap procedure. [c] $K = C_{\text{SHOH}^-}C_{\text{H}^-}/C_{\text{SH}}$ at ionic strength equal to zero.

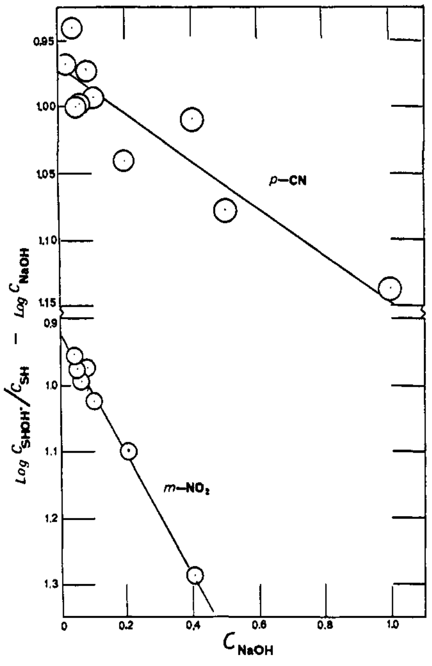

Figure 3. A plot of the spectrophotometrically determined values of log (C_{SHOH^-}/C_{SH}) − log C_{NaOH} as a function of the concentration of sodium hydroxide for the *p*-cyano- and *m*-nitrobenzaldehyde derivatives. The thermodynamic value of the pK for these indicators is the value of the ordinate at C_{NaOH} = 0.

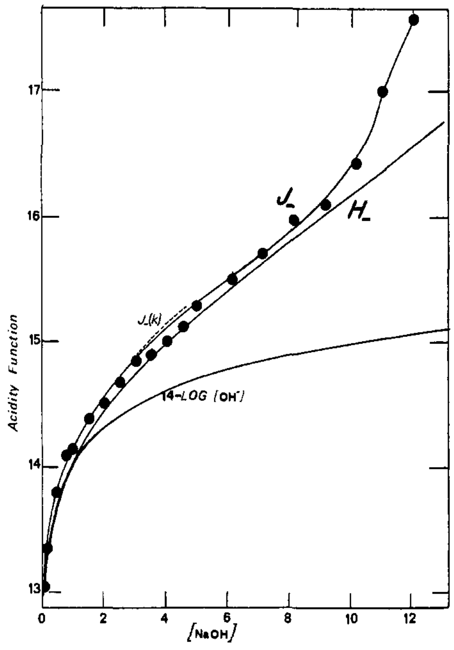

Figure 4. Some acidity functions plotted against the concentration of sodium hydroxide. The filled circles are the experimental points for the observed J_- function, while the curve (J_-) is the best fit through the points. The J(k) curve corresponds to Rochester's[12b] kinetic scale, the H_- scale is as reported by Yagil,[6b] and the "pH" scale corresponds to "pH" = 14 − log [OH].

using the standard overlap procedure[16] involving assumption of similar activity coefficient ratios. To test the internal consistency of the data, the values of pK' for *m*-NO$_2$, *p*-CN, and *m*-CN were determined by the overlap procedure based on the thermodynamic pK value for the *p*-NO$_2$ derivative and compared with thermodynamic pK values obtained for the former three compounds from the values extrapolated to ionic strength equal to zero. The two sets of data agreed within 0.02 pK unit, which is inside the experimental error, and hence the pK' values of the four compounds are consistent and together can serve as a basis for the overlap procedure. Because of the closeness of some pK_2 values (Table II), it was often possible to use one known value of pK_2 for calculation of p$K_2{}^b$ values for two or three indicators with higher pK_2 values. The calculated values of pK_2 were converted into pK' (Table II), which enables comparison with the strength of proton donating acids by the relation pK' = pK_2 + pK_w.

J_- Acidity Function. Determination of values of pK_2 for individual indicators and of the expression log C_{SHOH^-}/C_{SH} at a given C_{OH^-} enables us to calculate the value J_- by means of eq 3. Calculated values of J_- have been tabulated (Table III) and plotted as a function of concentration of sodium hydroxide (Figure 4). The calculated values of J_- below J_- = 16.3 show an accuracy of ±0.03 J_- unit, those at higher sodium hydroxide concentration of about ±0.10 J_- unit. Because indicators with pK' > 16.0 were not available, determinations of J_- > 16.3 were based only on 2–5 experimental data.

Discussion

In a development of a new acidity function, it is essential to prove that all the indicators used undergo the same type of acid–base reaction and to make sure that nature of this acid–base process is understood.

The uniformity of the process involved was indicated by the similarity of the change in uv absorption spectra of the benzaldehydes studied with increasing concentration of sodium hydroxide. Irrespective of whether

Table III. Comparison of Values of the Acidity Function J_- Obtained Employing Benzaldehyde Indicators with Other Reported Acidity Functions in Aqueous Solutions of Sodium Hydroxide (25°)

NaOH, M	"pH"[a]	H_-[b]	J_-[c] (obsd)	J_-(k)[d]
0.1	13.0	12.99	13.04	
0.2	13.30	13.30	13.35	
0.5	13.70	13.71	13.80	
0.8	13.90	13.92	14.09	13.98
1.0	14.00	14.02	14.14	14.13
1.5	14.18	14.20	14.35	14.34
2.0	14.30	14.37	14.52	14.52
2.5	14.40	14.54	14.67	14.67
3.0	14.48	14.65	14.80	14.84
3.5	14.54	14.81	14.92	14.95
4.0	14.60	14.95	15.05	15.12
4.5	14.65	15.08	15.15	15.25
5.0	14.70	15.20	15.27	15.38
6.0	14.78	15.40	15.50	
7.0	14.85	15.62	15.70	
8.0	14.90	15.75	15.89	
9.0	14.95	15.97	16.10	
10.0	15.00	16.20	16.37	
11.0	15.04	16.42	17.00	
12.0	15.08	16.58	17.58	
13.0	15.12	16.76		
14.0	15.15	16.93		
15.0	15.18	17.10		

[a] "pH" = 14 − log [OH]. [b] After G. Yagil.[5b] [c] Our values observed in solutions containing 1% ethanol. [d] After C. H. Rochester.[12b]

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(16) L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, **54**, 2721 (1932).

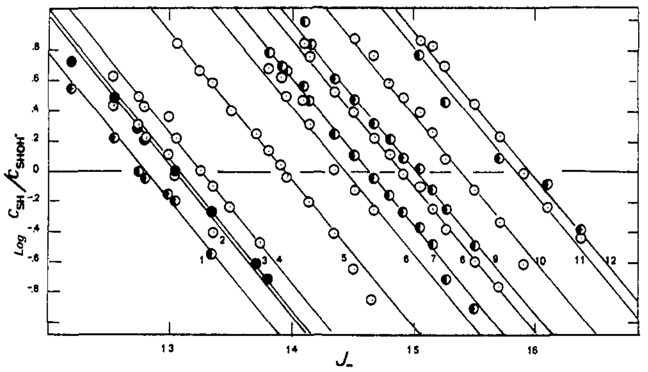


Figure 5. Values of log ([aldehyde]/[anion]) determined from spectrophotometric results are plotted against the J_- acidity scale for these benzaldehydes: (1) *p*-NO_2, (2) *m*-NO_2, (3) *p*-CN, (4) *m*-CN, (5) *m*-Cl, (6) *p*-Cl, (7) *m*-OCH_3, (8) H (benzaldehyde), (9) *m*-CH_3, (10) *p*-CH_3, (11) *m*-OH, and (12) *p*-OCH_3.

the benzaldehydes carried as substituents auxochromic or chromophoric groups, in all cases the benzenoid absorption band in the region between 250 and 280 nm decreased with increasing hydroxide concentration. This decrease was accompanied by a decrease of the $n \rightarrow \pi^*$ absorption band of the carbonyl group. This behavior in addition to confirmation that a single process is operating throughout the reaction series also indicated that in the formation of the corresponding base the conjugation between the aromatic ring and the side chain is suppressed and the nature of the carbonyl group changed, as corresponds to the acid–base process 6.

The uniformity of the process involved has been further confirmed by the fact that plots of log C_{SHOH^-}/C_{SH} against J_- are parallel and show a unit slope (Figure 5). This plot also indicates that J_- is an acceptable acidity function for the studied reaction series. Moreover, the linearity of the plots in Figure 5 indicate that formation of the dianion (9) has a pK_3 value which is

$$ArCH(OH)O^- + OH^- \underset{K_3}{\rightleftharpoons} ArCH(O)_2^{2-} + H_2O \qquad (9)$$

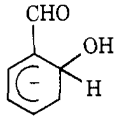
more than two p*K* units larger than pK_2 for the majority of compounds studied.

The trend of deviations shown for the plot in Figure 5 for *m*-methoxy- and *m*-chlorobenzaldehyde at higher J_- values is of the type and size expected for pK_3 approximately equal to pK_2 + 2. On the other hand, it is necessary to consider that at values of log $C_{SHOH^-}/C_{SH} > 0.8$ the experimental error considerably increases.

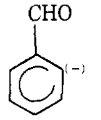
Further support of the uniformity of the acid–base reaction can be seen in the comparison of the obtained J_- values with the values obtained in aqueous solutions of sodium hydroxide by kinetic measurements[12] and with the H_- acidity function.[1] Over the region of J_- values over which values J_-(k) have been reported[12] the two acidity functions practically overlap (Figure 4). The relationship of J_- and H_- functions is similar to that of J_0' (or J_0''') and H_0. In solutions which resemble aqueous solutions, the J_- and H_- follow a similar trend. Differences are observed at the highest studied sodium hydroxide concentrations (Figure 4). Discussion of the nature of these deviations is meaningless until information will be available about the variation of activity coefficients of individual species with sodium hydroxide concentration.

Further support for the suitability of the studied system can be seen in the fact that in all cases the acid–base equilibrium has been rapidly established, and that by decreasing the basicity of the solution, equilibrium 6 has been found to be shifted quantitatively in favor of the corresponding benzaldehyde.

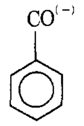
Finally, the internal consistency of the pK_2 (or pK', respectively) for the reaction series studied involving substituents X in meta and para position has been confirmed[14] by the linearity of the pK_2^x *vs.* σ_x plot. Alternatives to proposed reaction 6 were formation of a Meisenheimer type complex I, and of carbanions II and III. Formation of Meisenheimer complexes



I



II



III

results in a formation of a new long-wave band. Similarly, carbanions are known to form an intensive new absorption band in the 300-nm region. Such behavior is in direct contradiction with experimental results. Hence, reaction 6 seems to be the best description of the acid–base equilibrium used in definition of J_- acidity functions.

Extension of this study to the use of substituted benzaldehydes and related compounds for definition of J_- functions for solutions of other hydroxides in aqueous, nonaqueous, and mixed solvents is in progress.