Lewis Acid Properties of Benzaldehydes and Substituent Effects

By **William J. Bover** and **Petr Zuman,*** Department of Chemistry, Clarkson College of Technology, Potsdam, New York 13676, U.S.A.

Benzaldehydes, which do not exist in the hydrated form at lower pH values, have been found to add hydroxide ions in a reversible, rapidly established acid–base reaction in strongly alkaline media. In the reaction in aqueous solutions, an anion of the geminal diol is formed in reaction (1). Measurement of the decrease of absorbance in the 250—280 nm region as a function of sodium hydroxide concentration made it possible to determine equilibrium constants of reaction (1) for substituted benzaldehydes. The pK values follow a Hammett $\rho\sigma$ plot with ρ = 2·76. Deviations from the linear plot observed for *m*-hydroxybenzaldehyde and isophthalaldehyde are discussed.

SOME reactions in alkaline media of aldehydes in which the β-carbon has no hydrogen attached (*e.g.* systems CX_3CHO, $C{\equiv}C{-}CHO$, $COC{-}OH$ and ArCHO) where no interaction with hydrogen on the α-carbon is possible, were assumed to proceed *via* the monoanion of the hydrated form $CH(OH)O^-$ or even *via* the dianion $^-OCHO^-$. Examples of such processes are the Cannizzaro reaction,[1,2] Favorskii rearrangement,[3] benzilic acid rearrangement,[4-6] and deformylation reactions [7-10] in alkaline media.

Formation of anions of the type $CH(OH)O^-$ has been observed with increasing pH for strongly hydrated carbonyl compounds [10,11] and has been confirmed by equilibrium [10,11] and kinetic studies based on measurements of polarographic currents.[12,13] The pH above which the monoanion $CH(OH)O^-$ predominates in the solution depends on the pK value of the geminal diol

[1] K. B. Wiberg, *J. Amer. Chem. Soc.*, 1954, **76**, 5371.

[2] T. A. Geissman, *Org. Reactions*, 1944, **2**, 96.

[3] A. S. Kende, *Org. Reactions*, 1960, **11**, 261.

[4] F. H. Westheimer, *J. Amer. Chem. Soc.*, 1936, **56**, 2209; *J. Org. Chem.*, 1936, **1**, 1339.

[5] J. F. Eastman, R. G. Nations, and C. J. Collins, *J. Org. Chem.*, 1958, **23**, 1764.

[6] G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

[7] C. Gustafsson and M. Johanson, *Acta Chem. Scand.*, 1948, **2**, 42.

[8] E. Pfeil, H. Strache, and F. Lomker, *Annalen*, 1959, **623**, 74.

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

[10] J. Hine and G. F. Koser, *J. Org. Chem.*, 1971, **36**, 1348.

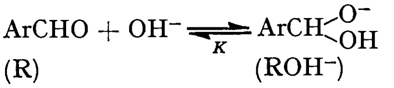
[11] R. P. Bell, *Adv. Phys. Org. Chem.*, 1966, **4**, 1.

[12] K. Veselý and R. Brdička, *Coll. Czech. Chem. Comm.*, 1947, **12**, 313.

[13] P. Zuman, D. Barnes, and A. Ryvolová-Kejharová, *Discuss. Faraday Soc.*, 1968, **45**, 202.

[*e.g.*, for $\mathrm{CF_3CH(OH)_2}$, pK 10·2;[14] $\mathrm{CCl_3CH(OH)_2}$, pK 10·0;[11] $\mathrm{PhC(OH)_2CF_3}$, pK 10·0;[15] $\mathrm{H_2C(OH)_2}$, pK 13·3;[11] and $\mathrm{PhC{\equiv}CC(OH)_2}$ pK 11·8[10]].

Benzaldehyde and most of its derivatives substituted on the aromatic ring, together with heterocyclic aldehydes with five-membered rings, show, nevertheless, no substantial formation of the geminal diol at lower pH values. In equilibrium less than a few percent are present in the hydrated form. For the reaction (1) no experimental evidence has been reported for the parent

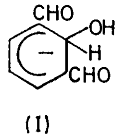


$$\underset{\text{(R)}}{\mathrm{ArCHO}} + \mathrm{OH^-} \underset{K}{\rightleftharpoons} \underset{\text{(ROH}^-\text{)}}{\mathrm{ArCH}\genfrac{}{}{0pt}{}{\mathrm{O^-}}{\mathrm{OH}}} \qquad (1)$$

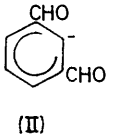
benzaldehyde or its *meta*- or *para*-substituted derivatives. The only values of equilibrium constants reported were obtained for 2,6-dichlorobenzaldehydes[9] and since no attempt has been reported since, it might be concluded that the reaction was considered restricted to some *ortho*-substituted benzaldehydes.

Principal differences observed in the comparison of polarographic curves[16] and spectra[17] of the three isomeric phthaldehydes[17] lead us to a preliminary investigation[18] which has shown that whereas the *ortho*- and *para*-isomers are strongly hydrated at lower pH values, isophthalaldehyde behaved like other substituted benzaldehydes and has shown no indication of formation of a geminal diol at lower pH values. An investigation of changes in u.v. spectra with varying sodium hydroxide concentration in strongly alkaline media indicated the presence of a reversible, rapidly established acid–base reaction. The spectra have shown a decrease both of the benzenoid (at *ca.* 250 nm) and $n \longrightarrow \pi^*$ carbonyl (at *ca.* 300 nm) bands with increasing hydroxide concentration.

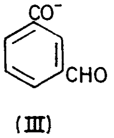
Four possible products (I)—(IV) of the interaction of isophthalaldehyde with hydroxide ions were considered.



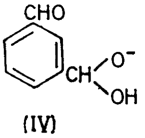
(I)



(II)



(III)



(IV)

Formation of a Meisenheimer type complex or of one of the carbanions (II) or (III) can be excluded from consideration, because a decrease of absorbance was observed for the longest wavelength band. Meisenheimer adducts[19,20] and carbanions[21] show the formation of a new long-wave band with increasing hydroxide concentration. Moreover, when solutions of isophthalaldehyde in tetrahydrofuran and other nonaqueous solvents were treated with sodium hydride,[18] no formation of hydrogen occurred and no increase in a long-wave absorption band was registered, as observed for *m*-dinitro-compounds.[19,20]

Whereas, formation of (I) or (II) (eventually with the attack in another position) can be expected only for *meta*-derivatives, structures (III) or (IV) depend on the presence of the second group only as a substituent. To support further our preference for structure (IV), we extended the study to other benzaldehydes bearing both electropositive and electronegative substituents in the *meta*- and *para*-positions. The observation that for all benzaldehydes studied, irrespective of whether the substituent is a chromophore or an auxochrome, a similar decrease of an absorption band at 250—300 nm occurs with increasing sodium hydroxide concentration, was considered to support structure (IV) as the conjugate base.

Reaction (1) is hence considered the best description of benzaldehydes as Lewis acids reacting with hydroxide ions.

As reaction (1) takes place in more or less concentrated solutions of sodium hydroxide, it was necessary to determine thermodynamic pK values of those substituted benzaldehydes which are strongest acids in dilute sodium hydroxide solutions by using extrapolation to zero ionic strength. Based on these values, pK values of the other very weak Lewis acids can be determined by an overlap procedure.[22] The values of pK of substituted benzaldehydes can be used as those of indicators in the development of the J_- acidity scale.[23] The pK values for substituted benzaldehydes enable us also to investigate substituent effects on the acid–base equilibrium (1).

EXPERIMENTAL

Most of the aldehydes employed were supplied by Aldrich. Purity was checked by measurement of their m.p.s or b.p.s and by g.l.c. The few benzaldehydes the purity of which proved to be unsatisfactory were recrystallized from ether or ethanol.

The 0·01M stock solutions of aldehydes in absolute ethanol or water were prepared every day and kept in the dark at 4 °C. Ethanol was preferred as a solvent for preparation of the stock solution, with respect to the solubility. For benzaldehydes (*p*-methyl- and -methoxy- and *m*-hydroxy-derivatives) where it was necessary to carry out experiments at concentrations of sodium hydroxide $>$8M, aqueous stock solutions of the benzaldehydes were prepared, because of the limited miscibility of ethanol with such solutions.

Spectrophotometric experiments were carried out by addition of 0·1 ml of the stock solution (delivered by a 100 μl pipette) to 9·9 ml of the buffer or sodium hydroxide

---

[14] R. Stewart and M. M. Mocek, *Canad. J. Chem.*, 1963, **41**, 1160.

[15] R. Stewart and R. Van der Linden, *Canad. J. Chem.*, 1960, **38**, 399.

[16] L. Holleck and H. Marsen, *Z. Elektrochem. Ber. Bunsengesellschaft Phys. Chem.*, 1953, **57**, 944.

[17] D. Barnes, unpublished results.

[18] W. J. Bover, B.Sc. Thesis, Clarkson College of Technology, Potsdam, New York, 1971.

[19] T. N. Hall and C. F. Poranski, jun., 'Polynitroaromatic Addition Compounds,' in 'The Chemistry of the Nitro and Nitroso Groups,' ed. H. Fever, Interscience, New York, 1970, p. 329.

[20] E. Buncel, A. R. Norris, and K. E. Russell, *Quart. Rev.*, 1968, **22**, 123.

[21] D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965.

[22] C. H. Rochester, 'Acidity Functions,' Academic Press, New York, 1970.

[23] W. J. Bover and P. Zuman, *J. Amer. Chem. Soc.*, in the press.

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

A preliminary spectrophotometric investigation of all the benzaldehydes studied has been performed prior to the detailed study of the alkaline solution. To cover the entire aqueous pH range, 0·1N-H_2SO_4, 0·1N-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 0·1N and 1·0N 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 18·86N. From this solution 11, 12, and 13M solutions of sodium hydroxide were prepared by dilution with distilled, carbonate-free water, as well as 10 and 5M stock solutions of sodium hydroxide, and standardized against potassium acid phthalate. From these two stock solutions 1—9M solutions were prepared by dilution. The transfer of 50%, 10M, and 5M solutions for dilution was carried out under nitrogen. The 0·1—1·0M-sodium hydroxide solutions were prepared by dilution of 1·0M-Dilut-it standard solution, and the 0·01—0·1M sodium hydroxide solutions by dilution of 0·1M-Dilut-it standard.

Equipment.—A Unicam SP 800-A recording spectrophotometer was employed for all measurements of the u.v. absorption spectra. Matched fused quartz cells (10 mm sample path) were placed in a thermostatted compartment through which water was circulated by means of a Mark F. J. (Haake, Berlin) thermostat so that the temperature of the solution in the cell was kept 25 ± 0·1 °C. The cells were cleaned with a dilute, 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 preliminary experiments. A Varian Aerograph series 1200 with a flame ionization detector and Sargent model SR recorder were employed for g.l.c. The 5 ft × $\frac{1}{8}$ in stainless steel column used contained 3% SE-30 on 100–120 Varaport No. 30. Evaluation of numerical data has been carried out by means of a modified PDP-8 computer (Digital Equipment Corp.).

RESULTS

To determine p*K* values of the substituted aldehydes, the change in u.v. spectra in aqueous solutions of varying sodium hydroxide concentration containing 1% ethanol and 1×10^{-4}M aldehyde was followed.

Optical data and p*K* values for reaction of substituted benzaldehydes with hydroxide ions

Aldehyde	λ_{max}/nm [a] ε/l mol^{-1} cm^{-1}	λ_{calc}/nm [b]	p*K* [c]	p*K′* [d]	σ [e]
m-Nitrobenzaldehyde	270 2800	238	−0·96	13·04	0·71
p-Nitrobenzaldehyde	268 14,000	260	−1·21	12·79	0·78
m-Cyanobenzaldehyde	245 8000	245	−0·74	13·26	0·68
p-Cyanobenzaldehyde	254 19,000	258	−0·94	13·06	0·66
Isophthalaldehyde	250 13,000	230	−1·00	13·00	0·38
m-Chlorobenzaldehyde	249 10,000	250	−0·08	13·92	0·37
p-Chlorobenzaldehyde	260 16,000	260	0·44	14·44	0·23
m-Anisaldehyde	255 9000	250	0·61	14·61	$0{\cdot}11_5$
Benzaldehyde	250 12,800	250	0·90	14·90	0
m-Tolualdehyde	254 13,800	255	1·00	15·00	−0·07
p-Tolualdehyde	261 17,000	263	1·39	15·39	−0·17
p-Anisaldehyde	280 16,000	280	1·96	15·96	−0·27
m-Hydroxybenzaldehyde	266 6000	265	1·81	15·81	(−0·71) [f]

[a] Wavelength of the absorption maximum (B and K band) and molar absorptivity coefficient. [b] Wavlength at which the ratio c_{ROH^-}/c_R was determined. [c] $K = c_{ROH^-}/c_R c_{OH^-} \times y_{ROH^-}/y_R y_{OH^-}$. [d] $K' = KK_w = c_{ROH^-} c_{H^+}/c_R \times y_{ROH^-} y_{H^+}/y_R$. [e] Hammett substituent constant used. [f] Uncertain value.

Benzaldehydes generally show three main absorption bands in the u.v. region, *viz.* an $n \longrightarrow \pi^*$ carbonyl absorption band (R band) of low intensity at *ca.* 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 *ca.* 210 nm corresponding to $\pi \longrightarrow \pi^*$ transitions (E band). Since at higher sodium hydroxide concentration the cut off due to the OH^- absorption shifted to *ca.* 230 nm, measurements of the 210 nm band were impractical. The forbidden transition bands at 300 nm were in a region where most anions ROH^- do not show measurable absorption, but because of low sensitivity due to the low extinction coefficient, measurement of this band has been made use of only in some few instances where further confirmation was necessary.

Since the anion ROH^- 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_{ROH^-}/c_R. The molar absorptivity (extinction) coefficient of this absorption band for various benzaldehydes (R) ranged from 7000 to 19,000 l mol^{-1} cm^{-1} (Table). These values were obtained at $pH < 12$ where the formation of the anion can be neglected.

Furthermore, the absorption band in the 250—280 nm region shows, for the majority of the benzaldehyde studied, an almost negligible residual absorbance at higher sodium hydroxide concentrations (Figure 1) where the anion ROH^- predominates. The only exceptions were *m*- and *p*-nitrobenzaldehyde, where it was necessary to make corrections for the absorption caused by the nitrobenzene portion of the molecule. Similarly for isophthalaldehyde corrections were necessary for the absorption due to C_6H_4CHO grouping in $HCO{-}C_6H_4{-}CH(OH)O^-$. The wavelength actually chosen for the measurement of the absorbance in the p*K* determination was generally at or close to the wavelength of the absorption maximum to achieve the highest accuracy.

The p*K* values of substituted benzaldehydes were determined by means of the spectrophotometrically measured ratio of c_{ROH^-}/c_R using standard procedures.[22] Thermodynamic p*K* values for the four strongest acids (*p*-NO_2, *p*-CN, *m*-NO_2, and *m*-CN derivatives) were determined by means of extrapolation to $[OH^-] = 0$ (*i.e.*, to $\mu = 0$) and the values for the other benzaldehydes were determined by an overlap procedure. Plots of log c_{ROH^-}/c_R against the J_- function derived by us [23] were linear and had a unit slope (Figure 5 of ref. 23). This indicates the validity of the assumption [24] of equality of activity coefficients ratio.

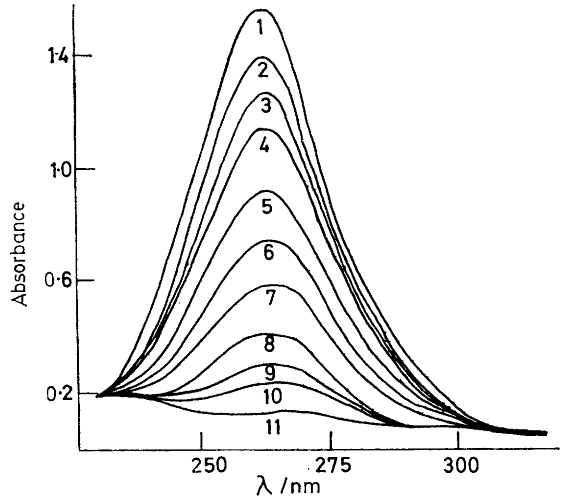


FIGURE 1 The u.v. absorption spectra of *p*-tolualdehyde in aqueous solutions containing sodium hydroxide: (1) 0·8; (2) 2·0; (3) 3·0; (4) 4·0; (5) 5·0; (6) 6·0; (7) 7·0; (8) 8·0; (9) 9·0; (10) 10·0; and (11) 12·0M. The solutions (25 °C) were 1 × 10^{-4}M in aldehyde with curves (1)—(8) containing 1% ethanol

To test the internal consistency of the data, the values of p*K* for *m*-NO_2, *p*-CN, and *m*-CN were determined by the overlap procedure based on the p*K* value for the *p*-NO_2 derivative. The p*K* values so obtained were then compared with p*K* values obtained by extrapolation to zero ionic strength. These two sets of data agreed within 0·02 p*K* units which is inside the experimental error, which is *ca.* 0·03 p*K* units below p*K* 14·7 and *ca.* 0·05 p*K* units for weaker acids.

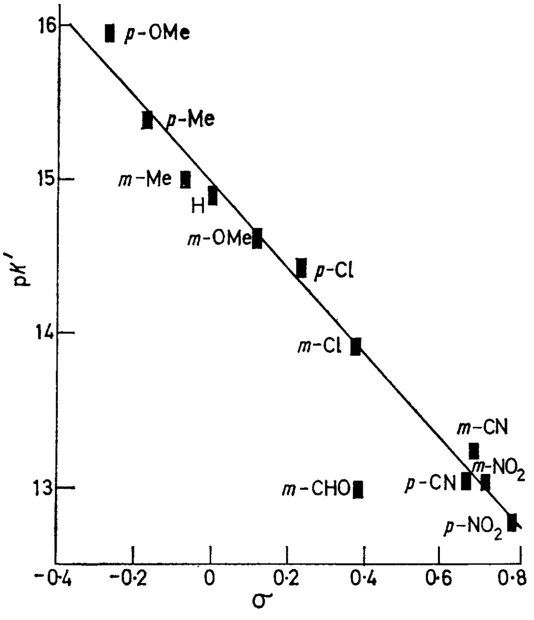


FIGURE 2 Spectrophotometrically determined values of acid dissociation constants p*K'* for the reaction of substituted aldehydes with hydroxide ions at 25 °C plotted against Hammett substituent constants σ. Plotted line corresponds to $\varepsilon = 2{\cdot}76$. The value for *m*-CHO was not included in the correlation.

To enable comparison with the strength of proton-donating acids, the calculated p*K* values were converted into p*K'* defined as $pK' = pK + pK_w$ (Table).

To express the effect of substituents the values p*K'* were plotted as a function of the Hammett [25,26] substituent constants σ (Figure 2). The slope of the linear plot corresponded to a reaction constant ρ of 2·76. For the values for the 11 compounds shown, the correlation coefficient *r* was found 0·994 and the standard error of estimate *S* (est) for the slope was 0·012. When the p*K'* values were plotted as a function of the substituent constant σ^+ a linear plot (ρ 2·19) has also been obtained but the correlation was worse [*r* 0·939, *S*(est) = 0·049].

DISCUSSION

The regular effect of introduction of substituents on the p*K'* value corresponding to the equilibrium of the benzaldehydes with hydroxide ions as expressed by the linearity of the p*K*–σ plot confirms that all the aldehydes studied undergo an acid–base reaction of the same type in alkaline media. This is confirmed by analogous changes in the u.v. spectra with increasing sodium hydroxide concentration. It is concluded that the acid–base reaction involved is best described by equation (1)

---

[24] L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721.

[25] L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1st edn., 1940, p. 188.

[26] J. E. Leffler and E. Grunwald, 'Rates and Equilibria of Organic Reactions,' Wiley, New York, 1963, p. 173.

which shows benzaldehydes acting as Lewis acids susceptible to a nucleophilic attack by hydroxide ions.

The positive value of the reaction constant ρ indicates a reaction in which a negative charge is developed on the side chain.[27] This is in agreement with reaction (1) and structure (IV) for the conjugate base. As structure (IV) carries a unit charge in the side chain similar to benzoates, the observed value (2·76) of the reaction constant ρ observed for benzaldehydes being larger than that for benzoic acid dissociation ($\rho = 1{\cdot}0$) indicates that grouping $CH(OH)O^-$ is able to interact with substituents on a benzene ring to a larger extent than CO_2^-. This may due to resonance stabilization of the carboxylate group.

For two substituents deviations from the linear pK–σ were observed: *m*-hydroxy (not shown in Figure 2) and *m*-formyl (in isophthaldehyde). Treatment of the effects of substituents bearing a unit charge is considered to be complicated by various factors and substituent constants expressing the effect of charged substituents are rather limited in their application. Use of a tabulated value for $\sigma_{m\text{-}O^-} = -0{\cdot}71$ and the ρ value 2·76 gives for *m*-hydroxybenzaldehyde a value which is far below the line plotted in Figure 2. If, on the other hand, our experimental pK values for benzaldehyde and *m*-hydroxybenzaldehyde and the ρ value 2·76 are used, a value of $\sigma_{m\text{-}O^-} = -0{\cdot}32$ can be calculated. Even this value is the most negative one found for a *meta*-derivative, that for $\sigma_{m\text{-}NH_2} = -0{\cdot}16$ being closest.

The introduction of a second formyl group in isophthalaldehyde results in a pK' value (13·0) which is *ca* 0·9 Kp units lower than the value obtained for the linear plot and $\sigma_{m\text{-}CHO} = 0{\cdot}38$. The shape of the log c_{ROH^-}/c_R *vs.* pH plot for isophthalaldehyde indicates that only one of the formyl groups reacts with hydroxide ions at pH 12—14. The problem of aromatic compounds with two reactive centres has not been discussed in general terms from the point of view of the substituent effect of the second centre on the first. In some cases, kinetic evidence [28] indicates that the second group can be treated as another substituent. In the case of acid reactions of benzaldehydes, this cannot be assumed. The deviation of pK' observed is in the same direction and roughly of the same magnitude ($\Delta_{theor} = 0{\cdot}6$) as predicted by the probability factor.[29]

Hence none of the observed substituent effects is at variance with equation (1) which best describes the observed acid–base reaction of substituted benzaldehydes. Extension of this study to other types of aldehydes is in progress.

The support of this work by an Eastman Kodak Fellowship (1971—1972) and by the Edward Western Fellowship of the Electrochemical Society (summer 1972) awarded to one of us (W. J. B.) is acknowledged.

[2/2222 *Received, 25th September,* 1972]

---

[27] Ref. 26, p. 177.

[28] P. Zuman, ' Substituent Effects in Organic Polarography,' Plenum Press, New York, 1967.

[29] N. Bjerrum, *Z. physik. Chem.*, 1923, **106**, 219.