of magnitude is observed. This effect is attributed to the reversible formation of the acetal and will be discussed in paper II of this series.

Summary

The absorption spectra of the three *o*-hydroxynaphthaldehydes and their negative ions has been determined in a variety of solvents. A theory, based on resonance possibilities in the ground and excited states, accounts for the striking differences in the low frequency absorption bands of these compounds.

CHICAGO 12, ILL. RECEIVED APRIL 27, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Absorption Spectra of *o*-Substituted Aldehydes. II. Aldehyde–Acetal Equilibrium in Methanol–Water Solutions[1]

BY NORTEN C. MELCHIOR[2]

The striking effect of temperature change upon the absorption spectrum of 3-hydroxy-2-naphthaldehyde in acidified 80 mole per cent. methanol–water,[3] and the fact that temperature change had no such effect on the spectra of either 1-hydroxy-2-naphthaldehyde or 2-hydroxy-1-naphthaldehyde under identical conditions led to the extension of these studies to related compounds. Under the same conditions it was found that the spectrum of salicylaldehyde was somewhat affected by temperature, while that of *o*-methoxybenzaldehyde showed a pronounced temperature effect. Further experiments showed that the temperature dependence vanished when *neutral* methanol or methanol–water was used as solvent, and that temperature dependence appeared when acidified 98 mole per cent methanol was used as solvent for either 1-hydroxy-2-naphthaldehyde or 2-hydroxy-1-naphthaldehyde. These experiments suggested that the changes observed were caused by acid catalyzed formation of· acetals or hemiacetals. To distinguish between these possibilities, and to define the differences existing among these related compounds, their spectra were determined in neutral and acid methanol–water solutions over a range of temperature and methanol concentration.

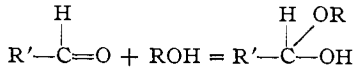
Experimental

Absorption Measurements.—A Beckman model D. U. spectrophotometer was used in all measurements. One-cm. fused silica cells with standard taper stoppers prevented solvent loss by evaporation. The temperature of the cells was controlled as previously described.[3] As a precaution, the previously purified aldehydes were distilled or sublimed immediately before use and were handled in nitrogen. Methanol was reagent grade, and blanks were prepared from the same sample of solvent in all cases.

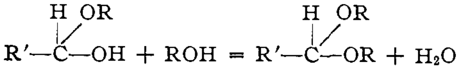
Preparation of Salicylaldehyde Methyl Acetal.—Twenty-five ml. (29 g.) of salicylaldehyde was dissolved in 100 ml. of methanol which contained 0.002 mole of hydrochloric acid. The solution was cooled in stages to Dry-Ice temperature and stored in Dry Ice for one week. It was then neutralized at that temperature with 1 *N* sodium hydroxide, and the methanol and water removed below 0.1 mm. as the mixture warmed to room temperature. The precipitated salt was filtered off with the aid of an anhydrous ether wash, and the product distilled at less than 0.01 mm. after removal of the ether below 25°. After the lapse of a week, this fraction was redistilled, and after preliminary evolution of a low-boiling liquid (possibly methanol), a 9-g. fraction (b. p. 64.5–65.0°, 0.01 mm.; d^{25}_4 1.107, $n^{25}\text{D}$ 1.5119) was obtained. The colorless residue weighed 9 g. Analysis of the distillate gave C, 64.8, 64.8; H, 7.2, 7.3. Calculated for $C_9H_{12}O_3$: C, 64.27; H, 7.19. This is apparently the same substance prepared by Pauley and v. Buttlar,[4] but these authors report only the boiling point.

Calculations and Results

The equilibria considered are



$$R'\text{—}\overset{\text{H}}{\text{C}}\text{=O} + ROH = R'\text{—}\overset{\text{H OR}}{\text{C}}\text{—OH} \qquad (1)$$



$$R'\text{—}\overset{\text{H OR}}{\text{C}}\text{—OH} + ROH = R'\text{—}\overset{\text{H OR}}{\text{C}}\text{—OR} + H_2O \qquad (2)$$

The equilibrium constant for the sum of reactions 1 and 2 is

$$K_{1+2} = \frac{a_{\text{acetal}}a_{\text{water}}}{a_{\text{aldehyde}}a^2_{\text{methanol}}} = \frac{\gamma_{\text{Ac}}N_{\text{Ac}}\gamma_{\text{H}_2\text{O}}N_{\text{H}_2\text{O}}}{\gamma_{\text{Al}}N_{\text{Al}}\gamma^2_{\text{MeOH}}N^2_{\text{MeOH}}} \qquad (3)$$

If we assume that hemiacetal formation is small, the ratio $N_{\text{Ac}}/N_{\text{Al}}$ can be obtained from the measured absorption spectra as

$$\frac{N_{\text{Ac}}}{N_{\text{Al}}} = \frac{\epsilon_0 - \epsilon}{\epsilon - \epsilon_1} \qquad (4)$$

where, at a given wave length,[5] ϵ_0 is the measured extinction coefficient of the aldehyde in neutral methanol, ϵ_1 is that of the acetal in neutral methanol and ϵ is the apparent extinction coefficient of the aldehyde in a given acidified methanol–water solution. If ϵ_1 is zero or small compared to ϵ_0 and ϵ, the equation reduces to (1)

$$N_{\text{Ac}}/N_{\text{Al}} = \epsilon_0 - \epsilon/\epsilon \qquad (5)$$

Measurements of the spectra of the acetals of salicylaldehyde and *o*-methoxybenzaldehyde showed that ϵ_1 was small at the wave lengths chosen in each case, and consideration of the spectra of α- and β-naphthol indicated that this

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[1] Presented at the meeting of the American Chemical Society in San Francisco, March, 1949.

[2] Present address: Stritch School of Medicine, Loyola University, Chicago 12, Illinois.

[3] Paper I, THIS JOURNAL, **71**, 3647 (1949).

[4] H. Pauley and R. v. Buttlar, *Ann.*, **383**, 283 (1911).

[5] The preferred wave length is that of an absorption maximum which can be ascribed to the carbonyl group.

was also the case at the rather long wave lengths chosen for the naphthaldehyde calculations.

Preliminary calculations of K_{1+2} (equation 3) assuming that $\gamma_{Ac} = \gamma_{Al}$ and using values from the literature[6] for the activities of methanol and water gave only fair agreement between values calculated from measurements at different methanol–water ratios. Examination of the published data revealed that no measurements had been made in the range of concentration which is of interest here, although in some cases data from smoothed curves had been tabulated in this range.

It was, therefore, necessary to obtain some assurance as to the meaning of the numbers which could so easily be obtained from laboratory measurements. Rearrangement of equation (3) and combination with (5) gives

$$\frac{\epsilon_0 - \epsilon}{\epsilon} = \frac{N_{Ac}}{N_{Al}} = K_{1+2}\frac{\gamma_{Al}\gamma^2_{MeOH}N^2_{MeOH}}{\gamma_{Ac}\gamma_{H_2O}N_{H_2O}} \qquad (6)$$

If the plot of $(\epsilon_0 - \epsilon)/\epsilon$ against N^2_{MeOH}/N_{H_2O} is a straight line, the quantity $(\gamma_{Al}\gamma^2_{MeOH})/(\gamma_{Ac}\gamma_{H_2O})$ is a constant over the range considered, and if that constant is unity, the slope of the line is K_{1+2}. Figure 1 shows typical measurements from which these data can be obtained, and Fig. 2 shows this test applied to the data for salicylaldehyde.[7] The linear relationship found is confirmed by the data on *o*-methoxybenzaldehyde and 3-hydroxy-2-naphthaldehyde. This test simultaneously verifies the assumption that hemiacetal formation is small, since any appreciable hemiacetal formation would cause a deviation from the straight line observed.

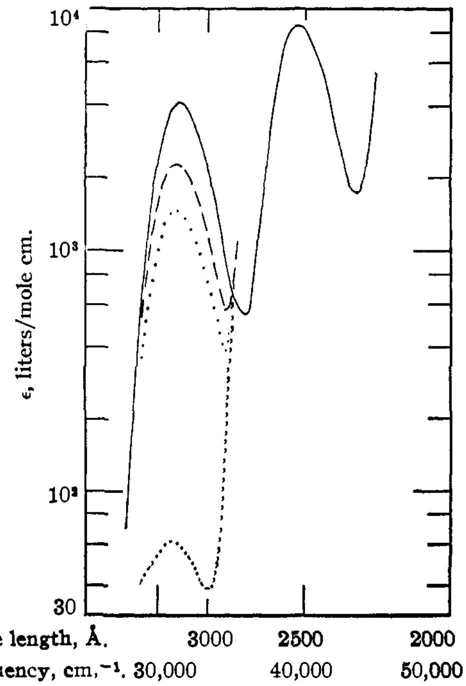

Fig. 1.—Absorption spectra of *o*-methoxybenzaldehyde in methanol–water solutions: — neutral methanol, 25°; — — eighty mole % methanol, 0.01 *M* HCl, 25°; ...... eighty mole % methanol, 0.01 *M* HCl, 2°; - - - - methanol, 99.8 mole %, 0.01 *M* HCl, 25°.

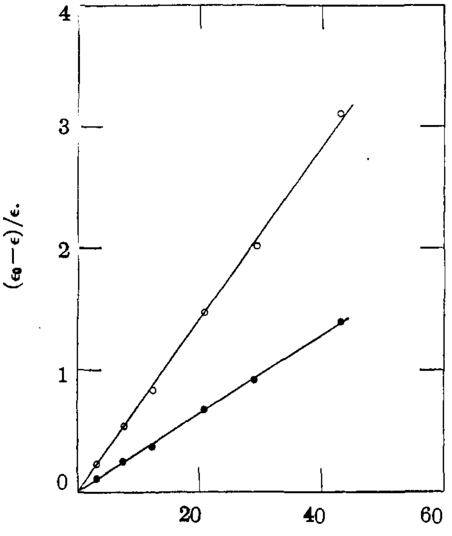

Fig. 2.—Extinction coefficients of salicyaldehyde in acidified methanol–water solutions, λ = 3250 Å.: filled circles, 25°, open circles, 2°.

One can then calculate equilibrium constants on a comparative basis. The values obtained will be subject to a constant correction when the activity coefficient of water in these solutions is available, but are useful for comparative purposes and can be used in calculation of comparative values for ΔH and ΔS without ambiguity. The data obtained are given in Table I and the calculated thermodynamic values are collected in Table II.

Discussion

The data in Table I show clearly the reason temperature has so much less effect on the spectra of 2-hydroxy-1-naphthaldehyde and 1-hydroxy-2-naphthaldehyde than on those of the other aldehydes studied. In most methanol–water solutions so little acetal is formed from either of these aldehydes that the spectrum is only slightly affected, and in 80 mole per cent. methanol even a 100% change in the amount of acetal would scarcely be measurable.

The values obtained for the equilibrium constants cannot, unfortunately, be compared with

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[6] (a) Ferguson and Funnell, *J. Phys. Chem.*, **33**, 1 (1929); (b) M. Ewert, *Bull. soc. chim. Belg.*, **45**, 493 (1936); (c) Butler, Thomsen and Maclennan, *J. Chem. Soc.*, 674 (1933); (d) Dulitkaya, *J. Gen. Chem.* (*U. S. S. R.*), **15**, 9 (1945).

[7] Although the straight line relationship is found, it has not been shown that $\gamma_{Al}/\gamma_{Ac} = 1$, nor that $\gamma^2_{MeOH}/\gamma_{H_2O} = 1$. The first is probably correct, since the solutions of aldehyde were very dilute and the standard state chosen is the infinitely dilute solution. The second relation is probably not correct. In this range γ_{MeOH} is probably unity, while γ_{H_2O} is somewhat greater than unity. Over the range of interest, however, both appear to be constant.

TABLE I

ACETAL FORMATION IN METHANOL–WATER SOLUTIONS

Compound	N_{MeOH}	$\epsilon \times 10^{-3}$ 25°	$\epsilon \times 10^{-3}$ 2°	K_{1+2} 25°	K_{1+2} 2°
Salicylaldehyde, λ = 3250 Å.	1.00[a]	3.51	3.61	.....	.....
	0.978	1.46	0.88	0.0325	0.0722
	.968	1.83	1.19	.0318	.0696
	.956	2.10	1.46	.0324	.0706
	.925	2.56	1.97	.0326	.0733
	.895	2.82	2.32	.0325	.0714
	.802	3.16	2.92	.0345	.0721
				.0324[b]	.0714[b]
o-Methoxybenzaldehyde, λ = 3200 Å.	1.00[a]	4.11	4.11	.....	.....
	0.895	1.39	0.753	0.256	0.591
	.802	2.24	1.46	.257	.559
	.802	2.28	1.45	.248	.565
	.648[c]	3.12	2.34	.262	.633
				.256[b]	.582[b]
3-Hydroxy-2-naphthaldehyde, λ = 3846 Å.	1.00[a]	1.76	1.74	.....	.....
	0.956	0.447	0.217	0.141	0.337
	.895	0.847	.488	.142	.336
	.802	1.17	.511	.157	.362
				.142[b]	.336[b]
2-Hydroxy-1-naphthaldehyde, λ = 3580 Å.	1.00[a]	5.22	5.22	.....	.....
	0.978	4.04	3.44	0.0067	0.0120
1-Hydroxy-2-naphthaldehyde, λ = 3720 Å.	1.00[a]	4.90	4.90	.....	.....
	0.978	4.22	3.95	0.0037	0.0056

[a] In *neutral* methanol. [b] Value from the slope of the line as in Fig. 2. [c] Value probably outside the range of constancy of γ_{MeOH} and γ_{H_2O}.

TABLE II

THERMODYNAMIC QUANTITIES[a] FOR THE FORMATION OF ACETALS IN METHANOL–WATER SOLUTIONS

Compound	$\Delta F°_{298}$ cal.	ΔH, cal.	ΔS, e. u.
o-Methoxybenzaldehyde	+ 800	−5800	−22.2
Salicylaldehyde	+2000	−5600	−25.5
3-Hydroxy-2-naphthaldehyde	+1200	−6200	−24.6
2-Hydroxy-1-naphthaldehyde	+3000	−4100	−23.6
1-Hydroxy-2-naphthaldehyde	+3300	−2800	−20.5

[a] For comparative purposes, see note (7) and the text.

those obtained by Adkins and co-workers,[8] since, as these workers recognized, one cannot estimate the activities of any of the substances in their reaction mixtures. The only advantage the spectroscopic measurement can claim is the use of very dilute solutions of aldehyde and acetal; so that the problem is reduced to the estimation of the activities of water and the alcohol concerned. For the first time we are able to examine the separate factors which influence the formation of acetals from different aldehydes with some degree of assurance.[9]

The driving force of the reaction is found in ΔH, and is comparable to that for the formation of ethers from alcohols. The entropy of the system decreases in all cases. A portion of this decrease can be ascribed to the decrease in the number of particles, while some of the remainder may be due to differences in hydrogen bonding of water molecules as compared to alcohol molecules. These factors are constant in all the cases considered. The *differences* observed must be due to differences in the aldehydes and their corresponding acetals and their respective solvent envelopes. Comment on these differences is restricted because of the lack of a common plane of reference, but cautious analysis may yield some information.

In comparing the equilibrium formation of acetal from salicylaldehyde with that from *o*-methoxybenzaldehyde one might reason that, since a chelated hydrogen bond must be broken in the case of the salicylaldehyde but not in *o*-methoxybenzaldehyde, the formation of acetal from the latter should be favored over that from the former. This is exactly what is observed. However, the data in Table II show that this argument, based on energy considerations, has substantially nothing to do with the result, and that differences in ΔS are the basis of the observed changes. The values for ΔH, which is closely related to energy change, indicate that energy required to replace that of the chelated hydrogen bond is supplied, most probably by the formation of several new hydrogen bonds with the solvent. If, then, we accept the values for ΔH as evidence that the *increase* in the number of solvent molecules bound is greater in the formation of salicylaldehyde methyl acetal than in the formation of *o*-methoxybenzaldehyde methyl acetal, we are prepared for the experimental result that the increase in order (decrease in entropy) is greater in the former reaction. It may be noted that the values of ΔS for the sterically similar compounds salicylaldehyde and 3-hydroxy-2-naphthaldehyde are more nearly alike. This same small but, the author believes, real difference is observed in the values of ΔS in the reactions of 3-hydroxy-2-naphthaldehyde and 2-hydroxy-1-naphthaldehyde, both of which yield substituted β-naphthols with the hydroxyl group sterically available to the solvent. This is not the case with 1-hydroxy-2-naphthaldehyde, and we find definitely different values for both ΔH and ΔS, a result which is consistent with a much smaller change in solvation in the reaction than in those of the isomeric compounds considered. There are two qualitative indications that the hydroxyl group is a solvation site even when the chelate ring is presumably intact. One is the almost negligible effect of the solvent

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[8] For leading references to the work of Adkins, Adams, Hartung, Street, Broderick, Minne and Dunbar, see THIS JOURNAL, **56**, 442 (1934).

[9] Parks and Huffman have calculated some standard free energies from the equilibrium data of Adkins and co-workers ("The Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, N. Y., 1932, pp. 169–170). These authors estimate the uncertainty in these free energies to be of the order of 100 calories. Since this corresponds to values of the ratio of the activity coefficients in the range 0.8 to 1.2, this author believes that their estimate of the uncertainty is too low.

change hydrocarbon to water on the spectrum[3] of 1-hydroxy-2-naphthaldehyde, while its isomers show a real, albeit small, effect which is not due to acetal formation. The second is the fact that this compound steam distils with ease, its isomers with considerable difficulty.

Further, if we assume the energies of the acetals which are substituted β-naphthols to be the same, we find that the values for ΔH indicate that the ground state of 3-hydroxy-2-naphthaldehyde is some 2,000 calories above that of 2-hydroxy-1-naphthaldehyde. This is the order deduced in the previous paper,[3] but the numerical difference is less than half that expected. It seems probable that this is due to differences in solvent interaction which were much less important in the measurements made in hydrocarbon solvents.

Summary

The differences observed in the spectra of certain aldehydes in neutral methanol as compared to solutions in acidified methanol have been shown to be due to the reversible formation of the corresponding acetal in the acid solutions. The equilibrium constants for these reactions have been determined at 25 and 2°, and from these data comparative values for ΔH and ΔS have been calculated. Comparison of these data suggests the importance of solvation in interpreting the differences observed. The spectroscopic method offers a tool for the study of this reaction which is capable of separating to some extent energy factors from orientation factors.

CHICAGO 12, ILL. RECEIVED APRIL 27, 1949

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORQUIMA, S. A.]

Ferrous Mono-α,α'-dipyridyl

BY P. KRUMHOLZ

It has been assumed until recently, that only one type of complexes between ferrous ion and α-α'-dipyridyl (D) or *o*-phenanthroline (Ph) exists in solution and that the 6-coördinated ions FeD_3^{++} and $FePh_3^{++}$ are present.[1]

The formation of lower Fe^{++}–D complexes as intermediates in the formation of FeD_3^{++} has been recently assumed and confirmed by the observation that the formation of FeD_3^{++} is less complete with an excess of Fe^{++} than with equivalent concentrations.[2]

Analogous yellow-colored complexes exist in the system Fe^{++}–Ph, and it seems that both complexes $FePh_2^{++}$ and $FePh^{++}$ may be formed under favorable conditions.[3]

We found strong evidence for the existence of the complex ion FeD^{++} studying the kinetics of formation of FeD_3^{++},[4] by the observation, that the reaction velocity, initially proportional to the Fe^{++} concentration, is retarded by a large excess of Fe^{++}. The kinetics could be correctly interpreted, assuming the very rapid formation of FeD^{++} with an equilibrium constant $K_{FeD} = 2.7 \times 10^4$ at 25° and $\mu = 0.33$.

In the present paper we confirm this indirect finding by an entirely different and direct method. We found that acid solutions of α,α'-dipyridyl, containing only a small amount of free D, form with a large excess of Fe^{++} yellow solutions which turn reddish more or less rapidly, due to the formation of FeD_3^{++}. Under suitable conditions such solutions are stable enough to determinate their extinction in dependence on the concentrations of the reactants, and thus the composition and equilibrium constant of the yellow compound. Solutions containing a very large excess of Fe^{++} are stable enough to measure the absorption spectrum of the yellow compound. As the calculation of the equilibrium constants involves the acid constant of the α,α'-dipyridylium ion (HD^+), this constant has been determined.

Experimental

Material Used.—α,α'-Dipyridyl was purified by vacuum distillation and recrystallized from diluted alcohol and hexane; m. p. 70°. Ferrous chloride solutions were prepared by dilution of a filtered 0.5 *M* solution, kept over iron powder with 0.005 *N* hydrochloric acid.

Determination of the Acid Constant of α,α'-Dipyridylium Ion.—The acid constant of HD^+ was computed from *p*H values of solutions of D and its hydrochloride, the ionic strength being adjusted with potassium chloride. The *p*H values were determined with a glass electrode, calibrated with standard biphthalate and acetate buffers at the same temperature as the sample. Temperatures were kept constant to within ±0.3°. The potential readings could be reproduced within ±0.5 m. v. Even accounting for possible errors due to diffusion potentials between the saturated potassium chloride bridge and the measured solution and for the uncertainty in the *p*H values of the buffer, the error of the absolute values of the constants should be less than 10%.

Determination of the Extinction of Fe^{++}-D Solutions.—To obtain reproducible extinction values of solutions of the yellow complex, it is necessary to establish very rapidly a high concentration of Fe^{++}, because at low Fe^{++} concentrations there appears almost immediately the red color of FeD_3^{++}. The mixing set up consisted of a 250-ml. beaker provided with two propeller stirrers rotating with the maximum speed, not yet introducing air bubbles into the liquid. About 125 ml. of the HD^+ solution, containing various amounts of hydrochloric acid and potassium

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(1) C. Ferrari, *Gazz. chim. ital.*, **67**, 604 (1937); R. K. Gould and W. C. Vosburgh, THIS JOURNAL, **64**, 1631 (1942). In the solid state F. M. Jaeger and J. A. van Dijk, *Z. anorg. Chem.*, **227**, 273 (1936), prepared 1:1 compounds between α,α'-dipyridyl and ferrous sulfate.

(2) J. H. Baxendale and Ph. George, *Nature*, **162**, 177 (1948).

(3) T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, **70**, 3596 (1948).

(4) P. Krumholz, *Nature*, **163**, 724 (1949). The formulation FeD^{++} does not exclude that other groups, as water or Cl^- are coördinated to Fe^{++}.