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.

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[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^{++}.

chloride, were placed in the beaker and the Fe^{++} solution introduced by means of a 25-ml. pipet with a large opening. The time of complete mixing is less than one second. A parallel light-beam was directed across the beaker, between the shafts of the stirrers, the light intensity being measured by a photronic cell and a spotlight galvanometer of 5×10^{-9} amp./mm. sensitivity, calibrated, within 0.1%. The light-beam was filtered with an interference filter in combination with a blue glass, with a transmission maximum of 438 mμ, very closely to the absorption maximum of the yellow complex. As the isolated spectral band is very narrow and the absorption curve flat, it may be taken for granted that the measured extinctions are proportional to the concentration of the yellow complex.

As ferrous chloride solutions in the concentrations used show a marked absorption, slightly dependent on the amount of free acid present, the extinction values were referred to the extinction of a blank solution containing all components except α,α'-dipyridyl.

The final galvanometer reading could be made within about two seconds after the introduction of the Fe^{++} solution. If the reading did not persist at least for a few seconds, the absorptions were read at different times and the zero time value determined by extrapolation.

The photometric accuracy was about 1% at extinctions > 0.1, decreasing to about 3% at $E = 0.03$.

Due to the large volume of the solution and the short time of measurement, the temperature could be kept constant within ±0.5° without thermostatic device.

Determination of Absorption Spectra.—Solutions containing a very large excess of Fe^{++} were prepared in the mixing device already described, rapidly transferred in a 50-mm. Korex cell, and the extinctions determinated in intervals of 5 mμ using a Beckman spectrophotometer. The extinctions were referred as above to a α,α'-dipyridyl free blank. Readings remained constant within 2% during about two minutes.

Results

Acid Constant of α,α'-Dipyridylium Ion.—Tables I and II show *p*H values of 1:1 mixtures of α,α'-dipyridyl and α,α'-dipyridylium hydrochloride in 4×10^{-3} *M* solution at different ionic strengths and temperatures, as the corresponding values of the concentration dissociation constant K_c.

TABLE I

μ	*p*H	γ_{H^+}	$K_c{}^a \times 10^{-5}$
4.7×10^{-3}	4.38	0.92	4.6
2.4×10^{-2}	4.41	.86	4.6
4.2×10^{-2}	4.43	.84	4.5
7.8×10^{-2}	4.45	.82	4.4
1.1×10^{-1}	4.47	.81	4.3
1.8×10^{-1}	4.50	.80	4.0
3.3×10^{-1}	4.53	.81	3.7
5.5×10^{-1}	4.59	.87	3.0

[a] $T = 25°$.

TABLE II

T, °C.[a]	*p*H	$K_c \times 10^{-5}$
15	4.61	3.1
20	4.57	3.4
25	4.53	3.7
30	4.49	4.1
35	4.45	4.5
40	4.40	5.0
45	4.36	5.5
50	4.32	6.1

[a] $\mu = 0.33$.

K_c was calculated by means of

$$K_c = \frac{(H^+)(D)}{(HD^+)} = \frac{(H^+)\{(D)_0 + (H^+)\}}{(HD^+)_0 - (H^+)} = K_a \frac{\gamma_{HD^+}}{\gamma_{H^+}\gamma_D} \quad (1)$$

where γ represents the activity coefficient and $(HO)_0$ the initial analytical concentrations. (H^+) was calculated from the *p*H values, using the values of γ_{H^+} indicated in Table I computed by the method of individual activity coefficients from the known mean activities of potassium chloride and hydrochloric acid. At low ionic strengths K_c approaches, as shown in Table I, the steady value of the thermodynamic constant K_a, which may be taken as $K_a = 4.6 \times 10^{-5}$ at 25°.[5]

From the temperature dependence of K_c, the mean heat of formation of the α,α'-dipyridylium ion may be calculated as 3.5 ± 0.5 kcal.[6]

Elucidation of the Nature of the Yellow Complex.—To establish the composition and the dissociation constant of the yellow complex, we determined the extinctions of solutions containing various amounts of Fe^{++}, HD^+ and H^+ (at 25° and $\mu = 0.33$). As the extinction coefficient of the yellow compound was unknown, we calculated first of all the concentration of the yellow complex, *supposed to be FeD*$^{++}$, using the previously reported "kinetic" value of the stability constant

$$K_{FeD} = \frac{(FeD^{++})}{(Fe^{++})(D)} = 2.7 \times 10^4 \quad (2)$$

To calculate (FeD^{++}) from (2), (D) has to be expressed as function of $(HD)_0$ and $(H^+)_0$, $(HD)_0$ representing the total initial concentration of α,α'-dipyridyl. In Fe^{++} free solutions this relation is given by

$$(D) = K_c \frac{(HD^+)}{(H^+)} = K_c \frac{(HD)_0 - (D)}{(H^+)_0 + (D)} \sim K_c \frac{(HD)_0}{(H^+)_0 + K_c} \quad (3)$$

Because in our experiments always $(H^+)_0 \gg (D)$, we used the last approximation throughout. Due to the formation of FeD^{++}, (HD) and (Fe^{++}) decrease by the amount of (FeD^{++}) formed, (H^+) increasing by the same amount. (FeD^{++}) may then be calculated from

$$(FeD^{++}) = K_c \times K_{FeD} \times \{(Fe^{++})_0 - (FeD^{++})\} \frac{(HD)_0 - (FeD^{++})}{(H^+)_0 + (FeD^{++}) + K_c} \quad (4)$$

The mean value of the relation of the thus calculated concentrations to the measured extinctions was used as proportionality factor (f) in the calculation of the experimental values of (FeD^{++}).

As shown in Table III, theoretical and experimental values of (FeD^{++}), calculated from E with $f = 4.95 \times 10^{-4}$, are in excellent numerical agreement. As easily may be shown, this agreement does not hold with values of K_{FeD}, differing more than 5% from the "kinetic" value, confirming thus the numerical value of this constant previously obtained by an entirely different method.

It is, of course, impossible to correlate theoretical and experimental values on the assumption that the yellow complex is FeD_2^{++}, using any value of K_{FeD_2}. Our experiments, however, do not disprove the possible existence of this complex, which hardly could be detected, if $K_{FeD_2} \lesssim K_{FeD}$ (and $\epsilon_{FeD_2} \sim \epsilon_{FeD}$).

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[5] Baxendale and George, ref. 2, found $K_a = 4.2 \times 10^{-5}$ at 17° and $\mu = 0.025$ in close agreement with our corresponding value (4×10^{-5}). A. Albert, R. Goldacker and J. Philips, *J. Chem. Soc.*, 2247 (1948), indicate the rather high value of about 6×10^{-5} at 25°.

[6] Baxendale and George, ref. 2, found the lower value of about 2 kcal.

TABLE III

$(Fe^{++})_0$ $\times 10^3$	$(HD)_0$ $\times 10^5$	$(H^+)_0$ $\times 10^3$	E $\times 10^3$	$(FeD^{++}) \times 10^6$ Found	Calcd.
74	13.3	8.0	242	120	120
37	13.3	8.0	218	108	109
30	13.3	7.15	216	107	107
14.2	13.3	7.4	177	87.5	86.5
3.75	13.3	14.6	54	26.5	27
14.2	13.3	2.4	225	111.5	112.5
14.2	13.3	7.4	177	87.5	86.5
14.2	13.3	14.1	134	66.5	66
14.2	13.3	34	79	39	39
14.2	13.3	67.5	46	22.8	23
14.2	13.3	135	26.5	13.1	12.6
14.2	13.3	335	11	5.5	5.4
14.2	3.33	7.4	44	21.8	21.8
14.2	6.66	7.4	89	44	43.5
14.2	33.3	7.4	436	216	215
1.8	6.66	3.55	43	21.3	22
1.8	13.3	3.5	87	43	44
1.8	20.0	3.4	133	66	66
1.8	33.3	3.3	228	113	110

Table IV shows the dependence of K_{FeD}, calculated by means of (4) from $(FeD^{++})_{expt.}$, on the ionic strength.

TABLE IV

$(Fe^{++})_0 = 3.75 \times 10^{-3}$, $(HD)_0 = 1.33 \times 10^{-4}$, $(H^+)_0 = 1.46 \times 10^{-2}$, $T = 25°$

μ	E $\times 10^3$	$(FeD^{++})_{expt.}$ $\times 10^6$	K_{FeD} $\times 10^{-4}$
0.03	56.5	28	2.3
.10	56	27.7	2.4
.20	55	27.2	2.6
.33	54	26.7	2.7

K_{FeD} decreases slowly with the decrease in μ, approaching the value of the thermodynamic constant, which may be taken to $2.3 \pm 0.3 \times 10^4$ at 25°, accounting for the possible error introduced with K_c.

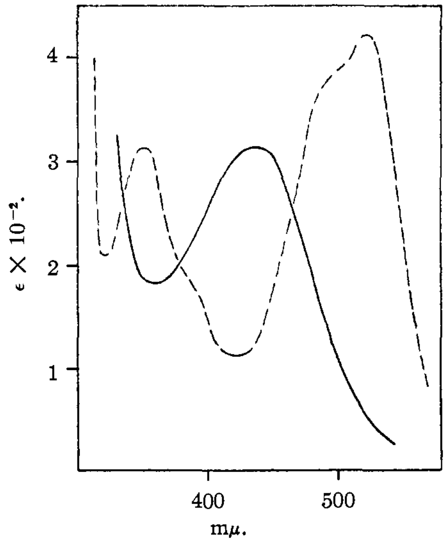

Fig. 1.——— FeD^{++}, - - - FeD_3^{++}. Values of ϵ for FeD_3^{++} to be multiplied by 20.

We tried furthermore to determine the dependence of K_{FeD} on the temperature. As shown in Table V the values of K_{FeD} at 45° vary considerably with the composition of the solution, if (FeD^{++}) is calculated from E with the mean proportionality factor f, obtained at 25°.

TABLE V[a]

$(Fe^{++})_0$ $\times 10^3$	$(HD)_0$ $\times 10^4$	$(H^+)_0$ $\times 10^3$	$E_{25°}$ $\times 10^3$	$E_{45°}$	$K_{25°}$ $\times 10^{-4}$	$K_{45°}$	$\bar{K}_{45°}$
74	1.33	8.0	242	220	2.65	0.9	1.45
30	1.33	3.8	236	215	2.6	0.95	1.45
30	1.33	7.15	216.5	190.5	2.75	1.1	1.4
30	1.33	13.8	183	157	2.7	1.2	1.4
30	1.33	34	126.5	102	2.75	1.25	1.4
30	1.33	67	83	65	2.7	1.3	1.4
3.75	1.33	14.6	54.5	42.5	2.7	1.35	1.45

[a] $\mu = 0.33$.

Using however the proportionality factor $f_1 = 5.3 \times 10^{-4}$, that is assuming that the extinction coefficient decreases by about 7% from 25 to 45°, the values of $\bar{K}_{45°}$ agree perfectly.

If this assumption is valid, the heat of formation of FeD^{++} may be calculated to approximately 6 kcal.

We measured finally the absorption spectrum of FeD^{++} in the visible and near ultraviolet, shown in Fig. 1, in comparison with the spectrum of FeD_3^{++}. The extinctions were determined in a solution of the composition: $(Fe^{++})_0 = 7 \times 10^{-2}$, $(HD)_0 = 1.33 \times 10^{-4}$, $(H^+)_0 = 1.4 \times 10^{-2}$ at 25°, corresponding to a concentration of FeD^{++} of 1.1×10^{-4}. The extinction coefficient at the absorption maximum $\lambda = 435$ mμ is 3.1×10^2, and thus about 25 times less than the extinction coefficient of FeD_3^{++} at $\lambda = 523$ mμ ($\epsilon = 8.5 \times 10^3$).

Summary

The acid constant of α,α'-dipyridylium ion has been determinated at various ionic strengths and temperatures. The value of the thermodynamic constant at 25° was found to be 4.6×10^{-5}. The heat of formation was calculated to about 3.5 kcal.

The previously assumed existence of a ferrous mono α,α'-dipyridyl complex has been confirmed and its thermodynamic equilibrium constant determinated as 2.3×10^4 at 25°. An approximative value of 6 kcal. for the heat of formation of this complex has been calculated.

The absorption spectrum of the ferrous mono-α,α'-dipyridyl complex has been measured in the visible and near ultraviolet.

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