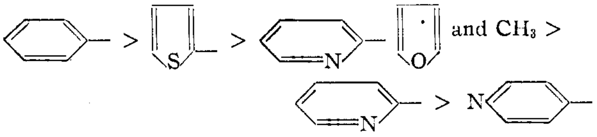
form as the mole fraction of dioxane is increased up to 0.1.

Wheland[5] has pointed out that most 1,3-dicarbonyl compounds are more enolic in a non-polar solvent than in a polar one. However, dimedone is predominately in the enol form even in water. Wheland[6] gives data which indicate that in water 15.5% of acetylacetone is in the enol form while 95.3% of dimedone exists in the enol form. This difference arises from the structure of dimedone and is enough to make any shift to a higher enol–keto ratio with changes in solvent insignificant in comparison to acetylacetone. Hence there is no deviation from linearity in this case.

Figure 2 shows a comparison of the pK_D values determined in the presence of sodium ion (apparent pK_D) and in solutions containing quaternary ammonium ions instead of sodium ion. The differences between the curves shown for each β-diketone are attributed to chelation with the sodium ion.

Dibenzoylmethane is typical of the β-diketones containing two aromatic ring systems and shows a greater tendency to chelate with the sodium ion than do the methyl-containing β-diketones. When one employs Calvin and Wilson's adaptation of Bjerrum's calculation procedure[7] in conjunction with the necessary theoretical considerations previously set forth,[2] it is found that the formation constants for the sodium salts of dibenzoylmethane and the other β-diketones containing two aromatic ring systems at a mole fraction of dioxane of 0.40, approximate log K_f = 4.4. For acetylacetone, which is typical of the β-diketones containing the methyl group, at a dioxane mole fraction of 0.40 log K_f is approximately one unit less or 3.2. For dimedone, the difference in the curves obtained with or without sodium ion is within the experimental error, so that no appreciable coördination of the sodium ion occurs in this case. The structure of dimedone is such that chelation is very improbable. The pK_D curve for acetic acid from the previous paper[2] is included for a comparison of the slopes of the curves.

If one assumes that the β-diketones are largely in the enol form at $n_2 = 0.45$ (> 50%), the following order of influence of end-groups on increasing the pK_D for a β-diketone can be written



The pK_D values for acetylacetone are higher than would be expected from the effect of the methyl group in this series.

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[5] G. W. Wheland, "Advanced Organic Chemistry," Second Edition, John Wiley and Sons, New York, N. Y., 1949, p. 607.

[6] G. W. Wheland, ref. 5, p. 602.

[7] M. Calvin and K. W. Wilson, THIS JOURNAL, 67, 2003 (1945).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

Studies on Coördination Compounds. III. The Chelating Tendencies of β-Diketones with the Chlorides of Copper(II), Nickel and Barium in Water–Dioxane Solutions

BY LEGRAND G. VAN UITERT, W. CONARD FERNELIUS AND BODIE E. DOUGLAS

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The variation of the logarithms of the formation constants (K_f) of the coördination compounds of copper, nickel and barium with structurally similar β-diketones (HCh) has been found to be an essentially linear function of the negative logarithms of the acid dissociation constants (pK_D) of the β-diketones. The β-diketones that have two aromatic rings as end-groups form more stable chelate compounds than those with an aliphatic end-group for comparable pK_D values. The slopes of the pK_D *vs.* log K_f lines increase with an increase in the chelating ability of the metal ions involved. Nickel compounds of the composition $NaNiCh_3 \cdot C_4H_8O_2$ are precipitated from the water–dioxane solutions used. The trifluoromethyl and silicon-containing β-diketones hydrolyze under the conditions employed in these titrations.

Introduction

The work of Calvin and Wilson[1] on the stability of chelate compounds formed between copper(II) and several chelating agents in 50 volume per cent. dioxane solution indicated the desirability of a more thorough investigation of the problem. The formation constants of a series of β-diketones with copper, nickel and barium which are in solution as the dichlorides are herein reported and compared to the respective acid dissociation constants of the chelating agents.[2] The mathematical treatment and theoretical considerations were outlined in a previous communication.[3]

Experimental

The metal salts employed were reagent grade. The dibenzoylmethane, benzoylacetone and acetylacetone were purchased from the Eastman Kodak Company. The hexafluoroacetylacetone was obtained from M. Calvin of the University of California. The silicon-containing β-diketones were synthesized by R. Pioch.[4] The remaining β-diketones were furnished by R. Levine of the University of Pittsburgh.

The acid dissociation constants of the β-diketones were all

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[1] M. Calvin and R. W. Wilson, THIS JOURNAL, 67, 2003 (1945).

[2] L. G. Van Uitert with W. C. Fernelius, B. E. Douglas and C. G. Haas, *ibid.*, 75, 455 (1953).

[3] L. G. Van Uitert and C. G. Haas, *ibid.*, 75, 451 (1953).

[4] L. H. Sommer and R. P. Pioch, unpublished work at The Pennsylvania State College.

measured in 74.5 volume per cent. dioxane (mole fraction of dioxane = 0.380) under the conditions previously described.[2] The formation constants of the metal chelate compounds were measured in a solution of approximately the same water–dioxane ratio by titrating, with 1.302 N sodium hydroxide, a solution containing the following: 75 ml. of dioxane, 25 ml. of H_2O, 4×10^{-3} mole of chelating agent and 1×10^{-3} mole of the metal chloride. The measurements were made with a Beckman pH meter in a 4-necked flask thermostated at 30 ± 0.1° as previously described.[3] The base was added from a buret which could be read to ±0.02 ml.

Analysis of the blue precipitate (dried at 100° *in vacuo*) formed in the titration of nickel ion with acetylacetone: Calcd. for $NaNi(C_5H_7O_2)_3 \cdot C_4H_8O_2$: C, 48.85; H, 6.26. Found: C, 48.95, 48.73; H, 6.05, 6.25.

Discussion of Results

The method of calculation is essentially the same as that outlined by Calvin and Wilson[1] with the exception that C values are used as outlined previously.[3]

$$C = \log [H^+]/[HCh] \equiv \log K_f - pK_D$$

at half integral values of $\bar{n}$. The C curves are related to the formation curves of Bjerrum[5] by the constant value pK_D of the particular chelating agent. The C curves may be treated in the same manner as the regular formation curves for obtaining the temporary formation constants and converting these to the correct constants by the use of Verhoek's convergence equations.[6] The application of these equations for bichelate compounds is greatly simplified by plotting the convergence correction *versus* the temporary values of $C_{1/2} - C_{3/2}$, or $pK_{f_1} - pK_{f_2}$, that is the numerical difference between the C constants or the formation constants. This plot is independent of the absolute values of C or pK_f. The calculated points of the convergence curve are given in Table I. The corrected values of $C_{1/2}$ and $C_{3/2}$ are always closer together than the temporary values. The curve approaches the value $C_{1/2} - C_{3/2} = 0.4343$ asymptotically as the second formation constant approaches a value which is infinitely larger than the first. The values of log K_{f_1}, log $K_{f(av)}$ and log K_{f_2} for the copper and nickel chelate compounds and log $K_{f(av)}$ for the barium compounds are presented along with the pK_D values for the chelating agents in Table II. The average values alone are given for barium since it was difficult to calculate the data accurately enough in this case to apply convergence corrections. It should be noted that high B values (pH meter readings[3]) are not to be unexpected since the dissociation constant of water is 4×10^{-19} in this solvent mixture.[7]

Table I

The Convergence Curve for the Correction of Temporary Constants

$C_{1/2} - C_{3/2}$	$\pm \Delta C$	$C_{1/2} - C_{3/2}$	$\pm \Delta C$
2.00	0.012	0.85	0.240
1.50	.043	.80	.279
1.25	.080	.75	.330
1.00	.154	.70	.394

Formation Constants.—Since association occurs to a marked extent in a medium of low dielectric constant such as 75 volume per cent. dioxane solutions, the formation constants obtained are interpreted in terms of the equations

$$MCl_2(H_2O)_x + HCh \rightleftarrows HCl + MChCl(H_2O)_y + (x - y)H_2O$$

$$MChCl(H_2O)_y + HCh \rightleftarrows HCl + MCh_2(H_2O)_z + (y - z)H_2O$$

In accordance with the definitions given in an earlier publication,[3] the value of a given formation constant is a function of the difference in the coördi-

Table II

The Acid Dissociation Constants for a Series of β-Diketones and the Formation Constants for the Corresponding Chelate Compounds Formed with Copper, Nickel and Barium Ions

		pK_D for n_2 = 0.380	log $K_{f\text{av}}$						
			Cu⁺⁺			Ni⁺⁺			Ba⁺⁺
	Chelating agent		(1)	(av.)	(2)	(1)	(av.)	(2)	(av.)
1	Dibenzoylmethane	13.75	12.98	12.50	12.00	10.46	10.09	9.71	5.7
2	2,2-Dimethyl-2-sila-5,7-octadione	13.50	12.28	11.85	11.42	9.65	9.18	8.70	4.9
3	2-Thenylbenzoylmethane	13.30	12.68	12.19	11.70	10.30	9.95	9.60	5.9
4	2-Furoylbenzoylmethane	12.95	12.48	11.95	11.44	10.10	9.70	9.29	5.7
5	2,2,10,10-Tetramethyl-2,10-disila-5,7-hendecanedione	12.9	11.5	11.1	10.7	8.6	8.3	8.1	3.9
6	Benzoylacetone	12.85	12.05	11.51	10.96	9.58	9.00	8.42	4.7
7	Di-2-thenoylmethane	12.63	12.23	11.76	11.28	9.93	9.58	9.23	5.7
8	Acetylacetone	12.70	11.85	11.30	10.74	9.34	8.69	8.06	4.5
9	2-Thenoylpicolinoylmethane	12.45							6.0
10	2-Thenoyl-2-furoylmethane	12.30	11.92	11.46	10.01	9.78	9.41	9.03	5.6
11	2-Thenoylacetone	12.35	11.70	11.19	10.68	9.38	8.80	8.22	4.6
12	2-Thenoylisonicotinoylmethane	11.75							5.4
13	Isonicotinoylacetone	11.25							4.4
14	Picolinoylacetone	12.15							5.0
15	Naphthoyltrifluoroacetone	9.3		9.2			7.4		5.0
16	Benzoyltrifluoroacetone	9.2		9.4			7.7		5.2
17	2-Thenoyltrifluoroacetone	9.1		9.5			8.0		5.3
18	Trifluoroacetylacetone	8.7		8.6			7.1		4.4
19	2-Furoyltrifluoroacetone	8.5		8.6			7.1		5.1
20	Hexafluoroacetylacetone	6.0	4.3						4.0

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[5] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[6] F. H. Verhoek, This Journal, **67**, 1334 (1945).

[7] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y. 1950, p. 509.

nating ability of the ionized chelating agent with the metal ion and the coördinating ability or association tendency of the other species present in solution with the same metal ion.

The chloride salts were used to obtain a sufficient degree of salt anion coördination in the case of copper so that relative measurements of the first formation constants of its chelate compounds could be obtained. Otherwise, the first chelation would have been completed and, in most cases, a precipitate would have formed immediately on mixing unless strongly acidic solutions were used. It is difficult to evaluate the formation constants in such solutions where the fraction of protons produced by chelation are few compared to the total number present.

The β-diketones which have trifluoromethyl end-groups were found to undergo rapid hydrolysis under the conditions used.[8] Their acid dissociation constants are probably reliable, but their pK_D values are quite low and the acid liberated in the process of chelation with metal ions appears to result in more rapid hydrolysis of the β-diketone. Hence, it was necessary to obtain measurements quickly and the results must necessarily be considered as approximations. The β-diketones with silicon-containing end-groups undergo basic hydrolysis and the data obtained at high pH values must also be considered as approximations.

The Variation of Log K_f as a Function of pK_D.—Figure 1 presents a plot of the log K_{f_1} and log K_{f_2} values for the copper and nickel chelate compounds *vs.* the pK_D values of the stable β-diketones. The points fall on a common line for those compounds containing structurally similar end-groups. In the case of each formation constant (log K_1, log $K_{av.}$, log K_2) the β-diketones containing two ring systems as end-groups fall on a common line. Those compounds which have one methyl end-group fall very nearly on a common line parallel to the first. Acetylacetone which has two methyl end-groups and the disilane compound do not fall on either line, but lie below them. It can be concluded that a β-diketone containing a methyl end-group would have a smaller chelating ability than a β-diketone which contains two ring systems as end-groups and a comparable pK_D value.

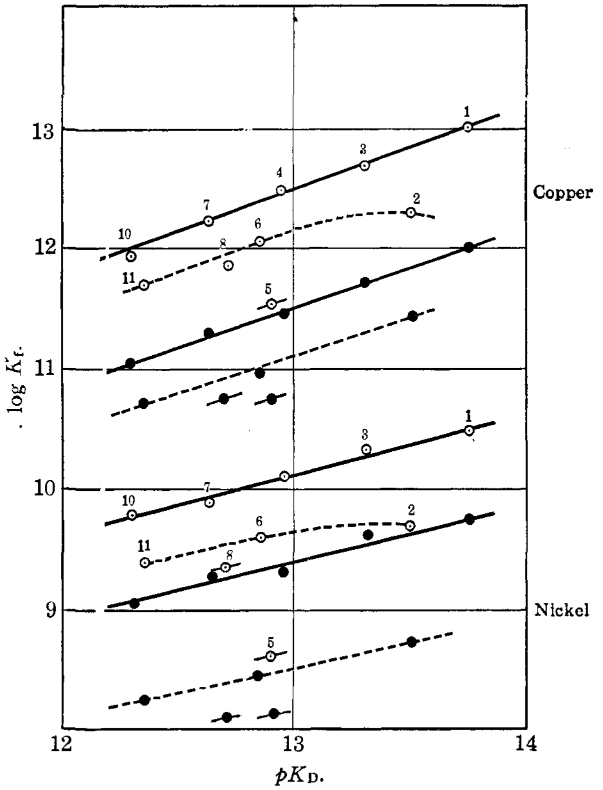

Fig. 1.—log K_{f_1} and log K_{f_2} *vs.* pK_D, see Table II: O for log K_{f_1} and ● for log K_{f_2}; —— di-ring end group β-diketones, ---- β-diketones with one methyl end-group.

A possible explanation of this methyl-substitution effect is found in the less effective shielding by the methyl group of the metal ion from external contacts as compared to the larger ring-type end-groups. The effect is much larger for the second chelation than for the first. This difference in shielding occasionally results in changes in the order of the formation constants for the same series of β-diketones with different metal ions.

Figure 2 shows the plot of log $K_{f\,av.}$ *vs.* pK_D for the several chelating agents. The pK_D values for the trifluoromethyl compounds are quite low. In this solvent mixture they appear to be below the value for acetic acid. The greater acid strength of the trifluoromethyl compounds is in accordance with the strong electron affinity of the fluorine atoms. Since appreciable ionization of the trifluoromethyl compounds occur at low pH values, they form chelates with copper and nickel in acidic solution. In the case of copper, the ionized trifluoromethyl β-diketones have about an equal tendency to associate with the metal ion as with the proton. Compounds with higher pK_D values show an increased preference for the proton. Copper first combined with one molecule of hexafluoroacetylace-

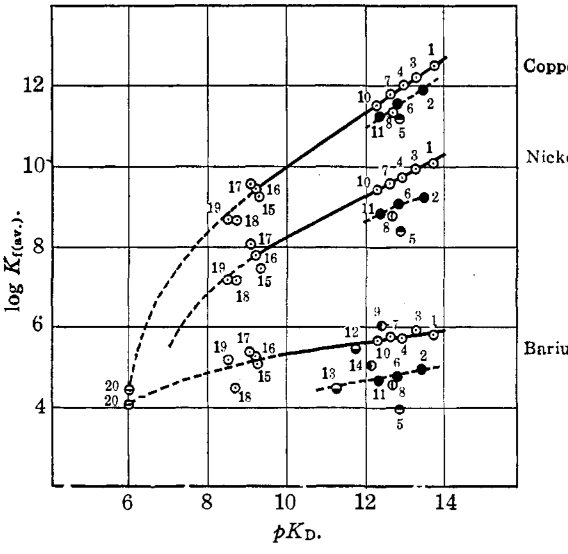

Fig. 2.—log $K_{f(av.)}$ *vs.* pK_D (see Table II) β-diketone end-groups: -O- two ring structures, --O-- one trifluoro, --●-- one methyl, ⏀ two methyl, ⊖ two trifluoro, ◐ one picolinyl, ◒ one isonicotinoyl, ● two tetramethylsilane.

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[8] Further studies of this hydrolysis are being carried out in this Laboratory.

tone under the conditions employed and then, as the pH increased, hydrolyzed to precipitate $Cu_2(OH)_3Cl$. The value of the first formation constant for this compound is plotted in lieu of the average value. This value is believed to be fairly accurate since no evidence of hydrolysis of the β-diketone was detected in the titration of this compound. It is apparent from Fig. 2 that the slopes of the pK_D *vs.* log K_{av} lines increase with an increase in the chelating tendency of the metal ion involved.

The pK_D values of the β-diketones are over four units larger in 74.5 volume per cent. dioxane than in water. Hence, if barium chloride can be considered to behave as a strong electrolyte as it does in pure water,[3] its chelate compound formation constants can be expected to be over four units lower in water or of the order of unity.

The average formation constants for the β-diketones with a pyridine ring end-group are given only for the case of barium since additional complex equilibria must be taken into account in the cases of copper and nickel. It is apparent that the picolinoyl group β-diketones have a greater chelation tendency than the comparable β-diketones containing one and two aromatic rings. This can be attributed to the ortho position of the ring nitrogen atom which can also enter into the chelation. The isonicotinoyl group (p-nitrogen) has no comparable effect.

The Hydrolysis of the Trifluoro-β-diketones.—In the titrations involving the trifluoro-β-diketones the expected stoichiometric rise in the pH of the solutions did not occur until approximately one-half of the excess chelating agent present had been converted to a species that titrates as a strong acid. If a known amount of hydrochloric acid is added to a solution of the chelating agent and the solution is then titrated, the stoichiometric pH rise is again passed as in the previous case. This behavior is only interpretable as being due to hydrolyses of the β-diketone itself in the titration process.

The Solid Nickel Chelate Compounds.—An interesting series of compounds were obtained as the chelation products of the β-diketones with nickel in water–dioxane solutions. A typical case is that of acetylacetone. The dichelate compound of nickel was formed over the first two equivalents of base added in the chelation titration. At the stoichiometric point the B value rises to approximately 10, the region in which the excess acetylacetone titrates. However, a pale blue precipitate separates and the B value falls to approximately 7. The concentration of the ionized species of acetylacetone is kept at a minimum over the third equivalent part of the titration. A rise of the B value to the level of titration of acetylacetone occurs at the point where three moles of NaOH have been added per mole of nickel salt present in the solution.

The titration shows that the blue precipitate formed during the addition of the third equivalent of NaOH contains three equivalents of acetylacetonate ion and hence must also contain a sodium ion to preserve electrical neutrality. The compound precipitates most readily from solutions containing large concentrations of dioxane, thus indicating salt-like properties. The solubility of the compound in this solvent medium (n_2 = 0.380) is less than 10^{-5} mole/liter.

The fact that the pH curve follows the titration pattern of acetylacetone until precipitation of the blue compound occurs suggests that the dissociation of the third equivalent of acetylacetone is not influenced by the presence of the nickel ion or that at least the species $NiCh_3^-$ probably does not exist in this solution. This is confirmed by the fact that when the titration is carried out using tetramethylammonium hydroxide as the base no precipitation occurs and a stoichiometric equivalent of two acetylacetonates per nickel is realized.

On the basis of the analytical data, the formula for the compounds corresponds to $NaNi(Ch)_3 \cdot C_4H_8O_2$, although this formula is not intended to indicate the nature of the third acetylacetonate ion or the way in which it is held. Similar lithium and potassium double salts form, but they are much more soluble than the sodium salt and have a deeper blue color. Other oxygen containing organic solvents will also cause the precipitation of similar compounds. The precipitate from ethanol is a brighter blue than that from dioxane.

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