In experimental work to be communicated later, it will be shown that for certain metals and certain chelating agents, C_2 is nearly independent of the inorganic anion present and of the solvent in which the determination is made, whereas for certain other systems large variations are observed for both of the changes. The cases in which such variations are observed will be interpreted as examples of specific interactions of the two types mentioned.

The same type of treatment can be extended to the first chelation step (equation 1) by defining K_{f_1} in a manner analogous to K_{f_2}. As before, multiplying by K_D and setting γ_{HCh} equal unity one obtains

$$\log k_{f_1} = pK_D + \log \frac{[MCh^+]}{[M^{++}]} + \log \frac{[H^+]}{[HCh]} + \log \frac{\gamma^2_{\pm 1-1}}{\gamma_{\pm 2-1}} \qquad (13)$$

where the subscripts on the activity coefficients signify 1–1 and 2–1 electrolytes. The activity coefficient term here causes uncertainty, since it can be approximated only in a rough manner. In the limiting case in which the Debye–Hückel limiting law applies, $\log \gamma_{\pm 2-1} = 2 \log \gamma_{\pm 1-1}$. Hence $\log \gamma^2_{\pm 1-1}/\gamma_{\pm 2-1} = 0$. This result is for ideal behavior and will not be completely valid at finite concentrations.

Again at the point at which $[MCh^+] = [M^{++}]$ (where Bjerrum's $\bar{n} = 1/2$) one obtains

$$\log K_{f_1} = pK_D + \log ([H^+]_{\bar{n}=1/2}/[HCh]_{\bar{n}=1/2}) = pK_D + C_1$$

the log of the concentration ratio being represented by C_1. C_1 has a significance analogous to that of C_2.

Acknowledgment.—The authors gratefully acknowledge financial support furnished for this work by the United States Atomic Energy Commission through Contract AT(30-1)-907.

STATE COLLEGE, PENNSYLVANIA

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

Studies on Coördination Compounds. II. The Dissociation Constants of β-Diketones in Water–Dioxane Solutions[1]

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

RECEIVED MAY 2, 1952

The variation of the pK_D values for several β-diketones with changes in composition of water–dioxane solutions has been found to follow the general pattern for simple acids above a mole fraction of dioxane (n_2) of 0.10. Shifts in the keto–enol equilibrium cause deviations from linearity below $n_2 = 0.10$ for some compounds studied. A comparison has been made of the effect of various end-groups on the acid strength of the β-diketones and their tendency to coördinate with the sodium ion.

A previous publication[2] reported data to verify the thermodynamic significance of results obtained with a pH meter in water–dioxane solutions. The present paper contains the results of the determination of dissociation constants for a series of β-diketones in water–dioxane solutions. It is of interest to know the values for the dissociation constants of β-diketones with some accuracy in order to make better comparisons of the formation constants of chelate compounds formed between metal ions and the β-diketones. The measurements were made at a mean molarity of strong electrolyte which was the same as that in the previous paper, so the corrections established in that paper were applied to the readings of the pH meter to obtain the final data. The calculation of the negative logarithm of the dissociation constant, pK_D, at each mole fraction of dioxane, n_2, for solutions containing equal concentrations of ionized and un-ionized β-diketones is carried out as

$$pK_D = B + \log U_H + \log 1/\gamma^2$$

where

B = the reading of the pH-meter scale

$\log U_H$ = $-B - \log [H^+]$, this is a constant correction factor for the scale reading in a particular solvent mixture at a mean molality of 0.0172[2]

$\log 1/\gamma^2$ = the negative log of the square of the mean stoichiometric activity coefficient for HCl at the same mean molality (interpolated from the data of Harned and Owen)[3]

Experimental

The tetramethylammonium hydroxide, dibenzoylmethane, benzoylacetone and acetylacetone were obtained from the Eastman Kodak Company; the dimedone (1,1-dimethyl-3,5-cyclohexanedione)[4] and tetra-*n*-butylammonium iodide were student preparations from this Laboratory. Dr. Robert Levine of the University of Pittsburgh kindly supplied the remainder of the diketones.

The measurements were made using solutions containing equal concentrations of ionized and un-ionized diketone employing a Beckman model G pH meter equipped with a calomel electrode and a "type E" glass electrode in accordance with the procedure previously described.[2]

Solutions used for the measurements contained 0.00172 mole of diketone, 0.72 ml. of 1.20 *N* tetramethylammonium hydroxide, 40 ml. of dioxane and 10 ml. of distilled water. For the first eleven compounds listed in Table I, these solutions were progressively diluted with a 0.0172 *M* aqueous solution of tetra-*n*-butylammonium iodide. For the remaining water-soluble diketones the initial solutions were progressively diluted with an aqueous solution containing the same concentration of ionized and un-ionized β-diketone. By these means a series of water–dioxane solutions of the same mean strong electrolyte molality was obtained. The tetrabutylammonium iodide could not be used as a neutral electrolyte in pure water solutions because the pH meter was found to behave erratically under these conditions.

---

[1] A portion of a thesis presented by L. G. Van Uitert in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1952.

[2] L. G. Van Uitert and C. G. Haas, THIS JOURNAL, **75**, **451** (1953).

[3] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 547.

[4] R. L. Shriner and H. R. Todd, "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 200.

TABLE I

pK_D EQUATIONS FOR THE RANGE n_2 = 0.10 TO 0.45[a]

		pK_D equals
1	Dibenzoylmethane	$9.10 + 12.20\ n_2$
2	2-Thenoylbenzoylmethane	$8.85 + 11.70\ n_2$
3	2-Furoylbenzoylmethane	$8.55 + 11.60\ n_2$
4	Benzoylacetone	$8.40 + 11.70\ n_2$
5	Di-2-thenoylmethane	$8.30 + 11.40\ n_2$
6	2-Thenoylacetone	$8.10 + 11.20\ n_2$
7	2-Thenoyl-2-furoylmethane	$8.10 + 11.00\ n_2$
8	Di-2-furoylmethane	$7.80 + 11.20\ n_2$
9	2-Thenoylpicolinoylmethane	$7.90 + 12.00\ n_2$
10	2-Thenoylnicotinoylmethane	$7.80 + 11.20\ n_2$
11	2-Thenoylisonicotinoylmethane	$7.40 + 11.40\ n_2$
12	Isonicotinoylacetone	$6.95 + 11.30\ n_2$
13	Picolinoylacetone	$7.65 + 11.80\ n_2$
14	Acetylacetone	$8.35 + 11.60\ n_2$
15	Dimedone (1,1-dimethyl-3,5-cyclohexandione)	$5.23 + 10.95\ n_2$
16	Acetic acid	$4.78 + 11.00\ n_2$

[a] These equations fit the points to ±0.05 log unit.

This is possibly associated with the low water-solubility of the salt.

Similar measurements were made using sodium hydroxide and sodium chloride under the same conditions instead of the quaternary ammonium compounds in order to determine the extent of association between the β-diketones and the sodium ion. The concentrations of the β-diketone, the sodium salt of the β-diketone and sodium chloride were the same as for the previous measurements.

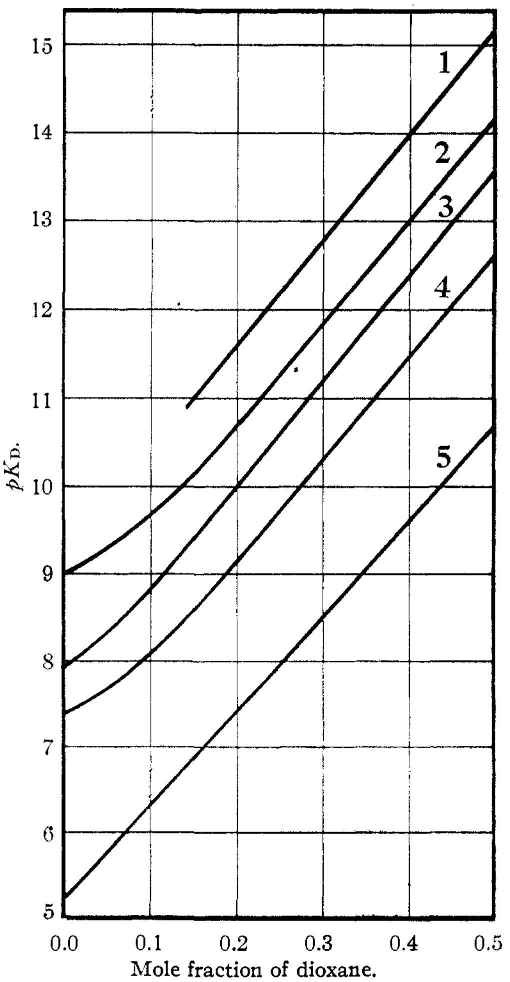


Fig. 1.—pK_D as a function of the mole fraction of dioxane: 1, dibenzoylmethane; 2, acetylacetone; 3, picolinoylacetone; 4, isonicotinoylacetone; 5, dimedone.

Discussion of Results

The work of Harned and Owen[3] has shown that an approximately linear relationship exists between the pK_D values of water, acetic acid and propionic acid and the mole fraction of dioxane in the aqueous solvent mixture. The slopes of the lines vary from 10.5 to 12. The β-diketones have been found to behave similarly for the range of dioxane mole fractions from 0.10 to 0.45. The upper limit is an arbitrary choice while the lower limit represents the approximate dioxane mole fraction in which the β-diketones containing two aromatic ring systems are no longer soluble. The lower limit also represents the range in which the β-diketones containing one or more methyl groups deviate from linearity due to a shift in their keto–enol equilibria. The results are shown in Figs. 1 and 2. Table I gives mathematical expressions for the curves which fit the experimental data within ±0.05 log unit for the region of linearity.

Figure 1 shows the variation of pK_D with mole fraction of dioxane for dibenzoylmethane, acetylacetone, picolinoylacetone, isonicotinoylacetone and dimedone. The dibenzoylmethane is characteristic of the β-diketones studied which contain two aromatic ring systems. The other compounds are water soluble and could be studied over a wider range. All of these compounds except dimedone deviate from linearity as the mole fraction of dioxane approaches zero. The direction of the deviation suggests that there is a shift from the predominately keto form to a large fraction of the enol

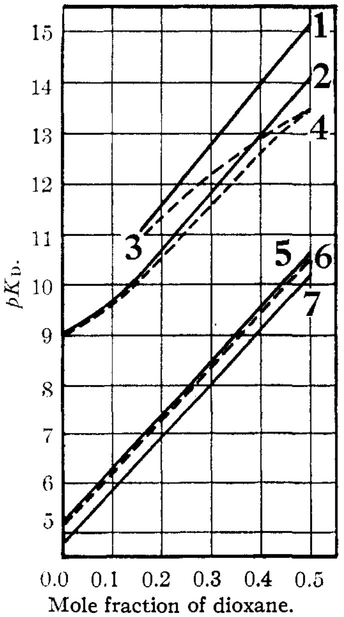


Fig. 2.—The effect of sodium ion chelation upon the "measured" values of pK_D. The solid lines are the pK_D curves for: 1, dibenzoylmethane; 2, acetylacetone; 5, dimedone; 7, acetic acid. The broken lines are the measured pK_D curves in the presence of sodium ions for: 3, dibenzoylmethane; 4, acetylacetone; 6, dimedone.

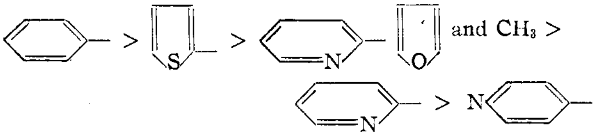
form as the mole fraction of dioxane is increased up to 0.1.

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.

Acknowledgment.—The authors gratefully acknowledge financial support furnished for this work by the United States Atomic Energy Commission through Contract No. AT(30-1)-907.

STATE COLLEGE, PENNSYLVANIA

---

[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

RECEIVED MAY 2, 1952

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

---

[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.