pected $Co_2(CO)_8(C_3H_7C{\equiv}CH)_2$ but to a mixture containing more than two moles of alkyne per mole of $Co_2(CO)_8$.

Anal. Calcd. for $Co_2(CO)_8(C_3H_7C{\equiv}CH)_2$: C, 45.21; H, 3.35. Found: C, 54.40; H, 5.30. Calcd. for $Co_2(CO)_8(C_3H_7C{\equiv}CH)_4$: C, 54.73; H, 5.25.

The infrared spectrum of the oil differs from that of $Co_2(CO)_9C_3H_7C{\equiv}CH$. The two bands located at 5.42 and 5.68 are shifted to 5.33 and 5.70 and two bands at 10.52 and 15.17 present in $Co_2(CO)_9C_3H_7C{\equiv}CH$ are absent in the spectrum of the oil.

(c) **$Co_2(CO)_9CH{\equiv}CH$ and Acetylene.**—An erlenmeyer flask was charged with 1.053 g. (2.66 mmoles) of $Co_2(CO)_9CH{\equiv}CH$, the flask attached to a gas buret and the apparatus filled with acetylene. During the first 2 hr. little if any gas was absorbed, while the bright red crystals of the complex turned darker. After this period, the gas volume decreased at a rate of approximately 3 ml. per hour. The reaction was interrupted after 26 hr., during which time the crystals had turned dark red. An analysis of the gas showed that 0.33 mole of carbon monoxide had been evolved per mole of complex. From the amount of carbon monoxide evolved and the observed decrease in gas volume, the amount of acetylene absorbed per mole of $Co_2(CO)_9CH{\equiv}CH$ was found to be 1.18 moles per mole of complex.

The infrared spectrum of the reaction product dissolved in carbon disulfide showed these bands (in μ): 4.74, 4.82, 4.86, 4.90, 5.30, 5.41, 5.63, 5.70, 9.15, 9.20, 10.05, 12.38, 13.59 and 13.79.

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Studies on Coördination Compounds. XVII. Stabilities of Bivalent Metal Complexes of Some Methylene-substituted β-Diketones[1]

BY BARBARA B. MARTIN AND W. CONARD FERNELIUS

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Acid dissociation constants of several methylene-substituted β-diketones and formation constants of some of their metal derivatives have been determined. The acidity of the β-diketones and the stability of their metal chelates appear to depend upon the type of substitution and, in the case of cyclic compounds, upon the type of ring system present.

Introduction

Although the dissociation constants of a number of β-diketones have been determined as well as the formation constants of a variety of metal derivatives, the literature contains only one reference to such measurements for a β-diketone with a substituent on the methylene carbon atom.[2] In this case the effect of the substituent was to lower both the acidity and the stability of the copper chelate, relative to that of the unsubstituted compound. The present study was undertaken to obtain more data concerning stabilities of metal chelates of substituted β-diketones and to determine whether such substitution always lowers the stability. Previously no formation constant data concerning β-diketones in which one of the carbonyl groups is contained in a ring (α-acylcyclanones) have been reported.

In the present communication, acid dissociation constants of methylene-substituted β-diketones and α-acylcyclanones and formation constants of some of their metal chelates are reported. Results of infrared and ultraviolet spectral studies are presented

Experimental

β-Diketones.—1. The preparation of **3-*n*-butyl-2,4-pentanedione** is described in another publication[3]; b.p. 98–102° (16–17 mm.), reported[4] b.p. 90–94° (10 mm.).

2. **3-Allyl-2,4-pentanedione** was prepared by the procedure of English[5]; b.p. 88–90° (21 mm.), reported[5] b.p. 82–83° (16 mm.).

3. **Dibenzoylmethyl bromide** was prepared by the method of de Neufville and von Pechmann[6]; m.p. 91–92°, reported[6] m.p. 93°.

4. **2-Acetylcyclohexanone** was prepared by the method of Hauser, *et al.*[7]; b.p. 103–109° (17–18 mm.), reported[7] b.p. 110–115° (20 mm.).

5. **2-Benzoylcyclohexanone** was prepared by the method of Hauser, *et al.*[8]; m.p. 85–87°, reported[8] m.p. 88–89°.

6. **2-Benzoylhydrindone** was prepared by the method of Hauser, *et al.*[8]; m.p. 98.8–100°, reported[8] m.p. 100–101°.

7. **2-Acetylcyclopentanone** was generously supplied by the American Petroleum Institute Project 42.

The titrations were preformed as previously described.[9] Acid dissociation constants were determined according to the method of Van Uitert.[10] Calculations were made by the method of Block and McIntyre.[11]

Infrared absorption spectra were obtained with a Perkin-Elmer model 21 Double Beam Recording Spectrophotometer using a sodium chloride prism. The spectra of liquid samples were obtained as thin liquid films pressed between plates of sodium chloride, and those of solid samples were obtained in disks of potassium bromide.

Ultraviolet absorption spectra were obtained with a Warren Spectracord having a hydrogen lamp light source and using 2-cm. quartz cells. Samples were prepared by dilution of stock solutions which contained from 7 to 15 mg. of material per 100 ml. of redistilled 95% ethanol.

Results and Discussion

The plots of the pK_D values for the β-diketones studied as a function of mole fraction of dioxane at 30° were linear. Table I gives mathematical expressions for the curves which fit the mathematical data within ±0.05. The formation constants (log K for the reactions $M^{++} + Ch^- \rightleftarrows$

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[1] Abstracted from a thesis presented by Barbara B. Martin in partial fulfillment of the requirements for the degree of Master of Science, January, 1959.

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

[3] D. F. Martin, M. Shamma and W. C. Fernelius, *ibid.*, to be published.

[4] H. Adkins, W. Kurtz and D. D. Coffman, *ibid.*, **56**, 3212 (1930).

[5] J. P. English, *et al.*, *ibid.*, **68**, 453 (1946).

[6] R. de Neufville and H. von Pechmann, *Ber.*, **23**, 3375 (1890).

[7] R. Levine, J. A. Conroy, J. T. Adams and C. R. Hauser, THIS JOURNAL, **67**, 1510 (1945).

[8] C. R. Hauser, B. I. Ringler, F. W. Swamer and D. F. Thompson, *ibid.*, **69**, 2649 (1947).

[9] L. G. Van Uitert, *et al.*, *ibid.*, **75**, 451, 457 (1953).

[10] (a) L. G. Van Uitert, *et al.*, *ibid.*, **75**, 455 (1953); (b) **76**, 5887 (1954).

[11] B. P. Block and G. H. McIntyre, Jr., *ibid.*, **75**, 5667 (1953).

MCh^+ and $MCh^+ + Ch^- \rightleftarrows MCh_2$) obtained in 75 volume % dioxane ($N_2 = 0.380$) are listed in Table II.

TABLE I

pK_D EQUATIONS FOR THE RANGE $N_2 = 0.137$ TO 0.380[a]

β-Diketone	pK_D equals
3-*n*-Butyl-2,4-pentanedione	$9.92 \pm 12.82N_2$
3-Allyl-2,4-pentanedione	$9.63 \pm 11.51N_2$
Dibenzoylmethyl bromide	$7.21 \pm 12.90N_2$
2-Acetylcyclopentanone	$7.41 \pm 11.73N_2$
2-Benzoylhydrindone	$7.32 \pm 12.93N_2$
2-Acetylcyclohexanone	$9.65 \pm 11.65N_2$
2-Benzoylcyclohexanone	$10.02 \pm 12.90N_2$
Acetylacetone[10a]	$8.35 \pm 11.60N_2$
Benzoylacetone[10a]	$8.40 \pm 11.70N_2$

[a] Reliable within ±0.05.

TABLE II

FORMATION CONSTANTS (LOG K_n) OF SOME BIVALENT METAL CHELATES OF β-DIKETONES IN 75 VOLUME % DIOXANE ($N_2 = 0.380$) AT 30°

β-Diketone	*n*	Cu	Ni	Zn	Co	Cd	Mn
3-*n*-Butyl-2,4-pentanedione	(1)	13.50	Ppt.	Ppt.	Ppt.	Ppt.	Ppt.
	(2)	11.18					
3-Allyl-2,4-pentanedione	(1)	13.12	9.41	Ppt.	Ppt.	Ppt.	Ppt.
	(2)	8.46	8.43				
Dibenzoylmethyl bromide	(1)	8.69	Ppt.	Ppt.	Ppt.	Ppt.	Ppt.
	(2)	8.35					
2-Benzoylhydrindone	(1)	11.59	9.85	9.59	9.46	8.37	8.72
	(2)	11.31	7.96	8.10	7.80	6.94	6.99
2-Acetylcyclohexanone	(1)	12.66	9.90	Ppt.	Ppt.	Ppt.	Ppt.
	(2)	10.85	7.89				
2-Benzoylcyclohexanone	(1)	13.69	10.58	Ppt.	Ppt.	Ppt.	Ppt.
	(2)	11.53	8.92				
Acetylacetone[12a]	(1)	(12.78)	10.19	9.52	9.68	7.79[a]	8.50
	(2)	11.24	8.21	8.05	7.92	6.75[a]	6.84
Benzoylacetone[12b]	(1)				9.42[a]	7.79[a]	
	(2)				8.41[a]	6.57[a]	

[a] These values were obtained using nitrate salts rather than perchlorates.

It is interesting to note that the dissociation constant of 3-*n*-butyl-2,4-pentanedione is lower than that of 3-allyl-2,4-pentanedione. Apparently a steric factor is involved, since molecular models show that steric interaction is present between the butyl group and the methyl groups of the enol form. There is much less interaction in the allyl compound.

The dissociation constant of 2-benzoylcyclohexanone is smaller than that of 2-acetylcyclohexanone, as would be expected from the increased resonance possible in the benzoyl derivative. Van Uitert[10a] found a similar difference in acidity between acetylacetone and benzoylacetone and in general that the phenyl group as a terminal group of a β-diketone has a greater influence on increasing the pK_D than does a methyl group.

It is interesting to note that 2-acetylcyclopentanone is a much stronger acid than is 2-acetylcyclohexanone. Schwarzenbach and Felder[13] have shown that the enol content of 2-acetylcyclohexanone (29%) is roughly twice that of 2-acetylcyclopentanone (15%), measured in water. Extrapolating to 75% dioxane, it may be assumed that 2-acetylcyclohexanone still has the higher enol content. If this is the case, 2-acetylcyclohexanone would be expected to be the stronger acid. The opposite behavior observed may be due to ionization of the keto form of 2-acetylcyclopentanone. The large difference in acidity between 2-benzoylhydrindone and 2-benzoylcyclohexanone also may be due to ionization of the keto form of 2-benzoylhydrindone.

It may be seen from Table II that 2-benzoylhydrindone is the only β-diketone studied for which constants for the chelates of zinc, cobalt, cadmium and manganese could be calculated. The constants for these metals occur in the order of increasing stability determined by Van Uitert[12b] with the exception of the reversal of zinc and cobalt.

If the β-diketones in Table II are arranged in order of increasing pK_D, the log K_{av} values for their copper chelates fall in the same order. This behavior is what would be expected, since the weaker the acid, the greater the base strength and chelating power of the conjugate base.

The data of Table I show that substitution of an alkyl radical on the methylene carbon atom of a β-diketone lowers the acidity as found previously.[2] The substitution of an electronegative atom like bromine, of course, increases the acidity. Ring closure involving the methylene carbon atom of a β-diketone may result in increased or decreased acidity depending upon the nature of the ring. In a general way the stability of the metal derivatives expressed as log K_{av} is proportional to the pK_D of the β-diketones except for dibenzoylmethyl bromide.

Spectra Results

The infrared absorption bands of interest are listed in Table III. These bands are grouped according to tentative assignments as proposed by Bellamy.[14]

TABLE III

INFRARED ABSORPTION SPECTRA OF β-DIKETONES

β-Diketone	Hydroxyl, μ	Carbonyl, μ	Enol-chelate, μ
3-*n*-Butyl-2,4-pentanedione	2.98w[a]	5.83s	6.24m
3-Allyl-2,4-pentanedione	3.00w	5.87m	6.25m
Dibenzoylmethyl bromide	3.27w	5.88vs	6.24s
2-Acetylcyclopentanone	3.42m	5.85vs	6.22vs
2-Benzoylhydrindone	3.30m	5.87w	6.21vs
2-Acetylcyclohexanone	2.92m	5.83m	6.20s
2-Benzoylcyclohexanone	3.04w	5.78s	6.25w

[a] vs = very strong, s = strong, m = moderate, w = weak.

It is interesting to note whether a correlation can be found between enol content and acidity. A rough indication of enol content of β-diketones can

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(12) (a) L. G. Van Uitert, *et al.*, THIS JOURNAL, **75**, 2741 (1953); (b) **75**, 2736 (1953).

(13) G. Schwarzenbach and E. Felder, *Helv. Chim. Acta*, **27**, 1044 (1944).

(14) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen, London, 1958, p. 123.

be obtained from the ratio of the intensity of the band attributed to the free carbonyl group to that of the band attributed to the enol–chelate structure. In 2-benzoylhydrindone this ratio is roughly 0.1:1; 2-benzoylcyclohexanone, 4:1; 2-acetylcyclohexanone, 0.4:1; 2-acetylcyclopentanone, 1:1. Apparently, in the compounds just mentioned no correlation exists. For example, 2-benzoylhydrindone is a stronger acid than 2-benzoylcyclohexanone but appears to have the lower enol content of the two compounds. On the other hand, 2-acetylcyclohexanone is the stronger acid and has a higher enol content than 2-benzoylcyclohexanone. The strongest acid of the β-diketones studied, *i.e.*, 2-acetylcyclopentanone, has a lower enol content than does 2-acetylcyclohexanone.

Among the straight-chain β-diketones in this study, a correlation appears to exist. The intensity ratios of these compounds are: dibenzoylmethyl bromide, 1.58:1; 3-allyl-2,4-pentanedione, 1.77:1; 3-*n*-butyl-2,4-pentanedione, 2.17:1. Dibenzoylmethyl bromide, the strongest acid, has the highest enol content; 3-*n*-butyl-2,4-pentanedione, the weakest acid, has the lowest enol content.

The ultraviolet absorption maxima of interest for the β-diketones studied are listed in Table IV. It will be seen from the table that, for these β-diketones, the logarithm of the extinction coefficient of a given peak remains essentially constant as the concentration is changed. This adherence to Beer's law usually is observed among β-diketones and is interpreted to mean that the ratio of keto to enol forms is not changed with concentration.

TABLE IV

ULTRAVIOLET ABSORPTION SPECTRAL DATA OF β-DIKETONES

β-Diketone	Molarity $\times 10^5$	mμ	l	log ϵ_{max}
3-*n*-Butyl-2,4-pentanedione	4.88	291	0.258	3.42
	9.75	291	0.418	3.40
3-Allyl-2,4-pentanedione	18.7	288	1.34	3.56
	9.35	288	0.72	3.59
Dibenzoylmethyl bromide	4.23	232	1.39	4.21
	1.69	235	0.50	4.17
2-Acetylcyclopentanone	6.26	289	1.02	3.91
	5.01	289	0.77	3.89
	2.50	289	0.37	3.87
2-Benzoylhydrindone	4.62	249	1.30	4.15
	0.965	249	0.27	4.15
		355	0.46	4.38
2-Acetylcyclohexanone	11.3	290	2.01	3.95
	5.64	290	0.808	3.89
2-Benzoylcyclohexanone	5.05	315	0.56	3.71
		249	1.12	4.01
	11.0	315	1.04	3.68

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

Carbonium Ions. VII. An Evaluation of the H_R Acidity Function in Aqueous Perchloric and Nitric Acids[1,2]

BY N. C. DENO, HENRY E. BERKHEIMER, WILLIAM L. EVANS AND HENRY J. PETERSON

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The H_R acidity function (previously termed C_0 and J_0 as well as H_R) has been evaluated for 0–60% perchloric acid and 0–58% nitric acid. Values of $pK_{R^+} + \log (c_{ROH}/c_{R^+})$ are equal when determined in different aqueous mineral acids; and values of $d \log (c_{ROH}/c_{R^+})/d$ % acid are independent of the structure of R. The symbol c refers to the concentration in moles/l. These two facts demonstrate that a class of cation exists, the arylmethyl cations, for which the values of the activity coefficient (f_{R^+}) are equal in aqueous mineral acids. The structural characteristics of this class are discussed in light of solubility measurements on perchlorate salts in aqueous sulfuric acid. The equilibrium between HNO_2 and NO^+ follows the H_R function in aqueous perchloric acid.

Evaluation of H_R in Perchloric and Nitric Acids.—The H_R acidity function previously had been evaluated in 0–97% sulfuric acid using eq. 1 and a series of arylmethanols as indicators.[3] It has now been evaluated in 0–60% perchloric acid and 0–58% nitric acid. The values of H_R as a function of % acid and moles/l. of acid are summarized in Table I.

$$H_R = pK_{R^+} + \log (c_{ROH}/c_{R^+}) \qquad (1)$$

It was found that values of $d \log (c_{ROH}/c_{R^+})/d$ % acid were independent of the structure of the arylmethyl group, R. The data in Table II show that pK_{R^+} values are the same for a particular ROH even though measured in different aqueous mineral acids. Both of these results demonstrate that for arylmethanols, values of f_{ROH}/f_{R^+} are independent of the arylmethyl group chosen. This generalization can be extended with perhaps some loss of precision to stating that f_{R^+} is the same for different R groups at each acid concentration since it has al-

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[2] The acidity function defined as equal to $pK_{R^+} + \log (c_{ROH}/c_{R^+})$ has been known as C_0 in our publications, J_0 in publications by V. Gold and co-workers, and H_R in publications by G. Williams and co-workers. The symbol H_R seems preferable since it indicates the close relationship to the H_0 acidity function. This fact coupled with its priority (A. M. Lowen, M. A. Murray and G. Williams, *J. Chem. Soc.*, 3321 (1950)) has led us to abandon the symbol C_0 (and J_0) and to use H_R in all future publications.

[3] N. Deno, J. J. Jaruzelski and A. Schriesheim, THIS JOURNAL, **77**, 3044 (1955).