[CONTRIBUTION OF THE CENTRAL EXPERIMENT STATION, BUREAU OF MINES, AND CENTRAL RESEARCH LABORATORIES OF AIR REDUCTION COMPANY, INC.]

Addition of Carbon Monoxide to Acetylene Dicobalt Hexacarbonyl. A New Type of Complex

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RECEIVED OCTOBER 23, 1958

A new complex, $Co_2(CO)_9RC\equiv CR'$, obtained by the addition of acetylene and carbon monoxide to $Co_2(CO)_8$ is described. The possible significance of this complex as an intermediate in the catalytic carbonylation of unsaturated hydrocarbons is discussed.

When dicobalt octacarbonyl is treated with acetylene or a substituted acetylene and carbon monoxide at elevated temperature and pressure a stable, crystalline nonacarbonyl, $Co_2(CO)_9RC\equiv CR'$ (I), is formed according to equation 1

$$Co_2(CO)_8 + RC\equiv CR' + CO \longrightarrow \underset{\text{I}}{Co_2(CO)_9RC\equiv CR'} \quad (1)$$

This new complex also can be obtained according to equation 2, by treating dicobalt hexacarbonyl acetylene (II)[1] with carbon monoxide at elevated pressure and temperature

$$\underset{\text{II}}{Co_2(CO)_6RC\equiv CR'} + 3CO \longrightarrow \underset{\text{I}}{Co_2(CO)_9RC\equiv CR'} \quad (2)$$

When I is treated with a solution of iodine in pyridine approximately 7 of the 9 carbonyl groups are liberated as carbon monoxide. This indicates that 2 of the 9 carbonyl groups in I are probably not present either as bridge or terminal carbonyl groups, since both bridge and terminal carbonyl groups are readily liberated under these conditions as carbon monoxide. For example, $Co_2(CO)_8$, which contains 2 bridge and 6 terminal carbonyl groups,[2,3] gives off 8 moles of carbon monoxide[4,5] and II, which contains 6 terminal carbonyl groups,[6] gives off 6 moles of carbon monoxide.

When complex I is treated with pyridine, 4 moles of $[Co(CO)_4]^-$ are formed and 5 moles of carbon monoxide are evolved per 3 moles of I (equation 3)

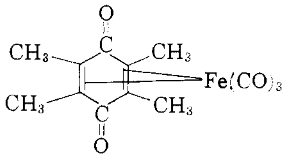
$$3\text{I} \longrightarrow 2Co[Co(CO)_4]_2 + 5CO + \text{unidentified products} \quad (3)$$

i.e., only 7 of the 9 moles of carbon monoxide per mole of I appear in the form of $[Co(CO)_4]^-$ and carbon monoxide. In the treatment of $Co_2(CO)_8$ with pyridine on the other hand (equation 4)

$$3Co_2(CO)_8 \longrightarrow 2Co[Co(CO)_4]_2 + 8CO \quad (4)$$

all of the eight moles of carbon monoxide per mole of $Co_2(CO)_8$ appear either in the form of $[Co(CO)_4]^-$ or as carbon monoxide.[7]

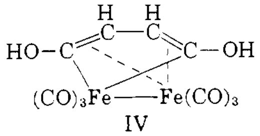
Exposure of I to radioactive carbon monoxide at room temperature, decomposition of the radioactive product with a solution of iodine in pyridine and analysis of the gas evolved and the residue showed that all the activity was present in the 7 moles of carbon monoxide evolved and none in the residue. In the case of the duroquinone iron tricarbonyl complex, III, it could be demonstrated[8] that the 3 terminal carbonyl groups but not the quinone carbonyls exchange with radioactive carbon monoxide. The fact that 2 carbonyl groups in I do not exchange may be an indication that these carbonyl groups are combined with acetylene in a ligand.



III

Treatment of I with excess alkyne results in the liberation of 1 mole of carbon monoxide. This displacement of the carbonyl group is accompanied by polymerization of the alkyne, and attempts to isolate a dicobalt octacarbonyl dialkyne complex from the reaction mixture were unsuccessful.

To date, two examples involving addition of acetylene to a metal carbonyl have been reported. These are the addition of 2 moles of acetylene to $Fe(CO)_5$ to give a quinone iron tricarbonyl complex, III, and the reactions[9-11] between an aqueous solution of $NaHFe(CO)_4$ and acetylene to form $[Fe_2(CO)_8C_2H_2]^=$ which in acid solution adds two protons to give $H_2Fe_2(CO)_8C_2H_2$ (IV) whose structure recently was established.[12]



IV

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[1] H. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiz, R. Markby and I. Wender, THIS JOURNAL, **78**, 120 (1956).

[2] J. W. Cable, R. S. Nyholm and R. K. Sheline, *ibid.*, **76**, 3373 (1954).

[3] R. A. Friedel, I. Wender, S. L. Shufler and H. W. Sternberg, *ibid.*, **77**, 3951 (1955).

[4] W. Hieber, F. Muhlbauer and E. A. Ehmann, *Ber.*, **65**, 1090 (1934).

[5] H. W. Sternberg, I. Wender and M. Orchin, *Anal. Chem.*, **24**, 174 (1952).

[6] W. G. Sly, THIS JOURNAL, **81**, 18 (1959).

[7] I. Wender, H. W. Sternberg and M. Orchin, *ibid.*, **74**, 1216 (1952).

[8] H. W. Sternberg, R. Markby and I. Wender, *ibid.*, **80**, 1009 (1958).

[9] W. Reppe and H. Vetter, *Ann. Chem. Justus Liebig*, **582**, 133 (1953).

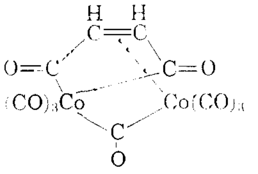
[10] H. W. Sternberg, R. A. Friedel, R. Markby and I. Wender THIS JOURNAL, **78**, 3621 (1956).

[11] R. Clarkson, E. R. H. Jones, P. C. Wailes and M. C. Whiting *ibid.*, **78**, 6206 (1956).

[12] A. A. Hock and O. S. Mills, *Proc. Chem. Soc.*, 233 (1958).

In both cases two of the carbonyl groups have combined with acetylene to form a new ligand.

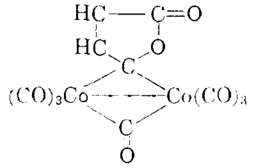
A possible structure analogous to that of IV and consistent with the chemical behavior of I is shown in A.



A

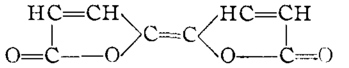
Structure A implies that both cobalt atoms have rare gas configuration, with the double bond furnishing two electrons.

In accordance with structure A, the infrared spectra of the complexes (Table I) show bands attributable to terminal carbonyl groups[1-3] one band (in the acetylene and pentyne complex) attributable to olefinic C–H and a band at 5.42 μ due to bridge carbonyl.[2,3] On the basis of structure A, one might expect two rather intense bands in the organic carbonyl region due to the two carbonyl groups in the ring. However, only one such band is found at 5.62 μ in the acetylene complex and at 5.67 and 5.68 μ in the dimethylacetylene and pentyne complex, respectively. A band in this region might be produced by vinyl-type esters or lactones. A structure containing a lactone ring and consistent with chemical and infrared evidence is shown in B.



B

Structure B is supported by the recent finding of G. Albanesi and M. Tovaglieri who isolated a compound of structure C



C

from the reaction products obtained by treating acetylene in methanol with carbon monoxide in the presence of $Co_2(CO)_8$.[13] While other plausible structures can be written for I, proof for the correct structure will have to await the result of an X-ray study now in progress.[14]

TABLE I

INFRARED SPECTRA OF DICOBALT NONACARBONYL ALKYNE COMPLEXES IN CS_2 AND CCl_4

$Co_2(CO)_9HC{\equiv}CH$		$Co_2(CO)_9C_3H_7C{\equiv}CH$		$Co_2(CO)_9$-$CH_3C{\equiv}CCH_3$	
μ	Relative intensity	μ	Relative intensity	μ	Relative intensity
2.40	0.2	2.41	0.2	2.40	0.2
2.46	.2	2.47	.2	2.45	.2
2.75	.2	2.76	.2	2.76	.2
2.87	.2	2.88	.2	2.87	.2
3.21	.2	3.27	.2		
		3.39	1		
		3.42	1	3.42	.2
3.5	Trace	3.50	0.5		
4.04	0.5	4.03	0.2	4.03	.2
4.74	3	4.74	3	4.74	4
4.83	9	4.83	9	4.82	9
4.87	9	4.87	9	4.87	9
4.91	10	4.91	10	4.91	10
5.42	6	5.42	6	5.42	6
5.62	7	5.68	5	5.67	7
5.75	1	6.05	0.2	6.16	0.5
		6.24	.5	6.33	1
6.47	1	6.74	.5	6.95	0.2
6.47	1	7.24	.2	7.20	.5
		7.48	.2	7.56	.2
		7.97	.2		
8.50	1	8.29	.5	8.19	.5
		8.76	1		
9.20	2	9.17	0.2	9.12	1
9.36	2	9.53	1	9.42	0.2
10.05	2	9.95	0.2	10.2	1
10.30	1	10.52	4	10.48	4
		11.11	1		
11.50	2	11.73	0.2		
		12.07	.2		
12.40	3	12.36	.2		
13.80	2				
14.25	1	15.17	4	14.81	4

In spite of uncertainty regarding a detailed structure, it seems fairly certain that I contains two carbonyl groups attached to an acetylene. The existence of complex I with structural features as in A or B sheds light on the mechanism of the cobalt carbonyl catalyzed carbonylation of acetylene. When acetylene is treated with carbon monoxide and methanol in the presence of $Co_2(CO)_8$, a smooth reaction occurs at 100° yielding chiefly dimethyl succinate.[15] The formation of this diester has been postulated[16] to proceed through the intermediate formation of methyl acrylate

$$HC{\equiv}CH + CO + CH_3OH \xrightarrow[110^\circ]{Co_2(CO)_8}$$

$$H_2C{=}CHCOOCH_3 \xrightarrow[CH_3OH]{CO} CH_3OOCCH_2CH_2COOCH_3$$

Methyl acrylate, however, reacts very slowly under the same conditions, and there is little doubt that this compound is not an intermediate. The ready addition of two carbon monoxide molecules to acetylene to form I furnishes a good basis for postulating that I or a similar complex is an intermediate in the succinate synthesis. The formation of A according to equation 2 involves the insertion of carbon monoxide between acetylenic carbons and cobalt in $Co_2(CO)_6RC{\equiv}CR'$ whose structure has been established recently.[6] Insertion of carbon monoxide between a carbon atom and a transition

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[13] G. Albanesi and M. Tovaglieri, *La Chimica e L'Industria*, in press.

[14] O. S. Mills, private communication.

[15] P. Pino and A. Miglierina, THIS JOURNAL, **74**, 5551 (1952).

[16] G. Natta and P. Pino, *La Chimica e L'Industria* (*Milan*), **34**, 449 (1952).

metal recently was demonstrated by Coffield, Kozikowski and Closson[17] who found that $CH_3Mn(CO)_5$ treated with carbon monoxide yielded the corresponding acetyl compound $CH_3COMn(CO)_5$. Formation of B may involve a similar insertion of carbon monoxide followed by rearrangement. It is very likely that in the case of a heterogeneous catalyst, carbon monoxide can be similarly inserted between the metal and the chemisorbed hydrocarbon substrate.

Experimental[18]

Preparation of I. (a) $Co_2(CO)_9C_3H_7C{\equiv}CH$.—A 500-ml. autoclave was charged with 89.5 g. (262 mmoles) of $Co_2(CO)_8$ and 80 ml. of *n*-heptane. A test-tube containing 25 ml. (265 mmoles) of 1-pentyne then was placed in the autoclave in a vertical position. By means of this arrangement it was possible to prevent contact between $Co_2(CO)_8$ and alkyne until the reagents had been placed under elevated carbon monoxide pressure. The autoclave was placed in a mechanical rocker, sealed and flushed with carbon monoxide. After the autoclave had been pressured up to 190 atm. of carbon monoxide and the autoclave heated to 70°, the mechanical rocker was started. After heating at 70° for 12 hr. with continuous rocking, the autoclave was allowed to cool to room temperature, the pressure released, and the autoclave opened. The reaction product consisted of a dark red liquid and red crystals. The liquid was decanted from the crystals and the crystals thoroughly washed with 300 ml. of petroleum ether (35–45°). The crystals, dried at 40° (20 mm.), weighed 74 g. (64% based on the amount of 1-pentyne used). They decomposed in air at 76° and melted in an evacuated tube at 75–77°.

Anal. Calcd. for $C_{14}H_8O_9Co_2$: C, 38.38; H, 1.84; Co, 26.91; mol. wt., 438.08. Found: C, 38.33; H, 1.91; Co, 26.76; mol. wt., 465 (cryoscopic in benzene).

(b) $Co_2(CO)_9CH{\equiv}CH$.—The starting material II (R = R′ = H) was prepared by treating $Co_2(CO)_8$ with acetylene according to

$$Co_2(CO)_8 + HC{\equiv}CH \longrightarrow Co_2(CO)_6HC{\equiv}CH + 2CO$$

and distilling the crude reaction product.[1] The distillate, 22.65 g. (72.6 mmoles), was transferred to a 180-ml. autoclave with 20 ml. of *n*-hexane. The bomb was sealed, placed in a mechanical shaker, purged with carbon monoxide and then pressured to 210 atm. at room temperature. After heating for 13 hr. at 70–75°, the autoclave was allowed to cool to room temperature. After the pressure had been released and the autoclave opened, the solution was decanted from the crystals that had formed. The crystals were washed with petroleum ether and recrystallized by dissolving in boiling petroleum ether (35–45°) and cooling the petroleum ether solution to −35°. The red crystals decomposed on heating in an evacuated tube at 113–115° and weighed 25.9 g., corresponding to a yield of 90.1% based on the amount of II used.

Anal. Calcd. for $C_{11}H_2O_9Co_2$: C, 33.36; H, 0.51; Co, 29.77; mol. wt., 396.01. Found: C, 33.32; H, 0.61; Co, 30.25; mol. wt., 421 (cryoscopic in benzene).

(c) $Co_2(CO)_9CH_3C{\equiv}CCH_3$.—The starting material II (R = R′ = CH_3) was prepared as follows. A round-bottom flask provided with a mercury seal was charged with 90 g. (263 mmoles) of $Co_2(CO)_8$ and 50 ml. (637 mmoles) of $CH_3C{\equiv}CCH_3$ added to the flask in five 10-ml. portions in the course of 3 hr. Care was taken to prevent access of air to the reaction mixture. After standing overnight, the flask was evacuated to remove excess 2-butyne and the dark-red semi-solid residue transferred to a 500-ml. bomb with 150 ml. of petroleum ether (35–45°). The bomb was sealed, placed in a mechanical rocker, purged with carbon monoxide, pressured to 290 atm. and the mechanical rocker started. After heating at 70–75° for 32 hr. with continuous rocking, the bomb was allowed to cool to room temperature, the pressure released and the bomb opened. The dark red liquid was decanted and the crystals washed with petroleum ether until the color of the washings changed from dark red to orange. The weight of the crystals was 24 g. corresponding to a yield of 21.5% based on the amount of $Co_2(CO)_8$ used. After recrystallization from petroleum ether as described under b, the crystals melted in an evacuated tube at 108.5–109.5°.

Anal. Calcd. for $C_{13}H_6O_9CO_2$: C, 36.82; H, 1.42; Co, 27.80. Found: C, 36.73; H, 1.43; Co, 27.80.

Decomposition of I, $Co_2(CO)_9C_3H_7C{\equiv}CH$, with Pyridine and Iodine.—The decomposition of I and the determination of the amount of gas evolved was carried out in an apparatus described previously.[5,7]

To 0.7907 g. (1.80 mmoles) of I was added 20 ml. of pyridine and the solution stirred until the evolution of gas had stopped. The amount of gas evolved corresponded to 1.66 moles of CO per mole of I. Equation 4 requires the evolution of 1.67 moles of CO per mole of I. The presence of $[Co(CO)_4]^-$ in the pyridine solution was established by its characteristic[3] absorption band.

The amount of $[Co(CO)_4]^-$ in the pyridine solution was determined by treating an aliquot with excess iodine.[5] The amount of CO evolved corresponded to 4.97 moles of CO or 1.24 moles of $[Co(CO)_4]^-$ per mole of I. The total amount of CO evolved was $1.67 + 4.97 = 6.64$ moles of CO per mole of I.

Exchange of I, $Co_2(CO)_9C_3H_7C{\equiv}CH$, with Carbon Monoxide Containing $C^{14}O$.—A solution of 5.14 g. (11.74 mmoles) of I in 15 ml. of toluene was placed in a 70-ml. stainless steel bomb, the bomb sealed, placed in a mechanical rocker and pressured up to 33 atm. with carbon monoxide containing $C^{14}O$. The bomb was rocked at room temperature for 32 hr., then cooled to −40° and a gas sample withdrawn for counting. A barium carbonate planchet obtained from the sample had an activity of 5270 c.p.m. The bomb was allowed to warm to room temperature, the pressure released and the bomb opened. The mother liquor was decanted and the residue was crystallized from petroleum ether (35–45°) as described under b. To 0.5416 g. (1.24 mmoles) of the crystallized radioactive complex was added a solution of 3 g. of iodine in 20 ml. of pyridine. The volume of the evolved gas sample corresponded to 6.60 moles per mole of I. The barium carbonate planchet obtained from the gas sample had an activity of 5625 c.p.m. There was no activity in the pyridine solution of the decomposed sample. The higher count of the gas sample obtained from the decomposition of I (5625) as compared to that of the equilibrium mixture (5270 c.p.m.) was probably due to insufficient purging of the lines.

Treatment of I with Alkynes. (a) $Co_2(CO)_9C_3H_7C{\equiv}CH$ **and Phenylacetylene.**—Preliminary experiments had indicated that carbon monoxide was evolved when $Co_2(CO)_9C_3H_7C{\equiv}CH$ was treated with an excess of an acetylene. To determine the amount of gas evolved, $Co_2(CO)_9C_3H_7C{\equiv}CH$ was treated with excess phenylacetylene. The reason for using phenylacetylene in this experiment rather than 1-pentyne was that the determination of the evolved gas is carried out more accurately in the absence of compounds having a high vapor pressure.

In a flask provided with a side arm and a glass-enclosed stirring bar was placed 1.9294 g. (4.40 mmoles) of $Co_2(CO)_9C_3H_7C{\equiv}CH$ in toluene, the flask attached to a gas buret and the apparatus purged with helium. Through the side arm 2.5 ml. (22.8 mmoles) of phenylacetylene was added and the solution stirred. Gas evolution was completed in 4 hr., during which time 4.29 mmoles of CO or 0.975 mole per mole of $Co_2(CO)_9C_3H_7C{\equiv}CH$ was evolved.

(b) $Co_2(CO)_9C_3H_7C{\equiv}CH$ and 1-Pentyne.—To determine whether or not the carbon monoxide displaced by excess alkyne was replaced by alkyne, another experiment was carried out.

A flask provided with a mercury seal was charged with 5.04 g. (11.5 mmoles) of $Co_2(CO)_9C_3H_7C{\equiv}CH$ and 6 ml. (63.7 mmoles) of 1-pentyne added. After completion of the gas evolution, the excess pentyne was removed at 70° (20 mm.). Attempts to distil the remaining oil or to crystallize it from low-boiling petroleum ether failed. The composition of this oil did not correspond to that of the ex-

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[17] T. H. Coffield, J. Kozikowski and R. D. Closson, *J. Org. Chem.*, **22**, 598 (1957).

[18] Analyses by W. Dieter and W. Rosinski, Analytical Chemists, Central Experimental Station, Bureau of Mines, U. S. Department of the Interior, Region V, Pittsburgh, Pa.

pected $Co_2(CO)_6(C_3H_7C{\equiv}CH)_2$ but to a mixture containing more than two moles of alkyne per mole of $Co_2(CO)_8$.

Anal. Calcd. for $Co_2(CO)_6(C_3H_7C{\equiv}CH)_2$: 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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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY]

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

RECEIVED NOVEMBER 29, 1958

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] I. 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).