Reaction of Bis(acetylacetonato)copper(II) with Bromine*

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The halogenation of β-dicarbonyl compounds such as acetylacetone and ethyl acetoacetate proceeds in two steps:[1]

$$R_1COCH_2COR_2 + X_2 = R_1COCHXCOR_2 + HX$$

$$R_1COCHXCOR_2 + X_2 = R_1COCX_2COR_2 + HX$$

These reactions were found to be of first order with respect to the β-dicarbonyl compound, independent of the halogen concentration, and catalyzed by bases in general.[2] Bell and his collaborators analyzed these reactions in aqueous solution and determined the catalytic constants of various bases.[3]

Pedersen investigated the bromination of ethyl acetoacetate in aqueous solution and found that the first of the two consecutive reactions was catalyzed by copper(II)[4] and other divalent metal ions.[5] The intermediate metal chelate of the keto-form of the ester was assumed to transfer a proton to the catalyst base more easily than the substrate itself does. However, details of the succeeding reaction, that is, the bromination of the normal metal enolate ester are not yet clear. Furthermore, the reason why the second bromination step is not catalyzed by these metal ions is not certain at all. The present paper reports reactions of bromine with copper(II) chelates of acetylacetone and 3-bromoacetylacetone which were studied for the purpose of obtaining some information about these points.

Experimental

Materials. — Bis(acetylacetonato)copper(II) was prepared[6] by adding an ammoniacal solution of copper(II) acetate to an ethanolic solution of acetylacetone and was recrystallized from chloroform. (Found: Cu, 23.86; C, 45.90; H, 5.38%)

Bis(3-bromoacetylacetonato)copper(II) can be prepared either by the reaction between 3-bromoacetylacetone and copper(II) ion,[7] or by bromination of bis(acetylacetonato)copper(II) with *N*-bromosuccinimide.[8] We adopted the former route, but prepared 3-bromoacetylacetone in higher purity by the reaction of bis(acetylacetonato)copper(II) with an appropriate quantity of bromine. To a vigorously stirred solution of 33 g. (0.125 mol.) of bis(acetylacetonato)copper(II) in 1.3 l. of chloroform, 250 ml. of a chloroform solution of bromine (0.76 mol./l.; 0.19 mol. bromine) was added dropwise from a burette. The precipitate, copper(I) bromide, was filtered off and most of the solvent was distilled under reduced pressure at room temperature. The residual yellow liquid was then added drop by brop to an acetone solution of copper(II) acetate (0.125 mol. in 400 ml.) under vigorous agitation. The reaction mixture was kept at 0°C for 24 hr. The resulting green powder was filtered off, dried, and then recrystallized twice from benzene. M. p. 180—182°C (decomp.).

Found: Cu, 15.19; C, 28.92; H, 3.30; Br, 37.00. Calcd. for $Cu(C_5H_6O_2Br)_2$: Cu, 15.14; C, 28.39; H, 2.88; Br, 38.09%.

In Fig. 1 the absorption spectrum of bis(3-bromoacetylacetonato)copper(II) in chloroform is compared with that of bis(acetylacetonato)copper(II).

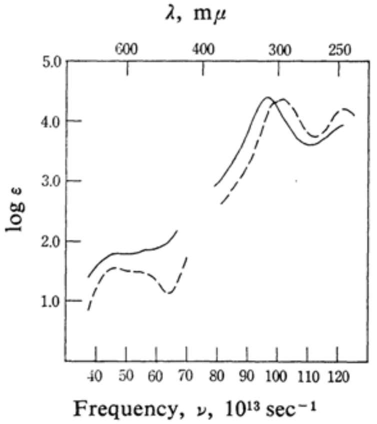

Fig. 1. The absorption spectra of bis(acetylacetonato)copper(II) (dashed curve) and bis(3-bromoacetylacetonato)copper(II) (full curve) in chloroform.

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[1] K. J. Pedersen, *J. Phys. Chem.*, **37**, 751 (1933); **38**, 581, 601 (1934); *Trans. Faraday Soc.*, **34**, 237 (1938).

[2] R. P. Bell and O. M. Lidwell, *Proc. Roy. Soc.*, **A176**, 88 (1940).

[3] e.g., R. P. Bell, E. Gelles and E. Möller, ibid., **A198**, 308 (1949).

[4] K. J. Pedersen, *Acta Chem. Scand.*, **2**, 252 (1948).

[5] K. J. Pedersen, ibid., **2**, 385 (1948).

[6] H. F. Holtzclaw, Jr., A. H. Carlson and J. P. Collman, *J. Am. Chem. Soc.*, **78**, 1838 (1956): H. F. Holtzclaw, Jr., K. W. R. Johnson and F. W. Hengeveld, ibid., **74**, 3776 (1952).

[7] H. F. Holtzclaw, Jr., and J. P. Collman, ibid., **79**, 3318 (1957).

[8] R. W. Kluiber, ibid., **82**, 4839 (1960).

Commercial bromine, after being washed with water more than five times, was dissolved in an aqueous solution of potassium bromide, and then distilled. The distillate was redistilled three times over calcium oxide.

Commercial dichloromethane was washed with concentrated sulfuric acid, then with a dilute solution of sodium hydroxide and finally with pure water. The washed solvent was dried over calcium chloride and distilled in a 60 cm. Widmer column.[9]

Absorption Spectra.—Visible and ultraviolet absorption spectra were measured with Beckman Model DU spectrophotometer. Infrared absorption spectra were obtained on an infrared spectrophotometer Model IR-S of the Japan Spectroscopic Co.

Analysis of the Precipitate. — The precipitate produced by the reaction between the copper chelate and bromine was dissolved in aqueous ammonia and allowed to stand overnight. The solution was then treated with a small quantity of sodium hydroxide and heated. The precipitate of copper(II) oxide was filtered off, dissolved in nitric acid and submitted to electrolytic analysis. The above filtered solution was acidified and treated with silver nitrate to determine the bromine content gravimetrically.

Results

Reaction of Bis(acetylacetonato)copper(II) with Bromine at Room Temperature. — The reaction was carried out in dichloromethane solution. Bis(acetylacetonato)copper(II) solution was prepared in the same concentration, 3.48×10^{-2} mol./l., as that of bromine. A desired amount of the bromine solution was added from a burette to a given amount of the chelate solution under vigorous agitation. Mole ratios of 1 : 1, 1 : 1.5, and 1 : 2 copper chelate to bromine were examined. When 1 mol. of bromine was added to 1 mol. of the chelate, the solution still showed the light blue color of residual chelate, but after 1.5 mol. or more of bromine had been added the solution was slightly yellow. A white precipitate was produced when the mole ratios were 1 : 1 and 1 : 1.5, but a brownish black precipitate resulted from a 1 : 2 mol. ratio. Analitical results for the precipitate from each experiment are summarized in Table I.

The white precipitate formed in the 1 : 1 and 1 : 1.5 reaction mixtures was copper(I) bromide; the black one formed in the 1 : 2 reaction mixture was found to consist mainly of copper(II) bromide. However, when the latter was allowed to remain in the reaction mixture for a long time, the precipitate gradually turned white and was found to be copper(I) bromide.

After the precipitate had been filtered off from the reaction mixture in Exp. Nos. 3 and 4, most of the solvent was driven off at room temperature under reduced pressure. The residual yellow liquid was submitted to infrared spectroscopy. Frequencies of the main absorption bands are listed in Table II (product A) together with those for acetylacetone. Absorption bands due to the methylene group in acetylacetone are not exhibited by this product. The absorption bands at 1720 and 1701 cm^{-1}, which are assigned to the two carbonyl groups in the keto-form of actylacetone, are shifted by 15 and 5 cm^{-1}, respectively, to the higher frequency side. This coincides with the shift of the carbonyl stretching frequency of a haloketone, suggesting the liquid product to be 3-bromoacetylacetone. That this is indeed so was unequivocally demonstrated by the preparation and analysis of its copper(II) chelate as descrived in the Experimental.

Reaction of Bis(3-bromoacetylacetonato)-copper(II) with Bromine.—The reaction between bis(3-bromoacetylacetonato)copper(II) and bromine in dichloromethane solution was carried out in a manner similar to that described in the preceeding section. Bromine was added to the chelate solution in mole ratios of 1 : 1, 1.5 : 1, and 2 : 1. In each case the precipitate was analyzed for copper and bromine, and the filtrate was examined by infrared spectroscopy after evaporation of the solvent.

Bis(3-bromoacetylacetonato)copper(II) reacts with bromine as rapidly as bis(acetylacetonato)-copper(II) does and gives quite similar precipitates (Table III). When 2 mol. or more of bromine is used for 1 mol. of the chelate, copper(II) bromide is precipitated, but when 1.5 mol. or less bromine is employed, copper(I) bromide results.

The main infrared absorption bands of the liquid product in Exp. Nos. 10, 11 and 12 are listed in Table II (product B) together with literature data for 3, 3-dichloroacetylacetone.[10] The absorption bands due to the two carbonyl groups appear at 1737 and 1714 cm^{-1}, exhibiting shifts of 17 and 13 cm^{-1}, respectively, compared with those of acetylacetone. This shift can be ascribed to the effect of halogen substitution in the 3-position; the magnitude of the shift is larger than that observed for product A, suggesting a dibromo substitution product. The strong absorption band around 1600 cm^{-1}, which was observed for the enol-form of acetylacetone and the product A, is not observed for the product B indicating the absence of an enol-form. Similar features were also reported for 3, 3-dichloroacetylacetone by Mecke

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[9] A. Weissberger et al. (ed.), "Organic Solvents," 2nd ed., Interscience Publisher, New York (1955), p. 409.

[10] R. Mecke and E. Funck [1], *Z. Elektrochem.*, **60**, 1124 (1956).

TABLE I. ANALYSIS OF THE PRECIPITATE FROM THE REACTION BETWEEN BIS(ACETYLACETONATO)COPPER(II) AND BROMINE

Exp. No.	Mole ratio of chelate : bromine	Precipitate analyzed, mg.	Copper found, mg.	Bromine found, mg.	Atom ratio Cu : Br
1	1 : 1	77.9	32.4	45.5	1 : 1.12
2	1 : 1	83.6	35.7	44.5	1 : 1.00
3	1 : 1.5	115.8	50.4	65.0	1 : 1.04
4	1 : 1.5	119.4	52.2	72.2	1 : 1.10
5	1 : 2	98.1	28.1	68.2	1 : 1.84
6[a]	1 : 2	61.4	25.0	33.4	1 : 1.06
7[a]	1 : 2	77.2	32.0	41.8	1 : 1.04

a) Precipitate allowed to remain in the reaction mixture for two weeks before analysis.

TABLE II. INFRARED ABSORPTION DATA OF REACTION PRODUCTS (cm^{-1})

Assignment	Acetylacetone	Product A[a]	Product B[a]	3,3-Dichloro-acetylacetone[b]
ν(OH)	~2800(1)	~2800(1)	—	—
ν(C=O)	1720(3)	1735sh(6)	1737(7)	1758(9)
ν(C=O)	1701(4)	1706(6)	1714(8)	1740(9)
ν(C=O) ν(C=C)	1610(8)	1597(8)	—	—
ν(C-O)	1445sh	1412(5)	1407(2)	1422(3)
$\delta_a(CH_3)$ δ(OH) $\delta(CH_2)$	1408(4)			
$\delta_s(CH_3)$	1359(5)	1362(6)	1360(6)	1361(8)
$\gamma(CH_2)$	1300(3)	—	—	—

a) Product A refers to the liquid product from the reaction between bis(acetylacetonato)copper(II) and bromine in the mole ratio of 1 : 1.5 (Exp. Nos. 3 and 4). Product B refers to the liquid product from the reaction between bis(3-bromoacetylacetonato)copper(II) and bromine in the mole ratio of 1 : 2 (Exp. Nos. 11 and 12).

b) Data from Ref. 10.

TABLE III. ANALYSIS OF THE PRECIPITATE FROM THE REACTION BETWEEN BIS(3-BROMOACETYLACETONATO)COPPER(II) AND BROMINE

Exp. No.	Mole ratio of chelate : bromine	Precipitate analyzed, mg.	Copper found, mg.	Bromine found, mg.	Atom ratio Cu : Br
8	1 : 1	58.7	25.2	28.6	1 : 0.90
9	1 : 1	48.7	24.8	26.5	1 : 0.84
10	1 : 1.5	66.7	25.9	35.1	1 : 1.08
11	1 : 2	92.4	25.7	61.2	1 : 1.90
12	1 : 2	96.6	27.0	64.2	1 : 1.90

and Funck.[10] Product B can thus reasonably be regarded as 3,3-dibromoacetylacetone.

Reaction of Bis(acetylacetonato)copper(II) with Bromine at a Low Temperature. — When the reaction was conducted in chloroform at about −60°C, the color of the solution changed from blue to green, to brown, and eventually to red, but no precipitate was formed after two moles of bromine had been added per mole of the chelate. However, when the solution was warmed to room temperature, a dark precipitate of copper(II) bromide appeared and the solution became colorless.

Discussion

When bis(acetylacetonato)copper(II) is attacked by bromine in organic solvents, the chelate ring is broken resulting in copper bromides and 3-bromoacetylacetone. When two moles or more of bromine is added to one mole of the chelate, copper(II) bromide is produced (Exp. No. 5). The reaction is represented by the equation,

$$\mathrm{Cu(HA)_2 + 2Br_2 = CuBr_2 + 2HABr} \qquad (1)$$

where H_2A stands for acetylacetone and

HA^- for the acetylacetonate anion $(CH_3COCHCOCH_3)^-$. Copper(II) bromide thus formed can further react with the other product 3-bromoacetylacetone (HABr) at a much lower rate, and thus is completely converted to copper(I) bromide when allowed to stand for a long period in the reaction mixture (Exp. Nos. 6 and 7).

$$2CuBr_2 + HABr = 2CuBr + ABr_2 + HBr \qquad (2)$$

When 1.5 mol. of bromine is employed for 1 mol. of the chelate, the following reaction occurs (Exp. Nos. 3 and 4).

$$Cu(HA)_2 + {}^3/_2Br_2 = CuBr + 2HABr \qquad (3)$$

In these cases the copper chelate employed is consumed completely, but when 1 mol. of bromine is added to 1 mol. of the chelate, the excess of the chelate remains unchanged in the solution.

Bis(3-bromoacetylacetonato)copper(II) reacts with bromine in a similar fashion to bis(acetylacetonato)copper(II), producing 3, 3-dibromoacetylacetone and copper bromide. The reaction in the mole ratio of 1 : 1.5 is represented by

$$Cu(ABr)_2 + {}^3/_2Br_2 = CuBr + 2ABr_2 \qquad (4)$$

Similarly the reaction in the mole ratio of 1 : 2 is written as

$$Cu(ABr)_2 + 2Br_2 = CuBr_2 + 2ABr_2 \qquad (5)$$

In this case the product 3, 3-dibromoacetylacetone has no active hydrogen to react with copper(II) bromide, and thus the latter remains unchanged even after standing a long time in the product solution.

Thus copper(II) chelates, not only of acetylacetone but also of 3-bromoacetylacetone, react instantaneously with bromine in dichloromethane giving 3-bromoacetylacetone and 3, 3-dibromoacetylacetone, respectively. The reason why copper(II) ion does not show any catalytic activity in the second step of the bromination of ethyl acetoacetate in aqueous solution[4] might be due to the instability of the intermediate copper(II) chelate of the ester in these reaction conditions. In fact, crystalline copper(II) chelate of ethyl α-bromoacetoacetate could not be isolated[11] in contrast to good stability of the chelate of the nonsubstituted ester. However, the copper(II) chelate of 3-bromoacetylacetone is very stable and can be synthesized in good yield as described in the present paper, and thus the copper(II) ion may be expected to promote the second step of the bromination of acetylacetone.

In the reaction of bis(acetylacetonato)copper(II) with bromine, copper(I) bromide is formed when less than two moles of bromine is employed for one mole of the chelate. This is very interesting in view of the oxidizing characteristic of bromine. The mechanism of the reactions represented by Eqs. 1 and 2 is not at all clear, but they seem to proceed through a common intermediate. The experiment performed at a low temperature indicates that the intermediate species is quite stable at about −60°C. Further investigation of the reaction mixture at a low temperature should shed light on the nature of the intermediate.

Summary

In the reaction of bis(acetylacetonato)copper(II) with bromine the chelate ring is broken and 3-bromoacetylacetone and copper(I) or copper(II) bromide are formed depending on the mole ratio of the reactants.

Bis(3-bromoacetylacetonato)copper(II) also reacts with bromine in a similar fashion resulting in 3, 3-dibromoacetylacetone and copper(I) or copper(II) bromide. The possibility of the copper(II) ion functioning as a catalyst in the second step of the bromination of acetylacetone is suggested.

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[11] T. Ogura, Y. Nakamura and S. Kawaguchi, This Bulletin, to be published.