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The Reactions of Bis(acetylacetonato)beryllium with Bromine and Hydrogen Bromide in Dichloromethane

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The main product in the reaction of bis(acetylacetonato)beryllium with bromine in the mole ratio of one to two was found to be bis(3-bromoacetylacetonato)beryllium. The mass-spectrometric analysis of the product of the same reaction in the mole ratio of one to one revealed the coexistence of mono- and dibrominated chelates, but the quantitative information concerning the product distribution has not been obtained. In this reaction a small amount of white precipitate was produced as a minor product. The same compound was obtained in the reaction of bis-(acetylacetonato)beryllium with hydrogen bromide in dichloromethane containing water, and identified as diaquoacetylacetonatoberyllium bromide on the bases of the elemental analysis, the anion exchange experiment and the infrared assay.

The bromination of ethyl acetoacetate in aqueous solution is catalyzed by copper(II)[1] and other bivalent metal ions,[2] whose catalytic activities were correlated with the stability of their acetylacetone chelates.[2] However, beryllium and aluminum ions do not show any catalytic activity for this reaction even though their acetylacetone chelates show the highest stability comparable with that of copper(II).[3]

We have studied the reactions of bromine with copper chelates of acetylacetone[4] and ethyl acetoacetate[5] in dichloromethane and found that in both cases the chelate is decomposed, forming the brominated β-dicarbonyl compound and copper(I) or copper(II) bromide depending on the reactants' mole ratio. The object of this paper is to report the behavior of bis(acetylacetonato)beryllium toward bromine and hydrogen bromide in dichloromethane.

Experimental

Materials. Bis(acetylacetonato)beryllium was synthesized according to a standard method.[6]

Found: Be, 4.35; C, 58.30; H, 7.14%. Calcd for $Be(C_5H_7O_2)_2$: Be, 4.35; C, 57.96; H, 6.81%.

Commercial bromine was purified by repeated distillation after water-washing.[5] Bp 58.2—58.8°C. Hydrogen bromide was prepared by the reaction of purified bromine with purified tetraline, passed through a calcium bromide column and condensed in a trap cooled by a dry ice - methanol bath. The gas was then evolved gradually and absorbed in dry dichloromethane.

Commercial dichloromethane was also purified by a standard method[7] and its water content was measured by the Karl Fischer method to be 4.9×10^{-3} mol/*l*.

The Reaction of Bis(acetylacetonato)beryllium with Bromine. The reaction of bromine with the chelate was performed in a three-necked flask equipped with a burette, and dry air inlet and outlet tubes. To the chelate solution of a desired concentration (usually in the range from 0.1 to 0.5 mol/*l*) in the flask was added bromine solution of the same concentration from the burette under a vigorous manual agitation. The gas outlet tube was connected to a suction pump *via* a washing bottle containing an aqueous alkaline solution. Hydrogen bromide gas evolved by the reaction was sweeped by a gentle stream of dry air and absorbed in the alkaline solution. In the course of this reaction a small amount of precipitate appeared. In one experiment this precipitate was filtered and analyzed. In another experiment, after the desired amount of bromine solution was added and dry air passed further for a while, the solution was washed with water. The precipitate suspended in the dichloromethane is soluble in water and extracted in this procedure. The water layer was combined with the alkaline solution in the washing bottle, acidified and treated with silver nitrate solution to determine hydrogen bromide evolved in this reaction. The dichloromethane layer was dried with anhydrous sodium sulfate and then evaporated *in vacuo*. The solid product thus obtained was dried and recrystallized twice from benzene. Both the crude and the recrystallized specimen were submitted to elemental analysis.

The Reaction of Bis(acetylacetonato)beryllium with Hydrogen Bromide. For the reactions of bis-(acetylacetonato)beryllium with hydrogen bromide, dichloromethane containing water in various concentration up to saturation (*ca.* 0.1 mol/*l*) was employed as a

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1) K. J. Pedersen, *Acta Chem. Scand.*, **2**, 252 (1948).

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

3) L. G. Sillén and A. E. Martell (Eds.) "Stability Constants of Metal-ion Complexes," The Chemical Society, London (1964).

4) Y. Nakamura and S. Kawaguchi, This Bulletin, **38**, 954 (1965).

5) T. Ogura, Y. Kojima, Y. Nakamura and S. Kawaguchi, *ibid.*, **38**, 1468 (1965).

6) W. C. Fernelius (Ed.), "Inorganic Syntheses," Vol. 2, McGraw-Hill, New York (1946), p. 17.

7) A. Weissberger *et al.* (Eds.), "Organic Solvents," 2nd ed., Interscience Publishers, New York (1955), p. 409.

solvent. The concentration of hydrogen bromide stock solution was determined just before use by pouring an aliquot into a large quantity of water and titrating with 0.1 N sodium hydroxide solution by means of a pH meter. Necessary amount of dichloromethane solution of hydrogen bromide was added from a burette to the chelate solution. White precipitate produced was filtered, washed with anhydrous dichloromethane and dried.

The Synthesis of Bis(3-bromoacetylacetonato)-beryllium. Anhydrous sodium acetate was suspended in the reaction medium, in advance, to avoid the effect of hydrogen bromide produced by the reaction. After the reaction the solid was filtered off and the solvent was evaporated as descrided above.

Analysis of Products. The solid product, which was obtained by solvent evaporation in each case, was submitted to elemental analysis. Beryllium was determined gravimetrically as the oxide.[8] To measure the bromine content, weighed amount of the solid specimen was heated with concentrated aqueous solution of sodium hydroxide for a few hours. After the chelate was destructed, the solution was acidified with nitric acid and treated with silver nitrate.

The white precipitate obtained in the reaction of bis-(acetylacetonato)beryllium with hydrogen bromide in dichloromethane of various water content was dissolved in methanol and passed through a column of the anion-exchange resin Diaion SA No. 100 (Mitsubishi Chemical Industries, Ltd). The resin had been treated in advance with 2 N solutions of sodium hydroxide, ammonium nitrate and nitric acid, successively, and washed with methanol repeatedly.

The infrared spectrum of the reaction product was examined by means of a Model IR-S Spectrophotometer of Japan Spectroscopic Co., Ltd. The NMR spectrum was observed with a Model JNM C-60 NMR Spectrometer of Japan Electron Optics Laboratory Co. The mass analysis was performed with a Hitachi RMU-6 Mass-spectrometer.

Results and Discussion

The Reaction of Bis(acetylacetonato)beryllium with Bromine in Dichloromethane. The main product in the reaction of bis(acetylacetonato)beryllium with bromine in the mole ratio of one to two is soluble in dichloromethane. Results of the elemental analysis of this product obtained after the solvent evaporation are as follows:

Found for the crude product: Be, 2.27; Br, 41.7; C, 33.27; H, 3.60%. Found for the recrystallized specimen: Be, 2.44; Br, 44.3; C, 33.38; H, 3.94%. Calcd for $Be(C_5H_6O_2Br)_2$: Be, 2.47; Br, 43.78; C, 32.90; H, 3.31%.

The analytical data of the recrystallized specimen coincide well with values calculated for bis(3-bromoacetylacetonato)beryllium, and the observed mp 179—180°C also coincides with that in the literature.[9] The infrared spectrum of this product shows the characteristic feature of the metal complex of 3-bromoacetylacetone.[10] In the region of 1500—1600 cm^{-1} only one strong peak is observed at 1564 cm^{-1} in place of two peaks for the acetylacetone complex, and the weak bands at 1194 and 792 cm^{-1} assigned for the C-H bending in the latter compound are lost in the reaction product. These facts are well reconciled with the above conclusion that the reaction product is bis-(3-bromoacetylacetonato)beryllium.

The quantity of hydrogen bromide evolved in the reaction of bis(acetylacetonato)beryllium with bromine in the mole ratio of one to two was determined to be twice as many moles as the original chelate. In one experiment, for example, 5.20 mmol of hydrogen bromide was produced from 2.586 mmol of the chelate. Thus the stoichiometry of the main reaction is represented by Eq. (1), where HA stands for acetylacetonate anion and BrA for 3-bromoacetylacetonate.

$$Be(HA)_2 + 2\,Br_2 = Be(BrA)_2 + 2\,HBr \qquad (1)$$

As described in the Experimental Section, a small amount of white precipitate is produced as a minor product in this reaction. The reproducibility of the analytical data for this precipitate is very poor, but some trend is noticed. Thus, one specimen obtained from a reaction in the mole ratio of one to one showed the empirical formula, $BeBr_{0.95}C_{4.54}H_{10.6}O_{3.15}$ and another sample obtained from a reaction in the mole ratio of one to two, $BeBr_{1.77}C_{4.84}H_{11.0}O_{3.86}$. In either case only one molecule of acetylacetone is contained per beryllium atom, but the bromine content is much larger in the latter sample than in the former. These results suggest that hydrogen bromide produced in the reaction may attack the original or the brominated chelate in accordance with the stage of the main reaction, to give a beryllium complex containing bromine and acetylacetone or 3-bromoacetylacetone as ligands. The fluctuation of analytical data might be due to the variation in the mixing ratio of these two products. To clarify this situation, the reactions of hydrogen bromide with bis(acetylacetonato)beryllium and bis(3-bromoacetylacetonato)beryllium were examined.

The Product in the Reaction of Bis(acetylacetonato)beryllium with Hydrogen Bromide in Dichloromethane. The yield of the white insoluble product obtained in the reaction of hydrogen bromide with bis(acetylacetonato)-beryllium was found to increase with the water content of dichloromethane but was very low in either case. Some typical experimental results are shown in Table 1. Results of the elemental analysis nearly coincide with values calculated for $Be(C_5H_7O_2)Br\cdot 2H_2O$. The water content of this

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[8] W. F. Hillebrand *et al.*, "Applied Inorganic Analysis," 2nd ed., Wiley, New York (1953), p. 522.

[9] R. W. Kluiber, *J. Am. Chem. Soc.*, **82**, 4839 (1960).

[10] R. P. Dryden and A. Winston, *J. Phys. Chem.*, **62**, 635 (1958); J. P. Collman, R. A. Moss, S. D. Goldby and W. S. Trahanovsky, *Chem. Ind. (London)*.

TABLE 1. PRODUCT OF THE REACTION BETWEEN HYDROGEN BROMIDE AND BIS(ACETYLACETONATO)-BERYLLIUM IN DICHLOROMETHANE CONTAINING VARIOUS AMOUNT OF WATER*

Mole ratio of chelate to HBr	Chelate employed mmol	Water content mmol	Ppt. yield mg	Analytical data of the ppt.(%) Be	Br	C	H
1 : 1	18.1	0.50	54	—	36.8	26.08	5.05
1 : 1	18.1	4.90	291	4.26	35.7	27.49	4.81
1 : 2	18.1	5.15	287	4.25	35.7	28.26	4.68
1 : 1	5.05	5.38	323	4.09	36.3	26.32	5.14
	Calcd for $Be(C_5H_7O_2)Br\cdot 2H_2O$:			4.02	35.66	26.80	4.95

* The concentration of the chelate and hydrogen bromide solutions was 0.36 mol/*l* in either case.

compound was directly determined to be 17.4% by the Karl Fischer method employing methanol as solvent. This figure corresponds fairly well with the value, 16.1% calculated for the above formula. Beryllium usually prefers the coordination number of four and the structure of this compound should be either $[BeBr(HA)(H_2O)]\cdot H_2O$ or $[Be(HA)(H_2O)_2]Br$. In the former case bromine is coordinated directly to beryllium and the compound should be a nonelectrolyte. On the other hand, if the latter is the case two molecules of water are both contained in the inner sphere and the compound should be an electrolyte.

Dried sample of this compound was dissolved in methanol and passed through a column of the anion-exchange resin as described in the Experimental Section. From the filtrate 92.4% of the beryllium employed was recovered, but any trace of bromine was found there. The bromide ion held in the column was eluted with 100 m*l* of 2 N sodium nitrate solution, and recovered in the yield of 99.6%. These results clearly indicate that the compound is diaquoacetylacetonatoberyllium bromide, $[Be(HA)(H_2O)_2]Br$.

The infrared spectrum of this reaction product well corresponds with that of the original chelate except six new bands: 3123(s, broad), 2503(vw), 2323(vw), 1643(m), 883(m) and 765 cm^{-1}(m). Of these 3123 and 1643 cm^{-1} bands are attributed to the O–H stretching and H–O–H bending modes of water, respectively. Two absorption bands at 883 and 765 cm^{-1} could be assigned to the rocking and wagging, respectively, of the coordinated water.11)

The reaction of hydrogen bromide with bis(3-bromoacetylacetonato)beryllium was also examined in dichloromethane containing various amount of water, but muddy intractable solid was produced and further experiment has not been performed.

Products Obtained in the Reaction of Bis(acetylacetonato)beryllium and Bromine in the Mole Ratio of One to One. The fact that the main product in the reaction of bis(acetylacetonato)beryllium with bromine in dichloromethane in the mole ratio of one to two is bis(3-bromoacetylacetonato)beryllium, suggests that there occurred the "pseudo aromatic" substitution12) at the 3-position of ligated 2, 4-pentanedione. The minor product diaquoacetylacetonatoberyllium bromide should be considered to have been produced in the secondary reaction of hydrogen bromide with the original chelate in the presence of water.

There seem to be three possibilities as to products in the reaction of bis(acetylacetonato)beryllium with bromine in the mole ratio of one to one. If the first bromination reaction of the chelate (Eq.(2)) is much faster than the second stage (Eq. (3)), the mixed complex Be(HA)(BrA) should

$$Be(HA)_2 + Br_2 = Be(HA)(BrA) + HBr \qquad (2)$$

$$Be(HA)(BrA) + Br_2 = Be(BrA)_2 + HBr \qquad (3)$$

be produced exclusively. On the other hand if the reverse is the case, only one half amount of the original chelate employed will be transformed to the dibrominated chelate $Be(BrA)_2$. Thirdly, if rates of the two steps are comparable, the final system will be a mixture of three kinds of beryllium chelates. Thus the information concerning the products distribution is expected to indicate the relative rates of the two reactions.

The absorption spectrum of the solid product obtained by the solvent evaporation was just the same as that of a one to one mixture of $Be(HA)_2$ and $Be(BrA)_2$. However, any conclusion can not be drawn since the absorption spectrum of the mixed complex Be(HA)(BrA) is unknown. The infrared absorption spectra and the NMR spectra were not diagnostic either, and thence the mass-spectrometric analysis was tried.

The mass-spectrometer is becoming a valuable instrument for structural investigations of metal chelates, and acetylacetone chelates of various

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11) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York (1963), p. 156.

12) J. P. Collman, *Advan. Chem. Ser.* No. 37, 78 (1963).

metal have been examined by this method,[13] but no report has appeared on the metal chelates of substituted acetylacetone. The mass-spectrum of bis(3-bromoacetylacetonato)beryllium is very complex containing many fragment ion peaks. The pattern coefficients of only several peaks are listed in Table 2 together with those for the product compound in question. Three parent peaks, $m/e=367$, 365 and 363 are observed in accordance with the natural abundance ratio of bromine isotopes, ^{79}Br, 50.52 and ^{81}Br, 49.48%. The highest peak of these, $m/e=365$, was taken as the base peak. The pattern coefficients for parent ions and other ions derived from them show a very good correspondence down to the m/e value of 300 for the two kinds of sample. However, the peaks of $m/e=287$ and 285 due to Be(HA)(BrA)$^+$ ion are very much higher for the one to one reaction product than for dibrominated chelate. The same situation is also noticed for all peaks of m/e less than 280.

TABLE 2. THE MASS-SPECTRA OF BIS(3-BROMOACETYLACETONATO)BERYLLIUM AND PRODUCT OF REACTION BETWEEN BIS(ACETYLACETONATO)BERYLLIUM AND BROMINE IN THE MOLE RATIO OF ONE TO ONE

Ion	m/e	Be(BrA)$_2$	Product from 1 : 1 reaction
Be(CH$_3$COCBrCOCH$_3$)$_2^+$	367	50.7	50.9
	365	100	100
	363	51.8	50.9
$-$CH$_3$	352	34.8	34.5
	350	69.6	68.6
	348	35.7	35.3
$-$2CH$_3$+H	338	1.6	1.5
	336	2.9	2.6
	334	1.7	1.5
Be(CH$_3$COCBrCOCH$_3$)-(CH$_3$COCHCOCH$_3$)$^+$	287	53.1	235.9
	285	53.7	237.8
$-$CH$_3$	272	75.8	344.6
	270	76.4	347.8
$-$2CH$_3$+H	258	4.2	12.7
	256	4.9	13.6

These results clearly indicate that the product of reaction between bis(acetylacetonato)beryllium and bromine in the mole ratio of one to one is a mixture of mono- and dibrominated chelates. Unfortunately, however, those mass-spectra were observed for vapors from solid samples kept at about 150°C in the ion source, and so the quantitative information concerning the product distribution could not be obtained.

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[13] J. S. Shannon and J. M. Swan, *Chem. Commun.*, **1965**, 30; E. P. Dudek and G. O. Dudek, *Inorg. Nucl. Chem. Letters*, **2**, 56 (1966); S. Sasaki *et al.*, Paper to the 19th Annual Meeting of the Chemical Society of Japan, March 31, 1966.