BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2572—2574 (1967)

The Reaction of Tris(acetylacetonato)aluminum with Bromine in Dichloromethane

Yukio NAKAMURA, Masaaki HIRATA and Shinichi KAWAGUCHI

Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka

(Received May 22, 1967)

The reaction between tris(acetylacetonato)aluminum and bromine in dichloromethane was studied. The main product of this reaction was tris(γ-bromoacetylacetonato)aluminum which was soluble in dichloromethane. A small amount of slightly yellow precipitate was also produced as a minor product. The same compound was obtained in the reaction of tris(γ-bromoacetylacetonato)aluminum with hydrogen bromide in dichloromethane containing water, and identified as bromoaquobis(γ-bromoacetylacetonato)aluminum on the bases of the elemental and water analyses, the ion exchange study, and the infrared spectroscopy.

In the reactions of bromine with copper chelates of acetylacetone[1] and ethyl acetoacetate[2] in dichloromethane, the chelate is decomposed forming the brominated β-dicarbonyl compound and copper(I) or copper(II) bromide depending on the mole ratio of reactants. However, the main product in the similar reaction of bis(acetylacetonato)beryllium was found to be bis(γ-bromoacetylacetonato)beryllium.[3] This paper reports the experimental results obtained in the reaction of tris(acetylacetonato)aluminum with bromine.

Experimental

Materials. Tris(acetylacetonato)aluminum was prepared according to a standard method[4] and recrystallized twice from the benzene solution by adding petroleum ether. Mp 194.8°C (literature, 194.6°C).

Found: C, 55.77; H, 6.68; Al, 8.23%. Calcd for $AlC_{15}H_{21}O_6$: C, 55.57; H, 6.53; Al, 8.32%.

Commercial bromine and dichloromethane were purified by the standard methods,[2] and the water content of the "dry" solvent was determined by the Karl Fischer method to be 4.9×10^{-3} M.

The solution of dry hydrogen bromide in dichloromethane was also prepared by the method described previously.[2]

The Reaction of Tris(acetylacetonato)aluminum with Bromine. The reaction of tris(acetylacetonato)aluminum with bromine was performed in a three-necked flask equipped with a burette, and dry air inlet and outlet tubes. To a chelate solution of about 0.15 M in the flask was added a bromine solution of the same concentration from the burette under vigorous manual agitation. The solution remained transparent in the initial stage of the reaction, but became turbid when about 1.5 mol of bromine was added per 1 mol of the chelate. A small amount of slightly yellow precipitate was formed when 3 mol of bromine was added. This precipitate was filtered, washed with dichloromethane repeatedly, dried *in vacuo* and submitted to the elemental analysis.

The main product of the reaction is soluble in dichloromethane. The filtrate was washed with water repeatedly, dried with anhydrous sodium sulfate, and then evaporated to dryness at room temperature by passing dry

---

[1] Y. Nakamura and S. Kawaguchi, This Bulletin, **38**, 954 (1965).

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

[3] Y. Nakamura and S. Kawaguchi, *ibid.*, **40**, 1179 (1967).

[4] R. C. Young, "Inorganic Syntheses," Vol. II, ed. by W. C. Fernelius, McGraw-Hill Book Company, New York, N. Y. (1946), p. 25.

air. The solid product thus obtained was submitted to the elemental analysis.

In one experiment a washing bottle containing a 2 N aqueous solution of sodium hydroxide was inserted between the reaction vessel and a suction pump. Hydrogen bromide gas evolved by the reaction was sweeped by a gentle stream of dry air and absorbed in the alkaline solution. After the desired amount of bromine solution was added and dry air was passed further for a while, the product solution was washed repeatedly with water. The hydrogen bromide solution thus obtained was combined with the alkaline solution in the washing bottle and added with a solution of silver nitrate after acidification to determine hydrogen bromide produced in this reaction.

The Reaction of Tris(γ-bromoacetylacetonato)aluminum with Hydrogen Bromide. Dichloromethane almost saturated with water (9.85×10^{-2} M) was employed as a solvent. Tris(γ-bromoacetylacetonato)aluminum was synthesized by the reaction of tris(acetylacetonato)aluminum with bromine in dichloromethane suspended with anhydrous sodium acetate and recrystallized twice from benzene-petroleum ether.

Found: C, 32.73; H, 3.54; Br, 41.75; Al, 4.36%. Calcd for $AlC_{15}H_{18}Br_3O_6$: C, 32.12; H, 3.23; Br, 42.73; Al, 4.81%.
Mp 212.0—213.4°C (literature, 215.5—216.0°C[5]). The concentrations of the chelate and hydrogen bromide solutions were both 9.73×10^{-2} M, and the reaction was performed in the reactants' mole ratio of 1 : 1 and 1 : 2. The precipitate produced was dried at 80°C for about 7 hr to reach a constant weight.

Analyses. The concentration of hydrogen bromide solution used in the above reaction was determined just prior to each experiment. An aliquot from the stock solution was poured into a large excess of water and titrated with a 0.1 N solution of sodium hydroxide by the aid of a pH meter.

Aluminum contained in the reaction product was determined gravimetrically as aluminum oxide[6] after decomposition with nitric acid.

The bromine content of the reaction product was measured gravimetrically as silver bromide by heating a specimen with a concentrated sodium hydroxide solution for a few hours and then adding a solution of silver nitrate after acidification with nitric acid.

The product in the reaction of tris(γ-bromoacetylacetonato)aluminum with hydrogen bromide was dissolved in methanol and passed through a column (10 mm × 15 cm) of the cation exchange resin, Dowex 50W-X8. The resin had been treated in advance with 3 N hydrochloric acid and a 2 N solution of potassium chloride, and then washed repeatedly with methanol.

The infrared spectrum of the reaction product was examined as a pressed disc in potassium bromide by means of a Model IR-S Spectrophotometer of Japan Spectroscopic Co., Ltd.

Results

The Reaction of Tris(acetylacetonato)aluminum with Bromine. When 2.34 mmol of the aluminum chelate was forced to react with three times as many moles of bromine in dichloromethane, 7.92 mmol of hydrogen bromide was produced. This figure is a little larger than that of bromine employed.

The result of the elemental analysis of the main product which is soluble in dichloromethane coincides with those calculated for this (γ-bromoacetylacetonato)aluminum.

Found: C, 32.83; H, 3.44; Br, 39.62; Al, 4.34%. Mp 208.6—209.4°C.

The infrared absorption spectrum of this compound shows some remarkable differences from that of the original chelate. Two peaks at 1598 and 1530 cm^{-1} characteristic for C=O and C=C groups in tris(acetylacetonato)aluminum changed to a single peak at 1575 cm^{-1}. Furthermore two bands at 1193 and 782 cm^{-1} assigned for the C–H bending vibrations in the original chelate are lost in the reaction product. These are the characteristic features of the metal complex of γ-substituted acetylacetone.[7]

Thus, the main reaction at the reactants' mole ratio of 1 : 3 seems to be represented by the following equation:

$$Al(AH)_3 + 3Br_2 = Al(ABr)_3 + 3HBr$$

where AH and ABr stand for acetylacetonate and γ-bromoacetylacetonate anions respectively.

The minor insoluble product which was produced in the later stage of this reaction showed the following analytical results: Found: C, 23.98; H, 3.61; Br, 47.13; Al, 5.61%. The infrared spectrum of this compound showed a complete coincidence with that of the product of the reaction between tris(γ-bromoacetylacetonato)aluminum and hydrogen bromide in dichloromethane containing water.

The Reaction of Tris(γ-bromoacetylacetonato)aluminum with Hydrogen Bromide in Dichloromethane. The yield of the light yellow insoluble product obtained in the reaction of tris(γ-bromoacetylacetonato)aluminum with hydrogen bromide was found to increase with the amounts of water and hydrogen bromide contained, but was very low in either case. For instance, when 2.734 g (4.87 mmol) of the chelate was added with equimolar hydrogen bromide in dichloromethane containing 5.18 mmol of water, 0.885 g of precipitate was obtained, but when twice as many moles of hydrogen bromide was used, 1.052 g of the product was given. Results of the elemental analysis of this product was very poor, but seemed to lie between the calculated values for $Al(C_5H_6O_2Br)_2Br\cdot H_2O$ and $Al(C_5H_6O_2Br)_2Br\cdot 2H_2O$.

Found: C, 24.53; H, 3.69; Br, 46.38; Al, 5.48%. Calcd for $AlC_{10}H_{14}O_5Br_3$: C, 24.97;

---

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

[6] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analysis," 2nd ed., Wiley, New York, N. Y. (1953), p. 500.

[7] 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)*, **1960**, 1213.

H, 2.93; Br, 49.85; Al, 5.61%. Calcd for $AlC_{10}H_{16}O_6Br_3$: C, 24.07; H, 3.23; Br, 48.05; Al, 5.41%.

The direct determination of water content by the Karl Fischer method gave the value of 3.37%. This value coincides closely with 3.75% calculated for the monohydrate and differs appreciably from 7.22% for the dihydrate. Thus it is assumed that this product is $Al(C_5H_6O_2Br)_2Br\cdot H_2O$. Hydrogen bromide seems to have attacked tris(γ-bromoacetylacetonato)aluminum together with water, replacing one molecule of γ-bromoacetylacetone with a bromide ion and a water molecule. This compound is soluble in methyl, ethyl and other alcohols and tetrahydrofuran, but not in water or benzene, chloroform, carbon tetrachloride, acetone and other organic solvents.

To ascertain the bonding nature of bromine to aluminum in this compound, the methanol solution was passed through a column of the potassium form cation exchange resin, Dowex 50W-X8. The complex was not adsorbed at all, but recovered completely (102% as to aluminum and 98% as to bromine) in the effluent. This result indicates that the bromide ion coordinates to aluminum forming a nonelectrolyte complex molecule.

The infrared spectrum of this compound resembles that of tris(γ-bromoacetylacetonato)-aluminum, but the strong peak due to the C=O group appears at 1598 cm^{-1} in contrast with 1575 cm^{-1} for the latter chelate. Furthermore a weak band is observed at 1530 cm^{-1} which is not found for tris(γ-bromoacetylacetonato)aluminum, but it is certain that tris(acetylacetonato)aluminum is not contained as an impurity since the latter compound is soluble in dichloromethane. Furthermore a C–H bending peak at 1193 cm^{-1} observed for the unbrominated acetylacetone chelate does not appear at all. The above change in the C=O stretching region must be due to the bromide coordination to aluminum.

The absorption bands due to water coordinated to aluminum were reported by Gamo[8] to appear at 3030(s, b), 2420(m), 1640(m), 844(m), 1950(w), 1160(w, vb) cm^{-1} in $AlCl_3\cdot 6H_2O$, and at 3330(s), 2460(w), 1640(w), 704(w), 2940(s) cm^{-1} in $Al_2(SO_4)_3\cdot 18H_2O$. In the present case a strong and very broad band is observed at 3240 cm^{-1}, but no other peaks can be identified. Thus the conclusive evidence supporting the coordination of water to aluminum could not be obtained. However, the coordination number of five is unusual for aluminum and the octahedral structure $[AlBr(C_5H_6O_2Br)_2(H_2O)]$ (I) may be assumed for this compound.

Discussion

The behavior of tris(acetylacetonato)aluminum against bromine in dichloromethane is very similar to that of bis(acetylacetonato)beryllium. The main reaction is the quasi-aromatic substitution of γ-hydrogen with bromine. Hitherto *N*-bromosuccinimide was used exclusively for brominating these chelates,[5] but now it was disclosed that bromine does work as well in dichloromethane. In contrast with acetylacetonates of other metals examined, such as copper(II),[1] cobalt(II),[9] cobalt(III),[10] and nickel(II),[11] the brominated chelates of beryllium and aluminum are surprisingly stable. This might be a reason why beryllium and aluminum ions do not show any catalytic activity for the bromination of β-dicarbonyl compounds.[12]

Metal acetylacetonates are acid labile in general. Bis(acetylacetonato)beryllium is partly decomposed by the attack of hydrogen bromide together with water in dichloromethane.[3] On the other hand tris(acetylacetonato)aluminum is not decomposed by hydrogen bromide and water, but the brominated chelate is partly decomposed in the same condition. These facts are in good accordance with the observation that precipitate appears in the later stage of reaction between the aluminum chelate and bromine, while precipitate appears from the start of reaction in the case of beryllium.[3] The acid lability seems to decrease in the following order: beryllium chelate > brominated beryllium chelate $\gtrsim$ brominated aluminum chelate $\gg$ aluminum chelate.

The molecular formula (I) was tentatively assumed for the non-ionic product in the reaction between tris(γ-bromoacetylacetonato)aluminum and hydrogen bromide in dichloromethane containing water. However, the coordination of water molecule is not established and another possibility of the dimeric structure $[(ABr)_2Al\langle{}^{Br}_{Br}\rangle Al(ABr)_2]\cdot 2H_2O$ can not be denied. The determination of molecular weight is desired, but no suitable solvent has been found. When this compound was dissolved in tetrahydrofuran and forced to recrystallize, a disproportionation reaction occurred and tris(γ-bromoacetylacetonato)aluminum was obtained.

The authors are grateful to Dicel, Ltd. for the generous gift of acetylacetone. The cost of this research has been partly defrayed by a Scientific Research Grant from the Ministry of Education, to which the authors' thanks are also due.

---

8) I. Gamo, This Bulletin, **34**, 760 (1961).

9) Y. Nakamura, N. Kanehisa, M. Gotani and S. Kawaguchi, Abstracts of the 16th Symposium on the Coordination Chemistry held at Tokyo by the Chemical Society of Japan, December, 1966, p. 113.

10) Y. Nakamura, M. Gotani and S. Kawaguchi, Abstracts of the 20th Annual Meeting of the Chemical Society of Japan held at Tokyo, April, 1967, p. II-88.

11) Y. Nakamura, K. Noda and S. Kawaguchi, Abstracts of the 14th Symposium on the Coordination Chemistry held at Fukuoka by the Chemical Society of Japan, November, 1964, p. 126.

12) K. J. Pedersen, *Acta Chem. Scand.*, **2**, 385 (1948).