The Reaction of the Copper(II) Chelate of Ethyl Acetoacetate with Bromine* and the Reactions of the Copper(II) Chelates of Acetylacetone and Ethyl Acetoacetate with Dry Hydrogen Bromide**

By Tetsuya OGURA, Yoshitane KOJIMA, Yukio NAKAMURA and Shinichi KAWAGUCHI

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In a previous paper[1] we have reported on the reaction of bis(acetylacetonato)copper(II) with bromine in dichloromethane. When 2 mol. of bromine was added to 1 mol. of the chelate at room temperature, copper(II) bromide and 3-bromoacetylacetone were formed, but if 1.5 mol. or less of bromine was employed against 1 mol. of the chelate, copper(I) bromide resulted instead of copper(II) bromide. The pathway of the reaction is not yet clear. Therefore, similar reactions of the copper(II) chelate of ethyl acetoacetate with bromine and dry hydrogen bromide have been studied, as has been the reaction of bis(acetylacetonato)-copper(II) with the latter reagent, in hopes of determining some reaction intermediates.

Experimental

Materials.—The copper(II) chelate of ethyl acetoacetate was prepared according to the method of Wislicenus[2] by adding an ether solution of ethyl acetoacetate to an ammoniacal solution of copper sulfate. The complex thus obtained was then recrystallized from a hot chloroform solution. M. p. 193°C (lit., 192—193°C). (Found: Cu, 19.65; C, 44.79; H, 5.96%). Bis(acetylacetonato)copper(II) was also synthesized by a standard method reported previously.[1]

Commercial bromine was washed with pure water repeatedly (more than five times) and then distilled from an aqueous solution containing potassium bromide. The distillation of bromine was further repeated over calcium oxide in order to exclude all water.

Dry hydrogen bromide was prepared by dropping purified bromine into tetralin which had previously been dried and fractionally distilled. The evolved gas was passed through a column of calcium bromide and condensed in a trap immersed in a dry ice-methanol bath. Hydrogen bromide was then evaporated and absorbed in dry dichloromethane.

Dichloromethane from a commercial source was washed with a 5% solution of sodium hydrogen carbonate and then with pure water. After having been dried with calcium chloride, it was fractionally distilled through a Widmer column.[3]

Reaction Procedure. — In the reaction of the copper(II) chelate of ethyl acetoacetate with bromine, dry or wet dichloromethane was adopted as the reaction medium. The "dry" solvent was found by the Karl Fischer method to contain water in the concentration of 4.9×10^{-3} mol./l. (8.8 mg. water in 100 ml. dichloromethane). In the experiment to clarify the role of water, dichloromethane saturated with water was employed; the water content was estimated to be 0.14 mol./l. (0.189 g. water in 100 g. dichloromethane) at 25°C.[4] The

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** Presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

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

[2] W. Wislicenus, *Ber.*, **31**, 3151 (1898).

[3] A. I. Vogel, *J. Chem. Soc.*, **1948**, 1833.

[4] Weissberger, et al. (ed.), "Organic Solvents," Interscience Publishers, Inc. (1955), p. 192.

reaction was caused to proceed by dropping the bromine solution of a particular concentration (around 0.1 mol./l.) into a chelate solution of a similar concentration under vigorous agitation. Mole ratios of the metal chelate to bromine of 1 : 1, 1 : 1.5 and 1 : 2 were examined. In the latter two cases, the precipitate formed in the reaction mixture was filtered, washed with the solvent, dried, weighed and then analyzed for copper and bromine. The filtrate was also applied to the analysis of organic bromine. In the first case (1 : 1), when the desired amount of the bromine solution was added, a gray colloidal precipitate was formed; this was difficult to filter and so was separated from the solution by centrifugation after it had stored one day in a dessicator.

In the reaction of the copper(II) chelate of acetylacetone or ethyl acetoacetate with hydrogen bromide, dry dichloromethane was employed exclusively as a solvent. A desired amount of a hydrogen bromide solution was added from a burette to a chelate solution drop by drop or at full speed under vigorous agitation. Alternatively, a chelate solution was added gradually to a hydrogen bromide solution in experiments to investigate the effect of an excess of hydrogen bromide.

Analysis. — The concentration of hydrogen bromide in the dichloromethane solution was determined by titration, after the addition of dilute acetic acid, with a silver nitrate solution employing Eosin as the indicator.

The precipitate formed in the dry reaction medium was generally a mixture of copper(I) and copper(II) bromide. It was dissolved in aqueous ammonia and was kept standing in air overnight. A small amount of sodium hydroxide was then added to the solution, and it was heated in order to expel any ammonia. A black precipitate of copper(II) oxide was filtered off to be submitted to the electrolytic analysis of copper, and the bromide ion in the filtrate was determined gravimetrically to be silver bromide.

The precipitate formed in the reaction of the copper(II) chelate of ethyl acetoacetate with bromine in a wet solvent was a mixture of copper(I) bromide, copper(II) bromide and copper(II) hydroxide. When the precipitate was treated with acetic acid, copper(II) compounds were dissolved, but copper(I) bromide remained insoluble. The solution was then submitted to iodometry in order to determine the copper(II) content. On the other hand, the whole copper and bromine contents in the precipitate were determined as above.

The brominated β-dicarbonyl compound contained in the organic filtrate of each experiment was concentrated under reduced pressure and added to an acetic acid solution of potassium iodide. Iodine liberated in the solution was titrated with a solution of sodium thiosulfate.

Results

The Reaction of the Copper(II) Chelate of Ethyl Acetoacetate with Bromine in Dry Dichloromethane.—The results of the analysis of reaction products under the dry conditions are listed in Table I. When the copper(II) chelate reacted with bromine in the mole ratio of 1 : 2, the precipitate formed was found to be practically copper(II) bromide. The filtrate contained ethyl α-bromoacetoacetate; this was determined by iodometry as has been described in the Experimental section. Copper could not be detected in the filtrate. Thus, the net reaction may be represented by the following equation:

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

where H_2A stands for the ethyl acetoacetate molecule, HA, for the enolate anion, and HABr, for ethyl α-bromoacetoacetate. The yield of the bromoester listed in the last column of Table I was calculated on the basis of Eq. 1.

In the reaction of the 1 : 1.5 mole ratio, the precipitate formed was essentially copper(I)

TABLE I. PRODUCTS OF REACTION BETWEEN COPPER(II) CHELATE OF ETHYL ACETOACETATE AND BROMINE IN DRY DICHLOROMETHANE AT ROOM TEMPERATURE

Mole ratio chelate to bromine	Chelate used, g. (mmol.)	Ppt. recovered g.	Composition of precipitate			α-Bromoester formed, mmol. (% yield)
			Cu, g. (mg.-atom)	Br, g. (mg.-atom)	Atom ratio Br/Cu	
1 : 2	3.073 (9.548)	2.069	0.5872 (9.243)	1.471 (18.89)	1.991	18.71 (97.85)
	1.024 (3.182)	0.7078	0.2012 (3.168)	0.4608 (5.766)	1.820	5.912 (92.88)
1 : 1.5	1.022 (3.176)	0.4779	0.1997 (3.143)	0.2755 (3.448)	1.097	5.659 (89.10)
	3.455 (10.74)	1.501	0.6578 (10.35)	0.8414 (10.53)	1.017	21.16 (98.52)
1 : 1*	5.174 (16.03)	1.560	0.6712 (10.56)	0.7742 (9.694)	0.9190	21.29 (99.62)

* The solution contained excess of chelate, which was determined by the electrolytic analysis of copper to be 5.031 mmol. (94.14% of the theoretical value calculated on the basis of Eq. 3).

TABLE II. PRODUCTS OF THE REACTION BETWEEN THE EQUIMOLAR COPPER(II) CHELATE OF ACETOACETATE AND BROMINE IN DICHLOROMETHANE SATURATED WITH WATER AT ROOM TEMPERATURE

Chelate used, g. (mmol.)	Ppt. recovered g.	Composition of ppt.			α-Bromoester formed, mmol. (% yield)
		Total Cu, g. (mg.-atom)	Cu(II) mg.-atom	Br, g. (mg.-atom)	
5.537	2.601	0.9099		1.026	18.1
(17.21)*		(14.34)*	12.52	(12.84)	(105)
2.891	1.396	0.4072		0.4862	9.08
(8.983)		(6.61)	6.554	(6.092)	(101)

* The difference between these figures is due to incomplete transfer of the muddy precipitate from the reaction vessel into the glass filter.

bromide, and no copper remained in the solution. The stoichiometry of the reaction may satisfactorily be represented by the equation:

$$\mathrm{Cu(HA)_2 + 3/2\,Br_2 = CuBr + 2HABr} \qquad (2)$$

When an equimolar amount of bromine was added to the chelate solution, copper(I) bromide precipitated. In this case the solution still contained unchanged copper(II) chelate, which was determined to amount to about one-third of the original quantity. The material balance may be represented by the equation:

$$\mathrm{Cu(HA)_2 + Br_2 = 1/3\,Cu(HA)_2 + 2/3\,CuBr + 4/3\,HABr} \qquad (3)$$

The net change in this case should also be shown by Eq. 2.

Besides dichloromethane, chloroform and benzene (in the dark) were also used as solvents. The pattern of the reactions was the same as in dichloromethane.

The Reaction of the Copper(II) Chelate of Ethyl Acetoacetate with Bromine in Wet Dichloromethane.—When dichloromethane saturated with water was employed as the solvent, the precipitate formed in the reaction of the 1 : 1 mole ratio consisted essentially of copper(II) compounds, as is shown in Table II. This is in marked contrast to the case in a dry solvent, where copper(I) bromide was exclusively obtained in the 1 : 1 reaction (Table I). These results may be well reconciled with the following equation:

$$\mathrm{Cu(HA)_2 + Br_2 + H_2O = 1/2\,CuBr_2 + 1/2\,Cu(OH)_2 + HABr + H_2A} \qquad (4)$$

No trace of copper could be detected in the filtrate. The difference between the total copper content and that of copper(II) corresponds to that of copper(I), and ethyl α-bromoacetoacetate is obtained beyond the theoretical yield calculated on the basis of Eq. 4. These are considered to be formed in the following slow reaction:

$$\mathrm{2CuBr_2 + H_2A = 2CuBr + HABr + HBr} \qquad (5)$$

Copper(II) halide is known to react easily with acetone[5] and other compounds containing active hydrogen.[6] Reaction 5 really proceeds gradually at room temperature.

The Reaction of the Copper(II) Chelate of Ethyl Acetoacetate with Bromine under Other Conditions.—When dichloromethane containing ethyl alcohol or diethyl ether instead of water is employed as the reaction medium, the color of the reaction mixture changes from deep green to light blue on the addition of bromine, and the appearance of a precipitate is remarkably retarded. However, the precipitate is formed immediately on the addition of water.

When a 1 : 1 reaction is conducted in dry dichloromethane at −78°C, a grayish black muddy precipitate is formed; this changes to white copper(I) bromide when it is warmed to room temperature, reproducing thereby some quantity of the original copper(II) chelate. The dark precipitate is soluble in alcohol or ether, giving a light blue solution which is stable even at room temperature.

The Reactions of Copper(II) Chelates of Acetylacetone and Ethyl Acetoacetate with Dry Hydrogen Bromide.—In the reaction of these chelates with bromine in a mole ratio of 1 : 2, copper(II) bromide is formed exclusively, as has been reported above. However, it is not certain whether copper(II) bromide is directly produced through some intermediate or is formed secondarily by the reaction between copper(I) bromide and an excess of bromine. This problem is expected to be solved by an investigation of the reaction of the copper(II) chelates with hydrogen bromide, since even an excess of hydrogen bromide has no ability to oxidize copper(I) bromide once produced.

The analytical results of reaction products when the hydrogen bromide solution was added gradually to the chelate solution in various mole ratios, are summarized in Tables III and IV. In either case the sum of copper and

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[5] J. K. Kochi, *J. Am. Chem. Soc.*, **77**, 5274 (1955).

[6] E. M. Kosower, W. J. Cole, G.-S. Wu, D. E. Cardy and G. Meisters, *J. Org. Chem.*, **28**, 630 (1963); E. M. Kosower and G.-S. Wu, ibid., **28**, 633 (1963).

TABLE III. REACTION PRODUCTS FORMED WHEN A HYDROGEN BROMIDE SOLUTION WAS ADED GRADUALLY TO A SOLUTION OF BIS(ACETYLACETONATO)COPPER(II)

Mole ratio chelate to HBr	Chelate used, g. (mmol.)	Ppt. obtained g.	Composition of the precipitate				3-Bromoketone	
			Cu, g. (mg.-atom)	Br, g. (mg.-atom)	CuBr mmol. (%)	$CuBr_2$ mmol. (%)	Found mmol.	Calcd. mmol.
1 : 2	0.7171 (2.739)	0.3186	0.1345 (2.117)	0.1825 (2.284)	1.950 (92.1)	0.167 (7.9)	1.200	1.261
	0.7171 (2.739)	0.3103	0.1306 (2.055)	0.1794 (2.245)	1.865 (90.8)	0.190 (9.2)	1.009	1.243
	0.3545 (1.354)	0.1734	0.0751 (1.18)	0.0979 (1.23)	1.13 (95.8)	0.05 (4.2)	0.645	0.652
1 : 1.5	0.6417 (2.451)	0.2872	0.1257 (1.978)	0.1600 (2.002)	1.954 (98.8)	0.024 (1.2)	1.136	1.210
	0.5299 (2.024)	0.2535	0.1115 (1.755)	0.1426 (1.784)	1.726 (98.4)	0.029 (1.6)	0.921	0.995
1 : 1*	0.6417 (2.451)	0.2497	0.1085 (1.708)	0.1386 (1.735)	1.681 (98.4)	0.027 (1.6)		
	0.3545 (1.354)	0.1249	0.0547 (0.861)	0.0700 (0.876)	0.846 (98.3)	0.015 (1.7)		

* The product solution of a 1 : 1 reaction contains some quantity of remaining excess of chelate which disturbs the determination of 3-bromoacetylacetone.

TABLE IV. REACTION PRODUCTS FORMED WHEN A HYDROGEN BROMIDE SOLUTION WAS ADDED GRADUALLY TO A SOLUTION OF COPPER(II) CHELATE OF ETHYL ACETOACETATE

Mole ratio chelate to HBr	Chelate used, g. (mmol.)	Ppt. obtained g.	Composition of the precipitate				α-Bromoester	
			Cu, g. (mg.-atom)	Br, g. (mg.-atom)	CuBr mmol. (%)	$CuBr_2$ mmol. (%)	Found mmol.	Calcd. mmol.
1 : 2	0.5139 (1.597)	0.2114	0.0920 (1.45)	0.1194 (1.494)	1.41 (96.9)	0.044 (3.1)	0.720	0.773
	0.5139 (1.597)	0.2144	0.0932 (1.47)	0.1207 (1.510)	1.43 (97.3)	0.040 (2.7)	0.722	0.775
1 : 1.5	0.8090 (2.514)	0.3235	0.1424 (2.241)	0.1805 (2.259)	2.223 (99.2)	0.018 (0.8)	1.167	1.245
1 : 1*	1.0278 (3.194)	0.3325	0.1436 (2.260)	0.1812 (2.267)	2.253 (99.7)	0.007 (0.3)		
	0.8598 (2.672)	0.2787	0.1186 (1.867)	0.1495 (1.871)	1.863 (99.8)	0.004 (0.2)		

* The bromination product in the solution could not be determined accurately because of the disturbance by the remaining chelate.

bromine found in the precipitate coincides quite well with the weight of the precipitate, indicating that the latter contains nothing but copper and bromine. The atomic ratio of bromine to copper in the precipitate is slightly larger than 1, showing that the reaction product is a mixture of copper(I) bromide and a small amount of copper(II) bromide. The number of millimoles of copper(I) bromide and that of copper(II) bromide were calculated from these equations:

$$CuBr = 2\ \text{Total Cu} - \text{Total Br}$$

$$CuBr_2 = \text{Total Br} - \text{Total Cu}$$

They are listed in Tables III and IV.

The results obtained in reactions at mole ratios of 1 : 1 and 1 : 1.5 are essentially simillar to those obtained in analogous reactions with bromine; they can be represented by the following equation:

$$Cu(HA)_2 + 3/2\ HBr = CuBr + 3/2\ H_2A + 1/2 HABr \qquad (6)$$

where H_2A stands for acetylacetone or ethyl acetoacetate, and HABr, for 3-bromoacetylacetone or ethyl α-bromoacetoacetate. The presence of free acetylacetone or ethyl acetoacetate in the solution was confirmed, after solvent evaporation in vacuo, by the nuclear magnetic resonance absorptions. The theoretical yield of brominated β-dicarbonyl compounds listed in the last column of Tables III and IV was calculated on the ground that 2 mol. of the original chelate produced 1 mol. of the

TABLE V. REACTION PRODUCTS FORMED WHEN A HYDROGEN BROMIDE SOLUTION WAS ADDED RAPIDLY FROM A BURETTE TO A SOLUTION OF COPPER(II) CHELATE OF ACETYLACETONE OR ETHYL ACETOACETATE (MOLE RATIO OF THE CHELATE TO BROMINE, 1 : 2)

Cu chelate of	Chelate used, g. (mmol.)	Ppt. obtained g.	Composition of the precipitate				Brominated product	
			Cu, g. (mg.-atom)	Br, g. (mg.-atom)	CuBr mmol. (%)	$CuBr_2$ mmol. (%)	Found mmol.	Calcd. mmol.
Acetyl-acetone	0.3545 (1.354)	0.1744	0.0710 (1.12)	0.1032 (1.292)	0.948 (84.8)	0.172 (15.2)	0.547	0.571
	0.7027 (2.684)	0.3759	0.1437 (2.262)	0.2263 (2.832)	1.692 (74.8)	0.570 (25.2)	0.911	1.004
Ethyl aceto-acetate	0.5139 (1.597)	0.1875	0.0760 (1.20)	0.1115 (1.395)	1.005 (83.3)	0.195 (16.7)	0.667	0.667
	0.5139 (1.597)	0.2159	0.0894 (1.41)	0.1263 (1.580)	1.240 (87.9)	0.170 (12.1)	0.679	0.700

TABLE IV. ANALYSIS OF THE PRECIPITATE FORMED WHEN A SOLUTION OF COPPER(II) CHELATE OF ACETYLACETONE OR ETHYL ACETOACETATE WAS ADDED GRADUALLY TO A SOLUTION OF HYDROGEN BROMIDE (MOLE RATIO OF THE CHELATE TO HYDROGEN BROMIDE, 1 : 2)

Cu chelate of	Chelate used, g. (mmol.)	Ppt. obtained g.	Composition of the precipitate			
			Cu, g. (mg.-atom)	Br, g. (mg.-atom)	CuBr mmol. (%)	$CuBr_2$ mmol. (%)
Acetylacetone	0.4147 (1.584)	0.2941	0.0861 (1.36)	0.2099 (2.602)	0.118 (8.7)	1.242 (91.3)
Ethyl acetoacetate	0.8090 (2.514)	0.5070	0.1475 (2.321)	0.3602 (4.508)	0.134 (5.8)	2.187 (94.2)

brominated compound, according to Eq. 6. A necessary correction for the occurrence of reaction 7 was made on the basis of the yield of copper(II) bromide.

As Tables III and IV show, a very small amount of copper(II) bromide is formed in the reaction at a mole ratio of 1 : 1.5 or 1 : 1; this is considered to result from the following reaction, which is analogous to Eq. 1:

$$Cu(HA)_2+2HBr=CuBr_2+2H_2A \qquad (7)$$

The relative amount of copper(II) bromide produced in comparison with copper(I) bromide indicates the relative probability of the occurrence of reaction 7 compared with reaction 6. Even in the reaction at a mole ratio of 1 : 2, the quantity of copper(II) bromide formed is far less than that of copper(I) bromide, suggesting that the reaction according to Eq. 6 proceeds far more rapidly than the reaction represented by Eq. 7 under such reaction conditions. The yield of copper(II) bromide might depend upon the speed of feeding hydrogen bromide to the intermediate.

Table V shows the results obtained when the hydrogen bromide solution was caused to flow at full speed from a burette into the chelate solution. The amount of copper(II) bromide produced in each experiment is much larger than that shown in Tables III and IV. In other experiments, the chelate solution was dropped gradually from a burette into a solution containing twice as many moles of hydrogen bromide. In these cases copper(II) bromide was produced predominantly, as was expected (Table VI). It must be noticed, however, that a small amount of copper(I) bromide was also produced, even when such a circumstance as an excess of hydrogen bromide should favor the reaction path of Eq. 7.

Discussion

The stoichiometry of the reaction between the copper(II) chelate of ethyl acetoacetate and bromine in dry dichloromethane has been established for the two cases of the reactants mole ratio represented by Eqs. 1 and 2. In either case, the copper(II) chelate is decomposed by the attack of bromine, and the product is copper(II) or copper(I) bromide, depending upon whether 2 or 1.5 mol. of bromine is added to 1 mol. of the chelate. There are two possible reaction pathways to be considered: (i) copper(I) bromide is produced first, and then it is oxidized to copper(II) bromide by an excess of bromine. (ii) Copper(II) bromide is formed at first, and then it is reduced to copper(I) bromide by an excess of the chelate or the free ester produced. Copper(I) bromide is oxidized by bromine very rapidly, but copper(II) bromide is reduced by these compounds rather slowly; thus, the second pathway could not be responsible for the rapid formation of

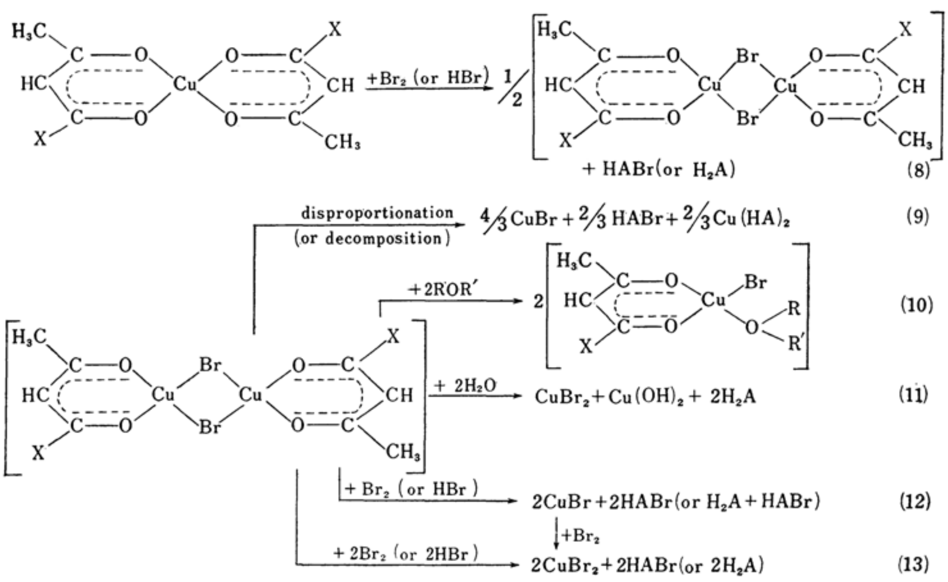

Fig. 1. Suggested pattern of the reaction between the copper(II) chelate of acetylacetone (X=CH_3) or ethyl acetoacetate (X=C_2H_5O) and bromine or hydrogen bromide. Bracketed species are still unidentified; their structures are only postulated here. ROR′ represents alcohol or ether.

copper(I) bromide in the present case. Furthermore, the results obtained in the reaction of copper(II) chelates with hydrogen bromide strongly support the former reaction course under such reaction conditions.

The dark precipitate which is produced in the 1 : 1 reaction mixture of copper(II) chelate of ethyl acetoacetate and bromine at −78°C looks like a precursor of copper(I) bromide in the reaction pathway; it changes, in fact, to copper(I) bromide whenever warmed to room temperature. The precipitate is, however, soluble in alcohol or ether and does not produce copper(I) bromide in these solutions, even when warmed. Furthermore, in dichloromethane containing alcohol or ether, the formation of copper(I) bromide is greatly suppressed in the 1 : 1 reaction at room temperature. The water contained in dichloromethane also prohibits the formation of copper(I) bromide, so copper(II) bromide and hydroxide are produced instead. Thus, we may presume an intermediate with some stability, which decomposes (or disproportionates), spontaneously to copper(I) bromide and the original chelate, reacts with alcohol or ether to form some more stable species, or reacts with water to produce copper(II) bromide and hydroxide. It must be emphasized that, though one-third of the chelate employed is recovered in a 1 : 1 reaction (Eq. 3), it is not really unchanged, but is reproduced through an intermediate. We may now assume the following structure for this intermediate, and can picture the entire reaction pattern by virtue of it, as Fig. 1 shows. The experimental results obtained in the reactions of the copper(II) chelates with hydrogen bromide can also be explained by means of the same pattern.

An intermediate containing a double bridge of bromine is assumed to be formed in process 8. In the reactions at a mole ratio of 1 : 1, the intermediate disproportionates (or decomposes) according to Eq. 9, reproducing one-third of the original chelate. In the reaction at a mole ratio of 1 ; 1.5, copper(I) bromide is formed by process 12. In reactions with hydrogen bromide, copper(II) bromide can be produced only when two molecules of hydrogen bromide attack an intermediate molecule cooperatively, as is shown by Eq. 13.

The reactions represented by Eqs. 9, 12 and 13 are all very fast, and the competition between them is influenced by the chance of an encounter between the intermediate and the bromine or hydrogen bromide molecule. These reactions may not be elementary processes, and even their relative rates are not yet certain. Further extensive investigations are needed to elucidate the mechanisms of these reactions.

The preparation of the copper chelate of ethyl α-bromoacetoacetate was attempted but was unsuccessful, in contrast with that of 3-bromoacetylacetone.1) This was due to the lower stability of the copper(II) chelate of the α-bromoester, and is related to Pedersen's finding[7] that copper(II) ions can not catalyze the second step of the bromination of ethyl acetoacetate by bromine in an aqueous solution, although it can accelerate the first step remarkably.

Summary

When the copper(II) chelate of ethyl acetoacetate reacts with bromine in dry dichloromethane, the chelate is broken, forming the α-bromoester and copper(I) or copper(II) bromide depending on the reactants' mole ratio. However, in the reaction between bromine and the chelate at a mole ratio of 1 : 1 in dichloromethane saturated with water, copper(I) bromide is not produced primarily; instead copper(II) hydroxide is formed, as is copper(II) bromide.

In the reactions of the copper(II) chelate of acetylacetone or ethyl acetoacetate with dry hydrogen bromide at the mole ratio of 1 : 1 or 1 : 1.5, more than 98% of the total copper precipitated as copper(I) bromide. Even when 2 mol. of hydrogen bromide was employed against 1 mol. of the chelate, more than 90% of the original copper changed to copper(I) bromide, in contrast with the results obtained in a similar reaction with bromine.

The entire reaction pattern has been suggested employing a presumed intermediate binuclear complex containing a bromine double brigde.

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Faculty of Science
Osaka City University
Sumiyoshi-ku, Osaka

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