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On the Mechanism of Bromination of Olefins with Cupric Bromide

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Although it is generally accepted that cupric chloride does not liberate chlorine molecule in chlorination of organic substances,[1] the active species has not been established in bromination of organic compounds with cupric bromide. The bromination of acetone to bromoacetone in methanol at 0°C has been explained as the reaction of cupric bromide molecule,[2] while in the nuclear bromination of alkylbenzenes at 110—120°C a possibility of participation of bromine molecule has been suggested.[3] Rate of the bromination of allyl alcohol to form 2,3-dibromopropanol in refluxing methanol has been reported to be second order in cupric bromide and independent of olefin.[4] This rate equation was

$$\text{rate} = k[\text{CuBr}_2]^2 \qquad (1)$$

explained by assuming the dissociation of cupric bromide to molecular bromine, which was claimed to be the actual brominating agent in the reaction. Consumption of bromine[4] or removal of cuprous bromide by complex formation with olefin[5] has been believed to be a driving force for the dissociation of cupric bromide.

$$2\text{CuBr}_2 \underset{k_b}{\overset{k_a}{\rightleftarrows}} 2\text{CuBr} + \text{Br}_2 \qquad (2)$$

In order to obtain further experimental results to discuss the reaction mechanism, the bromination of 1-hexene has been kinetically investigated in methanol.

The products were the dibromide (I) and the methoxybromide (II) with a small amount of by-products ($<1\%$). To avoid complication by the effect of resulting cuprous bromide, the rates are expressed by initial rates and shown in Table 1.

Plots of log[CuBr$_2$] and log[hexene] *vs.* log v showed straight lines, and rate orders were calculated from these lines. The rates were expressed by following equations, where v_1 and v_2 are the rates of formations of I and II, respectively.

$$v_1 = k_1[\text{hexene}][\text{CuBr}_2]^{1.8-2.0} \qquad (3)$$

$$v_2 = k_2[\text{hexene}][\text{CuBr}_2] \qquad (4)$$

Since the rate order in [CuBr$_2$] is smaller for II, I can not be a precursor of II, that is, II was not formed by methanolysis of I.

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[1] T. Koyano, This Bulletin, **43**, 1439 (1970), and references cited therein.

[2] S. Kawaguchi and Y. Kojima, *Shokubai*, **8**, 239 (1966).

[3] P. Kovacic and K. E. Davis, *J. Amer. Chem. Soc.*, **86**, 427 (1964).

[4] C. E. Castro, E. J. Gaughan, and D. C. Owsley, *J. Org. Chem.*, **30**, 587 (1965).

[5] W. C. Baird, Jr., and J. H. Surridge, *ibid.*, **35**, 2090 (1970).

Table 1. Rate of reaction

Method	Temp. (°C)	hexene (mol/l)	$CuBr_2$ (mol/l)	$v_1 \times 10^6$ (mol/l·sec)	$v_2 \times 10^6$ (mol/l·sec)	n_1	n_2	m_1	m_2
A	40	0.184	0.197	3.96	2.99	2.0	1.1		
		0.182	0.288	8.56	4.73				
		0.192	0.374	14.3	5.82				
B	50	0.088	0.291	4.23	3.47	1.8	1.0	1.1	1.0
		0.175	0.290	9.38	6.75				
		0.350	0.287	18.3	12.5				
		0.350	0.453	41.3	19.3				

$v_1 = k_1[\text{hexene}]^{m_1}[CuBr_2]^{n_1}$ $v_2 = k_2[\text{hexene}]^{m_2}[CuBr_2]^{n_2}$

If the equilibrium of Eq. 2 had been attained rapidly, Eq. (5) must have been realized.

$$k_a[CuBr_2]^2 = k_b[CuBr]^2[Br_2] = 4k_b[Br_2]^3 \qquad (5)$$

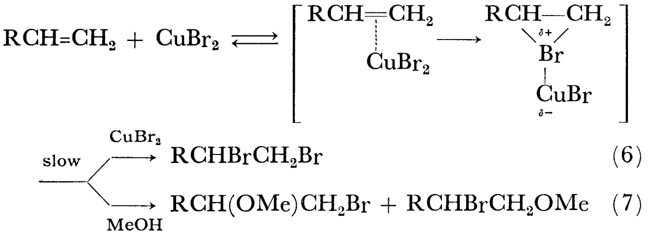
Then, concentration of bromine should be approximately proportional to the 2/3 power of cupric bromide added. The present data are hardly interpreted as the bromination with bromine.

If the reaction proceeds by bromination with bromine, an allylic bromination may be expected.[6] However, the bromination of cyclohexene with cupric bromide in refluxing carbon tetrachloride afforded 1,2-dibromocyclohexane but no 3-bromocyclohexene.

A possible explanation is that the olefin initially forms a complex with cupric bromide, followed by competitive attack of this complex by solvent methanol and another cupric bromide molecule or bromide ion. The latter step should be rate-determining.

We have also studied the bromination of isomeric 2-butenes in refluxing methanol. The resulted dibromides were composed exclusively of those expected from "*trans*" addition of bromine, in contrast to the case with cupric chloride, where a mixture of diastereomeric dichlorides was obtained.[7] Similarly, the products from cyclohexene have been reported to be only *trans*-dibromide and *trans*-methoxybromide,[5] while cupric chloride yielded the corresponding *cis*-compounds at the same time.[7] Therefore, the intermediate complex must resemble a bridged bromonium ion type species.

In summary, the reaction may be represented by the following scheme.



$$RCH{=}CH_2 + CuBr_2 \rightleftarrows \left[\underset{CuBr_2}{RCH{=}CH_2} \longrightarrow \underset{\underset{\delta-}{CuBr}}{\overset{RCH{-}CH_2}{\underset{\delta+}{Br}}} \right]$$

$$\xrightarrow{\text{slow}} \begin{cases} \xrightarrow{CuBr_2} RCHBrCH_2Br & (6) \\ \xrightarrow{MeOH} RCH(OMe)CH_2Br + RCHBrCH_2OMe & (7) \end{cases}$$

Experimental

Materials. All the reagents were the commercially available purest reagents, purified appropriately when necessary. I and II, 1,2-dibromocyclohexane, and diastereomeric 2,3-dibromobutanes were synthesized by addition of bromine to 1-hexene in methanol,[8] cyclohexene in CCl_4,[9] and *trans*- and *cis*-2-butenes in CH_2Cl_2,[10] respectively. 3-Bromocyclohexene was prepared by allylic bromination of cyclohexene with NBS in CCl_4 in the presence of benzoyl peroxide[11] (bp 65—66.5°C/20 mmHg).

Analysis. Cupric ion was determined by iodometry.[12] Cuprous ion was titrated with the standard ceric solution using ferroin as the indicator.[13] Glpc was performed on a Shimadzu GC-4AF gas chromatograph (dioctyl sebacate on Chromosorb W, 135°C, H_2 flame detector).

Kinetic Measurements. *Method A*: A solution of cupric bromide in methanol was placed in a Schlenk tube under N_2 and prewarmed in a constant temperature bath (±0.05°C). A measured amount of 1-hexene was added in the solution and the reaction was started. From time to time 10ml of the reaction solution was removed and was poured into 20ml of 0.05 M ferric ammonium sulfate solution (in 3N H_2SO_4) immediately after taking a small amount of sample for glpc, and the cuprous ion was titrated.

Method B: A sealed tube technique was employed; in each 15ml glass sealed tube 10ml of the reaction mixture was placed under N_2. At intervals the tube was taken out from the bath (±0.05°C), cooled in ice-water, and kept in a freezer (−20°C). After the last tube was removed, the reaction solutions were analyzed as quickly as possible.

The amount of consumed cupric bromide was divided between the dibromide and the methoxybromide in the ratio of the glpc analysis. Then, amounts of the products were calculated on assumption that one mole of either product was formed by consumption of two moles of the cupric salt. The methoxy-bromide was composed of approximately 18% of 1-methoxy-2-bromohexane and 82% of 1-bromo-2-methoxyhexane (by Hitachi 063 gas chromatograph with Apiezon L capillary column at 90°C).

Reaction of Cyclohexene. A mixture of cyclohexene (3.3g, 0.04 mol) and cupric bromide (8.9g, 0.04mol) in CCl_4 (40 ml) was refluxed for 1hr under N_2. The resulted grey powder was dissolved in aqueous methanol after drying under reduced pressure, and cupric ion was titrated. The conversion was *ca.* 98%. The main reaction product was 1,2-dibromocyclohexane with some by-products (*ca.* 5%), and 3-bromocyclohexene was

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[6] B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, **1961,** 80.

[7] T. Koyano, This Bulletin, **43,** 3501 (1970).

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[9] H. R. Snyder and L. A. Brooks, "Organic Syntheses", Coll. Vol. II. p.173 (1943).

[10] J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91,** 1469 (1969).

[11] L. F. Hatch and G. Bachmann, *Chem. Ber.*, **97,** 132 (1964).

[12] W. T. Elwell and D. Price, "Comprehensive Analytical Chemistry", Vol. Ic. ed. by C. L. Wilson and D. W. Wilson, Elsevier Publishing Co., Amsterdam (1962), p.371.

[13] I. M. Kolthoff and R. Belcher, "Volumetric Analysis", Vol. III, Interscience, New York (1957), p. 121.

not detected by glpc.

Reaction of 2-Butenes. A solution of cupric bromide in methanol (0.50 mol/*l*) was refluxed for 4 hr under 2-butene atmosphere (1 atm). The results were (the starting 2-butene, conversion, and ratio of the dibromide (III) to the methoxybromide (IV)): *trans*, 14.1%, 0.87; *cis*, 25.3%, 1.07. The dibromides formed were exclusively the "*trans*" addition products, *i.e.*, *meso* from *trans* and *dl* from *cis*.

The dibromides were sufficiently stable under the reaction conditions. When III (4 mmol) was heated in refluxing methanol (30 m*l*) with cupric bromide (15 mmol) for 4 hr under N_2, 1.1% of *erythro*-IV was formed from the *meso*-III and 0.2% of *threo*-IV from the *dl*-III.