data. In F potassium hydroxide alone the optical value is 2.50 and the polarographic value is 2.49.[2] Other values of pC found from spectrophotometric measurements are reported in Table I.

TABLE I

OPTICAL CRITICAL CONCENTRATIONS OF GELATIN IN VARIOUS MEDIA

Supporting electrolyte	Copper (II), millimolar	pC
1 F KOH–1 F K_3Cit	5.0	2.16
	1.0	2.19
1 F KOH–0.5 F K_3Cit	5.0	2.20
	2.0	2.11
	0.80	2.09
1 F KOH–0.1 F K_3Cit	2.0	2.22
	0.50	2.31
0.1 F KOH–1 F K_3Cit	0.50	2.11
0.1 F KOH–0.5 F K_3Cit	0.50	2.14
1 F KOH–0.5 F Na_2Tart	2.0	2.39
	1.0	2.37
1 F KOH	1.0	2.50
5 F KOH	2.0	2.74

This phenomenon might be thought to be due to the successive formation of two complexes between gelatin and the complex metal ion. Of these two complexes, the one formed at lower gelatin concentrations would have to have an absorption curve substantially identical with that of the original metal complex, while the other, formed above the optical critical concentration, must have an absorption curve differing from that of the original complex only in having much higher extinction coefficients.

Such a combination of characteristics is improbable but by no means impossible, an actual example being shown by Fig. 2. This represents the data secured in the spectrophotometric titration of copper(II) (as cuprate) with potassium citrate in F potassium hydroxide. The breaks in this curve correspond to the successive formation of complexes containing one and two citrates per copper atom, and there is little evident difference between this curve and those of Fig. 1. However, the positions of the end-points in titrations like those of Fig. 2 depend in the expected stoichiometric fashion on the amount of copper present, while there is no such dependence in the gelatin experiments. Thus, in F potassium hydroxide–0.5 F potassium citrate the optical critical concentration is independent of the copper concentration between 0.8 and 5 mM within about $\pm 10\%$, which is approximately the experimental error.

Therefore the optical critical concentration must represent the point at which binding of copper begins, rather than the point at which a second type of complex begins to form. It seems probable that the reaction above the optical critical concentration consists essentially of the binding of the complex metal ions at loci of attachment (presumably the carboxylate groups) on the gelatin micelles which appear near the critical concentration. There is little or no evidence that gelatin at concentrations below the critical concentration is capable of binding any of these complexes.

(2) E. L. Colichman, THIS JOURNAL, **72**, 4036 (1950).

In view of the marked effect on pH on the binding of cupric ions by bovine serum albumin demonstrated by Klotz and Curme,[3] it is of interest that at pH values near 7, Klotz[4] found no effect of even as much as 1% gelatin on the spectra of the methyl orange or azosulfathiazole anions, while in the present study no spectra alterations were produced by the addition of gelatin to the anionic carbonate, citrate, oxalate or tartrate complexes of copper(II) at pH values between 9 and 11.5.

It should be mentioned that the increasing absorbancy above the optical critical concentration is not due to the slight turbidity of the stock gelatin solution used, as shown by the dashed line in Fig. 1. Nor is it due to the formation of a turbidity in the solutions containing copper(II) and gelatin, for the absorbancy at 475 mμ invariably remained constant at 0.002 ± 0.003 up to the highest concentration of gelatin used: this could not have been the case if any significant amount of dispersed solid had been formed.

(3) I. M. Klotz and H. G. Curme, THIS JOURNAL, **70**, 939 (1948).
(4) I. M. Klotz, *ibid.*, **68**, 2299 (1946).

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Concerning the Reduction of α-Bromoketones by Hydrogen Bromide

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It is known that the reaction of bromine with a ketone to yield α-bromoketone and hydrogen bromide is reversible.[1]

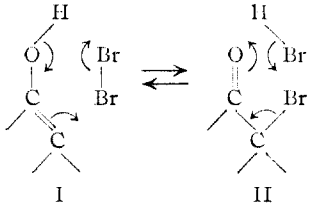
$$RCOCH(R)_2 + Br_2 \rightleftarrows RCOC(R)_2Br + HBr$$

It has been shown that the equilibrium constant ($K_{eq} = [RCOC(R)_2Br][HBr]/[RCOCH(R_2)][Br_2]$ is quite small when the hydrogen replaced in the ketone is acidic,[1d] but considerably larger in ketones such as acetophenone.[1c] It has also been shown that the rate of acid-catalyzed bromination is independent of the bromine concentration and that the bromination proceeds through the enol form.[2] There has been little discussion of the way in which bromine reacts with the enol form to yield bromoketone, possibly because the rate is too fast to measure.[2] Addition of bromine to an olefin is commonly represented by the formation of an intermediate cyclic bromonium ion,[3] and, in the absence of an alternate explanation, this mechanism might be assumed to apply to the bromination of an enol. However, it is possible to write a cyclic intermediate involving a six atom ring, I, which will account for the bromination of the enol form and also a similar six atom ring, II, which will picture the reduction of a bromoketone by hydrogen bromide.

(1) (a) A. Lapworth, *Mem. Manchester Phil. Soc.*, **64**, ii, 8 (1920); (b) R. Robinson, *Ann. Reports Chem. Soc.*, 1922, p. 100 ff; (c) F. Kröhnke and H. Timmler, *Ber.*, **69**, 614 (1936); F. Kröhnke, *ibid.*, **69**, 921 (1936); (d) R. Altschul and P. D. Bartlett, *J. Org. Chem.*, **5**, 623 (1940).

(2) The evidence is summarized in L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 231 ff.

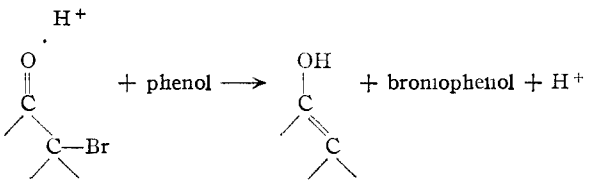
(3) The evidence is summarized in ref. 2, p. 147 ff.



I II

There has not been much discussion of the mechanisms of the forward and backward reactions other than the statement that the mechanism of the reduction of bromoketone must be the exact reversal of the bromination of ketone.[1d]

In studies of the reduction of bromoketones by hydrogen bromide bromine acceptors, 2-naphthol[1c] and cyclohexene,[1d] were used. We were interested to know whether free bromine was the brominating agent or a positively charged complex involving bromoketone and a proton was involved. Experiments were conducted by sealing a mixture of a bromoketone, phenol and an acid in glacial acetic solution and allowing the reactions to proceed for varying periods. At first, *p*-bromophenacyl bromide was used but this was later replaced by bromoacetomesitylene. This change was made because self-condensation side reactions involving *p*-bromoacetophenone did not occur with the hindered ketone. Furthermore, since the rate of reaction was about the same in the case of bromoacetomesitylene, any mechanism involving addition to the carbonyl group (in the usual sense) may be ruled out. These experiments indicated that the acid strength of the acid used was not the dominating factor. For example in comparable experiments using bromoacetomesitylene and hydrogen bromide or perchloric acid the yield of acetomesitylene was over 90% in the former case and of unchanged bromoacetomesitylene over 80% in the latter. This rules out the reaction sequence pictured below.



Thus it is evident in the reduction of bromoketones by hydrogen bromide that: (1) the bromine moiety of the hydrogen bromide plays a definite role; (2) the process does not involve a direct acid-catalyzed transfer of bromine from bromoketone to phenol.

From the above discussion and evidence we believe it likely that both the acid-catalyzed bromination of ketones and the reduction of bromoketones by hydrogen bromide proceed by a cyclic mechanism involving a common cyclic activated state (not pictured). This conclusion is consistent with the fact that bromination of a ketone involves the enol form.[2] However, this work does not rule out a rate controlling stepwise reduction[1d] as shown below.

$$[RCOC(R_2)Br\cdot H]^+ + Br^- \longrightarrow RCOCH(R)_2 + Br_2$$

Experimental[4]

Reduction of *p*-Bromophenacyl Bromide.—In a typical experiment a moderate stream of gaseous hydrogen bromide was bubbled into a mixture of 3.0 g. of bromoketone and 1.5 g. of phenol in 12 cc. of glacial acetic acid in an ampoule which was then sealed. This mixture containing undissolved crystals of bromoketone was shaken frequently and left at room temperature (about 25°). After three days a small amount of solid remained but after four days the mixture was homogeneous. On the fifth day the tube was opened and the products taken into ether–benzene. After washing well with water, alkali and saturated sodium chloride solution the solvents were removed and the residue distilled to yield 1.16 g. (54%) of colorless oil, b.p. about 135° at 34 mm., and a tarry residue. The distillate solidified and on crystallization from diluted alcohol there was obtained with little loss pure *p*-bromoacetophenone, m.p. and mixed m.p. with authentic material, 49.5–51.5°. The oxime, formed in 93% yield from hydroxylamine hydrochloride and pyridine, melted alone and mixed at 128–130°.

In a similar experiment except that 1.0 g. of *p*-toluenesulfonic acid replaced the hydrogen bromide, the reaction mixture remained unchanged for 49 days. On heating such a mixture to 80° for four hours, it darkened and only tar was obtained. In another experiment in which hydrogen chloride replaced the hydrogen bromide the rate of disappearance of undissolved bromoketone was much slower, 24 days being required before the mixture became homogeneous. After 37 days the mixture was processed as above to yield a smaller amount (about 20%) of *p*-bromoacetophenone.

Reduction of Bromoacetomesitylene.—In an experiment similar to the above except that 2.0 g. of bromoacetomesitylene[5] was used instead of *p*-bromoacetophenone the reaction mixture was allowed to stand for seven days. After the usual procedure there was obtained 1.87 g. (93%) of acetomesitylene, b.p. about 140° at 40 mm., $n^{26}D$ 1.5145.[6] This compound was further identified by nitration to 3,5-dinitroacetomesitylene,[7] m.p. and mixed m.p. 139–140.4°. In another experiment 2.6 g. of 60% perchloric acid was treated with a solution of 5 cc. of acetic anhydride in 5 cc. of glacial acetic acid. This solution was then added to bromoketone and phenol so that the final reaction mixture was similar to that above except for the change of acids. After standing for seven days the mixture was processed as above to yield 2.6 g. (86%) of unchanged starting bromoketone, m.p. and mixed m.p. 55.0–56.0°.

(4) The author is indebted to the Graduate School for providing a grant and to Mr. C. C. Cochrane for preparing some of the compounds used.

(5) W. A. Jacobs and M. Heidelberger, *J. Biol. Chem.*, **21**, 455 (1915).

(6) C. R. Noller and R. Adams, THIS JOURNAL, **46**, 1893 (1924), give $n^{20}D$ 1.5175.

(7) R. C. Fuson and J. T. Walker, *ibid.*, **52**, 3269 (1930).

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The Preparation of *n*-Butyl α-D-Glucoside

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The new compound *n*-butyl α-D-glucoside has been prepared by a *trans*-glycosidation procedure from methyl α-D-glucopyranoside. Since relatively few α-glucosides are known, the preparation and properties of the new compound are reported.

Experimental

Preparation.—To 170 cc. of dried *n*-butanol was added 50 g. of methyl α-D-glucopyranoside, and the solution was heated to the boiling point. Then, 30 cc. of butanol (0.44 *N* with respect to HCl) was added, and the solution was refluxed for a total of 20 hours. New 20-cc. portions of the butanol–HCl were added after 7 and after 8 hours. After 9 hours, 100 cc. of the solution was removed by distillation, and 30 cc. of the butanol–HCl was added. (Hydrogen chloride is lost easily under reflux conditions.) The cooled solution was then treated with activated carbon (Darco),