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The Oxidation of Alcohols by Bromine in the Presence of Bromate

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The kinetics of the oxidation of ethyl alcohol by bromine alone[1] and by a mixture of bromine and bromate[2] have been discussed in previous investigations. The present paper describes certain aspects of the latter reaction which appear to be of value for preparative work.

In the case of a primary aliphatic alcohol the oxidation reaction with bromine in the presence of bromate is represented by the following two reactions[2]

$$2RCH_2OH + 2Br_2 = RCOOCH_2R + 4H^+ + 4Br^- \quad (I)$$

$$BrO_3^- + 6H^+ + 5Br^- \rightleftarrows 3Br_2 + 3H_2O \quad (II)$$

The effect of the presence of bromate is that during the main part of the reaction the concentration of the total titrated bromine undergoes but little change and the pH is maintained at about 2.5. The bromine concentration is fixed by the amount of bromine or acid added and is adjusted to the value which yields optimal results with a given starting material.[3]

If the reaction is carried out at a controlled and relatively low acidity, the formation of organic bromine compounds is suppressed. A high reaction temperature, and still more a low pH, increase the rate of formation of substitution products. Table I shows the influence of the acidity upon the formation of bromine substituted products during the oxidation of ethanol. When the bromate is added slowly and its quantity is less than the amount required by equation (II), the pH falls below the normal value of 2.5.

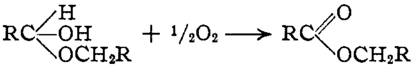
TABLE I

INFLUENCE OF ACIDITY ON THE EXTENT OF SUBSTITUTION IN THE OXIDATION OF ETHANOL

	Temp.:	b. p. 80°	
Initial concn. HBr, *N*	Time of addition of bromate, min.	Yield in acetyl groups, % theor.	Ratio of organically bound bromine atoms to acetyl groups formed
0.75	180	80	0.18
1.40	180	75	.52
1.85	180	71	.80
0.75	22[a]	89	.02

[a] Normal reaction conditions.

The oxidation of primary aliphatic alcohols (*cf.* eqn. I) leads to the formation of ester accompanied by a small amount of free fatty acid. As soon as two equivalents of oxygen are consumed per mole of alcohol, the reaction slows down considerably and interaction of the bromine–bromate mixture with the ester leads to the formation of bromine substituted compounds. Other oxidizing agents, such as chloric acid[4] and chromic acid[5] and the electrolytic oxidation[6] of alcohols also yield esters as the principal products of oxidation. The formation of esters may be explained[4,5] by assuming that the aldehyde which is formed in the first step of the oxidation[1] combines with the excess alcohol to form a hemiacetal, and that the oxidation of the latter takes place according to



$$RC\begin{smallmatrix}H\\OH\\OCH_2R\end{smallmatrix} + {}^1/_2O_2 \longrightarrow RC\begin{smallmatrix}O\\OCH_2R\end{smallmatrix} + H_2O \quad (III)$$

On the other hand, the oxidation of ethylene chlorohydrin leads to chloroacetic acid,[7] and benzyl alcohol principally yields benzaldehyde (see below).

The method is not particularly suitable for the oxidation of secondary alcohols. Their oxidation is more rapid than that of primary alcohols; however the ketones obtained are too easily substituted by bromine. Nevertheless, when working with an excess of alcohol at low temperatures and with low bromine concentrations, it is possible to balance the reaction conditions in such a way that only a small amount of substitution takes place, and the reaction is complete within a few hours. Since the substitution reaction consumes bromine, acid must be added to the mixture after a while.

The present method may be used with advantage in particular for the preparation of aliphatic ester. When it is compared with the method of G. R. Robertson, for example,[8] it is seen that the yield is considerably higher. The procedure is simpler, since cooling in an ice–salt-bath is dispensed with, the volumes handled are much smaller and fractionation is not necessary.

Experimental

The following examples will illustrate the application of the method:

1. **The Oxidation of Butyl Alcohol.**—One hundred forty-eight grams *n*-butyl alcohol (C. P.), 120 g. of water, 108.9 g. of potassium bromate and 7.4 g. of bromine (or 111.4 g. of potassium bromate and 18.5 g. of 40% hydro-

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[1] Farkas, Perlmutter and Schächter, THIS JOURNAL, **71**, 2829 (1949).

[2] Farkas, Perlmutter and Schächter, *ibid.*, **71**, 2833 (1949).

[3] The concentration of free bromine decreases considerably during the reaction on account of tribromide formation. When all the bromate is consumed, the bromine yields hydrobromic aicd, the concentration of which reaches the value corresponding to the quantity of bromine initially added (as a rule 0.25 to 0.5 *N*). Over 97% of the total oxidant is consumed when this last phase of the reaction sets in. If the oxidation products of the alcohols are strong acids, these considerations do not apply.

[4] Milas, THIS JOURNAL, **50**, 493 (1928).

[5] Schulz, Ann. Rept., "Essential Oils, Synthetic Perfumes etc.," Schimmel & Co., 1938, p. 119.

[6] Radchenko, *J. Appl. Chem.* (*U. S. S. R.*), **10**, 683 (1937), **13**, 1348 (1940); *cf. C. A.*, **31**, 6612 (1937); *C. A.*, **35**, 2469 (1941).

[7] Part of the chloroacetic acid is transformed into bromoacetic acid according to

$$CH_2ClCOOH + Br^- \rightleftarrows CH_2BrCOOH + Cl^- \quad (IV)$$

[8] Gilman, Blatt, "Organic Syntheses," 2nd ed., John Wiley & Sons, Inc., New York, N. Y., 1941, Coll. Vol. I, p. 138.

bromic acid) are put in a 600-ml. flask equipped with a reflux condenser, thermometer and stirrer (ground glass joint). Since the reaction is strongly exothermic (about 120 kcal. per mole of ester formed), the temperature must be carefully controlled. For the first twenty minutes the mixture is kept at about 40°; then the temperature is raised to 50° and kept constant until the color of the bromine begins to disappear (three hours). The temperature is then slowly raised to 70° and finally to 100° at which temperature the reaction is brought to completion.

The upper layer weighs 147 g. and contains 84% butyl butyrate and 9% butyric acid, the rest being water and butyl alcohol. The total yield of oxidation products corresponds to the bromate used. Only 0.0024 equivalent of organic bromine compounds is formed. The aqueous layer contains potassium bromide and hydrobromic acid in virtually the theoretical amounts.

The reaction product is washed with 200 ml. of 4% sodium carbonate solution, then with 50 ml. of 0.5 *N* sodium hydroxide, finally three times with water, and then dried over sodium sulfate. The final product contains 99% butyl butyrate (as shown by the saponification number), less than 0.1% acid, and is free from organic bromine (negative Beilstein reaction); 118 g. of butyl butyrate of b. p. 164–166° is obtained (yield 82%).

Ethyl alcohol, isobutyl alcohol and various amyl and hexyl alcohols were oxidized by similar procedures. The yield of total oxidation products (esters + organic acids) was in all cases over 90%. Concentrated solutions of calcium bromate (about 50% b. w.) in place of potassium bromate may be used. With the hexyl alcohols the oxidation was carried out at lower temperatures (35°). In this case, the reaction took about seven hours instead of the four hours that are required at 50°.

2. **The Oxidation of Cyclohexanol.**—Two hundred grams of cyclohexanol (2 moles), 83.5 g. of potassium bromate (0.5 mole) and 150 g. of water are put in the vessel described above and 10.7 g. of hydrobromic acid (40%) or an equivalent quantity of potassium bromide and sulfuric acid are added. The reaction is carried out at 35–40° with vigorous stirring. After two hours, when the color of the bromine has brightened considerably, 5.4 g. of 40% hydrobromic acid is added, and after another thirty minutes, 2.7 g. more. Toward the end of the reaction the water-bath is slowly heated to boiling. After a total time of about three and one-half hours the mixture becomes colorless and separates into two layers. The upper layer (211 g.) contains 1.38 moles of ketone[9] instead of the theoretical yield of 1.5 moles, corresponding to 92% of the bromate used. The reaction product contains 0.083 equivalent of organic bromine.

The aqueous layer contains 0.50 equivalent of bromide, *i. e.*, 84% of the theoretical quantity; 0.06 mole of ketone is also present in this layer, which corresponds to an additional yield of 4%.

The bromine-substituted compounds are separated from the reaction product by fractionation. If the presence of cyclohexanol is undesirable, the ketone can be purified by mixing the reaction product with twice the required amount of a 12% sodium bisulfite solution, extracting the alcohol with ether, cleaving the bisulfite compound with sodium carbonate and distilling it with steam. In this way, 110 g. of a product containing 95% of cyclohexanone (determined with the hydroxylamine chlorohydrate) and 5% of cyclohexanol was obtained. The yield based on bromate consumption was 71%. (Over 75% of the unreacted cyclohexanol can be recovered from the ether extract.)

Similar results were obtained with isopropyl alcohol, *s*-heptanol, undecanol-2, dodecanol-2, *s*-tetradecanol and *s*-heptadecanol, using potassium bromate and working at 35–40°.

3. **The Oxidation of Benzyl Alcohol.**—Two hundred sixteen g. of benzyl alcohol (2 moles), 111.4 g. of potassium bromate ($^2/_3$ mole) and 120 g. of water are mixed, and 20 g. of 40% hydrobromic acid is added. The temperature is kept at about 50°. After thirty minutes, the temperature is raised to 80°; the reaction is complete in ninety minutes.

The upper layer weighs 216 g. According to analysis it contains 79% benzaldehyde, 5.6% benzoic acid and 10.6% benzyl benzoate. This means that about 80% of the bromate is consumed for the production of aldehyde and the remainder about equally for the production of benzoic acid and ester; 0.011 equivalent of bromine were organically bound.

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Summary

The oxidation of alcohols with bromine in the presence of bromate is described. The bromate maintains a nearly constant bromine concentration and a *p*H of about 2.5. Under these conditions bromine substitution can be kept low, even in the temperature range between 50 to 80°.

Upon oxidation, primary aliphatic alcohols give esters, secondary alcohols—ketones, and benzyl alcohol—mainly the aldehyde.

Examples of all these groups are given.

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[9] It should be noted that the bisulfite method of analysis does not give reproducible results in the case of cyclohexanone, since the bisulfite compound dissociates readily in aqueous solution. The amount of ketone was determined volumetrically with hydroxylamine hydrochloride, which checked well with the gravimetric method using 2,4-dinitrophenylhydrazine.