Spectrophotometric and Titrimetric Studies on Alkyl Hypobromites

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Investigations on the oxidation of simple alcohols by bromine in aqueous solution were initiated by Bugarszky.[1] He found that oxidation of dilute aqueous solutions of ethanol (1 to 4% by weight) gave acetic acid as the main product. Swain et al.[2] studied the oxidation of 2-propanol by bromine in aqueous solution and found 2-propanone. Kudesia[3] had investigated the oxidation of *n*-butanol and found butyraldehyde to be the only product.

Little work had been done on the reaction of alcohols with bromine in nonaqueous solution. Sneen and Matheny[4] treated a pentane solution of 1,3,3-trimethylcyclohexanol with Br$_2$ and HgO in the dark to give a hypobromite intermediate:
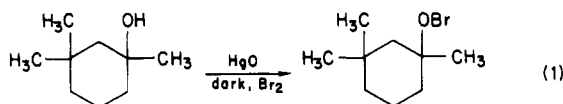
They did not isolate the hypobromite intermediate but confirmed its identity through ultraviolet and infrared spectroscopy and compared the spectroscopic data to those of known hypobromites, which had been reported by Anbar and Dostrovsky.[5]

We investigated the formation of alkyl hypobromites from tertiary and secondary alcohols. A titrimetric method was adopted to determine the percent yield of the alkyl hypobromites. Molar absorptivities for each reaction were calculated from the spectrophotometric and titrimetric data.

Results and Discussion

Factors that effected the most favorable condition for the formation of the alkyl hypobromites were light, solvent, temperature, and the concentration of the reactants.

Tertiary hypobromites are stable in the dark at a 0 °C temperature for prolonged periods. Secondary hypobromites deteriorate over prolonged periods under the same conditions. The nature of the products formed from the decomposition of hypobromites is discussed in a report by Brun and Waegell.[6]
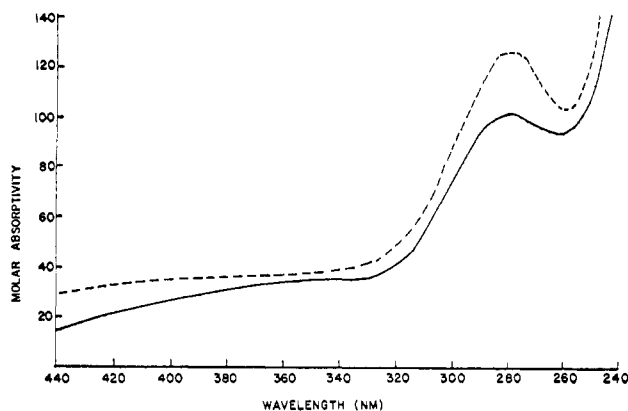
(1) Bugarszky, S. *Z. Phys. Chem.* **1901,** *38,* 561; **1910,** *71,* 705.
(2) Swain, C. G.; Wills, R. A.; Bader, R. F. W. *J. Am. Chem. Soc.* **1949,** *71,* 2829.
(3) Kudesia, V. P. *Bull. Soc. Chim. Belg.* **1971,** *80,* 213.
(4) Sneen, R. A.; Matheny, N. P. *J. Am. Chem. Soc.* **1964,** *86,* 5503.
(5) Anbar, M.; Dostrovsky, I. *J. Chem. Soc.* **1954,** *1105.*
(6) Brun, P.; Waegell, B. *Tetrahedron* **1976,** *32,* 517.

Figure 1. Absorption spectra. Reaction of alcohols with bromine and mercuric oxide in pentane with a reaction time of 60 min: *tert*-amyl alcohol (--); 2-pentanol (—).

The reaction to form alkyl hypobromite proceeded at room temperature with the mercuric oxide and distilled pentane as solvent:
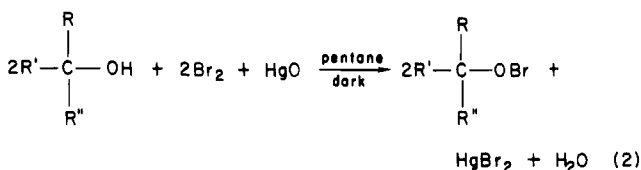
Mercuric oxide is assumed to act as it does in the reaction with water and bromine to generate hypobromous acid.[7]

The reaction flask was covered with Al foil as the alkyl hypobromite was found to be stable in the dark.[4]

Earlier work[2] suggested that secondary alcohols reacted directly with bromine to give their corresponding ketones and the HBr produced would cause the acid-catalyzed addition of bromine to the enol form of the ketone product to take place.[8] Hence, when secondary alcohols were employed, Na$_2$CO$_3$ was added.

Reaction of Alcohols with Bromine and Mercuric Oxide in Pentane. Twelve alcohols were employed in the preparation of their corresponding alkyl hypobromites. After 1 h, samples were removed for the spectrophotometric and titrimetric studies.

Absorption Spectra. The absorption spectra, measured after 1 h, displayed no appearance of Br$_2$ at 415 nm and a strong absorbance of the alkyl hypobromite at 280 nm. Representative spectra of the alkyl hypobromites prepared from a secondary alcohol and a tertiary alcohol are displayed (Figure 1).

Tritrimetric Determination. The alkyl hypobromite was analyzed by two methods, following treatment of an aliquot of the solution with excess KI and a known excess of HCl (eq 3). The liberated iodine was estimated by

$$ROBr + H^+ + 2I^- \rightarrow ROH + I_2 + Br^- \quad (3)$$

titration against standard sodium thiosulfate, following which the excess HCl remaining after decomposition of the hypobromite was determined by titration against standard alkali. Each titration gives an independent estimate of the amount of alkyl hypobromite present, i.e.,

[alkyl hypobromite] = [I$_2$] = [H$^+$ used in reaction 3]

(7) Moeller, T. "Inorganic Chemistry"; Wiley: New York, 1952; p 439.
(8) March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; pp 537–39.

Table I. Titrimetric Data and Spectrophotometric Data: Reactions of Alcohols with Bromine and Mercuric Oxide in Pentane

alcohols	yields of alkyl hypobromite, %			average molar absorptivity, ϵ_{ave}
	iodometry	acidimetry	average	
tert-butyl alcohol	100 ± 1	102 ± 0	101	135
tert-amyl alcohol	99.3 ± 1.6	97.7 ± 0.1	98.5	128
2-methyl-2-pentanol	94.0 ± 2.6	96.2 ± 0.3	95.1	149
3-methyl-3-hexanol	98.5 ± 0.4	94.4 ± 1.0	96.5	151
2-methyl-2-octanol	93.1 ± 2.3	94.9 ± 0.3	94.0	153
2-methyl-2-nonanol	97.8 ± 0.6	96.6 ± 2.2	97.2	154
2-pentanol	94.1 ± 0.2	99.1 ± 0.4	96.6	102
cyclohexanol	95.0 ± 0.2	98.7 ± 0.4	96.9	97.3
3-methyl-2-pentanol	93.1 ± 0.2	95.0 ± 0.0	94.0	102
2-hexanol	80.9 ± 0.4	86.1 ± 0.4	83.5	111
2-heptanol	80.6 ± 1.6	84.5 ± 1.0	82.6	114
2-octanol	66.0 ± 0.5	68.6 ± 0.7	67.3	125

Percent Yields of Alkyl Hypobromites. The percent yields of alkyl hypobromites from tertiary alcohols are high and consistent (Table I) and seem to decrease slightly as the length of the alcohol chain increases. This trend may be caused by steric effects which give rise to different reaction rates as the mass of the alcohol chain is altered[9] or to a competing side reaction to form the ketone.[4]

The percent yields of secondary alkyl hypobromites vary within a large range, between 66% and 99% (Table I), and decrease markedly as the length of the alcohol chain increases. Cyclohexanol and 3-methyl-2-pentanol were also found to give higher yields of their corresponding alkyl hypobromites than 2-hexanol would under the same conditions. This is analogous to earlier work[10] which indicated that the more complicated molecules have smaller steric factors or steric hindrance and that different distributions of masses usually led to a change in the rate of a reaction.

Molar Absorptivity. Molar absorptivities were calculated on the basis of the concentration of the alkyl hypobromites in solution as determined by titration. The molar absorptivity (average of both methods of titration) is reported in the last column of Table I.

The values of the molar absorptivities of the secondary alkyl hypobromites increase as the length of the alcohol chain increases. The alkyl hypobromite prepared from cyclohexanol has the smallest calculated ϵ values, and that prepared from 2-octanol has the largest ϵ values. The molar absorptivities calculated for the tertiary alkyl hypobromites are somewhat greater than the values for the secondary.

Experimental Section

Instrument. Spectrophotometric measurements were conducted on a DMS 90 UV–vis spectrophotometer or a 634 Varian Series model.

Chemicals. Pentane (98%, Fisher) was shaken with small amounts of concentrated H_2SO_4, distilled, collected, and stored in closed containers.

2-Pentanol (Aldrich), tert-amyl alcohol (J. T. Baker), tert-butyl alcohol and 2-octanol (Fisher), and 2-hexanol and cyclohexanol (Eastman) were used as received. 2-Methyl-2-pentanol, 3-methyl-3-hexanol, 2-methyl-2-octanol, 2-methyl-2-nonanol, 3-methyl-2-pentanol, and 2-heptanol were obtained from Chemical Samples Company.

Bromine (Reagent ACS, Fisher) was used without further purification. Anhydrous Na_2CO_3 (J. T. Baker analytical reagent) was dried at 110 °C for at least 2 h and cooled to room temperature before use. Mercuric oxide (Fisher Certified Reagent) was used as received.

Reagent Solutions. A stock $Na_2S_2O_3$ (Reagent ACS, Allied Chemical) solution (0.02301 N) was prepared in distilled water

and stored in a closed container. Similar preparations were carried out for making a NaOH (Fisher Scientific Co.) solution (0.04930 N) and a HCl (Mallinckrodt) solution (0.05327 N). All three solutions were standardized before use.

The alcohol solution was prepared by weighing each alcohol in a volumetric flask (10 mL) on an analytical balance (to the nearest 0.0001 g) and diluting to the mark with distilled pentane.

Bromine solution was prepared by pipetting Br_2 (1.00 mL) into pentane in a volumetric flask (100 mL) and diluting to the mark. About 24 mL was used in the reaction involving secondary alcohols and 12 mL was used for reaction with tertiary alcohols.

Reaction of Alcohols with Bromine and Mercuric Oxide in Pentane. Twelve alcohols were employed in this study, using the following sample procedure.

Mercuric oxide (0.4612 g) was added to the three-necked reaction flask, wrapped in Al foil. Pentane (278 mL) was introduced and the tert-butyl alcohol (2.128×10^{-3} mol) solution was dissolved in the HgO/pentane mixture. The bromine solution (containing 0.12 mL or 2.124×10^{-3} mol) was added to the reaction mixture, which was being stirred constantly by a magnetic stirrer and maintained at ambient room temperature. Time was recorded when the bromine solution was added to the reaction mixture. For reactions involving secondary alcohols, anhydrous Na_2CO_3 was introduced to the reaction flask and the concentrations of all reactants were doubled.

Spectrophotometric Determination. After 1 h, samples were removed and placed in a quartz cuvette (1 cm). Care was taken to avoid removing any HgO along with the samples. The absorbance was measured against the solvent blank, scanning from 440 to 240 nm.

Titrimetric Determination. The following method was taken from Furman[11] and adapted accordingly.

To 25 mL of a HCl solution (0.05327 N) in a 250-mL Erlenmeyer flask, was added KI, and the resulting solution was stirred. To this solution was added a 25-mL aliquot of the alkyl hypobromite solution, and the resulting mixture was stirred for 5 min. The mixture was then titrated against a $Na_2S_2O_3$ solution (0.02301 N) to the iodine end point. The addition of modified methyl orange indicated that there was unreacted, leftover HCl solution. The mixture was then titrated against a NaOH solution (0.04930 N) to the methyl orange end point.

(9) Gould, S. "Mechanism and Structure of Organic Chemistry"; Holt and Company, Inc.; New York, 1953; pp 234–35, 275.
(10) Brown, H. C.; Berneis, H. L. *J. Am. Chem. Soc.* **1953**, *75*, 10.

(11) Furman, N. H., Ed. "Standard Methods of Chemical Analysis, Volume 1–The Elements"; 6th ed."; D. Van Nostrand Co.; London, 1963.