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Studies on Bromites. III. Isolation and Characterization of Quaternary Ammonium Bromites

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Synopsis. Bromite, BrO_2^-, could be easily stabilized and isolated as quaternary ammonium salts by the reaction of sodium bromite with the corresponding ammonium halides. The bromites are more stable and non-hygroscopic in comparison to sodium bromite. The stability of the ammonium bromites depends a great deal on the structure of the ammonium groups.

Sodium bromite (**1**) (in aqueous solution) has been used as an oxidative desizing agent for textiles because of its mild oxidizing property.[1] The aqueous solution of **1** (*ca.* 4%) can be easily prepared by the reaction of sodium hydroxide with bromine, followed by dispropotionation.[2,3] However, troublesome operations such as concentration and purification at low temperature are necessary for the isolation of pure **1** from dilute solution.[4,5] Sodium bromite thus obtained contains small amounts of impurities, NaBr, $NaBrO_3$, and NaOH, even the most purified product being hygroscopic and unstable.

For studies on physical and chemical properties of BrO_2^-, stability of the compound is required. We could isolate an extremely stable bromite, tetrabutylammonium bromite (**3a**), during the course of the oxidation reaction using **1** in the presence of phase transfer catalyst, tetrabutylammonium chloride (**2**). In the present paper, we wish to describe the isolation and characterization of the quaternary ammonium bromites containing **3a**.

Isolation of the bromites **3** is very simple as shown in the following. An equimolar amount of **1** in water

$$\underset{\mathbf{1}}{NaBrO_2} + \underset{\mathbf{2}}{R^1{}_3R^2N^+\,Cl^-} \longrightarrow \underset{\mathbf{3}}{R^1{}_3R^2N^+\,BrO_2^-}$$

and tetrabutylammonium chloride **2** were mixed in water. The pH of the resulting solution was so adjusted with acetic acid that an orange crystal of **3a** almost insoluble in water was precipitated. The structure of **3a** was confirmed by means of IR and NMR spectra (in the presence of tetrabutylammonium) and analytical data of Br (total) and BrO_2^- obtained by titration with sodium arsenite[6] after dissolution in alkaline solution.

$$R^1{}_3R^2N^+\,BrO_2^- + NaOH \xrightarrow[\text{in } H_2O]{} NaBrO_2 + R^1{}_3R^2N^+\,OH^-$$

Other quaternary ammonium bromites, tetraethylammonium (**3c**), dodecyltrimethylammonium (**3d**), octadecyltrimethylammonium (**3e**) and benzyltrimethylammonium bromite (**3f**), were prepared in a similar way. However, tetramethylammonium bromite (**3b**) was not isolated because of decomposition with time. The results are given in Tables 1 and 2.

Most of the bromites **3** obtained have definite melting points and are stable and non-hygroscopic enough to be kept at room temperature for over half a year.

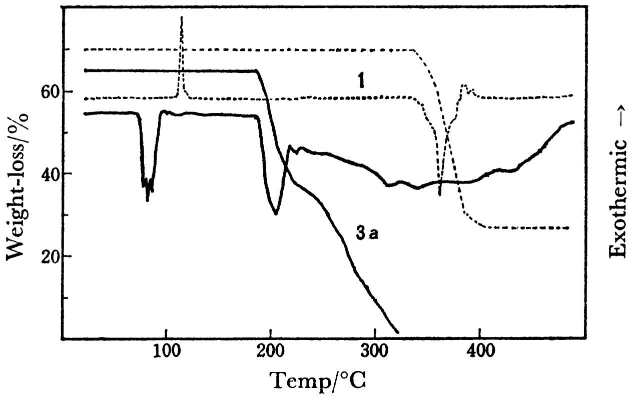

Fig. 1. DTA and TG curves of **1** and **3a**.

The instability seems to depend remarkably on the structure of the cation. The bromites having large and bulky groups on nitrogen are more stable than those containing no such groups, the order of stability being **3a**>**3c**≫**3b** in bulkiness and **3e**>**3d**≫**3b** in size of group.

The same tendency was observed quantitatively by means of thermal analysis. In the DTA curve of **3a** (Fig. 1) two peaks were observed at 74 and 188 °C. The former might correspond to melting point and the latter to decomposition temperature on the basis of thermogravimetry. The DTA curves of the other bromites showed the same pattern. The decomposition temperatures obtained from their curves are 115 (**3c**), 110 (**3d**), 167 (**3e**), and 115 °C (**3f**) and can be arranged in the order mentioned above.

The DTA curve of sodium bromite (dotted line, Fig. 1) has two peaks at 109 °C (exothermic, on the basis of dispropotionation) and at 359 °C (endothermic, on the basis of decomposition of sodium bromate).[5a)] There is a remarkable difference between the curves of the bromites **3** and **1**, which seems to be due to the difference in their decomposition patterns.

The isolation of the quaternary ammonium bromites **3** is of importance not only as regards the stabilization of BrO_2^- but also because of their use in oxidation reactions in an organic medium, since **3** is soluble in benzene, dichloromethane, and chloroform.

Experimental

The IR spectra were recorded on a Hitachi 285 spectrophotometer and NMR spectra on a JNM-C-100 spectrometer (Japan Electron Optics Lab.), the thermal analysis being carried out on a DTA-TG apparatus 8055-EI, Rigaku Denki Co. Ltd.

Determination of BrO_2^- was carried out after dissolution in alkaline solution containing two fold amount of NaOH (in mol) to sample **3**.

Materials. Sodium bromite was prepared by the method described in a previous paper.[5a)] Quaternary am-

Table 1. Preparation of quaternary ammonium bromites **3**

	$R^1_3R^2N^+$ BrO_2^-	Mp/°C	Yield/%	Found (%)		Calcd (%)	
				Br	BrO_2^-	Br	BrO_2^-
a	$R^1=R^2=C_4H_9$	74.0—74.5	≈100	22.4	31.6	22.5	31.6
b	$R^1=R^2=CH_3$	—	0				
c	$R^1=R^2=C_2H_5$	82.5—84.0	≈100	33.1	46.0	33.0	46.2
d	$R^1=CH_3$, $R^2=C_{12}H_{25}$	81.0—83.5	≈100	23.4	32.6	23.5	32.9
e	$R^1=CH_3$, $R^2=C_{18}H_{37}$	88.5—91.0	≈100	17.0	26.3	17.1	26.4
f	$R^1=CH_3$, $R^2=C_6H_5CH_2$	92.0—94.0	96	23.9	42.4	23.9	42.7

Table 2. IR and NMR spectra

	IR(KBr) $\tilde{\nu}$/cm^{-1}	NMR($CDCl_3$) δ/ppm
3a	2920, 2870, 1450, 1375, 990, 920, 880, 790, 730	1.11(t, 12H), 1.2—2.0(m, 16H), 3.26(t, 8H)
3c	2920, 1445, 1180, 1000, 790	decompn. during measurement
3d	2920, 2850, 1460, 965, 920, 725	0.89(t, 3H), 1.0—2.1(m, 20H), 3.36(s, 9H), 3.2—3.7(m, 2H)
3e	2920, 1470, 970, 900, 760	0.91(t, 3H), 1.1—2.0(m, 32H), 3.49(s, 9H), 3.3—3.8(m, 2H)
3f	3020, 2960, 1470, 1400, 975, 920, 890, 780, 730, 700, 620	decompn. during measurement

monium bromides and chlorides of reagent grade were used.

*Isolative Preparation of Quaternary Ammonium Bromites **3**. General Procedure*: To an aqueous solution (18%) of 10 mmol of sodium bromite was added 10 mmol of quaternary ammonium halide. After stirring for 30 min, the pH of the resulting solution was adjusted to 8—9 by the addition of acetic acid, stirring being continued for 60 min. An orange crystal of quaternary ammonium bromite **3** deposited. The crystal was dissolved in CH_2Cl_2 without filtration and the solution was extracted with CH_2Cl_2 (15 cm^3 × 3). The combined extracts were dried over anhydrous sodium sulfate and evaporated to dryness *in vacuo* to give an orange crystal of **3** which was purified by reprecipitation from CH_2Cl_2–Et_2O. The results are given in Tables 1 and 2.

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References

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4) About 18% solution of **1** was obtained by the modified method.[5a)]

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