CHEMISTRY LETTERS, pp. 671-672, 1980.

ELECTROLYTIC PREPARATION OF TETRAALKYLAMMONIUM BROMITES FROM THE CORRESPONDING BROMIDES[1)]

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Electrolytic oxidation of tetraalkylammonium bromides to give the corresponding bromites was found. This method is convenient and applicable to the preparation of the stable tetraalkylammonium bromites.

As is well known the electrolysis of sodium bromide[2)] or chloride[3)] gives the corresponding bromate or chlorate. In the course of the electrolysis, the intervention of BrO_2^- or ClO_2^- may be assumed. However, there has been no report in which the confirmation of the presence of the intermediates is described.

In a previous paper,[4)] we described that labile BrO_2^- can be stabilized as water-insoluble tetraalkylammonium salts. During the electrolytic oxidation of Br^-, if tetraalkylammonium ions are present, BrO_2^- formed is expected to deposit from the aqueous electrolyte as the tetraalkylammonium salt. If bromite can be obtained in such a simple manner, it should become more effective method of preparation of BrO_2^- than the known time-consuming methods[5)] which require severe control of pH and temperature.

We attempted anodic oxidation of tetrabutylammonium bromide (**1a**) and succeeded in obtaining the corresponding bromite (**2a**) in a quantitative yield with an almost 100% current efficiency. The procedure is as follows. The electrolytic cell used was a cylindrical vessel (500 cm^3 capacity) having anode and cathode compartments separated by a cylindrical porcelain cup (4.5 cm diameter x 15 cm). The electrodes used were a cylindrical platinum net anode (3 cm diameter x 5 cm) and a cylindrical lead cathode (6.5 cm diameter x 9 cm). In the electrolytic cell, **1a** (10 mmol in 100 cm^3 of water in anode room) was electrolyzed at 0.05 A/cm^2 and 40-50°C for 26 min using a catholyte of potassium bromide (10 mmol in 110 cm^3 of water). The orange crystals deposited during electrolysis were dissolved in chloroform and the anolyte was extracted with chloroform. The resulting chloroform solution was washed with water, dried over anhydrous sodium sulfate, and evaporated to dryness to give orange crystals of **2a** in a quantitative yield. The structure of **2a** was confirmed by agreement of the IR and NMR spectra and the melting point with those of authentic sample,[4)] and by the assay of BrO_2^- [Found: 31.5%, Calcd: 31.6%].[6)]

In a similar way, other tetraalkylammonium bromides **1** listed in Table 1 were electrolyzed to give the corresponding bromites **2**. From the results given in the

Table, it is noted that the bromites having bulky groups are obtained in better yield than those having smaller groups. This seems to be attributed to their stability as described in the previous paper.[4)] Therefore, the present method is applicable to the preparation of comparatively stable tetraalkylammonium bromites.

Table 1. Electrolysis of **1** to **2**

	1	**2**	
	$R^1{}_3R^2N^+\ Br^-$	Mp / °C	Yield/%[b]
a	$R^1=R^2=C_4H_9$	74.0-75.0 (74.0-75.0)[a]	≈100
b	$R^1=R^2=C_2H_5$	82.5-84.0 (82.5-84.0)	3
c	$R^1=CH_3$, $R^2=C_{12}H_{25}$	82.0-83.5 (81.0-83.5)	≈100
d	$R^1=CH_3$, $R^2=C_{18}H_{37}$	88.5-91.0 (88.5-91.0)	≈100
e	$R^1=CH_3$, $R^2=C_6H_5CH_2$	92.0-94.0 (92.0-94.0)	8

a, The values in parentheses are those described in the reference No. 4. b, The yields were obtained by the electrolysis with passage of 4F/mol. Anode, Pt; cathode, Pb.

Though the exact mechanism is still not clarified, as the above expectation the transformation of **1** to **2** is considered to occur along the following scheme.

Scheme

$$\underset{\mathbf{1}}{R^1{}_3R^2N^+\ Br^-} \rightleftharpoons R^1{}_3R^2N^+ + Br^-$$

$$Br^- + 2H_2O \xrightarrow{\text{electrolysis}} BrO_2^- + 4H^+ + 4e$$

$$R^1{}_3R^2N^+ + BrO_2^- \rightleftharpoons \underset{\mathbf{2}}{R^1{}_3R^2N^+\ BrO_2^-}\downarrow$$

We wish to thank Professor Dr. M. Okawara, Tokyo Institute of Technology, for his advice and Mr. Nakamura, Tokyo Institute of Technology, for the measurement of NMR spectra.

References and Notes

1) Part IV of ''Studies of Bromites''.
2) T. Osuga and K. Sugino, J. Electrochem. Soc., 104, 448 (1957).
3) K. Sugino and M. Yamashita, Denki Kagaku, 16, 123 (1948).
4) T. Kageyama and T. Yamamoto, Bull. Chem. Soc. Jpn., 53, 1175 (1980).
5) (a) T. Kageyama, Nippon Kagaku Kaishi, 1972, 1064. (b) Societe d'Etudes Chimques pour l'Industrie et Agriculture, Brit. Patent, 843 559 (1960).
6) The contents of BrO_2^- were determined by the reference method; M. H. Hashme and A. A. Ayaz, Anal. Chem., 35, 908 (1963).

(Received February 22, 1980)