

ELECTROLYTIC PREPARATION OF TETRAALKYLAMMONIUM BROMITES  
FROM THE CORRESPONDING BROMIDES<sup>1)</sup>

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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<sup>2)</sup> or chloride<sup>3)</sup> gives the corresponding bromate or chlorate. In the course of the electrolysis, the intervention of  $\text{BrO}_2^-$  or  $\text{ClO}_2^-$  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,<sup>4)</sup> we described that labile  $\text{BrO}_2^-$  can be stabilized as water-insoluble tetraalkylammonium salts. During the electrolytic oxidation of  $\text{Br}^-$ , if tetraalkylammonium ions are present,  $\text{BrO}_2^-$  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  $\text{BrO}_2^-$  than the known time-consuming methods<sup>5)</sup> 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<sup>3</sup> 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<sup>3</sup> of water in anode room) was electrolyzed at 0.05 A/cm<sup>2</sup> and 40-50°C for 26 min using a catholyte of potassium bromide (10 mmol in 110 cm<sup>3</sup> 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,<sup>4)</sup> and by the assay of  $\text{BrO}_2^-$  [Found: 31.5%, Calcd: 31.6%].<sup>6)</sup>

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.<sup>4)</sup> Therefore, the present method is applicable to the preparation of comparatively stable tetraalkylammonium bromites.

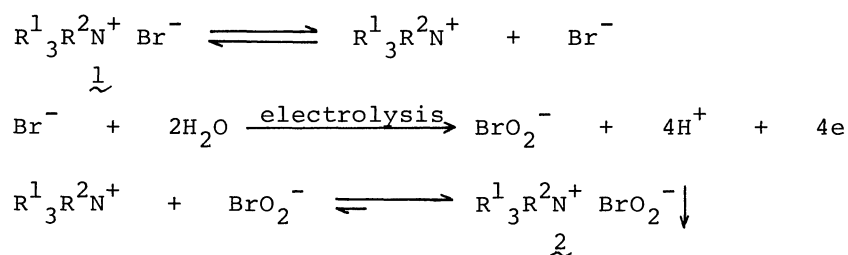
Table 1. Electrolysis of  $\underline{1}$  to  $\underline{2}$

	$\underline{1}$ $R^1_3R^2N^+ Br^-$	Mp / °C	$\underline{2}$	Yield/% <sup>b</sup>
a	$R^1=R^2=C_4H_9$	74.0-75.0	(74.0-75.0) <sup>a</sup>	≈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  $\underline{1}$  to  $\underline{2}$  is considered to occur along the following scheme.

Scheme



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References and Notes

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- 6) The contents of  $BrO_2^-$  were determined by the reference method; M. H. Hashme and A. A. Ayaz, Anal. Chem., 35, 908 (1963).

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