CARBON-BROMINE BOND CLEAVAGE

BY ELECTROOXIDATION OF ALKYL BROMIDES

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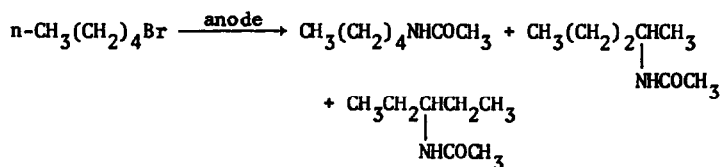
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In the past, some difficulties were encountered in the anodic oxidation of "simple" alkyl halides other than iodoalkanes.[1] Up until now, the only oxidized bromoalkanes were adamantyl derivatives,[2] which form carbenium ions by breaking carbon-hydrogen, as well as carbon-bromine bonds. Furthermore, it has been claimed that this process involves initial electron transfer from an orbital primarily located on the adamantyl moiety.[2b]

We report here the exclusive anodic cleavage of C-Br bonds of simple bromoalkanes and suggest that this process involves direct oxidation of the bromoalkane resulting from abstraction of an electron from the non-bonding orbital of the bromine atom. The products isolated after work-up are acetamidated fragments.

The following procedure is described for the conversion of 1-bromopentane to the corresponding acetamido derivatives, in about equal amounts:

$$n\text{-}CH_3(CH_2)_4Br \xrightarrow{\text{anode}} CH_3(CH_2)_4NHCOCH_3 + CH_3(CH_2)_2\underset{\underset{NHCOCH_3}{|}}{C}HCH_3$$

$$+ CH_3CH_2\underset{\underset{NHCOCH_3}{|}}{C}HCH_2CH_3$$

A three compartment cell of the type described elsewhere,[3] containing 0.5M of supporting electrolyte (Table) in twice distilled acetonitrile (from phosphorus pentoxide) was used. The reference electrode was a silver wire immersed in 0.1 M $AgNO_3$ in acetonitrile and the anode was platinum gauze. The reaction was conducted at controlled anode potential of 2.35 V with the temperature maintained at ~ 25°C. The background current was 4-5 mA and it increased to ~ 70 mA upon addition of 20 mmole of the depolarizer. The electrolysis was continued until 4mF were utilized (during the course of the reaction the potential was pulsed to ca. 0V for 1 sec every

15 sec). The products were isolated by concentrating the anolyte, adding water and extracting

it with chloroform and dichloromethane. The combined organic layers were washed with water and

dried over anhydrous magnesium sulfate. The products were collected by preparative gas-chroma-

tography, identified by standard spectroscopic methods and in some cases compared with authentic

samples.

<center>Table</center>

<center>Voltammetric Data[a] and Oxidation Products</center>

Reactant(20 mmoles)	Supporting Electrolyte	Current Yield(%)[b]	Products
t-butyl bromide	TEAF[c]	83	N-t-butylacetamide (1)
2-bromopropane	LiClO$_4$	70	N -2-acetamidopropane (2)
	TEAF	40	
2-bromobutane	LiClO$_4$	60	N-2-acetamidobutane (3)
	TEAF	41	
1-bromopentane	LiClO$_4$	40	N-1- (4), N-2- (5), N-3-acetamidopentane (6)
1-bromo-2-methylpropane	LiClO$_4$	50	1 + 3 + N-isobutylacetamide (7)

[a] All preparative oxidations have been carried out at 2.35 V vs. Ag/AgNO$_3$ 0.1 M in

10 ml of acetonitrile at room temperature. Cyclic voltammograms of all the listed

compounds give E_p values in the range 2.4-2.7 V (vs. Ag/Ag+) at 0.5 V/s scan rate.

[b] Based on 2e/mole.   [c] Tetraethylammonium Fluoborate.

The Table shows unambiguously that cleavage of carbon-bromine bond is the reaction followed

under the conditions studied and that in general tertiary and secondary alkyl bromides give higher

current yields than primary ones. It is noteworthy that in the anodic oxidation of 2-bromoada-

mantane[2a] the scission of the carbon-hydrogen bond at the 1 position competes favorably with that of a carbon-bromine bond. However, in the present study, none of the compounds listed in the Table yields a product due to C-H bond breaking (bifunctional alkanes would have been the expected products from this breaking). Therefore, the reaction seems to be highly selective towards bromine substitution. This is striking especially in the case of primary bromoalkanes (Table) compared to the secondary bromoadamantane.

The mechanism for the oxidation of alkanes is believed to involve direct electron transfer from the hydrocarbon to the electrode.[4] The same mechanism has been proposed for the anodic oxidation of haloadamantanes on the basis of photoelectron spectroscopy measurements which indicated that the vertical ionization potential (IP) observed for 1-haloadamantanes is higher than that of adamantane.[5] However, the discussed simple bromoalkanes have lower IP than the corresponding hydrocarbons[6] and indeed, they oxidize at lower potentials (~ 2.4 V) than alkanes (3-3.5 V).[4] It therefore seems likely that an electron is initially removed from the nonbonding orbital of the bromine followed either by cleavage of the carbon-bromine bond to generate a highly energetic carbenium ion and/or by S_N2 type displacement on an initially formed cation-radical.[1b,7] In support of these two possible pathways, products $\underset{\sim}{5}$ and $\underset{\sim}{6}$ (Table) from 1-bromopentane and $\underset{\sim}{1}$ and $\underset{\sim}{3}$ from 1-bromo-2-methylpropane point to carbenium ion rearrangements (there is a clear precedent for carbenium ions as precursors in acetonitrile[2b]), whereas $\underset{\sim}{4}$ and $\underset{\sim}{7}$ point to S_N2 type mechanism. It is, however, clear that both intermediates could account for the above observations.

It should be emphasized that the bromoalkane's oxidation can be performed at potentials at which the background current is very low and thus it does not seem reasonable to invoke a mechanism involving attack of oxidized solvent or electrolyte species on the reactants.

In an effort to detect unsaturated hydrocarbon(s), the following experiments have been carried out independently, for 2-bromopropane and 2-bromobutane: argon was continuously sparged through the anolyte throughout various runs to sweep any volatile olefinic product into a bromine-carbon tetrachloride solution. No dibromo product was identified after removing the excess bromine with aqueous thiosulfate and the organic solvent by evaporation. In contrast, propene has been detected in the anodic oxidation of 2-iodopropane.[1a] Although olefinic products are not observed in this study, we cannot exclude their existence as intermediates.

Further studies on a wider range of bromoalkanes as well as other haloalkanes are in progress.

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