ft × 0.25 in. FFAP column, 160 °C) showed a gradual disappearance of **20** and the concomitant appearance of two photoproducts. The reaction was essentially complete after irradiation for 80 min. Evaporation of the solvent at reduced pressure gave a yellow oil. Purification of the photoproducts by GLC (above conditions) provided **4-isopropylidenepentanolide (24)** as an oil [ν (CHCl$_3$) 3015, 2925, 1740, 1445, 1375, 1340, 1290, 1255, 1140, and 1035 cm^{-1}. Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.28; H, 8.44.] and **2-isopropylidenepentane-1,5-dial (25)** as an oil [ν (CHCl$_3$) 3025, 1722, 1661, 1631, 1375, and 1160 cm^{-1}.]

Analysis of the crude photolysate by ^{1}H NMR showed that **24** and **25** were obtained in yields of ca. 65 and 5%, respectively.

Photolysis of 22. A solution of 205 mg of **22** in 12 mL of diethyl ether was irradiated through a Corex filter with a Hanovia L 450-W high-pressure mercury lamp. Monitoring the photolysis by GLC (5 ft × 0.25 in. Carbowax column, 175 °C) indicated a gradual disappearance of **22** with the concomitant formation of two photoproducts. After irradiation for 2 h, ca. 95% of **22** had reacted. Evaporation of the solvent at reduced pressure provided a yellow oil. Purification of the photoproducts by GLC (above conditions) gave **3,3-dimethyl-5-isopropylidenehexanolide (26)** as an oil [δ_{Me_4Si} (CDCl$_3$) 4.57 (s, 2 H), 2.49 (s, 2 H), 2.22 (s, 2 H), 1.77 (s, 3 H), 1.71 (s, 3 H), and 1.01 (s, 6 H); ν (CHCl$_3$) 2970, 1724, 1380, 1315, 1280, 1115, and 1025 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.32; H, 9.67.] and **4,4-dimethyl-2-isopropylidenehexane-1,6-dial (27)** as an oil [δ_{Me_4Si} (CDCl$_3$) 10.09 (s, 1 H), 9.76 (m, 1 H), 2.40 (br s, 2 H), 2.20 (m, 5 H), 1.97 (m, 3 H), and 0.99 (s, 6 H); ν (CHCl$_3$) 3025, 2965, 2880, 1716, 1665, 1635, 1380, 1190, and 1155 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.40; H, 9.76.].

Analysis of the crude photolysate by ^{1}H NMR showed that **26** and **27** were obtained in yields of 45 and 20%, respectively.

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Registry No.—**19,** 3883-58-7; **20,** 63704-11-0; **21,** 702-50-1; **22,** 63704-12-1; **23,** 63704-13-2; **24,** 63704-14-3; **25,** 63704-15-4; **26,** 63704-16-5; **27,** 63704-17-6.

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Formation of Carbonium Ions from Electrooxidation of Alkyl Bromides

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Primary, secondary, and tertiary bromoalkanes were potentiostatically oxidized at platinum gauze. The anolyte was acetonitrile–lithium perchlorate or tetraethylammonium fluoborate and the reference electrode Ag/0.1 M $AgNO_3$. Carbon–bromine bond cleavage, leading to the formation of *N*-alkylacetamides, was observed to be the exclusive route of these oxidations. Each of the oxidations of 2-bromopropane, 2-bromobutane, *tert*-butyl bromide, and neopentyl bromide yielded a sole amide, whereas 1-bromobutane, 1-bromopentane, 1-bromohexane, 1-bromo-2-methylpropane, 1-bromo-3-methylbutane, 2-bromopentane and 3-bromohexane gave mixtures of amides. A mechanism involving an initial electron transfer from the nonbonding orbital of the bromine is proposed. This intermediate is thought to undergo attack by the nucleophilic solvent and/or undergo carbon–bromine bond breaking to generate highly energetic carbonium ions, which react with the acetonitrile directly or after rearrangement.

The anodic oxidation of aliphatic halides has been studied on relatively few systems to date. Iodoalkanes and haloadamantanes were studied by several groups.[1,2] However, the electrochemical oxidation of simple alkyl bromides, with the sole exception of bromoadamantyl derivatives, has been unsuccessful. Preliminary study has recently demonstrated that covalently bound bromine makes the selective electrooxidation of organic bromides feasible in acetonitrile solution.[3] Carbon–bromine bond cleavage was found to occur exclusively, resulting in the formation of carbonium ion intermediates which reacted to form *N*-alkylacetamide products. This paper reports the results of a comprehensive study on anodic oxidation of a variety of primary, secondary, and tertiary bromoalkanes. The nature of the products and gross mechanistic features of the oxidation process are discussed.

Results

Preparative electrolyses were performed potentiostatically in a three-compartment cell at room temperature. Acetonitrile–lithium perchlorate or tetraethylammonium flouborate were used in both anode and cathode compartments. The solvent was routinely distilled from phosphorus pentoxide before use. The background current in all experiments was ~0.5 mA/cm^2 at 2.35 V. Initial currents with added substrates were 10–100 times the background, depending on the nature of the substrate. Coulometry was accomplished with an electronic counter. The coulometric data reported are uncorrected for background current, but if the coulometry were corrected (assuming that the current due to background oxidation was that which was determined without added substrate) the n values would be lowered by less than 0.1. In the electrooxidations of primary alkylbromides, the anode potential was pulsed to about 0.5 V for 1 s every 20 s. This resulted in higher currents and more rapid oxidations. For secondary bromoalkanes only an occasional pulsing was needed. The work-up included concentration of the anolyte followed by extraction with chloroform, methylene chloride, and water. Evaporation of the organic solvents after drying over anhydrous magnesium sulfate usually gave oily acetamido derivatives. The products reported in Table I were isolated after preparative GLC collection and identified by standard spectroscopic techniques and by comparison with authentic samples.

Table I. Voltammetric Data[a] and Oxidation Products

Substrate	Registry no.	Electrolyte[b]	mF consumed	Current yield, %[c]	Products[d]
$(CH_3)_3CBr$	507-19-7	A	4.0	83	$(CH_3)_3CNHCOCH_3$ (**1**) (98%)
$(CH_3)_2CHBr$	75-26-3	A	3.6	41	$(CH_3)_2CHNHCOCH_3$ (**2**) (92%)
		B	3.2	70	**2** (95%)
$CH_3CH(Br)CH_2CH_3$	78-76-2	A	4.0	31	$CH_3CH(NHCOCH_3)CH_2CH_3$ (**3**) (95%)
		B	4.0	50	**3** (98%)
$(CH_3)_3CCH_2Br$	630-17-1	B	4.6	33	$(CH_3)_2C(NHCOCH_3)CH_2CH_3$ (**4**) (43%) CH_3CONH_2 (**5**) (14%)
$(CH_3)_2CH(CH_2)_2Br$	107-82-4	B	4.0	28	**4** (16%) $(CH_3)_2CHCH(NHCOCH_3)CH_3$ (**6**) (25%) $(CH_3)_2CHCH_2CH_2NHCOCH_3$ (**7**) (53%)
$(CH_3)_2CHCH_2Br$	78-77-3	B	4.4	50	**1** (56%) + **3** (3%) $(CH_3)_2CHCH_2NHCOCH_3$ (**8**) (1%) **5** (15%)
$n\text{-}C_4H_9Br$	109-65-9	B	4.6	40	**3** (67%) $n\text{-}C_4H_9(NHCOCH_3)$ (**9**) (33%)
$n\text{-}C_5H_{11}Br$	110-53-2	B	4.0	40	$1\text{-}C_5H_{11}(NHCOCH_3)$ (**10**) (30%) $2\text{-}C_5H_{11}(NHCOCH_3)$ (**11**) (33%) $3\text{-}C_5H_{11}(NHCOCH_3)$ (**12**) (33%)
$2\text{-}C_5H_{11}Br$	107-81-3	B	4.0	51	**11** (33%) + **12** (67%)
$n\text{-}C_6H_{13}Br$	111-25-1	B	5.1	54	$1\text{-}C_6H_{13}(NHCOCH_3)$ (**13**) (27%) $2\text{-}C_6H_{13}(NHCOCH_3)$ (**14**) (41%) $3\text{-}C_6H_{13}(NHCOCH_3)$ (**15**) (31%)
$3\text{-}C_6H_{13}Br$	3377-87-5	B	4.0	40	**14** (12%) + **15** (88%)

[a] All E_p values were in the range of 2.5–2.8 V vs. Ag|$AgNO_3$ 0.1 M in CH_3CN except for *tert*-butyl bromide (2.4 V). Electrooxidations were carried out at controlled potential of 2.35 V; 20 mmol of alkyl bromide in 10 mL CH_3CN was used in each experiment. [b] The electrolyte concentration was 0.5 M (A, tetraethylammonium fluoborate; B, $LiClO_4$). [c] Current yields are based on 2 e/mol. [d] Percentages shown express product distributions of isolated materials. On this basis the current yield is treated as 100%. In the oxidations of neopentyl bromide, 1-bromo-2-methylpropane, and 1-bromo-3-methylbutane, unidentified materials were also present in the product mixtures.

Table II. The Effect of Concentration on the Yield of 2 in the Anodic Oxidation[a] of Isopropyl Bromide at 2.35 V vs. Ag|$AgNO_3$ 0.1 M

[*i*-PrBr]	Current yield, %[b]
0.025	8
0.1	10
0.5	20
1.6[c]	45

[a] In all runs, tetraethylammonium fluoborate (0.2 M) was used as an electrolyte. [b] Yields are based on isolated products after passing 4 mF in each experiment, assuming 2 e/mol. [c] At concentrations higher than 1.6 M two phases were formed due to a limited solubility of certain bromoalkanes. Therefore current yield comparisons for all compounds listed in Table I are with substrate concentration of 1.6 M.

Table III. The Effect of Electrolytes on the Yields of 2 and 3[a]

Substrate	Concn, M	Supporting electrolyte	Current yield, %[c]
2-Bromobutane	1.6	TEAF	31
	1.6	$LiClO_4$	50
	1.6	TEAP[b]	41
	1.6	NH_4BF_4	22
2-bromopropane	0.5	TEAF	20
	0.5	$LiClO_4$	41

[a] All experiments were carried out potentiostatically at 2.35 V vs. Ag|$AgNO_3$ 0.1 M, at room temperature. Electrolyses were stopped after utilizing 4 mF. [b] TEAP = tetraethylammonium perchlorate. [c] Based on 2 e/mol calculation.

Cyclic voltammograms were recorded for each compound using tetrabutylammonium fluoborate as an electrolyte. Each bromoalkane shows one anodic peak in the range 2.5–2.8 V vs. Ag/Ag^+ at 0.2 V/s scan rate. *tert*-Butyl bromide and all secondary bromides gave a reasonably well-defined wave whereas primary bromoalkanes gave ill-defined ones. The anodic peak positions were dependent on sweep rate and there was no evidence of a reversible cathodic peak even at sweep rates of 60 V/s.

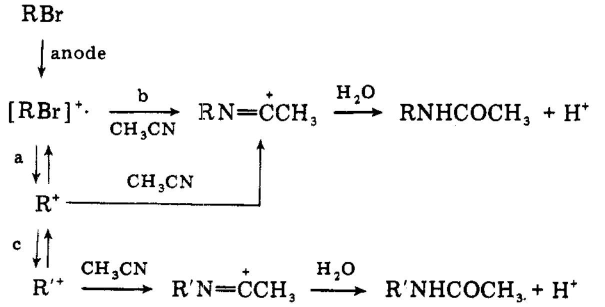
N-Alkylacetamido products which resulted from carbonium ion fragments are listed in Table I. The oxidations of *tert*-butyl bromide, 2-bromobutane, and 2-bromopropane each gave a sole amide derivative, while other primary and secondary bromides yielded mixtures of acetamidated products, due to one or more hydride shifts (e.g., from the oxidation of *n*-bromoalkanes) or a methyl shift (in the oxidation of neopentyl bromide) or both shifts (in the case of 1-bromo-2-methylpropane).

Several sets of experiments were conducted in order to optimize the product yields. The dependence of current yields on the concentration of the substrate is illustrated in Table II for the oxidation of 2-bromopropane. It shows clearly that the more concentrated the solution, the higher the current yield achieved. According to these results all preparative oxidations were carried out at a substrate concentration of 1.6 M.

The effect of the n value on the yield for the oxidation of *tert*-butyl bromide has been studied. When $n = 3$ or 4 the product mixture was contaminated with unidentified materials other than *N*-(*tert*-butyl)acetamide. However, when $n \leqslant 2$ the desired amide was obtained in over 95% purity. As a consequence of these results, the calculated current yields for all the electrooxidations presented in Table I are based on 2 e/mol.

Table III illustrates the influence of several supporting electrolytes on the extent of carbon–bromine bond breaking in the case of oxidation of 2-bromobutane and 2-bromopropane. For both substrates, higher yields of the corresponding

Scheme I



amides were achieved with lithium perchlorate. Thus, this electrolyte was employed in most preparative electrolyses described in this work.

Regarding the yields obtained from the experiments described above it seems reasonable to assume that the oxidation of alkyl bromides competes with oxidation of products and/or intermediates. Consequently, the reactions were arbitrarily discontinued when ~10% of the charge calculated for a two-electron process had been utilized. This procedure was used in order to avoid further oxidation of the products.[4a]

Discussion

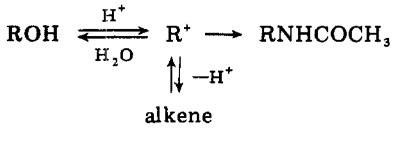
Table I illustrates that the cleavage of the carbon–bromine bond in the anodic oxidation of bromoalkanes is the sole process which appears to occur in the entire range of the substrates studied. This is in contrast to the behavior of secondary bromoadamantanes.[2a] This high selectivity is particularly noteworthy in the case of isobutyl bromide and 1-bromo-2-methylbutane, where tertiary hydrogens are present and for which no products due to C–H breaking were detected.

On the basis of an earlier argument[3] it seems likely that in the electrooxidation of simple alkyl bromides an initial electron is removed from the nonbonding orbital of the bromine (Scheme I) followed either by C–Br cleavage to generate a carbonium ion (path a), possibly a highly energetic one, and/or S_N2 type displacement on an initially formed cation radical (path b).[1b,4b] The carbonium ion, R$^+$, can undergo a reversible rearrangement (path c) to the isomeric carbonium ion (R$'^+$) and then react with the nucleophilic solvent to give amides different from those obtained via paths a and b. In support of the pathways in Scheme I, products **11** and **12**, for instance, from the oxidations of 1- and 2-bromopentanes, point to carbonium ion rearrangements (there is clear precedent for carbonium ion precursors in acetonitrile[2b]), whereas products **9**, **10**, and **13** point to an S_N2 type mechanism. It is clear, however, that the above results could be attributed to both cation radical and carbonium ion intermediates as well.

As is evidenced by the product distribution for 1-bromoalkanes (Table I), the isomerizations normally tend from primary to secondary and from secondary to tertiary alkyl products, that is, in the direction of the more stable carbonium ion. However, the oxidation of another primary alkyl bromide, 1-bromo-3-methylbutane, for instance, yielded a mixture of three amides derived from primary, secondary, and tertiary carbonium ions. This fact implies (assuming an S_N1 mechanism) that the rearrangement of the carbonium ion by hydride migration occurs in competition with the direct addition of the nucleophilic solvent acetonitrile to the carbonium ion.

Table I also indicates that carbonium ions "prefer" to rearrange toward the center of the molecule. This trend was observed for the oxidations of several compounds, e.g., 2-bromopentane and 1- and 3-bromohexanes. The rationale for this tendency may be attributed to a slightly greater inductive effect which the ethyl group exerts in comparison to the methyl group.[5] Consequently, a carbonium ion substituted with two ethyl groups is more stable than that substituted with one ethyl and one methyl group.

Scheme II



The carbonium ion intermediates might have been expected to produce alkenes and/or alcohols in addition to the acetamide, as demonstrated in Scheme II.

As we noted previously,[3] no olefins or alcohols were detected in the product mixtures of the various oxidized bromoalkanes (e.g., no dibromide from the formation of isobutylene or *tert*-butyl alcohol was observed from the oxidation of *tert*-butyl bromide). If one discounts the possibility of modifying the reactivity of a cation with a highly positively charged anode, i.e., adsorbed cations, one is then left with the proposition that the alkene, if formed, is converted to acetamide in a Ritter reaction.[6a] This is quite probable near the anode surface at which a high acid concentration must exist. Such acid-catalyzed processes converting alcohol or alkene to acetamide are not uncommon under these conditions.[7] Furthermore, aliphatic alcohols and olefins are known to oxidize below[8] the potential applied for the oxidation of bromoalkanes and such a possibility could also explain their absence.

In order to investigate the influence of acid on the formation of products, one would have expected that anodic oxidation of alkyl bromides in a basic medium would result in a decrease in the yield of *N*-alkylacetamides. Indeed, when 2-bromobutane was oxidized in the presence of an excess of anhydrous Na_2CO_3, under the same oxidation conditions described in Table I, the yield of **3** went down from 50% (without the presence of Na_2CO_3) to 32%. It is unlikely that all of this difference in yield is due to experimental error and therefore it seems that at least some of the 18% difference "belongs" to other products which, unfortunately, were difficult to identify under the conditions studied, for the reasons described in the preceding paragraph.

Mechanisms involving intramolecular remote abstration of hydrogen, by an RBr$^{+}\cdot$ type of intermediate, as found in mass spectroscopy of alkyl halides[9] and similarly in electrooxidation of ketones,[10] are ruled out since no bifunctional alkanes (e.g., acetamidated bromoalkane, biacetamidated products, etc.) were observed, as one would have expected from such a process. A mechanism involving intermolecular hydrogen abstraction is also ruled out for the same reasons. However, intermolecular interaction between a neutral alkyl bromide and an oxidized molecule could be involved.

The fate of the bromine is not clear at present. However, neither Br_2 nor products containing bromine functionality were observed. The possibility of the formation of "Br$^+$" intermediate and its role as an electrophile (as demonstrated by Miller et al.[1b] in the case of "I$^+$") is under investigation.

Summary

This work has demonstrated not only the high selectivity of the heterolysis of the carbon–bromine bond but also the selectivity of the type of products isolated. Although the detailed mechanism of carbonium ion formation has not been elucidated, it most reasonably arises from a fleeting bromoalkyl cation radical initially generated by the electrochemical process. In fact, all of the data presented here for alkyl bromide oxidations can be rationalized in terms of an initial one-electron transfer from the highest filled molecular orbital of the organic bromide to the electrode. In subsequent steps bromoalkyl cations undergo scission of the carbon bromine bond to form carbonium ions and oxidizable bromine.

These carbonium ions are responsible for the *N*-alkylacetamide products. Attack on nitriles by carbonium ions has ample precedent in the literature[6b] and, indeed, the formation of only rearranged *N-tert*-pentylacetamide from oxidation of neopentyl bromide, for example, requires a mechanism involving carbonium ions. This mechanism bears a striking resemblance to that for the decomposition of alkyldiazonium ions.[11] The latter are highly unstable and decompose to alkyl carbonium ions.

Experimental Section

Preparative Oxidations. For all experiments listed in Table I, the electrolysis cell consisted of a 20-mL water-jacketed flat-bottomed glass cylinder with a four-neck flat flange lid equipped with a platinum gauze as anode, a flat stainless steel spatula as a cathode, an Ag|0.1 M $AgNO_3$ in MeCN reference electrode with a fine fritted cylinder at one end, and a magnetic stirrer bar. The separation of the anode cell and the cathode cell was achieved by a medium fritted cylinder at one end of the cathode. In some preparative oxidations, especially with primary bromoalkanes, the anode potential was pulsed to $\sim$0 V for 1 s each 25 s. This was generally unnecessary, however, and had no discernible effect on the product. The potential was set at 2.35 V and the reactions were arbitrarily terminated, usually after passage of $\sim$4 mF/mol of added substrate. The workup procedure consisted of evaporation of much of the acetonitrile (*Caution:* not to dryness. If perchlorate electrolyte is used the anolyte contains perchloric acid!), addition of water, and extraction twice with chloroform and twice with methylene chloride. The combined organic layers were washed once with water and then dried over anhydrous magnesium sulfate. After filtration and evaporation to an oil the product mixtures were isolated by preparative gas chromatography (GLC), using a 10% SE-30 column, 2 m × 0.25 in., on Chromosorb W. The products isolated (Table I) were characterized by NMR and GLC comparisons with authentic samples.

In electrolysis experiments at lower substrate concentrations (Table II) a different type of three-compartment cell was used which has been described elsewhere.[12]

Cyclic Voltammetry. Voltammograms were recorded for each bromoalkane in twice-distilled acetonitrile. The cell volume was 10 mL and the electrolyte was tetrabutylammonium fluoborate. The Ag|0.1 M $AgNO_3$ reference electrode was separated from the working electrode by a glass frit. The auxiliary electrode was a platinum sheet (10 × 20 mm), and the working electrode was a platinum wire sealed in glass and ground smooth making a small platinum button. All the voltammograms showed no cathodic peak corresponding to reduction of an initially formed cation radical.

Instrumentation. A Perkin-Elmer IR spectrometer Model 137 and Varian XL100 NMR spectrometer were used for structure determination. Gas-liquid chromatography (GLC) analyses were performed by Varian Aerograph Model 920 gas chromatograph equipped with a thermal conductivity detector. The potentiostat employed is a Princeton Applied Research Model 173. Coulometry during preparative electrolysis was performed with a counter constructed from an Acromag integratortotalizer. A Universal Programmer Model 175 from Princeton Applied Research was used as a function generator to pulse the anode potential during preparative oxidations and to determine scan rates during cyclic voltammetry measurements. The recorder employed during these cyclic experiments is a Model 26000 A4 X–Y recorder from Bryans.

Materials. Acetonitrile (Fluka 99.5%) was purified by distillation from phosphorus pentoxide under nitrogen and stored over 4A molecular sieves. Anhydrous lithium perchlorate (Alfa Products) was used without any further treatment. Tetraalkylammonium fluoborates and perchlorate were purchased from Fluka AG and used without further purification. All bromoalkanes were commercial samples (Aldrich and BDH Labs).

Authentic Samples. *N*-Alkylacetamide derivatives (Table I) were prepared by two procedures described elsewhere.[1a] The availability of the starting material determined the method of choice. Thus, aminoalkanes were treated with acetic anhydride and tertiary alcohols were reacted with H_2SO_4 in acetonitrile. The NMR data for all products listed in Table I are in accordance with the literature and the elemental analyses of all the *N*-alkylacetamide products were satisfactory. The amides show characteristic absorptions in the IR in the regions 1650, 1670, and 3300 cm^{-1}.

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