Tetrahedron Letters No. 15, pp 1331 - 1334, 1978. Pergamon Press. Printed in Great Britain.

THE EFFECT OF CHAIN LENGTH ON THE ANODIC OXIDATION OF 1-BROMOALKANES

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(Received in UK 9 February 1978; accepted for publication 27 February 1978)

In a recent publication on the electrochemical oxidation of alkyl bromides, mostly branched ones, we found these substrates to undergo an exclusive carbon-bromine bond cleavage to form N-alkylacetamides via carbenium ion type intermediates. The present work reports on the effect of chain-length on the course of the anodic oxidation of 1-bromoalkanes in acetonitrile. The chain-length affects both yield and product distribution.

The alkyl bromides investigated were $Br(CH_2)_nCH_3$ (n = 1-7). The reactions were performed potentiostatically in a three compartment cell which was previously described[1], at room temperature. Platinum anode and lithium perchlorate (0.2N) as supporting electrolyte were employed. The oxidations were arbitrarily terminated after passage of ~ 4.5 Faraday per mole of added bromide. The work-up procedure and product isolation were conducted as described in ref. 1 and the results are summarized in the Table.

It can be seen from the Table that all substrates produce acetamido derivatives due only to C-Br bond breaking with no competition of C-H bond cleavage as was found in the electrooxidation of bromoadamantanes[2]. The current yield is strongly affected by chain-length; it decreases when the latter increases. It is also affected by change of concentration as can be seen from the Table in the case of the electrooxidation of 1-bromohexane.

Table

Electrochemical Data[a] and Oxidation Products

$Br(CH_2)_nCH_3$ n (conc.,M)	Total mF consumed	Current yield(%)[b]	Relative % of oxidation products[c]			
			$1-NHCOCH_3$ alkane	$2-NHCOCH_3$ alkane	$3-NHCOCH_3$ alkane	$4-NHCOCH_3$ alkane
1(1.6)	4.4	79	100			
2(1.6)	4.5	52	40	60		
3(1.6)	4.6	40	32	68		
4(1.56)	4.0	40	33	33	33	
5(1.54)	5.0	50	27	41	32	
5(1.0)	4.4	34	26	44	30	
5(0.2)	4.5	23	25	40	35	
6(1.47)	4.0	12	22	45	30	3
7(1.47)[d]	5.2	10	5	24	16	44

[a] All oxidations were carried out at 2.35V vs. Ag/0.1N $AgNO_3$ in acetonitrile. The cyclic voltammogram of each of the alkyl bromides mentioned above gave an ill-defined wave in the range 2.6 - 2.8.

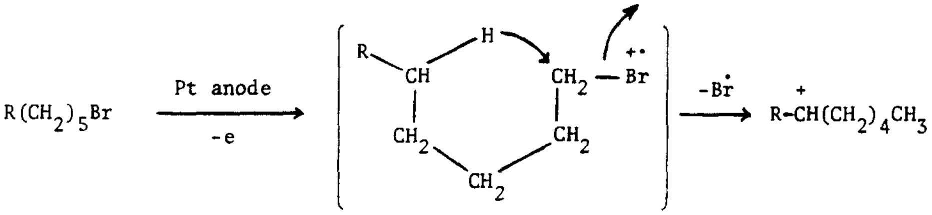
[b] Based on $2e^-$/mole.

[c] Percentages shown express product distributions of isolated materials determined by glc. On this basis the current yield is treated as 100%.

[d] A small amount of acetamide and other impurities were observed.

As is evident from the product distribution the isomerizations normally tend to form secondary alkyl products from primary ones, that is, in the direction of the more stable carbenium ion. However, isomerization does not always result in the total formation of the most stable carbenium ion. This fact implies that the rearrangement of the carbenium ion by hydride migration occurs in competition with the direct addition of the nucleophilic solvent acetonitrile to the carbenium ion type intermediate.

The formation of most of the products containing a secondary alkyl group attached to the nitrogen of the acetamide can be explained by presuming a series of consecutive 1,2-hydride shifts. However, $Br(CH_2)_nCH_3$ (n = 5-7) gave somewhat unusual results as indicated in the Table by the product distribution. For instance, the 4-acetamido derivative obtained from 1-octyl bromide is the major product whereas the corresponding derivative achieved from the electrooxidation of 1-heptyl bromide is a minor product. These results may be rationalised by postulating not only a series of consecutive 1,2-hydride shifts but also a remote rearrangement pathway. This is illustrated by the following scheme:



Although the scheme indicates hydride transfer and bromine atom departure as concerted, the possibility of a carbenium ion type intermediate formed as a result of initial bromine atom departure from the cation radical cannot be ruled out. It is clear that such a route, based on a six-membered ring transition state can only occur for compounds in which n ≥ 5. In fact, the anomalous product distribution is observed for hexyl, heptyl and octyl bromides. The driving force for the reaction is presumably the formation of a secondary carbenium ion type intermediate in place of the less stable primary one. Such a mechanism rationalises also the striking result that out of the four isomers of amides obtained from 1-octyl bromide, the 4-(N-acetamido) octane is the major product. For R = H, as in 1-bromopentane, the above rearrangement is less likely since there is no energy gain. In any event, such a transformation is degenerate and could only be detected with a labeling experiment. For compounds with n = 1-3, in which the remote rearrangement is impossible, the product distribution is consistent with a rearrangement mechanism based on a series of consecutive 1,2-hydride shifts.

References

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2. F. Vincent, R. Tardivel and P. Mison, Tet. Lett., 603 (1975); Tetrahedron, **32**, 1681 (1976).