

ANODIC ACETAMIDATION OF ADAMANTANE AND 1-HALOADAMANTANES

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The discovery^{2,3,4} that large alkanes can be directly oxidized in acetonitrile at a platinum anode provides access to the anodic chemistry of a variety of aliphatic compounds. In the present investigation, we have oxidized several adamantyl compounds as an initial step in elucidating this chemistry. This system was chosen because of the availability of 1-adamantyl derivatives, their low oxidation potential (compared to simpler analogs) and the simplicity of the observed chemistry. We report the first product studies of alkane, alkyl chloride and alkyl fluoride oxidations in aprotic media.

The reactions were performed potentiostatically in a three-compartment cell at room temperature. The anode was a platinum sheet of total area 12.5 cm². The reference electrode was Ag/0.1 N AgNO₃ in acetonitrile. The acetonitrile solvent was twice distilled from phosphorus pentoxide and lithium perchlorate was the electrolyte. The background current density at 2.50 V was less than 0.3 mA/cm². Initial currents were proportional to substrate concentration and were 15-100 times the background level. Up to 2 mmoles of the adamantyl derivative were oxidized exhaustively in each run. The reaction was terminated when the current fell to the background level. The products reported in Table I were isolated and were identified by standard spectroscopic techniques and comparison with published data.

The potentiostatic oxidation of adamantane thus produced only N-(1-adamantyl)acetamide.⁵ This implicates the 1-adamantyl carbonium ion in the reaction since it is known to lead to this product in acetonitrile^{5,6} and it is probable that this ion arises from direct anodic oxidation of adamantane since the steady state currents are proportional to adamantane

Table I. Products of Electrooxidation

Substrate	v^a	n^b	Products	% Yield of Amide ^c
Adamantane	2.35	2.1	N-(1-adamantyl)acetamide ⁵	(75)
1-Adamantyl bromide	2.35	3.2	N-(1-adamantyl)acetamide	(89)
1-Adamantyl chloride	2.50	2.1	N-(3-chloro-1-adamantyl)-acetamide	(91)
1-Adamantyl fluoride	2.50	2.4	N-(3-fluoro-1-adamantyl)-acetamide	(51)

^a Measured with respect to Ag/0.1 N AgNO₃ in acetonitrile.

^b Number of electrons transferred per molecule of added substrate.

^c Yields based on isolated products compared to added reactant.

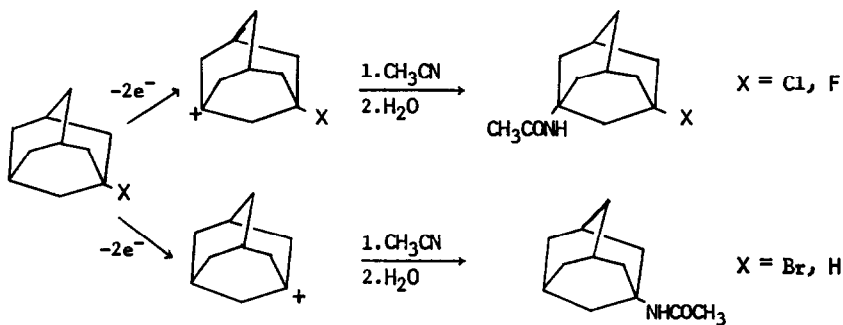
concentration. Cyclic voltammetry gave the $E_{p/2}$ shown on Table II. No cathodic peaks on the reverse sweep were seen at sweep rates up to 100 V/sec. For adamantane a plot of i_p vs. [sweep rate]^{1/2} was linear. This is consistent with a rate determining, diffusion controlled

Table II. Voltammetric Data

Substrate	$E_{p/2}^a$
Adamantane	2.36
1-Adamantyl bromide	2.54
1-Adamantyl chloride	2.64
1-Adamantyl fluoride	2.64

^a Sweep rate 0.5 V/sec. Ag/0.1 N AgNO₃ reference electrode.

electron transfer. It should be emphasized that the adamantane oxidation can be performed at potentials where the background current is very low and it does not seem reasonable to invoke a mechanism involving attack of oxidized solvent or electrolyte species on adamantane.⁷ A more reasonable scheme is the following:



Products from the direct oxidation of alkanes,⁸ alkyl chlorides, and alkyl fluorides in aprotic media have not been previously reported. Our initial results indicate that alkanes will produce carbonium ions and that the chloride and fluoride of aliphatic halides will not be reactive at the anode. The oxidation of n-propyl bromide has been suggested to give propyl cations⁹ in agreement with the above scheme.¹¹ Furthermore, it is known that a variety of alkyl iodides lead to alkyl acetamides via carbonium ions under these conditions.¹² These results give an initial delineation of the anodic chemistry of aliphatic halides.

We are continuing to use the adamantyl system to test the anodic reactivity of functional groups. It is hoped that these results will allow electrochemical techniques to be applied to simpler aliphatic systems and to synthetic problems.

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