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THE ELECTROCHEMICAL OXIDATION OF SOME ALIPHATIC HYDROCARBONS IN ACETONITRILE

M. Fleischmann and D. Pletcher

Department of Chemistry, The University, Southampton SO9 5NH

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In recent years, there has been considerable interest in the electrochemical oxidation of organic compounds in acetonitrile. The results reported in this communication show that, by using tetrafluoroborates or hexafluorophosphates instead of more common salts as the inert electrolyte, it is possible to extend the potential range in this solvent and that this extension in the anodic limit allows the study of aliphatic hydrocarbons containing weak carbon-hydrogen bonds (e.g. allylic or tertiary C-H bonds).

Previous work on the electrochemical oxidation of organic compounds in acetonitrile has almost exclusively used a perchlorate as the inert electrolyte. However, the results in table I indicate the considerable increase in potential range which may be obtained by using tetrafluoroborate or hexafluorophosphate as the inert electrolyte and these salts should allow the study of many compounds with high oxidation potentials. E_1 and E_{10} are the potentials at which 1 mA/cm^2 and 10 mA/cm^2 current, respectively, flow through the cell in the presence of inert electrolyte alone. The potentials are given with respect to the Ag$|10^{-2}$M Ag$^+$ reference electrode.

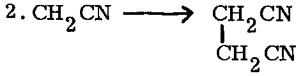
TABLE I

	E_1	E_{10}
0.1 M perchlorate	2.48	2.70
0.1 M tetrafluoroborate	2.91	3.35
0.1 M hexafluorophosphate	3.02	3.45

In perchlorate medium, the electrode reaction which governs the anodic limit has been suggested to be the oxidation of the anion (1), and the variation in the anodic limit with inert electrolyte is strong evidence that this is indeed the case. The complete oxidation mechanism was reported to be

$$ClO_4^- \longrightarrow ClO_4^\cdot + e$$

$$ClO_4^\cdot + CH_3CN \longrightarrow .CH_2CN + HClO_4$$



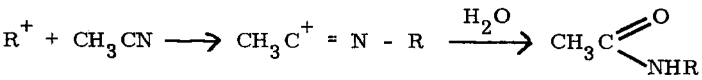
$$2.CH_2CN \longrightarrow \begin{array}{c} CH_2CN \\ | \\ CH_2CN \end{array}$$

and similar schemes could be written for the other anions.

Although the electrochemical oxidation of aromatic hydrocarbons has been widely studied (2,3), few reports on the oxidation of aliphatic hydrocarbons in acetonitrile have been published (3). In table II, electrochemical data are reported for a selection of aliphatic hydrocarbons in 0.14 M Et_4NBF_4/CH_3CN and a correlation between half wave potential and ionisation potential is shown in diagram I. Such a correlation has previously been reported for a series of more easily oxidised species in acetonitrile (4). The ionisation potentials are taken from Field and Franklin (5). The correlation suggests that it should be possible to study the oxidation of hydrocarbons with ionisation potentials less than 10.1, and this range corresponds to hydrocarbons with a weak C-H bond. Thus it can be seen that hydrocarbons with a tertiary or allylic C-H bond are oxidisable in BF_4^-/CH_3CN. As the data for ethylene do not fit the correlation in diagram I, it is likely that its oxidation mechanism is entirely different to that of the other hydrocarbons. The higher n-alkanes have ionisation potentials only slightly higher than 10.1 and it seems likely that in some similar solvent system, their oxidation would be possible.

Comparison of the diffusion currents for these aliphatic hydrocarbons with diffusion currents for compounds of known n value, suggests that two electrons are involved in the oxidation of these hydrocarbons. Thus the oxidation path is probably

$$RH \longrightarrow R^+ + H^+ + 2e$$



$$R^+ + CH_3CN \longrightarrow CH_3C^+ = N - R \xrightarrow{H_2O} CH_3C\begin{array}{l} {=}O \\ \diagdown NHR \end{array}$$

which is similar to the mechanism reported for the oxidation of alkyl iodides (6).

TABLE II

	$E_{\frac{1}{2}}$(volts)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (mV)	I.P.(e.V)
cyclohexene	2.05	128	9.05
2-octene	2.23	220	9.11
2-butene	2.26	162	9.29
1-octene	2.70	284	9.52
1-pentene	2.74	194	9.66
1-butene	2.78	260	9.72
propene	2.84	270	9.80
ethylene	2.90	290	10.56
iso-pentane	3.00	140	10.10
2-methylpentane	3.01	128	10.00
2, 2-dimethylbutane	3.28	120	10.19
n-octane	>3.4	-	10.24
n-heptane	>3.4	-	10.35
n-hexane	>3.4	-	10.24

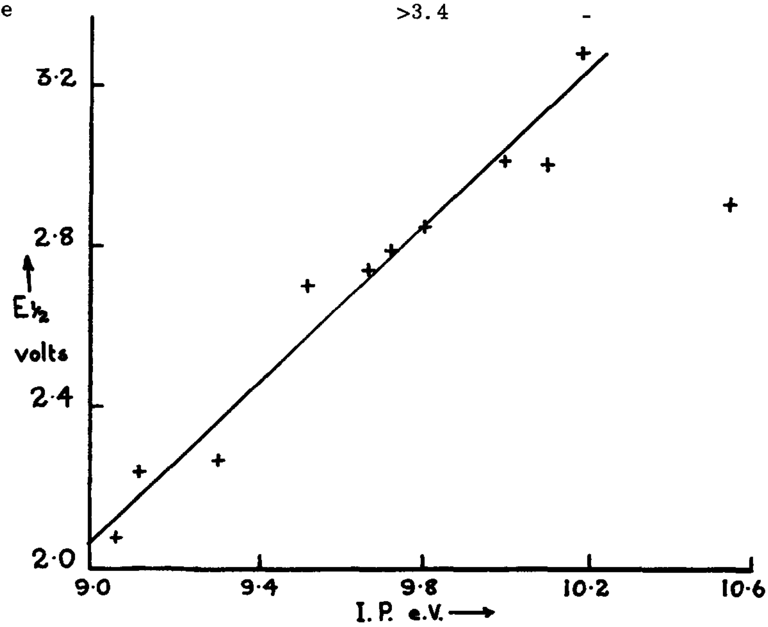


DIAGRAM I

Moreover, the oxidations are irreversible as would be expected for a mechanism which involves a bond fracture.

The current-potential curves were recorded using a platinum disc electrode, 0.12 sq. cm. in area and rotating at 1000 r.p.m., a three compartment cell and a potentiostat.

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