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THE ANODIC OXIDATION OF ALKANES IN FLUOROSULPHONIC ACID; A NOVEL SYNTHESIS OF αβ-UNSATURATED KETONES

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Previous work in these laboratories has shown that it is possible to produce carbonium ions by the direct anodic oxidation of certain aliphatic hydrocarbons in aprotic media.[1,2] Carbonium ions are, however, very short-lived in such solvents and it was therefore considered worthwhile to investigate the oxidation of aliphatic hydrocarbons in a solvent where carbonium ions are known to have greater stability; anhydrous fluorosulphonic acid is such a solvent.[3]

Since fluorosulphonic acid is not itself a conducting medium, it is necessary to add a base electrolyte, for example a metal fluorosulphorate or an ionisable organic compound. However, in view of the more interesting products, this report is restricted to results using acetic acid as the base electrolyte. It is a strong base in this solvent and exists mainly as the ion I[4] since water reacts with the fluorosulphonic acid thereby pulling the equilibria to the right

$$CH_3COOH + FSO_3H \rightleftarrows CH_3COOH_2^+ + FSO_3^- \rightleftarrows \underset{\text{I}}{CH_3CO^+} + FSO_3^- + H_2O$$

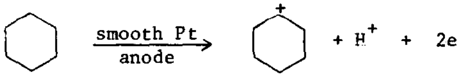
Current-potential curves were run at a smooth platinum electrode and at room temperature for various alkanes in fluorosulphonic acid containing 1.15 M acetic acid. It was found possible to oxidise all alkanes other than n-alkanes containing less than five carbon atoms. Half wave potentials for some alkanes are reported in Table 1; the potentials are quoted against a Pd/H_2 electrode in the solvent. All the oxidations are irreversible since cyclic voltammograms run at rapid potential sweep rates show no reduction peaks prior to hydrogen evolution. This does not necessarily indicate that the carbonium ions are unstable since it is not clear that the carbonium ion/radical couple is positive to hydrogen evolution at platinum in this medium.

TABLE 1

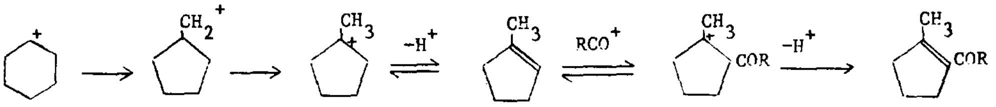
Hydrocarbon	$E_{\frac{1}{2}}$ (Volts)	Hydrocarbon	$E_{\frac{1}{2}}$	Hydrocarbon	$E_{\frac{1}{2}}$
n-pentane	2.01	n-decane	1.56	3-methylhexane	1.60
n-hexane	1.86	2-methylbutane	1.89	cyclopentane	2.01
n-heptane	1.73	3-methylbutane	1.73	cyclohexane	1.77
n-octane	1.64	3-methylpentane	1.68	cycloheptane	1.67
n-nonane	1.57	2-methylpentane	1.68	cyclooctane	1.20

A preparative scale controlled potential electrolysis was carried out at 1.85V on a solution of cyclohexane in fluorosulphonic acid containing 1.15M acetic acid at room temperature; the cyclohexane concentration was maintained by stirring the anode compartment with dry nitrogen saturated with cyclohexane. The anolyte was added to ice, neutralised and extracted with ether; v.p.c. analysis showed the presence of a single product together with some high boiling tars.

After isolation of the product by preparative v.p.c., it was examined by N.M.R., U.V., I.R. and mass spectroscopy. These spectra are consistent with the product (current yield 30%) being the αβ-unsaturated ketone II (R = Me). Identification was confirmed by comparison of its v.p.c. and spectral properties with those of an authentic sample of II (R = Me) prepared by the acetylation of 1-methylcyclopentene.[5] The source of the extra two carbon atoms in the product was confirmed as being the acetic acid by carrying out another electrolysis using propionic acid as the added electrolyte. In this case the product isolated was II (R = Et). These products are best explained by a mechanism involving the primary electrode process



followed by the series of reactions



II

It was found that the cyclohexyl carbonium ion formed by a chemical reaction, the addition of cyclohexene to a mixture of fluorosulphonic acid and acetic acid at -45°C also yielded II (R = Me) as the major product. It would seem from the completeness of the rearrangement of the cyclohexyl carbonium ion that it has considerable stability in this medium.

Controlled potential electrolyses have also been carried out in solutions of n-hexane, n-heptane, n-pentane, isopentane and cyclooctane in fluorosulphonic acid containing acetic acid. In each case the major products are αβ-unsaturated ketones but the products are a mixture of isomers whose carbon skeletons have not yet been defined. The electrochemical oxidation of alkanes in fluorosulphonic acid/acetic acid,however, appears to be a general reaction leading to αβ-unsaturated ketones.

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