The Partial Anodic Oxidation of n-Alkanes in Acetonitrile and Trifluoroacetic Acid

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The partial anodic oxidation of several n-alkanes at a smooth platinum electrode in acetonitrile or trifluoroacetic acid containing a tetra-alkylammonium tetrafluoroborate as the electrolyte have been studied. In both media these hydrocarbons give well-formed oxidation waves and a detailed investigation of the oxidation of n-octane in acetonitrile showed that at high potentials the electrode reaction is a diffusion-controlled two electron process while on the rising portion of the *i–E* curve, electron transfer is rate determining. Preparative electrolyses showed that in both acetonitrile and trifluoroacetic acid, the initial products of the electrode reaction are secondary carbonium ions which then react rapidly with the solvents to give mixtures of isomeric *N*-s-alkylacetamides (total yield 35—40%) and isomeric s-alkyl trifluoroacetates (total yields 50—80%) respectively.

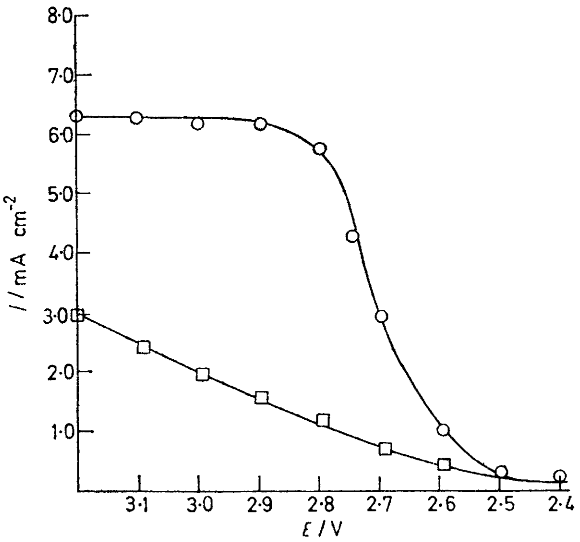
EARLIER papers have reported that the anodic oxidation of a wide range of aliphatic hydrocarbons is possible in several aprotic and weakly acidic solvents [1-3] which are highly resistant to oxidation. Furthermore detailed studies of the anodic oxidation of several olefins have appeared [2,4-6] and the common feature of these electrode reactions is that they involve direct oxidation of the hydrocarbon molecule and lead to cleavage of a carbon–hydrogen bond in the allylic position; the resulting carbenium ion undergoes a rapid reaction with the solvent or with added nucleophiles to yield allylically substituted products.

In this paper we report the extension of this work to the study of four alkanes in acetonitrile and of six alkanes in trifluoroacetic acid, two solvents from which the electrolysis products have been successfully isolated. Electroanalytical studies have shown that these alkanes may also be oxidised in other solvents including methylene chloride and nitroethane but in these less nucleophilic media the products have not yet been identified.

RESULTS

Oxidation of n-Octane in Acetonitrile + 0·1M-*Tetraethylammonium Tetrafluoroborate.*—Conventional steady state current–potential curves could not be run for this system since over *ca.* 1 min, the electrode became deactivated and the current decreased. This phenomenon is general for all hydrocarbons in these solvents but is readily overcome by pulse activation of the electrode (a short, periodic pulse to a potential around 0·0 V is applied to the electrode and this procedure prevents the current at the working potential from falling abnormally). This technique is not fully understood but can be widely utilised [2,4] and was employed in all experiments with a timescale of >10 s. For example the Figure shows an *i–E* curve for octane ($2{\cdot}5 \times 10^{-2}$M) in acetonitrile containing tetrabutylammonium tetrafluoroborate (0·1M) obtained in this way and it may be seen that octane gives a well formed oxidation wave with a half wave potential of 2·71 V *versus* the Ag/Ag$^+$ reference electrode and that $E_{\frac{3}{4}} - E_{\frac{1}{4}} = 110$ mV. Furthermore similar curves run for various concentrations of octane showed that over the whole potential range of the wave, the current is proportional to the concentration of octane ($10^{-2}\text{M} < [C_8H_{18}] < 10^{-1}\text{M}$).

Both cyclic voltammetry and experiments with a rotating disc electrode may be used to show that the plateau on the *i–E* curve is due to diffusion control of the electrode process; in cyclic voltammetry the peak current for the oxidation of octane varies as the square root of the potential scan rate and in the limiting current region, the current varies as the square root of the rotation rate of the disc electrode. In addition cyclic voltammetry shows the absence of stable, reducible intermediates in the electrode reaction since even at rapid potential sweep rates there are no peaks on the scan towards negative potentials.



Steady state curves for: □ acetonitrile + 0·1M-Bu$_4$NBF$_4$; ○ acetonitrile + 0·1M-Bu$_4$NBF$_4$ + 25mM-n-octane

Coulometry was carried out on a solution of octane (0·1M) in the solvent–electrolyte combination at 3·1 V, a potential well into the limiting current region and *n*, the number of electrons per molecule of octane transferred during the electrode process, was determined as a function of the octane consumed, the removal of octane being followed by g.l.c. analysis. The *n* values, corrected

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[1] M. Fleischmann and D. Pletcher, *Tetrahedron Letters*, 1968, 6255.

[2] D. B. Clark, M. Fleischmann, and D. Pletcher, *J. Electroanalyt. Chem.*, 1973, **43**, 133.

[3] G. Fiori, personal communication.

[4] D. B. Clark, M. Fleischmann, and D. Pletcher, *J. Electroanalyt. Chem.*, 1972, **36**, 137.

[5] T. Shono and A. Ikeda, *J. Amer. Chem. Soc.*, 1972, **94**, 7892.

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for the contribution to the current from the background, are given in Table 1. It is apparent that early in the electrolysis $n = 2$, but in the later stages this value increases probably due to the further oxidation of products accumulating in the electrolysis solution. Certainly it has been shown that *N*-alkylacetamides do oxidise under the conditions of the experiment.[7]

TABLE 1

n Value as a function of octane consumed. The coulometry was carried out on a solution containing octane (0·1M) and $(C_4H_9)_4NBF_4$ (0·1M) in CH_3CN and at a potential of +3·1 V *versus* the Ag/Ag^+ reference electrode. The octane consumed was determined by g.l.c. analysis. The *n* values are corrected for the contribution to the current from the background and are the average of several experiments

Octane consumed (%)	*n* Value
10	2·00
20	2·01
40	2·15
65	2·50

TABLE 2

Yields and distribution of isomers of acetamidoalkanes from the controlled potential of alkanes at a Pt anode in CH_3CN–0·1M-Bu_4NBF_4

Alkane	$E_{p/2}$/V [a]	Total current [b] yield (%)	Total organic [c] yield (%)	Isomer distribution (%) 2-Isomer	3-Isomer	4-Isomer
n-Octane	2·80	35	45	33	35	32
n-Heptane	2·80	38	48	45	45	10
n-Hexane	2·84	35	45	55	45	
n-Pentane	2·88	40	50		Not resolved	

[a] Half peak potential from a linear potential sweep at 50 mV s^{-1} quoted *versus* the Ag/10^{-2}M-$AgNO_3$ reference electrode. [b] Current yield after the passage of 2·5 C cm^{-3} of anolyte. At higher conversions, these yields decreased slightly. [c] Based on alkane consumed.

The *i–E* curves obtained for solutions of n-pentane, n-hexane, and n-heptane in acetonitrile showed their behaviour to be essentially the same as that of n-octane. The lower alkanes (*i.e.* methane—butane) did not give well defined oxidation waves.

Preparative Electrolyses in Acetonitrile.—Controlled potential electrolyses were carried out on saturated solutions of each of the four n-alkanes in acetonitrile containing tetrabutylammonium tetrafluoroborate (0·1M) at a potential on the plateau of an *i–E* curve. The major products isolated from each electrolysis were a mixture of isomeric acetamidoalkanes; the yields and the isomer distributions are summarised in Table 2. In all cases the anolyte became acidic during the electrolysis.

During studies of the anodic oxidation of propene in acetonitrile it was noted that the presence of acetic acid in the electrolysis solution increased the yield of *N*-allylacetamide.[4] This was not the case with the n-alkanes as the addition of 0·5% v/v acetic acid did not significantly alter the yield of acetamidoalkanes. Higher quantities of acetic acid caused a decrease and with 5% acetic acid, a low yield (<5%) of the corresponding alkyl acetates was detected in the products.

Electrolyses in Trifluoroacetic Acid.—*i–E* Curves were run on solutions of the n-alkanes in trifluoroacetic acid containing tetrabutylammonium tetrafluoroborate (0·4M) and these showed well formed oxidation waves for the hydrocarbons at potentials slightly less positive than those where solvent decomposition occurred. The characteristics of these oxidation waves were similar to those found for n-octane in acetonitrile.

Controlled potential electrolyses were performed for each of the four n-alkanes in this medium, the potentials chosen being just on the plateau of the *i–E* curves. In all cases the major products were alkyl trifluoroacetates; their yield and the isomer distributions are shown in Table 3. *i–E* Curves run on solutions of cyclohexane and isobutane indicated that these hydrocarbons also undergo oxidation in this solvent. Analysis of the products from preparative electrolyses showed that for these alkanes, a single isomer is produced. The current yield of cyclohexyl trifluoroacetate was 60% and of isobutyl trifluoroacetate 55%.

DISCUSSION

The slope of the *i–E* curve for the oxidation of n-octane in acetonitrile in the region where the current changes rapidly with potential indicates that, probably, a single electron is transferred prior to and during the rate-determining step. Furthermore it is apparent from coulometry for this alkane in acetonitrile and from the products identified in both solvents that overall, two electrons are involved in the electrode process. Hence in the case of octane the mechanism of the anode reaction is analogous to that found for propylene,[4] *i.e.* $C_8H_{18} \xrightarrow{-e} C_8H_{18}^{\cdot+} \xrightarrow[\text{fast}]{-e-H^+} C_8H^+_{17}$.

Certainly the limiting current plateau is due to diffusion control of the electrode process. There is also every indication that the oxidation of the other alkanes proceeds in an identical manner. The contrast in the

TABLE 3

Yields and distribution of isomers of trifluoroacetoxyalkanes from the controlled potential oxidation of alkanes at a Pt anode in CF_3CO_2H–0·4M-Bu_4NBF_4

Alkane	Total current yield (%)	Isomer distribution (%) 2-Isomer	3-Isomer	4-Isomer
n-Octane	75	33	33	33
n-Heptane	75	45	45	10
n-Hexane	60		Not resolved	
n-Pentane	50		Not resolved	

[a] Current yield after the passage of 2·5 C cm^{-3} of anolyte. Yield decreases only very slightly with increasing duration of the electrolysis.

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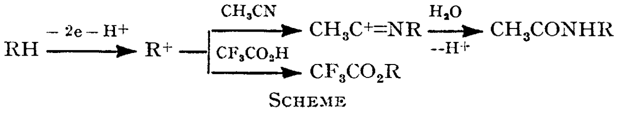
[7] J. F. O'Donnell and C. K. Mann, *J. Electroanalyt. Chem.*, 1967, **13**, 157 and 162.

mechanism for the oxidation of these alkanes in these solvents and the strongly acidic solvent, fluorosulphonic acid, should be noted; in the latter solvent, the electroactive species is the protonated form of the alkane.[8]

The final products from the anodic oxidation of the n-alkanes in acetonitrile and trifluoroacetic acid are a proton and the solvolysis product of the carbenium ion intermediate. Hence the major organic products are *N*-s-alkylacetamides and s-alkyl trifluoroacetates respectively (Scheme).



$$\mathrm{RH} \xrightarrow{-2e-\mathrm{H}^+} \mathrm{R}^+ \begin{cases} \xrightarrow{\mathrm{CH_3CN}} \mathrm{CH_3C^+{=}NR} \xrightarrow[-\mathrm{H}^+]{\mathrm{H_2O}} \mathrm{CH_3CONHR} \\ \xrightarrow{\mathrm{CF_3CO_2H}} \mathrm{CF_3CO_2R} \end{cases}$$

SCHEME

Furthermore the current yields of the products are substantial, particularly in trifluoroacetic acid. Indeed, the nucleophilic strength of these two solvents must represent about the optimum for high yields of products from alkane oxidation; in less nucleophilic solvents, degradation and tarring seem to be the predominant reactions while more nucleophilic media undergo oxidation more readily than the alkane.

It is of interest to consider further the nature of the carbenium ions produced in the electrode reaction and their subsequent rearrangements. First, the similarity in the isomer distribution in acetonitrile and trifluoroacetic acid and the absence of rearrangement to a tertiary cation should be noted. Secondly, although electrode reactions are generally considered to involve ' free cations ' rather than the stabilised cations met in solvolysis reactions,[9] comparison of the isomer distributions found in this work with those found in other reactions involving ' free cations ' shows marked differences. For example the deamination of n-octylamine in acetic acid[10] and the condensation of oct-1-ene and acetonitrile in liquid hydrogen fluoride[11] lead to totally different isomer distributions and this would suggest that the isolated electrolysis products do not arise by rearrangement of a single carbonium ion. Further the latter work[11] showed that the proportion of *N*-1-methylheptylacetamide increases with an increase in the ratio $[\mathrm{CH_3CN}]:[1\text{-}\mathrm{C_8H_{16}}]$ and extrapolation to our conditions would indicate that little or no carbonium ion rearrangement would occur prior to solvolysis. Indeed it would seem that the isomer distributions observed from the electrolysis of n-alkanes must arise from the formation of a mixture of secondary carbonium ions at the electrode, *i.e.* the first electron transfer leads to a cation radical in which the secondary C–H bonds are of similar strength and hence unselective cleavage results. If the C–H bond cleavage were totally unselective one would predict an isomer distribution of 1 : 1 : 1 for octane, 2 : 2 : 1 for heptane, and 1 : 1 for hexane and these are very close to the distribution found in this work. The absence of a solvent effect between the results in acetonitrile and in trifluoroacetic acid also argues against an important role for carbonium ion rearrangement as does the isolation of single isomers from the oxidation of cyclohexane and isobutane in trifluoroacetic acid.

In contrast to the work of Whiting,[10] no olefin was detected amongst the electrolysis products. Although olefins are readily oxidised at the potentials used for the electrolyses, the products of their oxidation are allylically substituted compounds[2,5] and these were also absent from the electrolysis products. Hence loss of proton from the carbonium ion does not appear to be an important reaction route.

The lower yield of products in acetonitrile compared with trifluoroacetic acid requires some comment. Certainly the alkylacetamides are less stable to oxidation under the electrolysis conditions than the corresponding trifluoroacetates but this is unlikely to be the sole factor. It seems likely that, as postulated to explain the data on the oxidation of propene in acetonitrile, the intermediate nitrilium ions must have alternative reaction paths. This is also indicated by the results from the condensation of oct-1-ene and $\mathrm{CH_3CN}$ in HF[11] where the extrapolated yield of amide in pure acetonitrile would be very low.

EXPERIMENTAL

Reagents.—Acetonitrile (Koch-Light) was purified as described earlier.[4] The resulting solvent contains a significant quantity of an impurity which azeotropes with acetonitrile[12] and it is not removed until the greater part of the charge has been distilled. Unfortunately this impurity is electroactive in the region of interest and the *i–E* curves with least interference were obtained with later solvent fractions.

Trifluoroacetic acid and the n-alkanes (B.D.H.) were used as supplied. Alkyl trifluoroacetates were prepared by mixing equimolar quantities of the corresponding alcohols and trifluoroacetic anhydride followed by distillation. The secondary octyl- and pentyl-acetamides were prepared by literature methods.[11]

Tetra-n-butylammonium tetrafluoroborate was precipitated from water by mixing aqueous solutions of tetra-n-butylammonium hydrogen sulphate (AB Biotec Labtjanst) and sodium tetrafluoroborate, filtering, and extracting into methylene chloride. After removing the bulk of the methylene chloride the product was precipitated by addition of ether, recrystallised from acetone–ether and dried in a vacuum oven at 80 °C for 48 h.

Equipment.—The electrochemical experiments were carried out in three electrode cells using a Chemical Elec-

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[9] J. T. Keating and P. S. Skell, ' Carbonium Ions,' eds. G. Olah and P. von R. Schleyer, Interscience, New York, vol. II, 1970.

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[12] J. F. O'Donnell, J. T. Ayres, and C. K. Mann, *Analyt. Chem.*, 1965, **37**, 1162.

tronics valve potentiostat, a Chemical Electronics pulse generator, type R.B.1 and, where necessary, a Bryan's Series 26000 XY recorder, a Telequipment oscilloscope type D53, or an electronic integrator.

In acetonitrile, the reference electrode was a silver wire dipping into acetonitrile containing tetrabutylammonium tetrafluoroborate (0·1M) and silver nitrate (10^{-2}M) while for work in trifluoroacetic acid a commercial saturated calomel electrode (Radiometer) was used. In both solvents the reference electrode was separated from the working electrode by a Luggin capillary and tap while the working and Pt secondary electrodes were separated by a No. 2 glass sinter. For rotating disc experiments the working electrode was a Pt disc (diameter 2 mm) surrounded by a Teflon sheath and the cell had a vertical Luggin capillary while in other kinetic experiments the working electrode was a Pt wire, area 0·1 cm^2 and the cell had a horizontal Luggin capillary. In preparative experiments the working electrode was a 1 cm^2 Pt gauze. All cells were closed to the atmosphere.

G.l.c. analysis was carried out on a Pye 104 chromatograph with a flame ionisation detector. N.m.r. spectra were recorded on a Perkin-Elmer R12 spectrometer at 60 MHz, i.r. spectra with a Unicam SP 200 instrument, and mass spectra with an AEI-MS 12 mass spectrometer which had a direct inlet system from a Pye 104 chromatograph.

Experimental Procedures.—' Steady state ' and rotating disc experiments were carried out using pulse activation of the Pt electrode. A potential–time square wave with 7 s at the potential of interest and 3 s at 0·0 (in acetonitrile) or +0·2 V (in trifluoroacetic acid) was applied to the electrode. The current was read at the end of the pulse to the working potential which was varied manually. For controlled electrolyses the square wave pulse sequence was slightly different, 2·7 s at the working potential followed by 0·3 s at 0·0 V (0·2 V in trifluoroacetic acid). The quantitative g.l.c. analysis was carried out as follows. The amides were analysed on a 3 m column of 25% Apiezon L on Celite, temperature programmed from 70 to 200 °C at 8° min^{-1} with a nitrogen flow rate of 70 ml min^{-1}. The trifluoroacetates were anslysed on a 3 m column of 20% silicone oil (SE 30) on Celite at 100 °C or a 2 m column of 10% polyethylene glycol adipate at 70%; in both cases the nitrogen flow rate was 50 ml min^{-1}.

For preparative electrolyses the cell was filled with solvent containing electrolyte and the anolyte was saturated with the alkane. Excess of alkane was present so that its concentration was maintained constant. The anode compartment was stirred with nitrogen throughout the electrolysis and the electrode was kept active using the potential–time profile described above. Quantitative yields of products were estimated by injecting the anolyte solution directly onto the g.l.c. apparatus; solutions of known concentrations of octylacetamide and octyl fluoroacetate were used as standards for all products. Initial identification of the products were made by reducing the anolyte solution to a small volume, precipitating the electrolyte with ether and after filtering off the solid, vacuum distilling the residue and examining the residue as follows.

In acetonitrile. (i) Octane electrolysis. The residue from this electrolysis showed three peaks on g.l.c. analysis. The retention times of these peaks were identical to those for a mixture of secondary *N*-octylacetamides prepared by a literature method.[11] Further comparison of the i.r. and n.m.r. spectra for the residue with that for the mixture and g.l.c.–mass spectra for each of the three isomers confirmed the nature of the electrolysis products, δ(CDCl$_3$) 0·6—1·6 (17H, m), 1·95 (3H, s), $\nu_{max.}$ (liquid film) 1160, 1310, 1380, 1470, 1550, 1640, 2900, 3050, and 3250 cm^{-1}, *m/e* (1-methylheptyl) 86, 44, 43, 60, 41, 58, 171, 100, 114, and 142, *m/e* (1-ethylhexyl) 100, 58, 142, 43, 41, 60, 30, 171, 72, and 29, *m/e* (1-propylpentyl) 86, 72, 114, 128, 43, 30, 41, 60, 171, 100.

(ii) Heptane electrolysis. Products were identified on the basis of g.l.c.–mass spectra only, *m/e* (1-methylhexyl) 44, 86, 43, 60, 58, 100, 157, 41, 87, and 128, *m/e* (1-ethylpentyl) 58, 86, 100, 43, 128, 72, 157, 41, 60, and 114, *m/e* (1-propylbutyl) 72, 114, 43, 30, 60, 41, 86, 56, 55, and 73.

(iii) Hexane electrolysis. Products were identified on the basis of g.l.c.–mass spectra only, *m/e* (isomer mixture) 44, 58, 72, 43, 86, 100, 114, 60, 41, and 143.

(iv) Pentane electrolysis. The g.l.c.–mass spectrum of the electrolysis residue was identical to that of an authentic sample prepared by a chemical method.[11] The isomers were not resolved by our g.l.c. method, *m/e* 58, 44, 86, 43, 100, 129, 72, 41, 60, and 30.

In trifluoroacetic acid. (i) Octane, cyclohexane, and isobutane electrolysis. Identification of the electrolysis products was by comparison of g.l.c. retention times and g.l.c.–mass spectra with those of authentic samples prepared from the corresponding alcohol with trifluoroacetic anhydride. (a) n-Octane: *m/e* (1-methylheptyl) 70, 55, 41, 43, 56, 69, 57, 83, 42, and 29, *m/e* (1-ethylhexyl) 41, 55, 83, 45, 69, 70, 56, 43, 57, and 29, *m/e* (1-propylpentyl) 55, 69, 45, 41, 70, 56, 43, 57, 112, and 51; (b) cyclohexane: *m/e* 82, 67, 54, 41, 83, 55, 69, 39, 81, and 56; (c) isobutane: *m/e* 41, 57, 155, 69, 39, 29, 55, 56, 43, and 61.

(ii) Other electrolyses. Products were identified on the basis of g.l.c.–mass spectra. Heptane: *m/e* (1-methylhexyl) 56, 69, 41, 43, 45, 55, 57, 70, 98, and 141, *m/e* (1-ethylpentyl) 41, 69, 56, 57, 98, 29, 70, 43, and 55, *m/e* (1-propylbutyl) 69, 45, 41, 55, 51, 56, 57, 29, and 43; hexane: *m/e* (isomer mixture) 55, 43, 41, 84, 56, 69, 42, 141, 91, and 113; pentane: *m/e* (isomer mixture) 55, 43, 41, 70, 71, 91, 141, 69, 58, and 155.

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