The Electrochemical Behaviour of Alkanes in Fluorosulphonic Acid

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The anodic oxidation of several alkanes in fluorosulphonic acid containing various carboxylic acids has been studied, the product in each case being an αβ-unsaturated ketone. These species can undergo further oxidation and electroanalytical techniques have been used to define the optimum conditions for the formation of the αβ-unsaturated ketones. The oxidation potential for an alkane in fluorosulphonic acid is shown to depend on the proton donating ability of the medium and the nature of this ' pH ' dependence shows that there is a rapid protonation equilibrium prior to the electron transfer step and that it is the protonated alkane which undergoes oxidation. In addition, in more acid solutions, the alkanes are shown to undergo spontaneous chemical reactions which yield similar products. Possible mechanisms for the chemical and anodic reactions are discussed and it is shown that electroanalytical techniques may be used to investigate the chemistry of alkanes in fluorosulphonic acid. The application of these reactions to synthesis is considered.

In an earlier communication [1] it was reported that alkanes with more than four carbon atoms could be oxidised at a smooth platinum anode in fluorosulphonic acid which had been made to be 1M in acetic acid (a strong base in this solvent). The products of these anode reactions were αβ-unsaturated ketones with two more carbon atoms than the starting materials and it was shown that the acetyl fragments in the product are derived from the acetic acid.

Later work reported in this paper has shown that in fluorosulphonic acid solutions which contain less added base the anodic oxidation of butane, propane, and ethane becomes possible. Further, in fluorosulphonic acid solutions to which an acid or only small quantities of the base have been added, it is clear that the alkanes undergo spontaneous chemical reactions which can give the same products as the electrode reactions provided acetyl cations are present in the system; the ' pH ' at which the chemical reaction occurs depends on the temperature and on the structure of the hydrocarbon.

These experiments clearly demonstrate that the proton donating ability of the medium is of key importance in determining both the electrode behaviour and the chemistry of alkanes in fluorosulphonic acid solution. Regrettably the data required to set up an exact pH scale for solutions with fluorosulphonic acid as the solvent are not presently available but using acetic acid, sodium fluorosulphonate, and antimony pentafluoride, known strong acids and bases in this system,[2-4] it is possible to study the electrochemistry in fluorosulphonic acid

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[1] J. Bertram, M. Fleischmann, and D. Pletcher, *Tetrahedron Letters*, 1971, 349.

[2] G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, 1967, **89**, 3591.

[3] R. C. Thompson, J. Barr, R. J. Gillespie, J. B. Milne, and R. A. Rothenbury, *Inorg. Chem.*, 1965, **4**, 1641.

[4] J. Barr, R. J. Gillespie, and R. C. Thompson, *Inorg. Chem.*, 1964, **3**, 1149.

solutions containing various quantities of acid or base.

This paper reports the results of such a study, discusses the mechanism of the electrode process, and illustrates the use of electroanalytical techniques to investigate the chemistry of alkanes in this highly acidic solvent.

RESULTS

Preliminary Experiments.—Half wave potential data have been reported earlier[1] for alkanes in fluorosulphonic acid which had been made to be 1·14M in acetic acid. The Table shows half peak potentials for a series of alkanes in a medium which contains approximately one tenth as much base. The major difference between these media is that in the less basic solution, propane and butane undergo anodic oxidation. It should be noted that the value reported previously for the anodic oxidation of cyclohexane in fluorosulphonic acid containing acetic acid (1·14M) is erroneous; the correct value is +1·07 V. In addition the half peak potentials for the oxidation of alkanes depend on the proton donating ability of the medium and this will be discussed later. All the oxidation potential data reported are taken from *i–E* curves run under conditions where only one major oxidation wave is observed; under slightly modified conditions more complex behaviour is found and this will again be discussed later.

Half peak potentials for the oxidation of alkanes in fluorosulphonic acid containing 0·1M-KSO_3F and 25 mM-HOAc. The potentials are quoted *versus* the Pd–H_2 electrode in this solvent–electrolyte combination. Curves run with potential scan rate of 0·1 V s^{-1} at a smooth Pt electrode and at room temperature

Alkane	$E_{p/2}$	Alkane	$E_{p/2}$
Propane	2·21	n-Octane	1·42
n-Butane	1·85	n-Decane	1·37
n-Pentane	1·74	Cyclohexane	1·12
n-Hexane	1·54	Isobutane	1·00

At both concentrations of added base, the cyclic voltammograms show no peaks on the sweep towards negative potentials for the reduction of stable or quasi-stable intermediates produced in the electrode reaction and the variation of the peak currents with potential scan rate shows the peak current to be diffusion controlled. The half peak widths, *i.e.* $E_p - E_{p/2}$ are in the range 110—140 mV.

The curves in Figure 1 show the effect of using the acid, antimony pentafluoride, as the supporting electrolyte. Curve (i) shows the background current for fluorosulphonic acid which has been made to be 0·15M in fluorosulphonate ion and curve (ii) the background current after the addition of sufficient antimony pentafluoride to make the solution contain excess of the acid. The difference clearly shows that with the solutions which contain an added base the limiting process is the oxidation of fluorosulphonate ion. Curve (iii) shows that in the medium containing 0·1M-acid (SbF_5) the oxidation of ethane becomes possible.

At room temperature and in the solutions containing high concentrations of added base (>0·1M), the alkanes are stable. In solutions which contain an added acid or low concentrations of added base (<0·01M), the *i–E* curves for the oxidation of alkanes can show changes with time. In particular the oxidation wave for the parent alkane decreases with time and other waves can appear. Thus it is clear that a chemical reaction is occurring. The rate of this reaction depends on the structure of the alkane (branched >n-alkanes) and increases with acidity and temperature. Hence in solutions where such changes occur, the electrochemistry is limited to experiments on a short time-scale.

Preparative Experiments.—Preparative scale anodic oxidations were carried out on saturated solutions of a series of alkanes in fluorosulphonic acid containing acetic acid (1·14M) at room temperature and at a potential just on the plateau of an *i–E* curve. The products isolated or identified from these electrolyses allow certain general features of the anodic oxidation of alkanes in fluorosulphonic acid solutions containing carboxylic acids to be deduced. (i) When the supporting electrolyte is acetic acid the products are αβ-unsaturated ketones with two more carbon atoms than the starting material; the total yield is good (in the region of 50—70%). (ii) The origin of the acetyl fragment is the acetic acid. This may be shown using different carboxylic acids, RCO_2H, when an αβ-unsaturated ketone containing an additional RCO group is formed. (iii) The n-alkanes give rise to a mixture of isomers. (iv) The distribution of products shows that the carbon skeletons have undergone rearrangements typical of carbenium ion intermediates. (v) The products show that C–C bond cleavage does not occur during the reaction.

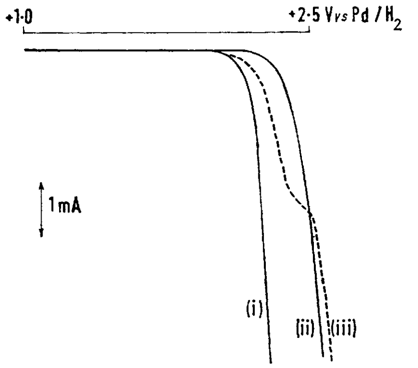
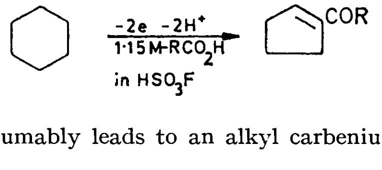


FIGURE 1 *i–E* Curves run at 0·1 V s^{-1} for solutions in fluorosulphonic acid containing (i) 0·1M-potassium fluorosulphonate and 25 mM-acetic acid, (ii) 0·1M-potassium fluorosulphonate, 25 mM-acetic acid, and 0·25M-antimony pentafluoride, and (iii) solution (ii) saturated with ethane

A typical example is the anodic oxidation of cyclohexane which leads to a single product with a rearranged carbon skeleton. The yield is 50—60% when the carboxylic acid is acetic, propionic, or hexanoic acid. The electrode reaction presumably leads to an alkyl carbenium ion intermediate.

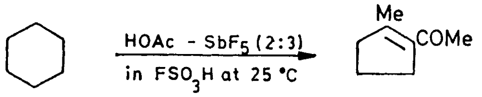


It has already been stated that in solutions which had been made to be less than 0·1M in added base, the alkane can undergo a spontaneous chemical reaction. Certain alkanes may also be activated in the more basic solutions at elevated temperatures. For example isobutane may be converted to methyl 2-methylprop-1-enyl ketone at 60 °C. This ketone accounted for 95% of the product isolated but the rate of the reaction is not fast and the conversion low in a single pass of the gas through the solution. The same

$$Me_3CH \xrightarrow[60\ ^\circ C]{FSO_3H\text{-}HOAc\ (2{\cdot}0M)} Me_2C{=}CH{\cdot}COMe$$

product may be isolated from an anodic oxidation of isobutane at room temperature.

Where thermal activation of the alkane in the basic fluorosulphonic acid solution is not possible a chemical synthesis of the αβ-unsaturated ketones can be attempted using the chemical reaction which occurs at lower ' pH '. For the synthesis to proceed at a reasonable rate, it is normally necessary to have a high concentration of acetyl cations in the system and this situation is only possible at a suitable ' pH ' if the acetyl cations are produced by titrating the acetyl fluorosulphonate with an acid such as antimony pentafluoride in fluorosulphonic acid. For example, methyl 2-methylcyclopent-1-enyl ketone is readily produced in 45% yield (based on cyclohexane) from the addition of cyclohexane to a fluorosulphonic acid solution of acetic acid (1·0M) which has been approximately neutralised by the addition of the calculated quantity of antimony pentafluoride. Under similar conditions ethane formed methyl 2-methylprop-1-enyl ketone. In these chemical reactions the same intermediate carbenium ions are formed probably *via* protonation and loss of hydrogen (see Olah *et al.*[5-13] and Brouwer and Hogeveen).[14]



$$C_2H_6 \xrightarrow[\text{in } FSO_3H \text{ at } 25\ ^\circ C]{HOAc\ -\ SbF_5\ (1{:}1)} Me_2C{=}CH{\cdot}COMe$$

Experiments where the syntheses were attempted by protonation of the olefin were less successful and considerable tarring was observed, even at −45 °C when the olefin was added to fluorosulphonic acid which had been made to be 1·0M in acetic acid. Low yields of the αβ-unsaturated ketones could, however, be identified.

In comparing the anodic and chemical synthesis of substituted olefins from saturated alkanes in fluorosulphonic acid, the difficulties of using antimony pentafluoride must be weighed against the cost of electricity and the availability of electronic control equipment. However, both techniques show promise of some generality since a number of cations, *e.g.* NO_2^+, I^+, are readily formed in this solvent and would be expected to be capable of reacting in an analogous fashion to the acetyl cation. The preparative aspects of these reactions are the subject of further study.

Mechanistic Studies.—A. Chemical reaction following electron transfer. During preliminary studies of the *i–E* curves for the anodic oxidation of alkanes in fluorosulphonic acid to which acetic acid had been added as the supporting electrolyte, it was noted that under certain conditions, some hydrocarbons gave a second oxidation peak at more anodic potentials to that for the alkane oxidation. Cyclohexane was one of these hydrocarbons and it was chosen for a more detailed investigation.

Linear potential sweep voltammetry was carried out at a stationary platinum electrode on solutions of cyclohexane in fluorosulphonic acid to which acetic acid had been added. Figures 2—4 respectively show the results of experiments where the *i–E* curves were recorded as a function of (i) potential sweep rate at constant acetic acid concentration and temperature, (ii) acetic acid concentration at constant potential sweep rate and temperature, and (iii) temperature at constant acetic acid concentration and potential sweep rate. It can be seen that the ratio of the height of the second peak to that of the first increases with increasing temperature and increasing concentration of acetic acid but decreases with an increase in the potential scan rate. This is exactly the type of behaviour to be expected if the second peak is due to the oxidation of a species formed in a slow chemical reaction from the product of the first process while the rate of this chemical reaction is dependent on the concentration of acetic acid and determines the quantity of the electroactive species for the second process. In these

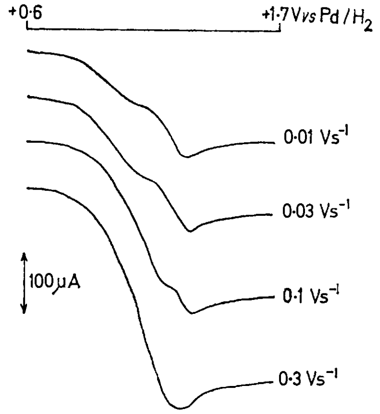


FIGURE 2 *i–E* Curves for the oxidation of 5mM-cyclohexane in fluorosulphonic acid containing 0·4M-acetic acid at various sweep rates

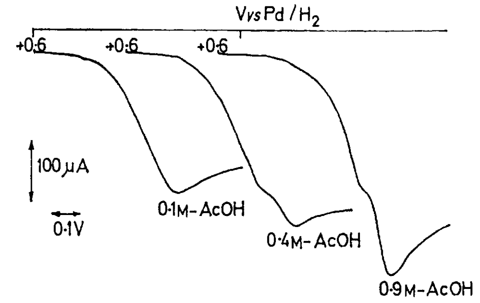


FIGURE 3 *i–E* Curves for the oxidation of 5mM-cyclohexane in fluorosulphonic acid containing various acetic acid concentrations. Potential sweep rate 0·1 V s^{-1}

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[5] G. A. Olah, J. M. Bollinger, C. A. Cupas, and J. Lucas, *J. Amer. Chem. Soc.*, 1967, **89**, 2692.

[6] G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, 1967, **89**, 2227.

[7] G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, 1967, **89**, 4739.

[8] G. A. Olah and R. H. Schlosberg, *J. Amer. Chem. Soc.*, 1968, **90**, 2726.

[9] G. A. Olah, Y. Halpern, J. Shen, and J. K. Mo, *J. Amer. Chem. Soc.*, 1971, **93**, 1251.

[10] G. A. Olah and J. A. Olah, *J. Amer. Chem. Soc.*, 1971, **93**, 1256.

[11] G. A. Olah, G. Klopman, and R. H. Schlosberg, *J. Amer. Chem. Soc.*, 1969, **91**, 3261.

[12] G. A. Olah, *J. Amer. Chem. Soc.*, 1972, **94**, 808.

[13] G. A. Olah, *Chem. in Britain*, 1972, 281.

[14] D. M. Brouwer and H. Hogeveen, *Progr. Phys. Org. Chem.*, 1972, **9**, 179.

systems acetic acid has the dual role of base and source for acetyl cations [2] and it is not apparent from these experiments whether the rate-determining chemical reaction involves loss of proton or attack by an acetyl cation.

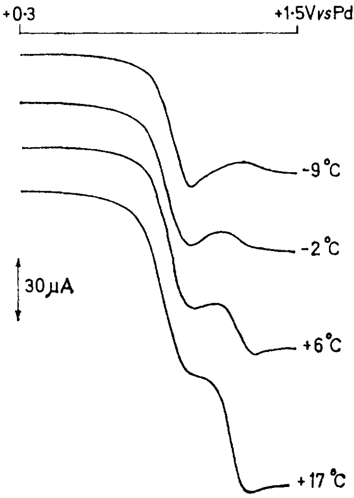

FIGURE 4 i–E Curves for the oxidation of 5mM-cyclohexane in fluorosulphonic acid containing 0·1M-acetic acid at various temperatures. Potential sweep rate 0·01 V s^{-1}

However an experiment in fluorosulphonic acid, which had been made to be 0·1M in acetic acid where the ' pH ' of the medium was varied by addition of potassium fluorosulphonate, showed that the ratio of the peak heights was independent of ' pH ' and therefore that the rate-determining chemical reaction must involve the acetyl cation.

Furthermore a rotating disc electrode may be used to show that at a potential on the plateau of the second wave the overall process is an e.c.e. reaction.* In solutions of fluorosulphonic acid which had been made to be between 0·1 and 1·0M in acetic acid and at a potential on the plateau of the second wave the rotating disc electrode was used to construct plots of $i/\omega^{\frac{1}{2}}$ *versus* ω (rotation rate); at rotation rates above 500 r.p.m. $i/\omega^{\frac{1}{2}}$ is independent of the rotation rate but below this value positive deviations are observed indicating an increase in the total number of electrons transferred in the electrode process, *i.e.* only at low rotation rates does the chemical reaction occur prior to the intermediate being swept from the electrode surface.

The more anodic peak in these systems may be shown to be due to the oxidation of methyl 2-methylcyclopent-1-enyl ketone by comparison of the i–E curves with that of an authentic sample. The αβ-unsaturated ketone gives a diffusion controlled peak whose $E_{p/2}$ is independent of ' pH ' and acetic acid concentration over the range studied. Indeed, it is to be expected that the cyclopentenyl ketone is the source of the second peak since this is the product isolated by controlled potential electrolysis of cyclohexane at a potential on the plateau of the first wave.

The alkanes which are much less readily oxidised than cyclohexane show only a single peak. This is to be expected since in these cases the αβ-unsaturated ketone formed initially will undergo oxidation at the same potential. If it is desired to isolate the αβ-unsaturated ketone the electrolysis must be carried out under conditions where the acetylation is slow, *i.e.* at low acetic acid concentration, at low temperature, or in stirred solution.

B. Protonation equilibrium preceding the electron transfer step. In the preliminary experiments it was noted that the wave for the oxidation of the parent hydrocarbon shifted as the concentration of acetic acid added to the fluorosulphonic acid was varied. Hence a detailed study of this phenomenon was undertaken. i–E Curves were run for cyclohexane in fluorosulphonic acid containing concentrations of acetic acid in the range 0·1—5·0M and the curves were used to construct an $E_{p/2}$–log [HOAc] plot. The half peak potential becomes more positive with increasing acetic acid concentration and the plot is linear with a slope ($dE_{p/2}/d$ log [HOAc]) = 80 mV. It has been pointed out previously, however, that in these systems acetic acid has the dual role of base and source of acetyl cations so to distinguish whether the shift in half peak potential is due to a change in ' pH ' or to a change in the concentration of the acetyl cation, two further experiments were carried out. First, i–E curves were run in fluorosulphonic acid containing acetic acid (25mM) and cyclohexane (1mM) and the ' pH ' was varied using potassium fluorosulphonate. Secondly the acetic acid concentration was varied and the solutions were maintained at a constant total fluorosulphonate ion concentration by addition of potassium fluorosulphonate. The first experiment resulted in a linear plot of $E_{p/2}$ *versus* log $[FSO_3^-]$ (see Figure 5) with a slope ($dE_{p/2}/d$ log $[FSO_3^-])_{MeCO^+}$ = 100 mV while the second experiment showed that there was a slight tendency for the half peak potential to become less positive with increasing acetyl cation concentration. Hence the major change is conclusively shown to be due to a ' pH ' effect and it must be emphasised that the half peak potential becomes more positive with increasing concentration of added base, *i.e.* the oxidation of alkanes takes place more easily in the more acidic solutions.

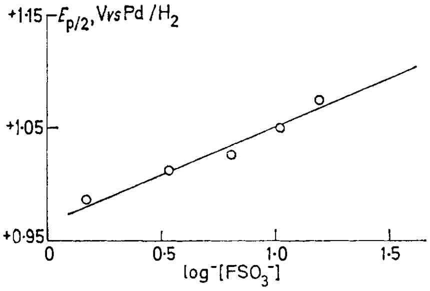

FIGURE 5 Plot of $E_{p/2}$ *versus* log $[SO_3F^-]$ for cyclohexane in fluorosulphonic acid. The $E_{p/2}$ data is taken from i–E curves run on solutions in fluorosulphonic acid containing saturated cyclohexane, 25mM-acetic acid, and various concentrations of potassium fluorosulphonate. The potential sweep rate was 0·1 V s^{-1}

Unfortunately the ' pH ' range which can be used for these experiments is in practice severely limited. At the low ' pH ' end of this range, the experiments are limited by the absence of suitable buffers in fluorosulphonic acid while at high ' pH ' the two anodic waves for the cyclohexane tend to merge since the potential of the peak for the oxidation of the cyclopentenyl ketone is independent of ' pH ' in the range studied. In addition it did not prove possible to carry out these experiments at constant ionic strength since no highly soluble, neutral salts in fluorosulphonic acid could be identified.

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* An e.c.e. reaction is an electrode process involving electron transfer, chemical reaction, and a second electron transfer.

Further experiments with n-butane and heptane showed linear $E_{p/2}$–log [HOAc] dependences with slopes of 80—90 mV and again the half peak potential becomes more positive with increasing acetic acid concentration.

The potential of the reference electrode used in this work, the Pd–H_2 electrode would be expected to be ' pH '-dependent. Hence all experiments were carried out with the same acetic acid concentrations and ' pH ' in the reference electrode compartment and a tap was used to form a boundary between the reference electrode and the test solutions.

DISCUSSION

The i_p–$v^{\frac{1}{2}}$ plots taken from the cyclic voltammograms for the oxidation of alkanes in fluorosulphonic acid containing acetic acid and/or potassium fluorosulphonate as the supporting electrolyte show that the peak currents for the first process are controlled by the diffusion of alkane to the electrode surface. Further the half peak widths of *ca.* 120 mV indicate that the current in the rising portion of the i–E curve is controlled by the rate of an electron transfer process; since the half peak width is theoretically equal to $2{\cdot}3\alpha nF/RT$, it is probable that a single electron is transferred before and during the rate controlling step and that the transfer coefficient $\alpha = 0{\cdot}5$.

i–E Curves where the half wave potential varies with pH but the limiting current is diffusion controlled and hence independent of pH have been commonly observed during polarographic studies in aqueous solution.[15,16] For such an oxidation process where $2{\cdot}3\alpha nF/RT = 120$ mV and the half wave potential shifts by 120 mV per ' pH ' unit in an anodic direction as the solution is made more basic, it may be concluded that (i) there is an equilibrium preceding the electron transfer step which involves a single proton since the shift per ' pH ' unit is equal to $2{\cdot}3\alpha nF/mRT$ where m is the number of protons involved in the pre-equilibrium, (ii) the electroactive species is a protonated form of the major species in the bulk solution and the unprotonated form is not electroactive at the potential of the wave, and (iii) the protonation equilibrium is rapid compared to diffusion since the limiting current is controlled by diffusion and not the rate of the protonation reaction.

In the case of the three alkanes, cyclohexane, heptane, and n-butane, whose i–E curves were studied as a function of ' pH ' in this work in fluorosulphonic acid, the shift in half wave potential was 100 mV per ' pH ' unit, the oxidation potentials become less positive with increasing acidity. In view of the half peak widths found for these oxidations, it is probable that a single proton is involved in a pre-equilibrium and the only plausible mechanism is shown in equations (1) and (2). If

$$RH + HFSO_3 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} RH_2^+ + FSO_3^- \qquad (1)$$

$$RH_2^+ - e \longrightarrow RH_2^{2+} \qquad (2)$$

k_f and k_b are written as pseudo-first-order constants (HSO_3F and FSO_3^- are always present in excess during the quantitative studies reported) it is possible to obtain a minimum value for k_f since, for the steady state limiting current to be controlled by diffusion and not the rate of protonation, $k_fK > 25$ where $K = k_f/k_b$.[17,18] Thus since K must be less than 10^{-2} for RH to be the major species in the bulk solution, $k_f \geqslant 2{\cdot}5 \times 10^3$ s^{-1}.

Protonated alkanes were postulated as intermediates in chemical reactions as early as 1946 [19] and are now widely accepted species in strongly acidic solvents such as fluorosulphonic acid, liquid hydrogen fluoride, and solutions containing antimony pentafluoride.[12–14] The minimum rate of the protonation deduced from these electrochemical studies is, however, considerably faster than that reported by Van Pelt and Buck [20] who measured the rate of tritium–proton exchange for the tertiary hydrogen of isobutane; their data (second-order rate constant $= 3{\cdot}9 \times 10^{-3}$ l mol^{-1} s^{-1} at 25 °C) may be used to calculate a value of $k_f \simeq 6{\cdot}5 \times 10^{-2}$ s^{-1}. This measurement, however, was obtained from a heterogeneous system which therefore involves equilibrium between a gaseous isobutane phase and a fluorosulphonic acid phase and two observations taken from experiments in homogeneous solution would support the larger rate constant indicated by this work. First, using n.m.r. as a simple analytical technique it may be shown that a saturated solution of deuteriated cyclohexane in fluorosulphonic acid containing potassium fluorosulphonate (0·5M) undergoes complete exchange in a few minutes and, bearing in mind the large statistical factor between the rate of the protonation of a single C–H bond and the rate of complete exchange, this clearly shows the protonation step to be rapid. Secondly, Olah *et al.*[21] have determined by n.m.r. line-broadening techniques the rate constant for reaction (3) to be 3×10^4 l mol^{-1} s^{-1}

$$Me_3\overset{*}{C}H + Me_3C^+ \longrightarrow Me_3C^{*+} + Me_3CH \qquad (3)$$

at 25 °C. If one accepts their postulate that this reaction occurs by attack of the cation on the C–H bond to form an intermediate containing a pentaco-ordinated carbon atom and a three-centred bond in an exactly analogous manner to the intermediate formed by protonation of the alkane,[9,10,13] one would expect the protonation to be even faster.

In addition to requiring the rate of protonation to be rapid, the proposed explanation of the ' pH ' dependencies of the i–E curves for the oxidation of alkanes requires that the unprotonated alkane is stable at the potentials where the oxidation wave occurs, *i.e.* the protonated form is more radily oxidised than the parent alkane. At first sight this is a somewhat surprising postulate but there are MO calculations to support this

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[15] P. Zuman, *Progr. Phys. Org. Chem.*, 1967, **5**, 81.

[16] P. Zuman, 'The Elucidation of Organic Electrode Processes,' Academic Press, New York, 1969.

[17] J. Koutecký, *Coll. Czech. Chem. Comm.*, 1953, **18**, 597.

[18] R. Brdička, *Adv. Polarography*, 1960, **2**, 655.

[19] H. P. Block, H. Pines, and L. Schmerling, *J. Amer. Chem. Soc.*, 1946, **68**, 153.

[20] P. Van Pelt and H. M. Buck, *Rec. Trav. chim.*, 1972, **91**, 195.

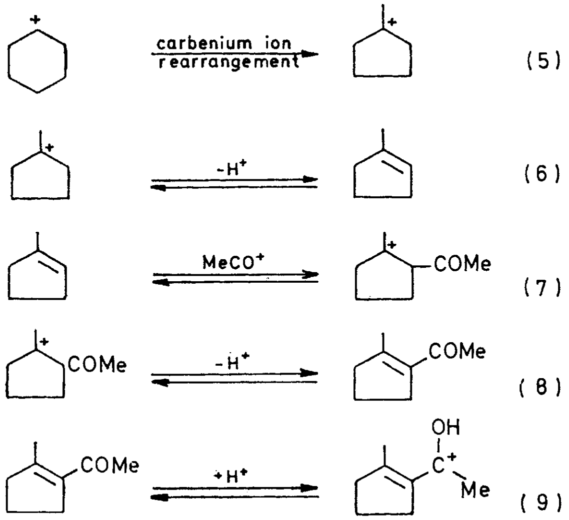
[21] G. A. Olah, Y. K. Mo, and J. A. Olah, personal communication.

view.[22-24] For example, Kollmar and Smith[24] have reported CNDO molecular orbital calculations which conclude that the CH_5^+ cation in its most stable configuration contains a bond with energy (9·5 eV) significantly less than the C–H bond of methane (16 eV) and there is generally a correlation between oxidation potential and the bond energy of the weakest bond in a molecule.

Thus the electrochemical evidence for a rapid protonation step prior to the initial electron transfer process would seem to be compatible with the known behaviour of the alkanes in these highly acidic media. Since the product studies, particularly the carbon skeletal rearrangements, strongly indicate that a carbenium ion is generated in the electrode process, the species formed in the initial electron transfer process must rapidly lose two protons and a further electron [reaction (4)]. It is not possible to define the order in which these steps occur.

$$\mathrm{RH_2^{2+}} \xrightarrow{-2\mathrm{H}^+\ -e} \mathrm{R}^+ \qquad (4)$$

In the earlier paper[1] the mechanism for the formation of the methyl 2-methylcyclopent-1-enyl ketone from the cyclohexyl cation was written as equations (5)—(9) and this mechanism may be modified to explain the products observed from the anodic oxidation of the other alkanes. A recent paper has shown that the product αβ-unsaturated ketone exists, in a similar medium, protonated on the carbonyl oxygen[25] and the absence of a shift in the half peak potential for the oxidation of cyclopentenyl ketone with ' pH ' proves that it is the species present in the bulk solution which take part in the electrode process.



The effect of stirring, potential scan rate, temperature, and the concentrations of the fluorosulphonate anion and the acetyl cation on the ratio of the heights of the peaks for the oxidation of cyclohexane and of methyl 2-methylcyclopent-1-enyl ketone clearly show that reaction (7) is the slow chemical step which occurs between the two anodic processes. Further the rate of reaction (7) is such that by correct choice of the electrolysis parameters, *i.e.* temperature, stirring, and the concentration of acetyl cation, it should always be possible to isolate an αβ-unsaturated ketone from the oxidation of an alkane even when the oxidation potential of the αβ-unsaturated ketone is less positive than the parent hydrocarbon. The absence of an oxidation peak for the olefin intermediate when the *i–E* curve is run under conditions where reaction (7) does not occur during the time-scale of the experiment suggests that in this solvent the olefin is also much less readily oxidised than the protonated alkane.

Hence the evidence suggests that the anodic oxidation of alkanes in fluorosulphonic acid containing acetyl cations from an αβ-unsaturated ketone is a general reaction which occurs by a mechanism summarised by equations (1), (2), and (4) followed by processes analogous to reactions (5)—(9).

The spontaneous chemical reactions which may be induced at elevated temperatures or at lower ' pH ' and which lead to similar products to the anodic reaction are probably initiated by the reactions (10) followed by the sequence (5)—(9). The loss of hydrogen from protonated alkane has been studied previously.[8,9,13,14] It is to be expected that the rate of this reaction will be increased at elevated temperatures and the ' pH ' dependence of the rate of product formation will arise if the rate of carbenium ion formation is first order with respect to the steady-state concentration of protonated alkane. The equilibrium constant K for the protonation reaction of alkanes will, of course, depend on the size and structure of the alkanes and this controls the ' pH ' and temperature where the chemical reaction becomes important.

$$\mathrm{RH} + \mathrm{H}^+ \rightleftharpoons \mathrm{RH_2}^+ \rightleftharpoons \mathrm{R}^+ + \mathrm{H_2} \qquad (10)$$

It can be seen that the product from the chemical reaction of ethane in fluorosulphonic acid containing acetic acid and antimony pentafluoride, methyl 2-methylprop-1-enyl ketone, must be formed *via* the isobutyl cation. This indicates that the major fate of the ethyl cation, generated by loss of hydrogen from the protonated ethane, must be the process (11) followed by reactions analogous to (6)—(9). Reaction (11) would be expected in view of the earlier results reported by Olah *et al.*;[9,11] they found that all hydrocarbons with less than five carbon atoms gave mainly products derived from the isobutyl cation. Indeed, they also report that higher alkanes underwent C–C bond cleavage due to protonation of a C–C bond, a reaction which they suggest is energetically more favourable than protonation at a C–H bond

$$\mathrm{C_2H_5}^+ + \mathrm{C_2H_6} \longrightarrow \mathrm{Me_3C}^+ + \mathrm{H_2} \qquad (11)$$

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[22] W. A. Latham, W. J. Hehre, and J. A. Pople, *Tetrahedron Letters*, 1970, 2699.

[23] W. Th. A. M. Van der Lugt and P. Ros, *Chem. Phys. Letters*, 1969, **4**, 389.

[24] H. Kollmar and H. O. Smith, *Chem. Phys. Letters*, 1970, **5**, 7.

[25] G. A. Olah, Y. Halpern, Y. K. Mo, and Gao Liang, *J. Amer. Chem. Soc.*, 1972, **94**, 808.

and it is somewhat surprising that during the anodic oxidations no C–C bond cleavage was found to occur.

Both the anodic and chemical substitution reactions of alkanes have obvious applications in synthesis for the introduction of substituents into aliphatic hydrocarbons and these synthetic reactions are currently being investigated further. The electrolytic technique has the advantage of avoiding the use of antimony pentafluoride which is expensive and unpleasant to handle.

EXPERIMENTAL

Chemicals.—Fluorosulphonic acid (Allied Chemicals) was distilled twice at atmospheric pressure prior to use. Acetic acid (B.D.H. AnalaR), cyclohexane and other alkanes (B.D.H.), antimony pentafluoride (Fluorochem), and [$^2H_{12}$]cyclohexane (Prochem) were all used as supplied. Potassium fluorosulphonate was prepared by the addition of fluorosulphonic acid to an aqueous solution of potassium hydroxide (5M); by cooling in ice, crystals were formed. These were filtered off, recrystallised from water, and dried under vacuum. The αβ-unsaturated ketones required as standards were prepared by literature methods.[26,27]

Equipment.—The electrochemical experiments were carried out using a Chemical Electronics transistorised potentiostat, model TR40-3A and wave-form generator type R.B.1. *i–E* Curves were recorded on a Hewlett–Packard 7035B x–y recorder and during controlled potential electrolyses an electronic integrator was used to measure the quantity of current passed. The rotation speed of a disc electrode was controlled by a Servomex type MC 43 control unit.

For voltammetry, a two compartment cell was used. The working electrode compartment (volume 5 cm^3) contained a platinum wire anode (area 0·6 cm^2) surrounded by a helical platinum wire cathode. The reference electrode was in a separate compartment connected by a Luggin capillary and tap to the working electrode compartment. The reference electrode was a platinum wire carrying a palladium bead charged with hydrogen by successively anodising and cathodising in aqueous sulphuric acid.[28] The reference electrode was dipped into the cell solution except in experiments where the ' pH ' effects were studied. In these cases the reference electrode solution was maintained unchanged throughout the experiment and a boundary between the solutions of differing ' pH ' was formed in the tap. A given reference electrode was found to be reproducible in potential.

For rotating disc electrode experiments a two compartment cell with a vertical Luggin capillary was used. The working electrode was a 2 mm diameter platinum disc surrounded by Teflon.

For preparative scale experiments a three compartment cell was used. A 1 cm^2 platinum gauze anode was separated from the cathode by a No. 2 glass sinter. The anode compartment had a volume of *ca.* 30 cm^3. The reference electrode was again the Pd–H_2 electrode and it was separated from the working electrode by a sinter and Luggin capillary. The secondary electrode was a Pt sheet (area 2 cm^2).

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. G.l.c. was carried out with a Pye 104 chromatograph with a flame ionisation detector.

Preparative Electrolyses.—(*a*) *Cyclohexane in fluorosulphonic acid–acetic acid* (1·14M). All compartments of the electrolysis cell were filled with fluorosulphonic acid which had been made to be 1·4M in acetic acid. The anolyte was then saturated with cyclohexane and stirred with dried nitrogen which had been pre-saturated with the hydrocarbon; in this way the concentration of cyclohexane was maintained constant throughout the electolysis. The electrolysis was carried out with a controlled anode potential of +1·15 V *versus* the Pd–H_2 reference electrode until 600 C of electricity had been passed through the cell.

At the end of the electrolysis the solution in the anode compartment was quenched by pouring onto crushed ice. The resulting aqueous solution was neutralised with sodium carbonate and the organic content was extracted with ether. The extract was dried (Na_2SO_4) and then subjected to g.l.c. and g.l.c.–mass spectroscopic analysis. The g.l.c. analysis showed there to be a single major product; in order to identify this product conclusively, it was isolated by preparative scale g.l.c. and subjected to spectroscopic analysis, $\nu_{max.}$ (liquid film) 970, 1220, 1260, 1365, 1440, 1620, 1660, 1685, and 3000 cm^{-1}, $\lambda_{max.}$ (EtOH) 253 nm (ε 9·54 × 10^3), δ ($CDCl_3$) 1·5—2·0 (2H, m), 2·05br (3H, s), 2·15 (3H, s), and 2·3—2·9 (4H, m), *m/e* 124, 109, 81, 67, 53, and 43. These spectra suggested that the product was methyl 2-methylcyclopent-1-enyl ketone. This was confirmed by comparison with an authentic sample. The yield of ketone from the electrolysis was 54% based on the current passed.

(*b*) *Cyclohexane in fluorosulphonic acid–propionic acid* (1·0M). This electrolysis was carried at an anode potential of +1·15 V. The procedure for the electrolysis and for the extraction and identification of ethyl 2-methylcyclopent-1-enyl ketone (52%) was as in (*a*), $\nu_{max.}$ (liquid film) 970, 1225, 1270, 1365, 1440, 1620, 1665, 1690, and 3000 cm^{-1}, $\lambda_{max.}$ (EtOH) 253 nm (ε 9·5 × 10^3) δ ($CDCl_3$) 1·00 (3H, t), 1·50—2·20 (2H, m), 2·05 (3H, s), and 2·15—2·80 (6H, m), *m/e* 138, 123, 81, 67, 57, and 53.

(*c*) *Cyclohexane in fluorosulphonic acid–hexanoic acid* (1·00M). The electrolysis and extraction procedure was as described in (*a*). 2-Methylcyclopent-1-enyl n-pentyl ketone (50%) was identified on the basis of g.l.c.–mass spectroscopy only, *m/e* 180, 165, 99, 81, 65, and 53.

(*d*) *n-Pentane in Fluorosulphonic acid–acetic acid* (1·14M). The electrolysis procedure and extraction were as in (*a*) except that the anode potential was controlled at +1·98 V. G.l.c. analysis of the ether extract showed the presence of three main products; furthermore, g.l.c.–mass spectral analysis showed all three products to be isomeric with parent ion peaks at *m/e* 112. After separation by preparative scale g.l.c., the major product was subjected to spectral analysis, $\nu_{max.}$ (liquid film) 980, 1080, 1400, 1470, 1623, 1693, 2900, 2960, and 3000 cm^{-1}, $\lambda_{max.}$ (EtOH) 240 nm, *m/e* 112, 97, 83, 69, and 43. This product is probably methyl 2-methylbut-1-enyl ketone but it is clear that all three products are isomeric methyl pentenyl ketones.

(*e*) *n-Hexane in fluorosulphonic acid–acetic acid* (1·14M). The electrolysis conditions and extraction procedure were as in (*a*) except the anode potential was controlled at +1·83 V. G.l.c. analysis of the ether extract showed the

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[26] W. S. Rapson and R. Robinson, *J. Chem. Soc.*, 1935, 1287.

[27] I. Tabushi, K. Fujita, and R. Oda, *Tetrahedron Letters*, 1968, 4247.

[28] M. Fleischmann and N. Hiddlestone, *J. Instrumental Sci.*, 1968, 1, 667.

presence of four products. G.l.c.–mass spectral analysis showed them to be isomeric hexenyl methyl ketones, *m/e* 126, 111, 97, 83, and 43.

(*f*) *n-Heptane in fluorosulphonic acid–acetic acid* (1·14M). The electrolysis conditions and extract procedure were as in (*a*) except the anode potential was controlled at +1·75 V. G.l.c. analysis of the ether extract showed the presence of four peaks. All gave parent ions at *m/e* 140 and were hence probably isomeric heptenyl methyl ketones. The major product was again separated by preparative scale g.l.c. and identified as $\nu_{max.}$ (liquid film) 960, 1060, 1080, 1440, 1470, 1620, 1690, 2900, 2960, and 3000 cm^{-1}, *m/e* 140, 125, 97, and 43.

(*g*) *Isobutane in fluorosulphonic acid–acetic acid* (1·0M). This electrolysis was carried out at +1·5 V *versus* the Pd–H_2 reference electrode and the anolyte was continually stirred with isobutane. Otherwise the electrolysis and extraction procedure were as in (*a*). G.l.c. showed a single peak and after separation by preparative scale g.l.c. this was shown to be methyl 2-methylprop-1-enyl ketone (55%), *m/e* 98, 83, 55, and 43, δ ($CDCl_3$) 1·87 (3H, s), 2·10 (6H, s), and 6·05br (1H, s), $\nu_{max.}$ (liquid film) 975, 1170, 1220, 1365, 1385, 1455, 1620, 1680, and 3000 cm^{-1}.

Procedure for Electroanalytical Experiments.—In most experiments both compartments of the electrochemical cell were filled with the same solution, fluorosulphonic acid to which a measured volume of acetic acid and/or a weighed amount of anhydrous potassium fluorosulphonate had been added. In experiments where the *i–E* curves were studied as a function of the ' pH ' of the medium a tap separated the working and reference electrode solutions. The reference electrode was always immersed in the same solution so that its potential was constant and the solution in the working electrode compartment was varied from experiment to experiment.

All cells were closed to the atmosphere and where not stated differently, all experiments were carried out at room temperature. Low temperature experiments were carried out by immersing the cell in a suitable cooling bath.

Chemical Reactions.—(*a*) *Isobutane in Fluorosulphonic acid–acetic acid* (2·0M) at 60 °C. Isobutane was bubbled for 5 h through fluorosulphonic acid (50 cm^3) to which acetic acid (0·1 mol) had been added and the solution was maintained at 60 °C. The solution was then quenched with ice and neutralised with sodium carbonate. The product was extracted with ether and after removal of this solvent, the product, a yellow oil, was distilled. G.l.c. analysis showed this to be methyl 2-methylprop-1-enyl ketone.

(*b*) *Cyclohexane in fluorosulphonic acid–acetic acid and antimony pentafluoride.* Cyclohexane (0·01 mol) was added to fluorosulphonic acid (50 cm^3) which had been cooled to room temperature after the addition of acetic acid (0·02 mol) and antimony pentafluoride (0·04 mol) and the mixture was stirred for 1 h. The product, a yellow oil (1·0 g), was extracted as in (*a*) and then distilled. G.l.c. analysis showed it to be methyl 2-methylcyclopent-1-enyl ketone (44%).

(*c*) *Ethane in fluorosulphonic acid–acetic acid and antimony pentafluoride.* Ethane was bubbled for 2 h through fluorosulphonic acid (25 cm^3) to which had been added acetic acid (0·005 mol) and antimony pentafluoride (0·015 mol) and the solution was maintained at room temperature. Crude product (300 mg) was obtained by the extraction procedure employed in (*a*). G.l.c. analysis showed this to contain several components of which the major was methyl 2-methylprop-1-enyl ketone.

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