THE ANODIC OXIDATION OF ALKANES IN ANHYDROUS HYDROGEN FLUORIDE AND RELATED SUPERACID MEDIA

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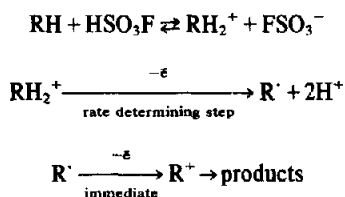
Abstract—The anodic oxidation of several alkanes in anhydrous hydrogen fluoride at various acidity levels, from "basic" media (KF) to "acid" media (SbF$_5$) has been studied to establish optimum conditions for the formation of carbenium ions. The oxidation potential of an alkane depends on structure and on the acidity level of the medium. Taking into account thermodynamical data, possible mechanisms for the anodic oxidation are proposed. Furthermore, it is shown that alkanes undergo spontaneous chemical oxidation in acid media (HF + SbF$_5$) which may be investigated in its kinetic and thermodynamic aspect by means of electroanalytical methods.
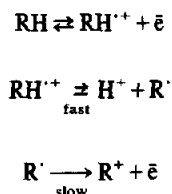
Since the pioneering work of Olah which gave impetus to studies of reactions in superacids, these media have been shown to be of great interest in the field of organic synthesis, especially for the isomerization and alkylation of hydrocarbons because of their stabilizing power for carbocations.

Although the chemical reactivity of alkanes in these media is well understood, electrochemical studies[1-6] have been, up to now, limited to media that may be called "basic" (i.e. acidity levels below $H_0 \approx -13$ or $R_0(H) \approx -19$) and not in "strongly acidic" media such as HF + SbF$_5$ mixtures. The acidity scale in anhydrous hydrogen fluoride (AHF) has been determined in previous work.[7] It runs from pH = 0, corresponding to a 1 M SbF$_5$ solution, up to pH = pK$_i$ = 13.7, corresponding to a 1 M KF solution. The acidity functions H_0 or $R_0(H)$ have been used to compare the acidity levels of the various superacids and to connect this pH scale in AHF to the usual pH scale in aqueous solution: pH = 0 in AHF corresponds to $R_0(H) - 27.9$ or $H_0 = -22.1$.[8]

From the study of the products of the anodic oxidation of alkanes in FSO$_3$H containing acetic acid and of the cyclic voltammetry, Pletcher *et al.* have proposed the following scheme.[1-3]

$$RH + HSO_3F \rightleftharpoons RH_2^+ + FSO_3^-$$

$$RH_2^+ \xrightarrow[\text{rate determining step}]{-\bar{e}} R^\cdot + 2H^+$$

$$R^\cdot \xrightarrow[\text{immediate}]{-\bar{e}} R^+ \rightarrow \text{products}$$

This process has been infirmed by Herlem *et al.*[5,6] who have suggested an other scheme on the basis of voltammetric results at cryogenic temperatures:

$$RH \rightleftharpoons RH^{\cdot+} + \bar{e}$$

$$RH^{\cdot+} \underset{\text{fast}}{\rightleftharpoons} H^+ + R^\cdot$$

$$R^\cdot \xrightarrow[\text{slow}]{} R^+ + \bar{e}$$

In the absence of a "trapping agent" (a base) such acetic acid[2,3] the products of the anodic oxidation of alkanes are polymers. Thus, the situation concerning the electrochemical behaviour of these compounds is not clear.

Recently, we have described the chemical behaviour of two alkanes, isopentane[9] and methylcyclopentane,[10] from results of electrochemical studies. We have given evidence for the existence of carbonium ion RH$_2^+$ in very acidic media (SbF$_5$ solutions) and of a radical oxidation state (which leads to polymers) in basic media (KF solutions). These results completed with thermodynamic data from the literature lead us to predict the chemical behaviour of various alkanes (methane to pentanes) according to the acidity level of the medium in which they are dissolved.[11]

In the present paper we describe the anodic oxidation of alkanes (from methane to pentanes) and cycloalkanes (cyclopentane, cyclohexane and methylcyclopentane) in AHF at different acidity levels. Taking into account thermodynamic data,[11] we propose several schemes for the anodic oxidation of these compounds in such media.

EXPERIMENTAL

The experimental line used for handling AHF solutions has been described in detail in a previous paper.[12] All measurements were performed at 0°C. Hydrogen fluoride (Matheson) was purified by two successive condensations; SbF$_5$ (Allied Chemical) was twice distilled before experiments in an all-glass distillation apparatus. The other fluorides used to prepare pH buffers: TaF$_5$, NbF$_5$ (Fluorochem), BF$_3$ (Matheson), PF$_5$ (Pfaltz and Bauer) and KF (Merck), and the alkanes (gas Matheson) and liquids (Fluka) are analytical grade reagents and were used without further purification.

The gaseous alkanes (from methane to butanes) were dissolved by bubbling in the solution and liquid ones were introduced by means of a microsyringue (Hamilton).

Voltammograms were obtained by means of Tacussel PRG5 polarograph, the potential scanning being achieved by means of a Tacussel GSTP3 generator and the voltammograms recorded with a Sefram TRP 10-100 XY recorder. Controlled potential electrolyses were carried out with a Tacussel GCU coulometer and a Tacussel IG6N current integrator.

The working electrode was a platinum disc (diameter 1 mm) coated in a Teflon rod. The reference electrode, described previously,[12] was formed with the Ag/Ag(I) system placed in a Teflon

in a Teflon compartment, the junction with the working solution being made through a porous Teflon disc.

The following abbreviations have been used: C_1H: methane; C_2H: ethane; C_3H: propane; nC_4H: n-butane; iC_4H: isobutane; nC_5H: n-pentane; iC_5H: isopentane; $neoC_5H$: Neopentane; cyC_5H: cyclopentane cyC_6H: cyclohexane; MCPH: methylcyclopentane.

RESULTS

The anodic oxidation of alkanes was investigated by linear sweep voltammetry. The solutions of hydrocarbons are electroactive, giving rise to voltammetric curves such as those shown in Figs. 1 and 2. All the oxidations are irreversible since cyclic voltammograms show no reduction peaks prior to hydrogen evolution.

The shape and position of the curves depend on the nature of the alkane and on the acidity level; their characteristics for different pH values are given in Table 1.

Basic and weak acidic media

One oxidation peak potential Ep undergoes a shift towards higher values when pH decreases (Fig. 3). The peak current is linearly related to the square root of the potential scan rate (v), showing that the electrochemical process is diffusion controlled.

As is known, the peak potential Ep depends on the structure of the hydrocarbon (Table 1). The alkanes with tertiary structure are more easily oxidizable (i.e. have a lower oxidation potential) than the ones with secondary or primary structure.

The controlled potential electrolysis yield polymeric species which passivate the electrode and hinder from determining the number of electrons exchanged per molecule.

Acid media (SbF₅ solutions)

The voltammetry of alkanes with a primary structure (methane, ethane, neopentane) gives rise to curves showing one peak like in basic media but the peak potential is more positive according to the expected evolution with pH decreasing.

In the case of neopentane, the recording of the voltammetric curves versus time shows a decrease of the peak current due to the chemical oxidation of this compound (by H^+ ion). This reaction is known to be a protolysis.[13,14]

$$neoC_5H + H^+ \to iC_4^+ + C_1H \qquad (1)$$
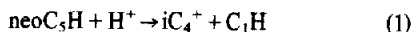
Thus, voltammetry can be used to study the kinetics of such an oxidation.[11]

The other alkanes (except MCPH) give rise to voltammetric curves showing two peaks (Figs. 1 and 2). The first one $(0.8 < Ep < 1.3)$ has been proved to be controlled by an adsorption process.[9] The second peak corresponds to the ones observed in less acidic media, taking into account their displacement with pH (Fig. 3). The hydrodynamic voltammetric curve (at a rotating electrode) shows only one wave whose half-wave potential is close to that of the first peak.

In each case, we have observed a slow decrease of the anodic peak height with time, characteristic of a decrease of the alkane concentration since they are linearly related. This fact gives the evidence of the slow chemical oxidation of alkane into carbenium ion. A kinetic analysis of

the isopentane oxidation has shown that the limiting step of the reaction is the protonation of the hydrocarbon.[11]

$$RH + H^+ \xrightarrow[slow]{} RH_2^+ \to R^+ + H_2. \qquad (2)$$
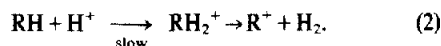
Taking into account the variation of concentration resulting from the chemical reaction superposed to the electrochemical one, coulometric analysis at constant electrode potential shows that anodic oxidation is a process involving two faradays per mole of alkane whatever the electrode potential is (0.9 V < Electrolysis < 1.7 V).[9]

For the last hydrocarbon,[10] methylcyclopentane, only one peak is always observed, but with an oxidation peak potential value close to the one observed in basic media. The decrease of the peak current, which is linearly related to the concentration of MCPH, is very rapid (half time about 2 min).

DISCUSSION

Interpretation of the experimental results necessitates to take into account the thermodynamic data deter-
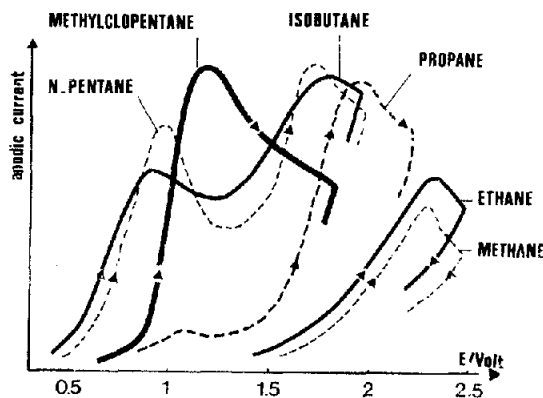

Fig. 1. Voltammograms of alkanes in $AHF + 0.5$ M SbF_5: Stationary platinum microelectrode ($\emptyset$ 1 mm), potential scanning rate: p.s.r. 0.5 V s⁻¹.
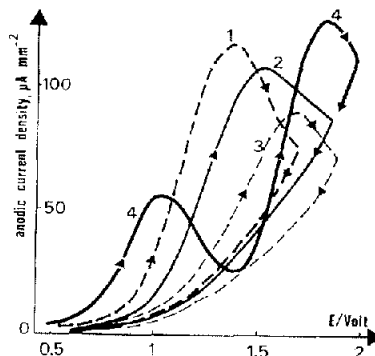

Fig. 2. Voltammograms of isopentane (i–C_5H) in AHF at various pH: 1. pH(HF) = 13.2 (0.14 MKF), $|i$–$C_5H| = 41$ mM; 2, pH(HF) = 6.6 (0.24 M BF_3/BF_4^-), $|i$–$C_5H| = 24$ mM; 3, pH(HF) = 4.2 (0.27 M TaF_5/TaF_6^-), $|i$–$C_5H| = 18$ mM; 4, pH(HF) = 0.4 (0.44 M SbF_5), $|i$–$C_5H| = 24$ mM.

E_p /V	BASIC AHF pH(HF)≈12.7 $H_o = -9.4$	NEUTRAL AHF pH(HF)≈6.5 $H_o = -15.6$	ACID AHF pH(HF)≈0.5 $H_o ≈ -21.6$
2.0	C1H, C3H, C2H	C1H, C2H, neo-C5H, n-C4H, C3H	C1H, C2H, neo-C5H, cy-C6H, C3H
1.5	neo-C5H, cy-C5H, n-C4H, cy-C6H, i-C4H	cy-C6H, cy-C5H, n-C5H, i-C4H	n-C4H, cy-C5H, i-C4H, n-C5H, i-C5H
1.0	n-C5H, MCPH, i-C5H	i-C5H, MCPH	MCPH$_2^+$, n-C4H$_2^+$, cy-C6H$_2^+$, cy-C5H$_2^+$, C3H$_2^+$
			n-C5H$_2^+$, i-C4H$_2^+$, i-C5H$_2^+$

Table 1. Oxidation peak potentials Ep of alkanes in AHF at various pH, p.s.r. $0.5\,V\,s^{-1}$.
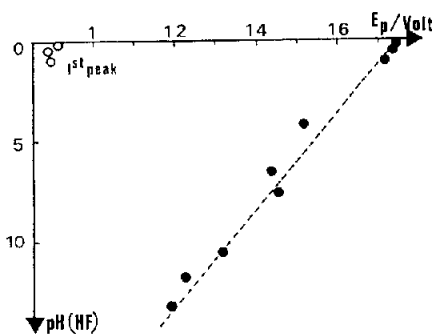
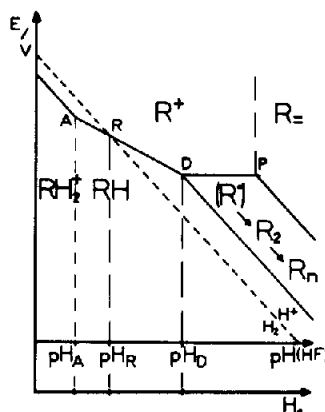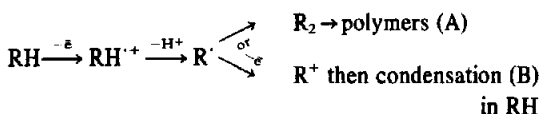Fig. 3. Plot of the oxidation peak potential Ep of isopentane (i-C$_5$H) vs pH(HF).

Fig. 4. General potential-acidity diagram of an alkane RH[9,10] vs the hydrogen system: R = alkene, conjugate base of R$^+$. The x-axis represents the acidity by reference to the pH scale in HF[7] and to the Hammett acidity function H_0.

minations, recently published,[9-11] which are represented under the form of potential-acidity diagrams (Fig. 4). Such diagrams show that (a) on the acidic side (pH < pH$_A$), the equilibrium potential of the R$^+$/alkane system is represented as a function of pH by a line of the same slope as for H$^+$/H$_2$ when the carbonium ion RH$_2^+$ is the predominating form; the slope turns to one half of the former when RH becomes the predominating form (pH$_A$ < pH < pH$_D$). The ensuing crossing of the two lines of the R$^+$/RH and H$^+$/H$_2$ systems means that spontaneous oxidation of the alkane into R$^+$, which can run to practical completeness at the highest acidity levels (pH < pH$_R$), no longer takes place when the acidity level is low enough (pH > pH$_R$); (b) on the basic side (pH > pH$_D$), the two lines take into account the condensation reaction between RH and R$^+$ (or protonated alkene R =) yielding first the dimer and then polymers. This reaction may be interpreted by the production of a redox reaction between R$^+$ and RH to form two R$^.$ radicals.

Case 1. pH > pH$_D$. The chemical oxidation of RH does not lead directly to the carbenium ion R$^+$ but goes through the radical oxidation state R$^.$ enhancing condensation reactions. In the same way, the anodic oxidation yield polymers; two processes can be proposed, corresponding to two different evolutions of the radical R$^.$:

$$RH \xrightarrow{-e} RH^{.+} \xrightarrow{-H^+} R^{.} \begin{cases} \nearrow & R_2 \rightarrow \text{polymers (A)} \\ \searrow_{-e} & R^+ \text{ then condensation (B)} \\ & \text{in RH} \end{cases}$$

A process implying the exchange of one electron per molecule of RH (type A) and a process implying the exchange of two electrons per molecule of RH,[5,6] followed by condensation reactions (type B):

$$R^+ + RH \rightarrow R_2 + H^+$$

$$R^+ + R_nH \rightarrow R_{n+1} + H^+.$$
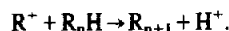
Taking into account the very high overvoltage (above 1 V, Ep – E° (standard potential),[11]) observed in the anodic process and the fact that in presence of bases (acetic acid[1-3]) carbenium ions are trapped during electrolysis, the anodic oxidation could rather be a B type.

Case 2. pH$_A$ < pH < pH$_D$. At these acidity levels, RH is not yet protonated but its chemical oxidation, which is very slow, leads directly to the carbenium ion R$^+$.

In the same way, the results of electrolysis at constant potential (yielding carbenium ion through a two electron process) suggest the following interpretation:

From the thermodynamic potential-acidity diagram, an electrochemical oxidation which is followed by a disproportionation:

$$RH \xrightarrow{-e^-} RH^{.+}$$

$$2RH^{.+} \rightarrow R^+ + RH + H^+$$
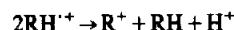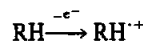
or, as above, taking into account the very high overvol-

tage, an E.C.E. process:[5,6]

$$RH \xrightarrow{-e} RH^{+} \xrightarrow{-H^{-}} R^{\cdot} \xrightarrow{-e} R^{+}.$$
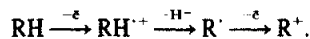
Case 3. pH < pH$_A$. In those media, RH is thermodynamically protonated into the carbonium ion RH$_2^+$ which is oxidized into the carbenium ion R$^+$. As concerns aliphatic alkanes, the oxidation is slow and its rate is determined by the protonation of RH (reaction (2)).[11] On the contrary, MCPH is rapidly oxidized into MCP$^+$ according to a reaction where the limiting step is the decomposition of the carbonium ion MCPH$_2^+$:[10]

$$MCPH + H^+ \rightleftharpoons MCPH_2^+ \xrightarrow{k} MCP^+ + H_2. \quad (3)$$
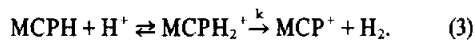
At these acidity levels, the electroactive species are different from those observed in basic media: carbonium ions are more readily oxidized that the parent alkanes as it was reported by Kollmar and Smith[15] on the basis of CNDO molecular orbital calculations. They concluded that the CH$_5^+$ cation 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.[16]

Thus, the oxidation potential of MCPH, protonated in the medium, is less positive than we could expect from its displacement with pH. Furthermore, when the protonation is slow (a) on the time scale of cyclic voltammetry, we observed two peaks, the first one corresponding to the carbonium ion RH$_2^+$ and the second one to the alkane RH, not yet protonated (its Ep value corresponds to the ones observed in less acidic media, taking into account the displacement with pH); (b) on the longer time scale of hydrodynamic voltammetry, only one wave is observed, whose half wave potential is close to the peak potential of the first peak above mentioned. Thus, the electrochemical reaction giving rise to the second peak, observed by cyclic voltammetry, must be the same scheme as the one described in case 2.

The first peak (single for MCPH) could be attributed to the carbonium ion and the process, presenting adsorption characters,[9] could be following:

$$RH + H^+ \rightarrow RH_2^+ \rightarrow RH_2^+{}_{ads.}$$
$$\downarrow$$
$$R^+ + 2H_{ads}$$
$$\downarrow -2\bar{e}$$
$$R^+ + 2H^+.$$
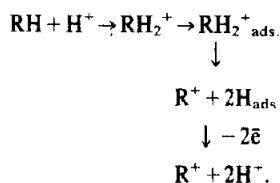
The peak potentials of the oxidation of alkanes are related to their structure (see Table 1) and to their gas phase ionization potential.[15,16]

Primary alkanes present the most positive potentials and no first peaks due to the protonated forms are observed. Those compounds are much too unreactive to yield either the carbenium ions or the carbonium ions.[11] The media investigated in this paper (up to 2 M SbF$_5$) are not enough acid yet for this purpose, with regard to the mixtures HF–SbF$_5$ (10-1/mole) in which such species have been postulated.[17,18]

The electrochemical behaviour in the acidity range of HF is limited to case 1. Tertiary alkanes possess less positive oxidation potentials and the peaks attributed to the carbonium ions in SbF$_5$ diluted solutions. These compounds behave as weak bases and are oxidized into carbenium ions.

In the acidity range of HF, we have observed the three types of electrochemical behaviour mentioned above (a) in basic media, case 1 takes place; then, in slightly acidic media case 2 appears and in the highest acid media (SbF$_5$ solutions) case 2 is displaced by case 3; (b) secondary alkanes present an intermediate behaviour between the two other alkane types. In acid media (SbF$_5$), one can notice that n-pentane behave as a tertiary alkane: it can be attributed to the fact that n-pentane is isomerized into isopentane[19] while n-butane is not.[20]

In the acidity range of HF, these compounds present electrochemical behaviours similar to those observed for tertiary alkanes.

CONCLUSION

The electroanalytical techniques are suitable for the *in situ* study of the alkanes conversion in superacid media. Meanwhile, the irreversibility of the electrochemical processes restricts the possibilities of these methods: (i) no direct thermodynamical interpretation could be obtained on the redox properties of alkanes (ii) the resulting large width of the oxidation peaks prevents to analyse, by voltammetry, a solution of various alkanes.

However, the linear relation between the oxidation peak height and the alkane concentration allows to follow the evolution of the hydrocarbon; thus, voltammetry has been shown to be particularly useful for the study of the oxidation reactions of alkanes in view of thermodynamical or kinetical determinations.[9,10] As concerns the electrochemical activation of alkanes, two principal aspects have been investigated (a) the anodic oxidation into carbenium ion, in order to promote isomerization reactions. Such reactions have to be performed in a medium where the alkane oxidation leads directly to the carbenium ion (i.e. in a medium of acidity level lower than the value of pH$_D$ of the alkane to prevent condensation reactions through the radical oxidation state[11]); (b) the direct electrochemical fluorination (mild conditions) of alkanes in basic media (KF), by trapping the carbenium ions by F$^-$ ions. Since the anodic oxidation of alkanes in basic media yields polymeric species, the F$^-$ ions are much too solvated and not basic enough for this purpose.[21]

REFERENCES

[1] J. Bertram, F. Fleischmann and D. Pletcher, *Tetrahedron Lett.* 349 (1971).
[2] J. Bertram, J. P. Coleman, M. Fleischmann and D. Pletcher, *J. Chem. Soc. Perkin II* 374 (1973).
[3] J. P. Coleman and D. Pletcher, *J. Electroanal. Chem.* **87**, 11 (1978).
[4] H. P. Fritz and T. Wurminghausen, Ibid. **54**, 181 (1974).
[5] S. Pitti, F. Bobilliart and M. Herlem, *Anal. Lett.* **8**, 241 (1975).
[6] S. Pitti, M. Herlem and J. Jordan, *Tetrahedron Lett.* 3221 (1976).

[7]J. Devynck, A. Ben Hadid, P.-L. Fabre and B. Tremillon, *Anal. Chim. Acta* **100**, 343 (1978).

[8]A. Ben Hadid, Thesis Doct. Etat, Paris (1980).

[9]J. Devynck, P.-L. Fabre, A. Ben Hadid and B. Tremillon, *J. Chem. Res.* (s)200, (M)2469 (1979).

[10]P.-L. Fabre, J. Devynck and B. Tremillon, *J. Electronal. Chem.* **113**, 251 (1980).

[11]P.-L. Fabre, Thesis Doct. Etat, Paris (1980).

[12]J. Devynck, P.-L. Fabre, A. Ben Hadid and B. Tremillon, *J. Electroanal. Chem.* **91**, 93 (1978).

[13]G. A. Olah and J. Lukas, *J. Am. Chem. Soc.* **89**, 2227 and 4739 (1967).

[14]H. Hogeveen and A. F. Bickel, *Rec. Trav. Chim. Pays-Bas* **86**, 1313 (1967) and **88**, 371 (1969).

[15]H. Kollmar and H. O. Smith, *Chem. Phys. Lett.* **5**, 7 (1970).

[16]L. L. Miller, G. Nordblom and E. A. Mayeda, *J. Org. Chem.* **37**, 916 (1972).

[17]G. A. Olah and R. H. Schlosberg, *J. Am. Chem. Soc.* **90**, 2726 (1968).

[18]G. A. Olah and G. Klopman and R. H. Schlosberg, *Ibid.* **91**, 326 (1969).

[19]R. Bonifay, B. Torck and M. Hellin, *Bull. Soc. Chim. Fr.* 808 and 1057 (1977) and 36 (1978).

[20]D. M. Brouwer, *Rec. Trav. Chim. Pays-Bas* **87**, 1435 (1968).

[21]F. Huba, E. B. Yeager and G. A. Olah, *Electrochim. Acta* **24**, 489 (1979).