

Chemical Oxidation of Alkanes by Fluoranil in HF-SbF₅ Superacid Solutions

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The chemical oxidation of methane, propane, and n-pentane by fluoranil [Q(F)] was investigated in HF-SbF₅ superacid media; it was shown that the oxidation of n-pentane by Q(F) is faster than by H⁺ and that Q(F) can be regenerated by coulometry, hence, an electrocatalytic oxidation process of alkanes is proposed.

The chemistry of alkanes in superacid media has been widely investigated, particularly in the context of isomerizations or alkylations.¹ The first step of these reactions is described as oxidation, generally by the H⁺ ion. This oxidation is possible with all alkanes but it was shown that lighter ones (especially methane) are oxidized only under high pressure and in concentrated superacid mixtures.²

The relation between the acidity level and the nature of the H⁺ oxidation products has been recently investigated in the case of isopentane in HF-superacid media. Redox potentials of different couples involving isopentane have been determined.³ From the results, and taking into account the thermodynamic data of the hydrocarbons, redox potentials for various alkanes have been calculated.⁴ Thus, it was shown that H⁺ is a poor oxidizing agent towards light alkanes, even in acidic solutions such as 1 M SbF₅ in HF. So, in order to activate these compounds, new agents with higher oxidizing power were needed. Among them, quinone derivatives⁵ seemed of interest, particularly fluoranil [2,3,5,6-tetrafluoro-

p-benzoquinone:Q(F)] whose potential-acidity diagram had previously been established (Figure 1).⁶

Fluoranil is suitable for our purpose because: i, its oxidation potential is high enough to oxidize alkanes (Figure 1); ii, fluoranil couples are stable towards electrophilic species such as carbenium ions (the fluorine atoms prevent electrophilic addition at the nucleus); iii, fluoranil can be regenerated by electrolysis. It is thus possible to suggest an electrocatalytic activation process for the hydrocarbons.

This paper describes the oxidizing properties of fluoranil towards alkanes in HF-SbF₅ solutions and the kinetic properties of the reactions. The experiments were carried out at 0 °C in a Teflon and Kel-F apparatus.⁷ To a 50 ml solution of 0.5 M SbF₅ in HF (pH_{HF} = 0.3, *i.e.* R₀(H) *ca.* -27.6 or *H₀* *ca.* -21.8) containing fluoranil, was added the alkane: n-pentane was introduced using a syringe (0.1 M up to saturation, 0.2 M). Methane and propane were dissolved under atmospheric pressure (propane concentration of *ca.* 0.65 M⁸). The concentration of fluoranil is linearly related to

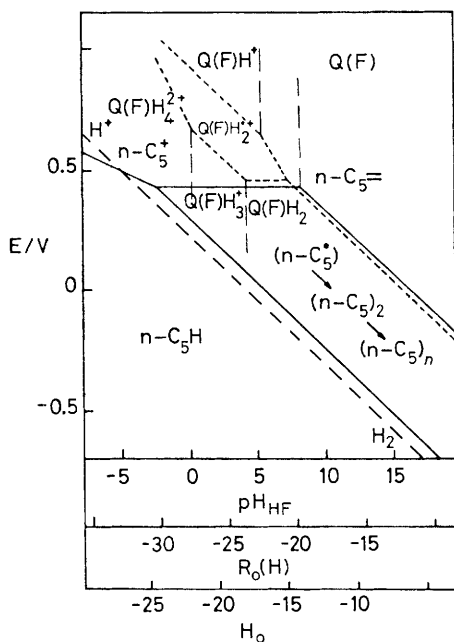
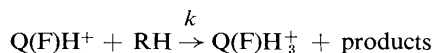


Figure 1. Potential-acidity diagram in HF of the redox systems, showing the oxidizing power of fluoroanil [Q(F)] towards n-pentane (potentials are expressed vs. the Ag^+/Ag system⁷). The x-axis represents the acidity by reference to the pH-scale in HF ($\text{pH}_{\text{HF}} = 0$ for $[\text{SbF}_5] = 1 \text{ M}$) and the STREHLOW acidity function [$R_0(\text{H})$], and the HAMMETT acidity function (H_0). Experimental diagrams: (—): hydrogen; (---): fluoroanil Q(F). Calculated diagram: (—): n-pentane ($\text{n-C}_5\text{H}$), n-pent-2-ene ($\text{n-C}_5=$).

the measured current and therefore was determined by chronoamperometry (fixed potential $+0.35 \text{ V}$) using a gold micro-electrode.

Under the experimental conditions, the oxidation



was pseudo-first order with respect to fluoroanil. Hence the electrochemical determination of the concentration of Q(F) as a function of time led to the kinetic constant k . For n-pentane, the rate of oxidation by fluoroanil is higher than the rate of oxidation by H^+ (Table 1). Under atmospheric pressure, the gaseous alkanes which are difficult to oxidize by H^+ are slowly oxidized by fluoroanil. In the case of methane the reaction is too slow to be measured.

Having demonstrated the utility of fluoroanil, we investigated its electrochemical regeneration. The voltampero-

Table 1. Kinetic constants for alkane oxidation by fluoroanil in 0.5 M SbF_5 in HF ($\text{pH}_{\text{HF}} = 0.3$)^a: $k = \frac{-d[\text{Q(F)}]}{dt[\text{Q(F)}]}$

RH	Methane	Propane	n-Pentane
k/s^{-1}	ca. 0	1.5×10^{-4}	5.5×10^{-4}

^a The kinetic constant for n-pentane oxidation by H^+ in the same medium is ca. $0.8 \times 10^{-4} \text{ s}^{-1,4,9}$

metric study of the oxidation of dihydrofluoroanil⁸ and alkanes⁴ showed that: i, the oxidation of dihydrofluoroanil is quasi-reversible with a Pt or Au electrode, and electrolysis at 0.85 V of this compound yields the quinone; ii, light alkanes whose electrochemical systems are irreversible are oxidized at potentials higher than 1 V . So the electrochemical oxidation of dihydrofluoroanil regenerates the quinone at a potential when alkanes are not oxidized.

The experiments were performed as follows: once fluoroanil had reacted with the hydrocarbon, electrolysis of the hydroquinone was carried out using a gold electrode at constant current (50 mA , 40 min). From the recording of the chronoamperograms (before and after electrolysis), the concentration of quinone was determined and the yield of electrolysis was calculated to be 80% .

These first results show that the chemical oxidation of alkanes in superacid media is possible with an oxidant like fluoroanil whose oxidizing power is very high. The electrochemical regeneration of the reduced quinone suggests the possibility of new electrocatalytic reactions, which increases the interest in such media.

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