

ELECTROOXIDATION OF CYCLOPENTANE AT CRYOGENIC TEMPERATURES

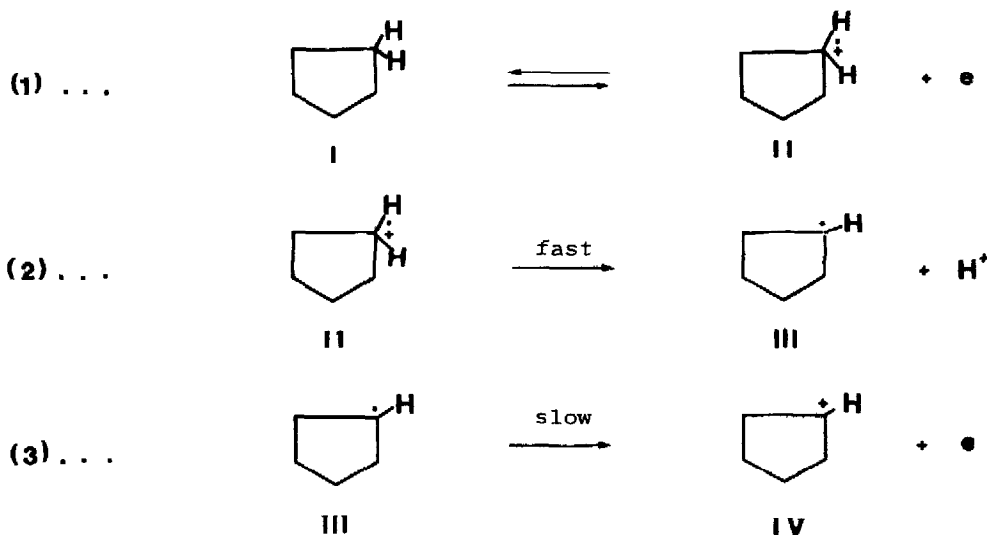
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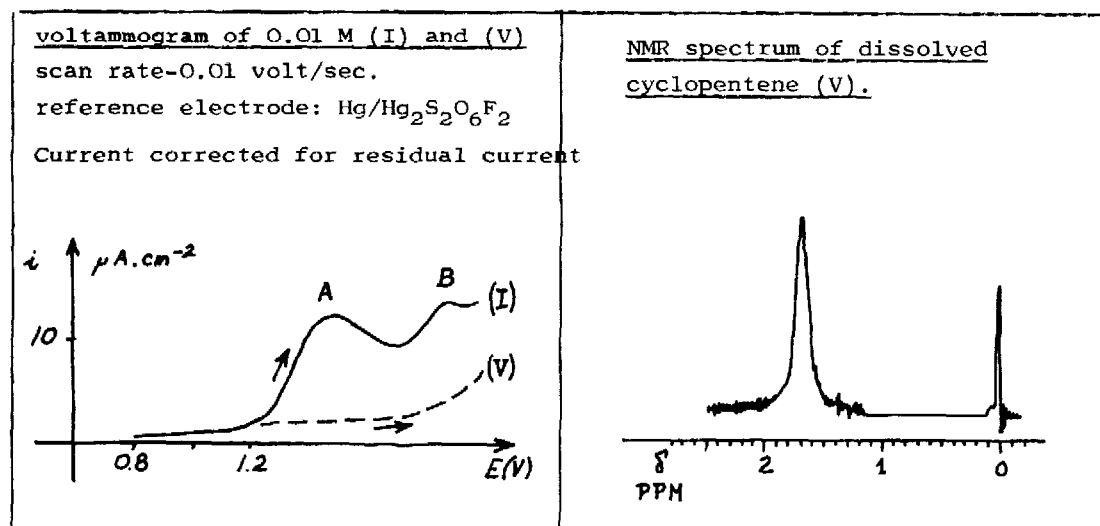
The discovery of the reactivity of aliphatic hydrocarbons in Olah's superacid media has revolutionized carbonium chemistry¹. In recent years several laboratories have reported² the anodic electrogeneration of carbenium ions from alkanes in various non aqueous solvents including fluorosulfuric acid (FSA). It was concluded that charge transfer is preceded by a fast protonation of the alkane and is followed by the abstraction of a H₂ molecule, yielding the corresponding carbenium ion. Recently³ we have found a different electrochemical behaviour of several alkanes including cyclopentane. Experimental results were not compatible with this reaction sequence. Consequently the electroactive species could not be in the form of protonated alkane molecules. A relevant mechanism is of evident crucial interest in the context of electrosynthetic possibilities. We wish to report the electrogeneration of the cyclopentyl ion (IV) at -60°C, via the reaction sequence:



This communication is the first known report of the electrogeneration of a carbenium ion at cryogenic temperatures. Reilley and Van Duyne⁴ have recently shown that low temperature electrochemistry is a powerful tool for elucidating primary electron transfer steps in complex mechanisms, because side reactions are likely to be quenched. The novel feature of our work is that we have segregated and conclusively identified the basic single electron-transfers (1) and (3), substantiating the classical Haber-Weiss postulate⁵ that multi-electron transfers occur by mono-electronic steps via free radical intermediates. The choice of cyclopentane (I) for a model study was predicated by the fact that species (II) and (IV) are unique in the sense that - in contradistinction to all other alkylcarbenium ions - they do not isomerize¹.

The experimental evidence which substantiates the sequence (1), (2) and (3) is outlined below. Representative findings are presented based on about fifty experiments which yielded consistent results. Three principal methods were used viz., cyclic voltammetry, coulometry at controlled potential and NMR. A relevant section of the anodic sweep of a typical cyclic voltammogram of cyclopentane is illustrated in Figure 1, revealing at -60°C two peaks in a range of potentials between zero and +1.9 volt.

Figure 1. Typical experimental results obtained at -60°C in fluorosulfuric acid + 2M NaF



The reverse cathodic scan showed no corresponding peaks. Well known diagnostic criteria⁶ revealed the following (where capital letters refer to peaks identified in the figure, \underline{v} denotes sweep rate and \underline{c} cyclopentane concentrations)

$$\frac{F}{RT} \frac{dE_{p/2}}{d \ln v^{1/2}} = 0.6 \pm 0.1 .$$

$$A \left\{ \frac{F}{RT} \frac{d(E_{p/2} - E_{p/2})}{d \ln v^{1/2}} = 0.06 ; \quad \frac{dE_{p/2}}{d \ln c} > 0 \right.$$

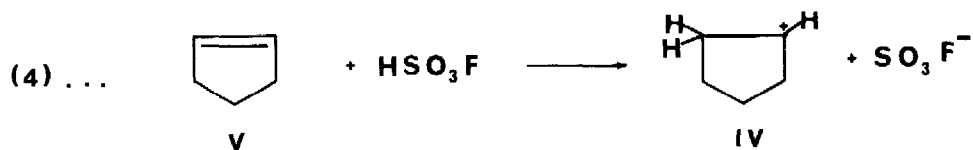
Plot of current function ($i_p / c v^{1/2}$) vs. $\ln v^{1/2}$ is sigmoid in shape.

$$B \left\{ \begin{aligned} \frac{F}{RT} \frac{dE_{p/2}}{d \ln v^{1/2}} &= 0.6 ; \quad \frac{dE_{p/2}}{d \ln c} = 0 \\ \frac{F}{RT} \frac{d(E_{p/2} - E_{p/2})}{d \ln v} &= 0.06 ; \quad \frac{d(i_p / c v^{1/2})}{d \ln v} = 0 \end{aligned} \right.$$

The data indicate unambiguously that peak A correspond to a one-electron transfer coupled with a fast chemical "follow-up" reaction, a so called EC' mechanism with $\alpha n_a = 0.6 \pm 0.1$, where $n_a = 1$ is the number of electrons involved in the rate determining step. Coulometry at an appropriate controlled potential ($E_{3/4 p}$) revealed that the overall number of electrons was the same as n_a , viz. $n = 1$. The reaction sequence (1) and (2) is obviously consistent with these requirements. The diagnostic findings for peak B are consistent with a slow one-electron transfer preceded by a rapid chemical equilibrium ("C'E" mechanism). Again $\alpha n_a = 0.6 \pm 0.1$ and (by coulometry) $n = n_a = 1$. Reaction sequence (2) plus (3) is evidently compatible with these results.

The crux of the argument in favour of the overall sequence is that it corresponds to a reasonable assumption that the same chemical reaction (C') be interposed between the two one-electron transfer steps. The proposed sequence also appears reasonable in the light of contemporary knowledge of carbenium ion chemistry. The absence of converse cathodic peaks is accounted for the short lifetime of the radical ion (II).

In order to substantiate conclusively the prevalence of reactions (1), (2) and (3) the voltametry of cyclopentane was compared with that of cyclopentene. The rationale behind this particular type of experiment was that (V) was found to protonate in FSA (via reaction 4) at cryogenic temperatures, yielding quantitatively species (IV), which is identical with the final product of reaction (3):



This is documented by the low temperature proton NMR spectrum shown on the right side of figure 1, which was obtained in a sample prepared by dissolving compound (V) in FSA at -60°C . The singlet is known to be characteristic of cyclopentyl ion (IV) ¹ which should be non oxidizable in the range of potentials corresponding to peaks A and B in figure 1, if the proposed mechanism is correct. This indeed was found experimentally as is apparent from the voltamogram labeled cyclopentene in the figure: peaks A and B were conspicuous by their absence.

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