

Study on the Electro-reduction of Perfluorodecalin

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Abstract: The reduction of perfluorodecalin was studied by the method of electrochemistry. The results indicated that the electrochemical reduction of perfluorodecalin was a multi-step reaction. The mechanism of the first consecutive reaction showed that it is to diffusion controlling step.

Keywords: Electrochemical reduction, perfluorocarbons compounds, electrocatalytic, organometallic compounds.

The special chemical properties of perfluoro-carbon compounds (PFCs) led their multiple industrial and domestic applications. Recent interest has focused on the selective activation of C-F bond and functionization of saturated PFCs¹⁻³. Alkali metals, organometallic compounds, metallocene compounds with stronger reductive ability^{2,4,5} and photosensitizer⁶ have been used effectively for selective defluorination of saturated PFCs. Meanwhile, decamethylferrocene (FcCp₂), with many advantages, was chosen as reducing agent to reduce perfluoromethylcyclohexane⁵. Most of the research of selective defluorination of saturated PFCs was carried out by chemical and photochemical methods. Only in a few works, the electrochemical method was used². The present study is to investigate the electrochemical behavior of perfluorodecalin and exhibit the neglected but important electrochemical approaches in the field of selective defluorination of saturated PFCs. Here we show an attractive phenomenon: the multi-step reaction was observed in the electrochemical reduction of perfluorodecalin.

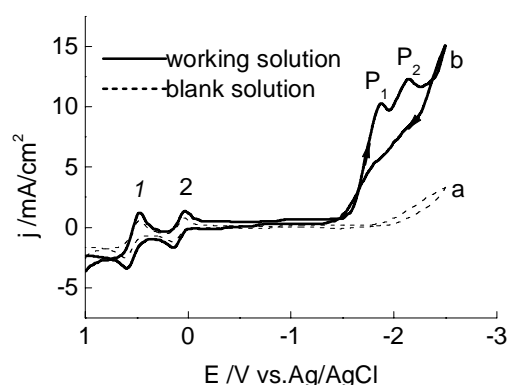
Experimental

Electrochemical measurements were carried out using a CHI650A electrochemical workstation controlled by a PCII computer. The conventional three-electrode electrochemical cell was used for cyclic voltammetric experiments. The working electrode was Pt with a disk area of 0.159 mm², sealed in glass tube. The surface of working electrode was renewed by polishing with 0.1 μm SiC powder followed by ultrasonication in ultra-pure water and tetrahydrofuran (THF), subsequently. A Pt sheet (1cm²) was used as the counter electrode. A silver chloride-coated silver wire electrode was used as the reference electrode and ferrocene/ferrocenium (Fc⁺/Fc) redox couple was

used as internal potential standard. The electrolytic solutions were prepared by THF (distilled over NaBzph and degassed prior to use). Tetra-n-butylammonium hexafluorophosphate ((n-Bu)₄NPF₆) was used in 0.2 mol/L concentration as an inert electrolyte without further purification. The working solution concentration of perfluorodecalin was typically 4×10^{-3} mol/L and the solution without perfluorodecalin was used as blank solution. Before electrochemical measurements, the electrolytic solutions have been deaerated by bubbling with high pure nitrogen gas. All results were obtained at ambient temperature (about 25°C).

Results and Discussion

Figure 1 Cyclic voltammogram



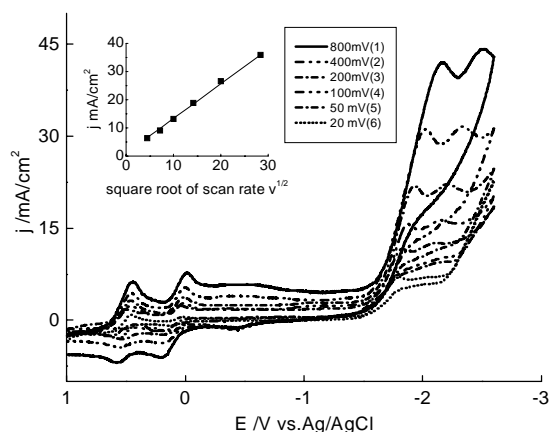
In the blank solution, two pairs of redox peaks appeared in the researched potential region, from 1.0V to -2.6V vs. Ag/AgCl in THF medium (see **Figure 1a**). The first pair of redox peak, with more positive potential value, was produced by the ferrocene/ferrocenium(Fc^+/Fc) redox couple. The second pair of redox peak, with more negative potential value, was produced by the decamethylferrocene / decamethylferrocenium ($\text{FcCp}^*_{2}/\text{FcCp}^*_{2}$). The value of $|E_{P_1} - E_{P_2}|$ of ferrocene/ferrocenium(Fc^+/Fc) redox couple is about 122 mV. It indicated that the redox reaction of the couple was quasi-reversible process. It should be ascribed the nature of the eletro-chemical system. At the same time, the result proved that the blank was suitable for the researches of defluorination of perfluorodecalin. **Figure 1b** showed the cyclic voltammogram curve of the cathodic reduction of 4×10^{-3} mol/L perfluorodecalin in 0.2 mol/L (n-Bu)₄NPF₆ on Pt electrode (arrows show the scan direction). On the negative-going sweep, there are two peaks at -1.871 V and -2.150 V (the scan rate was 50 mV), which will be termed P₁ and P₂ cathodic peaks, respectively. On the return sweep there is not any anodic peak (except two anodic peaks of ferrocene and decamethylferrocene) in research potential region. This fact proved that defluorination reaction of perfluorodecalin is a very difficult course. It should be ascribed to the great strength of the C-F bond and the

remarkable resistance to chemical attack by most reagents^{4,5}, it is the reason that leads to most scientists using strong reducing agent to selectively active C-F bond and achieve the defluorination products. At the same time, defluorination reaction of perfluorodecalin was proved for the first time as a consecutive step reaction by the technique of electrochemistry. It suggests us that the mechanism of defluorination reaction of perfluorodecalin will be explained and the selective defluorination reaction of perfluorodecalin might be achieved by the critical control some of parameter of electrochemistry during the process of defluorination reaction. Meanwhile, some drawback of chemical methods might be avoided. In addition, we found that the degree of reversibility of ferrocene/ferrocenium (Fc^+/Fc) redox couple will affect the clearness appearance of peaks of P_1 and P_2 .

Furthermore, the primary electrochemical dynamic behavior of defluorination reaction of perfluorodecalin was also investigated. The scan rate was changed from $20 \text{ mV}\cdot\text{s}^{-1}$ to $800 \text{ mV}\cdot\text{s}^{-1}$. The cyclic voltammograms of perfluorodecalin were showed in **Figure 2**. The first cathodic peak and the second cathodic peak showed a negative shift of potential 398 mV and 400 mV, respectively, between scan rate of 20 mV and $800 \text{ mV}\cdot\text{s}^{-1}$. Diffusional control of the cathodic could be proved by the proportionality between the peak current of P_1 and the square root of the scan rate (shown in the insert plot).

The detailed study on defluorination of perfluorodecalin is being carried out by the technique of *in-situ* electrochemistry in our group.

Figure 2 Cyclic voltammogram curves of Pt electrode in working solution with different scan rate. (The insert plot is the relationship between the peak current of P_1 and the square root of scan rate)



Conclusions

The results proved that perfluorodecalin could be reduced by the technique of electrochemistry for the first time. The electrochemical reduction of perfluorodecalin was an irreversible and multi-step electrochemical process. The mechanism of the first

electrochemical step belongs to diffusion controlling mechanism.

Acknowledgments

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