

Electrochemical Studies of 9-Fluorenone Complexation by Aluminum in Ionic Liquids

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Introduction

Recent work from this laboratory has involved the interaction of various Lewis acids with 9-fluorenone in ionic liquids (1). The basic nature of 9-fluorenone allows these interactions to be followed electrochemically by the extent of potential shifts caused by complexation at the carbonyl oxygen. Much of this work has been carried out in 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate [BMPY TfO] with various transition metal triflates (2, 3). The use of aluminum triflate ($\text{Al}(\text{TfO})_3$) in the present work helps to complete the picture of ketone complexation in ionic liquids.

Experimental

9-fluorenone and aluminum trifluoromethanesulfonate were obtained from Aldrich Chemical Company. BMPY TfO was prepared by the method of Welton (4). Voltammograms were taken with a PAR283 potentiostat using PowerSuite™ software. Potentials are reported with respect to a Ag/AgCl (0.1M EMICl in EMI BF_4) reference electrode (Cypress Systems). Vitreous carbon electrodes were obtained from Cypress Systems. All experiments were carried out in a Vacuum Atmospheres drybox.

Results and Discussion

The electrochemical behavior of 9-fluorenone in BMPY TfO is shown in Figure 1. Two successive one-electron redox processes are observed as shown in the black curve. Upon addition of $\text{Al}(\text{TfO})_3$, new reduction processes appear at -0.25 V and -0.90 V, indicative of complexation of 9-fluorenone by the added $\text{Al}(\text{TfO})_3$. The complexation is not complete, however, as shown by the small currents associated with these peaks. Reversal of the potential scan at -1.60 V, past the first 9-fluorenone reduction process, shows that the process is not reversible. This behavior is interpreted to mean that the 9-fluorenone radical anion is complexed rather extensively by the $\text{Al}(\text{TfO})_3$ remaining in solution. This general voltammetric situation is very similar to that for 9-fluorenone in BMPY TfO to which $\text{Sc}(\text{TfO})_3$ was added (2), as well as $\text{La}(\text{TfO})_3$ and $\text{Yb}(\text{TfO})_3$ (3). In these cases, the metal cation is evidently very extensively complexed by the large concentration of triflate in the ionic liquid, preventing complete interaction with 9-fluorenone (1). It is interesting to note that complexation of 9-fluorenone by aluminum in the acidic aluminum chloride : 1-ethyl-3-methylimidazolium chloride ionic liquid is very complete (1), illustrating the importance of the anionic environment to the activity of a Lewis acid.

Acknowledgement

Grateful acknowledgement is made to the United States Naval Academy Chemistry Department for its support.

References

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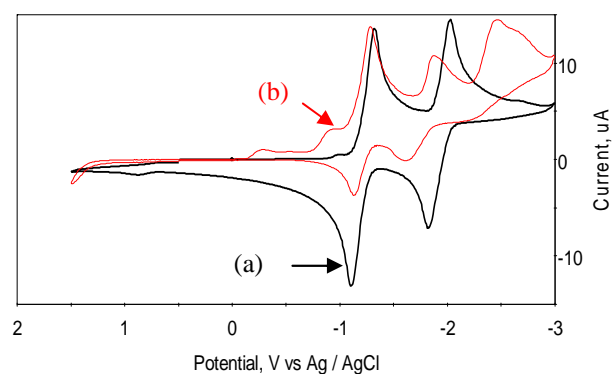


Figure 1. Cyclic voltammograms of 63 mM 9-fluorenone in BMPY TfO, at vitreous carbon, 100 mV/s. [(a), black curve] Before addition of $\text{Al}(\text{TfO})_3$. [(b), light red curve] After addition of 1:1 FI : $\text{Al}(\text{TfO})_3$.

Scans with 60 mM $\text{Al}(\text{TfO})_3$ in BMPY TfO (separate solution) gave no appreciable ($< 1 \mu\text{A}$) response above background current.