ELECTROCHEMICAL REDUCTION OF AROMATIC KETONES
IN A ROOM-TEMPERATURE MOLTEN SALT

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ABSTRACT

The electrochemical behavior of fluorenone and benzophenone has been investigated in the aluminum chloride : 1-methyl-3-ethylimidazolium chloride molten salt system. Cyclic voltammetric studies have shown that melt acidity greatly influences the reduction potential of these ketones by complexation of the carbonyl oxygen in the acidic melt. The lifetime of the electrochemically generated ketyl also depends on melt acidity, becoming longer (more stable) as acidity increases. Preparative electrolyses have shown that reduction of fluorenone in the basic melt gives the pinacol (one-electron, dimeric) product, whereas benzophenone reduction forms the alcohol (two-electron, monomeric) product. In the neutral melt, buffered with sodium chloride, both ketones undergo reduction to form a pinacolone product, resulting from initial pinacol formation followed by rearrangement induced by oxide abstraction by the melt. Further evidence of oxide uptake by the melt is found in the reduction of fluorenone in the acidic melt, in which the pinacolone product and a small amount of bifluorenylidene (alkene, both oxygens removed) is formed.
INTRODUCTION

Previous studies of carbonyl compounds in this room-temperature melt (1-4) have shown that the electrochemical properties are markedly affected by melt acidity, an increase of which causes the reduction potentials for these compounds to be shifted to more positive values. Complexation of the carbonyl groups by aluminum chloride in acidic melts is responsible for this phenomenon and seems to be rather general in these melts. In preliminary work, it has been found that the reduction process for ketones (4) is not as reversible as that for quinone systems (1,2), affording an opportunity to study the effect of melt acidity on the type and distribution of ketone reduction products. Of particular interest here is the possibility of oxide abstraction from the reduction products by aluminum species in the melt. This pathway has not been extensively investigated in this molten salt system, and provides an interesting insight into additional aspects of reactivity for oxygen-containing compounds.

EXPERIMENTAL

1-Methyl-3-ethylimidazolium chloride (MEIC) was prepared by reaction of 1-methylimidazole and a three-fold molar excess of ethyl chloride in a pressure bottle (5). Ethyl chloride (Aldrich Chemical Company) was used as received, and 1-methylimidazole (Aldrich Chemical Company) was vacuum-distilled over calcium hydride before use. Aluminum chloride was purified by distillation in a sealed tube (1). For removal of trace amounts of protonic impurities, either addition of ethyl aluminum dichloride or placement of the melt under vacuum was employed.

Voltammetric experiments were carried out at a PARC Model 174A Polarographic Analyzer, coupled with a Bioanalytical Systems CV-27 as potential scanner. A PARC Model 273 Electrochemistry System was used for preparative electrolysis and coulometric experiments. Cyclic voltammograms were recorded at 3 mm diameter vitreous carbon rod (Tokai GC-30 sealed in Pyrex) and are referenced against aluminum wire immersed in 2:1 aluminum chloride : MEIC melt.

Preparative electrolyses were run at reticulated vitreous carbon working electrodes using a PARC Model 273 Potentiostat. Following electrolysis, the melt was extracted with hexane or pentane while still in the drybox in order to separate neutral compounds from the melt. The melts were then taken outside the drybox, poured over ice, and then extracted with benzene to obtain the remainder of the electrolysis products.
RESULTS AND DISCUSSION

Electrochemistry of Fluorenone System.

The electrochemical behavior of fluorenone in the aluminum chloride : MEIC molten salt system has been described in a previous contribution (4) and will be summarized here. As is the case for other carbonyl compounds, the reduction potential for fluorenone is shifted to more positive values as the melt composition is changed from the basic region (−1.00 V) to the acidic domain (+0.10 V), this shift being due to complexation of the carbonyl oxygen by aluminum chloride. This complexation also has a profound effect on the spectroscopic properties of the solute, in this case causing a change from yellow (basic melt) to red (acidic melt). The voltammetric behavior of fluorenone has been rather well characterized, and subsequent work has involved determination of electrolysis products formed in fluorenone reduction in melts of various acidity levels.

In the basic melt, fluorenone undergoes a one-electron reduction, there being no anodic process on the return sweep at 100 mV/s. At 500 V/s, however, an anodic process appears approximately 500 mV positive of the reduction process and corresponds to the oxidation of the ketyl back to fluorenone. The ketyl anion, being negatively charged, apparently displaces chloride from tetrachloroaluminate, resulting in a ketyl species complexed by aluminum chloride. This interaction results in the separation in the observed potentials for the redox processes. At slower scan rates, the anodic process decreases in importance as the ketyl species couple to produce the pinacol, the oxidation of which is not observed in the basic melt. A preparative reduction of fluorenone in the basic melt resulted in the formation of fluorenone pinacol in 80% yield, there being also some pinacolone (10%) produced as well. As shown in Figure 1, the pinacolone results from rearrangement of the initially produced pinacol species in the melt.

From previous work on anthraquinone (1), chloranil (2), and fluorenone (4) in room-temperature molten salt systems, it has been observed that voltammetric studies in the neutral region typically involve the presence of many species and/or voltammetric responses, and that the relative amounts of these species depend critically on slight changes in melt acidity. For this reason, investigations in the neutral melt were carried out using the sodium chloride buffer system recently investigated by Wilkes et al. (6) Neutral conditions result from the addition of NaCl to a slightly acidic melt, the NaCl reacting with Al₂Cl₇⁻ to produce AlCl₄⁻. The effect
on the voltammetry of fluorenone is shown in Figure 2, in which the behavior typical of the acidic melt (1) changes to that seen in the buffered neutral melt. In particular, it is seen that conditions are still acidic enough that fluorenone exists primarily in the complexed form, and that the one-electron reduction process (Ic) in the acidic melt becomes more complex in the neutral melt. The presence of multiple processes in the neutral melt is probably due to depletion of the small amount of AlCl₃ next to the electrode surface as complexation of the reduction product occurs, resulting in a slight shift in reduction potential as the local acidity changes. It can also be seen that the Ia process in the acidic melt, due to oxidation of the ketyl in the acidic melt, is absent in the neutral melt. Preparative electrolysis showed that fluorenone pinacolone was produced in 75% yield, with a trace of bifluorenylidene also being formed. This result implies that reduction results in initial formation of the pinacol product from rapid coupling of the ketyl, followed by rearrangement to the pinacolone. In the more acidic conditions of the neutral melt, the rearrangement is much more complete than it is in the basic melt, reflecting the greater ease of oxide abstraction from the reduction product as acidity increases.

The electrochemical behavior of fluorenone in the acidic melt is more complicated than in either the basic or neutral regions. As seen in Figure 2, the first reduction process, shown by coulometry to involve one electron, results in the formation of the ketyl which couples more slowly than in less acidic melts. Variation of scan rate showed that the products undergoing oxidation at IIa (two peaks) are formed at the expense of the ketyl, suggesting that the IIa peaks are due to oxidation of the pinacolate product. Verification of this premise was found from a preparative electrolysis, in which the product oxidizing at the more positive potential in IIa was found to be stable and could be oxidized back to fluorenone, as shown on the return sweep. By performing another electrolysis just positive of the pinacolate oxidation wave, the amount of fluorenone regenerated served as a measure of the yield of the pinacol produced (25-35%). The presence of two waves in the IIa system suggests that the pinacolate exists in the acidic melt in two conformations, interconversion being difficult because of complexation of the oxygen anions by aluminum chloride. Even in more usual solvents such as DMSO and acetonitrile, some broadening of NMR resonances due to hindered interconversion of fluorenone pinacol conformers has been noted (7), giving support to this interpretation. As was stated earlier, only one form of the pinacolate is stable during the electrolysis, so that other products resulting from subsequent reactions should also be present. Product analysis showed that some of the pinacolone
product is also formed here. Bifluorenylidene (Figure 3) is also formed during the electrolysis (5-10% yield), giving a reversible couple at +1.20 V. Formation of this product evidently requires the abstraction of two oxide anions from the pinacolate and occurs only in the acidic melt.

**Electrochemistry of Benzophenone System.**

The series of cyclic voltammograms presented in Figure 4 illustrates the electrochemical behavior of benzophenone as the melt acidity is varied. As in the fluorenone system, complexation of the carbonyl group by aluminum chloride in the acidic melt results in a positive shift of the reduction potential; however, the benzophenone system as a whole is less easily reducible than is the fluorenone system. This is particularly evident in the acidic melt, in which reduction occurs immediately before the cathodic background process. Preparative electrolyses were attempted in the 1.2 : 1.0 acidic melt, but aluminum deposition eventually began and rendered the coulometric measurements meaningless.

As seen in Figure 4, reduction in the basic melt occurs in a rather broad process, there being no discernible reversibility at 100 mV/s. At higher scan rates, however, the ketyl oxidation process appeared, and at 10 V/s and higher the peak height ratios for the redox processes remained constant, indicating that further reaction of the ketyl occurs much more slowly than for the fluorenone system. Preparative electrolysis in the basic melt gave the alcohol (diphenylmethanol) as major product, with a smaller amount (10%) of tetraphenyloxirane also being produced. It was determined that the tetraphenyloxirane was formed in the electrolysis, and not during subsequent melt hydrolysis, by extraction of the melt with hexane immediately after the electrolysis, the epoxide product being found in the hexane extract. The more negative reduction potential of benzophenone apparently is responsible for the formation of a two-electron product (alcohol), as opposed to the one-electron product (pinacol) seen in the fluorenone system. The formation of tetraphenyloxirane is an indication that the pinacol is formed in low yield and undergoes subsequent abstraction of oxide by the melt to produce an epoxide system. This pathway is not followed for the fluorenone system, presumably because the steric constraints would be too severe in the analogous epoxide system. The epoxide formation in the basic melt is very interesting because it shows that the tetrachloroaluminate ion has the ability to abstract oxide from...
the products formed in the electrolysis.

In a weakly acidic melt (1.03 : 1.00), benzophenone reduction results in the formation of a relatively stable ketyl, as shown in Figure 5. Addition of sodium chloride to form the neutral buffered melt resulted in a situation much the same as that in the fluorenone system; that is, the reduction process shows evidence of multiple processes and following chemical reactions are now much faster than in the acidic melt. A preparative electrolysis produced pinacolone, so that the one-electron reduction mechanism (pinacol formation, followed by oxygen abstraction) is apparently followed here as well.

CONCLUSIONS

The products obtained in the electrolyses of fluorenone and benzophenone can be accounted for on the basis of both the structural aspects of the compounds themselves and on the melt acidity. In the basic melt, for instance, the structural differences between fluorenone and benzophenone cause the reduction of the latter compound to occur at rather more negative potentials, resulting in the production of the alcohol (two-electron) product as opposed to the formation of the pinacol (one-electron) product in the fluorenone system. The small amounts of epoxide formation in the benzophenone system and pinacolone formation in the fluorenone system show that the basic melt, in particular the tetrachloroaluminate ion, has the ability to abstract oxygen from the reduction products. The extent of this abstraction becomes greater, of course, as the melt acidity is increased, as is evident in the formation of pinacolone products from both systems in the neutral melt. Even further abstraction occurs in the acidic melt, at least in the fluorenone system, leading to the formation of bifluorenylidene. This uptake of oxide by the melt is undoubtedly driven by the large Al-O bond strength (8), coupled with the decrease in the carbon-oxygen bond order occurring upon ketone reduction. An interesting parallel between this work and recent synthetic methodology is found in the McMurry reaction, in which reaction of ketones with zero-valent titanium produces alkenes in very high yields (9).

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Figure 1. Reduction of fluorenone in the basic melt, showing formation of the pinacolate and pinacolone products.
Figure 2. Cyclic voltammetric behavior of fluorenone (31 mM).

(a) 1.04 : 1.00 acidic melt
(b) NaCl - saturated melt (buffered neutral)

100 mV/s

Temperature = 40°C
Figure 3. Reduction of fluorenone in the acidic melt, showing formation of the pinacolate and bifluorenylidene.
Figure 4. Cyclic voltammetric behavior of benzophenone.

Acidic melt: 24 mM
Neutral melt: 35 mM
Basic melt: 31 mM

100 mV/s, Temperature = 40°C
Figure 5. Cyclic voltammetric behavior of benzophenone (36 mM).

(a) 1.03 : 1.00 acidic melt
(b) NaCl - saturated melt (buffered neutral)

100 mV/s  Temperature = 40°C