FRIEDEL-CRAFTS ALKYATION REACTIONS
IN A ROOM TEMPERATURE MOLten SALT

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ABSTRACT

Room temperature molten salts have found usefulness as solvents for electro-organic studies because of their aprotic properties, wide electrochemical windows and reasonable conductivities as ionic liquids. The 1-methyl-3-ethylimidazolium chloride - aluminum chloride system was chosen for this study for its ease of preparation, its wide range of Lewis acidities and its carbocation stabilizing properties. We have studied the alkylation of benzene using the seven stable chloropentane isotopes. Cyclic voltammetry at a glassy carbon rotating disk electrode indicates carbocation formation from the chloropentanes only in acidic melts and no oxidation peaks are observed without prior reduction. Multiple reduction peaks and product analyses indicate that significant rearrangement occurs in the carbocations. Stabilization of carbocations probably results from complexation with the \( \text{Al}_2\text{Cl}_7 \) ion and this is strongly indicated by the delay of Al deposition in the presence of carbocations.

INTRODUCTION

The Friedel-Crafts reaction using anhydrous aluminum chloride as catalyst has been the most important method for attaching alkyl side chains to aromatic rings. The role of aluminum chloride is to abstract the halogen from the alkyl halide generating a carbocation which then acts as an electrophile attacking the aromatic ring. Friedel-Crafts systems are best considered as generalized acid-base systems with the electron deficient catalyst as the acid and the electron donor ability of the reagent as the base. Chloroaluminate room temperature molten salts provide a unique solvent system for Friedel-Crafts alkylations since the melts function as both solvent and catalyst. In the 1-methyl-3-ethylimidazolium chloride - aluminum chloride system, the catalyst has been
identified as the heptachloro-aluminate ion (4), the Lewis acid in the equilibrium:

\[ 2\text{AlCl}_4^- \rightleftharpoons \text{Al}_2\text{Cl}_7^- + \text{Cl}^- \]

Thus carbocation formation and alkylation reactions have not been observed in basic or neutral melts but only for acidic melts (mole fraction of AlCl$_3$ is greater than 0.500).

In alkylation reactions with a series of alkyl halides the long established sequence of reactivity is: tertiary halide > secondary halide > primary halide, which follows carbocation stability (2). Olah has also noted that Friedel-Crafts reactions are notoriously irreproducible, being traced to the presence of impurities which serve as co-catalysts without which Friedel-Crafts halides are often inactive (3). Following Olah, the carbocation generated as the alkylating species is most likely the classical trivalent carbenium ion rather than the penta- or tetracoordinated carbonium ion. Alkylation of benzene may proceed through a tetracoordinated aronium ion or $\pi$-complex or the trivalent arenium ion or $\sigma$-complex (4):

Olah has suggested that most Friedel-Crafts reactions probably do not involve formation of a free carbenium type reagent that reacts with the substrate. The alkylation of benzene with 1-chloropropane has shown an absence of isomerization of the alkylating agent indicating an $S_N2$ type displacement reaction (5):

\[ \text{CH}_2\text{CH}_2\text{Cl} + \text{AlCl}_3 \rightleftharpoons \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2\text{Cl} \rightleftharpoons \text{AlCl}_3 \]
Wilkes, et.al. have recently shown that in the MEIC-A1Cl₃ melt system, 1-chloropropane does isomerize with 57% of the alkylation product being isopropyl benzene and 24% n-propylbenzene with the remainder of product being di- and tri substituted benzenes (1). This is a strong indicator that these melt systems stabilize carbocations and that Friedel-Crafts alkylations may proceed somewhat differently than in conventional organic solvent systems.

EXPERIMENTAL

Procedures for melt preparation and general experimental conditions were those described by Wilkes, et.al. (1) All experiments were carried out in a helium environment in a Vacuum Atmosphere glove box system. Cyclic voltammetric measurements were made with a glassy carbon rotating disk electrode (normally with a rotation rate of 100 rpm), a tungsten counter electrode and an aluminum wire in 0.60 melt as reference. The chloropentane isomers were either Pfaltz-Bauer or Kodak and used as received.

Alkylation reactions for product analyses were generally run with 10 g melt / 1 g chloropentane / 10 g benzene, with the excess benzene to limit multiple substituted benzene products. After 48 hours in closed containers with magnetic stirring inside the glove box, each reaction sample was removed, reacted with 25 g crushed ice and then made basic with 6N NaOH. The liquid was added to a separatory funnel and extracted with 25 ml of diethyl ether. The ether samples were dried with anhydrous Na₂SO₄, then concentrated by evaporation of ether to final volumes of 10 ml which were then retained for analyses. Separation of various components was accomplished with GC on a fused glass capillary column with a stationary phase of SupelcoWax-10 and identified with MS using a HP model 5992 GC/MS instrument. (The GC/MS analyses were performed under contract with an independent analytical laboratory.)

RESULTS AND DISCUSSION

Cyclic voltammetry in acidic melts with the seven chloropentanes (1-C1-, 2-C1-, and 3-C1-pentane, 1-C1-2-methyl-, 1-C1-3-methyl-, 2-C1-2-methylbutane and neopentyl chloride) show two characteristic and consistent reduction peaks which are slightly dependent on melt acidity as follows:
No significant differences were observed for reductions with any of the seven isomers. With anodic sweeps, no oxidation was observed without prior reduction. Fig. 1 illustrates typical CV behavior in the MEIC-\(\text{AlCl}_3\) melts with Al deposition occurring at about \(-0.37\) V in 0.515 melt and at \(-0.26\) V in 0.55 melt. In following diagrams with added chloropentanes, we observe that Al deposition is either significantly delayed or prevented altogether. Formation of the carbenium ion results in a buffering action in the melt shifting it toward the neutral composition:

\[
\text{Al}_2\text{Cl}_7^- + \text{Cl}^- \xrightarrow{\text{buffering}} 2\text{AlCl}_4^- 
\]

For a typical CV experiment with 1 g of Cl-pentane in 20 g of 0.55 melt, there should be approximately twice as many heptachloroaluminate ions as Cl\(^-\) ions resulting from carbenium ion formation, assuming complete reaction. Thus we should still observe Al deposition based on melt acidity. That no deposition is observed is indicative of complex formation between the carbenium ion and Al\(_2\text{Cl}_7^-\).

Figures 2-8 present representative CV behavior for the chloropentanes with varying melt acidity. Compounds were selected to demonstrate the range of carbocations that should be formed, thus 1-chloro-pentane and neopentyl chloride should form primary carbenium ions, 3-chloropentane a secondary ion and 2-Cl\(^-\)2-methylbutane a tertiary ion. Essentially identical CV behavior was observed, not only for these four isomers, but in fact, for all seven of the chloropentane isomers studied. Figures 9-11 give qualitative comparisons of reaction rates of the alkylation reactions as a function of alkylation agent and melt acidity. These results show that the alkylation rate is strongly dependent on melt acidity (compare Figures 9 and 10). In addition, alkylation by a tertiary carbenium ion (assuming 2-Cl\(^-\)2-methylbutane forms a tertiary ion as the most stable species) occurs much faster and to a greater extent than by a primary carbenium ion (which would be the initial species formed from neopentyl chloride).

Product analyses were performed for products from alkylation reactions of benzene in 0.515 and 0.55 melts with 1-Cl\(^-\) and 3-Cl-pentane, 2-Cl\(^-\)2-methylbutane and
neopentyl chloride. Very little product could be isolated from reactions in the 0.515 melt and no reliable information can be reported. Results for 0.55 melt were as follows:

| alkylating agent   | products identified                                      |
|--------------------|----------------------------------------------------------|
| neopentyl chloride | isopentylbenzene                                         |
| 2-Cl-2-methylbutane| n-pentyl- and 2-pentylbenzene                            |
| 3-Cl-pentane       | n-pentyl-, 2-pentyl- and 3-pentylbenzene                 |
| 1-Cl-pentane       | 5 products as follows:                                   |

Benzene alkylation products with 1-Cl-pentane

| product                        | percent |
|--------------------------------|---------|
| 1,2-dimethyl-propylbenzene     | 78.5%   |
| 3-pentylbenzene                | 13.5    |
| 2-pentylbenzene                | 4.5     |
| isopentylbenzene               | 2.5     |
| n-pentylbenzene                | 1.0     |

Using a 10/1 benzene / chloropentane ratio effectively limited multiple alkylation products. Neopentyl chloride resulted in only a relatively small amount of alkylated benzene product. 1-Cl-pentane which should form the least stable carbocation and hence lead to the greatest degree of rearrangement resulted in the greatest variety of products as expected. The major product from 1-Cl-pentane alkylation of benzene (compound 1)

\[
\begin{align*}
\text{CH}_3 & \\
\text{C-H} & \\
\text{C-CH}_3 & \\
\text{H}_3\text{C-H} & \\
\end{align*}
\]

(1)

is not one we would have predicted. The isopentylbenzene (compound 2) is likewise an unexpected product. While \(-\text{CH}_3\) group migration is not as common as \(-\text{H}\) migration in carbocation rearrangements to form more stable ions, it is not unusual.
The products observed are not easily correlated with the electrochemical observations. The presence of two reduction peaks at essentially the same reduction potentials for each of the chloropentane isomers strongly suggests that the same two carbocation species are present in each case. The variety of products observed may be the result of rearrangements after alkylation has occurred. At present we cannot answer this question.

SUMMARY

Cyclic voltammetric studies of chloropentane isomers in MEIC-AlCl₃ acidic melts indicate the presence of two reducible species formed with each of the seven isomers studied. Similarity of the reduction potentials in every case suggests that significant rearrangements of the carbocations occur to produce similar carbenium ions from each of the isomers. Retardation and in some cases prevention of aluminum deposition indicate complex formation between the carbenium ions formed and the heptachloroaluminate ions of the acidic melt. Identification of several alkylation products suggest that rearrangements occur after the carbocation has attacked the benzene ring.

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3. Ibid, p. 414

4. Ibid, p. 516

5. Ibid, p. 533
Figure 1. Electrochemical windows of MEIC/AlCl$_3$ melts, $v = 100$ mV/sec.
Figure 2. Cyclic voltammetry of neopentyl chloride in 0.5067 melt. Anodic sweep limit: 2.4 V.
Figure 3. Cyclicvoltammetry of neopentyl chloride as a function of melt acidity.
Figure 4. Cyclic voltammetry of 3-Cl-pentane as a function of melt acidity.
Figure 5. Cyclic voltammetry of 3-Cl-pentane as a function of melt acidity.
Figure 6. Comparisons of cyclic voltammetric behavior in 0.515 melt. Voltage ranges: +2.6 to -1.6V; except (c) with +2.65V to -1.3V.
Figure 7. Comparisons of cyclic voltammetric behavior in 0.515 melt with extended cathodic sweep. Voltage ranges: 2.65V to -2.3V; except (d) to -2.4V.
a. 3-Cl-pentane  

b. 1-Cl-pentane  

c. 2-Cl-2-me-butane  

d. neopentyl chloride

Figure 8. Comparisons of cyclic voltammetric behavior in 0.55 melt. Voltage ranges: 2.6V to -0.75V.
Figure 9. Time dependence of cyclic voltammograms for reaction of benzene with 2-Cl-2-me-butane in 0.55 melt.
Figure 10. Time dependence of cyclic voltammograms for reaction of benzene with 2-Cl-2-me-butane in 0.52 melt.

a. no benzene

2.4V ———— -1.4V

b. 10 minutes after addition of benzene

2.4V ———— -1.4V

c. 20 minutes

2.1V ———— -1.4V

d. 18 hours

2.1V ———— -0.85V
Figure 11. Time dependence for reaction of benzene with neopentyl chloride in 0.52 melt. Anodic limit: 2.0V.

- a. -0.7V no benzene
- b. -0.7V 20 minutes after addition
- c. -0.6V 40 minutes
- d. -0.6V 60 minutes
- e. -0.6V 150 minutes
- f. -0.6V 15 hours