to pose no special problems.

Acknowledgment. The support of the U.S. Public Health Service (Grants GM-19450 and GM-21153) at Utah and the Robert A. Welch Foundation grant at Trinity is appreciated. B.P. thanks the Trinity Academic Leave Committee for faculty release time to support this investigation. We are grateful to Ms. L. Jonas and Mr. J. Radziszewski for technical assistance with the LD measurements.

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Electrochemistry of Carbonium Ions in Acidic Media. 1. Triphenylmethyl Ion in Aluminum Chloride Containing Melts

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The electrochemistry of the triphenylmethyl carbonium ion (1) has been studied in a room-temperature aluminum chloride containing melt. Formation of 1 is dependent on the acidity or pCl of a molten aluminum chloride/*n*-butylpyridinium chloride (1:1) binary mixture. The equilibrium constant for reaction 1 is 20.4 ± 0.3 mol L^{-1} at 40 °C as determined by spectroscopic techniques. Formation of 1 from triphenylmethyl chloride is too slow to quantitatively determine a rate constant (k_f) by conventional electrochemical techniques. Cyclic voltammetric and controlled-potential coulometric data reveal that 1 is reduced in an one-electron process to a triphenylmethyl radical (2). Formation of 2 in the $AlCl_3$ melt is verified by ESR spectroscopy. Dimerization of 2 produces an electrochemically oxidizable form of 1-(diphenylmethylene)-4-(triphenylmethyl)-2,5-cyclohexadiene (3); the rate constant for the dimerization of 2 is $1.33 \pm 0.08 \times 10^3$ l mol^{-1} s^{-1} at 40 °C. Workup of an exhaustively electrolyzed solution of 1 in the melt produces [4-(diphenylmethyl)phenyl]triphenylmethane, which is the result of proton isomerization of 3.

Molten salts, in particular tetrachloroaluminate melts, have been found to be useful solvents for organic electrochemical studies due to their totally aprotic and anhydrous properties.[1] Most recently aluminum chloride-/alkylpyridinium halide binary mixtures have been shown useful for such studies due to liquidus temperatures close to ambient temperatures.[2-4] This laboratory has recently become interested in the aluminum chloride/*n*-butylpyridinium chloride ($AlCl_3$/BPC) mixtures. Spectroscopic studies indicate that the predominant aluminum species in the $AlCl_3$/BPC melts are $AlCl_4^-$ and $Al_2Cl_7^-$, the relative ratio of which is dependent upon the composition.[5] The acid-base chemistry of these melts is of particular interest and can be described by the reaction $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$, with an equilibrium constant of 3.8×10^{-13} at 30 °C.[6] By varying the melt composition from 0.75:1 to 2:1 $AlCl_3$/BPC, the pCl of the melt can be varied from 0 to 15. Thus, the acidity range in these melts compares favorably with that found in conventional aqueous chemistry.

Several studies involving the electrochemical oxidation of aromatic amines and polycyclic aromatic hydrocarbons indicate improved stability of radical cations in the $AlCl_3$-containing melts.[2,3,7,8] In addition, recent work in this laboratory shows improved stability for monoamine dications as well as radical cations in the $AlCl_3$/BPC melt.[9] The most plausible explanation for this improved stability of cationic species is the absence of nucleophiles of appreciable strength in these $AlCl_3$ melts. It was therefore decided to take advantage of this property in the preparation and subsequent electrochemical study of carbonium ions in the $AlCl_3$ melt. The approach used in this laboratory included the generation of carbonium ions by the reaction $RCl + Al_2Cl_7^- \rightleftarrows R^+ + 2AlCl_4^-$, which can be controlled by adjustment of the pCl or $AlCl_3$ composition of the melt. The initial results of this approach for the generation of electroactive carbonium ions are presented here. Electrochemical studies on the triphenylmethyl carbonium ion in an $AlCl_3$/BPC melt are presented.

Experimental Section

Chemicals. Triphenylchloromethane (mp 110.5–111.5 °C) was prepared by reacting triphenylmethanol (Matheson) with freshly distilled acetyl chloride (Fisher) in benzene and was recrystallized from benzene.[10] 1-(Diphenylmethylene)-4-(triphenylmethyl)-2,5-cyclohexadiene (3) was obtained by reducing triphenylchloromethane with molecular silver:[11] For 3: ^1H NMR of ($CDCl_3$) δ 6.8–7.4 (20, aromatic), 5.8–6.4 (4, olefinic), 4.9 (1, methine); ^{13}C NMR ($CDCl_3$) 43.66, 62.44, 125.59, 126.05, 126.57, 127.67, 128.06, 130.27, 137.16, 141.44, 143.65, 146.64. [4-(Diphenylmethyl)phenyl]triphenylmethane (4, mp 225–227 °C) was prepared by bubbling HCl in a benzene solution of 3.[12] For 4: ^1H NMR ($CDCl_3$) δ 7.0–7.5 (29, aromatic) 5.5 (1, aliphatic); ^{13}C NMR ($CDCl_3$) δ 56.33, 64.58, 125.79, 126.18, 127.28, 128.19, 129.36, 131.05, 141.19, 143.85, 144.63, 146.71.

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The *n*-butylpyridinium chloride (BPC), which was used for melt preparation, was prepared by refluxing pyridine (Fisher) and *n*-butyl chloride (Fisher) in the absence of light. After the mixture was refluxed for 24 h, the excess reactants were decanted from crystalline BPC and refluxed until an 80% yield of BPC was obtained. The BPC was recrystallized four times from acetonitrile with decolorizing charcoal. The BPC was then dried for at least 24 h at 70 °C under vacuum and transferred to a drybox for use. The aluminum chloride used in melt preparation was purified by a modification of the method of Seegmiller and co-workers.[13] Aluminum chloride was sublimed in an evacuated sealed tube, which had been loaded with $AlCl_3$ (Fluka, AG, iron-free), aluminum wire (Alfa, m5N), and NaCl (Fisher, ACS).

Instrumentation. Cyclic voltammetric, chronoamperometric and rotating disk electrode (RDE) measurements were performed on a solid-state, three-electrode potentiostat–galvanostat which incorporates circuitry for electronic compensation of ohmic potential drop between the reference and working electrodes.[14] The data were acquired by either a Houston Instrument 2000 X-Y recorder or Tektronix 5103N storage oscilloscope. The latter was equipped with a Type 5A20N differential amplifier, Type 5B10N time base plug ins, and a Model C-5 Polaroid camera. A Pine Instrument ASR rotator was used to control rotation rates for RDE studies. Large-scale, controlled-potential electrolyses were performed on a high-power (150 V, 0.1 A), three-electrode potentiostat.[15] Potentiometric measurements were made with a Fluke 8600A digital multimeter.

Visible–UV spectroscopic measurements were made with a Cary 14 spectrophotometer equipped with a Haake temperature controller for the cells. ESR spectra were obtained with a Bruker ER-420 spectrometer. ^1H NMR spectra were obtained on a Varian EM390 and ^{13}C NMR spectra were obtained on a JEOL FX60 spectrometer. A Du Pont 21-491 mass spectrometer was used to obtain mass spectral data.

Melt Preparation. All melt preparations and electrochemical experimentation were performed in a Vacuum Atmospheres HE-43-2 Dri-Lab glovebox equipped with a HE-493 Dri-Train for constant recirculation of argon gas through a column consisting of activated copper and molecular sieves. Purified aluminum chloride was slowly added to BPC in a electrochemical cell, which was equipped with a glass-coated stirring bar. The reaction is exothermic, and care must be taken to maintain the temperature below 100 °C or thermal decomposition will occur. The resulting almost colorless melt was used in the electrochemical and spectroscopic experiments without further purification.

Cells and Electrodes. A Pyrex electrochemical cell with a machined Teflon top to fit into a 45/50 outer joint, which served as a cell bottom, was used. The Teflon top was fitted with opening for the auxiliary, reference, and working electrodes and a thermocouple well. Stirring was accomplished with a glass-coated magnetic stirring bar. The cell assembly was mounted in a tube furnace, and the temperature maintained ±1 °C by a Love 51J proportional temperature controller in conjunction with an iron/constantan thermocouple.

The reference electrode was a coiled Al wire (Alfa, m5N) immersed in a 2:1 $AlCl_3$/BPC melt and separated from the bulk melt with a medium-porosity glass frit. All potentials reported herein are with respect to this electrode. The auxiliary electrode in the voltammetric studies was a tungsten wire. The working electrode in voltammetric studies was glassy carbon (5-mm diameter, Tokai GC-30) rod mounted in Pyrex glass.[16] Dylon grade GC graphite cement was used to make electrical contact between the glassy carbon and a copper lead wire. The electrode surface was polished to a mirror-like finish by using alumina (Fisher type B) on a lap-wheel polisher. Rotating disk electrode studies were performed on glassy carbon (5 mm, Tokai GC-30) sealed in Pyrex glass and mounted on a spindle to fit the Pine ASR rotator.[17]

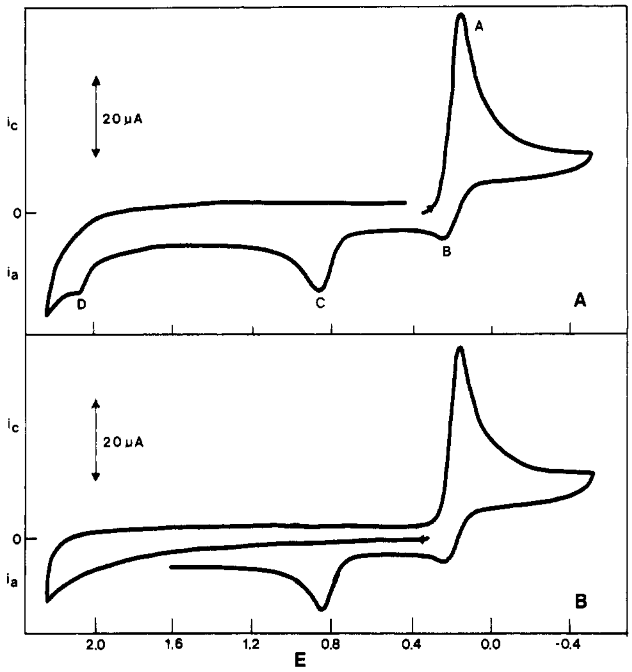

Figure 1. Cyclic voltammograms of 4.2×10^{-3} F triphenylmethyl chloride in a 1.1:1 $AlCl_3$/BPC melt at a pCl of 12 at 30 °C. The scan rate is 0.1 V/s on a glassy carbon electrode with an area of 0.20 cm^2: (A) initial cathodic scan from the rest potential, (B) initial anodic scan from the rest potential.

Exhaustive controlled-potential coulometric studies were carried out on a reticulated vitreous carbon basket (Fluorocarbon Corp., RVC 2X1-45-S). The auxiliary electrode for exhaustive electrolysis studies was a coiled Al wire (Alfa, m5N) in the 2:1 $AlCl_3$/BPC melt, which was isolated by means of a medium-porosity frit from the bulk melt. Stirring of the cell contents in the exhaustive experiments was accomplished by a magnetic stirring bar and stirrer.

The acidity of the melts were determined by placing an Al wire (Alfa, m5N) in the melt of interest and determining the potential difference between the Al wire and the 2:1 $AlCl_3$/BPC reference electrode. A 2:1 $AlCl_3$/BPC melt was assigned a pCl of 15.0.[6]

Product Analysis. Upon completion of an exhaustive electrolysis, the cell was brought out of the drybox, and the contents were carefully poured over ice in a fume hood. The aqueous layer was extracted three times with 50-mL portions of ether. The combined extracts were dried over magnesium sulfate and filtered, and the ether was removed on a rotary evaporator. Analysis of the resultant concentrated ether solution was accomplished by LC on a Waters Associates 6000A HPLC equipped with a Model 660 solvent programmer. The electrolyzed mixtures were separated on a 0.25-in. × 25-cm Alltech C18 (600 RP) column with 10-μm mean particle size packing. The flow rate of the eluting solvent (80/20 acetonitrile–water) was 1 mL/min.

Results and Discussions

Generation and Cyclic Voltammetry of Triphenylmethyl Carbonium Ions. Addition of triphenylmethyl chloride to a 1.1:1 $AlCl_3$/BPC melt produces a yellow solution containing a species which is reducible at 0.1 V. Figure 1A shows a cyclic voltammogram for triphenylmethyl chloride with an initial cathodic sweep from the rest potential at a moderately acidic pCl of 11.8. Reversal of the direction of potential sweep at a scan rate of 0.1 V s^{-1} produces a corresponding oxidation wave at 0.17 V (wave B), which indicates some stability for the product of the reduction process at 0.10 V (wave A). Rapid-scan voltammetric experiments show peak current ratios approaching unity for this couple at scan rates greater than 10 V s^{-1}. Upon continuing the anodic scan (Figure 1A), a second oxidation wave is noted at 0.8 V (wave C) with a small third oxidation wave at 2.1 V (wave

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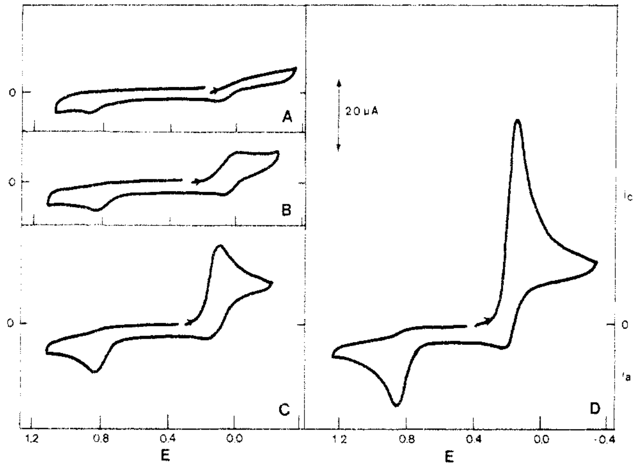


Figure 2. Cyclic voltammograms of 4.9×10^{-3} F triphenylmethyl chloride in an $AlCl_3$/BPC melt at 30 °C as a function of pCl: (A) pCl 10.2, (B) pCl 10.9, (C) pCl 11.0, (D) pCl 11.8. The scan rate is 0.1 V/s on a glassy carbon electrode with an area of 0.20 cm^2.

D). Both oxidation waves are chemically irreversible at scan rates of 1.0 V s^{-1}. Figure 1B illustrates a cyclic voltammogram with an initial anodic sweep from the equilibrium potential. The absence of oxidation waves on this sweep indicates that the oxidation waves at 0.8 and 2.1 V (C and D) are not due to an oxidizable species in the bulk melt but result from reaction pathways involving the product of the reaction process at 0.1 V. This conclusion is further verified by the decrease in peak currents for waves C and D with concomitant increase in wave B as the scan rate is increased.

The peak current for the reduction wave is linearly dependent on the concentration of triphenylmethyl chloride in the melt over a concentration range of 2–20 mM at a pCl of 12. The slope of the plot is 10.4 μA mM^{-1} at a scan rate of 0.1 V s^{-1}, which produces a diffusion coefficient of 3.9×10^{-7} cm^2 s^{-1} at 30 °C. The diffusion coefficient of ferrocene, a known one-electron process in the melt, has been reported as 4.7×10^{-7} cm^2 s^{-1} in the 1:1 $AlCl_3$/BPC melt at 30 °C.[2]

An increase in the acidity of the melt to pCl's greater than 12 does not appreciably change the peak current for the reduction wave at 0.1 V; however, as the melt is made basic, the peak current decreases smoothly as a function of pCl as illustrated in Figure 2A–D. Similar cyclic voltammetric behavior is obtained when the triphenylmethyl carbonium ion is added to a 1.1:1 $AlCl_3$/BPC melt as the triphenylmethyl hexafluorophosphate salt. A series of reactions consistent with these data are eq 1–3. The

$$Ph_3CCl + Al_2Cl_7^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Ph_3C^+ + 2AlCl_4^- \quad (1)$$

$$Ph_3C^+ + e^- \rightleftharpoons Ph_3C\cdot \quad (2)$$

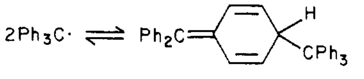
$$Ph_3C\cdot \xrightarrow{\text{slow}} \text{products} \quad (3)$$

redox couple at 0.1 V can be represented by reaction 2. Subsequent reactions of the triphenylmethyl radical in reaction 3 produce electroactive species, which are oxidized at 0.8 and 2.1 V. The further reduction of the triphenylmethyl radical to the anion is not possible in the 1.1:1 $AlCl_3$/BPC melt because of the deposition of aluminum at potentials more negative than −0.6 V at a pCl of 11. This cathodic limit is a function of melt acidity with a limit of approximately −0.1 V in the 2:1 melt and −1.1 V in the 1:1 melt (pCl 6).[2]

Spectroscopy. The equilibrium constant (K_{eq}) for reaction 1 was determined by using spectroscopic techniques.

The 1:1 mol ratio $AlCl_3$/BuPyCl melt is transparent from 800 nm in the visible region to 290 nm in the UV region. Addition of triphenylmethyl chloride to a melt at a pCl of 6 indicated no appreciable absorption at millimolar concentrations in the visible–UV window of the melt. However, upon increasing the acidity of the melt to a pCl of 8.5 or greater, a yellow color is formed whose intensity is dependent upon pCl as well as triphenylmethyl chloride concentration. The triphenylmethyl carbonium ion is apparently responsible for the observed yellow color; spectroscopic data on the system produce λ_{max} at 435 and 400 nm with log $\epsilon^{435} = 4.62$ and log $\epsilon^{400} = 4.64$. Triphenylmethylcarbonium ions, which are generated from the corresponding alcohol in a 95% H_2SO_4 solvent, have been reported with λ_{max} of 432 and 403 nm with log ϵ = 4.6 for both peaks.[18] Upon variation of the triphenylmethyl chloride concentrations from 1.17×10^{-4} to 1.17×10^{-3} F and pCl variations from 8.53 to 10.05, a series of spectroscopic measurements (eight determinations) produced a value of 20.4 ± 0.3 M for K_{eq}.

Controlled-Potential Electrolysis. Controlled-potential coulometry on a series of melts with triphenylmethyl carbonium ion concentrations of 10–40 mM in melts at pCl's of 12 indicated an *n* value of 1.04 ± 0.04 for the reduction process at 0.1 V. Cyclic voltammetric experiments on the resultant melts showed virtually exhaustive electrolysis with products from the reduction process which are respectively oxidized at 0.8 and 2.0 V (Figure 3A). Cyclic voltammetric experiments on 1-(diphenylmethylene)-4-(triphenylmethyl)-2,5 cyclohexadiene (**3**), which is the expected dimerization product of triphenylmethyl radical, produced an irreversible oxidation wave at 0.8 V (Figure 3B). Since **3** was added as a benzene solution to the melt, the diminished anodic limit due to oxidation of benzene did not allow potential sweeps beyond 1.8 V. Although there was unreacted triphenylmethyl chloride in the solution of **3** in the benzene/melt mixture, reversal of the potential sweep showed an increase in reducible species at 0.1 V. A reaction series consistent with these data is given by eq 4 and 5.

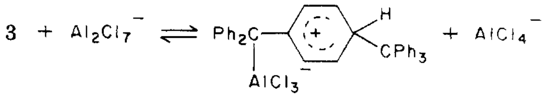


(4)

3

$$3 \xrightarrow{\text{wave C}} 2Ph_3C^+ + 2e^- \quad (5)$$

Further studies on the acid–base chemistry of **3** produced in situ by the electrochemical reduction of the carbonium ion indicate the importance of $AlCl_3$ complexation. The relative heights of the oxidation waves at 0.8 and 2.0 V are pCl dependent: wave C decreases as the pCl is increased with a concomitant increase in wave D. Complexation of the dimer **3** with $AlCl_3$ apparently produces dimer complex **5**, which is probably responsible for wave D.



(6)

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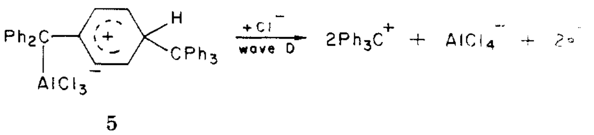

(7)

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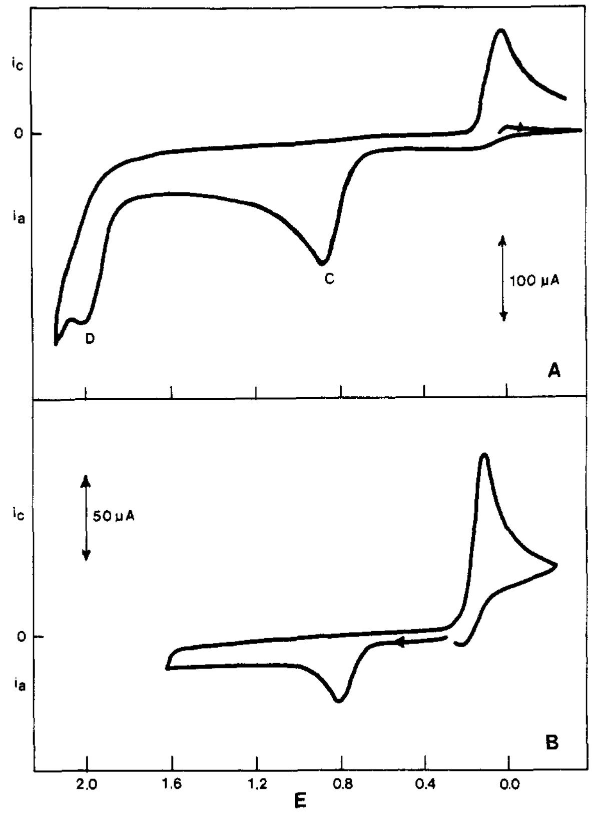


Figure 3. (A) Cyclic voltammogram after exhaustive electrolysis at an applied potential of −0.1 V (n value = 1.02 faradays/mol) of 3.5×10^{-2} F triphenylmethyl chloride in an $AlCl_3$/BPC melt at pCl 12. (B) Cyclic voltammogram of an approximately 10×10^{-3} F solution of 1-(diphenylmethylene)-4-(triphenylmethyl)-2,5-cyclohexadiene (**3**) in benzene–$AlCl_3$/BPC melt at pCl 12. The scan rate is 0.1 V/s on a 0.20-cm^2 glassy carbon electrode.

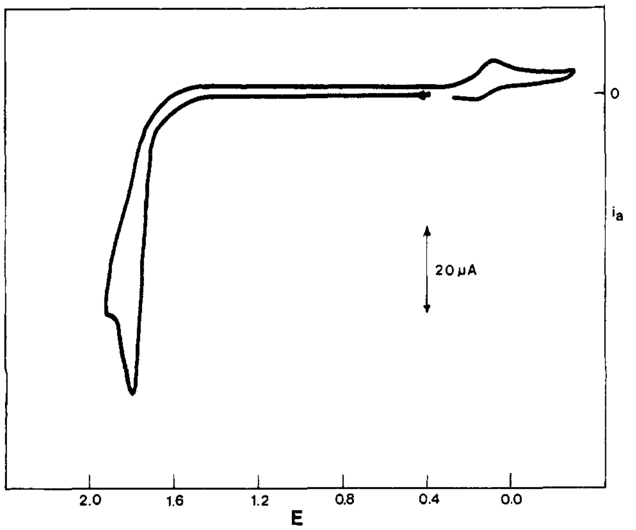


Figure 4. Cyclic voltammogram of 3.3×10^{-3} F [4-(diphenylmethyl)phenyl]triphenylmethane (**4**) in an $AlCl_3$/BPC melt at pCl 12. The scan rate is 0.1 V/s on a 0.20-cm^2 glassy carbon electrode.

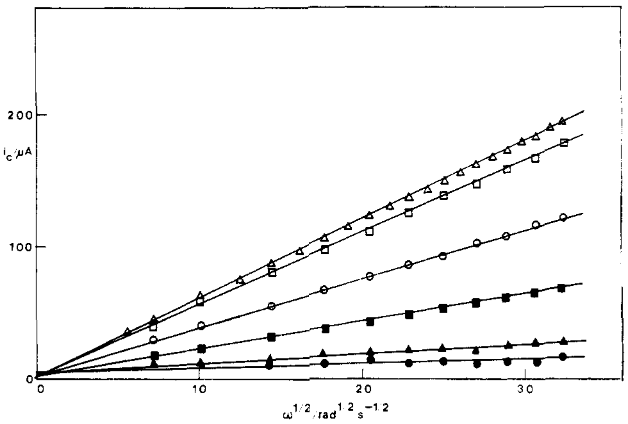
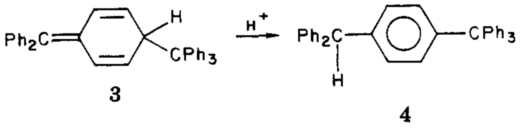
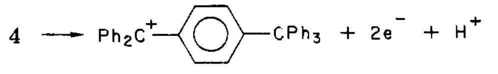


Figure 5. Rotating disk electrode (RDE) voltammetric plot of limiting cathodic current at −0.1 V vs. the square root of rotation rate ($\omega^{1/2}$) for 6.0×10^{-3} F triphenylmethyl chloride in the $AlCl_3$/BPC at 30 °C as a function of pCl: ●, pCl 10.6; ▲, pCl 10.9; ■, pCl 11.1; ○, pCl 11.3; □, pCl 11.6; △, pCl 12.1. The planar glassy carbon electrode had a area of 0.20 cm^2.



(8)

The electrochemistry of other possible dimeric forms were examined in the melt. **3** has been reported to undergo isomerization to [4-(diphenylmethyl)phenyl]triphenylmethane (**4**) under acidic conditions.[12] Cyclic voltammetric experiments on a melt solution of **4** show an irreversible oxidation wave at 1.8 V (Figure 4). A small, but significant, reduction wave at 0.1 V is observed on the reverse cathodic scan; this wave is consistent with the reduction of a substituted triphenylmethyl carbonium ion.[19] An electrode reaction consistent with this observation is shown in eq 9.



(9)

ESR spectroscopy after exhaustive electrolysis of the carbonium ion was used to confirm the formation of the triphenylmethyl radical. By use of external generation techniques, a complex spectrum, which had resolved more than 120 of the 196 theoretical lines for a triphenylmethyl radical, was obtained in the $AlCl_3$ melt. Splitting constants of a_p = 2.83, a_m = 1.13, and a_o = 2.55 G were calculated for the radical in the melt; splitting constants of a_p = 2.77, a_m = 1.11, and a_o = 2.53 G have been reported for the triphenylmethyl radical in benzene.[21]

The workup of the melt after exhaustive electrolysis followed by HPLC analysis (see Experimental Section) indicated that the major product was [4-(diphenylmethyl)phenyl]triphenylmethane (**4**). Since the ESR data indicated the presence of the triphenylmethyl radical and cyclic voltammetric data showed the presence of **3** after electrolysis, the workup of the melt apparently produces acidic conditions whereupon isomerization of **3** to **4** occurs (reaction 8). These observations are consistent with reports in the literature on the isomerization of Gomberg's trityl or **3** by Brønsted acids in conventional organic solvents.[12]

Kinetics of Homogeneous Chemical Reactions Preceding and Subsequent to Electron Transfer. The kinetics of the acid base chemistry, which is responsible for the formation of the triphenylmethyl carbonium ion in the melt, was studied by electrochemical methods. Rotating disk voltammetry (RDE) was used to determine the rate of formation of the electroactive carbonium ion from triphenylmethyl chloride (reaction 1). Excellent RDE data have been obtained in $AlCl_3$ melts at millimolar

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(19) Triphenylmethane exhibits an irreversible oxidation wave at 1.9 V with formation of the triphenylmethyl carbonium ion, which is noted as a reduction wave at 0.1 V on the reverse scan.

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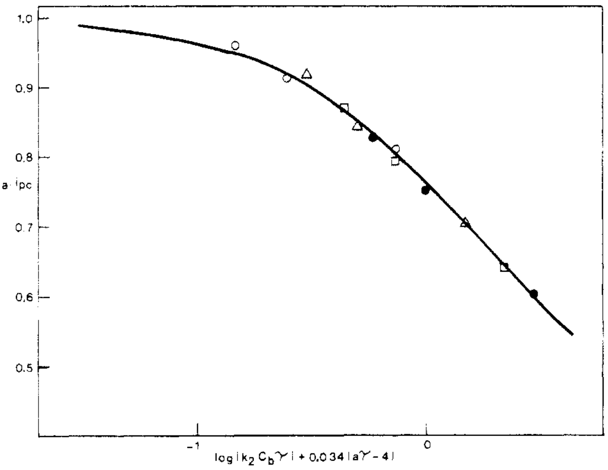

Figure 6. Cyclic voltammetric peak current ratio data for the dimerization of triphenylmethyl radicals at concentrations of 2.5 × 10^{-3} (●), 5.1 × 10^{-3} (▲), 7.5 × 10^{-3} (□), and 10 × 10^{-3} F (○) triphenylmethyl chloride in a $AlCl_3$/BPC melt (30 °C) at pCl 12. The solid line is calculated for a second-order rate constant of 1.3 × 10^3 L mol^{-1} s^{-1} by using the working curve of ref 27 (Table III).

concentration levels without background correction techniques.[22] The use of transient electrochemical techniques suffers in ionic melts due to significant charging currents at short measurement times ($t < 100$ ms). RDE voltammetry on the triphenylmethyl carbonium ions in melts at pCl ≥10 produces a single wave with an $E_{1/2}$ of 0.1 V. Plots of the limiting current of the wave vs. $\omega^{1/2}$ are linear over a rotation rate range from 10 to 1000 rad s^{-1} (Figure 5). The data indicate mass-transport control of the electroactive carbonium ion as the pCl is varied from values of 12.1 to 10.6; thus, the rate of formation of carbonium ion is relatively slow on the electrochemical time scale.[23] For example, there is no significant formation of carbonium ion beyond the equilibrium concentration at the slowest rotation rate of 10 rad s^{-1} and at pCl's where the ratio of bulk equilibrium concentrations of carbonium ion to chloride is greater than 0.1. A closer examination of the cyclic voltammetric wave shape obtained for the reduction of the carbonium ion at lower pCl's (e.g., Figure 2C) indicates mass-transfer control rather than kinetic control of the availability of the electroactive species at the electrode surface.[24]

Cyclic voltammetric data were used to evaluate the rate of dimerization of triphenylmethyl radicals to 1-(diphenylmethylene)-4-(triphenylmethyl)-2,5-cyclohexadiene (reaction 4). Figure 6 illustrates the cyclic voltammetric peak current ratios which were obtained as a function of scan rate and in a concentration range of 2.5–10 mM. The peak current ratios were calculated by Nicholson's empirical method.[26] The data were fitted to a working curve for second-order irreversible chemical reaction following electron transfer (EC mechanism) with a second-order rate constant of 1.3 × 10^3 L mol^{-1} s^{-1}.[27] The close agreement of the experimental curve with the EC model for four different concentrations strongly suggests that the reaction pathway in the melt involves dimerization of triphenylmethyl radicals. Furthermore, since the model is for an irreversible dimerization reaction, it would appear that the equilibrium constant for reaction 4 is significantly greater than unity (vide infra).

Conclusions

Cyclic voltammetric and spectroscopic evidence indicates that the formation of stable carbonium ions is feasible in the $AlCl_3$/BPC melt. Reaction 1 appears to be a facile and possibly general reaction for the generation of carbonium ions in a tetrachloroaluminate melt. More recent studies in our laboratory indicate that the formation of other tertiary and secondary carbonium ions including acylium ions is feasible by manipulation of the acidity of the melt. Proton elimination on the α-carbon appears to be a prominent pathway for some other tertiary carbonium ions in the melt.[28]

The electrochemistry of the triphenylmethyl carbonium ion has been reported by several workers in a variety of solvents. Breslow and co-workers observed the $E_{1/2}$ values for triphenylmethyl ion in order to carry out thermodynamic calculations for the pK_a of triphenylmethane. Values of $E_{1/2}$ for the triphenylmethyl carbonium ion of 0.24, 0.21, and 0.19 V vs. SCE have been reported in hexamethylphosphoramide,[29] acetonitrile,[30] and dimethyl sulfoxide,[31] respectively. In addition, Volz reported a value of 0.27 V vs. SCE in acetonitrile[32] and Plesch observed a value of -0.095V vs. Ag/$AgClO_4$ in methylene chloride.[33] The data obtained in the $AlCl_3$/BPC ionic melt can be compared to that reported in the above solvents by using ferrocene as an internal standard. The redox potential for the ferrocene–ferrocenium ion couple has been shown to be relatively independent of temperature and solvent.[34] The half-wave potential for ferrocene in a 1:1 melt is 0.26 V vs. Al,Al^{3+} (2:1 $AlCl_3$/BPC) as measured in our laboratory. This is in close agreement to a value of 0.24 V vs. the Al,Al^{3+} reference electrode for $E_{p/2}$ (29 mV negative of $E_{1/2}$) of the oxidation wave of ferrocene as reported by Osteryoung.[2] Breslow recently reported an $E_{1/2}$ for ferrocene in HMPA/THF as 0.51 V positive of the SCE. Since the half-wave potential for the triphenylmethyl carbonium ion/radical couple is 0.13 V vs. the Al,Al^{3+} reference, the $E_{1/2}$ for this couple in the melt would be 0.38 V vs. SCE. The $E_{1/2}$ for the triphenylmethyl carbonium ion is thus 0.14 V more positive in the melt than in polar organic solvents such as hexamethylphosphoramide. This is not the anticipated result if one assumes the tetrachloroaluminate melt to be more polar than conventional polar organic solvents. The loss of solvation energy in the reduction of a cation to the radical should be substantial and result in more negative reduction potentials with increasing polarity of the medium. However, it should be noted that similar behavior has been observed for the oxidation of aromatic hydrocarbons in the melt. The oxidation of polycyclic aromatics has been found to be more

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[23] Although an accurate rate constant for the formation of carbonium ions by eq 1 cannot be calculated, the RDE data indicate a upper limit of 10^3 l mol^{-1} s^{-1} for k_f.

[24] The general wave shape for a CE mechanism with a measurable rate constant indicates a polarographic-like wave with a limiting current rather than a peak current as noted in stationary-electrode voltammetry of a diffusion-controlled system.[25]

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difficult in the melt than in acetonitrile.[2] Solvation of the resultant radical cation should make the oxidation potential more negative (i.e., easier) in the more highly solvating medium. Thus, it is apparent that these room-temperature tetrachloroaluminate melts are not particularly strong solvating media when compared to polar organic solvents for organic cations.

The rate of dimerization of the triphenylmethyl radical in the $AlCl_3$ melt appears to be reasonably consistent with the reported stability of this radical in organic solvents. Cyclic voltammetric data reported on 5 mM triphenylmethyl perchlorate in dimethyl sulfoxide indicated chemical reversibility at 1.1 V s^{-1}.[31] However, a latter report states that the reoxidation of the triphenylmethyl radical to the carbonium ion became significant only at scan rates greater than 1.0 V s^{-1}.[30a] Although the scan rate is not reported, a more recent publication on the triphenylmethyl anion/radical couple in tetrahydrofuran reports a cyclic voltammetric peak current ratio of 1.06 for the couple, which indicates complete chemical reversibility.[35] Concentration effects on the rate of dimerization are important in any of the above data and need to be taken into account for comparison purposes.

The reasonably good fit of the kinetic data to an irreversible dimerization model (Figure 6) indicates a large equilibrium constant for reaction 4. An attempt was made to calculate the magnitude of this equilibrium constant from ESR data. The 2,2-diphenyl-1-picrylhydrazyl radical (DPPH) was used as a stable radical standard. Integration of peak areas was carried out on a known quantity of DPPH radical vs. the triphenylmethyl radical produced in the melt as a result of electrolysis of the carbonium ion. Upon addition of 1 faraday/mol of charge to a 10^{-2} M solution of carbonium ion, ESR peak integration of the resultant solution indicated a radical concentration of 5×10^{-4} M after a 24-h equilibration. Thus, the equilibrium constant for reaction 4 is on the order of 10^4 L mol^{-1}. The relatively low equilibrium concentration of triphenylmethyl radicals in the melt is consistent with the adequacy of an irreversible second-order EC model to calculate the rate constant for the dimerization reaction.

The rate of formation of triphenylmethyl carbonium ions in this melt was too slow to measure with transient electrochemical techniques. Rates of acid–base reactions in the low-temperature $AlCl_3$ melts in previous reports have apparently been too slow to quantitatively determine rate constants by cyclic voltammetry.[2,3] Further work on other carbonium ions including acylium ions is in progress and will be subsequently reported.

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Registry No. 1, 13948-08-8; **2**, 2216-49-1; **3**, 18909-18-7; **4**, 3416-63-5; triphenylmethyl chloride, 76-83-5.

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Mechanism of the Reaction between Benzylmagnesium Chloride and Carbonyl Compounds. A Detailed Study with Formaldehyde

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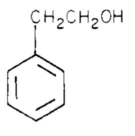
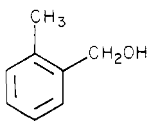
The reaction of benzylmagnesium chloride in THF with monomeric formaldehyde has been studied in detail. A mechanism is presented which accounts for the formation of the products, 2-phenylethanol, *o*-tolylcarbinol, and *o*-(2-hydroxyethyl)benzyl alcohol. A change in technique for Grignard titration and formaldehyde addition results in a much-improved mass balance than achieved previously. The decreased yield of the major product, *o*-tolylcarbinol, with increased reaction time is explained in terms of a hitherto unsuspected equilibrium influenced by the polymerization of monomeric formaldehyde. An intermediate organometallic species which could lead to some of the diol product, *o*-(2-hydroxyethyl)benzyl alcohol can be trapped as the trimethylsilyl derivative, but the quantity is insufficient to account for the amount of diol when an excess of formaldehyde is employed. An ene or Prins reaction is invoked for the formation of most of the diol. Deuterium tracer studies suggest competition between a proton abstraction pathway leading to the trimethylsilyl-trapped organometallic species and a base-catalyzed, stereospecific 1,3 hydrogen shift.

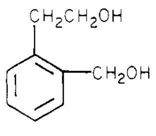
Ever since Grignard[1] first examined the reaction of benzylmagnesium chloride with formaldehyde, there has been considerable disagreement regarding the nature of the products formed in this reaction.[2-4] The most recent work[5] on the subject has clearly shown that three products, I–III, are all formed in varying amounts, depending upon the reaction conditions.



I



II



III

2-Phenylethanol (I), which normally would be the expected product, is found instead to be a consistently minor component of the final product mixture. The so-called "abnormal" *o*-tolylcarbinol (II) appears as the major product when low concentrations of formaldehyde are used. The amount of "abnormal" diol III [*o*-[2-hydroxyethyl)benzyl alcohol] increases from trace quantities at low formaldehyde concentration to a major component at high

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