An Electrochemical and Spectroscopic Study of Some Aromatic Hydrocarbons in the Room Temperature Molten Salt System Aluminum Chloride–*n*-Butylpyridinium Chloride

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Abstract: A molten salt system $AlCl_3$–*n*-butylpyridinium chloride has been developed which is molten at 40 °C over a wide composition range (0.75:1 to 2:1 mole ratio $AlCl_3$–*n*-butylpyridinium chloride) and the electrochemical and spectroscopic behavior of a number of aromatic hydrocarbons has been investigated in this medium. All the hydrocarbons studied were shown to undergo a one-electron oxidation to the cation radical at a potential that is independent of the melt composition and similar to the value in acetonitrile. The oxidation potential in the melt was found to vary fairly linearly with the value of the first ionization potential of the hydrocarbon and the cation radicals formed were observed to have a significantly greater stability in this molten salt medium than in acetonitrile. Spectroscopic studies showed that the hydrocarbons participate in an acid–base type equilibrium with the acid species in the melt, $Al_2Cl_7^-$, to yield complexes whose spectra were generally very similar to those of the carbonium ions of the parent hydrocarbons. The 2:1 melt was shown to be capable of oxidizing those hydrocarbons more readily oxidized than hexamethylbenzene to their radical cations. This oxidation ceased when the melt acidity was lowered.

Introduction

In view of their aprotic, totally anhydrous nature, and the ease with which their acid–base properties may be varied, tetrachloroaluminate melts ($AlCl_3$–alkali metal chloride mixtures) have been used as solvents in organic electrochemistry.[1-9] The most notable observation was the high stability of the radical cations of certain aromatic amines[2,4] and sulfur heterocycles.[3] There are, however, two major drawbacks associated with these systems for their use in organic electrochemistry: first, their operating temperature, ca. 175 °C, is above the boiling point of many organic species; and second, rapid homogeneous reactions occur between the melts and organic substrates at these temperatures.[10]

In order to overcome these problems there has been considerable effort extended recently in this laboratory toward developing similar solvents with lower melting points. In 1951 a molten salt system comprising 67 mol % $AlCl_3$ and 33 mol % ethylpyridinium bromide, which is molten at room temperature, was reported by Hurley and Wier,[11] and in the last few years there have been several reports by Osteryoung and co-workers of the use of this solvent for both electrochemical[12-14] and photochemical[15] investigations. It has also been shown[14] that this mixture is miscible with benzene, affording a solvent (50% volume ratio) suitable for both mechanistic and synthetic organic electrochemistry. The 2:1 $AlCl_3$–ethylpyridinium bromide and the $AlCl_3$–*n*-butylpyridinium chloride systems (also molten at room temperature), and their mixtures with benzene, have been studied by ^1H and ^{13}C NMR spectroscopy.[16] It was shown that the addition of benzene to the melt caused a marked increase in the conductivity and a marked decrease in the viscosity, but no benzene–$AlCl_3$ complexes were observed.

While the $AlCl_3$–ethylpyridinium bromide (2:1 mole ratio) system has been shown to be useful in organic electrochemistry and also to afford similar stabilization to cation radicals as the high-temperature tetrachloroaluminate melts, e.g., the hexamethylbenzene radical cation has been observed by cyclic voltammetry at sweep rates of 50 V s^{-1} in both the melt and the 50:50 melt–benzene mixture,[14] it has one major drawback: the mixture is only molten at room temperature for the 2:1 $AlCl_3$–ethylpyridinium bromide system with the melting point rising sharply as the ratio of $AlCl_3$ is reduced. We have, however, recently found a system which appears to be a very suitable substitute for the higher temperature tetrachloroaluminates in the study of organic species: the *n*-butylpyridinium chloride (BPC)–aluminum chloride system, which is molten at 40 °C over a wide composition range (0.75:1 to 2:1 $AlCl_3$–BPC). Raman studies of this system[17] show that in the 1:1 mixture the aluminum is present almost entirely as $AlCl_4^-$ ions whereas in the 2:1 system only $Al_2Cl_7^-$ ions can be detected. This is in contrast with the behavior of the alkali metal tetrachloroaluminates, where $AlCl_4^-$, $Al_2Cl_7^-$, and Al_2Cl_6 are all detectable in the 2:1 melt. These large concentrations of $Al_2Cl_7^-$ in the 2:1 $AlCl_3$–BPC mixture would suggest that this melt is more acidic than the comparable high-temperature system (2:1 $AlCl_3$–NaCl at 175 °C), which is indeed observed.[18]

The investigation discussed in this report is concerned with the electrochemical and spectroscopic behavior of some aromatic hydrocarbons in the low-temperature molten salt system $AlCl_3$–BPC. The electrochemical oxidation of a number of these hydrocarbons has been studied by Fleischmann and Pletcher in the high-temperature system KCl–NaCl–$AlCl_3$ (36:14:50 mol %)[1] and their results are compared with those in the low-temperature melt.

Experimental Section

Chemicals. All the aromatic hydrocarbons investigated were either sublimed, distilled, or recrystallized from ethanol prior to use. The pyridine (Aldrich Gold Star) and *n*-butyl chloride (Eastman) were used as received and the acetonitrile (Aldrich) and ethyl acetate (Fisher) were dried over P_2O_5 and K_2CO_3, respectively, distilled, and then stored over molecular sieves in tightly sealed glass bottles.

Preparation of *n*-Butylpyridinium Chloride. The *n*-butylpyridinium chloride (BPC) was prepared in 2–3 mol batches from pyridine and *n*-butyl chloride.[17] Equimolar quantities of the reactants were gently refluxed together, in the dark, in a standard reflux apparatus fitted with a drying tube containing Aquasorb (Mallinckrodt). The product appeared as long, white crystals, and when the reaction was about two-thirds complete the mixture was cooled and the excess reactants were decanted off (if the reaction was permitted to proceed further degradation of the product occurred, making purification exceedingly difficult). The product was then dissolved in a minimum amount of boiling acetonitrile and refluxed with decolorizing charcoal for 15 min. The mixture was then filtered under vacuum and approximately 10% by volume of ethyl acetate was added to the filtrate, which was then

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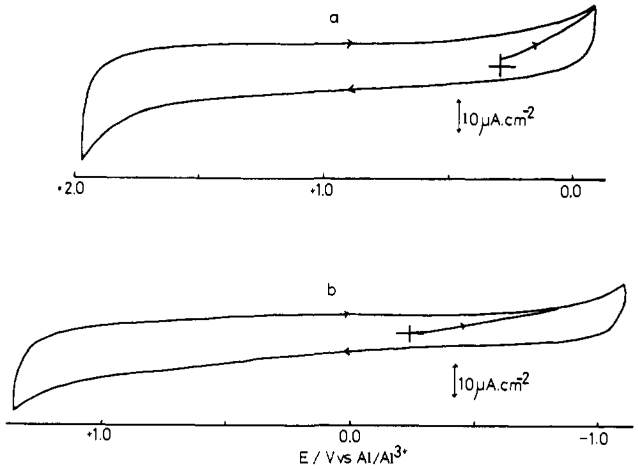


Figure 1. Background cyclic voltammograms of the $AlCl_3$-BPC melt at a glassy carbon electrode. Temperature 30 °C; sweep rate 100 mV s^{-1}. (a) 2:1 melt; (b) 1:1 melt.

Table I. Temperature Dependence of the Diffusion Coefficient of Ferrocene in a 1:1 Melt

temp/°C	$D \times 10^7/cm^2\,s^{-1}$	temp/°C	$D \times 10^7/cm^2\,s^{-1}$
30	4.7	123	32.7
40	5.4	152	41.9
72	12.7	175	56.1
97	21.4		

left to cool, isolated from atmospheric moisture by a drying tube. White crystals of BPC were precipitated and these were filtered off at a vacuum pump, washed with ethyl acetate, and rapidly transferred to a vacuum desiccator while still moist with solvent (the crystals of BPC were exceedingly hygroscopic). The excess solvent was then removed under vacuum. This recrystallization procedure was repeated at least three times with the decolorizing charcoal being omitted on the final one. Final traces of solvent were removed from the BPC by pumping at 70 °C for 24 h and it was then transferred to the drybox where it was stored in dark glass bottles. The product was determined to have a melting point of 131.5 ± 1.0 °C.

Sublimation of Aluminum Chloride. $AlCl_3$ (A.G. iron-free Fluka) was prepared by sublimation at 220 °C in sealed glass tubes in the presence of Al wire (m5N Alfa Inorganics) in a manner similar to that of Seegmiller et al.[19] except that about 1% by weight of NaCl (A.C.S. Fisher) was added to the contents of the tube. The NaCl combined with some of the $AlCl_3$ to form molten $NaAlCl_4$ which was both denser than and immiscible with the $AlCl_3$. This melt, being ionic in character, preferentially dissolved any ionic impurities and the molten layer of $AlCl_3$ in the sublimation tube was water white whereas the $NaAlCl_4$ layer had a yellow-brown color. The sublimation was permitted to continue until nearly all the $AlCl_3$ layer had sublimed and then the tube was cooled and transferred to the drybox. Once the tube was opened the $AlCl_3$ crystals were transferred to glass bottles fitted with ground glass closures for storage.

Melt Preparation. The melts were prepared by simple addition of $AlCl_3$ to BPC. BPC was placed in the glass electrochemical cell with a glass-coated magnetic stirring bar and the $AlCl_3$ was then very slowly added with stirring. The reaction of $AlCl_3$ with BPC was highly exothermic and care had to be taken not to permit the temperature of the mixture to rise above about 100 °C or thermal decomposition occurred. The resulting melt was water white and was used in both electrochemical and spectroscopic experiments without further purification. The melting point of the 1:1 melt was found to be 27.0 ± 1.0 °C while that of the 2:1 mixture was considerably below room temperature. The densities of the 1:1 and 2:1 melts were determined to be 1.234 and 1.345 g cm^{-3}, respectively.

Cells, Electrodes, and Instrumentation. All the essential details of the experimental techniques, electrochemical instrumentation, construction of glassy carbon working electrodes, and operation of the drybox (Vacuum Atmospheres Co.) have been presented in an earlier publication.[20] In all the electrochemical experiments the reference electrode was an Al wire (m 5N Alfa Inorganics) immersed in the melt and separated from the working electrode compartment by a fine porosity glass frit. Throughout this work all the potentials quoted have been converted to values with respect to an Al wire in the 2:1 melt unless otherwise stated. The ultraviolet and visible spectra were recorded on a Cary Model 17 spectrophotometer.

Results and Discussion

Melt Characterization. Previous experience in both the high-temperature $NaAlCl_4$ system[20] and, more recently, the 2:1 $AlCl_3$-ethylpyridinium bromide melt[14] has shown that one of the most suitable electrode materials for use in this type of solvent is glassy carbon and therefore this was chosen for use in the present study. Figures 1a and 1b show typical background cyclic voltammograms, at a glassy carbon electrode, for both the 2:1 and 1:1 $AlCl_3$-BPC melts (the reference electrode in both cases was an Al wire in the 2:1 melt). It can immediately be seen that in both cases the background is featureless, with the cathodic and anodic limits being the deposition of Al and the evolution of chlorine, respectively. The variation of the potential of these limits with melt composition is, however, very marked. The anodic limit of the 1:1 melt lies over 600 mV cathodic of that in the 2:1 system whereas the cathodic limit is about 1 V more cathodic in the 1:1 system (this latter difference is in part due to the large nucleation overpotential for Al deposition on glassy carbon in the 1:1 melt; the potential of an Al wire in the 1:1 mixture lies 690 mV more cathodic than in the 2:1 melt). These differences are significantly larger than those observed for the same composition change in the NaCl-$AlCl_3$ system at 175 °C, where the corresponding value is about 400 mV,[21] and can be attributed to the greater chloro-acidity variation that is possible in the $AlCl_3$-BPC system. A recent potentiometric study of this system[17] suggests that the pCl of the melt can be varied from about 0 to 15, comparable to the pH variation possible in aqueous solutions.

The ferrocene-ferricinium ion couple has been shown to be electrochemically stable and reversible in a wide variety of solvents including, most recently, the 2:1 $AlCl_3$-ethylpyridinium bromide room temperature melt.[14] Similar behavior was observed here in the $AlCl_3$-BPC system. For all melt acidities the ratio of the anodic and cathodic cyclic voltammetric peak currents was unity and the peak separation at 30 °C was 60 ± 1 mV, in agreement with the value predicted for a reversible one-electron process (60 mV). It was also observed that the value of the ferrocene oxidation potential was independent of melt acidity (the value of $E_{p/2}$ in cyclic voltammetry being 0.24 V vs. Al), indicating that no strong interaction between the melt and the ferrocene is occurring. The values of the diffusion coefficient (D) determined from cyclic voltammetry for ferrocene in a 1:1 melt as a function of temperature are given in Table I. At room temperature the value of D is very low but on heating to 175 °C increases to a value comparable with that observed in $NaAlCl_4$ melts. This large change in the value of D can probably be attributed to changes in the viscosity (η) of the medium. The values of D and η are related by the Stokes-Einstein equation:[22]

$$D = \frac{kT}{6\pi\eta r} \tag{1}$$

where k is the Boltzmann constant and r is the radius of the diffusing species. Robinson et al.[16] have determined the values of η for the 2:1 and 1:1 melts to 27.0 (25 °C) and 23.5 cP (40 °C), respectively, whereas the η values for the $NaAlCl_4$ system at 175 °C are 3.371 cP for the 1:1 system and 3.846 cP for the 2:1 melt.[23]

Electrochemical Oxidation of Some Aromatic Hydrocarbons. The electrochemistry of a wide range of aromatic hydrocarbons was investigated in these melts using cyclic voltammetry and

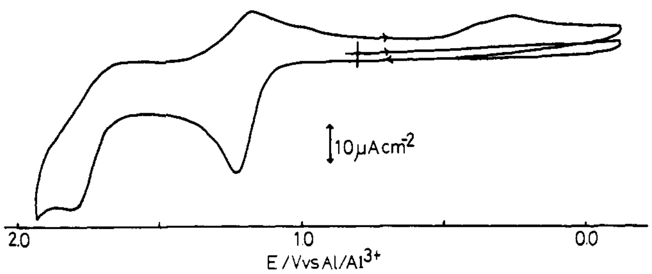


Figure 2. Cyclic voltammogram at a glassy carbon electrode of 1.43×10^{-3} M anthracene in 1.2:1 melt at 30 °C. Sweep rate 100 mV s^{-1}.

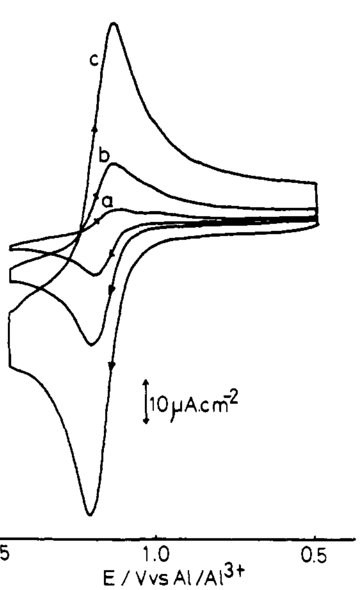


Figure 3. Cyclic voltammograms at a glassy carbon electrode of 1.43×10^{-3} M anthracene in 1.2:1 melt at 30 °C. The sweep rates were (a) 20, (b) 100, and (c) 500 mV s^{-1}.

Table II. First Oxidation Potentials of the Aromatic Hydrocarbons

compd	$E_{p/2}/V^a$	$E_{1/2}/V^b$
1. mesitylene	1.75	1.55
2. biphenyl	1.73	1.48
3. naphthalene	1.58	1.34
4. durene	1.59	1.29
5. phenanthrene	1.59	1.23
6. pentamethylbenzene	1.53	1.28
7. hexamethylbenzene	1.36	1.16
8. pyrene	1.09	0.86
9. anthracene	1.16	0.84
10. 9,10-diphenylanthracene	1.02	0.86
11. benzo[*a*]pyrene	1.09	0.64
12. benzo[*e*]pyrene	1.20	0.97

[a] Values with respect to Al/Al^{3+} in 2:1 melt. [b] Values recorded in CH_3CN with respect to Ag/Ag^+ (0.1 M) reference electrode. Data taken from ref 26-29.

typical voltammograms for anthracene in a 1.2:1 melt are shown in Figures 2 and 3. Figure 2 shows two oxidation waves of comparable heights with peak potentials of 1.22 and 1.82 V and peaks on the reverse sweep at 1.16 and around 0.3 V. Figure 3 shows the voltammograms that are observed when the potential sweep is reversed after the first oxidation. The forward and reverse peaks are separated by about 65 mV, which is close to the value predicted for a one-electron reversible process (60 mV at 30 °C), and also the peak potentials are independent of sweep rate. The ratio of the cathodic to anodic peak current, as determined by the method of Nicholson,[24] increases from 0.55 at 20 mV s^{-1} to 0.89 at 500 mV s^{-1}, indicating that the product of the electron transfer is undergoing a following chemical reaction. This overall behavior is very similar to that observed for anthracene in acetonitrile[25] and can be attributed to the oxidation of anthracene to its radical cation with the second oxidation being due to the formation of the dication. The only difference in the present case is the marked increase in the stability of the radical cation on changing from CH_3CN as the solvent to the melt as evidenced by the reduction peak on the reverse sweep of the cyclic voltammograms: in CH_3CN this reduction peak only becomes visible at sweep rates of several volts per second[25] whereas, as can be seen in Figure 3, it can readily be observed in the melt at sweep rates as low as 20 mV s^{-1}. This demonstrates the remarkable stability afforded to radical cations in these aluminum halide-alkylpyridinium halide melts, presumably due to the total absence of water. The broad peak seen on the reverse sweep around 0.3 V (Figure 2) is due to the reduction of various products of the following chemical reactions with the radical cation and dication.

Table II lists the values of $E_{p/2}$ (the potential at which the current is half the peak value) determined for the first oxidation wave on the cyclic voltammograms of a series of hydrocarbons. For comparison the values of $E_{1/2}$ determined in polarographic studies of these hydrocarbons in CH_3CN[26-30] are also given in Table II. All the values were independent of the melt composition and sweep rate up to 5 V s^{-1}. 9,10-Diphenylanthracene and benzo[*a*]pyrene both exhibited perfectly reversible behavior; benzo[*e*]pyrene and pyrene itself, as in acetonitrile,[25] as evidenced by the shape of the cyclic voltammetric peaks, showed a significant degree of product adsorption but the cation radicals appeared to be fairly stable. Anthracene, as shown above, exhibits significant cation radical stability and a reduction wave for the cation radical of hexamethylbenzene was seen at sweep rates above 1 V s^{-1}. No reduction peaks were observed for the cation radicals of the other hydrocarbons at the sweep rates used (up to 10 V s^{-1}). Anthracene, 9,10-diphenylanthracene, pyrene, and the benzopyrenes all showed further oxidation processes, but these will not be considered here. No reduction processes were ever observed for any of the hydrocarbons studied.

There have been several successful attempts in the literature[28,30] to correlate the electrochemical oxidation potential of hydrocarbons with the value of the first ionization potential (IP) and molecular orbital parameters. For example, the value of the polarographic half-wave potential ($E_{1/2}$) can be related to the value of IP by the equation[30]

$$E_{1/2} = \alpha \mathrm{IP}\ \Delta E_{\mathrm{solv}} - \beta \mathrm{EA} + C \qquad (2)$$

where α is the extent to which IP is modified by the electrical double layer at the electrode surface, ΔE_{solv} is the difference in solvation energy between R and $O^{+}\cdot$, EA is the electron affinity of the electrode material modified by the double layer by a factor β, and C is a constant determined by the potential of the reference electrode used. Since for any given working and reference electrode combination β, EA, and C are constants, $E_{1/2}$ will be proportional to IP if ΔE_{solv} is either constant or proportional to IP. The value of $E_{1/2}$ (or the related cyclic voltammetric parameter $E_{p/2}$) for a wide range of hydrocarbons has been found to vary fairly linearly with IP in several solvents, including acetonitrile[28,30] and, most recently, the KCl-NaCl-$AlCl_3$ melt at 150 °C.[1] In this latter paper the observed slope ($dE_{p/2}/d\mathrm{IP} = 0.5$) was used to postulate the existence of a strong interaction between $AlCl_3$ in the melt and the hydrocarbon. It was also suggested that, based on the potentials of the Al deposition and Cl_2 evolution in the melt, the oxidations were occurring at potentials much more negative than in any common solvent, again supporting the hypothesis

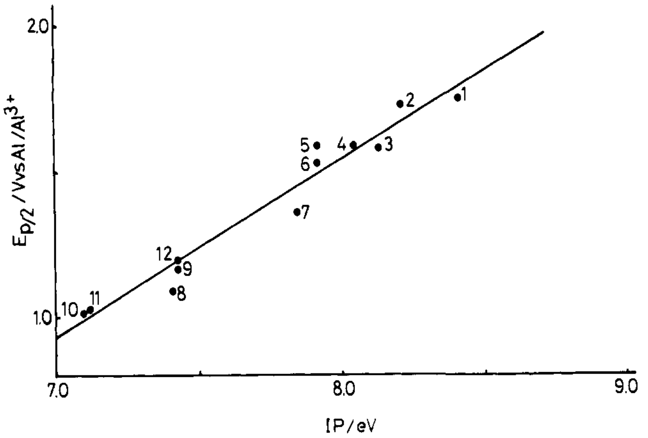


Figure 4. The correlation between $E_{p/2}$ values for the oxidation of various aromatic hydrocarbons and their photoionization potentials. The numbers refer to the different compounds as given in Table II.

Table III. Spectroscopic Data for Aromatic Hydrocarbon Complexes with $AlCl_3$ and H^+

compd	λ_{max}/nm complex in melt	λ_{max}/nm solid state complex with $AlCl_3$	λ_{max}/nm aromatic carbonium ion[d]
benzene	360	333[a]	
toluene	362		
mesitylene	367	365[b]	
durene	382	380[b]	355
pentamethylbenzene	380	385[b]	377
hexamethylbenzene	398	400[b]	
naphthalene	393	410,[b] 377[a]	390, 410 (sh)
phenanthrene	417	425,[b] 653[a]	510, 410
pyrene	451, 465, 475, 492	520,[b] 480[a]	475 and shoulders
anthracene	417	418,[a] 560,[b] 420[c]	410
9,10-diphenylanthracene	408, 432		
biphenyl	393, 452 (sh)		440
benzo[*a*]pyrene	553 (sh), 522, 491, 453, 390		520, 490, 475, 390
benzo[*e*]pyrene	542, 480, 432, 405		550, 490, 425, 400

[a] Reference 38. [b] Reference 36. [c] Reference 34. [d] Reference 39.

of a strong interaction between the $AlCl_3$ and the hydrocarbon.

It was decided to test the present data in a similar manner. Until recently the values of IP in the literature have been unreliable and inconsistent; however, there are now some very good values obtained from photoelectron spectroscopy[31,32] available. To test these values, they were correlated with the $E_{1/2}$ values given in Table II for the oxidation of the hydrocarbons in CH_3CN. The least-squares fit line was given by

$$E_{1/2} = 0.66\text{IP} - 4.00 \qquad (3)$$

with a correlation coefficient of 0.96. The result of plotting the $E_{p/2}$ values obtained in the melt against these same values of IP is given in Figure 4. The solid line is the least-squares fit as given by

$$E_{p/2} = 0.61\text{IP} - 3.34 \qquad (4)$$

and the correlation coefficient was 0.97. Both the correlations are reasonably good and it can also be seen that the slopes are quite similar, which, coupled with the invariance of the $E_{p/2}$ values to the melt composition, suggests no strong interaction between the acid species in the melt and the hydrocarbons.

Fleischmann and Pletcher[1] used the potentials of Al deposition and Cl_2 evolution to compare the oxidation potentials in their high-temperature melts and other common nonaqueous solvents. A much better reference is that of the ferrocene-ferricinium ion couple. The values of $E_{p/2}$ in CH_3CN[33] and in the melt at 0.06 V vs. 0.1 M Ag^+/Ag and 0.24 V vs. Al, respectively; therefore, the potential of the Al/Al^{3+} electrode lies 0.18 V cathodic of the Ag^+ (0.1 M)/Ag one. To compare the sets of values in Table II of $E_{p/2}$ and $E_{1/2}$ these two parameters have to be related and this is done in the equation

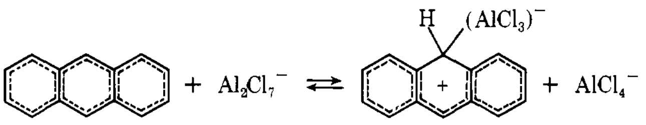
$$E_{p/2} = E_{1/2} - 1.09(RT/nF) \qquad (5)$$

At 30 °C $E_{p/2}$ is therefore 29.0 mV cathodic of $E_{1/2}$ for a one-electron oxidation. Making this correlation the oxidation potentials in the melt are found on average to be about 100 mV anodic of those in CH_3CN; i.e., contrary to the postulate of Fleischmann and Pletcher,[1] it is slightly more difficult to oxidize hydrocarbons in the melt than in CH_3CN (if Fleischmann and Pletcher's results in the high-temperature system are treated in the same way their values for the oxidation potentials of the hydrocarbons are also found to be very similar to those in CH_3CN). Corresponding similarities were also found between the oxidation potentials of a number of metal carbonyls in the $AlCl_3$-ethylpyridinium bromide system and CH_3CN.[13]

An interesting phenomenon was observed when any of the hydrocarbons with an $E_{p/2}$, in the melt, less than about 1.4 V was added to the most acidic melts: the hydrocarbon was spontaneously oxidized to the cation radical. Such behavior has also been observed when solid anthracene or tetracene is exposed to $AlCl_3$ vapor and heated slightly.[34,35] The UV-visible spectrum of 9,10-diphenylanthracene in a 2:1 melt was recorded 30 min after mixing and was found to be identical with that of the radical cation in acetonitrile[29] and was also found to be invariant over a period of 3 days. This is in contrast to the behavior in CH_3CN, where the half-life of the cation radical was found to be of the order of 50 min,[29] and provides further evidence for the remarkable stability of cation radicals in these melts. The spontaneous oxidation of hydrocarbons discussed above only occurred in the most acidic melts, ceasing when the mole fraction of $AlCl_3$ was reduced. Neither the nature of the oxidant nor its reduction product is at present known. In 1.2:1 melts no oxidation was observed and therefore the electrochemical studies on the more reactive hydrocarbons were carried out in this more basic melt.

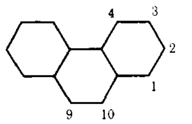
Spectroscopy. The electrochemical investigation discussed above suggests that no strong interactions between the melt and the hydrocarbons were operative; however, it was observed that when the hydrocarbons were added to acid melts, colored solutions were formed which could be reversibly decolored by making the melt basic. There are also several reports in the literature of the existence of solid-state complexes between $AlCl_3$ and hydrocarbons.[34,36-38] The UV-visible spectra of solutions of hydrocarbons in the room temperature melt were, therefore, recorded and the λ_{max} values are given in Table III. For the reasons already discussed concerning the spontaneous oxidation of certain hydrocarbons by the acid melts, the spectra were all recorded in the 1.2:1 system. In general the values of λ_{max} agree fairly well with those observed for the solid-state complexes[34,36-38] also given in Table III. Where differences exist, such as in the case of anthracene, the value reported here agrees with at least one of the literature values. It is probable that in some of the solid-state complexes some oxidation to the cation radical has occurred.[34]

No attempt was made to measure the values of the extinction coefficient, though qualitatively it can be stated that the most basic of the hydrocarbons gave the most intense spectra and reducing the melt acidity also reduced the spectral intensity such that in melts more basic than the 1:1 mixture the spectra reverted totally to that of the parent hydrocarbon. This behavior is indicative of an acid-base type equilibrium between the acid species in the melt, $Al_2Cl_7^-$, and the hydrocarbons. In view of the complexities of some of the spectra and the lack of any correlation between λ_{max} and IP values these complexes cannot be of the π-charge transfer type as has been suggested by Costanzo and Jurinski,[36] but rather they are σ complexes,[34,38] being formed in an equilibrium of the type given by eq 6. It is interesting, therefore, to compare the spectral properties of these complexes with those of the related aromatic carbonium ions (conjugate acids)[39] in HF and $HF-BF_3$ solutions (Table III). The similarities between the two sets of spectra are fairly good except for the cases of phenanthrene and biphenyl.



(6)

Dallinga et al.[39] have compared these spectra of the carbonium ions with the λ_{max} values they calculate for all the possible carbonium ions that can be formed by the hydrocarbon. In all cases the spectra agree very well with those calculated for the lowest energy carbonium ion, or for a mixture of ions when there are several possibilities for similar energy. Except for the cases of biphenyl and phenanthrene it is therefore reasonable to conclude that the $AlCl_3$ complexes are of the same structure as calculated for the carbonium ions with the $AlCl_3$ molecule replacing the proton. In the case of phenanthrene the calculations show that the 1 and 9 positions have the same π delocalization energy and for steric reasons it was also predicted that the 4 position will have a similar proton affinity. The observed spectrum for the carbonium ion corresponds to a mixture of the 9 and 4 (and possibly 1) ions; λ_{max} 510 (9 ion calculated 532 nm) and λ_{max} 410 nm (4 ion calculated 399 nm). The spectrum of the complex in the melt, λ_{max} 417 nm, therefore corresponds most closely with that of the 4 ion (the least sterically hindered ion) and the absence of any 9 ion in this case can be attributed to steric effects: the $AlCl_3$ molecule being much larger than the proton, the 9 ion becomes unfavorable. A similar argument can be used in the case of biphenyl. The carbonium ion spectra (λ_{max} 440 nm) corresponds to the ortho ion (λ_{max} calculated 468 nm) whereas the spectrum of the $AlCl_3$ complex (λ_{max} 393 nm) corresponds closely to that calculated for the para carbonium ion (λ_{max} 394 nm) while the shoulder at 452 nm is presumably due to some of the less favored ortho ion. Again in this case the ortho position is sterically unfavored for the $AlCl_3$ complex and the para ion is therefore preferentially formed.



From the above observations it can be concluded that aromatic hydrocarbons undergo acid-base equilibria of the type described in eq 6 to form complexes very similar to the carbonium ions (conjugate acids) of the hydrocarbons. Where differences exist between the spectra of the carbonium ions[39] and the $AlCl_3$ complexes these can be attributed to the much larger size of the $AlCl_3$ molecule compared to the proton, making certain complexes sterically less favored. From the absence of any acid-base effects in the electrochemical oxidation of the hydrocarbons it must be concluded that either the equilibrium of eq 6 is very fast and the hydrocarbon is more readily oxidized than the complex or alternatively the complex and the hydrocarbon oxidize at the same potential.

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References and Notes

(1) M. Fleischmann and D. Pletcher, *J. Electroanal. Chem.*, **25**, 449 (1970).
(2) H. L. Jones, L. G. Boxall, and R. A. Osteryoung, *J. Electroanal. Chem.*, **38**, 426 (1972).
(3) K. W. Fung, J. Q. Chambers, and G. Mamantov, *J. Electroanal. Chem.*, **47**, 81 (1973).
(4) H. L. Jones and R. A. Osteryoung, *J. Electroanal. Chem.*, **49**, 281 (1974).
(5) V. R. Koch, L. L. Miller, and R. A. Osteryoung, *J. Org. Chem.*, **39**, 2416 (1974).
(6) R. A. Osteryoung in Proceedings of the International Symposium on Molten Salts, the Electrochemical Society, 1976, p 240.
(7) H. L. Jones, K. Paulsen, D. Bartak, J. Robinson, and R. A. Osteryoung, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976, Abstract No. 52.
(8) D. E. Bartak and R. A. Osteryoung, *J. Electrochem. Soc.*, **122**, 600 (1975).
(9) D. E. Bartak and R. A. Osteryoung, *J. Electroanal. Chem.*, **74**, 69 (1976).
(10) H. L. Jones and R. A. Osteryoung, *Adv. Molten Salt Chem.*, **3**, 121 (1975).
(11) F. H. Hurley and J. P. Wier, *J. Electrochem. Soc.*, **98**, 203 (1951).
(12) H. L. Chum, V. R. Koch, L. L. Miller, and R. A. Osteryoung, *J. Am. Chem. Soc.*, **97**, 3264 (1975).
(13) H. L. Chum, D. Koran and R. A. Osteryoung, *J. Organomet. Chem.*, **140**, 349 (1977).
(14) V. R. Koch, L. L. Miller, and R. A. Osteryoung, *J. Am. Chem. Soc.*, **98**, 5277 (1976).
(15) H. L. Chum, D. Koran, and R. A. Osteryoung, *J. Am. Chem. Soc.*, **100**, 310 (1978).
(16) J. Robinson, R. C. Bugle, H. L. Chum, D. Koran, and R. A. Osteryoung, in preparation.
(17) R. Gale, B. Gilbert, and R. A. Osteryoung, in preparation.
(18) J. Robinson and R. A. Osteryoung, in preparation.
(19) D. W. Seegmiller, G. W. Rhodes, and L. A. King, *Inorg. Nucl. Chem. Lett.*, **6**, 885 (1970).
(20) J. Robinson and R. A. Osteryoung, *J. Electrochem. Soc.* **125**, 1454 (1978).
(21) L. G. Boxall, H. L. Jones, and R. A. Osteryoung, *J. Electrochem. Soc.*, **120**, 223 (1973).
(22) B. R. Sundheim in "Fused Salts," B. R. Sundheim, Ed., McGraw-Hill, New York, N.Y., 1964, p 165.
(23) J. A. Plambeck in "Encyclopedia of Electrochemistry of the Elements," Vol. X, "Fused Salt Systems," A. J. Bard, Ed., Marcel Dekker, New York, N.Y., 1976, p 235.
(24) R. S. Nicholson, *Anal. Chem.*, **38**, 1406 (1966).
(25) M. E. Peover and B. S. White, *J. Electroanal. Chem.*, **13**, 93 (1967).
(26) H. Lund, *Acta Chem. Scand.*, **11**, 1323 (1957).
(27) W. C. Niekam and M. M. Desmond, *J. Am. Chem. Soc.*, **86**, 4811 (1964).
(28) E. S. Pysch and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963).
(29) R. E. Sioda, *J. Phys. Chem.*, **72**, 2322 (1968).
(30) W. C. Niekam, G. R. Dimeler, and M. M. Deamond, *J. Electrochem. Soc.*, **111**, 1190 (1964).
(31) W. C. Herndon, *J. Am. Chem. Soc.*, **98**, 887 (1976).
(32) F. I. Vilesov, *Zh. Fiz. Khim.*, **35**, 2010 (1961).
(33) N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68** 449 (1968).
(34) M. Sato and Y. Aoyama, *Bull. Chem. Soc. Jpn.*, **46**, 631 (1973).
(35) A. N. Terenin, *Adv. Catal.*, **15**, 227 (1964).
(36) S. J. Costanzo and N. B. Jurinski, *Tetrahedron*, **23**, 2571 (1967).
(37) M. M. Perkampus and T. Kranz, *Z. Phys. Chem. (Frankfurt am Main)*, **34**, 213 (1962).
(38) M. M. Pekampus and T. Kranz, *Z. Phys. Chem. (Frankfurt am Main)*, **38**, 295 (1963).
(39) G. Dallinga, E. L. Mackor, and A. A. Verrijn Stuart, *Mol. Phys.*, **1**, 123 (1958).