

(15) See E. M. Arnett, L. E. Small, R. T. McIver, Jr; J. S. Miller, *J. Am. Chem. Soc.*, **96**, 5638 (1974), for a similar correlation for alkoxide ions in DMSO.

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Received February 10, 1975

An Electrochemical Scrutiny of Organometallic Iron Complexes and Hexamethylbenzene in a Room Temperature Molten Salt

Sir:

We wish to report on the first use of a room temperature, high Lewis acid molten salt system to study the electrochemistry of organometallics and an alkyaromatic compound. The redox behavior of two aliphatic diimine complexes of iron(II), ferrocene, and hexamethylbenzene are shown here to be accessible in a 2:1 aluminum chloride:ethylpyridinium bromide melt.¹

The chemical^{2,3} and electrochemical⁴ one-electron reversible oxidation of either tris(glyoxalbis(methylimine))iron(II), $\text{Fe}(\text{GMI})_3^{2+}$,⁵ or tris(biacetyl(methylimine))iron(II), $\text{Fe}(\text{BMI})_3^{2+}$,⁵ can only be observed at very high acid concentrations, e.g., $\geq 10 M \text{H}_2\text{SO}_4$. At lower acid concentrations using cerium(IV) as the oxidant, ligand oxidation takes place with the consumption of several equivalents of cerium(IV) accompanied by the formation of several new ligand-oxidized complexes.⁶ The electrochemical oxidation of these complexes at lower acidities results in nondestructive ligand oxidation with the transfer of several electrons.⁴

In the 2:1 aluminum chloride:ethylpyridinium bromide melt (potential range: -0.2 to $+1.8$ V vs. Al reference electrode) the electrochemical oxidation of $\text{Fe}(\text{GMI})_3^{2+}$ and $\text{Fe}(\text{BMI})_3^{2+}$ at a disc vitreous carbon working electrode at 25° can be described as a simple one-electron reversible process as shown by the cyclic voltammograms of Figure 1, and by the pulse voltammograms of Figure 2. The corresponding $\log(i/(i_d - i))$ vs. E plots for the pulse voltammograms yielded slopes of 59 ± 5 mV, and half-wave potentials of 1.59 and 1.12 V vs. Al wire reference electrode for $\text{Fe}(\text{GMI})_3^{2+}$ and $\text{Fe}(\text{BMI})_3^{2+}$, respectively. The difference of 0.47 V in the half-wave potentials of the two complexes indicates that in the molten salt the replacement of hydrogen by methyl groups at the diimine group stabilizes the ferric form more than the ferrous form due to an increase σ bonding ability of the ligand. A similar effect was found in $11 M \text{H}_2\text{SO}_4$, where a difference of 0.36 V was observed.

In the 2:1 aluminum chloride:ethylpyridinium bromide melt the two compounds studied show a characteristic intense inverse charge transfer band at 555 and 567 nm respectively for $\text{Fe}(\text{GMI})_3^{2+}$ and $\text{Fe}(\text{BMI})_3^{2+}$ which is practically identical with the λ_{max} values obtained in $11 M \text{H}_2\text{SO}_4$.⁷ In the melt these complexes exhibit a higher molar absorptivity, and the characteristic diimine chromophore⁸ seems to be preserved. If decomposition is allowed to occur, the presence of other species that absorb strongly around 400 nm can be detected. The rate of dissociation of the complexes in the melt proceeds ca. 10 times faster in the melt than in $11 M \text{H}_2\text{SO}_4$.

In $11 M \text{H}_2\text{SO}_4$ it was shown⁴ that these diimine complexes have larger solvodynamic mean radii (via the Stokes-Einstein equation) as compared to the structural mean radii. The correlation of solvodynamic mean radii vs. struc-

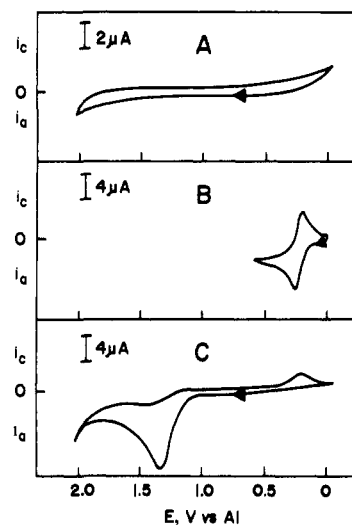


Figure 1. Cyclic voltammograms of $2.0 \times 10^{-3} M \text{Fe}(\text{GMI})_3^{2+}$ (A) and $2.0 \times 10^{-3} M \text{Fe}(\text{BMI})_3^{2+}$ (B), in the 2:1 aluminum chloride:ethylpyridinium bromide melt, at 25° . Scan rate = 0.4 V/sec .

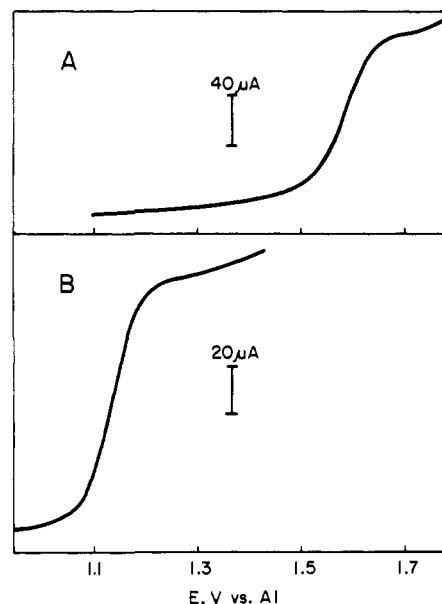


Figure 2. Pulse voltammograms; same conditions as in Figure 1.

tural mean radii was found to be linear within experimental error for a series of aliphatic diimine complexes, tris(2,2'-bipyridine)iron(II), and tris(1,10-phenanthroline)iron(II). The data obtained in water⁹ were interpreted in forms of a strong solvation of the complex ions by water molecules attached firmly to the complex ions in the pockets formed by the ligands. The linear correlation obtained for the aliphatic diimine complexes could imply that in $11 M \text{H}_2\text{SO}_4$ these ions are as strongly solvated as the aromatic ones in water. However, at such high acid concentration, where the activity of water is very low, it is more likely that the aliphatic diimine ions are strongly solvated by H_3O^+ ions due to the similarity of structural mean radii as compared to that of H_2O . This solvation could also explain the higher stability of the ferric complexes toward the internal redox reaction that leads to ligand-oxidized complexes by deterring nucleophilic attack by water molecules. (cf. ref 6).

In the melt, diffusion coefficients for the complex species obtained by the analyses of the cyclic and pulse voltammograms were found to be $(2.5 \pm 0.5) \times 10^{-7}$ and $(1.3 \pm 0.3) \times 10^{-7} \text{ cm}^2/\text{sec}$, respectively, for $\text{Fe}(\text{GMI})_3^{2+}$ and $\text{Fe}(\text{BMI})_3^{2+}$. These values are ca. two times smaller than

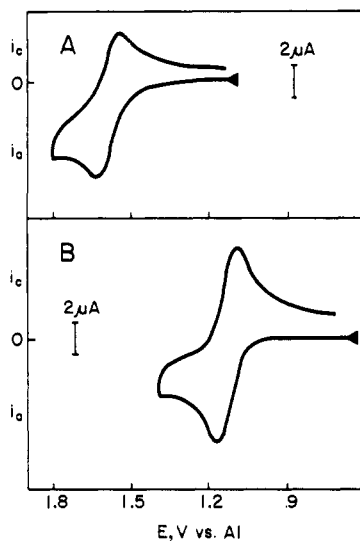


Figure 3. Cyclic voltammograms of melt background (A), 1.5×10^{-3} M ferrocene (B), and 1.5×10^{-3} M hexamethylbenzene, (C), in the 2:1 aluminum chloride:ethylpyridinium bromide melt, at 25°. Scan rate = 0.2 V/sec.

the corresponding diffusion coefficients of these complexes in 11 M H_2SO_4 . However, the viscosity of the melt is ca. three times greater than that for 11 M H_2SO_4 . An estimate of the solvodynamic mean radii for these complexes in the molten salt yields values very close to the structural mean radii. This indicates that in the melt solvation of the complex species is not of major importance. In point of fact, the potential solvating species would be the ethylpyridinium ion or aluminum chloride both of which have larger structural mean radii than simple water molecules or hydronium ions.

Cyclic voltammograms of the melt background, ferrocene, and hexamethylbenzene at a vitreous carbon electrode are shown in Figure 3. Ferrocene was found to undergo a reversible one-electron transfer ($E_{1/2} = 0.25$ V) over sweep rates ranging from 0.1 to 100 V/sec. The anodic to cathodic peak separation was found to be 60 ± 5 mV and the ratio of peak currents equaled one. A computer simulation of the data yielded voltammograms which were superimposable with the experimental curves.

At slow sweep rates hexamethylbenzene was observed to undergo an irreversible two-electron transfer ($E_p = 1.4$ V). A cathodic wave, $E_p = 0.15$ V, appeared only after cycling into or through the anodic wave. This was taken to be the reduction of proton to hydrogen by analogy with previous work.¹⁰

When hexamethylbenzene was subjected to sweep rates exceeding 10 V/sec a coupled cathodic wave ($\Delta E_p \sim 80$ mV) appeared and increased in height with faster sweep rates. To our knowledge, this is the first report of the hexamethylbenzene cation radical being electrochemically detected at room temperature.¹⁵ This reinforces previous results^{11,12} which propose that aluminum chloride based molten salts stabilize cation radicals. A comprehensive study of this phenomenon as well as preparative electrooxidations of hexamethylbenzene in this fused salt will be reported on shortly.¹³

It is clear from the data presented here that room temperature,¹⁴ strong Lewis acid, molten salt systems offer a new choice of media in which to study the chemical and electrochemical properties of a variety of compounds. Such solvents can easily be maintained free of proton, water, and oxygen.

Acknowledgments. The authors acknowledge helpful discussions with Professor J. H. Christie. One of us (H.L.C.)

would like to acknowledge an especially fruitful discussion with Professor Viktor Gutmann.

This work was supported in part by the Air Force Office of Scientific Research and Army Research Office, Durham, and by the Fundação de Amparo à Pesquisa do Estado de São Paulo.

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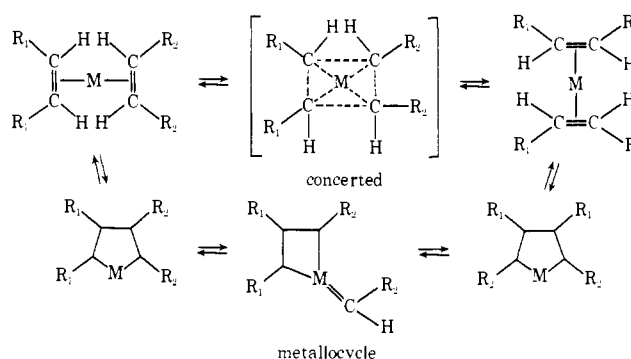
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Received February 25, 1975

Consideration of the Mechanism of the Olefin Metathesis Reaction

Sir:

One of the most intriguing problems in organometallic chemistry has been the determination of the mechanism of the olefin metathesis reaction.¹ Two classes of mechanism have received the most attention. The earliest suggestions involved a concerted switching of carbons through a "quasi-cyclobutane" transition state. This suggestion received much theoretical consideration.^{2,3} A later suggestion involved the rearrangement of a diolefin complex through a five-membered metallocycle.^{4,5}



This mechanism was supported by a number of studies of model systems.⁵⁻⁸ Both of these mechanisms require the pair-wise interchange of carbon atoms.

Recently, carbene-metal complexes have been demonstrated to be rather stable and relatively easy to generate in the early transition metal series.⁹ Schrock¹⁰ has demon-