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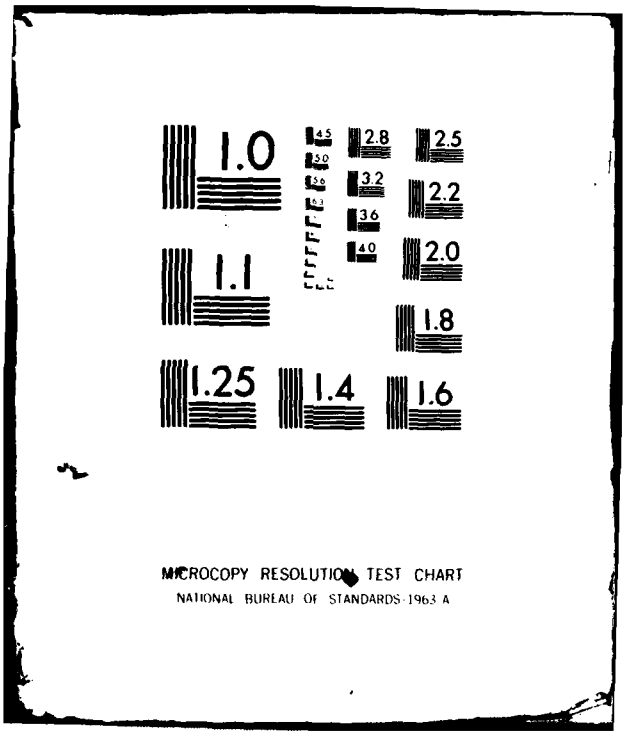
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FRANK J. SEILER RESEARCH LABORATORY

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MAY 1980

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61102F

PROJECT 2303

AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE

FJSRL-TR-80-0011

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by

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The MNDO method has been applied for the prediction of oxidation half-wave potentials of a series of aromatic compounds. A linear relation between HOMO energies and $E_{\frac{1}{2}}$ in N-alkylpyridinium chloroaluminate melts was demonstrated.

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SUMMARY

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INTRODUCTION

We have been interested in the possibility of predicting half-wave potentials for molecules being considered for electrochemical studies to determine if these potentials will fall within the electrochemical window of the solvent. Calculated molecular orbital energies are directly related to molecular ionization energies via Koopmans' theorem (1), and ionization energies should play a major if not predominant role in deteriming half-wave potentials (2,3); therefore, it appeared logical to seek a correlation between calculated molecular orbital energies and the measured half-wave potentials. Indeed, such correlations have previously been successful with Hückel-type calculations (2,4). We wish to report here the first use of the newly-developed MNDO (Modified Neglect of Diatomic Overlap) semiempirical technique for these correlations.

The MNDO method (5) is a semiempirical molecular orbital technique of a higher level than generally has been available in the past. The method is parameterized by comparison of calculated results with experimental results for a set of reference molecules. It has been shown to give reasonable predictions for the ionization energies (i.e., the negative of the calculated highest occupied molecular orbital [HOMO] energy) of a wide variety of molecules (mean absolute error of 0.48eV) even though parameterized specifically for molecular geometries and heats of formation (6). This accuracy should allow reasonable predictions of oxidation half-wave potentials, given the success of the simpler Hückel method.

Of particular interest in this laboratory is the electrochemical behavior of compounds in $AlCl_3$:N-(n-butyl)pyridinium chloride electrolytes,

which are molten at or near room temperature (7,8). These melts provide a completely anhydrous and aprotic medium in which organic electrochemistry may be performed.

RESULTS

Table I presents the results of the calculations for our correlation set of molecules compared to both measured ionization energies and measured half-wave potentials. The mean difference between the predicted ionization energies and the measured is 0.60eV, but the predicted value was consistently too large. The correlation was made between the predicted ionization energies and the oxidation half-wave potentials in acetonitrile/0.50M $NaClO_4$ vs. a $Ag/0.1MAg^+$ electrode. A least squares fit, shown in Figure 1, gave the following equation for the prediction of half-wave potential from the calculated ionization energy:

$$E_{\frac{1}{2}} = 0.725\ E_I - 4.95 \qquad [1]$$

$E_{\frac{1}{2}}$ is the half-wave potential in volts and E_I is the calculated ionization potential in eV.

Robinson and Osteryoung have shown a good correlation between ionization energy and half-wave potential for several aromatic species in $AlCl_3$:N-(n-butyl)-pyridinium chloride melts (9). They obtained an almost constant difference of 0.23V between the half-wave potentials measured in the melt vs. Al/Al^{+3} and those measured in acetonitrile/0.50M $NaClO_4$ vs. $Ag/0.1MAg^+$. (Potentials in the chloroaluminate melts in both the Robinson and Osteryoung study in the present work are reported with respect to an aluminum reference electrode immersed in 2:1 $AlCl_3$:N-(N-butyl)pyridinium chloride.) We modified Eq. [1] for this difference, and obtained the following equation for prediction of half-wave potentials in the melt:

TABLE I

CORRELATION BETWEEN IONIZATION ENERGIES AND HALF-WAVE POTENTIALS

Compound	Calculated Ionization Energy[a] (eV)	Observed Ionization Energy (eV)	Half-Wave Potentials in Acetonitrile Relative to Ag/0.1MAg$^+$[f] (V)
(1) Benzene	9.39	9.25[b]	2.00
(2) Toluene	9.28	8.82[b]	1.98
(3) o-Xylene	9.23	8.45[c]	1.57
(4) m-Xylene	9.24	8.50[c]	1.58
(5) p-Xylene	8.73	8.37[c]	1.56
(6) Biphenyl	9.12	8.20[d]	1.48
(7) Naphthalene	8.58	8.15[b]	1.34
(8) Anthracene	8.09	7.15[e]	0.84

[a] MNDO method, present work

[b] Reference 6

[c] Reference 11

[d] Reference 12

[e] Reference 13

[f] Reference 14

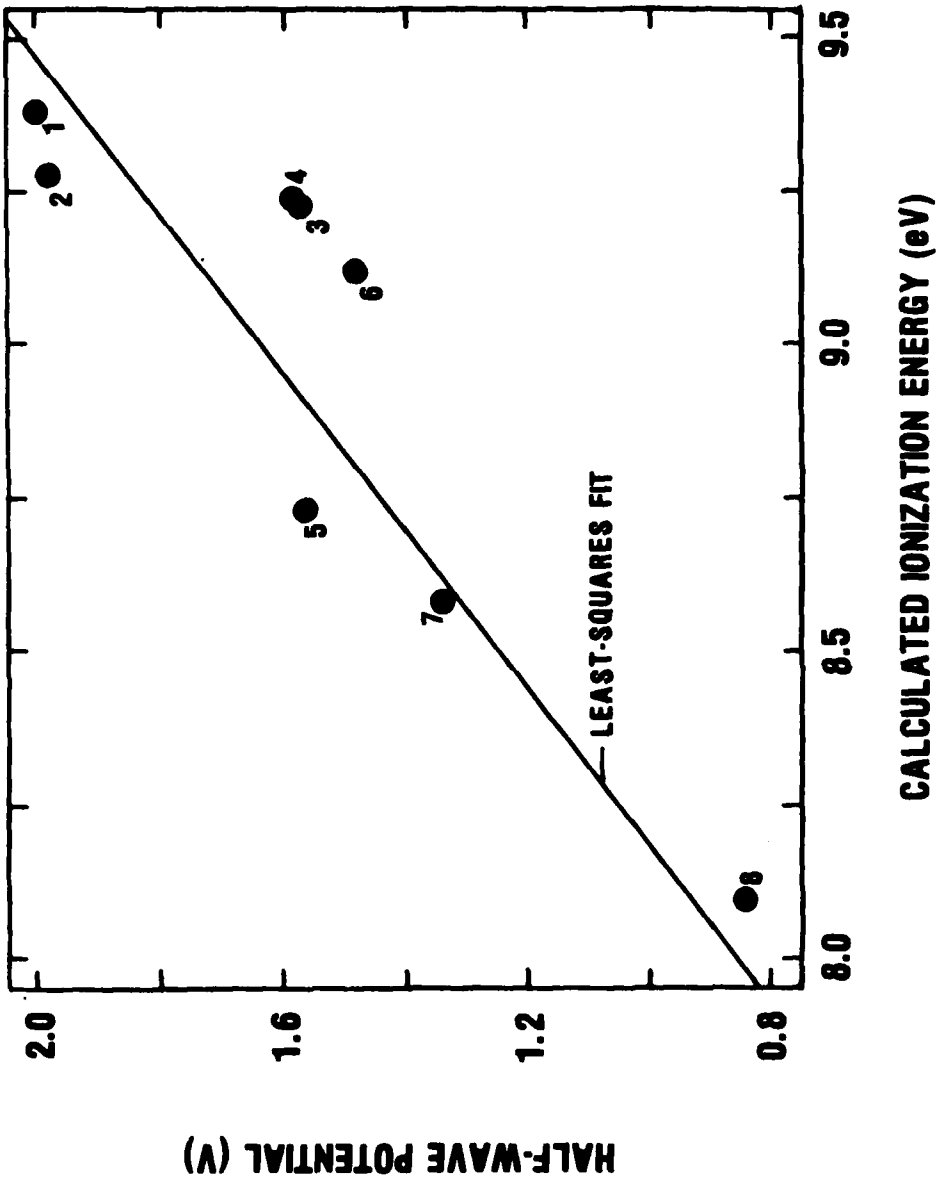

Figure 1. Least Squares Fit

$$\underline{E}_m = 0.725\ \underline{E}_I - 4.72 \qquad [2]$$

$\underline{E}_m$ is the half-wave potential in the melt in volts relative to Al/Al^{+3}.

Use of these equations resulted in predictions for half-wave potentials of the aromatic molecules given in Table II. These predictions also were compared with Robinson and Osteryoung's measured values in the melt (9) for three species; here the mean absolute difference was 0.08V.

Since the upper end of the electrochemical window of the room temperature melt is only about 2V *vs.* Al/Al^{+3}, the predictions preclude the possibility of anodic oxidation of the nitroaromatics in the melt. The prediction for thianthrene is for a very low oxidation potential, which might indicate the possibility of spontaneous oxidation if a suitable oxidant (or electron acceptor) is present in the system. The electronic and ESR spectra of thianthrene dissolved in an acidic $AlCl_3$:*N*-(*n*-butyl)pyridinium chloride solvent suggest that the radical cation of thianthrene is formed spontaneously (10). The measured half-wave potential for thianthrene was 1.17V in the melt (10), about 1V greater than the predicted potential. This discrepancy was the result of the different nature of the HOMO in thianthrene compared with the other molecules. In the case of thianthrene, the HOMO was a lone pair orbital on the sulfur atoms, while for the correlation set molecules the HOMO was a π orbital.

CONCLUSION

In summary, the MNDO method has been shown to reliably estimate half-wave potentials for a variety of aromatic molecules, providing that the same type of HOMO is involved. The predictions indicate that some compounds may be oxidized spontaneously while others will fall outside of the electrochemical window of the room temperature melt. The method will be used

TABLE II

PREDICTED HALF-WAVE POTENTIALS FOR SELECTED AROMATIC MOLECULES

Compound	Calculated Ionization Energy (eV)	Predicted Half-Wave Potential in Acetonitrile Relative to $Ag/0.1MAg^{+}$[a] (V)	Predicted Half-Wave Potential in Melt Relative to Al/Al^{+3}[b] (V)	Measured Half-Wave Potential in Melt Relative to Al/Al^{+3} (V)
Biphenyl	9.12	1.66	1.89	1.73[c]
Napthalene	8.58	1.27	1.50	1.58[c]
Anthracene	8.09	0.92	1.15	1.16[c]
Nitrobenzene	10.31	2.52	2.75	-
m-Dinitrobenzene	11.20	3.17	3.40	-
2,4,6-Trinitrobenzene	12.07	3.80	4.03	-
2,4,6-Trinitrotoluene	11.83	3.61	3.84	-
Thianthrene	6.70	-0.09	0.14	1.17[d]

[a] According to Eq. [1].

[b] According to Eq. [2].

[c] Referene 9.

[d] Reference 10.

to estimate half-wave potentials for a group of yet unsynthesized aromatic molecules being considered for electrochemical studies.

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