out under an atmosphere of dry nitrogen.

General Procedure. All of the experiments were carried out in a similar manner. The following is a typical procedure: Hexachlorocyclotriphosphazene (5.0 g, 0.014 mol) was dissolved in THF (150 mL). The methyllithium solution (22.4 mL, 0.028 mol) was slowly added over a period of ~20 min. The reaction mixture was allowed to stir overnight. Removal of the solvent under vacuum and filtration of the products dissolved in CH_2Cl_2 through neutral alumina gave the cyclic products. The yields are listed in Table I. For reactions involving TMEDA, the phosphazene (5.0 g, 0.014 mol) and TMEDA (8.45 mL, 0.056 mol) were first dissolved in the solvent and then the organometallic reagent was added as before. For reactions involving ethyl bromide, the phosphazene (5.0 g, 0.010 mol) and ethyl bromide (2.09 mL, 0.028 mol) were dissolved in the solvent and the above procedure repeated.

Acid Hydrolysis. The "ring-cleaved" products from the above reactions were all hydrolyzed in the same manner. The following is a typical procedue: A 1.0-g sample of the material was placed in a glass ampule with ethanol (30 mL) and 2 M HCl (30 mL). The ampule was then cooled to −196 °C, evacuated, and sealed and was then heated at 150 °C for 24 h. After this time, the ampule was allowed to cool at room temperature and opened, and the solvent was removed in vacuo. Sublimation of the solid residue at 80 °C (0.5 mm) yielded ~0.1 g of $(CH_3)_3P{=}O$ (identified by its mass spectrum and ^{31}P NMR). Extraction of the sublimator residue with toluene gave a mixture that proved to be $(CH_3)_2P(O)OH$, $CH_3P(O)(OH)_2$, and H_3PO_4 (identified by mass spectrometry and ^{31}P NMR).

Acknowledgment. We thank the taxpayers of Virginia for support of this work.

Registry No. Hexachlorocyclotriphosphazene, 940-71-6; methyllithium, 917-54-4.

Contribution from the Departments of Chemistry,
University of Rajasthan, Jaipur, India 302004,
University of Florida, Gainesville, Florida 32611, and
Clarkson College of Technology, Potsdam, New York 13676

Structural Effects on Polarographic Reduction of Substituted Dihydro(dimethylamine)(pyridine)boron(1+) Cations in Acetonitrile

Kamala Zutshi,[1a] G. E. Ryschkewitsch,[1b] and P. Zuman*[1c]

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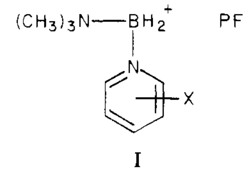
The polarographic reduction of trimethylamine–*N*-pyridylboronium hexafluorophosphates (I) (or dihydrido(tri-


$(CH_3)_3N{-}BH_2^+ \quad PF_6^-$

I

methylamine)(pyridine)boron(1+) hexafluorophosphates) is investigated in this paper, particularly from the point of view of effects of substituents on the reduction process. Such substituent effects were first treated qualitatively by the electronegativity rule by Shikata and Tachi.[3] More recently a linear free energy relationship was used for quantitative treatment of substituent effects in organic compounds on the basis of the modified Hammett equation:[4] $\Delta E_{1/2} = \rho\sigma_X$. This study is, to our knowledge, the first attempt to extend such an approach to compounds containing boron. The study has been carried out in acetonitrile, diminishing the role of proton transfers and resulting in a stabilization of the products of the one-electron uptake.[5]

Experimental Section

Compounds Ia–Is (Table I) were prepared according to ref 6. Spectroscopically pure acetonitrile dried over 4A molecular sieves was used as a solvent. Tetrabutylammonium perchlorate (G. F. Smith Chemical Co.) was used as delivered.

Polarographic curves were recorded with a Sargent XV polarograph using a capillary electrode with the following characteristics: m = 3.54 mg s^{-1}, t_1 = 6.6 s (in open circuit). The side arm of the electrolytic H-cell, filled with agar gel saturated with sodium chloride, was separated from the solution investigated by a medium-porosity sintered-Pyrex disk.

Solutions containing 0.25 mM boronium compound and 0.05 M tetrabutylammonium perchlorate in acetonitrile were freshly prepared by weighing. Such solutions were stable for at least 24 h. Half-wave potentials were measured with use of log $[i/(i_d - i)]$ vs. E plots, against a calomel reference electrode containing a saturated aqueous solution of sodium chloride. All values of half-wave potentials were corrected for the iR drop with use of measurements of resistance by means of a conductoscope.

The temperature of the solution was kept at 25 ± 1 °C. Solutions were purged by nitrogen passed through a heated copper furnace for 15 min. The temperatures of the gas and furnace were controlled so as to minimize variations in evaporation of the solvent.

Results

Most substituted trimethylamine–*N*-pyridylboronium hexafluorophosphates (I) studied are reduced in a single wave, which was proved by mercury pressure to be diffusion controlled. A comparison of limiting currents (i_d, Table I) indicates that most of the compounds studied are reduced by the same number of electrons. Calculation of diffusion coefficients by using the Ilkovič equation indicates that n = 1. The values of half-wave potentials, i_d/C, and αn_a were practically independent of concentration (Table II).

Only acetyl- (Ii) and benzoylpyridine (Ih) derivatives are reduced in two waves, one of them corresponding to the reduction of the carbonyl group. The shape of the plot of log $[(i_d - i)/i]$ vs. E indicates that for compounds Ib, If, Ig, Ij, and Is the process is close to reversible and for all others irreversible. Limiting currents for the 3-chloro- (Ic) and acetylpyridine (Ii) derivatives are significantly lower than those that would correspond to a one-electron process. An even more marked decrease was observed for the 3-methoxy-5-cyano derivative (Il). When maxima appeared on the limiting current, they were suppressed by using methylene chloride as cosolvent. The waves of the 4-methoxypyridine derivative (Ir) were so affected by maxima that measurement of the limiting current was impossible.

Discussion

The one-electron uptake leads to a formation of a radical, which may be followed by dimerization similar to that reported[7] for *N*-alkylpyridinium compounds or by cleavage of the bond between the boron atom and either the pyridine or the amine nitrogen. Even if the fate of the primary electrode product is not known, it is possible to use the polarographic data for structural correlations using the modified Hammett equation.[4]

For the application of the modified Hammett equation for the treatment of polarographic half-wave potentials for meta-

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Table I. Characteristic Properties of Trimethylamine-*N*-pyridylboronium Cations, Reduced Polarographically at the DME in Acetonitrile[a]

compd						
no.	X	i_d, μA	$-E_{1/2}$, V[b]	$RT/\alpha n_a$, V	rel *i*, μA[c]	% CH_2Cl_2
Ia	2-fluoropyridine	0.885	1.33	0.047	0.96	0
Ib	2-chloropyridine	1.14	1.215	0.057	1.24	0
Ic	3-chloropyridine	0.85	1.198	0.037	0.92	0
Id	3-bromopyridine	1.205	1.154	0.047	1.30	0
Ie	3-iodopyridine	1.07	0.804	0.043	1.16	20.0
If	4-cyanopyridine	0.97	0.77	0.055	1.05	0
Ig	4-benzylpyridine	0.93	1.53	0.055	1.01	6.0
Ih	4-benzoylpyridine 1W	0.865	0.766	0.053	0.94	0
	2W	0.885	1.441	0.159	0.96	
Ii	4-acetylpyridine 1W	0.74	0.81	0.054	0.80	0
	2W	0.80	1.527	0.20	0.86	
Ij	4-phenylpyridine	0.92	1.28	0.062	1.0	0
Ik	2-methoxypyridine	1.12	1.89	0.152	1.21	20.0
Il	3-methoxy-5-cyanopyridine	0.60	1.028	0.035	0.65	0
Im	4-methylpyridine	1.02	1.602	0.041	1.11	10.0
In	quinoline	0.88	1.05	0.035	0.96	0
Io	3,4-dimethylpyridine	0.98	1.66	0.038	1.06	0
Ip	2,4,6-trimethylpyridine	1.12	1.583	0.100	1.21	40.0
Ir	4-methoxypyridine			not measurable		
Is	hydrogen	1.22	1.473	0.055	1.20	0

[a] Conditions: 0.25 mM I, 0.05 M $(C_4H_9)_4NClO_4$, *h* = 75 cm, *T* = 25 ± 1 °C. [b] Vs. SCE. [c] Relative to Ij (*i* = 1.0).

Table II. Effect of Concentration on Electrochemical Characteristic Properties of Trimethylamine-*N*-pyridylboronium Fluorophosphate[a]

C, mM	i_d, μA	$-E_{1/2}$, V	i_d/C	$RT/\alpha n_a$, V
1	4.36	1.473	4.36	0.053
0.5	2.04	1.472	4.08	0.053
0.25	1.22	1.473	4.84	0.054
0.125	0.555	1.472	4.44	0.050

[a] Conditions: in acetonitrile, 0.05 M $(C_4H_9)_4NClO_4$.

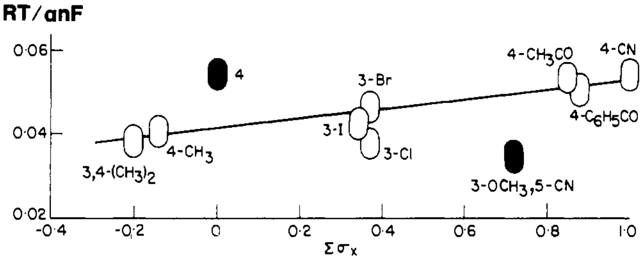


Figure 1. Dependence of the slope of the logarithmic analysis ($RT/\alpha n_a$) of polarographic waves of 0.25 mM solutions of substituted trimethylamine–*N*-pyridylboronium cations in acetonitrile containing 0.05 M $(C_4H_9)_4NClO_4$ on the sum of Hammett substituent constants ($\sum\sigma_X$). The solid points deviate.

and para-substituted compounds the processes involved in the electroreduction of all compounds compared must be identical.[4] In the present set of compounds this is indicated by the same wave height: For compounds Ic–Ig, Im, Io, and Is (Table I) used for establishment of the $\alpha E_{1/2}$–σ relationships the limiting currents vary by less than 14% from the average (1.04 μA). The only exception is the 3-methoxy-5-cyano derivative (Il), and its lower current may be due to insufficient purity.

The second condition[4] for the use of a modified Hammett equation is that within the group of compounds compared the values of the coefficient $RT/\alpha n_a$, obtained from logarithmic analysis, should either be practically constant or be a linear function of the substituent constants (σ_X). The latter condition is reasonably well fulfilled (Figure 1), with deviations for the unsubstituted compound and the 3-methoxy-5-cyano derivative.

Hence the values of the shift of the half-wave potential ($\Delta E_{1/2}$) can be plotted for the above mentioned compounds as a function of the sum of substituent constants ($\sum\sigma_X$). As a first approximation[4] substituent constants obtained for benzene derivatives were used. A good linear plot is obtained (r = 0.98) for the seven compounds with a slope corresponding to reaction constant ρ = 0.78 V (Figure 2).

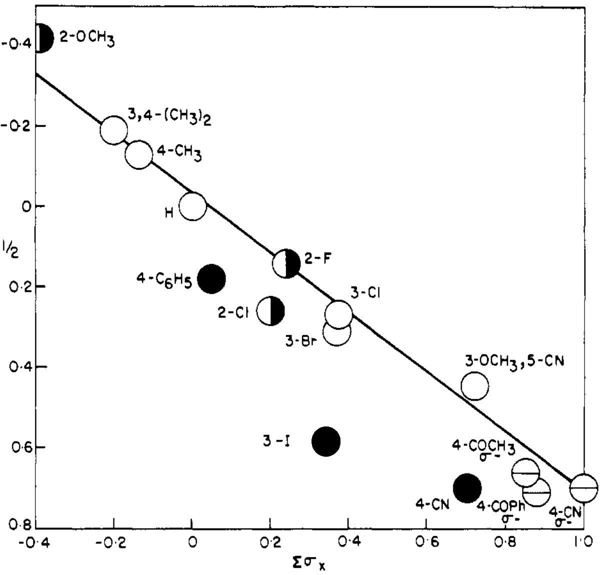


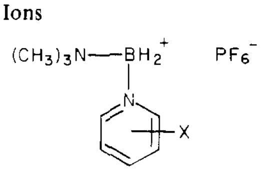
Figure 2. Dependence of the difference of the polarographic half-wave potentials ($\Delta E_{1/2}$) of the trimethylamine–*N*-pyridylboronium cation and those bearing substituents on the pyridine ring (Table III) on the sum of Hammett substituent constants ($\sum\sigma_X$): (●) compounds deviating from the line; (◑) compounds substituted at the ortho position; (⊖) compounds showing resonance interactions (σ^-_X substituted constants used). The half-wave potentials were measured for 0.25 mM cation in acetonitrile containing 0.5 M $(C_4H_9)_4NClO_4$.

For the 4-cyano derivative there is a choice of two values of substituent constants, $\sigma_{4\text{-CN}}$ and $\sigma^-_{4\text{-CN}}$ (Table III). The value for $\sigma_{4\text{-CN}}$ does not show a fit with the linear plot, whereas $\sigma^-_{4\text{-CN}}$ shows a very good fit. It can be thus concluded that the process involves a nucleophilic attack on the reduced molecule and that in the course of this attack the cyano group is in resonance interaction with the pyridine ring bearing the boron.

Considerable deviation for the 3-iodo derivative (Ie) (Figure 2) may be due to a participation of the iodine, possibly as a leaving group, in the electrode process.

For the acetyl and benzoyl derivatives (Ii and Ih) further complication was involved: It was not known whether a similar

Table III. Effects of Substituents on the Reduction of *N*-Pyridylboronium Ions



compd				
no.	X	$\Delta E_{1/2}$,[a] V	$\Sigma\sigma_X$[8]	σ^-_X[8]
Io	3,4-$(CH_3)_2$	−0.19	−0.20	...
Im	4-CH_3	−0.13	−0.14	...
Is	H	0.0	0.0	...
Ij	4-C_6H_5	0.17	0.05	...
Ic	3-Cl	0.27	0.37	...
Id	3-Br	0.32	0.37	...
Il	3-OCH_3, 5-CN	0.44	0.72	
Ii	4-CH_3CO	0.66	0.47	0.85
Ie	3-I	0.67	0.34	
If	4-CN	0.70	0.70	1.00
Ih	4-C_6H_5CO	0.70	0.46	0.88

[a] $(E_{1/2})_X - (E_{1/2})_H$.

conjugated system involving the carbonyl group and the pyridine ring is the site of the electron attack or if the first reduction occurs on the carbonyl group in the side chain. The values of $\Delta E_{1/2}$ for the acetyl and benzoyl derivatives show no correlation with $\sigma_{4\text{-}COCH_3}$ or $\sigma_{4\text{-}COC_6H_5}$ but very good correlation with $\sigma^-_{4\text{-}COCH_3}$ and $\sigma^-_{4\text{-}COC_6H_5}$ (Figure 2). This indicates that the trimethylamine–*N*-pyridylboronium moiety is involved in the reaction, as in the previous cases, rather than the acyl group. Moreover, in the course of the electron transfer the acyl group is in resonance with the pyridine ring as it is in the case for the 4-cyano derivative.

The character of the reduction resembling a nucleophilic attack (probably by the electron), concluded from substituent effects, is in agreement with the positive sign of the reaction constant ρ. It may be pointed out that the numerical value of ρ (+0.75 V) is much larger than values obtained for the transmission of substituent effects through benzenoid compounds, even on a reducible pyridine ring.[4] The limited evidence for the transfer of substituent effects through the pyridine ring on electroactive groups in the side chain, bound to a carbon of the heterocyclic ring, shows[4] also lower values (ρ varying between +0.13 and +0.43 V). This indicates a larger susceptibility of the pyridine ring to the transfer of substituent effects and a polarizability of the N–B bond larger than that of the C–X bonds.

As values for corresponding para-substituted compounds are not available for 2-F (Ia), 2-Cl (Ib), and 2-OCH_3 (Ik) derivatives, the value of the ortho shift[4] defined as $\Delta_o = (E_{1/2})_{o\text{-}X} - (E_{1/2})_{p\text{-}X}$ cannot be obtained. As a first approximation values of $\sigma_{o\text{-}X}$ obtained from the rate of hydrolysis of ortho-substituted benzoates[4] show relatively good correlation with the linear relationship obtained for the meta- and para-substituted boronium compounds (Figure 2). This means that the steric interaction between the substituents in the 2-position on the pyridine ring exerted on the N–B bond are similar to those affecting 2-substituted benzoates. The shift for the 2,4,6-trimethyl derivative (−0.13 V) is small, when compared with the half-wave potential of the unsubstituted *N*-pyridylboronium compound that would be predicted if the effects were additive ($-0.35\ V = (\sigma_{4\text{-}CH_3} + 2\sigma_{2\text{-}CH_3})\rho$). This indicates a possible hindrance of coplanarity, resulting in a decrease of interaction between the pyridine nitrogen and boron.

The substitution of phenyl in the 4-position (Ij) or the presence of the annelled ring in the quinoline derivative (In) exerts a much larger effect in the pyridine ring than predicted by the σ values obtained for benzenoid compounds ($\sigma_{4\text{-}C_6H_5} = 0.05$ and $\sigma_{\beta\text{-naphthyl}} = 0.17$). These effects, similarly to those causing the deviation for the 3-iodine derivative (Ie), can be affected by adsorption phenomena.

Thus, even in cases where the mechanism of the electrode process is not yet established, some information on the nature of the processes involved can be obtained when the linear free energy relationship is applied.

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Registry No. Ia, 22878-75-7; Ib, 22878-76-8; Ic, 22878-74-6; Id, 22878-72-4; Ie, 22878-73-5; If, 22654-00-8; Ig, 22654-03-1; Ih, 22654-04-2; Ii, 22654-05-3; Ij, 22654-02-0; Ik, 22654-08-6; Il, 83929-00-4; Im, 17439-16-6; In, 22653-99-2; Io, 22653-98-1; Ip, 22654-07-5; Is, 22653-96-9.

Contribution from the Department of Chemistry,
North Dakota State University, Fargo, North Dakota 58105

Quenching of the Substitutional Photochemistry of Tris(bipyridine)ruthenium(II) Bromide

Richard Fasano and Patrick E. Hoggard*

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The observation[1-3] of photoanation of $[Ru(bpy)_3]^{2+}$, bpy = bipyridine, which can be appreciable in organic solvents, leaves open the question of the mechanism of the substitution process and the related question of the excited state responsible. The extensive photoredox chemistry of $[Ru(bpy)_3]^{2+}$ suggests, as an alternative to direct substitution of Ru(II), the possibility of a pathway involving oxidation to Ru(III), followed by thermal substitution and reduction to Ru(II) again. Similar pathways through Ru(I) or through disproportionation to Ru(I) and Ru(III) are also reasonable. Both Ru(I) and Ru(III) should be less inert to substitution than Ru(II). The isolation of small amounts of blue and green species, stable for a few hours, from photolysis reaction mixtures[3,4] is intriguing in this regard.

Evidence has been presented for the existence of another excited state in the area of the luminescing charge-transfer state.[2,5,6] Thus another reasonable supposition is that photosubstitution results from a ligand field excited state.

To help characterize the photochemically reactive excited state, we have examined the quenching of the photoanation of $[Ru(bpy)_3]^{2+}$ by ferrocene in dimethylformamide (DMF) and compared it with the luminescence intensity quenching. The Stern–Volmer plots appear in Figure 1 and show a quenching constant 3 times greater for the photoanation reaction, which is shown both as disappearance of $[Ru(bpy)_3]^{2+}$ and as appearance of $[Ru(bpy)_2(DMF)Br]^+$, the major product under the conditions used.

The data point strongly to at least a partial partitioning of photosubstitution and luminescence among separate excited states. However, the experiment argues against a model in

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