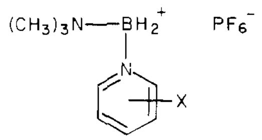
Table III. Effects of Substituents on the Reduction of *N*-Pyridylboronium Ions



compd				
no.	X	$\Delta E_{1/2}$,[a] V	$\Sigma\sigma_X$[8]	σ^-_X[8]
Io	$3,4\text{-}(CH_3)_2$	−0.19	−0.20	...
Im	$4\text{-}CH_3$	−0.13	−0.14	...
Is	H	0.0	0.0	...
Ij	$4\text{-}C_6H_5$	0.17	0.05	...
Ic	3-Cl	0.27	0.37	...
Id	3-Br	0.32	0.37	...
Il	$3\text{-}OCH_3$, 5-CN	0.44	0.72	
Ii	$4\text{-}CH_3CO$	0.66	0.47	0.85
Ie	3-I	0.67	0.34	
If	4-CN	0.70	0.70	1.00
Ih	$4\text{-}C_6H_5CO$	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 $\sigma_{4\text{-COC}_6\text{H}_5}$ but very good correlation with $\sigma^-_{4\text{-COCH}_3}$ and $\sigma^-_{4\text{-COC}_6\text{H}_5}$ (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 $2\text{-}OCH_3$ (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 ($-0.35\ \text{V} = (\sigma_{4\text{-CH}_3} + 2\sigma_{2\text{-CH}_3})\rho$). 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 ($\sigma_{4\text{-C}_6\text{H}_5} = 0.05$ 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.

Acknowledgment. K.Z. wishes to thank the University of Rajasthan for allowing a study leave for this period and the Chemistry Department of the University of Florida for financial support.

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.

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

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Received May 4, 1982

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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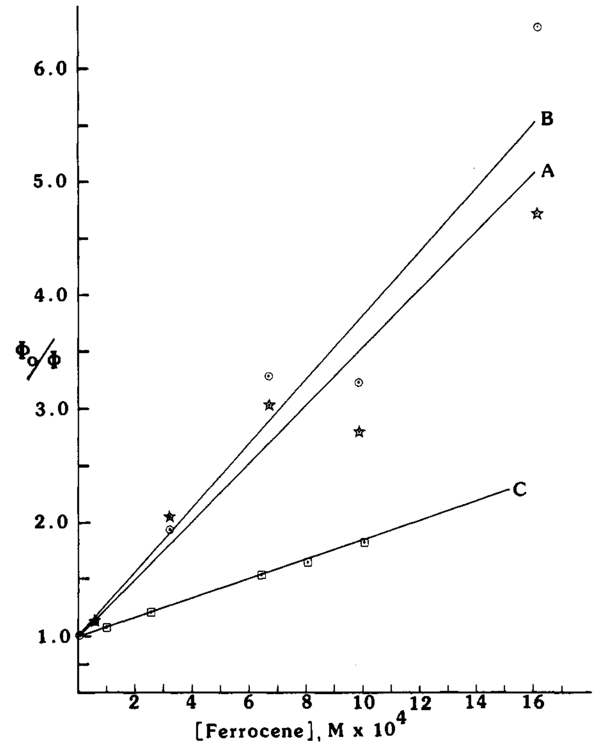

Figure 1. Stern–Volmer plots of the quenching by ferrocene of the luminescence intensity (C) of $[Ru(bpy)_3]^{2+}$ in DMF at 22 °C and of the photoanation reaction, in terms of the disappearance of $[Ru(bpy)_3{}^{2+}]$ (☆, line A) and the production of $[Ru(bpy)_2(DMF)Br]^+$ (⊙, line B). Slopes (M^{-1}): 2530 ± 620 (A); 2825 ± 580 (B); 826 ± 6 (C). 0.10 M Bu_4NBr was present in all samples.

which the states would be in thermal equilibrium.[6] Furthermore, the larger K_{SV} for the photosubstitution reaction implies either a longer lifetime for the ligand field state or a larger bimolecular quenching constant. A longer lifetime could result if the ligand field state were *lower* in energy than the luminescing charge-transfer state, whereas deactivation by more than one ferrocene electronic state could account for differences in the bimolecular quenching constant. Some evidence that the ligand field and charge-transfer states may not be in equilibrium has been presented recently.[7]

There remains the possibility that a chemical rather than a photophysical process is responsible for the observed differences in K_{SV}. Ion pairs and triplets are known to play a significant role in the photoanation reaction,[3] although we have at this time no suggestion for a way in which ferrocence might interfere with the process. Ferrocene was chosen as the quencher, in fact, precisely because it was neutral (thus unlikely to affect ion-pairing equilibria) and relatively robust in comparison with other neutral complexes that were tried. However, suggestive in this respect is the previously reported Stern–Volmer constant for quenching of $[Ru(bpy)_3]^{2+}$ emission (chloride salt) by ferrocene in ethanol[8] of 5300 M^{-1} (6 times greater than our value in DMF), which is more remarkable in that the viscosity of ethanol is greater than that of DMF.

Under the conditions of these experiments, ferrocene itself undergoes photolysis. Two photoproducts could be isolated after irradiation of solutions containing only ferrocene. Bromide had no effect on the photolysis. The quantum yields were very low (ca. 10^{-3}), and even at ferrocene concentrations in the range of those used in the quenching studies, analysis of the Ru photolysate absorption spectrum after 50% of the $[Ru(bpy)_3]^{2+}$ had reacted led to an estimate that less than 10% of the ferrocene had reacted. Nevertheless, oxidation of ferrocene by excited $[Ru(bpy)_3]^{2+}$ cannot be ruled out as an explanation of the present experiment.

Experimental Section

Solutions 4.85 × 10^{-5} M in $[Ru(bpy)_3]Br_2$ and 0.10 M in tetrabutylammonium bromide in DMF, with ferrocene concentrations between 0 and 1.61 × 10^{-3} M, were deoxygenated by bubbling N_2 through for 20 min and irradiated at 436 nm with use of an Oriel 500-W Hg lamp and a liquid filter train.[9] Photolysis was interrupted periodically and absorption spectra were recorded. The spectrum corresponding to the ferrocene present was subtracted. The resulting spectra were resolved[3] into the separate contributions from $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_2(DMF)Br]^+$, and $[Ru(bpy)_2Br_2]$. Plots of concentration vs. time were linear at least until 40% of the reactant had been consumed. Ferrioxalate actinometry[9] was used to determine the incident light intensity.

Registry No. $[Ru(bpy)_3]Br_2$, 15388-41-7; Br^-, 24959-67-9; $[Ru(bpy)_2(DMF)Br]^+$, 73663-67-9; DMF, 68-12-2; ferrocene, 102-54-5.

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The Mixed-Component Layered Tetravalent Metal Phosphonate System $Th(O_3P\text{-}C_6H_5)_x(O_3P\text{-}C_6H_4\text{-}C_6H_5)_{2-x}$

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Received June 15, 1982

Layered tetravalent metal phosphonates constitute a unique class of materials in which various organic groups are covalently appended in nearly close-packed arrays onto the basal surfaces of an inorganic sheet (Figure 1).[1] One feature of these solids that has particularly attracted our interest is the possibility of manipulation of their surface textural properties by variation of the organic groups. More specifically, we were concerned with the preparation and characterization of products having two different groups present within the microenvironment. Single-phase solid solutions, ordered single phases, or multiphase products could conceivably occur when precipitating mixtures of phosphonates with M^{4+}, and we have seen examples of all of these outcomes in our work.[2]

Conceptually, one simple means of introducing microporosity into mixed-component layered phosphonates is to have present both small and large groups, the latter serving to prop the layers apart, as is depicted in Figure 2. We chose to test this premise using for the two groups phenyl and biphenyl, since chemical similarity maximizes the likelihood of solid-solution formation. Thorium was used as the metal ion because it tends to yield more crystalline products (as gauged by the width of X-ray diffraction reflections). Therefore, we undertook the preparation of the series of products $Th(O_3P\text{-}C_6H_5)_x(O_3P\text{-}C_6H_4\text{-}C_6H_5)_{2-x}$ for x = 0, 0.2, 0.4, 0.6, ..., 2.0, that is, for the series in which the mole fraction ratios of phenyl and biphenyl varied from 0 to 1 at one-tenth increments.

Experimental Section

With use of methodology previously developed in our work, the preparation of the series was accomplished by adding together solutions

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† Deceased Aug 16, 1982.