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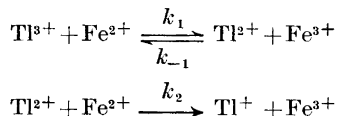
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Outer Sphere Electron Transfer through Substituted Pyridines

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In an earlier communication¹ it was shown that in perchloric acid solution the second step of the two-step redox reaction²



is strongly catalyzed by 2- and 4-aminopyridine, but not by 3-aminopyridine. The catalytic effect was interpreted as an outer-sphere remote attack mechanism in the $\text{Tl}^{2+} - \text{Fe}^{2+}$ reaction where an electron was assumed to be transferred through the pyridine in a manner similar to that occurring in heterogeneous catalysis by bright platinum.^{3,4}

We report here evidence that 2-hydroxypyridine (2-hp) has a similar but more pronounced catalytic effect, while 3-hydroxypyridine (3-hp), like 3-aminopyridine, produces a slight retardation of the overall reaction.

The reaction was followed, at 25°C, an ionic strength of 1.60 M in perchlorate and at $[\text{H}^+] = 0.500$ M, by the procedure described earlier for experiments in the presence of 3-aminopyridine.¹ The figure shows second-order plots in the absence of a catalyst, in the presence of

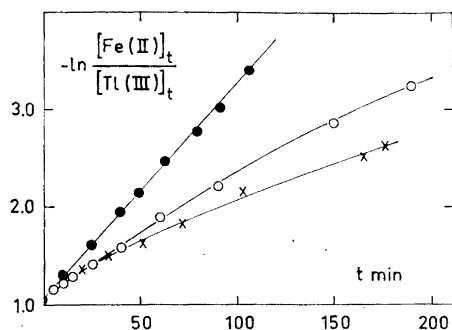


Fig. 1. Simple second-order plot. $[\text{Tl}^{3+}]_0 = 6.83 \times 10^{-3}$ M, $[\text{Fe}^{2+}]_0 = 4.76 \times 10^{-3}$ M, $[\text{Tl}^+]_0 = 1.33 \times 10^{-3}$ M. \circ no catalyst added, \bullet 0.021 M 2-hydroxypyridine, \times 0.054 M 3-hydroxypyridine.

0.021 M 2-hp, and in the presence of 0.054 M 3-hp. Straight lines are obtained for $[2\text{-hp}] \gtrsim 0.01$ M, corresponding to $k_2 \gg k_{-1}$. Also, k_1 increases with increasing $[2\text{-hp}]$, in contrast to what is observed in the presence of the aminopyridines and bright platinum, where k_1 is unaffected by the electron mediator. The rate constant of the reaction through the activated complex containing 2-hp has a value of 4.5 l/mole min, while that of Tl^{3+} and TlOH^{2+} are 0.33 and 9.4 l/mole min, respectively.

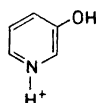
Addition of 3-hp results in a minor decrease in k_1 and k_2/k_{-1} , presumably due to the formation of complexes with Tl^{3+} , more inert than the aquo ion. This is similar to the effect of 3-aminopyridine.

The complex formation of 2-hp with Tl^{3+} , Fe^{3+} , and Fe^{2+} was measured by the same procedure as used earlier.¹ Within the limits of experimental error, no interaction was found with Fe^{2+} or Fe^{3+} , while a stability constant of 16 was found for the $\text{Tl}(\text{III})$ complex. Although the exact composition of the complex can not be stated from the present investigation, the value of the constant shows that the observed catalysis results from a very small amount of complex formation.

3-hp exists predominantly in the hydroxyform I, and in strongly acid solution as the protonated species II.⁵ No system of conjugated double bonds exists in an exchange path through the molecule, and in acid solution the free electron pair at the N-atom is not available



I



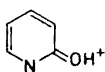
II



III



IV



V

leaving no possibility for a remote attack by a second metal ion. A possible kinetic effect would then be expected to be a retardation due to a decrease of the free energy of the overall reaction.

2-hp exists as the pyridone IV rather than the hydroxy form III.⁵ There is evidence⁶ that in acid solution the oxygen atom is protonated, and that the structure V is present. For this structure there is a possibility of interaction with a metal ion at both the O- and the N-atom, and there is also a conjugated double bond system in the exchange path through the molecule.

k_1 shows a minor increase only with increasing [2-hp], hence k_{-1} also can only show a minor dependence, and the main effect is a strong increase in k_2 . This is also what is observed for the aminopyridines which are present in acid solution in the same forms as V. It is thus plausible to assume that the same mechanism is valid, although more information is needed about the exact composition of the activated complex in the 2-hp catalyzed path.

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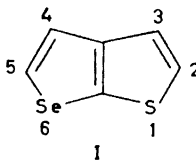
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The Synthesis of Seleno[2,3-b]-thiophene

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Seleno[3,2-b]thiophene has recently been prepared by Goldfarb *et al.*¹ but the isomeric seleno[2,3-b]thiophene (I) has hitherto not been described. The naming of these new heterocyclic compounds are based on the IUPAC 1957 rules using the thiophene ring as the base component and starting the peripheral numbering with the sulphur atom.



I

In order to obtain the seleno[2,3-b]thiophene, a method similar to the one described by Gronowitz and Persson² for the preparation of thieno[2,3-b]thiophene was adopted. 3-Thiophene aldehyde ethylene acetal (II) was metalated by butyllithium in the 2-position and the resulting thienyllithium compound reacted with selenium according to the method described previously by Goldfarb and Litvinov.³ The intermediate thienylselenolithium derivative was reacted with methyl chloroacetate and hydrolyzed. The methyl(3-formyl-2-thienylseleno)acetate formed was cyclized with alcoholic sodium ethoxide to give the 5-carboxyseleno[2,3-b]thiophene (III). Decarboxylation with copper and quinoline gave seleno[2,3-b]thiophene.

The structure of seleno[2,3-b]thiophene was confirmed by its NMR-spectrum. A discussion of the spectrum will appear elsewhere.