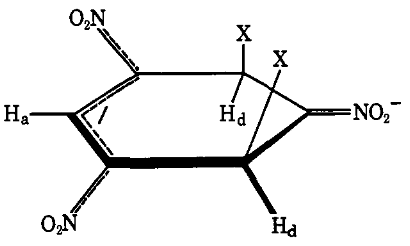
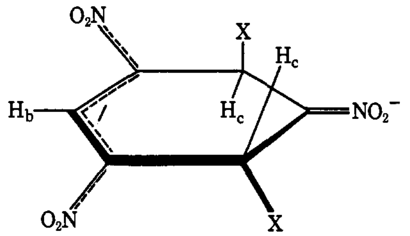


**1a**



**1b**

field, singlet resonances occur at $\tau$ 4.2 and 3.9 ppm (in a ratio of 45:55) for the $sp^3$ protons in the two isomers of **1** ($X = SO_3^-$). At low field, singlets for the corresponding nitronate protons occur at $\tau$ 1.6 and 1.5 (45:55). The $\tau$ 4.2 and 1.6 resonances integrate for 2 H and 1 H, respectively, as do the $\tau$ 3.9 and 1.5 absorptions. The shift difference between the nitronate protons in these isomers is much smaller than that of the corresponding $sp^3$ ring protons, as expected. The two sets of absorptions, one for each of the isomeric structures in a ratio of 45:55, are clearly in accord with the results of Bernasconi and Bergstrom.[1]

As we pointed out 2 years ago,[10] it is likely that *all* 1:2 $\sigma$-complex adducts can exist in isomeric cis and trans forms. Determination of equilibrium constants for such species by standard methods, *i.e.*, Benesi–Hildebrand or related procedures, must of course consider this fact, since the electronic spectral characteristics of these isomers are usually almost identical.

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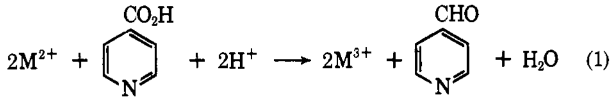
## Reactions of Pyridinecarboxylic Acids with $Eu^{2+}$(aq), $Cr^{2+}$(aq), and $V^{2+}$(aq). Selective Reduction of the Carboxylic Group

*Sir:*

The few reactions of pyridinecarboxylates with aqueous metal ions of low valence hitherto known involve the pyridine ring.[1] Here we report on the selective reduction of the carboxylic group by $Eu^{2+}$(aq), $Cr^{2+}$(aq), and $V^{2+}$(aq).

Usually, the reduction of the carboxylic group requires vigorous conditions. It is interesting in this respect, that even in the polarographic reduction of pyridinecarboxylic acids there is no general agreement among the various authors,[2] as to whether the observed waves are due to catalytic discharge of hydrogen, to reduction of the —CH=N— bond, or to the reduction of the carboxylic group. In the systems reported here, however, reduction of the carboxylic group does take place readily under mild conditions, namely at room temperature, in aqueous solutions acidified with HCl or $HClO_4$, under an inert argon atmosphere.

The consumption of $Eu^{2+}$(aq) during its reaction with isonicotinic acid can be followed by adding excess Fe(III) and titrating the Fe(II) amperometrically with Ce(IV). The products of the reaction are $Eu^{3+}$(aq) and isonicotinaldehyde. The latter was isolated in the form of its oxalate complex,[3] as well as in the form of the complex with sulfur dioxide,[4] after precipitating with $Na_2CO_3$ and filtering out the europium ions. The nmr spectrum of the organic product after reoxidation by air was found to be identical with that of the isonicotinic acid. The yield in excess isonicotinic acid was determined by titrating the aldehyde with $KMnO_4$. The stoichiometry corresponds to the overall reaction



$$2M^{2+} + C_5H_4N(CO_2H) + 2H^+ \longrightarrow 2M^{3+} + C_5H_4N(CHO) + H_2O \quad (1)$$

In a typical experiment for the determination of the stoichiometry the initial concentrations were $[Eu^{2+}]_0 = 0.2\ M$, $[\text{isonicotinic acid}]_0 = 0.6\ M$, and $[HCl] = 2\ M$.

Isonicotinaldehyde was also obtained using chromous and vanadous ions. It was isolated and identified as described above. Trivalent chromium was precipitated with alkali. During the neutralization a soluble red complex between Cr(III) and the excess isonicotinic acid is formed, which by further addition of alkali turns into an insoluble green complex. From a reaction mixture containing vanadous ion and an excess of isonicotinic acid, isonicotinaldehyde was also obtained, after precipitation of vanadium with alkali. The overall process with $Cr^{2+}$(aq) and $V^{2+}$(aq) is also described by reaction 1.

In solutions acidified with HCl or $HClO_4$, europous ion was found to give isonicotinaldehyde faster than chromous. The reaction with vanadous is overall slower. Typically, in a solution containing 1 $M$ $HClO_4$, 0.07 $M$ $Eu^{2+}$, and 0.11 $M$ isonicotinic acid, the reaction was completed in about 1.5 hr. In similar solutions the reaction with $Cr^{2+}$(aq) takes several hours, whereas the reaction with $V^{2+}$(aq) is even slower. All three ions react faster at lower acidities. A detailed investigation[5] indicated that the reaction between chromous and isonicotinic acid proceeds in two time-resolved one-electron transfer steps through formation

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of an intermediate complex having a maximum at 410 nm ([H$^+$] = 2 $M$, $\epsilon_{max}$ 38). This complex reacts further by a bimolecular reaction or decomposes back to the original species. In the case of $V^{2+}$(aq) the formation of the complex in the first stage of the reaction is completed within the time of mixing. Fast complex formation is also observed with $Eu^{2+}$(aq).

In the reaction between picolinic acid and $Eu^{2+}$(aq) direct formation of $Eu^{3+}$(aq) and free aldehyde is not observed. In a solution, for example, containing initially 0.3 $M$ $Eu^{2+}$(aq) and 0.7 $M$ picolinic acid at pH $\simeq$1, a yellow-gray complex (or complexes) is formed which is stable over a period of many days. It is believed that in this complex europium is in the +2 state, since it can be readily oxidized by air or by Fe(III). With $SO_2$ the Eu(II)–picolinic acid solution does not form a precipitate. If europium together with some organic material is first precipitated with soda, the $SO_2$ and 2,4-dinitrophenylhydrazine tests on the filtrate are positive. The yield, however, is small and irreproducible, as indicated by titrating with $KMnO_4$. It seems that aldehyde is formed only during the neutralization procedure.

A complex is also formed upon mixing a $Cr^{2+}$(aq) with a picolinic acid solution, *e.g.*, an acid solution 0.5 $M$ in $Cr^{2+}$ with an acid solution 1.8 $M$ in picolinic acid. This complex is deeply colored (red-brown), stable, and inert. Extraction with ether or chloroform gave no indication of a free organic product and chromium could not be precipitated with alkali. The complex was destroyed only by adding sodium pyrophosphate and boiling under reflux for several hours, but under these vigorous conditions the organic product underwent further reactions. Thus, ether extraction gave a product having a proton nmr spectrum consistent with what would be expected for *o*-hydroxymethylpyridine.[6] The boiled solution also contained other unidentified organic products.

The complex between V(III) and the product of the reaction between vanadous and picolinic acid is labile. It can be readily dissociated by acidifying the solution. Precipitation with $SO_2$ of picolinaldehyde can be achieved after removing vanadium with alkali, provided that picolinic acid is in excess. Even in acid solution, without removing the metal ion, the $SO_2$ test for the aldehyde is positive. At lower picolinic acid concentrations the organic product coprecipitates with V(III), if the solution is made alkaline. In the pH range between 1 and 3 the oxidation of $V^{2+}$(aq) by picolinic acid is second order in $V^{2+}$, having a maximum rate at pH $\simeq$2. At this pH, with a solution containing initially $1.5 \times 10^{-2}$ $M$ $V^{2+}$ and 0.19 $M$ picolinic acid the pseudo-second-order rate constant has the value 2.5 mol$^{-1}$ min$^{-1}$.

Under the conditions of our experiments nicotinic acid does not seem to be reduced by any of the three ions. Europous and chromous do not even seem to form complexes, while the complexes formed by vanadous are very unstable. Heating a mixture of $Cr^{2+}$(aq) with excess nicotinic acid at 80° for several hours leads to oxidation of Cr(II), but without apparent intermediate formation of a colored complex. Moreover, the organic product obtained in small yield, after removing chromium with alkali, does not give the characteristic reactions of the aldehyde group; it reduces $I_2$ and $KMnO_4$ but not methylene blue; with $SO_2$ it does not give a precipitate.

Our previous results[5] indicated that the first step in the two-electron reduction of isonicotinic acid by chromous ion involves an ion–radical intermediate rather than an organic free radical. Nevertheless, the spin densities of the radical anions, in the absence of the perturbing influence of the metal ion, obtained by esr spectroscopy and by theoretical calculations[7] have some relevance to the present work. They provide some basis for correlating the behavior of the three pyridinecarboxylic acids, since at the positions occupied by the carboxylic group isonicotinic and picolinic acids have higher spin densities than nicotinic acid. Correspondingly, isonicotinic and picolinic acids interact with the three ions strongly, whereas nicotinic acid does not. The interaction with isonicotinic acid leads to the formation of the aldehyde. Formation of aldehyde from picolinic acid and $Eu^{2+}$(aq) or $V^{2+}$(aq) is observed at low hydrogen ion concentrations, indicating an accelerating influence of chelation. Aldehyde formation from picolinic acid and chromous ion was not observed, presumably because of the substitution-inert character of the complex formed in the first step.

It must be recalled in this context, that Norris and Nordmeyer[8] found that free isonicotinamide catalyzes the reaction between $Eu^{2+}$(aq) and isonicotinamide-, pyridine-, and nicotinamidepentaamminecobalt(III) complexes, whereas the corresponding amide of nicotinic acid did not have any catalytic effect. It seems, therefore, that the study of the mechanism of the reduction of free ligands by metal ions is not only interesting for its own sake and for synthetic reasons but it can also help to gain a better understanding of the electron transfer process, when the ligand is bound to a metal ion center. Moreover, it can provide criteria for recognizing the cases in which the transfer of the electron proceeds by a radical–intermediate mechanism.

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[6] The presence of *o*-hydroxymethylpyridine could be attributed to the easiness with which picolinaldehyde undergoes a Cannizzaro reaction.

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## Structure of Tetracyclopentadienyluranium(IV)[1]

*Sir:*

When Fischer and Hristidu[2] first synthesized tetracyclopentadienyluranium(IV), $(C_5H_5)_4U$, they reported

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