

ment is good for C_p^0 for all three of the ΔH values calculated. For S^0 the agreement is certainly better for $\Delta H = \infty$ in accord with Scott et al.⁵ However, conversely we are not prepared to say that the discrepancy of 0.5 cal/°K/mol for $\Delta H = 600$ –800 cal/mol is significant in the light of experimental uncertainties and uncertainties in the calculated values. For 2,3-dimethylbutane the situation is similar, the C_p^0 values are in good agreement, and the calculated entropies are a bit high but probably not significantly so in view of the uncertainties.

In summary, it appears that the stabilities of the conformers of 2-methylbutane and 2,3-dimethylbutane are consistent with conformational energy calculations and have a simple qualitative explanation in terms of valence and torsional angle adjustments. Further, the stabilities are in reasonable accord with the thermodynamic functions.

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- (19) D. H. Wertz and N. L. Allinger have recently (*Tetrahedron*, **30**, 1579 (1974)) proposed that gauche H...H nonbonded interactions play a dominant role in the structure of conformational isomers. In our parameterization, at least, they play a relatively minor role. In *gauche*-vs. *trans*-n-butane for example, we find methyl...methyl nonbonded interactions contribute 0.50 kcal/mol to the *gauche*-*trans* energy difference with other contributions to the total difference of 0.66 kcal/mol from the following sources of Me...H -0.30, H...H 0.16, torsional angle distortion 0.11, valence angle distortion 0.21, bond length distortion 0.03, and non-bonded interaction differences on the same side of the center C-C bond -0.05. It also seems clear that most of the torsional and valence angle distortional energies are due to the methyl...methyl repulsions.

A Study on the Interaction of $\text{Eu}^{2+}(\text{aq})$ with Pyridinecarboxylic Acids

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Abstract: Europous ion forms with isonicotinic, *N*-methylisonicotinic, nicotinic, and picolinic acids one to one complexes having several features, which are rather unusual for a lanthanide ion. They are formed in strongly acidic aqueous solutions and have absorption maxima around 420 nm. The formation constants are 0.15 l. mol⁻¹ for nicotinic acid, 0.2 l. mol⁻¹ for picolinic acid, 1.9 l. mol⁻¹ for isonicotinic acid, and 0.4 l. mol⁻¹ for *N*-methylisonicotinic acid, respectively. Evidence is presented that the complexes involve charge transfer from the metal ion to the ligand. The complexes of nicotinic and picolinic acids are stable toward further redox reaction. The complexes of isonicotinic acid and its *N*-methyl derivative, however, undergo further reduction leading in the first case to isonicotinaldehyde and in the second very likely to the dihydro derivative. In the presence of $\text{Eu}^{3+}(\text{aq})$ the kinetics of the redox reaction of isonicotinic acid and its *N*-methyl derivative are second order in europous ion, first order in the organic acid, first order in hydrogen ion, and inverse first order in $\text{Eu}^{3+}(\text{aq})$. A unified mechanism is proposed to explain the results for both of these acids, which is also consistent with the results obtained on complex formation and with the postulate of a charge transfer from europous ion to the ligand.

The mechanism of electron transfer *through* reducible organic ligands is related to the mechanism of transfer *to* such ligands. It must be recalled that even when these ligands are bound, the electron is very likely first transferred to them, before finding its way to the central ion.²

If the ligands are bound, the presence of the central metal ion makes it impossible to detect and study some important details of the electron transfer process. In the reactions of free ligands³ with low valent metal ions some of these "missing aspects" become more pronounced and can be studied by conventional techniques. Focusing attention on substituted pyridine ligands, it is worth mentioning the following two such aspects. (i) In studies of electron trans-

fer through substituted pyridine ligands⁴ the electron may "reside" for a while on the ligand. The intermediate radical-complex is, however, difficult to detect. In the corresponding reactions of free ligands⁵ complex formation and subsequent reaction are time-resolved, and the course of the reaction from the precursor complex to the products can be explored more effectively. (ii) Kinetically, the reactions between substituted pyridine complexes and reducing metal ions are generally quite simple. The ligand, whether bound⁴ or free⁶ essentially acts as a catalyst. The differences in the overall chemistry caused by changes of the substituents on pyridine are rather trivial.

In the corresponding free ligand reactions the products

depend both on substitution on pyridine and on conditions. Thus, the final products may result either from a specific reduction of the carboxyl group^{5c} or from hydrogenation of the pyridine ring.⁷ These differences in the overall chemistry make the reactions of the free ligands more complicated, but at the same time provide additional information on the mechanism.

The study of free ligand reactions is also interesting in itself, independently of whatever relevance it might have on reactions between complexes. It is perhaps too early to speculate on whether the low valent metal ions or their complexes can become equally useful as specific reducing agents of organic molecules as the metal hydrides.⁸ The practically unlimited variety of possible combinations is undoubtedly a favorable factor. At any rate it seems worthwhile to look further into some of the possibilities.

Experimental Section

Solutions of Europous Ion. Eu(II) perchlorate solutions were prepared by electrolytic reduction of $\text{Eu}(\text{ClO}_4)_3$ in HClO_4 media, on a mercury pool cathode. The voltage during the electrolysis was 10 V and the current density 3.5–14 mA/cm² depending on the HClO_4 concentration.

Eu(II) chloride solutions were prepared in a similar way.

The solutions were kept in the dark, under inert atmosphere, and used immediately after preparation.

Oxygen is reduced by $\text{Eu}^{2+}(\text{aq})$ first to H_2O_2 , which accumulates and reacts further with $\text{Eu}^{2+}(\text{aq})$ slower.⁹ Consequently, unless oxygen is very carefully excluded, the kinetics results are irreproducible. Traces of oxygen were removed by purging with a gas mixture containing 99.5% Ar and 0.5% N_2 , which had passed through successive traps containing $\text{Cr}^{2+}(\text{aq})$, $\text{V}^{2+}(\text{aq})$, and zinc amalgam. In some of the experiments degassing was done by use of a high vacuum line.

Very low concentrations of $\text{Eu}^{2+}(\text{aq})$ were avoided as much as possible. Some oxidation of europous ion by impurities seems unavoidable and at low concentrations it causes large relative errors. Possible causes of this oxidation are traces of oxygen (left despite meticulous deaeration), dust, and grease. Even silicon grease was suspected. The light beam of the spectrophotometer also seems to enhance the rate of this irreproducible oxidation.¹⁰ Since our aim was not to study the photochemistry of the Eu^{2+} -pyridinecarboxylic acid solutions, we simply avoided long exposures of the samples to the spectrophotometer light source. Eu(II) solutions in aqueous HClO_4 or HCl remain unoxidized in the dark for only a few hours, even with the most careful control of the above mentioned factors.

Even in the absence of impurities and/or pyridinecarboxylic acid $\text{Eu}^{2+}(\text{aq})$ was slowly oxidized in aqueous HCl or HClO_4 . The time scale of the reactions with pyridinecarboxylic acids is, however, generally much shorter. Under the conditions of our experiments, hydrogen formation was not observed. Reaction mixtures carefully degassed on the vacuum line gave no gaseous products.

Preparation of the N-Methylbetaine of Isonicotinic Acid. We first prepared the methiodide of the isonicotinic methyl ester. A solution of the isonicotinic methyl ester in acetonitrile containing methyl iodide was boiled under reflux. The product was partially precipitated in crystalline form. An additional amount was obtained from the mother liquor by evaporation and addition of large excess of carbon tetrachloride. Recrystallization was from methanol containing carbon tetrachloride: yield 80%, mp 189°.

The betaine was prepared by passing an aqueous solution of the methiodide of the ester over a Dowex-1 resin in the hydroxide form and eluting with water, following the method of Kosower and Patton:¹¹ yield 85%, mp 286°, after recrystallization from methanol.

Other Materials. All other reagents were of analytical grade and were used without further purification. Pyridinecarboxylic acids were purchased from Koch-Light Laboratories, Ltd.

Preparation of Reaction Mixtures. A known volume of the Eu(II) solution was added to a known volume of the deaerated solution of the organic acid. The mixing was often done directly in the spectrophotometer cell. The cells were then closed tightly, further sealed with paraffin, and kept in the dark.

Analysis of the Reducing Species. Eu(II) and other reducing

species formed in the reaction were determined by oxidation with $\text{Fe}(\text{III})$, VO^{2+} , or KMnO_4 .

The analysis with $\text{Fe}(\text{III})$ was done by adding to the reaction mixture an excess of deaerated ferric solution in H_2SO_4 . The amount of $\text{Fe}(\text{II})$ formed was determined either by titration with a standard $\text{Ce}(\text{IV})$ solution or spectrophotometrically in the form of $\text{Fe}(\text{bpy})_3^{2+}$. The end point in the titration with $\text{Ce}(\text{IV})$ was determined amperometrically by use of a double platinum electrode or with 1,10-phenanthroline as indicator. The spectrophotometric method proved to be more sensitive and hence more appropriate for dilute solutions. The solution containing $\text{Fe}(\text{II})$ was neutralized to pH 4.5 by adding a saturated aqueous sodium acetate solution and then it was mixed with an excess of 2,2'-bipyridine. The red solution formed had an absorbance peak at 520 nm with $\epsilon = 8.24 \times 10^3$. Europium(III) or the pyridinecarboxylic acids do not interfere with the analysis.

The oxidation by KMnO_4 was simply followed by the decoloration of permanganate. Oxidation by VO^{2+} was followed spectrophotometrically at 760 nm ($\epsilon_{\text{VO}^{2+}} = 16.1$, $\epsilon_{\text{V}^{3+}} = 1.4$) and at 400 nm ($\epsilon_{\text{VO}^{2+}} = 0.0$, $\epsilon_{\text{V}^{3+}} = 8.12$).¹² Reduction of VO^{2+} to $\text{V}(\text{III})$ by europous ion is completed upon mixing.¹³ The slow reaction of $\text{V}(\text{III})$ with $\text{Eu}(\text{III})$ ^{14a} or perchloric acid^{14b} does not affect the results.

The analytical reagents used react with the reducing species present in our reaction mixtures fast compared to the rate of the reactions of $\text{Eu}(\text{II})$ with the pyridinecarboxylic acids.

Separation of Europium Ions from the Organic Components. Four methods were used to separate europium ions from the organic components in solution: (i) ion exchange (Dowex 50WX2, elution with HClO_4 , 2 M), (ii) precipitation of isonicotinic acid in the form of its copper salt, (iii) precipitation of europium ions with oxalic acid, and (iv) precipitation of europium ions with Na_2CO_3 , NaOH , or KOH .

Detection and Identification of the Organic Products. In our numerous attempts to detect and identify the organic compounds we used all the above mentioned separation techniques. The filtrates and/or precipitates were subjected to an exhaustive investigation in order to identify the organic products. The investigation included examination by ir and NMR in D_2O , by uv and visible spectrophotometry, by chromatography on silica gel and paper, and by polarography. The mixtures were also subjected to freeze-drying and extraction with ether or methanol in Soxhlet apparatus. Various qualitative tests were also tried for expected products. The reacting mixtures contained either HClO_4 or HCl .

Unreacted pyridinecarboxylic acids were determined polarographically by using a Metrohm AG Herisau rapid polarograph. The polarographic determinations were preceded by separation from europium.

Spectra. Electronic spectra were obtained by use of a Cary Model 14 spectrophotometer, NMR spectra by a Varian A-60A and ir spectra in KBr by a Perkin-Elmer Model 521 spectrometer.

Kinetics. The kinetics were followed spectrophotometrically in closed cells and by taking aliquots and determining the reducing species with $\text{Fe}(\text{III})$ or VO^{2+} . Under the conditions of the kinetics experiments the $\text{Fe}(\text{III})$ and VO^{2+} analyses gave identical results. Most of the kinetics experiments were carried out in perchloric acid solutions. All kinetics experiments were performed at 23°.

Results

Descriptive Chemistry. In acidic mixtures containing $\text{Eu}(\text{II})$ and isonicotinic acid (abbreviated INA) in the concentration range between 10^{-1} and 10^{-2} M the color becomes orange within the time of mixing. At lower concentrations it becomes intensely yellow. A few minutes after mixing the orange color turns intensely yellow too. The final color after the reaction is completed is very light yellow. Europium(III) solutions are colorless. The light yellow color is probably due to the organic products of the reaction. The intense colors indicate complex formation and the change from orange to intense yellow may be related to a change in the concentration of this complex, relative to unreacted europous ion.

The intense color is destroyed as soon as the $\text{Fe}(\text{II})$ analytical reagent is added. It is also gradually destroyed if the

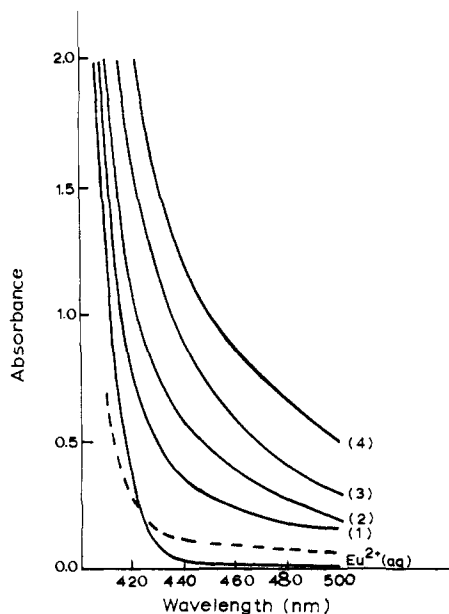


Figure 1. Spectra of Eu(II)-INA reaction mixtures taken 2 min after mixing. Perchloric acid concentrations were 3.8 M. Optical path length was 1 cm: (1) $\{\text{Eu}^{2+}\}_0 = 0.167 \text{ M}$, $\{\text{INA}\}_0 = 0.1 \text{ M}$; (2) $\{\text{Eu}^{2+}\}_0 = 0.167 \text{ M}$, $\{\text{INA}\}_0 = 0.2 \text{ M}$; (3) $\{\text{Eu}^{2+}\}_0 = 0.167 \text{ M}$, $\{\text{INA}\}_0 = 0.333 \text{ M}$; (4) $\{\text{Eu}^{2+}\}_0 = 0.333 \text{ M}$, $\{\text{INA}\}_0 = 0.2 \text{ M}$. The absorbance of the reaction mixtures can be compared to the absorbance of a 0.167 M $\text{Eu}^{2+}(\text{aq})$, 3.8 M HClO_4 solution. The absorption of isonicotinic acid in the wavelengths considered is roughly equal or smaller than that of $\text{Eu}^{2+}(\text{aq})$. Dotted line, same as (3), but 520 min after mixing.

solutions are exposed to air.

In very concentrated solutions (1–2 M in Eu(II) and isonicotinic acid) a brown-orange colloidal suspension is formed—it can be readily hydrolyzed with sodium carbonate.

Titration of the Eu^{2+} -INA reaction mixtures with KMnO_4 measures all the equivalents of the reductant added initially in the form of $\text{Eu}^{2+}(\text{aq})$.

The only organic product isolated at the end of the reaction between europous ion and isonicotinic acid was isonicotinaldehyde. In spite of our persistent efforts we were unable to isolate other europium-free organic products. We were in particular unable to isolate or directly characterize dimeric heterocyclic species or products of hydrogenation of the pyridine ring.

The presence of isonicotinaldehyde was confirmed by a variety of methods, including a test with 2,4-dinitrophenylhydrazine (after removing europium), the characteristic aldehyde odor, formation of its oxalate complex,¹⁵ and formation of the complex with sulfur dioxide¹⁶ after precipitating europium ions with soda and filtering.

After complete oxidation of Eu(II), isonicotinaldehyde was determined by titrating with KMnO_4 . Under the conditions of our experiments it is not oxidized by iodine or Fe(III). Neutralization and precipitation of europium ions before titration with KMnO_4 does not affect the results.

N-Methylisonicotinic acid forms with $\text{Eu}^{2+}(\text{aq})$ an intense orange-yellow solution, similar to that formed by isonicotinic acid. In excess *N*-methylisonicotinic acid the orange-yellow color disappears when Eu(II) is completely oxidized, but appears again if europium is removed with sodium carbonate and the remaining solution becomes neutral, having maximum absorbance around 440 nm. The colored solution obtained upon mixing *N*-methylisonicotinic acid with $\text{Eu}^{2+}(\text{aq})$ is strongly acidic, whereas the corresponding solution obtained after completion of the reaction and removal of europium is neutral. In fact, the latter solution,

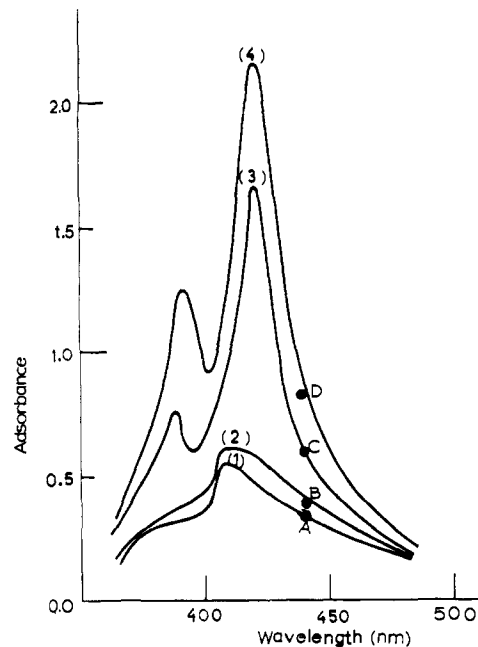


Figure 2. Comparison of difference spectra of mixtures containing initially 0.25 M europous ion, 0.25 M pyridinecarboxylic acid, and 1 M perchloric acid. Light path length is 1 cm. Reference europous and pyridine carboxylic acid solutions are of the same concentration but in two separate cells: (1) nicotinic acid; (2) picolinic acid; (3) isonicotinic acid; (4) *N*-methylisonicotinic acid. Points A, B, C, and D were calculated using the formation constants and absorptivities given in Table I.

when acidified, becomes reversibly colorless. This solution obviously contains the product of the *N*-methylisonicotinic acid and has reducing properties. It reacts with air, H_2O_2 , and KMnO_4 . It differs, however, from the product of the reaction of isonicotinic acid in that it does not give the reactions of the aldehyde group. Attempts to isolate the product from the solution failed, because it decomposed rapidly during the procedures. Its properties though in solution are similar to those of the dihydropyridines.

In acid solutions picolinic and nicotinic acids also form complexes with $\text{Eu}^{2+}(\text{aq})$ upon mixing. Under the conditions of our experiments, however, they do not seem to undergo further reaction.

Stoichiometry. The stoichiometry of the Eu^{2+} -INA reaction was determined by completely oxidizing known amounts of Eu(II) with excess isonicotinic acid. In a typical experiment the initial concentrations were $[\text{Eu}^{2+}]_0 = 0.2 \text{ M}$, $[\text{INA}]_0 = 0.6 \text{ M}$, and $[\text{HClO}_4]_0 = 2 \text{ M}$, and it was found that two europous ions gave one aldehyde molecule.

In order to determine the stoichiometry of the reducing species which react with Fe(III) we performed a second series of experiments using europous ion in excess. It was found that the decrease in the number of the reductant equivalents upon completion of the reaction corresponds to twice the number of moles of the initial isonicotinic acid.

Spectra. Typical spectra at different initial europous ion and isonicotinic acid concentrations are given in Figure 1. It is seen that the absorbance is larger at higher Eu(II) or isonicotinic acid concentrations.

In Figure 1 the large absorbance of $\text{Eu}^{2+}(\text{aq})$ and isonicotinic acid at short wavelengths obscures any structure that may exist in this wavelength region. An attempt was therefore made to magnify this structure by taking difference spectra, using $\text{Eu}^{2+}(\text{aq})$ and the corresponding solution of the organic acid in separate cells in the reference compartment of the double beam spectrophotometer. Typical results are included in Figure 2.

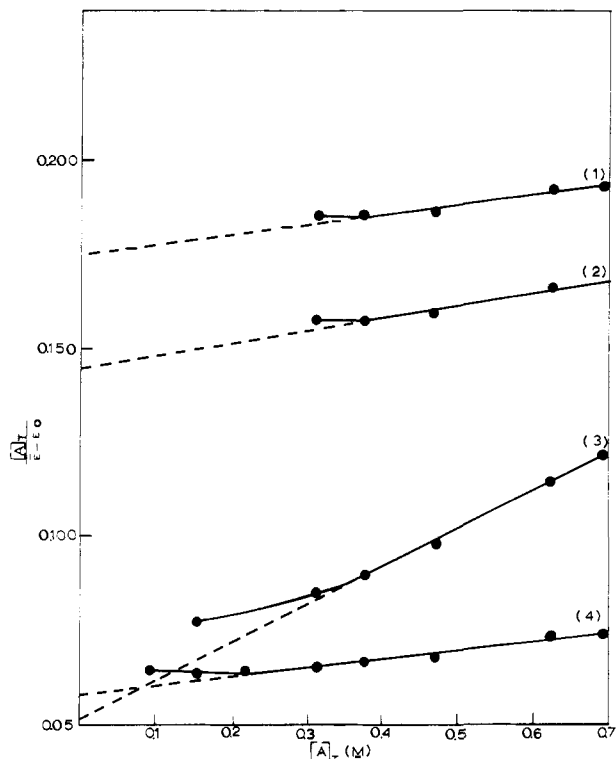


Figure 3. Plots of $[A]_T/(\bar{\epsilon} - \epsilon_0)$ vs. $[A]_T$ for the four pyridinecarboxylic acids: (1) nicotinic, $[Eu^{2+}]_0 = 0.0312 M$; (2) picolinic, $[Eu^{2+}]_0 = 0.0312 M$; (3) isonicotinic, $[Eu^{2+}]_0 = 0.312 M$; (4) *N*-methylisonicotinic, $[Eu^{2+}]_0 = 0.312 M$. Perchloric acid concentration in all cases is $2 M$. The measurements were made in 1-cm cells at 23° . Wavelength was $440 nm$.

Table I. Formation Constants and Absorptivities^a of Eu^{2+} -Pyridinecarboxylic Acids Complexes

	Nico- tinic	Pico- linic	Iso- nico- tinic	<i>N</i> -Methyl- iso- nico- tinic
ϵ_1 (l. mol ⁻¹ cm ⁻¹)	37	30	10	42
K (l. mol ⁻¹)	0.15	0.2	1.9	0.4

^a At $440 nm$.

In excess isonicotinic acid $Eu(II)$ is eventually oxidized completely to $Eu(III)$. In fact, a convenient criterion for completion of the reaction is the appearance of the characteristic weak spectrum of $Eu^{3+}(aq)$ in the visible spectrum. The strongest absorption of $Eu^{3+}(aq)$ is at $\sim 395 nm$ ($\epsilon = 3.06$). In the presence of $Eu(II)$ this absorption is effectively covered by the tail of the much stronger absorption of $Eu(II)$. Only after almost complete oxidation of $Eu(II)$ is the peak of $Eu^{3+}(aq)$ at $\sim 395 nm$ clearly observed.

The spectrum of the final $Eu(III)$ product is similar to that of $Eu^{3+}(aq)$.¹⁷ The presence of the remaining isonicotinic acid or of the products of the reaction has no effect. More generally we have no evidence for complex formation between $Eu(III)$ and any of the pyridinecarboxylic acids investigated or their reduction products.

In excess $Eu^{2+}(aq)$ the absorption at infinite time is larger than expected for $Eu^{2+}(aq)$ or $Eu^{3+}(aq)$, indicating complex formation between $Eu(II)$ and isonicotinaldehyde.

Formation Constants and Absorptivities of the Complexes. The formation constants and the absorptivities of the complexes formed upon mixing were estimated by determining the apparent absorptivity at different total pyridinecarboxylic acid concentrations. For relatively unstable

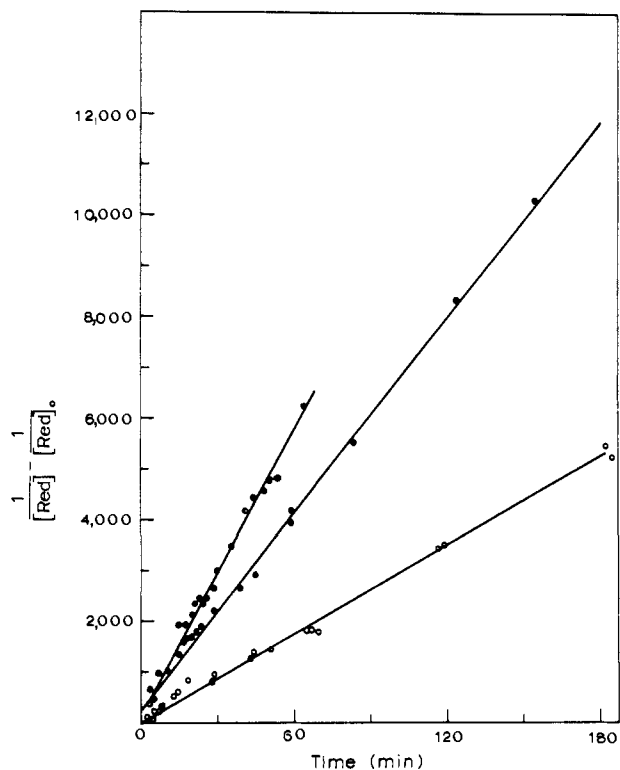


Figure 4. Typical pseudo-second-order plots for the reaction between $Eu^{2+}(aq)$ and an excess of isonicotinic acid. $[Red]$ is the concentration of the reducing species determined by our analytical methods. Concentrations are $[Eu^{2+}]_0 = 5 \times 10^{-4} M$, $[HClO_4]_0 = 1.955 M$; \odot , $[INA]_0 = 0.0144 M$, $[Eu^{3+}]_0 \approx 0$; \bullet , $[INA]_0 = 0.0111 M$, $[Eu^{3+}]_0 \approx 0$; \odot , $[INA]_0 = 0.0111 M$, $[Eu^{3+}] = 2.1 \times 10^{-3} M$. Ionic strength 2; temperature 23° .

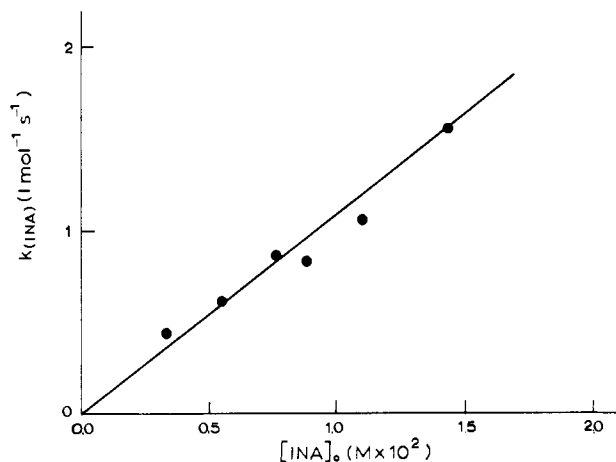


Figure 5. Pseudo-second-order rate constant with respect to $[Red]$ as a function of the initial isonicotinic acid concentration: $[Eu^{2+}]_0 = 5 \times 10^{-4} M$, $[HClO_4] = 1.955 M$, ionic strength 2, temperature 23° .

one to one complexes the apparent absorptivity $\bar{\epsilon}$ is given by the formula^{4b,18}

$$\bar{\epsilon} = (\epsilon_0 + \epsilon_1 K[A]_T) / (1 + K[A]_T)$$

where ϵ_0 and ϵ_1 are the absorptivities of $Eu^{2+}(aq)$ and the complex, respectively, K is the formation constant, and $[A]_T$ the total pyridinecarboxylic acid concentration, taken approximately equal to the free ligand concentration. On rearrangement the formula becomes

$$\frac{[A]_T}{(\bar{\epsilon} - \epsilon_0)} = \frac{[A]_T}{(\epsilon_1 - \epsilon_0)} + \frac{1}{K(\epsilon_1 - \epsilon_0)}$$

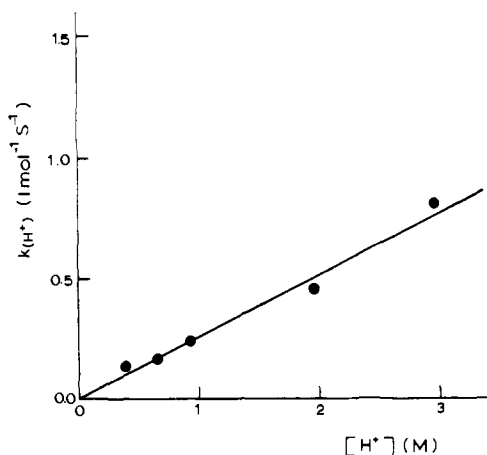


Figure 6. Hydrogen ion dependence of the pseudo-second-order rate constant with respect to [Red]. The solutions contained initially $[Eu^{2+}]_0 = 5 \times 10^{-4} M$, $[INA]_0 = 3.33 \times 10^{-3} M$; ionic strength 2, temperature 23° .

Figure 3 includes plots of $[A]_T/(\bar{\epsilon} - \epsilon_0)$ vs. $[A]_T$ for the four pyridinecarboxylic acids investigated, obtained in $1 M HClO_4$ media. Each point on the plot represents an average of several experiments. At low total pyridinecarboxylic acid concentrations the basic assumption of the method, namely that the concentration of the ligand is approximately equal to the total ligand concentration, is not valid any more, and the plots deviate from linearity. In the case of isonicotinic and *N*-methylisonicotinic acids, the determination of $\bar{\epsilon}$ requires an extrapolation of the spectrophotometric data to zero time, since we investigate the equilibrium which precedes the redox reaction. At concentrations of $[A]_T$ higher than those depicted in Figure 3 the redox step becomes too fast and the extrapolation inaccurate.

The results obtained from the slopes and intercepts of Figure 3 are given in Table I. At $2 M HClO_4$ we obtain approximately the same values.

Kinetics. Figure 4 contains pseudo-second-order plots of representative results obtained with excess isonicotinic acid. The concentrations plotted in this figure are those of the reductant (abbreviated Red) determined by $Fe(III)$ or VO^{2+} . The initial concentrations were much lower than those used to determine the equilibrium constants. It should be noted that after a relatively short initial period, the pseudo-second-order fit is satisfactory. The fast initial period seems to be real; under the conditions of our experiments it can be eliminated only by adding $Eu^{3+}(aq)$ from the beginning.

The observed rate constants obtained from the slopes of pseudo-second-order lines such as those of Figure 4, after the fast initial period, are plotted in Figure 5 as a function of the initial isonicotinic acid concentration. It follows from this figure that the pseudo-second-order rate constant in excess isonicotinic acid depends on $[INA]$ linearly.

Figure 6 depicts the dependence on hydrogen ion concentration of the pseudo-second-order rate constants obtained with excess isonicotinic acid. The results of this figure indicate that the rate law contains $[H^+]$ in the first power. A small contribution from a term second order in $[H^+]$ cannot be excluded, but the data are not accurate enough (Table II) to determine this term.

Figure 7 shows the dependence of the pseudo-second-order rate constant on $[Eu^{3+}]^{-1}$, which is linear for both the isonicotinic acid and its *N*-methyl derivative; the straight lines for the two compounds coincide. Deviations from linearity are observed only at low $Eu^{3+}(aq)$ concentrations.

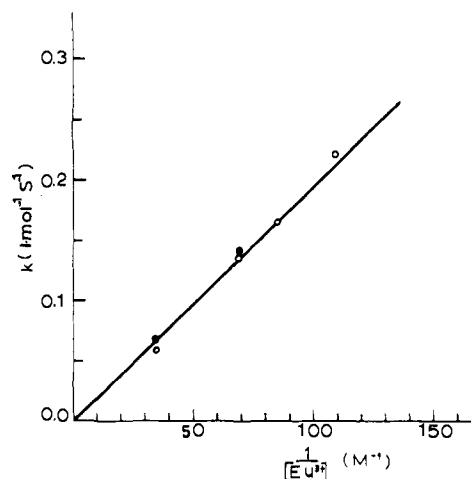
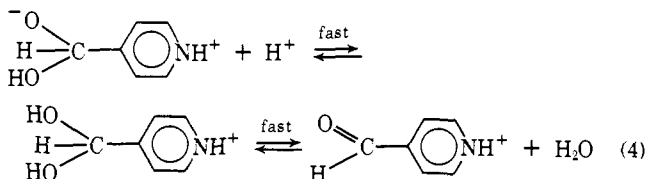
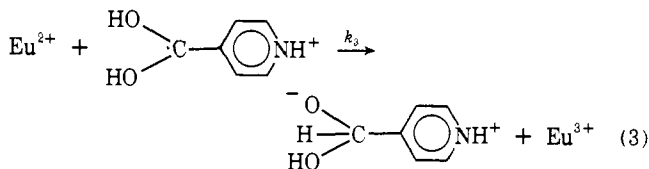
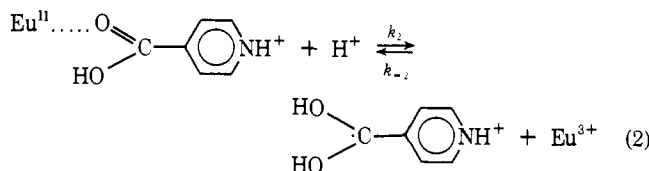
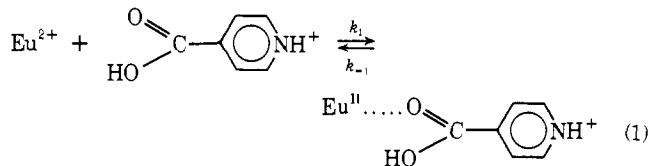


Figure 7. Effect of the $Eu^{3+}(aq)$ concentration on the pseudo-second-order rate constant with respect to [Red], of the reaction between europous ion and isonicotinic acid (open circles) and *N*-methylisonicotinic acid (full circles). The solutions contained initially $[Eu^{2+}]_0 = 1.4 \times 10^{-3} M$, $[INA]_0$ or $[N-MeINA]_0 = 0.0714 M$, and $[HClO_4] = 0.9 M$; temperature 23° .

Typical values of the pseudo-second-order rate constants for the reaction of $Eu^{2+}(aq)$ with isonicotinic acid and their least-squares errors are included in Table II. The last two entries in the table are for *N*-methylisonicotinic acid.

Discussion

All the observations reported in this paper for isonicotinic acid can be accounted for by a free radical mechanism.



Attempts to obtain more direct evidence for the formation of the organic free radical by studying acrylonitrile polymerization gave inconclusive results, because europous ion itself causes polymerization.

Hydration of isonicotinaldehyde is catalyzed by acid.¹⁹ Under the strongly acidic conditions of our experiments, equilibria (4) are therefore expected to be established quickly. Under the same conditions isonicotinic acid is expected to be fully protonated.²⁰ This would make attack on

Table II. Typical Pseudo-Second-Order Rate Constants of the Reaction between $\text{Eu}^{2+}(\text{aq})$ and Isonicotinic Acid^a

$[\text{Eu}^{2+}]_0$ ($M \times 10^3$)	$[\text{Eu}^{3+}]_0$ ($M \times 10^3$)	$[\text{INA}]_0$ ($M \times 10^3$)	$[\text{HClO}_4]$ (M)	k ($\text{mol l}^{-1} \text{sec}^{-1}$)
0.5	—	3.33	2.94	0.835 ± 0.050
0.5	—	3.33	1.96	0.456 ± 0.011
0.5	—	3.33	0.91	0.243 ± 0.055
0.5	—	3.33	0.65	0.165 ± 0.013
0.5	—	3.33	0.39	0.124 ± 0.004
0.5	—	5.56	1.96	0.619 ± 0.007
0.5	—	7.78	1.96	0.840 ± 0.019
0.5	—	8.89	1.96	0.779 ± 0.024
0.5	—	11.1	1.96	1.113 ± 0.022
0.5	—	14.4	1.96	1.491 ± 0.032
0.5	2.1	11.1	1.96	0.438 ± 0.017
1.4	9.1	71.4	0.9	0.225 ± 0.037
1.4	11.4	71.4	0.9	0.159 ± 0.008
1.4	14.3	71.4	0.9	0.133 ± 0.006
1.4	28.6	71.4	0.9	0.055 ± 0.006
1.4	14.3	71.4 ^a	0.9	0.139 ± 0.015
1.4	28.6	71.4 ^a	0.9	0.070 ± 0.008

^aThe last two entries are for *N*-methylisonicotinic acid.

nitrogen rather difficult, although not impossible. One reason for confining our investigation to strongly acidic solutions was in fact our desire to avoid this complication. Another reason was that we wanted to avoid competition between Eu^{2+} and H^+ for the same ligand site and to study complex formation in aqueous media, under the most unfavorable, for the metal ion, conditions.

At long enough times it can be assumed that both equilibria 1 and 2 have been established. In fact equilibrium 1 seems to be established upon mixing. Reaction 2 is proposed in order to explain the inhibition by $\text{Eu}^{3+}(\text{aq})$.

The odd electron of the free radical is conveniently symbolized by a dot on one of the carbon atoms. It is expected, however, to be highly delocalized. Further development of the reaction and even the nature of the final product must be related to this delocalization. The coincidence of the k vs. $[\text{Eu}^{3+}]^{-1}$ lines (Figure 7) for the reactions of $\text{Eu}^{2+}(\text{aq})$ with isonicotinic acid and its *N*-methyl derivative is indicative of a similarity in the intermediate steps. Yet, the final product in the $\text{Eu}^{2+}(\text{aq})$ -*N*-methylisonicotinic acid reaction does not have the properties of an aldehyde.

The rate law derived from the above mechanism by applying the steady state approximation for the intermediate free radical takes the form:

$$-\frac{d[\text{Eu}^{2+}]}{dt} = \frac{k_2 k_3 K_1 [\text{Eu}^{2+}]^2 [\text{INA}] [\text{H}^+]}{k_{-2} [\text{Eu}^{3+}] + k_3 [\text{Eu}^{2+}]} \quad (\text{I})$$

where

$$K_1 = k_1/k_{-1}$$

Under the conditions of our experiments the fraction of Eu^{2+} transformed to complex or radical was generally small. The analytically determined reductant [Red] is, therefore, approximately equal to $[\text{Eu}^{2+}]$. Ferric iron does not react with the final products. Equation I then becomes

$$-\frac{d[\text{Red}]}{dt} = \frac{k_2 k_3 K_1 [\text{Red}]^2 [\text{INA}] [\text{H}^+]}{k_{-2} [\text{Eu}^{3+}] + k_3 [\text{Red}]} \quad (\text{II})$$

If $\text{Eu}^{3+}(\text{aq})$ has not been added from the beginning, at short times the reverse of reaction 2 is negligible. This explains the intercepts obtained in the pseudo-second-order plots (Figure 4). At longer times $k_{-2}[\text{Eu}^{3+}]$ becomes larger than $k_3[\text{Red}]$ and the rate law takes the simpler form.

$$-\frac{d[\text{Red}]}{dt} = \frac{k_2 k_3 K_1 [\text{Red}]^2 [\text{INA}] [\text{H}^+]}{k_{-2} [\text{Eu}^{3+}]} \quad (\text{III})$$

The same approximate form (III) also applies when $\text{Eu}^{3+}(\text{aq})$ is added from the beginning.

From the slope of the k vs. $[\text{Eu}^{3+}]^{-1}$ line and the value of the formation constant we calculate $k_2 k_3/k_{-2} \approx 0.03 M^{-1} \text{sec}^{-1}$. The use of the data of Figures 5 and 6 for calculating this ratio is less reliable, because the concentration of $\text{Eu}^{3+}(\text{aq})$ changes as the reaction proceeds. In addition, there is always some $\text{Eu}^{3+}(\text{aq})$ present from the beginning even if not added intentionally, because oxidation of $\text{Eu}^{2+}(\text{aq})$ cannot be completely avoided. Nevertheless, rough estimates can be made from the data of Figures 5 and 6 as well and the values obtained for $k_2 k_3/k_{-2}$ lie around $0.03 M^{-1} \text{sec}^{-1}$, which is a fairly good cross check of the value obtained from the data of Figure 7.

From the minimum amounts of $\text{Eu}^{3+}(\text{aq})$ necessary to eliminate the intercept in the second-order plots (Figure 4) we can also conclude that k_3 must be smaller than k_{-2} . This information combined with the value of ~ 0.03 for $k_2 k_3/k_{-2}$ leads then to the conjecture that the value for the equilibrium constant of reaction 2 is not far from one. Direct determination of the formation constants (Table I) confirms this conjecture.

Mechanistic information can also be drawn from descriptive chemistry. Thus, it is not perhaps a coincidence that the complex formed in acid solution between *N*-methylisonicotinic acid and $\text{Eu}^{2+}(\text{aq})$ has the same color as the product obtained in neutral solution after removing europium ions with sodium carbonate. The similarity in the color may very well mean that corresponding ligand-centered orbitals of the nonprotonated form of the partially reduced carboxylic acid are involved in both cases (e.g., the corresponding n and π^* orbitals). According to this speculation the europium-free, partially reduced product is a weak acid and dissociates reversibly in neutral solution giving the colored dissociated form. The same effect is achieved by the transfer of an electron from europous to *N*-methylisonicotinic acid. In contrast then to the d orbitals of the elements of the main transition series, it is postulated that the inner ($4f$) orbitals of europous are essentially unaffected by the ligand. It is rather the orbitals of the reducible ligands that are affected by europous ion. The differences in the observed absorptivities (Table I) can be better understood too, if they are correlated to differences between the four ligands rather than to different effects of these ligands on the same central ion.

Interaction with the ligands of each of the well-shielded $4f$ electrons of europous is generally weak. For this reason and because of the shape of the f orbitals, no differentiation is expected into levels of σ and π symmetry. Thus, even though the overlap of each of the $4f$ orbitals with the ligand orbitals is not large, the mere number of the seven more or less equivalent $4f$ electrons of $\text{Eu}(\text{II})$ increases the probability that any one of them will be transferred.

Continuing the same line of reasoning we postulate that the formation of the complexes between europous and the pyridinecarboxylic acids studied involves a synergic mechanism of charge transfer from the metal to the ligand and bonding of essentially ionic character. It is interesting in this respect that picolinic acid has a smaller formation constant compared to isonicotinic or *N*-methylisonicotinic, in spite of the fact that it can be benefited by chelation. It must also be noted that the formation constant of vanadous ion with picolinic^{4b} acid under comparable conditions is almost one order of magnitude larger than that of europous.

According to the mechanism proposed the complex formed between $\text{Eu}^{2+}(\text{aq})$ and isonicotinic acid can break down into a free radical or be reduced further by another $\text{Eu}^{2+}(\text{aq})$ and can be formed with equal facility from the free radical and $\text{Eu}^{3+}(\text{aq})$ or from isonicotinic acid and $\text{Eu}^{2+}(\text{aq})$. In fact, the values of the equilibrium constants

indicate that at room temperature the standard free energy differences for the three states of the system, namely $\text{Eu}^{\text{II}} + \text{INA}$, $\text{Eu}^{\text{II}}\text{-INA}$ complex, and $\text{Eu}^{\text{III}} + \text{free radical}$, are small. This probably gives to the system its unusual stability for aqueous lanthanide species. The same remarks can be made for picolinic and nicotinic acids, except that in these cases reaction of the corresponding complexes with another europous ion does not take place. This implies that for these two acids not only the equilibrium constants K_1 but also the product of the rate constants k_2k_3 is considerably smaller. For explaining this, as well as the observation that the *N*-methyl derivative of isonicotinic acid gives a product of different nature than isonicotinic acid itself, it is not necessary to invoke new assumptions. It can be argued that the extent of charge transfer to the ligand is the factor that mainly determines not only the stability of the complexes but also the rate of their subsequent reduction and its path.

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Crystal and Molecular Structure of the Free Base Porphyrin, Mesoporphyrin IX Dimethyl Ester

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Abstract: The structure of the free base porphyrin, mesoporphyrin IX dimethyl ester, has been determined from three-dimensional X-ray diffraction data. The porphyrin crystallizes with two molecules per unit cell in the triclinic space group $C_2^1-P\bar{1}$ with $a = 23.458$ (8) Å, $b = 11.378$ (4) Å, $c = 5.971$ (2) Å, $\alpha = 93.25$ (2)°, $\beta = 94.23$ (2)°, and $\gamma = 93.82$ (2)°. The structure has been refined anisotropically to a final unweighted R index (on F^2) of 0.072 based on 5107 measured intensities. The R index (on F) for the 3336 reflections having $F_o^2 > 3\sigma(F_o^2)$ is 0.049. Bond lengths and bond angles within the porphyrin core have been determined to estimated standard deviations of ± 0.003 Å and ± 0.2 °, respectively. These bond lengths and angles closely resemble those in the porphyrin core of octaethylporphyrin. We conclude that the asymmetric pattern of substitution of mesoporphyrin IX dimethyl ester affects the bond lengths and bond angles within the porphyrin core to less than can be detected by this structure determination.

Complete X-ray crystallographic structure determinations of biologically important porphyrins,¹⁻³ corrins,⁴⁻⁵ and pheophorbides⁶⁻⁸ are relatively few in number. The asymmetric pattern of substitution of the naturally occurring compounds and the diverse nature of the substituents appear to make it difficult to obtain suitably crystalline samples. Nonetheless it is the asymmetry and substituent effects in these molecules which are of particular interest.

The structures of a number of symmetrically substituted free-base porphyrins have been reported⁹⁻¹³ and some gen-

eralizations inferred about the structure of the porphyrin core.¹¹⁻¹³ Prior to this investigation no structure of a free-base biologically relevant porphyrin had been reported, although the structures of three metalloporphyrins had been determined.¹⁻³ The latter three structures were plagued with crystallographic problems which lowered the accuracy of the determinations. Two of the crystal structures contained a disordered porphyrin, while the third contained a disordered solvent molecule. In contrast to these structures the free-base form of mesoporphyrin IX dimethyl ester