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Acid Hydrolysis of Ethyl Glycinate Complex of Pentaammineruthenium(III)

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Abstract: While ester hydrolysis for ethyl glycinate N-bonded to $Co(NH_3)_5{}^{3+}$ has a half-life in 1 M CF_3SO_3H at 25 °C in excess of 1 month, reaction for the corresponding Ru(III) complex under the same conditions is complete in 1 h. The reaction products in the latter case are ($[(NH_3)_5RuH_2O]^{3+}$ + $[C_2H_5O_2CCH_2NH_3]^+$), 30%, and ($[(NH_3)_5RuO_2CCH_2NH_3]^{3+}$ + C_2H_5OH), 70%. It needs to be emphasized that the facile ester hydrolysis takes place with the pentaammine unit remaining intact and does not involve replacement of NH_3. The rate of consumption of the reactant increases with acid but reaches a limiting value at high acid concentration. In the saturation region, the half-life for the consumption of the reactant is 12 min. When the noncomplexing acid is replaced by HCl, $[(NH_3)_5RuCl]^{2+}$ is formed in place of the aquo ion, but this change in stoichiometry does not affect the rate. The observations are fully accounted for by a rather facile ($k_1 = 1.14 \times 10^{-3}$ s^{-1}) rearrangement of $[(NH_3)_5RuNH_2CH_2CO_2C_2H_5]^{3+}$ to the linkage isomer $[(NH_3)_5RuOC(OC_2H_5)CH_2NH_2]^{3+}$. This intermediate is stabilized against reversion to the N-bound form by protonation and at 25 °C undergoes competition between ester hydrolysis (70%) or aquation/anation (30%). A trace of Ru(II) leads quantitatively to the anation product; at high acid this does not affect the half-life for consumption of the N-bound ester.

Catalysis by metal ions of the hydrolysis of amino acid esters has been the subject of intense study for more than a decade.[1] The most definitive conclusions about details of the mechanism have come from studies which have taken advantage of the substitution inertia of cobalt(III) ammines,[2-5] and little has been done to extend the work to other substitution-inert metal centers. A likely reason for the lack of interest in making the indicated extension is the conviction that nothing fundamentally new would be learned from such work. Thus, in comparing reactions on $Ru(NH_3)_5{}^{3+}$ with those in $Co(NH_3)_5{}^{3+}$, a quantitative difference is expected, arising from the greater polarizing power of the former as compared to the latter (pK_a for the aquo complexes are 4.2[6] and 6.1,[7] respectively), but at first sight there is no reason to expect any other great difference. However, a fundamental difference in reactivity between the two centers was demonstrated by the observation that isomerization of $[(NH_3)_5RuNH_2CH_2CO_2H]^{3+}$ to $[(NH_3)_5RuO_2CCH_2NH_3]^{3+}$ is facile in acidic medium;[8] a similar reaction for the corresponding Co(III) complex has not been reported in any of the numerous studies involving the N-bound glycine complex of $Co(NH_3)_5{}^{3+}$.[3]

In the course of the work in which the facile linkage isomerization on Ru(III) was discovered, an experiment was also done with $[(NH_3)_5RuNH_2CH_2CO_2C_2H_5]^{3+}$ in acidic solution.[9] It was observed that $[(NH_3)_5RuO_2CCH_2NH_3]^{3+}$ is readily formed in the system, but the result, suggestive though it was of an interesting effect, was not pursued. This investigation has now been done, confirming the supposition that there is a quite remarkable difference between Ru(III) and Co(III) with respect to a reaction of this kind.

Experimental Section

Chemicals and Reagents. Chloropentaammineruthenium(III) chloride was prepared according to the method of Vogt et al.[10] and was purified by recrystallization from 0.1 M HCl. Glycine ethyl ester hydrochloride (Aldrich Chemical Co.) was used without further purification. Neat glycine ethyl ester was prepared[9] by adding 10 g of thoroughly ground ester hydrochloride salt to 100 mL of dry ether. Ammonia gas was passed through this suspension for 15 min and then argon for an additional 15 min. Anhydrous sodium carbonate was added to remove traces of water and was subsequently removed. The solvent was removed by rotary evaporation and the resulting neat ester was used immediately to avoid the dimerization reaction.[11] All other chemicals were reagent grade and were used as received.

Analytical Methods. Visible and ultraviolet spectra were measured on a Beckman Acta MVII recording spectrophotometer. The infrared spectra were recorded on a Perkin-Elmer Model 621 grating infrared spectrophotometer in KBr pellets. The Varian T-60 was used to obtain proton NMR spectra for the cobalt complex. The complex was dissolved in 1 mL of deuterated oxide containing 1 M DCl. The microanalyses were performed by the Stanford Microanalytical Laboratory.

Preparation of Complexes. (Ethyl glycinato)pentaammineruthenium(II) hexafluorophosphate was prepared by a method similar to that described by Diamond.[9] A 75-mg sample of silver oxide was suspended in 2 mL of hot water, and concentrated trifluoroacetic acid was added dropwise until all the solids were dissolved and, then, 100 mg of $[Ru(NH_3)_5Cl]Cl_2$, with stirring to facilitate dissolution. The silver chloride which formed was filtered off, and the residue was washed with 3 mL of water. The solution, which included the washings, was reduced over zinc amalgam under an argon atmosphere for 20 min. At this point 0.30 g of glycine ethyl ester hydrochloride was added, and the pH of the solution was raised to 8 with 4 M NaOH. The reaction was allowed to proceed for 1 h, and then the pH was adjusted to ~1 with concentrated trifluoroacetic acid. A 0.60-g sample of ammonium hexafluorophosphate was added, and the solid formed was filtered and washed with ethanol and ether. The product was recrystallized from hot water (~50 °C) by using inert atmosphere techniques.[12] Anal. Calcd for $[(NH_3)_5RuNH_2CH_2CO_2C_2H_5](PF_6)_2$: C, 8.29; N, 14.50; H, 4.18. Found: C, 8.33; N, 14.50; H, 4.26.

(Ethyl glycinato)pentaamminecobalt(III) bromide was prepared according to the method of Buckingham et al.[3] with some modifications. $[Co(NH_3)_5N_3]Cl_2$[13] was converted to the perchlorate salt with silver perchlorate[14] by mixing concentrated solutions of the two in a 1:2 (Co:Ag) molar ratio. A stream of dry argon was passed through 30 mL of freshly distilled tributyl phosphate dried by 2 g of 4-Å molecular sieve for 20 min. A 1.5-g sample of $NOBF_4$ (Research Organic/Inorganic Chemical Corp.) was added, and the solution was kept bubbling with argon for another 15 min. A 2.5-g sample of $[Co(NH_3)_5N_3](ClO_4)_2$ was then added over a period of 20 min, and the reaction was allowed to proceed for 8 h under argon atmosphere until the solution turned reddish violet, indicating the formation of $[Co(NH_3)_5(n\text{-BuO})_3PO]^{3+}$. A 3-g

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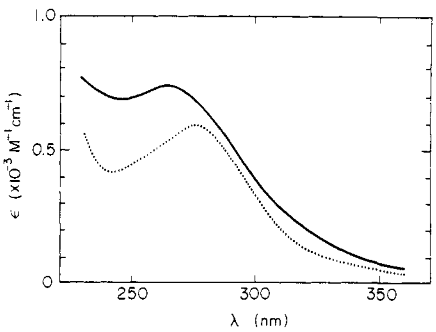

Figure 1. Absorption spectra for $[(NH_3)_5RuNH_2CH_2COOC_2H_5]^{2+}$ (—) and $[(NH_3)_5RuNH_2CH_2COOC_2H_5]^{3+}$ (···). Media: 0.1 NCF_3COOH for Ru(II) species and 0.1 N $HClO_4$ for Ru(III) species.

sample of neat ester was introduced, and the solution was heated at 65 °C for 20 min under a stream of dry argon until it turned dark orange. The solution was filtered while hot and the end product precipitated upon adding 400 mL of ethanol–ether mixture. The product was recrystallized twice by dissolving it in the minimum amount of hot 0.1 M HBr (~20 mL) and precipitated by sodium bromide. Anal. Calcd for $[Co(NH_3)_5(NH_2CH_2CO_2C_2H_5)]Br_3{\cdot}H_2O$: C, 9.5; N, 16.7; H, 5.2. Found: C, 8.9; N, 16.5; H, 4.9.

Kinetic Measurements. The reaction course was followed by using a Beckman Acta MVII recording spectrophotometer. The temperature was controlled by a Haake FK2 temperature bath. For each experiment a solution of $[Ru(NH_3)_5NH_2CH_2CO_2C_2H_5]^{2+}$ complex was oxidized with an equivalent amount of persulfate, and the absorbance at 285 nm was monitored until no further change was observed. The pseudo-first-order rate constants, k_{obsd}, for the experiments were obtained from the slope of the linear least-squares fit of log $(A_\infty - A_t)$ vs. time plots. The acid concentration of the solution was controlled with perchloric acid by using lithium perchlorate to maintain a constant ionic strength of 1.0. The choice of $HClO_4$–$LiClO_4$ as medium in this system is made to avoid interference by any trace amount of Ru(II) species which might exist in the solution.[15] As will be documented later, Ru(II) has a profound effect on the stoichiometry of the reaction.

Results

Stoichiometry. The electronic absorption spectrum of (ethyl glycinato)pentaammineruthenium(II) has a band maximum, λ_{max}, at 266 nm with an extinction coefficient of 7.2×10^2 M^{-1} cm^{-1} (cf. Figure 1). The infrared spectrum shows the ester carbonyl stretching band at 1740 cm^{-1}. Immediately on oxidizing the Ru(II) species in acid, the product shows an absorption band at 275 nm (530 M^{-1} cm^{-1}) which is similar to that of hexaammineruthenium(III) and which can be assigned to $[Ru(NH_3)_5NH_2CH_2CO_2C_2H_5]^{3+}$ (cf. Figure 1). As time elapses, the absorption shifts to longer wavelengths and intensifies, as will be described in detail in the following.

In Figure 2 are shown the absorption spectra of the Ru(III) species which account for the composition of our product solutions, namely, $[Ru(NH_3)_5OH_2]^{3+}$, $[Ru(NH_3)_5Cl]^{2+}$, and $[Ru(NH_3)_5O_2CCH_2NH_3]^{3+}$. For the glycinato complex, measured in 0.1 M $HClO_4$–0.9 M $LiClO_4$, we find λ_{max} = 288 nm and $\epsilon = 1.46 \times 10^3$ M^{-1} cm^{-1}; Diamond[9] reports for 0.1 M HCl, λ_{max} = 288 nm and $\epsilon = 1.45 \times 10^3$ M^{-1} cm^{-1}. For $[Ru(NH_3)_5Cl]^{2+}$ in 0.1 M HCl–0.9 M LiCl we find λ_{max} (ϵ) to be 327 nm (1.90×10^3 M^{-1} cm^{-1}). Armor[12] reports for 0.1 M HCl or 1 M NaCl as the medium λ_{max} (ϵ) to be 327 nm (1.90×10^3 M^{-1} cm^{-1}). The aquo ion is expected to be the most sensitive to medium effects. Accordingly the absorption spectrum was determined both in a chloride medium (0.1 M HCl–0.9 M LiCl) and in a perchlorate medium (0.1 M $HClO_4$–0.9 M $LiClO_4$) with the respective λ (ϵ) results 268 nm (7.24×10^2 M^{-1} cm^{-1}) and 268 nm (7.34×10^2 M^{-1} cm^{-1}). These can be compared to Krentzien's[16] result measured in 0.01 M HTFMS: 268 nm (7.48×10^2 M^{-1} cm^{-1}).

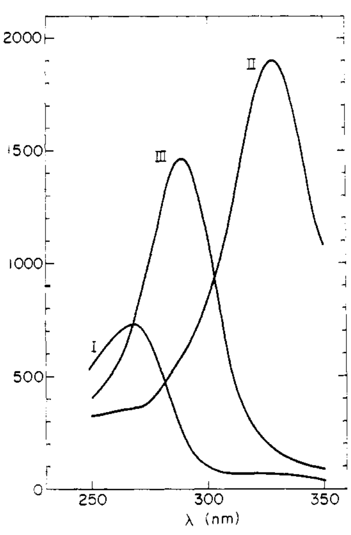

Figure 2. Absorption spectra for $Ru(NH_3)_5OH_2^{3+}$, $Ru(NH_3)_5Cl^{2+}$, and $Ru(NH_3)_5O_2CCH_2NH_3^{3+}$: (I) $Ru(NH_3)_5OH_2^{3+}$ (in 0.1 M HCl–0.9 M LiCl medium); (II) $Ru(NH_3)_5Cl^{2+}$ (in 0.1 M HCl–0.9 M LiCl medium); (III) $Ru(NH_3)_5O_2CCH_2NH_3^{3+}$ (in 0.1 M $HClO_4$–0.9 M $LiClO_4$ medium).

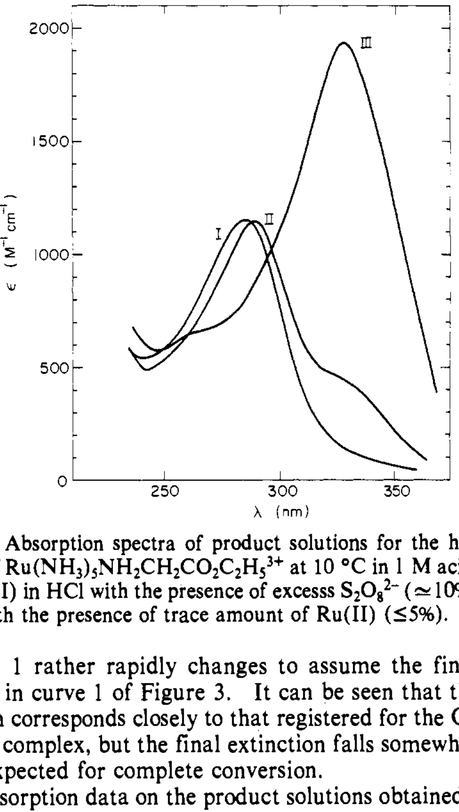

Figure 3. Absorption spectra of product solutions for the hydrolysis reaction of $Ru(NH_3)_5NH_2CH_2CO_2C_2H_5^{3+}$ at 10 °C in 1 M acid: (I) in $HClO_4$; (II) in HCl with the presence of excesss $S_2O_8^{2-}$ ($\simeq$10%); (III) in HCl with the presence of trace amount of Ru(II) ($\leq$5%).

When a solution of the N-bound glycine complex of Ru(III) is acidified with $HClO_4$, the absorption which begins as indicated in Figure 1 rather rapidly changes to assume the final form indicated in curve 1 of Figure 3. It can be seen that the band maximum corresponds closely to that registered for the O-bound glycinato complex, but the final extinction falls somewhat short of that expected for complete conversion.

The absorption data on the product solutions obtained in 1 M $HClO_4$ are fully accounted for by assuming that the aquo ion and the O-bound glycinate complexes are the sole products. With use of a variety of wavelengths in the range 280–300 nm, the glycinate content for the experiment at 25 °C was calculated as 71 ± 3% and at 10 °C as 72 ± 3%. The spectrum of the product solution was found to be insensitive to acid concentration over the range 0.1–1 M, and we conclude from this that the distribution of Ru(III) between the two products is not much affected by acidity. The Ru(III) glycinate contents of product solution with reaction media ($HClO_4$–$LiClO_4$) of 0.5 M:0.5 M, 0.2 M:0.8 M, and 0.1 M:0.9 M were 70, 67, and 72%, respectively.

That the glycinate complex is a major ingredient of product solutions of the kind we are describing was demonstrated by Diamond,[9] in obtaining a solid from an experiment in 0.10 M acid. This gave analyses identical with that of the species resulting from the isomerization of the N-bound glycine complexes and, when

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[15] It has been shown that ClO_4^- oxidizes $Ru(NH_3)_6^{2+}$ quite rapidly. J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **84**, 4984 (1962).

[16] H. Krentzien, Ph.D. Thesis, Stanford University, 1976.

dissolved, showed the same absorption spectrum, demonstrating that in fact ester hydrolysis had occurred. This work, however, did not serve to show that $[Ru(NH_3)_5H_2O]^{3+}$ is also an important component of the product mixture nor to establish just how much of the glycinate complex is formed.

The results of the spectrophotometric analysis were confirmed by determining the free amino acid ester content of the product solution for an experiment at 25 °C in 1 M $HClO_4$. The free amino acid ester was isolated by passing the product solution through a cation-exchange column (BioRad AG 50W-X2, 200–400 mesh) and eluted with 100 mL of 0.3 M $HClO_4$. The eluate was brought to pH ~12 with NaOH and was allowed to stand for 2 h for the hydrolysis of the ester to go to completion. The resulting solution was concentrated to ~10 mL by rotary evaporation, and the pH was adjusted to ~3 with $HClO_4$. The glycinic acid in the solution was then analyzed by the ninhydrin method according to published procedures.[17] The concentration of the free amino acid ester was found to be 29.6% that of $[Ru(III)]_0$ which is very close to the value obtained by spectrophotometric analysis for the aquo ion content of the product solution.

The results quoted thus far seem to constitute proof that the major Ru(III) products in a perchoric acid medium are $[(NH_3)_5RuO_2CCH_2NH_3]^{3+}$ and $[(NH_3)_5RuOH_2]^{3+}$. Nevertheless, we felt it necessary to investigate the possibility that some of the tetraammine $[(NH_3)_4RuNH_2CH_2CO_2]^{2+}$ is produced. Formation of this chelate requires NH_4^+ to be a coproduct, and analysis for the latter species was done by using the Nessler test. Reaction took place in a medium 8×10^{-4} M in $[(NH_3)_5RuNH_2CH_2CO_2C_2H_5]^{3+}$ and 1 M in $HClO_4$. Ammonium ion was separated from Ru(III) products by using a cation-exchange resin. The eluate (100 mL) containing NH_4^+ was concentrated and then diluted to a volume of 10.0 mL. No color indicative of NH_4^+ was produced on adding Nessler's reagent. A blank showed that NH_4^+ at the level of 1.0×10^{-5} M would have been detectable. We conclude that tetraammine corresponds to less than 2% of the total Ru(III) product.

When the reaction medium contains chloride ion, absorption also appears in the product solution characteristic of $[Ru(NH_3)_5Cl]^{2+}$ (cf. curve II on Figure 3). Analysis of the spectrophotometric data for an experiment in 1 M HCl at 25 °C, again using a number of wavelengths in the region covered, led to the conclusion that the solution contained 67%, 25%, and 8% of $[Ru(NH_3)_5O_2CCH_2NH_3]^{3+}$, $[Ru(NH_3)_5Cl]^{2+}$, and $[Ru(NH_3)_5H_2O]^{3+}$, respectively, with an uncertainty of ±3% on each of those results. Confirmation of these results at least in part was obtained by chromatographic separation of the chloro from the 3+ species. The product solution after dilution was passed through a Sephadex C25 column, and the chloro complex was eluted with 0.15 M $HClO_4$. The amount of the chloro complex by this method was found to be 20% of the total, in reasonable agreement with the spectrophotometric result. If the absorption data are corrected by subtracting that appropriate to 20% content of the chloro complex, the $[Ru(NH_3)_5O_2CCH_2NH_3]^{3+}$ is found to be 68% of the total and the aquo, 12%. At 10 °C in the same medium (cf. data of Figure 3), the spectrophotometric data yield for the content of the O-glycinate, chloro, and aquo complexes 68%, 17%, and 15%, respectively. At 25 °C in 0.10 M HCl–0.9 M $LiClO_4$, the figures are 70%, 7%, and 23%.

The stoichiometry is dramatically altered by Ru(II) even when this is present at low concentrations. The effect was encountered in an experiment at 10 °C in 1 M HCl in which the Ru(II) had not been fully oxidized, <5% of the complex having been left in the 2+ state. The sole ruthenium containing product was $[Ru(NH_3)_5Cl]^{2+}$, and it was formed at a specific rate indistinguishable from that at which the ester complex disappears in the absence of Ru(II). An experiment was also done at 25 °C in 1 M HCl with 10% of the ruthenium complex being left in the 2+ state. In this case also $[Ru(NH_3)_5Cl]^{2+}$ was formed quantitatively; the half-life of the reaction (14 min) was found to be somewhat longer than that of the reaction carried out with the fully oxidized form (12 min).

Table I. Pseudo-First-Order Rate Constants as a Function of Acid Concentrations[a]

$[HClO_4]$, M	T, °C	$10^4 k_{obsd}$, s^{-1}
0.917	25.0	9.71
	20.1	5.95
	15.4	3.11
	11.0	1.95
0.458	25.0	9.00
0.183	25.0	6.68
0.903	25.0	4.67
0.095	25.0	4.4[b]

[a] $[Ru(III)]_0 = (4–8) \times 10^{-4}$ M; $\mu = 1.0$ ($LiClO_4$). [b] Measured in the HCl–LiCl medium in the presence of 20% excess $S_2O_8^{2-}$ ion.

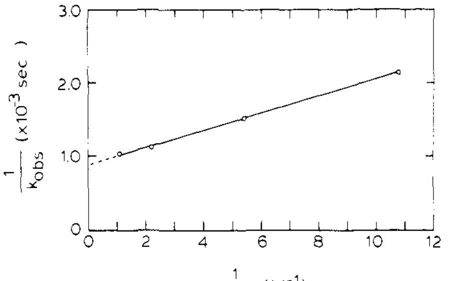

Figure 4. $1/k_{obsd}$ vs. $1/[H^+]$ plot (μ = 1.0 ($LiClO_4$)).

Rate Studies. The rate of the reaction following the rapid oxidation was studied at acid concentrations ranging from 0.093 to 0.92 M, and temperatures ranging from 11 to 25 °C. The concentration of Ru, except for an experiment at 3×10^{-3} M, was maintained in the range $(4–8) \times 10^{-4}$ M. Good first-order behavior was observed at least over three half-lives, thus showing that the rate is first order in Ru(III). The results of the rate measurements are summarized in Table I. It will be noted that k_{obsd} increases with $[H^+]$, but not linearly. When $1/k_{obsd}$ is plotted against $1/[H^+]$, as shown in Figure 4, a linear plot is obtained. The intercept in the plot is 880 ± 20 s, and the slope is 116 ± 4 M s. According to this plot

$$k_{obsd} = \frac{a[H^+]}{b + c[H^+]}$$

where b/a is the slope in Figure 4 and c/a the intercept.

The activation parameters for the system were determined for the experiments in the high acid concentration range where the rate is close to the saturation value (cf. Table I). The plot of ln (k/T) vs. $1/T$ shows a nice linear relationship yielding $\Delta H^\ddagger = 19.6 \pm 0.4$ kcal/mol and $\Delta S^\ddagger = -6.5 \pm 1.2$ eu.

The effect of Ru(II) on the rate of the reaction at high acidity was described in the previous section. In contrast to the behavior at high acid where rate acceleration is not observed, Ru(II) does enhance the rate when the acidity is low. In an experiment at 25 °C, in 0.1 M HCl–0.9 M LiCl, and with 10% of the ruthenium in the 2+ state, k_{obsd} was measured as 6.3×10^{-4} s^{-1} to be compared to 4.5×10^{-4} s^{-1} when Ru(II) is not present.

Cobalt Analogue. The hydrolysis of $[Co(NH_3)_5NH_2CO_2C_2H_5]^{3+}$ was followed in 1 M DCl in D_2O by using nuclear magnetic resonance spectroscopy. In 2 months at room temperature, less than 5% of the ester is hydrolyzed to produce ethanol. The N to O linkage isomerization of the complex was investigated under the same conditions by observing the change in absorption spectrum. The N-bound complex has a band maximum at 480 nm (ϵ = 63 M^{-1} cm^{-1})[3] while for the O-bound isomer it is at 500 nm (ϵ = 69 M^{-1} cm^{-1}).[18] The band maximum of the $[Co(NH_3)_5NH_2CH_2CO_2H_5]^{3+}$ solution stayed at 480 nm

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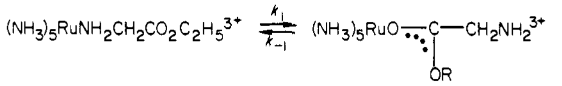
(17) J. P. Greenstein and M. Minitz, "Chemistry of the Amino Acids", Vol. 2, Wiley, 1961, p 1308.

(18) J. Fujita, T. Yashui, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **38** 654 (1965).

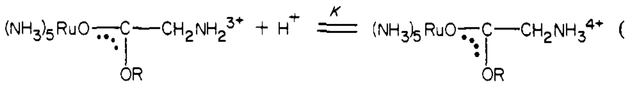
for more than 1 month. The absorbance decreased by 6% during this time, the same percent decrease being registered at both 500 and 480 nm. The cause of the decrease is not known but apparently involves reduction. Transformation of the N-bound to the O-bound complex would result in an absorbance increase at 500 nm where ϵ for the starting material is 53 M^{-1} cm^{-1}.

Discussion

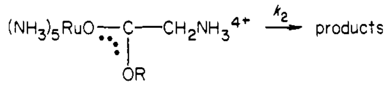
The mechanism comprised by reactions 1–3, together with the



$$(NH_3)_5RuNH_2CH_2CO_2C_2H_5^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (NH_3)_5RuO{\cdots}\underset{OR}{C}{-}CH_2NH_2^{3+} \quad (1)$$



$$(NH_3)_5RuO{\cdots}\underset{OR}{C}{-}CH_2NH_2^{3+} + H^+ \overset{K}{\rightleftharpoons} (NH_3)_5RuO{\cdots}\underset{OR}{C}{-}CH_2NH_3^{4+} \quad (2)$$



$$(NH_3)_5RuO{\cdots}\underset{OR}{C}{-}CH_2NH_3^{4+} \xrightarrow{k_2} \text{products} \quad (3)$$

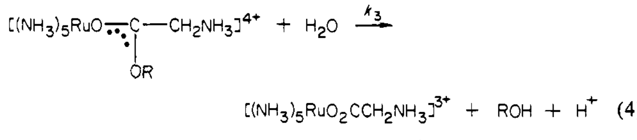
elaborations which will be introduced in due course, accounts for the results. The intermediate shown in reactions 2 and 3 can undergo a variety of reactions, but the distribution between them does not affect the rate of consumption of the reactant [RuN-glyc]. The rate law corresponding to this mechanism is

$$-\frac{d[\text{RuN-glyc}]}{dt} = \frac{k_1k_2K[H^+]}{k_{-1} + k_2K[H^+]}[\text{RuN-glyc}]$$

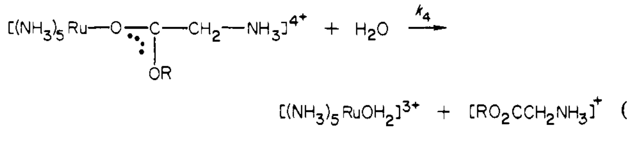
$$k_{obsd} = \frac{k_1k_2K[H^+]}{k_{-1} + k_2K[H^+]}$$

From the plot in Figure 4 we find that at 25 °C $k_1 = 1.14 \times 10^{-3}$ s^{-1} and $k_{-1}/k_2K = 0.13$. The value of k_1 is close to the rate constant of the acid-independent path in the rearrangement of $[(NH_3)_5RuNH_2CH_2CO_2H]^{3+}$ to $[(NH_3)_5RuO_2CCH_2NH_3]^{3+}$ for which 2×10^{-3} s^{-1} has been reported.[8] Assuming $K = 6 \times 10^5$ M^{-1}, which is estimated from the reported[19,20] value of 7.8 for pK_a, we have $k_{-1}/k_2 = 8 \times 10^4$. (The estimate was made by comparing pK_a for $C_2O_4H^-$ with that of $[(NH_3)_5CoC_2O_4H]^{2+}$.[21] This provides a reasonably good measure of the effect in the glycine case of attaching $(NH_3)_5Ru^{3+}$ to the ligand; in each of the cases, four atoms intervene between the tripositive center and the proton to be lost. The pK_a value for the cobalt complex is 2 units lower than that of $HC_2O_4^-$.) If either k_{-1} or k_2 were known, all of the kinetic parameters could be fixed. As we shall show, even short of a direct determination, reasonably good estimates can be obtained.

The fact that k_2 is composite provides us with a means of fixing the remaining kinetic parameters to within an order of magnitude. The stoichiometry shows that reaction 3 in perchloric acid is comprised of the parallel steps



$$[(NH_3)_5RuO{\cdots}\underset{OR}{C}{-}CH_2NH_3]^{4+} + H_2O \xrightarrow{k_3} [(NH_3)_5RuO_2CCH_2NH_3]^{3+} + ROH + H^+ \quad (4)$$



$$[(NH_3)_5Ru{-}O{\cdots}\underset{OR}{C}{-}CH_2{-}NH_3]^{4+} + H_2O \xrightarrow{k_4} [(NH_3)_5RuOH_2]^{3+} + [RO_2CCH_2NH_3]^+ \quad (5)$$

Taking account of the fact that at 25 °C the free ester formed in reaction 5 makes up 30% of the product, the relation $k_4 = 0.30k_2$ follows.

We turn now to an estimate of k_4. The rate constant for the aquation of the methyl acetate complex of pentaamminecobalt(III) has been reported[22] as being greater than 2×10^{-2} s^{-1}. Gaunder and Taube[23] have measured the aquation rate of the complex $[(H_2O)_5CrOC(OCH_3)\text{-4-}C_5H_4N]^{3+}$ which is produced in the reaction of $[Ru(NH_3)_5\text{-4-}COOCH_3C_5H_4N]^{3+}$ with Cr^{2+} as 3.65×10^{-2} s^{-1} at 25 °C at $\mu = 1.0$. Pentaammineruthenium(III) tends to be somewhat more labile than the corresponding complexes of Co(III) and Cr(III); thus, the aquation rates of the acetato complexes of both $Co(NH_3)_5^{3+}$[24] and $Cr(H_2O)_5^{3+}$[25] are approximately ten times slower than that of $Ru(NH_3)_5^{3+}$ complex.[26] It is therefore reasonable to assume that k_4, the rate constant for aquation of the ethyl glycinate complex of $Ru(NH_3)_5^{3+}$ (reaction 5), is 0.3 s^{-1}. With this value of k_4, k_3 is fixed at 0.7 s^{-1} and k_{-1} as 8×10^4 s^{-1}. Thus the equilibrium constant for reaction 1 is 10^{-8} (k_1/k_{-1}) which corresponds to a free-energy change $\Delta G° = 10.7$ kcal/mol for the conversion of the N-bound ester complex to the O-bound form. Because the activation parameters for the system were measured near the saturation region (i.e., at high acid concentration) the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained correspond closely to the activation parameters of the linkage isomerization process, reaction 1 in the forward direction.

The rate effects observed with Ru(II) present are in accord with the mechanism proposed. In the "saturation" region reaction 1 in the forward direction is rate determining, and the only effect exerted by Ru(II) is to dilute the reactant somewhat by converting it to the less reactive Ru(II) form. But at low acid, where in the limit the intermediate is in equilibrium with the reactants, Ru(II) accelerates the reaction by providing a new path for the aquation of the intermediate (the Ru(II) ester complex is expected to be more labile than the Ru(III)). A more detailed study is needed before the parameters for the additional path can be calculated.

An essential feature of the mechanism proposed is the formation of the intermediate $[(NH_3)_5RuOC(OR)CH_2NH_3]^{4+}$ which can undergo competitive reactions. The relative rates of these reactions can change without affecting the rate at which the N-bound ester complex disappears. Two such processes have already been considered, namely, ester hydrolysis and aquation to produce free ester. (These two reactions incidentally have about the same activation energies.) In the presence of chloride ion a third process intervenes, namely, the formation of the chloro complex. Production of this species does not affect the rate at which the N-bound glycinate complex disappears, nor does it significantly affect the yield of the O-bound glycinate complex. Two obvious mechanisms for the formation of the chloride complex can be excluded. We can be certain that $[(Ru(NH_3)_5H_2O)]^{3+}$ is not an intermediate for its production because substitution by Cl^- in the aquo ion is much too slow to account for the observations. Furthermore, we are certain that the formation of the chloro complex does not involve the direct attack of Cl^- on the ester complex. If this did occur, the yield of the carboxylato product would be adversely affected by Cl^- and this is not the case. The observations imply that the path leading to the aquo or chloro complex involves dissociation of the O-bound intermediate to produce $Ru(NH_3)_5^{3+}$, and that this species is rather efficiently scavenged by Cl^-. The ratio R = [chloro complex]/[aquo complex][Cl^-] from the experiment at 1 M Cl^- is found to be 3.1 and from that at 0.1 M Cl^-, also at 25 °C, 3.0. The agreement does of course not distinguish between the rate-determining formation of a species such as $Ru(NH_3)_5^{3+}$, Cl^- and H_2O then competing for reaction with it, or attack by Cl^- and H_2O on the O-bound ester intermediate in parallel processes. The second alternative however is not compatible with the observation that the chloro complex is not formed at the cost of the O-bound glycinate product. It is of interest that the yield of the chloro complex

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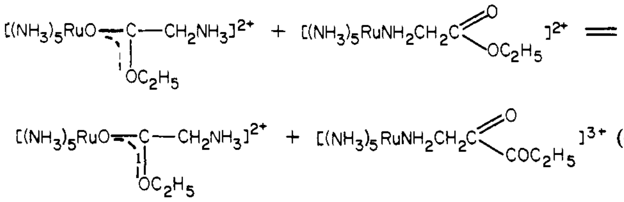
formed by the intermediate $Ru(NH_3)_5^{3+}$ is almost 10-fold greater than is the case for $Co(NH_3)_5^{3+}$. For the latter species $R = 0.33$[27] rather than 3 as observed in our system. The agreement of R in our systems at the two concentration of Cl^- is less good when the yield of Cl^- as determined by ion exchange is used. The difference is in the direction expected if some of the chloro complex is lost by aquation or by other means when the separation is done.

A third reaction of the intermediate, which again does not affect the rate at which the N-bound ester complex disappears, is evoked by the Ru(II) form of the N-bound complex. Even a trace of Ru(II) diverts the intermediate to produce $[(NH_3)_5RuCl]^{2+}$ quantitatively in 1 M Cl^-. Evidently, reaction 6, takes place rapidly



$$[(NH_3)_5RuO{=}C(OC_2H_5){-}CH_2NH_3]^{2+} + [(NH_3)_5RuNH_2CH_2C(=O)OC_2H_5]^{2+} = [(NH_3)_5RuO{=}C(OC_2H_5){-}CH_2NH_3]^{2+} + [(NH_3)_5RuNH_2CH_2C(=O)COC_2H_5]^{3+} \quad (6)$$

compared[28] to other reactions for the intermediate. The O-bound ester complex of Ru(II) is of course expected to aquate extremely rapidly. The increase in the half-life for the overall process when [Ru(II)] becomes large has a straightforward explanation. It is a consequence of the fact that part of the N-bound reactant is stored in the Ru(II) form, and this does not undergo the N → O transformation as rapidly as Ru(III), a difference that was noted also for the glycine complex.[8]

An alternative mechanism which involves the association of carboxylate ester with H^+ followed by the isomerization and the hydrolysis of the ethyl group has also been considered but can be excluded for the following reasons, among others. First, the absorption spectrum of the N-bound ester complex does not change with acid concentration. Second, our kinetic result according to this mechanism would fix pK_a for the ester at ~ 1; the pK_a reported[29] for the protonation of the carbonyl oxygen in a carboxylic acid is -6.5.

The rate of acid hydrolysis of free ethyl glycinate ester has a half-life of weeks at a pH of approximately 1.[20,30] For $[Co(NH_3)_5NH_2CH_2CO_2C_2H_5]^{3+}$ in 1 M H^+ the half-life for the hydrolysis has been shown to be longer than 2 months and longer than 1 month for the N to O isomerization. There is clearly a difference between Co(III) and Ru(III) in respect to the reaction we are studying which is quantitatively so great as to be qualitative. Another difference between $Co(NH_3)_5^{3+}$ and $Ru(NH_3)_5^{3+}$ is apparent from earlier work in relation to ours. The ethyl acetate complex of Co(III) reacts in water essentially quantitavely by aquation[22]—i.e., $k_4/k_3 > 10$; for the Ru(III) case, from the present work, $k_4/k_3 = 0.4$.

Some implications of the findings reported merit consideration. For polyfunctional ligands, once the bond to Ru(III) has been established, owing to the facile linkage isomerization, activation by the metal can in the right circumstances be transferred readily from one site on the substrate to another. Attachment of Ru(III) itself can be made facile for many systems by starting with Ru(II) and then oxidizing the Ru(II) complex to Ru(III). Because linkage isomerization is so facile for Ru(III), it is certain that activation for nucleophilic substitution by Ru(III) will not prove to be a simple extension of the effects observed for Co(III) and will be worthy of investigation in its own right.

A corollary of the facile attachment via Ru(II) is that release of a ligand from Ru(III) in an environment in which the ruthenium(III)-substrate complex is unstable can be catalyzed by Ru(II), at least when the ruthenium(II)-polar group bond is labile, as is the case for most ligands with oxygen as the donor atom. This is illustrated in the present work by the release of ester from $[(NH_3)_5RuNH_2CH_2CO_2C_2H_5]^{3+}$, a change which involves Ru(III)-N bond rupture, with a half-life of only 12 min at 25 °C when Ru(II) is present.

The data make it possible to estimate the catalysis of ester hydrolysis by a 3+ ion such as $(NH_3)_5RuOH_2^{3+}$, which provides only a single site for the attachment of the ester, if complex formation were a labile process. The quotient governing association of $NH_2CH_2CO_2C_2H_5$ with $(NH_3)_5RuOH_2^{3+}$ has been found to be $5.5 \times 10^2\ M^{-1}$ [31] so that K_{eq} for

$$(NH_3)_5RuOH_2^{3+} + [NH_3CH_2CO_2C_2H_5]^+ = [(NH_3)_5RuOC(OR)CH_2NH_3]^{4+}$$

would be ca. $5.5 \times 10^{-6}\ M^{-1}$. Multiplying this by k_1, the second-order specific rate governing the overall reaction to the glycine complex and alcohol would then be $6 \times 10^{-9}\ M^{-1}\ s^{-1}$. Even at 1-M levels of the "catalyst", the half-life of the reaction would be more than 3 years. The rate could of course be much improved if K_{eq} were made greater by, for example, chelation.

Finally we draw attention to the profound effect that the neighboring ester function has on the rate of aquation of NH_2-R on Ru(III). In the "saturation" regime, the rate constant for

$$[(NH_3)_5RuNH_2CH_2CO_2C_2H_5]^{3+} + H_2O + H^+ = [(NH_3)_5RuOH_2]^{3+} + [NH_3CH_2CO_2C_2H_5]^+$$

is $0.3 \times 1.1 \times 10^{-3}\ s^{-1}$ or $3 \times 10^{-4}\ s^{-1}$. The half-life for loss of NH_3 from $Ru(NH_3)_6^{3+}$ has been estimated[12] as >3 years, which corresponds to a specific rate of $2 \times 10^{-9}\ s^{-1}$. The rate of aquation of a primary amine is not expected to be much different from that of ammonia. It must be stressed that the proton plays an essential role in the labilization, because it raises the concentration of the O-bound ester complex to levels so that it provides a route to decomposition products.

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