= –0.75 V. Reduction past $n > 5^{10b}$ per dimer occurs to give $[Ru^{II}(NH_3)_5(H_2S)]^{2+}$ in high yield, as shown by the peak current of the wave for the $[Ru^{III}(NH_3)_5(SH)]^{2+}/[Ru^{II}(NH_3)_5(SH_2)]^{2+}$ couple at $E_{1/2}$ = –0.42 V ($E_{p,c}$ = –0.48 V; $E_{p,a}$ = –0.36 V vs. SCE)[12] in the cyclic voltammogram after the electrolysis. From cyclic voltammetric measurements under a variety of conditions, it is clear that the reduction of $[Ru^{II}(NH_3)_5(SO_2)]^{2+}$ occurs via at least one observable intermediate and that kinetic effects at the electrode are important.

The electrochemical results based on $[Ru^{II}(NH_3)_5(SO_2)]^{2+}$ are striking in showing the existence of a stepwise, net six-electron reduction of $[Ru^{II}(NH_3)_5(SO_2)]^{2+}$ to $[Ru^{II}(NH_3)_5(H_2S)]^{2+}$ with retention of the initially bound sulfur, at least in the net sense, and in showing the importance mechanistically of intermediate S–S coupling. The ruthenium complex is not an effective catalyst under these conditions, because of the relatively high affinity of ruthenium for sulfur in both oxidation states +IV and –II.

In Figure 2 are shown cyclic voltammograms and a differential-pulse polarogram[13] of solutions containing both $[Fe^{III}\text{-}(TPPS)(H_2O)_n]^{3-}$ and less than stoichiometric HSO_3^- (curve a) at pH 3.48 and 2.74, respectively. As shown in Figure 2, a new, irreversible wave appears at $E_{p,c}$ = –0.64 V with added HSO_3^-, which increases in peak current and becomes catalytic as the concentration of HSO_3^- is increased. As shown in Figure 2, the peak current for the wave at –0.64 V increases linearly with $[HSO_3^-]$ in the concentration range shown (curves b and c). A series of electrolysis experiments were carried out just past the wave at $E_{p,c}$ = –0.64 V at E_{appl} = –0.65 V (pH 3.00). In a typical experiment a solution containing 4.6×10^{-3} M HSO_3^- and 1.2×10^{-4} M $[Fe^{III}(TPPS)(H_2O)_n]^{3-}$ at pH 3.5 was electrolyzed to n = 3.9 per added HSO_3^- to give H_2S in yields up to 52% of the initial HSO_3^- based on GC and gravimetric analysis.[14] The background current in the absence of catalyst was negligible. Yields of less than 100% H_2S are expected under our conditions since an unavoidable complication in solutions containing high initial concentrations of HSO_3^- is the competitive formation of elemental sulfur formed by reaction between H_2S and HSO_3^-, which limits the yield of H_2S. Nonetheless, under the conditions of the experiment, H_2S was formed with a faradaic efficiency of 80%. The turnover number based on the total reductive equivalents passed was 170 or based on the moles of H_2S produced per mole of catalyst was 19.

Differential-pulse polarography and cyclic voltammetry experiments on the iron porphyrin in the presence of HSO_3^- (Figure 2) show that the new wave at E_p = –0.64 V appears following the reduction of Fe(III) to Fe(II) at E_p = –0.23 V. Presumably, reduction of Fe(III) to Fe(II) is followed by formation of an $Fe^{II}\text{-}SO_2$ or $Fe^{II}\text{-}SO_3H$ complex and the reduction at –0.64 V corresponds to the first stage of the net electrocatalytic reduction of bound HSO_3^- to H_2S. SO_2 complexes of Fe(II) porphyrins have been reported.[15]

In earlier work on the reduction of nitrile/nitrosyl to ammonia, coordinatively stable polypyridyl complexes of Ru provided useful insight into the probable mechanistic details by which the catalytically active iron porphyrins accomplish the net redox change.[16] The pentaammineruthenium(II) system may serve that role here as well. pH-dependent electrochemical studies show that the SO_2 complex, $[(NH_3)_5Ru(SO_2)]^{2+}$, is the reactive form toward re-

duction, and the key to its reactivity may be the availability of low-lying levels, largely $\pi^*(SO_2)$ in character, which provide a basis for the initial reduction.[17]   In the electrochemistry of $[Fe^{III}(TPPS)(H_2O)_n]^{3-}$ in the presence of SO_2/HSO_3^-, the irreversible reduction at –0.64 V is analogous to the initial reduction of $[Ru^{II}(NH_3)_5(SO_2)]^{2+}$ at –0.74 V. The wave at –0.64 V for the porphyrin complex only appears in acidic solutions where at least small amounts of SO_2 are present and the active form of the porphyrin in the catalytic system appears to be an SO_2 complex as well. As shown by the cyclic voltammetric scans in Figure 2, the net turnover of SO_2 to H_2S is rapid. With less than excess added HSO_3^- (curve a), scan reversal past the $HSO_3^-/SO_2 \rightarrow H_2S$ electrocatalyzed reduction gives back the aqua couple, suggesting that $HSO_3^-/SO_2 \rightarrow H_2S$ reduction and subsequent axial displacement of bound H_2S by water are both rapid. As shown by the dashed curves in the figure (curves b and c), in the presence of excess HSO_3^-, scan reversal shows a greatly diminished Fe-(III/II) aqua wave, suggesting that reduction, loss of H_2S, and re-formation of the active HSO_3^-/SO_2 complex are all rapid on the cyclic voltammetric time scale of 50 mV/s.

(17) Ryan, R. R.; et al. *Struct. Bonding (Berlin)* **1981**, *46*, 46–97.

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Uncomplexed Rather Than the Metal Ion Complexed α,α'-Carbanion as an Intermediate in Transamination between Pyridoxal and Pyridoxamine Schiff Bases

Sir:

A recent communication to the editor of this journal stated that an Al(III) α,α'-deprotonated complex is "a mandatory intermediate for the transamination process leading from ketimine to aldimine".[1]   With a starting solution containing pyridoxamine, pyruvate, and Al(III) in a 1:1:1 ratio, Figure 2 in ref 1 shows the ^{1}H NMR evidence for buildup of an intermediate with a maximum concentration at about 2 h and, separately, continuous production of aldimine as the main product of the reaction. However, the continuous increase does not conform to the requirements for a consecutive reaction sequence in which the intermediate lies on the reaction pathway from reactants to aldimine. Instead the results fit a competitive reaction scheme in which the presumed intermediate appears as a metastable byproduct produced in a reversible side reaction that does not lie on the reaction pathway from reactants to aldimine.

The proposed sequence of reactions in the consecutive reaction scheme may be represented as

$$A \rightleftharpoons B \rightarrow C$$
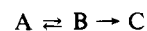
where A represents the reactants, B, the intermediate whose concentration builds and then declines, and C, aldimine as the main product of the reaction. Figure 2 of ref 1, however, does not display the required characteristics for consecutive reactions. Though there is a buildup and decline of an intermediate, the maximum alone is insufficient to establish an intermediate in a consecutive reaction sequence. The intensity vs. time curve for the aldimine product must display an induction period with an inflection point occurring at the same time as the maximum in the curve for the intermediate.[2]   The aldimine curve in ref 1 shows no clear induction period, and the required inflection point is

(12) Kuehn, C. G. Ph.D. Dissertation, Stanford University, Stanford, CA, 1975; p 63.

(13) Single-sweep voltammetry and differential-pulse polarography experiments were performed with a glassy-carbon working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode.

(14) GC analysis was performed by using an HP-5890 gas chromatograph and a Chromosorb 107, 80/100 Teflon column. Gravimetric analysis was performed by precipitation and weighing of ZnS·H₂O formed in a trap past the electrolysis cell. The H₂S formed during electrolysis was transferred to the trap by a continuous Ar purge. The trap contained 0.1 M zinc acetate dihydrate.

(15) Kuroi, T.; Nakamoto, K. *J. Mol. Struct.* **1986**, *146*, 111–121.

(16) Murphy, W. R., Jr.; Takeuchi, K. J.; Barley, M. H.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 1041–1053.

(1) Martell, A. E.; Taylor, P. *Inorg. Chem.* **1984**, *23*, 2734.

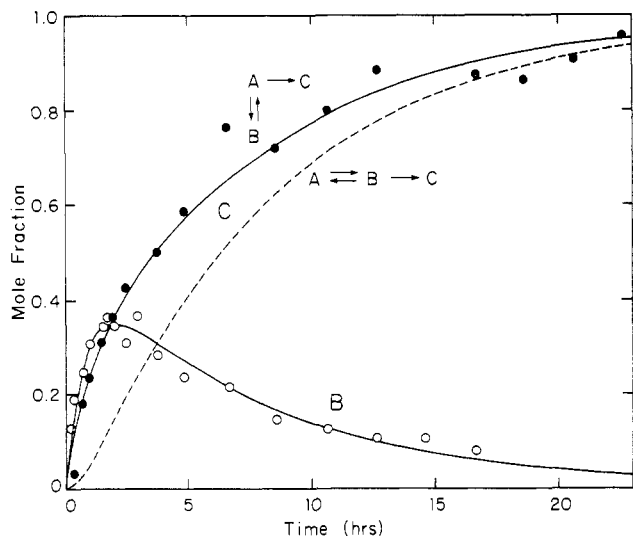(2) Martin, R. B. *J. Chem. Educ.* **1985**, *62*, 789.

Figure 1. Mole fraction vs. time in hours for species B (open circles) and final aldimine product C. The upper, solid C curve is for the competitive scheme, and the lower, dashed C curve is for the consecutive scheme. Parameters for the latter curve are wholly dictated by the fit of the B curve. Constants were derived by a nonlinear least-squares fit to the points in the competitive scheme formalism at $k_5 = 0.59$ h^{-1}, $k_6 = 0.46$ h^{-1}, and $k_7 = 0.37$ h^{-1}.

absent. Thus the proposed "mandatory intermediate" does not meet the criteria for an intermediate lying on the reaction pathway from reactants to products.

Points read from Figure 2 in ref 1 are replotted in Figure 1 of this communication. Solid circles represent the mole fraction sum of 1:1 and 2:1 complexes of aldimine product, C, and the open circles the similar sum for the intermediate, B. Parameters determined in the fit of the open circles for intermediate B completely determine the product C curve in the consecutive scheme. The resulting dashed curve for product C in Figure 1 does not fit the solid points, ruling out the consecutive scheme.
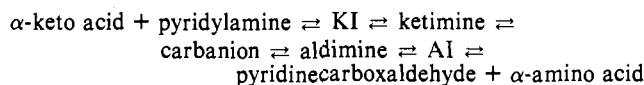
The results furnished in Figure 2 of ref 1 represent a classic case of the competitive reaction scheme

$$A \underset{k_6}{\overset{k_5}{\rightleftarrows}} B \qquad A \overset{k_7}{\longrightarrow} C$$
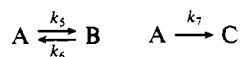
where the "intermediate" B is produced in a reversible side reaction not on the pathway from reactants A to main product C. This case has been explicitly considered in ref 2, and the same rate constant designations are used here for easy comparison. A nonlinear least-squares treatment of the complete curve over the course of the entire reaction for the intermediate in Figure 1 according to the prescription in ref 2 yields the rate constant values $k_5 = 0.59$ h^{-1}, $k_6 = 0.46$ h^{-1}, and $k_7 = 0.35$ h^{-1}. All values are to within about 10%. These constants predict a maximum at 2.0 h, as observed. A separate fit for production of aldimine, the main product, over the entire course of the reaction yields $k_7 = 0.37$ h^{-1}, in excellent agreement with the above value. Thus, the results in Figure 1 are quantitatively in agreement with the competitive reaction scheme. The resulting solid curve for aldimine product C in Figure 1 fits the solid points. Nonlinear least-squares analysis of the same results for aldimine formation by the consecutive sequence does not yield a refinement. The consecutive reaction sequence does not fit the results; the competitive scheme fits the results well within experimental uncertainties. Of course, the competitive reaction scheme may be filled out with more reaction intermediates.

What are the possibilities for species B, a metastable byproduct whose concentration builds initially and then declines as reactants

are converted to aldimine? The sequence of reversible reactions is

α-keto acid + pyridylamine $\rightleftarrows$ KI $\rightleftarrows$ ketimine $\rightleftarrows$
   carbanion $\rightleftarrows$ aldimine $\rightleftarrows$ AI $\rightleftarrows$
      pyridinecarboxaldehyde + α-amino acid

where KI and AI refer to tetrahedral carbinolamine intermediates. When one starts from the reverse or amino acid end, the metastable chelate species appears more slowly than the aldimine complex.[1] This result rules out a complex carbinolamine intermediate AI as species B. In the forward direction the concentration of the metastable byproduct builds more rapidly than that of the aldimine complex. Three complexes remain as possibilities for the metastable byproduct: tetrahedral carbinolamine intermediate KI, ketimine, and carbanion. Metal ions may trap carbinolamine intermediates.[3] However, the first two compounds contain an additional α'-carbon-bound proton that should be apparent in a ^{1}H NMR spectrum. In addition, the kinetic analysis presented above is not nearly so satisfactorily fit if the concentration of the metastable byproduct must be halved because it contains two rather than one α'-hydrogen. (There is, however, a perplexing, variable relationship between the concentrations of 1:1 and 1:1 complexes of the "intermediate" in Figure 2 of ref 1.) Therefore, identification of the metastable byproduct as a metal ion complex of the carbanion appears confirmed. Once made, partitioning of the uncomplexed carbanion must strongly favor aldimine over ketimine or else the observed α'-H would be washed out by deuterium in the third reaction of the above sequence from the D$_2$O solvent used in the NMR studies. Since no exchange is reported, the rate-limiting step cannot occur as late as the fourth reaction in the sequence and must occur in one of the first three reactions.

Thus, complexed carbanion does not lie on the reaction pathway from reactants to aldimine products. The carbanion complex is a metastable byproduct of a reversible side reaction. This conclusion should not detract from the original communication that reports trapping of the carbanion intermediate by complexation. Though the metal ion complexed carbanion does not lie on the reaction pathway, it remains likely that uncomplexed carbanion does. By complexation of the carbanion metal ions build up its concentration so the complexed carbanion becomes evident in ^{1}H NMR spectra.

That complexed carbanion where a metal ion substitutes for a proton is much less reactive than the carbanion protonated at the azomethine nitrogen may be ascribed to the many times greater polarizing power of the proton compared to even that of multiply charged cations.[4] Water-bound Al^{3+} loses a proton with pK_a = 5.5[5] while water bound to a proton exhibits pK_a = -1.7, indicating a 10^7 times greater polarizing capability of H$^+$ over that of Al^{3+}. Metal ions accelerate acid-catalyzed reactions more than a proton only in those special cases where, at a specific site, protonation is difficult and metalation facile.[4] Metal ions serve as catalysts in transamination reactions, not by coordinating starting amines in which only the free base form is nucleophilic, but rather by coordinating carbinolamine intermediates and changing the rate-limiting step.[3]

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