of this limitation, the method should be quite useful, since it nicely complements existing procedures. It uses cheap and readily available starting materials and is well suited for large-scale preparation of α-substituted, unsaturated amides. Its scope is broadened by the availability of smooth procedures allowing the conversion of tertiary amides into acids, esters, aldehydes, ketones, and amines.[12] Further applications of the newly described dehydrogenation method are under investigation.

Acknowledgment. We express our thanks to the Catholic University of Louvain (Secrétariat du Tiers Monde) and the "Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture" for fellowships to R. Da Costa, M. Gillard, and J. B. Falmagne, and the "Fonds de la Recherche Fondamentale et Collective" for financial support.

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(7) A mechanistic study of these reactions will be reported later with the full experimental details.

(8) When R^2 = H, it is advised to saturate the solution of amide with gaseous HCl prior to phosgenation. This precludes the formation of small amounts of β-acylated product.

(9) With the more reactive amides, cooling may be necessary during the early stages of phosgenation.

(10) If the phosgenation is not completed after 24 h, a few drops of dimethylformamide and more phosgene can be added to the mixture, which is allowed to stand 2 to 3 more days at room temperature.

(11) All these experiments require complete exclusion of moisture.

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Solar Energy Storage Reactions Involving Polynuclear Rhodium Isocyanide Complexes. Flash Photolysis Studies in Aqueous Sulfuric Acid Solutions

Sir:

We have recently reported[1] that 546-nm irradiation of solutions of the binuclear Rh(I) complex $Rh_2(bridge)_4^{2+}$ (bridge = 1,3-diisocyanopropane) in concentrated HX(aq) results in clean conversion to H_2 and $Rh_2(bridge)_4X_2^{2+}$ (X = Cl, Br).[2] Since these reactions are driven by visible photons, they represent one way of achieving conversion of solar to chemical energy. Recent work in our laboratory has shown that a thermal reaction between $Rh_2(bridge)_4^{2+}$ and HCl generates a blue photoactive species, $[Rh_2(bridge)_4Cl^{2+}]_n$, and hydrogen. Irradiation of $[Rh_2(bridge)_4Cl^{2+}]_n$ produces the ultimate products, according to the following scheme:

$$Rh_2(bridge)_4^{2+} + HCl \xrightarrow[12\ M\ HCl]{\Delta} (1/n)[Rh_2(bridge)_4Cl^{2+}]_n + \tfrac{1}{2}H_2$$

$$(1/n)[Rh_2(bridge)_4Cl^{2+}]_n + HCl \xrightarrow[12\ M\ HCl]{546\ nm} Rh_2(bridge)_4Cl_2^{2+} + \tfrac{1}{2}H_2$$

Analysis of the hydrogen evolved in the separate thermal and photochemical steps has established the above stoichiometric relationships.[3] The structure of the photoactive species, $[Rh_2(bridge)_4Cl^{2+}]_n$, or that of an analogue, $[Rh_2(bridge)_4^{3+}]_n$ (prepared by oxidation of $Rh_2(bridge)_4^{2+}$ in H_2SO_4 solutions), is being actively pursued. Evidence that bears on the structural question in the case of $[Rh_2(bridge)_4^{3+}]_n$ has been obtained in a series of flash photolysis experiments, as reported herein.

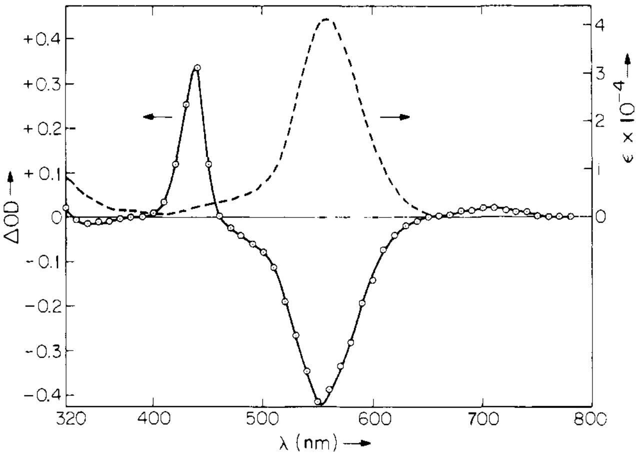

Figure 1. Absorption spectrum (- - -) and flash-generated transient difference spectrum (—) for $[Rh_2(bridge)_4^{3+}]_n$ in 1 N H_2SO_4(aq) at 25 °C.

Solutions of $[Rh_2(bridge)_4^{3+}]_n$ prepared by oxidation of $[Rh_2(bridge)_4](BF_4)_2$ in 1 N H_2SO_4(aq) possess an absorption maximum at 558 nm (ϵ/Rh_2 = 44 400) (Figure 1). Since the same λ_{max} is obtained for H_2O solutions with no added electrolytes, we assume that no sulfate or bisulfate is bound as a ligand to the rhodium complex.[4] Degassed H_2SO_4(aq) solutions of $[Rh_2(bridge)_4^{3+}]_n$ are indefinitely stable ($[H_2SO_4] \lesssim 20$ N). Flash photolysis reveals a transient(s), however, with absorption maxima at 438 ($\Delta\epsilon/Rh_2$ = 34 500) and 705 nm ($\Delta\epsilon/Rh_2$ = 2000) (Figure 1).[5] Extinction coefficients were calculated from the bleaching at 550-560 nm, making the assumption that transient(s) absorption is negligible at these wavelengths. The transient(s) is prompt, with a rise time of <10 ns, and undergoes clean second-order decay[6] to starting material. The rate constant in 1 N H_2SO_4(aq) is 3.3 (± 0.2) × 10^7 M^{-1} s^{-1}, where the calculation assumes that the bimolecular process involves identical reaction partners (vide infra). The rate constant is identical within experimental error in 1 N D_2SO_4 (D_2O).

Figure 2 depicts the dependence of the second-order rate constant on ionic strength.[7] The slope at low ionic strengths (+8.1) should equal the product of charges of the two reactants.[8] It is difficult to imagine how such a high product of

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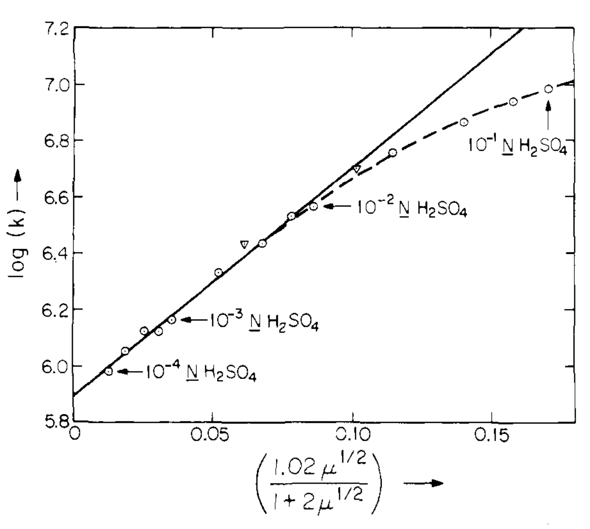

Figure 2. Plot of log (recombination rate constant) vs. Weller's ionic strength (μ) function.[8a] For the points (⊙), μ was adjusted only with H_2SO_4. For the points (▽), H_2SO_4 was 10^{-3} N, and μ was further adjusted with $Li_2SO_4 \cdot H_2O$.

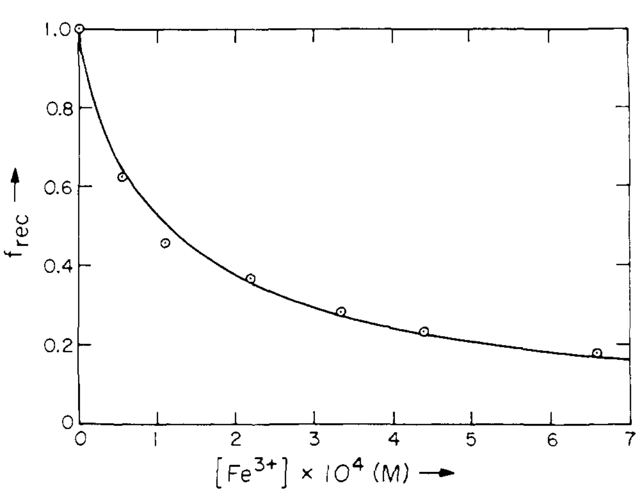

Figure 3. Theoretical fit of bleaching recovery data for Fe^{3+} scavenging in the flash photolysis of $[Rh_2(bridge)_4{}^{3+}]_n$ in 1 N H_2SO_4(aq) at 25 °C. The points (⊙) are experimental, whereas the curve (—) is eq 6 for $\alpha = 2.0 \times 10^{-3}$ and $(A)_0 = 2.8 \times 10^{-7}$ M. $(A)_0$ was determined from $(\Delta OD)_{t=0}$ at 550 nm and was constant over this series of experiments.

charges for the transients could obtain if the complex photolyzed has a charge of only +3. Thus, our results suggest that the complex present in aqueous sulfuric acid solution is *tetranuclear*, and that the reactions observed at low ionic strengths are (1) and (2):

$$\begin{array}{ccc} [\mathrm{Rh_2(bridge)_4}]_2{}^{6+} & \underset{\phi_0}{\xrightarrow{h\nu}} & 2[\mathrm{Rh_2(bridge)_4}]^{3+} \\ \lambda_{max}\ 558\ \mathrm{nm} & & \lambda_{max}\ 438,\ 705\ \mathrm{nm} \end{array} \qquad (1)$$

$$2[\mathrm{Rh_2(bridge)_4}]^{3+} \xrightarrow{k} [\mathrm{Rh_2(bridge)_4}]_2{}^{6+} \qquad (2)$$

The product of charges in this situation is +9, in reasonable agreement with experiment, and the clean second-order recovery that we observed is to be expected.

Calculations of diffusion-limited rates for two +3 charged ions yield[9] results closely comparable to the zero ionic strength intercept of Figure 2 ($k_0 = 7.9 \times 10^5$ M^{-1} s^{-1}). For example, Debye's equation[9a] predicts $k_0 = 4.3 \times 10^{-5} k_d$ in H_2O if the "ion radius" is taken to be 5.0 Å, where k_d is the diffusion-limited rate constant for two uncharged reactants. Thus, it is likely that the recombination is diffusion controlled. Flash photolysis of CH_3CN solutions of $[Rh_2(bridge)_4{}^{3+}]_n$ containing *p*-toluenesulfonic acid reveals a nearly identical transient; this transient also undergoes second-order decay, but with a smaller rate constant, 5.7 (±0.5) × 10^6 M^{-1} s^{-1} for 0.78 M acid, consistent[10] with the lower dielectric constant of the medium. Such long lifetimes (we have observed half-lives as long as 3 s) are totally inconsistent with the transient being an excited state.

Quenching studies provide strong support for our interpretation. A number of potential oxidants and reductants that do not react readily with the Rh-bridge solutions in the dark do react photochemically. In particular, the net photooxidation (eq 3) has been studied in detail.[11]

$$\tfrac{1}{2}[\mathrm{Rh_2(bridge)_4}]_2{}^{6+} + \mathrm{Fe}^{3+} \xrightarrow{h\nu} [\mathrm{Rh_2(bridge)_4}]^{4+} + \mathrm{Fe}^{2+} \qquad (3)$$

The quantum yield for product formation[12] in 1 N H_2SO_4(aq) with 546-nm irradiation is 0.020 ± 0.002, independent of $[Fe^{3+}]$ and light intensity for $[Fe^{3+}] \gtrsim 10^{-3}$ M. Flash photolysis studies show that the transient absorption immediately after the flash is identical with that already described, and of magnitude independent of $[Fe^{3+}]$. However, increasing $[Fe^{3+}]$ results in increasingly rapid pseudo-first-order decay at all wavelengths, and recovery of bleaching becomes incomplete, owing to product formation. Pseudo-first-order rate constants are identical for decay of 440- and 700-nm transient absorption, and a plot vs. $[Fe^{3+}]$ indicates $k_{Fe^{3+}}$ for eq 4 to be 6.9 (±0.5) × 10^4 M^{-1} s^{-1} either in 1 N H_2SO_4(aq) or 1 N D_2SO_4 (D_2O):

$$[\mathrm{Rh_2(bridge)_4}]^{3+} + \mathrm{Fe}^{3+} \xrightarrow{k_{\mathrm{Fe}^{3+}}} \text{products} \qquad (4)$$

Most interestingly, the pseudo-first-order rate constants for that portion of initial bleaching that does decay are *twice* those for transient absorption decay at high $[Fe^{3+}]$. This is in accord with our kinetic scheme (eq 1, 2, 4), as at high $[Fe^{3+}]$ we have

$$\begin{array}{c} 2[\mathrm{Rh_2(bridge)_4}]_2{}^{6+}/dt \simeq k[(A)_0]^2 \exp\{-2k_{\mathrm{Fe}^{3+}}[\mathrm{Fe}^{3+}]t\} \\ (A)_0 = [\mathrm{Rh_2(bridge)_4}]^{3+} \text{ at } t = 0 \end{array} \qquad (5)$$

Conclusively, the exact solution to this kinetic scheme yields eq 6 for the fraction (f_{rec}) of bleaching at $t = 0$ that has recovered at $t = \infty$.

$$\begin{array}{c} f_{rec} = 1 - \dfrac{\alpha(\mathrm{Fe}^{3+})}{2(A)_0} \ln\left\{\dfrac{2(A)_0}{\alpha(\mathrm{Fe}^{3+})} + 1\right\} \\ \alpha = k_{\mathrm{Fe}^{3+}}/k \end{array} \qquad (6)$$

Figure 3 shows a best fit of our experimental data for f_{rec} to eq 6. The derived value of α is 2.0×10^{-3}, in excellent agreement with that calculated from k and $k_{Fe^{3+}}$ measured in our other experiments ($\alpha = 2.1 \times 10^{-3}$).

In summary, our flash photolysis studies may be reasonably interpreted by assuming $n = 2$ for $[Rh_2(bridge)_4{}^{3+}]_n$. Preliminary results from flash experiments on solutions of the blue photoactive species, $[Rh_2(bridge)_4Cl^{2+}]_n$, also suggest $n = 2$ in that case. We are hopeful that EXAFS measurements on samples containing both polynuclear rhodium species will contribute to the solution of the structural problem. Such measurements are now underway.

Acknowledgment. We thank Professor Arthur W. Adamson for allowing us access to his laser flash photolysis equipment. Discussions of this work with Professor Adamson and his group, and with Dr. A. Gupta, were most helpful to us. Matthey-Bishop, Inc., is acknowledged for a generous loan of rhodium trichloride. Research at Caltech was supported by the National Science Foundation (Grant CHE75-19086). This research was also supported by the Director's Discretionary Fund at the Jet Propulsion Laboratory.

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(2) We have determined the structures of $Rh_2(bridge)_4^{2+}$ (ref 1b: and Mann, K. R.; Thich, J. A.; Bell, R. A.; Coyle, C. L.; Gray, H. B., to be submitted for publication) and $Rh_2(bridge)_4Cl_2^{2+}$ (ref 1c; and Mann, K. R.; Bell, R. A.; Gray, H. B. *Inorg. Chem.*, in press) in crystals.

(3) In a typical experiment 0.012 mmol of $Rh_2(bridge)_4^{2+}$ produced 0.005 mmol of H_2 upon reaction with 12 M HCl (5 mL) in the dark. Irradiation (>520 nm) of the resultant blue solution yielded an additional 0.006 mmol of H_2. Independent confirmation of the oxidation level of $[Rh_2(bridge)_4Cl^{2+}]_n$ was obtained in redox titrations. Thus, in 6 M HCl 1 equiv of Cr^{2+} reduces $Rh_2(bridge)_4Cl_2^{2+}$ to $(1/n)[Rh_2(bridge)_4Cl^{2+}]_n + Cl^-$, and 1 equiv of Ce^{4+} $(+Cl^-)$ reacts with $(1/n)[Rh_2(bridge)_4Cl^{2+}]_n$ to produce $Rh_2(bridge)_4Cl_2^{2+}$ (Sigal, I. S.; Gray, H. B., to be submitted for publication).

(4) Higher sulfate concentrations result in spectral shifts consistent with sulfate binding; thus, $\lambda_{max} = 590$ nm in 32 N H_2SO_4. We distinguish ligation from ion pairing, which our data suggest to be extensive for $N(H_2SO_4) > 10^{-2}$.

(5) (a) Flash photolysis experiments at Santa Cruz employed a homemade apparatus. Dilute (10^{-6}–10^{-5} M) degassed samples held in 15-cm pathlength cells were excited by a coaxialed xenon flash lamp (output ≤ 90 J, $\tau_{1/2} \sim 20$ μs), and monitored with a DC quartz/iodine lamp whose output was filtered to isolate appropriate spectral regions. (b) Laser flash photolysis measurements were made at the University of Southern California on an instrument that has been described previously (Gutierrez, A. R.; Adamson, A. W. *J. Phys. Chem.* **1978,** *82*, 902).

(6) Decay was second order for over 5 half-lives, and the rate constant was independent of total rhodium concentration and flash pulse intensity.

(7) The rate is nearly independent of ionic strength for >1 N H_2SO_4.

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(10) Scatchard, G. *Chem. Rev.* **1932**, *10*, 229–240.

(11) Fe(II) product was determined as the tris(*o*-phenanthroline) complex. The quantitative formation of the Rh(II) product, which has been independently characterized as the product of Ce(IV) thermal oxidation of the H_2SO_4(aq) solutions and has an absorption maximum at 311 nm (ε 33 600), was determined by the spectral changes that occur during the photoreaction, and by the clean reduction back to starting material that occurs upon addition of a large excess of Fe^{2+}.

(12) Assuming our kinetic scheme (eq 1, 2, 4), the limiting product quantum yield for (3) should be twice the primary quantum yield ϕ_0 for (1). Therefore, $\phi_0 \simeq 0.01$. Measurements of ϕ_0 from the magnitude of transient signal in the flash photolysis experiments were in reasonable agreement. The transient quantum yield increases at lower ionic strength and is much larger in CH_3CN, suggesting that cage recombination is important.

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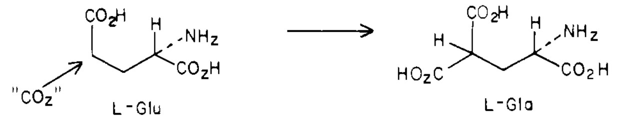
A Simple Synthesis of L-γ-Carboxyglutamate and Derivatives Thereof

Sir:

The curious amino acid, L-γ-carboxyglutamate (Gla), has been encountered in several of the vitamin K dependent blood clotting factors, including prothrombin.[1] Activation of prothrombin to thrombin apparently involves preliminary calcium ion mediated binding of the former to membrane phospholipids,[2] thereby increasing the effective concentrations of the necessary factors. Gla units, which comprise 10 of the first 38 amino acid residues in prothrombin, are thought to be implicated in the calcium binding sites of prothrombin.[3]

Not surprisingly, interest in the chemical synthesis of Gla (and derivatives that are suitably modified for convenient incorporation in peptides) has been high. Early approaches, however, resulted in racemic products.[4] Schwyzer did report the resolution of a synthetic Gla derivative,[5] as well as a multistep preparation of another optically active analogue by a chirally specific Strecker-like reaction.[6]

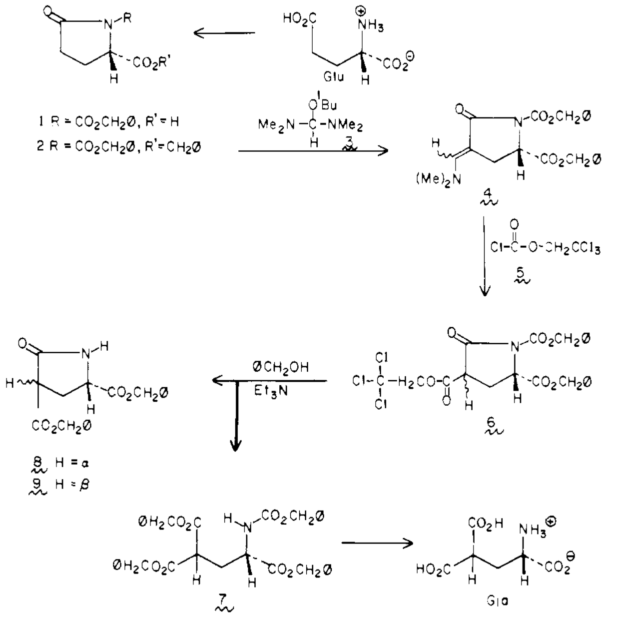
It was our intention to solve the challenge implicit in the synthesis of L-Gla by providing for the introduction of a carboxyl group on the 4 position of the readily available L-glutamic acid (L-Glu), while preserving its *S* chirality. The successful realization of this goal is described below.



Our starting material was the commercially available (Sigma) Glu derivative, *N*-carbobenzyloxy-L-pyroglutamate (**1**), which was converted (triethylamine–benzyl chloride–acetone) into the benzyl ester **2**: mp 107–108 °C; $[\alpha]_D$ −40.7° (*c* 1.1, ethanol); lit.[7] mp 110 °C; $[\alpha]_D$ −39.5°; 93% yield. Compound **3** reacts with Bredereck's reagent, **3**[8,9] (3 equiv of **3**; dimethoxyethane; 70 °C; 3.5 h), to afford a 95% yield of enamine **4**[10a,b] (mp 92–93°; $[\alpha]_D$ −32.8° (*c* 1.4, chloroform), which is apparently a single compound, though of undetermined geometric configuration (see Scheme I). An interesting transformation ensues when **4** is exposed to the action of 2,2,2-trichloroethoxycarbonyl chloride (**5**) (3 equiv of **5** in benzene; reflux; 36 h). Filtration and silica gel chromatography afford a 41% yield of the diastereomeric lactams, **6**.[10a] *It should be emphasized that this transformation was discovered by chance in a closely related series and its scope and limitations have not yet been ascertained.*

Compound **6** was treated with excess benzyl alcohol in the presence of triethylamine (3.80 g of **6**; 150 mL of benzyl alcohol; 0.5 mL of dry triethylamine; 104 °C; 27 h). Evaporation of the excess benzyl alcohol followed by chromatography of the residue on silica gel afforded the tribenzyl ester of N-Cbz-Gla (**7**):[10a] $[\alpha]_D$ +7.8° (*c* 1.6, $CHCl_3$); 62% yield. The infrared and NMR spectra as well as the chromatographic mobility of **7** were identical with those of an authentic sample of the racemic product, prepared according to Weinstein[4f] and

Scheme I



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