

The phosphorescence of in aqueous solution is quenched by 1,1'-bis(2-sulfoethyl)-4,4'-bipyridinium inner salt (BSEP). Transient absorption attributable to BSEP⁻ ($\lambda_{\max} \sim 610 \text{ nm}$)¹⁹ is observed in flash kinetic spectroscopic studies of aqueous solutions containing $\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8^{4-}$ and BSEP, thereby establishing an electron-transfer quenching mechanism:



Stern-Volmer analysis of the quenching yields $k_q = 5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ($[\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8^{4-}] \sim 10^{-4} \text{ M}$; 0.1 M NaClO_4 ; 25°C). Both the quenching reaction and the bimolecular back-electron-transfer ($k = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8^{3-}$ and BSEP⁻) are near the diffusion limit for such processes in aqueous solution at 25°C .

The $^3A_{2u}(\text{d}\sigma^*\text{p}\sigma)$ state of $\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8^{4-}$ is an extremely powerful one-electron reductant in aqueous solution. Preliminary experiments have shown that species such as $\text{Os}(\text{NH}_3)_5\text{Cl}^{2+}$ ($E_{1/2} = -1.09 \text{ V vs. SCE}$)²⁰ and nicotinamide ($E_{1/2} = -1.44 \text{ V vs. Ag/AgCl}$; CH_3OH , pH 7.2)²¹ are readily reduced by Pt_2 -

(19) Maverick, A. W. Ph.D. Thesis California Institute of Technology, 1982.

(20) Gulen, J.; Page, J. A. *J. Electroanal. Chem.* **1976**, *67*, 215-230.

(P_2O_5) $_4\text{H}_8^{4-*}$. From these and related experiments it is apparent that $\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8^{4-*}$ is a stronger reducing agent [$E^\circ(3-/4-*) < -1 \text{ V vs. NHE}$]²² than $\text{Ru}(\text{bpy})_3^{2+*}$ ($E^\circ = -0.88 \text{ V vs. NHE}$)²³ in aqueous solution. We are now exploring several aspects of the photoredox chemistry of $\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8^{4-}$, as the ease of generation of $\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8^{4-*}$ suggests that it will be a useful reagent for a variety of substrate reductions.

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(21) Meites, L.; Zuman, P.; Scott, W. J.; Campbell, B. H.; Kartos, A. M. "Electrochemical Data"; Wiley, New York, 1974; Part 1, AG85.

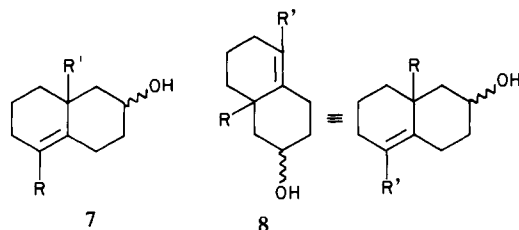
(22) It has not been possible to obtain a better estimate of $E^\circ(4-*/3-)$ from spectroscopic and electrochemical measurements, because the electrochemical oxidation of $\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8^{4-}$ in aqueous solution at 25°C is not reversible (cyclic voltammetric measurements; graphite electrode; scan speed, 500 mV/s ; $\text{K}_4[\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8]$, 0.1 M NaClO_4).

(23) Navon, G.; Sutin, N. *Inorg. Chem.* **1974**, *13*, 2159-2164.

Additions and Corrections

On the Nonconcertedness of Allylic Cation Promoted π -Cyclization Reactions [*J. Am. Chem. Soc.* **1981**, *103*, 1285]. MLADEN LADIKI, IVO BREGOVEC, and DIONIS E. SUNKO,* Department of Chemistry, Faculty of National Sciences and Mathematics, University of Zagreb, 41000 Zagreb, Yugoslavia.

Page 1286: Structures 7 and 8 should be:



Stereochemical Analysis of γ -Replacement and γ -Elimination Processes Catalyzed by a Pyridoxal Phosphate Dependent Enzyme [*J. Am. Chem. Soc.* **1981**, *103*, 4921]. MICHAEL N. T. CHANG and CHRISTOPHER T. WALSH,* Departments of Chemistry and Biology, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

Page 4925, Scheme VII: The last species is 4-S-2-ketobutyrate, not 4R as written.

Page 4925, 5th and 6th lines from the bottom, first column: The text should read "conversion of (Z)- and (E)-[4-²H]-vinyl-

glycines to (4S)- and (4R)-[¹H,²H,³H]-2-ketobutyrate, respectively, can be interpreted." The S and R designations were inadvertently transposed.

Page 4923, Table II, line 3: The numbers 1027.5 and 1029.3 are incorrectly transposed. The (E)-[4-²H]-vinylglycine yields the 1029.3 sample of homoserine, the (Z)-vinylglycine yields the 1027.5 sample.

Synthesis, Structure, and Stability of (i,o)-Bicyclo[6.2.2]dodeca-9,11-dienes. Generation of Unusually Expanded Carbon-Carbon Bond Angles [*J. Am. Chem. Soc.* **1981**, *103*, 215]. PAUL G. GASSMAN* and REBECCA C. HOYE, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455.

Page 217: In Table II for atom O2, the z value should be 0.4691 (1) instead of 0.4961 (1).

α -Disulfoxide and Sulfinic Anhydride in the Peroxy Acid Oxidation of 2-Methyl-2-propyl 2-Methyl-2-propanethiosulfinate [*J. Am. Chem. Soc.* **1981**, *103*, 6232-6235]. FILLMORE FREEMAN* and CHRISTOS N. ANGELETAKIS, Department of Chemistry, University of California, Irvine, California 92717.

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