to give a Pt(IV) silyl-silylene intermediate. Similar α-silyl shifts have been proposed by Pannell and by Ogino in photochemical reactions of polyisilyle ion complexes. However, an alternative route is via π-disilene intermediates, followed by fast back-reaction with dihydrogen. Stable platinum π-disilene complexes have been reported by Pham and West to undergo facile hydrogenolysis of the silicon–silicon bond to yield platinum bis(silyl)s. Investigations into the nature of this process are currently in progress.

Acknowledgment. M.J.F. thanks the Tulane Center for Biomolecular Research and the Tulane Committee on Research for support of this work. We also thank Drs. Fred Davidson and Joseph Lazar (Du Pont) and Drs. Brian Tobias and Deborah A. Grimm (Tulane University Instrumentation Facility) for assistance with NMR and mass spectra. The expert technical assistance of Chris Adams, Will Marshall, and John Nguyen is greatly appreciated.

Supplementary Material Available: Listings of NMR, MS, and elemental analysis data, tables of crystal data, atomic coordinates and temperature factors, hydrogen coordinates, and intramolecular bond distances and angles (12 pages); tables of calculated and observed structure factors of 3 (19 pages). Ordering information is given on any current masthead page.

Selective-Solvation-Induced Intramolecular Electron Transfer: Time Resolution via Pulsed Accelerated Flow Spectroscopy

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Received November 25, 1991
Revised Manuscript Received August 3, 1992

Despite extensive theoretical interest, relatively few experimental reports exist concerning nonphotochemical intramolecular electron-transfer (ET) kinetics, at least for chemically reversible (i.e., thermodynamically well-defined) redox systems. Nevertheless, the few that do exist have yielded important insights concerning donor-acceptor electronic coupling and solvent reorganization, especially over longer distances. We wish to report here an experiment which adds in an unusual way to the limited list of both chemical systems and chemical methodologies for inducing intramolecular ET. Our approach is based on the ability of added solvent to influence redox potentials, and therefore oxidation-state distributions, in selected asymmetric mixed-valence systems.

The system we have examined is a trimethylenebipyridine-bridged ruthenium-osmium complex (I) in nitromethane (NM) as the parent solvent:

As shown by Figure 1, addition of as little as 4 vol % dimethyl sulfoxide (DMSO) is sufficient to convert the visible absorption spectrum from one largely characteristic of (NH₃)₅Ru⁺⁺(pyridine-CH₃) to one indicative of the presence of a [(bpy)₂ClO₄⁻]⁻ fragment. (Note that the metal(III) fragments are nearly transparent in the green and red portions of the spectrum.) Quantitative spectral experiments show that, when 4% DMSO is present, redox trapping at Os is favored by 16-fold (ΔG° = −1.6 kcal mol⁻¹) over trapping at Ru. From previous studies the redox isomerization is known to arise from negative shifts in the Ru(III) oxidation state via specific ammine/solvent interactions. To time resolve the electron transfer we have employed a rapid (microsecond) mixing technique: pulsed accelerated flow (PAF) spectroscopy. PAF is a highly efficient (in terms of time and reagent consumption) multiple-velocity variant of continuous flow spectrophotometry and has been described in detail by Margerum and co-workers. In our experiments a solution of I in 100% NM was rapidly mixed with a solution containing 72% NM, 20% CH₃CN, and 8% DMSO. (Acetonitrile was required in order to achieve refractive index matching and eliminate Schlieren scattering effects which can accompany mixing.) The
progress of the reaction was monitored at 720 nm (appearance of Os(III), see Figure 1).

In the flow experiment, the appearance kinetics can be modeled by consecutive mixing and ET processes. (Microscopic re-solution is viewed, in this case, as faster than either.) Following Margerum, the appropriate transient absorbance expression is

$$A = \frac{A_0 - A_e}{A_0 - A_r} = 1 - e^{-Y}$$

where

$$Y = \frac{1}{b} \left( \frac{1}{k_{mixing}} + \frac{v}{k_{ET}} \right)$$

In the expression, $b$ is the reaction path length, $v$ is the flow velocity, and $A_0$, $A_r$, and $A_e$ are initial, intermediate, and final absorbances. For $1.4 \times 10^{-3} \text{M}$, measurements of $M_{ets}$ at each of 250 separate velocities (per push) between 3.5 and 12.5 meter s$^{-1}$ yielded $k_{ET} = 136 \pm 18$ s$^{-1}$.[10] Follow-up experiments with a 9-fold variation in reactant concentration overall yielded nearly identical ET kinetics, confirming the intramolecular (i.e., first-order) nature of the reaction. Finally, it should be noted that the observed ET rate falls well below the upper rate measurement limit of the current instrument (ca. $2 \times 10^8$ s$^{-1}$).[9]

A detailed comparison of this rate with the predictions of contemporary theory is clearly of interest, but is necessarily beyond the scope of the current paper. It is worth noting, however, that simple composite models suggest a metal-to-metal separation distance of ca. 16Å (fully extended bridged) and that thermal charge transfer over a similar distance in an isoproline-linked Os/Ru complex yields much faster kinetics ($k_{ET} = 3 \times 10^9$ s$^{-1}$).[2] For the isoproline case both the solvent and the Os coordination environment differ. The ligand environments for the ruthenium centers, however, are similar. For the two systems, driving-force effects should account for about a factor of 5 in reactivity difference. The balance may be due to a combination of (1) unique barrier effects associated with microscopic re-solution, and (2) enhanced nonadiabaticity effects associated with formal re-orthogonality effects along the length of the TMB bridging ligand. In addition to the theory comparisons, current work focuses on bridge modifications and on systematic driving-force variations. Indeed, the ability to employ solvent to obtain a continuously adjustable range of driving forces (and rates) may be the most promising feature of the new method.

Acknowledgment. We thank Prof. Dale Margerum and his students at Purdue University for generous and helpful advice on construction of the pulsed accelerated flow spectrophotometer and Matt Todd at Northwestern for computational assistance. We gratefully acknowledge support from the Department of Energy, Office of Energy Research, Division of Chemical Sciences (Grant No. DE-FG02-87ER13808). The PAF instrument was constructed with funds from an NSF equipment grant (CHE-8710014) and from a Presidential Young Investigator Award. J.A.R. acknowledges a Joseph W. Richards Fellowship from the Electrochemical Society. J.T.H. acknowledges support as an Alfred P. Sloan Fellow (1990–1992) and a Dreyfus Teacher–Scholar (1991–1996).

Supplementary Material Available: Figure S1 showing representative $M_{ets}$ vs velocity data for a single PAF push (1 page). Ordering information is given on any current masthead page.

Reductively Activated Mitomycin C: An Efficient Trapping Reagent for Electrophiles

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Received May 29, 1992

Mitomycin C, a clinically significant antineoplastic antibiotic, is considered to be the prototype of the bioreductive alkylating agents. Studies with models of mitomycin C and DNA restriction fragments documented that I selectively binds to the nucleophilic 2-aminosite of specific guaines.[2–5] It is accepted, however, that mitomycin C undergoes both C(1)-nucleophilic and electrophilic substitution transformations under aqueous reductive conditions in the absence of external nucleophiles (Scheme 1).[6] Investigations have shown that when the pH was above 7, the C(1)-nucleophilic adducts cis- and trans-1-hydroxy-2,7-diaminomitosenes[4] were produced almost exclusively, and when conditions were moderately acidic, the electrophilic adduct 2,7-diaminomitosene[5] predominated. It has been suggested that quinone methide[6,7] served as the central precursor to both 4 and 5. In this communication, we provide evidence that reductively activated mitomycin C functions primarily as a trapping agent for electrophiles in water at all operational pH values and that this pattern is altered only when nucleophiles are added under select conditions. The origin for previous misconceptions concerning the reactivity of reduced I has been identified.

Plots are provided in Figure 1 for the percentage of C(1)-electrophilic mitosenic products generated as a function of pH using two different Na$_2$S$_2$O$_4$-mediated reductive conditions (HPLC analysis, protocol 1). In method A, only 0.2 equiv of Na$_2$S$_2$O$_4$ was used, thereby ensuring substantial levels (≥64%) of unreduced 1. In method B, we employed excess Na$_2$S$_2$O$_4$ (1,2–2.0 equiv). Under these conditions, I accounted for less than 11% of the


(10) HPLC conditions using C$_{18}$ bonded (SOP) column 3.9 mm × 30 cm. (a) Protocol 1: linear gradient from 100% A (3 mM triethylammonium phosphate, pH 4.7) to 6% B (3 mM triethylamine in acetonitrile) to 50% A, 50% B in 35 min. (b) Protocol 2: isocratic for 5 min 98% A (0.1 M triethylammonium acetate, pH 6.5), 10% B (acetonitrile) and then linear gradient from 90% A, 10% B to 50% A, 50% B in 20 min.