cyanophenyl serves as a useful probe of excited-state electron distribution in the same way as in ground-state systems.
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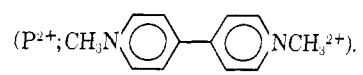
Kinetic Relaxation Measurement of Rapid Electron Transfer Reactions by Flash Photolysis. The Conversion of Light Energy into Chemical Energy Using the $Ru(bpy)_3^{3+}$–$Ru(bpy)_3^{2+}$* Couple

Sir:

There is growing evidence that the excited states of certain transition metal complexes can be quenched by electron transfer. Electron transfer quenching is potentially of importance in energy conversion, especially for metal complexes since they often absorb strongly in spectral regions of maximum solar insolation.

Quenching processes involving the excited states of tris(2,2′-bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$*, have been particularly well studied.[1-6] It has been found, for example, that net electron transfer occurs from $Ru(bpy)_3^{2+}$* to such oxidants as $Fe(H_2O)_6^{3+}$,[3] Tl(III),[5] $Ru(NH_3)_6^{3+}$,[3,4] and paraquat[3]



Flash photolysis and emission quenching studies have shown that $Ru(bpy)_3^{2+}$* can be quenched at, or near, the diffusion-controlled limit (eq 2), and that the quenching step is followed by a rapid thermal electron transfer reaction (eq 3).[3]

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} Ru(bpy)_3^{2+*} \quad (1)$$

$$Ru(bpy)_3^{2+*} + P^{2+} \longrightarrow Ru(bpy)_3^{3+} + P^{+} \quad (2)$$

$$(k = 2.4 \times 10^9\ M^{-1}\ sec^{-1})^3$$

$$Ru(bpy)_3^{3+} + P^{+} \longrightarrow Ru(bpy)_3^{2+} + P^{2+} \quad (3)$$

$$(k = 8.3 \times 10^9\ M^{-1}\ sec^{-1})^3$$

By combining eq 1, 2, and 3 under conditions where (3) becomes rate determining, the flash photolysis experiment can be used as a relaxation technique for measuring the rates of very rapid electron transfer reactions.[3]

A more general relaxation scheme can be devised if two *different* redox couples can be made to participate in reactions like 2 and 3. The thermodynamic limitations on such a scheme can be estimated from available reduction potential data (Table I). Estimates for the excited state couple, $Ru(bpy)_3^{3+}$–$Ru(bpy)_3^{2+}$*, are available from spectroscopic data[4] and from a recent quenching study using a series of neutral quenchers.[6]

From the data in Table I, it can be predicted that if a solution initially containing $Ru(bpy)_3^{2+}$, NPh_3, and P^{2+} is subjected to flash photolysis, the sequence of reactions outlined in Scheme I will occur. If reaction 4 can be made more rapid than reaction 3, the combination of reactions 1, 2, and 4 gives reaction 6 in which a chemical reaction has been driven in the nonspontaneous direction using light energy.

Table I. Reduction Potential Data in Acetonitrile Solution

Couple	E, V[a]
$Ru(bpy)_3^{3+} + e \rightarrow Ru(bpy)_3^{2+}$	1.29[b]
$NPh_3^{+} + e \rightarrow NPh_3$	1.00[c]
$P^{2+} + e \rightarrow P^{+}$	−0.45[d]
$Ru(bpy)_3^{3+} + e \rightarrow Ru(bpy)_3^{2+*}$	−0.81[6]

[a] At 25 ± 2°; in 0.1 M $Et_4N^+ClO_4^-$, or $(n\text{-}Bu)_4N^+ClO_4^-$, or $(n\text{-}Bu)_4N^+PF_6^-$–acetonitrile solutions. [b] G. M. Brown, Ph.D. Thesis, University of North Carolina, Chapel Hill, N.C., 1974. [c] S. C. Creason, J. Wheeler, and R. F. Nelson, *J. Org. Chem.*, 37, 4440 (1972). [d] A. Ledwith, *Acc. Chem. Res.*, 5, 133 (1972).

Scheme I

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} Ru(bpy)_3^{2+*} \quad (1)$$

$$Ru(bpy)_3^{2+*} + P^{2+} \longrightarrow Ru(bpy)_3^{3+} + P^{+} \quad (2)$$

$$Ru(bpy)_3^{3+} + NPh_3 \longrightarrow Ru(bpy)_3^{2+} + NPh_3^{+} \quad (4)$$

$$NPh_3^{+} + P^{+} \longrightarrow NPh_3 + P^{2+} \quad (5)$$

$$NPh_3 + P^{2+} \xrightarrow{h\nu} NPh_3^{+} + P^{+} \quad (6)$$

In an actual experiment, a 0.1 M $(n\text{-}Bu)_4N^+ClO_4^-$–acetonitrile solution which contained $Ru(bpy)_3^{2+}$ ($\sim 2 \times 10^{-5}$ M), P^{2+} (2.0×10^{-3} M), and NPh_3 (2.0×10^{-3} M) was flashed at 410 nm $< \lambda <$ 500 nm. The resulting spectral changes were monitored at a series of wavelengths from 380 to 700 nm. Absorption maxima for P^+ (395 and 603 nm) appeared rapidly, and their disappearance followed second-order, equal-concentration kinetics for two-three half-lives. In a similar experiment using NPh_2H as reductant, direct spectral evidence was obtained for the presence of both P^+ and NPh_2H^+ (λ_{max} 680 nm).[7] After the flash, no spectral changes were observed at 450 nm (λ_{max} for $Ru(bpy)_3^{2+}$). The reaction observed with NPh_3 present must be eq 5 and with NPh_2H present, eq 7.

There were no permanent spectral changes in the solutions after a series of flash photolysis experiments.

$$NPh_2H^{+} + P^{+} \longrightarrow NPh_2H + P^{2+} \quad (7)$$

The combination of flash photolysis and the series of reactions in Scheme I leads to a kinetic relaxation technique for measuring the rates of rapid, thermodynamically highly allowed, reactions. Rate constants for reactions 5 and 7 were $4.5 \times 10^9\ M^{-1}\ sec^{-1}$ (NPh_3) and $5.3 \times 10^9\ M^{-1}\ sec^{-1}$ (NPh_2H) at room temperature. The technique is potentially a general one with regard to the excited states and redox couples used, however, the potentials for the redox couples must fall between the ground and excited state potentials for the absorbing species. In practice, the technique is limited by several factors including: (1) efficient energy transfer quenching by either oxidant (P^{2+} in the scheme) or reductant (NPh_3), (2) numerically small rate constants for reactions like 2 and 4 when compared to 5, or much faster rates for reactions like 3 compared to 5, (3) instability of the components in the system, (4) overly competitive light absorption by either quencher or reductant, (5) an inability to observe redox products in the quenching step.[6]

The set of reactions in Scheme I is remarkable in that light energy is used to drive a highly favored redox reaction in the nonspontaneous direction, even though neither reac-

tant absorbs appreciably in the region photolyzed. In the case of reaction 5, $\Delta G^{\circ\prime} = 1.45$ V, which means that 69% of the excited state energy of $Ru(bpy)_3^{2+*}$ has been converted into chemical energy. Scheme I represents a useful inorganic model for photosynthesis. Ultimately, a related sequence of reactions may lead to the permanent storage of light energy as chemical energy.

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References and Notes

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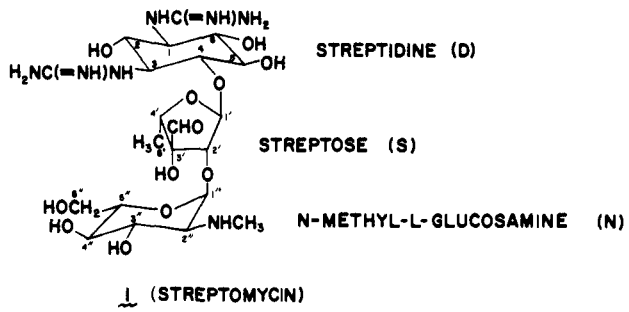
Carbon-13 Evidence for the Stereochemistry of Streptomycin Biosynthesis from Glucose[1,2]

Sir:

Streptomycin (**1**), the antibiotic produced by *Streptomyces griseus*, remains a medically important antibiotic. Studies in recent years[3] have argued for glucose as the precursor of all three subunits of streptomycin–streptidine, streptose, and *N*-methyl-L-glucosamine. Extensive chemical degradations of the latter two ^{14}C-labeled units of streptomycin indicate direct conversion of all carbons of glucose to like-numbered carbons of *N*-methyl-L-glucosamine[4] and conversion of carbons 1, 2, 4, 5, and 6 of glucose to carbons 1′, 2′, 3′, 4′, and 5′, respectively, and carbon-3 to the formyl carbon, of streptose.[5] However, the only reported degradation of ^{14}C-labeled streptidine involved periodate cleavage of *N,N*′-dibenzoylstreptamine following labeled glucose feeding.[6] These studies indicated that a majority (68,[6a] 83%[6b]) of the label was lost as formic acid, presumably from C-5 of streptidine, when [1-^{14}C]glucose was administered and that a majority of the label was retained in the cyclic dialdehyde hydrate when [2-^{14}C]-, [3,4-^{14}C]-, or [6-^{14}C]glucose was employed. This labeling pattern has been used in support of a biosynthetic pathway involving conversion of glucose to *scyllo*-inosose (**2**, Figure 1). Subsequent steps from **2** have been shown to involve its transamination, phosphorylation, and transamidination to guanidodeoxyinositol, and repetition of the keto → guanido steps at the β-carbon in the counterclockwise direction (path A), yielding streptidine (**3**).[7]



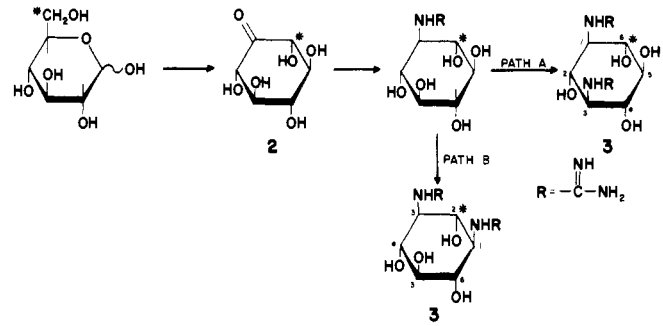
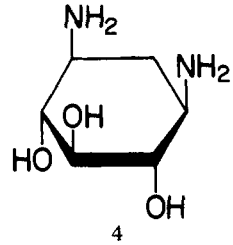


Figure 1. Biosynthetic conversion of glucose to streptidine via *scyllo*-inosose (**2**), with C-6 of glucose labeling C-6 of streptidine by path A, that apparently employed by *S. griseus*. Path B is not followed for streptidine formation but would be analogous to the pathway employed for deoxystreptamine formation by *S. fradiae*.[2b] The asterisks indicate the carbons expected to arise in each pathway from C-6 of glucose.

Unfortunately, no other carbons of streptidine have been correlated with its glucose precursor. For example, even if [1-^{14}C]glucose gives [5-^{14}C]streptidine, [6-^{14}C]glucose could label either C-4 or C-6 of streptidine. Moreover, we have recently found[2b] that deoxystreptamine (**4**) is formed



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in *Streptomyces fradiae* by an alternative to pathway A which apparently involves oxidation at the β-carbon in the clockwise direction (Figure 1, path B) followed by transamination. With pathway B operative in a closely related aminocyclitol, and in view of the occasional unreliability[8] of periodate oxidation[6] as a structural tool, it seemed advisable to define further the conversion of glucose to streptidine by reinvestigating the biosynthesis of streptidine using a ^{13}C-labeled precursor. We report here our results with [6-^{13}C]-D-glucose, which we have now shown to label carbon-6 of streptidine (pathway A).

A seed culture of *Streptomyces griseus* (MA-4583) was produced in the following medium: corn steep liquor, 30 g/l.; brewer's yeast, 1 g/l.; NZ-Amine, 0.5 g/l.; distilled water to 1 l. (final pH 7.3). Growth was carried out for 2 days at 28°, at which time the seed was used to inoculate six 250-ml erlenmeyer shakeflasks, with each flask containing 40 ml of the following synthetic medium: 31.86 g/l. of glucose (containing 3.86 g/l. of [6-^{13}C]glucose[2b] (64 atom %)); diammonium citrate, 10 g/l.; monosodium glutamate, 2.0 g/l.; K_2HPO_4, 0.5 g/l.; NaCl, 2.5 g/l.; $CaCO_3$, 1.0 g/l.; $MgSO_4 \cdot 7H_2O$, 1.0 g/l.; $FeSO_4 \cdot 7H_2O$, 0.02 g/l.; $ZnSO_4 \cdot NH_2O$, 0.01 g/l.; distilled water to 1 l. (pH 7.3). The culture was incubated on a rotary shaker (220 rpm) for 6 days at 28°, then filtered and acidified with phosphoric acid. The total filtered broth (205 ml) was diluted and passed through a CG-50 column in the NH_4^+ form. Elution with 1 *N* formic acid gave crude labeled streptomycin which was purified via the Reineckate salt.[9]

The ^{13}C NMR spectra of streptomycin show resonances for each of the 21 carbons, which will be assigned in a following communication.[10] The ^{13}C NMR spectrum of the