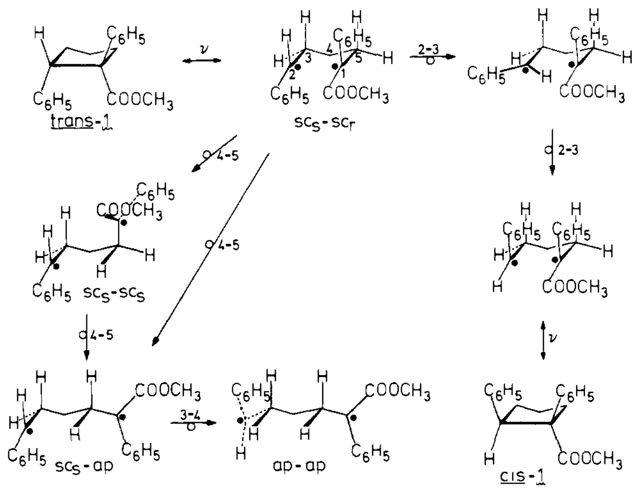

Figure 1. The path from *trans*-**1** to *cis*-**1** passes through the vibrational diradical, sc_s–sc_r, and over the continuous diradical as transition state by a C_2–C_3 internal rotation. The conformations on the lower left represent three of the five intermediary diradicals protected by the ~3-kcal/mol barriers around C_3–C_4 and C_4–C_5. [sc = synclinal; ap = antiperiplanar; subscripts s and r = left- and right-handed helix; 3–4 on arrow = rotation about bond between C_3 and C_4; ν over arrow = stretching vibrational mode.]

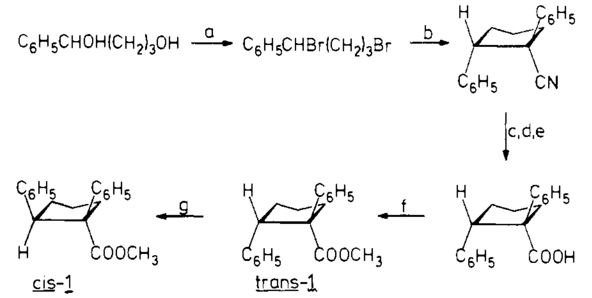

Figure 2. The synthesis of optically active *trans*-**1** is shown: (a) PBr_3; (b) phenylacetonitrile/C_6H_5–$CH_2N(C_2H_5)_3Cl$/NaOH; (c) diisobutylaluminum hydride; (d) tetra-*n*-butylammonium permanganate; (e) quinine; (f) diazomethane; (g) 400 °C, 15 min.

the nitrile until a two-step, reductive–oxidative procedure was developed. Even here, the highly hindered intermediate aldehyde resisted oxidation by conventional procedures, but could be oxidized by permanganate under conditions of phase transfer.[7]

The structure of *trans*-**1** rests on the method of synthesis, the exact mass (*m/e* 280.1465), the NMR [δ 7.45–7.20 (m, 10), 3.89 (dd, 1, J = 7.91, 13.84 Hz), 3.25 (s, 3), 2.21 (m, 1), 2.15 (m, 4), 2.12 (m, 1)], and the IR (1700 cm^{-1}) spectra.

cis-**1** is obtained in 39% yield on heating *trans*-**1** at 400° C for 33 min in decalin containing diphenylamine (50% of *trans*-**1** recovered) (the same result is obtained in the absence of diphenylamine and in diphenyl ether as solvent with or without diphenylamine): *m/e* 280.1465; NMR δ 7.14–6.85 (m, 10), 4.11 (t, 1, J = 7.2 Hz), 3.67 (s, 3), 2.62–2.56 (m, 2), 2.55–1.84 (m, 4); IR 1700 cm^{-1}.

The rearrangement is not effected, nor is deuterium incorporated in recovered *trans*-**1**, when *trans*-**1** is heated in perdeuterotoluene at 200 °C with 1 mol equiv of di-*tert*-butylperoxide.

In the presence of $Eu(fod)_3$, the benzylic hydrogen atom in *trans*-**1** shows a lanthanide-induced shift (LIS) of 0.80 relative to CH_3O as 1.00, while *cis*-**1** shows a relative shift of 1.44. The chiral LIS reagent, $Eu(hfbc)_3$, in perdeuterocyclohexane splits the CH_3O in *rac*-*trans*-**1** and *rac*-*cis*-**1** but gives good base-line separation only with the latter.

Resolution of the trans acid is effected partially by the quinine salt and is completed by recrystallization (CH_3OH) of the free acid to constant rotation: $[\alpha]^{25}_{589}$ −182° (*c* 0.733, $CDCl_3$). The enantiomer is obtained from the mother liquors: $[\alpha]^{25}_{589}$ +180° (*c* 0.508, $CDCl_3$).

Thermal rearrangement of optically active *trans*-**1** (0.207 g; $[\alpha]^{25}_{589}$ −132°; 73% of optical purity) in decalin (3.4%) containing 0.24 mol equiv of diphenylamine is effected by heating for 15 min at 400 °C. Analysis by capillary GLC of volatile recovered material (87%) shows 20.2% *cis*-**1** (>99.9%; $[\alpha]^{25}_{589}$ +20.1°; 40% of optical purity by chiral LIS), 65.2% recovered *trans*-**1** (containing 0.9% (+)-*cis*-**1**; $[\alpha]^{25}_{589}$ −93.3°; 52% of optical purity (corrected); 14.5% enantiomerization); and 14.6% unidentified products.

Corrected for 73% optical purity of starting *trans*-**1**, *cis*-**1** consists of 77.4% (+) and 22.6% (−), corresponding to an R_A factor of 3.4. When corrected for partial racemization of *trans*-**1** by assuming an average optical purity of *trans*-**1** of 62.5%, R_A becomes 4.5.

The dramatic degree to which chirality is retained in the face of unprecedented flexibility of the cyclopentadiyl system is understandable, if not uniquely so, in terms of the continuous diradical hypothesis outlined in Figure 1. To the extent that leakage over the 3 kcal/mol barriers aggravates enantiomerization in *cis*-**1** and recovered *trans*-**1** by generating intermediary diradicals, trapping by the likes of thiophenol becomes an exciting possibility.

Acknowledgment. We gratefully acknowledge that this material is based upon work supported by the National Science Foundation under Grant CHE-80-19427.

Registry No. (−)-**1**, 87883-15-6; (+)-**1**, 87883-16-7.

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Surface-Enhanced Raman Scattering Study of Bipyridyl-Modified Ag Electrodes

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We have observed enhancement of the electron-transfer rate between cytochrome *c* and a Ag electrode in the presence of 4,4′-bipyridine and have studied the origin of this effect using cyclic voltammetry and surface-enhanced Raman scattering (SERS) (a discussion of this technique may be found in references cited in ref 1). The results indicate that a Ag(I)–bipyridine complex forms on the electrode surface, and this complex has the appropriate redox properties to mediate cytochrome oxidation and reduction. This study illustrates an important application of SERS for the determination of chemical and mechanistic information about electrodes modified through adsorption.

Redox proteins generally exhibit poor electron-transfer kinetics at metal or semiconductor electrodes for reasons that are not well understood.[2] Cytochrome *c* has been one of the most frequently studied proteins by electrochemical techniques. Except in a few instances,[3] it behaves irreversibly in the absence of mediators. Recently, chemical modifications of electrode surfaces have been used to overcome the sluggish response of proteins at electrodes.[4]

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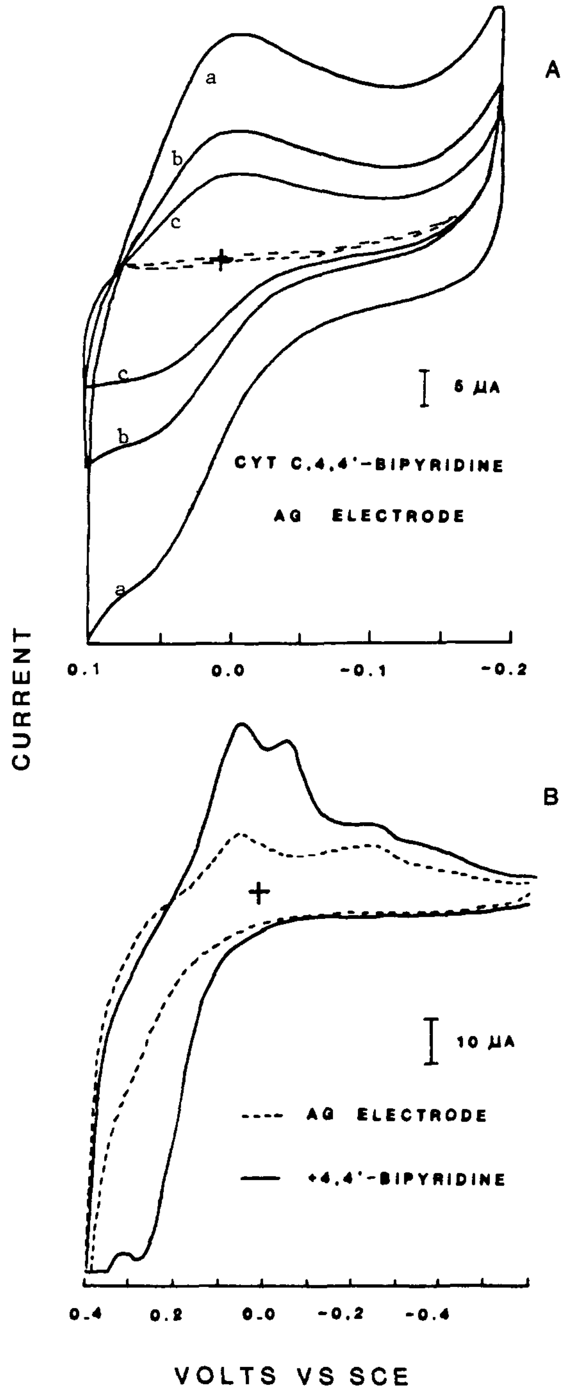

Figure 1. (A) Cyclic voltammogram of horse heart cytochrome *c* (4 × 10^{-4} M) in 0.1 M $NaClO_4$ and 0.1 M phosphate buffer (pH 7.0) (-----); same solution except with 1.0 × 10^{-2} M 4,4'-bipyridine added (—). Scan rates (a) 50, (b) 20, and (c) 10 mV/s; working electrode, Ag disk; auxiliary, Pt; reference, saturated NaCl, calomel (SSCE). Initial potential = −0.2 V; scan direction, anodic. (B) Cyclic voltammogram of a Ag electroode in above electrolyte–buffer solution (-----) and with 1.0 × 10^{-3} M 4,4'-bipyridine added (—). Scan rate = 10 mV/s. Cell and working electrode as described previously.[12]

Both covalent attachment of various mediators[5] and spontaneous adsorption of 4,4'-bipyridine on gold[6] or Pt[7] electrodes has resulted in improved kinetics. The 4,4'-bipyridine modification is of particular interest to us, since pyridine and its derivatives are known to produce strong SERS spectra.

Before examining the SERS behavior of 4,4'-bipyridine, we established that it functions on a Ag electrode in a manner analogous to that reported for Au[6] and Pt.[7] Figure 1A shows the cyclic voltammograms obtained for horse heart cytochrome *c* (Sigma Chemical Co,, type VI) in the presence of 1 × 10^{-2} M 4,4'-bipyridine (solid line) and in its absence (dashed line). The bipyridine clearly enhances the electron-transfer kinetics. Relevant electrochemical data include the following: $E_{1/2}$ = +0.03 V vs. SCE, anodic and cathodic peak separation = 63 mV for scan rate of 10 mV/s, and heterogeneous electron-transfer rate constant = 0.7 × 10^{-2} cm/s when calculated accoording to the procedure of Nicholson.[8] The latter value compares well to values observed for bipyridine-modified gold electrodes[6] and is significantly larger than values observed for other types of modifications.

The voltammetric response of the Ag electrode in the presence of 4,4-bipyridine (solid line) and in its absence (dashed line) was also examined (Figure 1B). The appearance of new peaks approximately 200-mV cathodic of the Ag oxidation and reduction peaks suggest that a Ag(I)–bipyridine complex is formed on anodization of the electrode. Ag(I)–bipyridine complexes have been prepared previously,[9] and a linear, two-coordinate structure has been postulated.[10] The overall stoichiometry of the solid is 1:1 Ag:bipyridine due to the tendency for the complex to form linear polymers with each bipyridine acting as a bridge between two Ag ions.

Further evidence for the formation of a Ag(I)–bipyridine complex was obtained from SERS data. Figure 2 shows spectra observed at three different electrode potentials (0.0, −0.8, and −1.4 V vs. SCE) following an oxidation–reduction cycle (ORC). This consisted of Ag oxidation at +0.45 V vs. SCE until 25 mC/cm^2 of charge had passed followed by reduction to Ag^0 at −0.6 V. The data are summarized in Table I. The following points are of particular importance. First, strong spectra are observed at each of the potentials shown, indicating that bipyridine is adsorbed and remains adsorbed throughout the potential range. Second, small shifts are seen in several bands as the electrode potential is made more negative (Figure 2, parts A and B).

These shifts are reversible with potential and are highly reproducible. Frequencies observed near 0.0 V correspond to those found for solid Ag(I)–bipyridine complex prepared according to Peard and Pflaum.[9] Frequencies observed at −0.2 V and more negative potentials are typical of uncomplexed bipyridine. Thus, the SERS data supports the electrochemical results and indicates the formation of a Ag(I)–bipyridine complex near 0.0 V, which is reduced to metallic Ag and adsorbed bipyridine at negative potentials (−0.2 V). The structure of the complex cannot be deduced from these data alone, but the similarity of the SERS spectrum with that of the solid complex suggests a linear, two-coordinate Ag(I) structure. Third, at very negative potentials (−1.4 V vs. SCE) the adsorbed bipyridine is reduced to an anion radical as evidenced by shifts in several bands to values observed for the anion radical in solution.[11]

The Ag–bipyridine-modified electrode was sufficiently stable that it could be removed from the SERS cell, placed in contact with a solution containing only cytochrome *c*, buffer, and electrolyte, and observed to exhibit reversible electron transfer with cytochrome *c* on repeated cycling between +0.1 and −0.2V. The cyclic voltammograms were identical with that shown in Figure 1A (solid line), indicating that the surface-bound bipyridine is responsible for the enhancement of electron-transfer kinetics.

In conclusion, the cyclic voltammetric and SERS data discussed above indicate that 4,4'-bipyridine forms a Ag(I) complex on Ag electrodes with the appropriate redox potential to mediate electron

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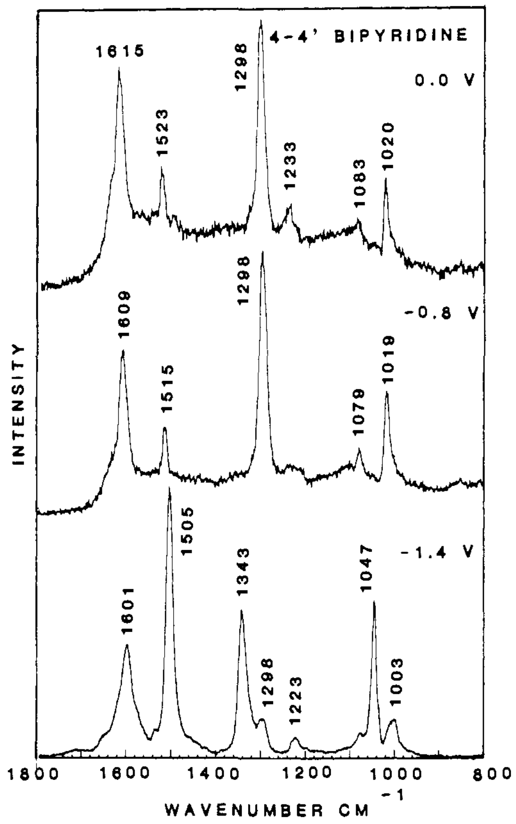

Figure 2. Surface-Enhanced Raman spectra of 4,4'-bipyridine adsorbed onto a Ag elctrode following the ORC described in the text as a function of electrode potential. Experimental procedure as described previously.[12]

Table I. Raman and SERS Vibrational Frequencies for 4,4'-Bipyridine and Its Ag Complex[a]

solid[b]	-0.8 V[c]	0.0 V[c]	Ag(I)-bipyridine[d]
1605	1609	1615	1617
1515	1515	1523	1529
1296	1298	1293	1293
1083	1083	1083	1083
998	1019	1020	1024

[a] Vibrational frequencies are in cm^{-1}. [b] Solid spectra were recorded in a 5-mm glass tube. [c] SERS spectra were recorded on anodized Ag electrodes as discussed in text. [d] Complex prepared according to Peard and Pflaum;[9] spectra recorded on solid in a 5-mm glass tube.

transfer between the electrode and cytochrome *c*. In addition, the 4,4'-bipyridine appears to inhibit adsorption of cytochrome *c* onto Ag, which is known to occur from previous studies.[12] The rapid displacement of cytochrome *c* from a Ag electrode by 4,4'-bipyridine can be monitored by SERS.[13] Finally, it should be noted that the mechanism proposed here for mediated electron transfer between a Ag(I)-bipyridine complex on Ag and cytochrome *c* is applicable to Ag only. The behavior of bipyridine on Au or Pt cannot be surmised from these results. However, since Au is also known to produce strong SERS, it should be possible to conduct a similar study of bipyridine-modified Au electrodes.

Acknowledgment. The support of the National Institutes of Health (GM 30240) is greatfully acknowledged by T.M.C.

Registry No. Ag, 7440-22-4; 4,4'-bipyridine, 553-26-4; cytochrome *c*, 9007-43-6.

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Isotope Effects as a Mechanistic Probe of Unimolecular Ion Decompositions. *tert*-Butoxide Anion

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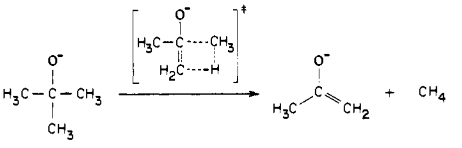
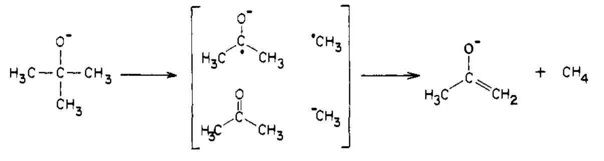
Although unimolecular reactions of gas-phase ions are important and are commonly observed, it is difficult to gain much mechanistic insight into how highly activated ions decompose.[1,2] We wish to report a detailed mechanistic study utilizing infrared multiphoton (IRMP) photochemistry[3] in an ion cyclotron resonance (ICR) spectrometer.[4] The mechanism of the IRMP-induced loss of methane from *tert*-butoxide ion to yield acetone enolate ion was probed by competitive kinetic isotope effects. The observation of unusually large secondary isotope effects (up to 6.9) and a small primary effect (1.6–2.0) is indicative of a stepwise mechanism involving bond cleavage as the first step and a subsequent hydrogen-transfer reaction from an intermediate ion-molecule complex.[5]

All experiments were performed on a pulsed ICR spectrometer.[6] The ICR spectrometer in which ions are generated, stored, irradiated, and studied temporally is well suited for IRMP photochemical studies, since experiments can be collisionless. Products and reactants are studied in situ following a single laser pulse.

Upon irradiation with the unfocused output of a pulsed CO_2 laser[7] *tert*-butoxide ion decomposed to yield acetone enolate ion (and presumably methane). The amount of acetone enolate produced was equal to the alkoxide decomposed. We envision at least two possible mechanisms for the decomposition: a concerted four-center elimination of methane (eq 1) or a stepwise mechanism involving an intermediate complex (eq 2).


(1)


(2)

The mechanism of this novel decomposition[8] was probed by

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