

Figure 2. Surface-Enhanced Raman spectra of 4,4'-bipyridine adsorbed onto a Ag electrode 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.

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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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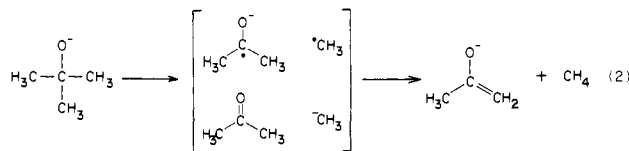
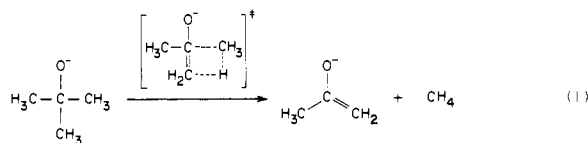
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Although unimolecular reactions of gas-phase ions are important and are commonly observed, it is difficult to gain much mechanistic insight into how highly activated ions decompose.^{1,2} We wish to report a detailed mechanistic study utilizing infrared multiphoton (IRMP) photochemistry³ 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 CO₂ laser⁷ *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).



The mechanism of this novel decomposition⁸ was probed by

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(7) Lumonics Model 103-2 TEA pulsed CO₂ laser.

(8) Overall elimination of methane has been observed in neutral radical chain processes⁹ as well as in alkane radical cations and other gaseous cations.¹⁰

measuring competitive kinetic hydrogen isotope effects in the IR laser photolysis of 2-methyl-2-propoxide-1,1,1- d_3 (**1**) and 2-methyl-2-propoxide-1,1,1,3,3,3- d_6 (**2**). Simultaneous detection of the relative intensities of the partially deuterated product enolate ions permitted measurement and separation of both secondary and primary effects.

An unusually large secondary isotope effect (loss of CH_3 favored over loss of CD_3 ; pulsed laser, 1.9 (1.2/D) for **1** and 1.7 (1.2/D) for **2**; CW laser, 6.9 (1.9/D) for **1**) and a small primary effect (pulsed, 1.6 for **1** and **2**; CW, 2.0 for **1**) were observed.^{11,12} Before these results could be interpreted it was imperative to ensure that the small primary effect was not an artifact of the pumping process. In a multiple-channel system, the branching ratio (isotope effect) is a function of the excess energy of the reacting species, which for an IRMP process is primarily determined by the CO_2 laser pumping rate. Since pulsed CO_2 lasers can give large pumping rate constants, it is likely that the ions are decomposing somewhat above threshold.¹⁴ So that the intensity dependence of the isotope effects could be investigated, the d_3 alkoxide **1** was subjected to low-power continuous-wave (CW) CO_2 laser photolysis.¹⁵ In this case, the reacting ions must be decomposing right at threshold. These experiments indicate only a slight change in the primary effect (2.0) but a very large amplification of the secondary effect (6.9).

We believe that the isotope effect results are consistent only with a stepwise mechanism (eq 2). The unusually large secondary effect essentially requires a severe loosening of the methyl group in the transition state relative to the ground-state reactant.¹⁶ Such a requirement is easily fulfilled by invoking an intermediate methyl radical¹⁷ or anion in which the ν_2 umbrella mode is considerably looser than that in a bound methyl (617 vs. 1364 cm^{-1}). The small primary effect is indicative of a highly asymmetric transition state, consistent with the large exothermicity (ca. 35–40 kcal/mol) of the second step in eq. 2. While the small primary effect may also be consistent with a bent four-center transition state (eq 1), it is difficult to rationalize the large secondary effect in terms of the relatively tight transition state in this concerted mechanism. The most convincing evidence against the concerted pathway is the large difference in energy dependence of the secondary and primary effects (i.e., the extreme variation in the secondary effect with little change in the primary effect). In a concerted mechanism involving only one transition state, the secondary and primary effects which result only from differences in zero-point energies and state sums¹⁸ would be expected to exhibit similar energy dependences. This large difference in energy dependence of the isotope effects strongly suggests that the secondary effect

occurs in a rate-limiting step while the primary effect occurs in a subsequent rapid product-determining step. Our multistep scheme (eq 2) can easily accommodate the large variation in the secondary effect due to the rate-limiting first step (loss of methyl), and the slight changes in the primary effect that would be expected for such an exothermic hydrogen transfer in the second step.¹⁹

This general stepwise mechanistic scheme can easily be extended to a variety of reactions. Since the photochemically generated intermediate in this scheme is also an intermediate in a proton-transfer reaction, bimolecular reaction dynamics²⁰ can be probed. These and related studies that rely heavily on the present mechanistic study will be forthcoming.

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Registry No. *tert*-Butoxide anion, 16331-65-0; deuterium, 7782-39-0.

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Rose Bengal and Nonpolar Derivatives

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Dyes were first used to sensitize oxidation by Windaus and Brunken¹ after the phenomenon of photodynamic action had been discovered by Raab in 1900.² Many synthetic applications of dye-sensitized oxidation processes preceded the papers of Foote and Wexler³ and Corey and Taylor,⁴ which established that singlet oxygen, a reactive intermediate originally postulated by Kautsky and de Bruijn,⁵ was responsible for such processes.

When immobilized to polystyrene/divinylbenzene beads, the xanthene dye rose bengal (**1**) is unique in being an effective heterogeneous photosensitizer.⁶ In the context of understanding the site of immobilization of the dye to the polymer support,^{6a}

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