Under identical reaction conditions, luminescence is observed during the photodecomposition of both **1** and **2**. The luminescence is collected at right angles to the laser beam by using a PMT (EMI 9635), transient recorder (Biomation 8100) combination. Luminescence occurs only under conditions where the oxetane decomposes, and there is a direct correlation between the single-pulse luminescence intensity and the single-pulse decomposition yield. Biacetyl or EVE irradiated alone under these conditions show no luminescence.[9] Rate constants for oxetane decompositions determined from the change in intensity with number of pulses are identical, within experimental error, with those obtained from pressure measurements. From a series of cutoff filter studies, an approximate emission spectrum from the decomposition of **1** may be reconstructed.[10] No luminescence is observed at $\lambda < 435$ nm, and less that 5% of the signal occurs at $\lambda > 550$ nm. The spectrum can be rationalized as a superposition of biacetyl singlet (λ_{max} = 460 nm) and triplet ($\lambda_{max'}$ = 520 nm).[11] The temporal behavior as well as the wavelength distribution appears to be consistent with the known gas-phase photophysics of photoexcited biacetyl.[12] At low pressures and sufficient internal energies, singlet, and triplet biacetyl interconvert. The decay rate constants for this mixed state are sensitive functions of internal energy ranging from 10^3 to 10^7 s^{-1} at 0-7000 cm^{-1} above the triplet zero-point level.[13] The kinetics of the multiphoton-induced chemiluminescence will be described in detail in a full paper. In contrast to **1**, luminescence from **2** is at least an order of magnitude less intense, and >70% of the intensity arises from $\lambda < 435$ nm as would be expected for electronically excited acetone.

We interpret these results in terms of competitive reaction channels from the highly vibrationally excited oxetane to excited triplet, singlet, and ground-state ketone. In the case of **1**, it is likey that the transition state for oxetane decomposition has a zero-point energy that lies above the combination of triplet biacetyl and ground-state EVE. An estimate of $\Delta H^{\ddagger} \sim 60$ kcal/mol may be made by using data from structurally similar oxetanes.[14] The overall ground-state reaction is roughly thermoneutral. The triplet energy of biacetyl is 57 kcal/mol and of the singlet 64 kcal/mol. In the case of **2**, the triplet channel probably requires 10-15 kcal/mol more energy than the ground-state channel. However, it is well-established that the average energies of IRMP-excited reactants are, in general, well in excess of reaction thresholds. Both RRKM calculations[15] and comparisons of the observed decay times with previous work[13] imply that reactant oxetane molecules reach internal energies at least 20 kcal/mol above the ground-state barrier. This excess energy will help make the higher energy diabatic channels competitive. Furthermore, the branching ratio, i.e., excited-state biacetyl/ground-state biacetyl, is probably small.[16]

Work is continuing on characterizing and modeling these reactions. We are particularly interested in obtaining diabatic/adiabatic branching ratios as a function of the average energy of reacting molecules and assessing the role played by the probable biradical intermediate in energy acquisition and intersystem crossing.

Acknowledgment. We are grateful for the financial support of the Department of Energy (DOE-AC02-80ER-10592). We also thank Professor Kent Mann for generous access to equipment.

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(10) The emission was examined with a series of long pass cutoff filters that covered a range from 375 to 550 nm at ~20-nm intervals. All intensities were adjusted for tube sensitivities.
(11) $^1\lambda_{max}$ = 460 nm; $^3\lambda_{max}$ = 520 nm. (a) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978. (b) Parmenter, C. S.; Poland, H. M. *J. Chem. Phys.* **1969**, *51*, 1551.
(12) Decay times were independent of any significant wall quenching contribution. Both the rise and the decay are significantly longer than the laser pulse width (tails to ~1 μs).
(13) van der Werf, R.; Kommander, J. *Chem. Phys.* **1976**, *16*, 125.
(14) Clements, A. D.; Frey, H. M.; Frey, J. G. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 2485.
(15) $k_{RRKM} = 10^6$ s^{-1} at ~45 kcal/mol above threshold.
(16) A rough estimae of luminescing biacetyl/nonluminescing biacetyl based on integrated signal intensity over the first 100 μs is $<10^{-4}$.

Mechanistic Study of the β-Hydroxyl Elimination from $[(H_2O)_5CrCH_2C(CH_3)_2OH]^{2+}$ in Aqueous Solution

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Carbon free radicals react very rapidly with aqueous Cr(II) to yield relatively stable alkyl chromium complexes, $[(H_2O)_5CrR]^{2+}$. Decomposition of these complexes can occur via either a heterolytic or a homolytic reaction pathway producing RH or RR, respectively.[1] Several workers have noted that alkyl chromium complexes bearing a β-hydroxyl group are anomalous in that (a) they are of much lower stability than other alkyl complexes and (b) their heterolytic decomposition is characterized by the formation of alkene products.[2,3] This exceptional reactivity of β-hydroxyalkyl complexes has been observed in Cu(II), Cu(III), and Co(III) systems as well.[3] Even though several mechanisms have been postulated to account for this behavior, no verification of any of these mechanisms has been published. We have discovered that C-H bond cleavage is not involved in the formation of 2-methylpropene from $[(H_2O)_5CrCH_2C(CH_3)_2OH]^{2+}$, and our results point to the existence of an unusual alkene complex, $[(H_2O)_5Cr(CH_2{=}C(CH_3)_2)]^{3+}$, as a long-lived species.

It had been previously observed that two species were involved in the reaction of $\cdot CH_2C(CH_3)_2OH$ with Cr(II).[2] The first-formed species, A, identified as the alkyl complex $[(H_2O)_5CrCH_2C(CH_3)_2OH]^{2+}$, has a short lifetime and rapidly rearranges to another more stable chromium complex, B.[4] The UV-vis spectrum of B and the kinetic parameters for its conversion to 2-methylpropene are typical of many alkyl chromium complexes.[5] Therefore, the conversion of A to 2-methylpropene had been proposed to occur via the protonolysis of either of two possible alkyl chromium complexes, $[(H_2O)_5CrCH_2C(CH_3){=}CH_2]^{2+}$, B-1, or $[(H_2O)_5CrC(H){=}C(CH_3)_2]^{2+}$, B-2. These alkyl complexes, corresponding to the long-lived species B, could be formed by loss of a proton from an unstable, electron-deficient and unobserved alkenechromium complex, $[(H_2O)_5Cr(CH_2{=}C(CH_3)_2)]^{3+}$, B-3 (Scheme I, paths 1 and 2).

Heterolytic cleavage of B-1 or B-2 in D_2O should yield monodeuterio-2-methylpropene where the deuterium occupies the site of the chromium atom in the precursor alkyl complexes. Cleavage of $[(H_2O)_5CrCH_3]^{2+}$ in D_2O has been shown to produce CH_3D, and a primary kinetic isotope effect; k_H/k_D of 6.3 has been measured for the reaction.[6] The location of the deuterium label in 2-methylpropene can be readily established from the mass spectrum of the molecule since a significant molecular ion peak (*m/e* 56), in addition to the most intense ion peak corresponding to loss of one methyl group (*m/e* 41) can be observed (Table I). Thus, exclusive operation of path 1 would furnish $CH_2{=}C(CH_3)CH_2D$. The mass spectrum would show full deuterium incorporation in the molecular ion but only 50% incorporation for

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(4) The decomposition of A and B follow the same rate law observed for the heterolytic cleavage of CrR^{2+} to RH and Cr^{3+}: $-d[CrR^{2+}]/dt = k_{obsd}[CrR]^{2+}$ where $k_{obsd} = k_{H_2O} + k_{H_3O}[H_3O^+]$.[1] The decomposition of A follows this rate law in the pH range 0-4.5 with $k_{H_2O} = 1.0 \times 10^2$ s^{-1}, $k_{H_3O^+} = 1.1 \times 10^3$ M^{-1} s^{-1}.[2]
(5) For B: $k_{H_2O} = 1.4 \times 10^{-4}$ s^{-1}, $k_{H_3O^+} = 3.9 \times 10^{-4}$ M^{-1} s^{-1}; λ^1_{max} = 310 nm ($\epsilon > 530$ M^{-1} cm^{-1}), λ^2_{max} = 410 nm ($\epsilon_{max} > 170$ M^{-1} cm^{-1}).[2]
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Scheme I

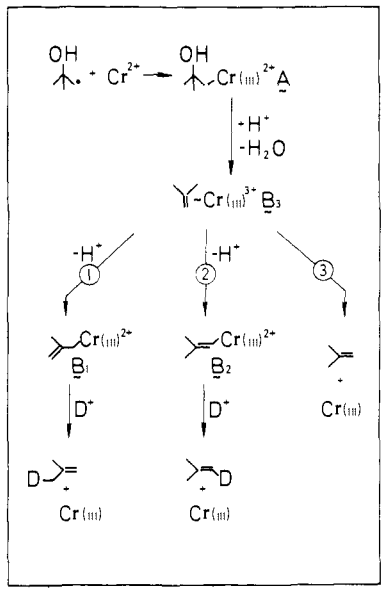

Table I. Partial Mass Spectra of 2-Methylpropene[a]

	intensity		
m/e	unlabeled[c]	experiment I	experiment II
41	1000[b]	1000[b]	1000[b]
42	38	45	57
55	186	187	165
56	461	469	414
57	22	26	24

[a] An Atlas Mass Spectrometer Model CH4 with 70-eV electrons in the ionization chamber was used. [b] Arbitrary units. [c] Same conditions as experiment I using H_2O in place of D_2O.

the parent fragment ion. On the other hand, $CHD{=}C(CH_3)_2$, formed via path 2, would produce a mass spectrum with full deuterium incorporation in both the molecular ion and the parent fragment ion.

Generation of the free radical precursors to A and B were carried out under two different experimental conditions. Helium-saturated D_2O containing *t*-BuOH (0.5 M), H_2O_2 (0.005 M), and Cr(II) (0.05 M) was made acidic with either $HClO_4$ (0.010 M, experiment I) or AcOH/AcONa (pH 4.7, total acetate = 0.012 M, experiment II). The deuterium content of the two solutions was established to be not less than 95% for both experiments.[7] The partial mass spectra produced by gas samples obtained from the two sets of experimental conditions are given in the table.

The 2-methylpropene produced in experiments I and II is almost identical with unlabeled 2-methylpropene indicating that little or no incorporation of deuterium occurs in these systems. Control experiments failed to detect any 2-methylpropene when Cr(II) was omitted from the reaction mixture, which confirms the A → B → 2-methylpropene sequence as the source of the unlabeled 2-methylpropene. The failure to observe deuterated 2-methylpropene rules out any significant participation of paths 1 and 2 in the formation of the alkene product. These results can be readily explained by identifying the alkenechromium complex, B-3, as the long-lived species B, which then undergoes subsequent decomposition releasing Cr(III) and 2-methylpropene directly (Scheme I, path 3). Even when a large primary kinetic isotope effect (k_H/k_D = 10) is assumed for the cleavage of the alkylchromium complexes, B-1 and B-2, less than 5% of the 2-methylpropene formation can be assigned to paths 1 and 2.

The simplest mechanism (Scheme I, path 3) consistent with these results requires that under the proper conditions $[(H_2O)_5Cr(CH_2{=}C(CH_3)_2)]^{3+}$, B-3, is an observable, surprisingly long-lived, species whose UV-vis spectrum is deceptively similar to those of alkyl chromium complexes.[9] Implicit in this mechanism is the assumption that electrophilic attack on alkylmetal complexes need not always be prefertially directed toward the metal-carbon bond. Loss of the hydroxyl group in A to generate an alkene complex, B-3, is formally the reverse reaction of nucleophilic attack on a metal-coordinated olefin by H_2O such as might occur in the Wacker process.[10] We intend to investigate the mechanism of the decomposition of other β-hydroxyalkyl complexes of chromium and of other metals as well.

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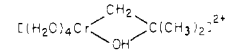
Registry No. A, 51965-50-5; B-3, 88801-82-5; 2-methylpropene, 115-11-7.

(7) Deuterium content of the aqueous reaction mixtures was determined from a mass spectrum of the hydrogen gas evolved by the thermal reaction of dry zinc powder with a few drops of the aqueous mixture. Incomplete drying of the zinc powder could produce a low analysis for deuterium.

(8) Gas samples were passed through a cold trap prior to analysis in order to remove *t*-BuOH vapors. Residual *t*-BuOH produces fragment ions of *m/e* 59, 57, 56, 52, and 41. The data in Table I have been corrected for the small contributions of fragment ions derived from *t*-BuOH by use of a mass spectrum of pure *t*-BuOH.

(9) One of the reviewers has suggested that the observed intermediate is



and not B_3. This intermediate might be formed by the labilizing effect of the alkyl-chrome bond on the Cr-OH_2 bond. However, the rate of formation of the intermediate[4] is over 2 orders of magnitude faster than the expected labilization of the trans Cr-OH_2 bond[1] and that of the cis bonds is even lower.[1] Furthermore it is difficult to envisage why the transformation of A into this intermediate would be acid catalyzed in the strongly acidic pH range.[1,4] In order to check this possibility we measured the rate of the A to B transformation for *trans*-$CrL(H_2O)CH_2C(CH_3)_2OH^{2+}$, where L = 1,4,8,12-tetraazacyclopentadecane, in neutral solutions. The specific rate of reaction observed under these conditions is $(1.0 \pm 0.2) \times 10^2\ s^{-1}$, i.e, identical with that observed for the aquo complex. This result clearly rules out any major role of the cis Cr-OH_2 bond.

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Allenic Amino Acids. 1. Synthesis of γ-Allenic GABA by a Novel Aza-Cope Rearrangement[1]

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The concept of enzyme suicide inhibition has been a powerful and intellectually appealing strategy for the design of specific enzyme inactivators.[2-6] Some of the most effective inactivators are acetylenic substrates that have been designed to exploit the high reactivity to Michael addition that is characteristic of a triple bond (or allene) when it is brought into conjugation with strongly electron-withdrawing groups. Thus, considerable success has been achieved toward inhibiting vitamin B_6 linked decarboxylases and transaminases by using the target enzyme to unmask the latent

(1) Contribution No. 183 from the Institute of Bio-Organic Chemistry, Syntex Research.

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