$Ph_3P{=}CH(CH_2)_3COO^-$ (Li^+ or Na^+).[13] Such direct observation of individual oxaphosphetanes allows the stereochemistry of initial carbon-carbon bond formation to be unambiguously determined for the first time.

We are currently using high-field ^{31}P, ^1H, and ^{13}C NMR to investigate reaction kinetics and thereby obtain a more complete picture of the Wittig reaction process.

Supplementary Material Available: Melting points, 360-MHz ^1H NMR data, and elemental analyses for **4a** and **5a** (1 page). Ordering information is given on any current masthead page.

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[13] Oxaphosphetane diastereomers prepared from ylides bearing anionic groups appear at roughly the same chemical shifts as those prepared from **3**. Results with these ylides will be described elsewhere.

Chemiluminescence in the Infrared Photochemistry of Oxetanes: The Formal Reverse of Ketone Photocycloaddition

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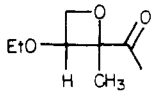
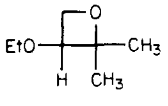
Multiphoton excitation using infrared lasers (IRMPE) is an excellent method for making ensembles of highly vibrationally excited ground-state molecules.[1] At low enough pressures and with sufficiently intense lasers, these "vibrationally hot" molecules may undergo chemical reaction. In general, the chemistry resembles thermal chemistry and the lowest energy pathway predominates. In certain cases, however, reaction channels that are not accessible under normal thermal conditions compete.[2] In this paper we report the observation of an IRMPE-induced decomposition leading to a diabatic, chemiluminescent channel that occurs in competition with the normal, adiabatic ground-state thermal reaction. The reaction we have studied is the fragmentation of oxetanes to ketones and olefins. The diabatic reaction produces electronically excited ketone. It represents the formal reverse of the well-known photochemical cycloaddition of ketones to olefins, the Paterno-Buchi reaction (Scheme I).[3] This constitutes a rare example of a diabatic organic reaction in which it is possible to access electronic surface crossing regions starting from either side of the reaction coordinate.[4]

Oxetanes **1** and **2** have been prepared by the photochemical cycloaddition of biacetyl[5a] and acetone,[5b] respectively, with ethyl vinyl ether (EVE).



1

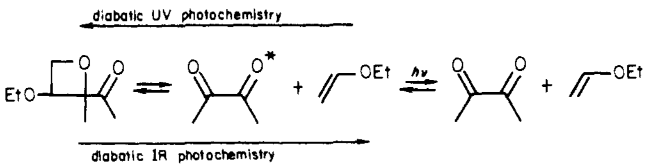


2

As has been previously noted, cycloaddition occurs regioselectively,[3] and with biacetyl, with relatively high stereoselectivity as well.[5a] **1** is formed as a 9:1 mixture of diastereomers. The diastereomers have not been separated, but the mixture has been purified by preparative gas chromatography for use in the IR photochemistry.

1 and **2** were irradiated in the gas phase with the collimated beam of a grating-tuned CO_2 TEA laser. Typical reaction conditions employed 0.1 torr of oxetane and 1.0 J/cm² fluence with a beam diameter of 6 mm, constant through the cell at a frequency of 969.15 cm⁻¹ [R(10) 001-100]. Progress of the reaction was conveniently followed by continuously monitoring the pressure in the cell. Up to 25% conversion, the pressure data give a good fit to a first-order rate constant calculated according to the stoichiometry of Scheme I:

Scheme I



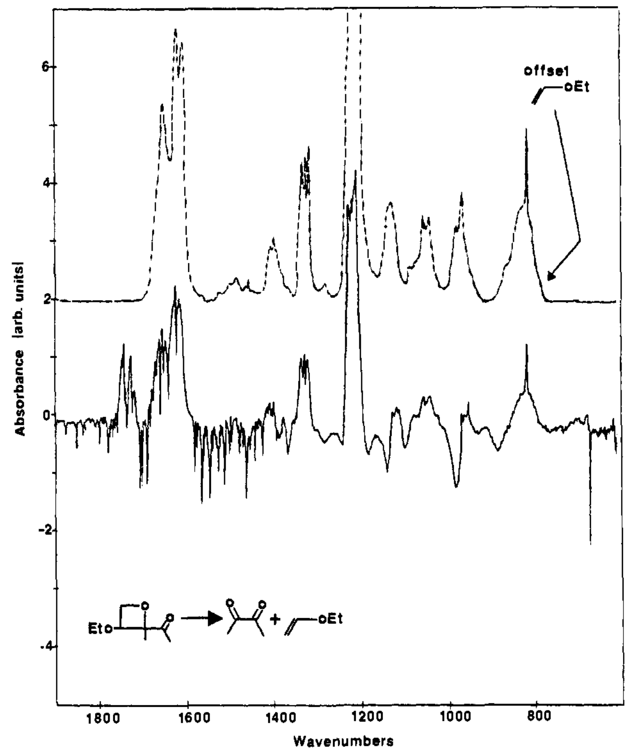


Figure 1. FTIR difference spectrum (photolysis mixture − starting material) after 600 pulses at ~2 J/cm². The dotted offset spectrum is ethyl vinyl ether vapor taken under similar conditions.

$$-k = \frac{1}{t}\ln\frac{2P_0 - P_t}{P_0}$$

For **1**, products have been analyzed by GC and IR.[6] Gas chromatography shows no significant products (<2%) other than biacetyl and ethyl vinyl ether, which are present in approximately equal concentration. Infrared spectroscopy clearly shows the growth of absorption features assigned to the ketone and olefin. Figure 1 is the FTIR difference spectrum of a sample of **1** irradiated for 600 pulses, from which the starting oxetane spectrum has been subtracted. It is clear from Figure 1 that all the major features in this spectrum can be assigned to ethyl vinyl ether (spectrum superimposed). The carbonyl bands of biacetyl at 1725 and 1735 cm⁻¹ are also evident.[7] The rate of IR photodecomposition of oxetanes appears to respond as would be expected from previous work to changes in fluence, frequency, and bath gas pressure.[8]

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(1) Danen, W. C.; Jang, J. C. In "Laser-Induced Chemical Processes"; Steinfeld, J. I., Ed.; Plenum Press: New York, 1981; and references therein.

(2) Farneth, W. E.; Thomsen, M. W. *J. Am. Chem. Soc.* **1983**, *105*, 1843.

(3) Jones, G., II *Org. Photochem.* **1981**, *5*, 227.

(4) Turro, N. J.; Chow, M.; Rigaudy, J. *J. Am. Chem. Soc.* **1979**, *101*, 1300.

(5) (a) Ryang, J.; Shima, K.; Sakuri, J. *J. Org. Chem.* **1973**, *38*, 2860. (b) Schroeter, S. H.; Orlando, C. M., Jr. *Ibid.* **1969**, *34*, 1181.

(6) Photolysis mixtures were directly injected into a gas chromatograph via a gas injection port. Columns of either 8% UCON-LB550X or 10% QF-1 (¹/₈ in. × 10 ft., Chromosorb W solid support) were used.

(7) Gas phase FTIR spectrum of biacetyl was taken under similar conditions.

(8) Farneth, W. E.; Thomsen, M. W.; Schultz, N. L.; Davies, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 4001.

0002-7863/84/1506-1875$01.50/0

J. Am. Chem. Soc. 1984, 106, 1876–1877

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 ($\lambda_{max} = 460$ 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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(9) Burak, I.; Queily, T. J.; Steinfeld, J. I. *J. Chem. Phys.* **1979**, *70*, 334.

(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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(1) Espenson J. H. In "Advances in Inorganic and Bioinorganic Mechanisms"; Sykes, G., Ed.; Academic Press: London, 1982; Vol. 1, p 1.

(2) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

(3) Ryan, D. A.; Espenson, J. H. *Inorg. Chem.* **1982**, *21*, 527. Elroi, H.; Meyerstein, D. *J. Am. Chem. Soc.* **1978**, *100*, 5540. Freiberg, M.; Meyerstein, D. *J. Chem. Soc., Faraday. Trans. 1* **1980**, *76*, 1825, 1838. Sorek, Y.; Cohen, H.; Mulac, W. A.; Schmidt, K. H.; Meyerstein, D. *Inorg. Chem.* **1983**, *22*, 3040.

(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}; $\lambda^1_{max} = 310$ nm ($\epsilon > 530$ M^{-1} cm^{-1}), $\lambda^2_{max} = 410$ nm ($\epsilon_{max} > 170$ M^{-1} cm^{-1}).[2]

(6) Schmidt, W.; Swinehart, J. H.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 1117. Ryan, D. A.; Espenson, J. H. *Inorg. Chem.* **1981**, *20*, 4401. Gold, V.; Wood, D. L. *J. Chem. Soc., Dalton Trans.* **1981**, 2452.

0002-7863/84/1506-1876$01.50/0