Femtosecond β-cleavage dynamics: Observation of the diradical intermediate in the nonconcerted reactions of cyclic ethers

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Femtosecond (fs) dynamics of reactions of cyclic ethers, symmetric and asymmetric structures, are reported. The diradical intermediates and their β-cleavages, which involve simultaneous C-C, C-H σ-bond breakage and C-O, C-C π-bond formation, are observed and studied by fs-resolved mass spectrometry. To compare with experiments, we present density functional theory calculations of the potential energy surface and microcanonical rates and product distributions. © *1998 American Institute of Physics.* [S0021-9606(98)02619-1]

I. INTRODUCTION

In elementary reactions, the processes of bond breaking and bond making involve transition states (TS's) which live for times comparable to the vibrational period. In complex reactions, however, the reaction channels for different products are multiple and may involve relatively stable intermediates which live for several vibrational periods or longer. With femtosecond (fs) time resolution it is possible to study these intermediates. Of particular importance are the *diradical* intermediates (see, e.g., Ref. 1), whose fs dynamics in many reactions, such as the Norrish,[2] Diels-Alder,[3] elimination[4] and other reactions,[5] are critical to the branching of product yields, to the stereochemistry, and to the reaction mechanism (see, e.g., Refs. 6 and 7). The strategies and techniques developed in these fs studies provide the opportunity to investigate other putative diradical intermediates, proposed as intermediates in high-energy reactions.

The thermal and photochemistry of cyclic ethers give rise to unsaturated hydrocarbons and carbonyl compounds. The vacuum ultraviolet photolysis of cyclic ethers has been interpreted to involve the cleavage of the carbon-oxygen bond as the major primary process. Since the early work by the groups of Pitts,[8] and Roquette,[9] there has been a number of studies of these cyclic ethers. Notably, von Sonntag and co-workers[10,11] have studied the 185 nm photochemistry of a number of cyclic ethers in the liquid phase; Diaz and Doepker[12] have reported the gas-phase results of tetrahydrofuran (THF) at 147.0 and 123.6 nm; Scala and Rourke[13] have investigated THF and its methyl derivatives at 147 nm in both the gas and solid (77 K) phase. The liquid-phase work may be characterized as involving oxy-polymethylene diradicals which undergo ring closure, β-cleavage fragmentation, and atom abstractions.

In the gas phase, the predominant reaction of the diradicals is fragmentation (hydrogen molecule is an important product in both the liquid and gas phase photochemistry). The elementary steps are described by our calculated potential energy surface (PES, shown in Fig. 1) for THF. As discussed below, the diradical intermediate ($\cdot CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\cdot$) could yield products A, B, C, and D by β-elimination involving the C-C π-bond formation (A and B) or the C-O π-bond formation (C and D), two resulting from
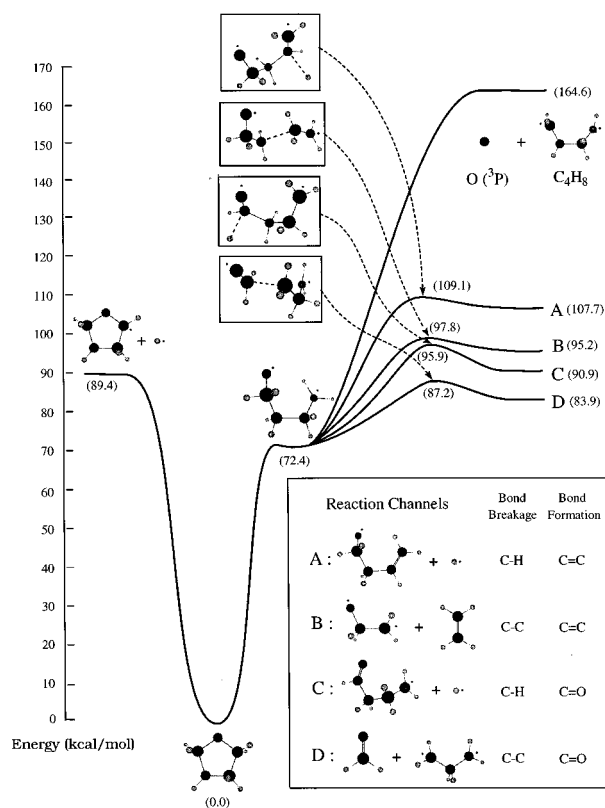
FIG. 1. Gound-state reaction paths of tetrahydrofuran (THF). The theoretical calculations were performed using density functional theory at the B3LYP/6-31G(d) level. Reaction channels $A–D$ correspond to four different β-cleavage reaction pathways, two involving the oxygen electron and two the carbon electron of the diradical intermediate. The channels to the right give the nonconcerted pathways, together with their calculated transition states. The values in parentheses are relative energies in kcal/mol with zero-point energy corrections.

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the electron on oxygen (C and D) and two from the electron on carbon (A and B).

In this communication, we report direct observation of the femtosecond dynamics of the intermediates in the reactions of THF and other cyclic ethers of related structures. We also report theoretical calculations of the reaction pathways and rates to compare with the experimental results. The C–O chemical bonds in THF break nonconcertedly in 65 ± 15 fs. The intermediate products of β-cleavage were observed to buildup in 55 ± 15 fs and decay in 120 ± 10 fs. Contrary to the traditional view of β-elimination involving only C–C bond breakage, we have observed a major channel of β-elimination which involves the C–H bond. To compare with experiment, we have calculated the potential energy surface for THF using density functional theory (DFT). Energies of various reaction channels were obtained at the B3LYP/6-31G(d) level of theory. Microcanonical reaction rate coefficients were then evaluated using the Rice–Ramsperger–Kassel–Marcus (RRKM) theory based on the calculated PES. Because they have only σ bonds, the cyclic ethers are unique for studies of bond cleavage and π-bond formation.

II. EXPERIMENT

The femtosecond laser and molecular beam apparatus used in these experiments has been described elsewhere.[14] Briefly, the output of a colliding-pulse, mode-locked oscillator (CPM) was amplified in a four-stage dye amplifier, pumped by a Nd:YAG laser. Typical output, after recompression by a four prism pair, was a 80 fs width (Gaussian) pulse with an intensity of ~300 μJ/pulse at 615 nm. The pulse was split to provide pump and probe beams. For the pump, the 615 nm output was frequency doubled by a KD*P crystal to give a 307 nm pulse which was isolated by a bandpass filter. The probe beam, 615 nm, was passed to a computer-controlled translation stage for the time delay with respect to the pump beam. The time zero was measured *in situ*.[14]

The two beams were spatially combined, using a dichroic mirror, and were focused onto the supersonic molecular beam. The laser pulses intersect the molecular beam in a differentially-pumped vacuum chamber containing a time-of-flight mass spectrometer. Both pump and probe beams were appropriately attenuated to minimize background signals. By gating the signal due to a particular ion and collecting the signal as a function of the time delay, the temporal evolution of each species was measured.

THF (99%), trimethylene oxide (98%), 2-methyltetrahydrofuran (99%), and tetrahydropyran (99%), all from Aldrich, were used without further purification. In order to avoid the formation of clusters, THF and trimethylene oxide were cooled to $-10\,°C$ before introduction to the chamber, and the molecular beam pulse valve was operated at $100\,°C$. The mass spectra in Figs. 2 and 3 clearly identify the molecules and show the relevant peaks.
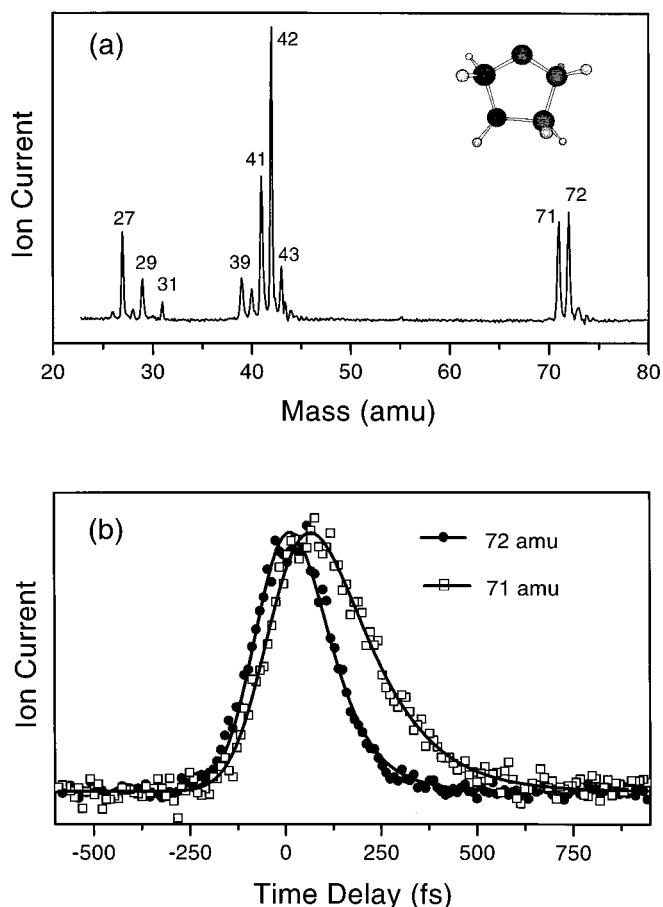

FIG. 2. (a) The mass spectrum of THF observed at 50 femtosecond delay time; (b) THF transients for the parent (72 amu) and the fragment (71 amu). For 72 amu, decay $\tau = 65 \pm 15$ fs; 71 amu, rise $\tau_1 = 55 \pm 15$ fs and decay $\tau_2 = 120 \pm 10$ fs.

III. THEORETICAL CALCULATIONS

A. Potential energy surfaces

The PES of THF was calculated at the B3LYP/6-31G(d) level of theory.[15–17] Briefly, the geometries of the closed-shell reactant and product species were optimized using restricted Kohn-Sham orbitals, whereas for the open-shell radicals, diradicals, and the corresponding TS's, the unrestricted orbitals were used. To properly localize both α and β spin densities for singlet diradicals, the spin-polarized procedure was used to destroy the α-β and the spatial symmetries by mixing the highest-occupied molecular orbital (HOMO) with the lowest-unoccupied molecular orbital (LUMO).[18] However, the attempt to locate a stationary point for the singlet state oxy-tetramethylene diradical using the current DFT approach was unsuccessful due to the instability of the singlet unrestricted Kohn-Sham orbitals.[19]

Assuming that the energy gaps between the singlet and the triplet ground states of the diradical are insignificant, all the diradicals and the β-cleavage TS's were first optimized at their triplet ground states and then followed by a single-point energy calculation using the same unrestricted B3LYP method for the singlet state. The vibrational frequencies of all species were calculated at the same level of theory to characterize the nature of the stationary points (no imaginary
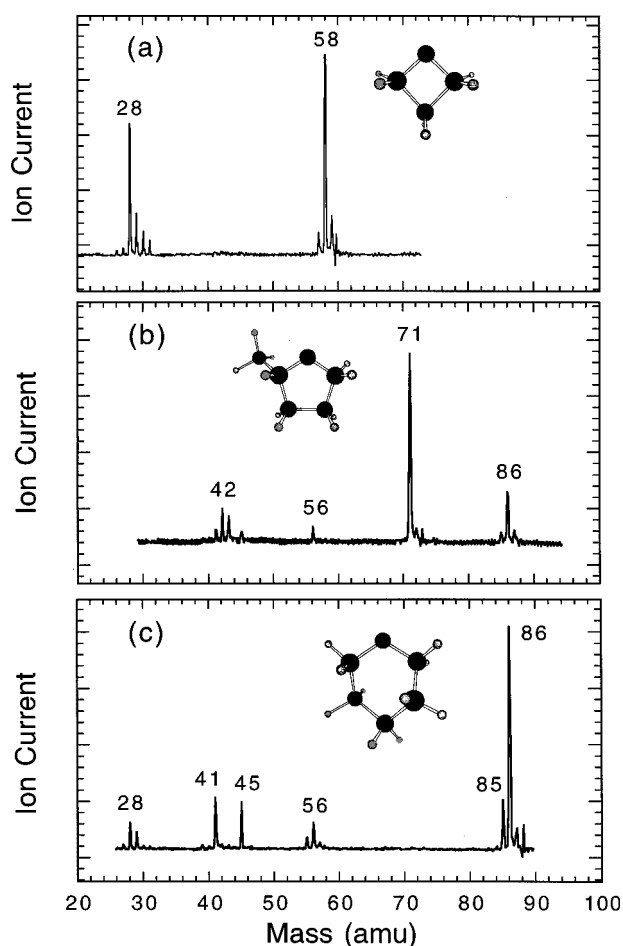
FIG. 3. The mass spectra of three structurally related cyclic ethers observed at 50 femtosecond delay time: (a) trimethylene oxide; (b) 2-methyltetrahydrofuran; (c) tetrahydropyran.

value for a minimum and only one imaginary value for a TS) and determine the zero-point energy (ZPE) corrections. All electronic structure calculations were performed using the G94 procedure.[20]

B. Reaction rates

To compare reaction rates to those calculated according to statistical theories, we invoked the standard RRKM formula, $k(E) = W^{\ddagger}(E - E_0)/h\rho(E)$, where h is Planck's constant, E_0 is the reaction barrier with ZPE corrections, $W^{\ddagger}(E - E_0)$ is the sum of states for the TS, and $\rho(E)$ is the reactant density of states. The vibrational frequencies were obtained from the electronic structure calculations outlined above, and the sum (and density) of states were then calculated using the Beyer-Swinehart direct counting algorithm.[21] The rates for the β-cleavage reactions were then calculated based on the PES shown in Fig. 1. With statistical theories, however, ergodicity is assumed in the calculation of the microcanonical rate coefficients, so that the total energy E is a property of the entire phase space of the system. The presence of a transition state along the reaction path also defines $W^{\ddagger}$ without invoking variational methods.

IV. RESULTS AND DISCUSSION

Figure 2(a) shows the mass spectrum for THF recorded at $t = 50$ fs and Fig. 2(b) displays the transients for the parent species (72 amu) and for a fragment intermediate (71 amu). The transient at 72 amu was fit to a single exponential decay, with proper convolution, to give a lifetime (τ) of 65 ± 15 fs. The transient signal at 71 amu shows a delayed rise followed by a subsequent decay. This transient was fit with a simple rise and decay function, giving a rise time (τ_1) comparable to the decay of the parent, i.e., $\tau_1 = 55 \pm 15$ fs, and a decay lifetime (τ_2) of 120 ± 10 fs. We have also observed the fs transients of the 42 and 43 amu species; the mass of trimethylene diradical and the oxy-dimethylene diradical minus one hydrogen atom. The transients are similar to that of 71 amu. This indicates that trimethylene diradical is produced from the parent diradical (72 amu) and that its decay time of ~ 120 fs is consistent with the one observed from another precursor, cyclobutanone, at the same total energy[2] (there may also be some contribution from the ionic fragmentation of the 71 amu species). The dominance of the mass peak of 42 amu is consistent with the product yield analysis (from trapping measurements at 77 K)[13] which gives the yield of D to be six times that of B channel. Note that all product channels will build up by the same total rate of the parent decay and only the yield and their decay will be different.

These observations illustrate the following points. First, oxy-polymethylene diradicals are true intermediates in the reactions of cyclic ethers, such as THF. These intermediates are formed by a nonconcerted mechanism involving the σ-bond (C-O) breakage. Second, for THF, the observation of transients for the parent (72 amu) and for the parent minus one hydrogen atom (71 amu), or 42 amu, indicates that the oxy-tetramethylene diradical decomposes by β-cleavage processes involving the C-H and C-C bonds. The corresponding reaction on the carbon end of the diradical, by H elimination from the adjacent carbon (channel A), is less probable because the formation of C-O π bond is energetically more favorable than the C-C π bond by ~ 25 kcal/mol, consistent with the results shown in Fig. 1 (for 0 K). The presence of the β-cleavage by H-elimination is significant because conventional mechanisms invoke only a C-C β-elimination.

Third, the concerted product from the breakage of two C-O bonds simultaneously is a much higher energy reaction path (see Fig. 1). This is consistent with the absence of a 56 amu (tetramethylene) signal in Fig. 2(a); the characteristic 700 fs lifetime of tetramethylene was not observed.[2] Also, prompt breakage of the C-H bond upon excitation is much less probable than the C-O breakage as the excitation involves the oxygen lone pair which promotes the neighboring (α) C-O cleavage.[13] Moreover, the energy required to break the C-H bond is 17 kcal/mol more than that of breaking a C-O bond as shown in Fig. 1 (left vs right energetics).

The β-cleavage of the diradical intermediate is facilitated by the simultaneous breaking of a C-H or C-C bond and the making of a C-C or C-O π bond. It is expected that a C-H σ bond would be stronger than a C-C σ bond by ~ 15 kcal/mol while a C-O π bond is stronger than a C-C π bond by ~ 25 kcal/mol. Our theoretical results of the relative enthalpies (at 0 K) of these reaction channels at the B3LYP/6-

31G(d) level are displayed in parentheses in Fig. 1, and indeed determine the expected energetic sequence for channels A to D. The corresponding TS's in the different channels A to D have also been successfully located at the reaction coordinate separation of $R/Å$ = 2.11, 2.34, 1.84 and 2.21, respectively. These TS's are relevant to provide accurate rate information via RRKM theory.

RRKM calculations using the PES in Fig. 1 give the lifetime of oxy-tetramethylene diradical undergoing β-cleavage through the different reaction channels: At the total available energy E = 113.6 kcal/mol,[22] the calculated rate coefficients in s^{-1} (predicted branching ratios given in parentheses) are 1.2×10^{10} (0.1%), 8.8×10^{11} (5.3%), 1.7×10^{12} (10.2%), and 1.4×10^{13} (84.4%) for channels A, B, C, and D, respectively. These results predict that channel D, which produces the trimethylene diradical (42 amu), is a significant reaction path, and that the total rate, which is the sum of all product-channel rates, is (60 fs)$^{-1}$. This would be consistent with the strong signal observed at 42 amu [Fig. 2(a)]. The implication is that channel C should be less by a factor of 10, different from the experimental results. However, the dynamical force into the channel is the important factor for branching yields and the statistical theory will predict neither the rates nor the yields on such time scales. As pointed out elsewhere,[23] the agreement between experimental rates and those obtained by assuming ergodic behavior is fortuitous as the rates approach the time scale of a vibrational period.

Studies of analog molecules (Fig. 3) illustrate the interplay between the dynamics and the molecular structure. This is most evident in the intensity of the peak for the parent minus one H atom. For trimethylene oxide there is little (M-1) in the mass spectrum because the β C-C cleavage gives two stable π-bonded products, ethylene and formaldehyde. For 2-methyltetrahydrofuran, the (M-1) is again very small but the (M-15) is quite large. This peak replaces the (M-1) because the bond to the methyl radical is weaker than the bond to the hydrogen atom. For tetrahydropyran the M-1 is again a prominent peak because there is no more favorable alternative reaction for the oxy-pentamethylene diradical.

The intermediacy of oxy-tetramethylene diradical unifies the proposed different reaction mechanisms. It is consistent with the observation that even in the liquid phase when *cis* or *trans* 2,5-dimethyltetrahydrofuran is photolyzed at 185 nm each isomerizes with a quantum yield of about 0.2.[11] This suggests that the quantum yield for ring closure of the oxy-tetramethylene diradical is about 0.4 in the liquid phase at 185 nm. The lifetime of this diradical in the liquid phase must be comparable to or longer than the period of rotation of the α-carbon-β-carbon bond in order for it to isomerize. The intermediacy of the diradical also explains the primary process in the reactions of aliphatic ethers for which both an alkyl and an alkoxyl radicals are formed.[11] The nonconcerted pathway is driven by the LUMO/HOMO interaction in the σ-bond framework (no π bonds) and this is consistent with the nature of the excitation and the bond strengths; the C-O is the weakest bond in the molecule.[24,25]

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