Direct femtosecond observation of the transient intermediate in the α-cleavage reaction of $(CH_3)_2CO$ to $2CH_3+CO$: Resolving the issue of concertedness

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When a reaction involving two equivalent bonds has sufficient energy to break both of them, it can proceed by either a *concerted* or a *stepwise* mechanism. For Norrish type-I and other reactions, this issue has been controversial since direct time resolution of the individual C–C cleavage events was not possible. Here, for the elementary α-cleavage of acetone, we report on the femtosecond resolution of the intermediates using mass spectrometry. The results show the nonconcertedness of the reaction, provide the times for the primary and secondary C–C breakage, and indicate the role of electronic structure (σ^*, antibonding impulse) and the vibrational motions involved. © *1995 American Institute of Physics.*

I. INTRODUCTION

For a chemical reaction with multiple-bond breaking or bond making, one of the most fundamental questions has been whether or not the events occur in a *concerted* or in a *stepwise* manner. Many experimental and theoretical studies (see, e.g., Refs. 1–3) have been devoted to answer such a question, and the issue in different reactions (pericyclic, S_N2, elimination, etc.) has been controversial. However, several *operational* concepts have been invoked.

A commonly used criterion between the concerted and stepwise mechanisms involves the kinetic time scale. A concerted reaction is defined as one that takes place in a single kinetic step without necessarily being synchronous.[2] In contrast, a stepwise reaction involves two kinetically distinct steps via a stable intermediate. Houston and co-workers[3] used the calculated molecular rotational time scale (~ps) of the intermediate as a dividing line between a concerted and a stepwise mechanism, defining concertedness when the intermediate lifetime becomes shorter than its rotational period.

The difference between a stepwise and a concerted process obviously rests with the direct detection of the intermediate species. What is critical is the nature of the transition-state region, e.g., a saddle-point concerted structure, an energy minimum describing an intermediate along the reaction coordinate, or a global potential energy surface with many degrees of freedom involved. Consequently, the dynamics of the nuclear motion on the femtosecond (fs) time scale must be established in order to conclusively define concertedness as a useful general concept.

In this contribution, we report direct femtosecond (fs) studies of the elementary processes in the three-body dissociation of $(CH_3)_2CO$ to CO and two CH_3 radicals. This two-bond (C–C) breakage is an ideal example for addressing the issue of concertedness and belongs to the general class of α-cleavage processes known as Norrish type-I reactions.[4,5] Our focus is on the fragmentation at excitation energies high enough for both bonds to, in principle, dissociate with a quantum yield for $2CH_3+CO$ close to unity.[6] We use the fs mass spectrometry approach[7] to identify the parent and transient intermediates, and to examine the energy and isotope effects on the dynamics.

The mechanism of α-cleavage in acetone has been investigated through spectroscopic, kinetic, and product-state studies (see, e.g., Refs. 8–12). For example, Baba *et al.* inferred from a nanosecond power dependence of the MPI signal of acetone and acetyl in the mass spectrum that neutral CH_3CO exist in a one-photon dissociation at 193 nm.[10] Vaida and co-workers, from the absorption spectra, suggested a predissociative mechanism for the photolysis of acetone at around 193 nm.[11] Leone and co-workers[12] found that the CO (at 193 nm excitation) is highly rotationally excited, and interpreted this as evidence for a stepwise mechanism. Houston and co-workers[3] measured the translational energy of the CH_3 fragments and did not observe a bimodal distribution (for two methyls) which they gave as evidence for a concerted dissociation. They also measured the internal energy of the methyl fragments to be very small, leading them to conclude that the dissociation of each C–C bond occurs prior to complete randomization of the available energy by a concerted mechanism.[3]

Later, Strauss and Houston[3] examined the same system with the information-theoretic approach to investigate the correlation of velocity vectors of two methyl fragments and concluded that the fragmentation at 193 nm proceeds in an intermediate way between the stepwise and concerted mechanisms. Subsequently, Hall *et al.*[13] removed an approximation in the information-theoretic analysis[3] and found that there is no correlation between the recoil directions of the two methyl radicals. They suggested that the lifetime of the reaction intermediate is long relative to the time of randomization.

Very recently, Lee and co-workers[14] carefully measured the fragments translational energy at two different wavelengths, 248 and 193 nm. From the fit of the distributions for CH_3 and CO, they provided evidence for a stepwise mechanism at 193 nm. The product-state distributions give valuable information on the energy changes in the exit channel, as discussed below.

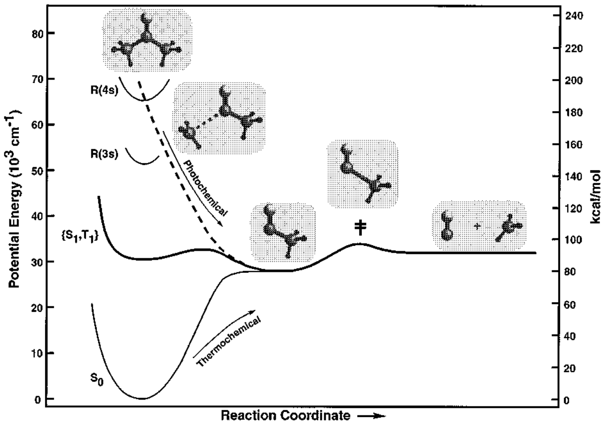

FIG. 1. A cut of the potential energy surface along the reaction coordinate illustrating the concerted vs stepwise mechanism of the reaction: $(CH_3)_2CO \rightarrow 2CH_3 + CO$, or $(CH_3)_2CO \rightarrow CH_3CO + CO \rightarrow 2CH_3 + CO$. Photochemical and thermochemical pathways are denoted by arrows, and the structures are shown only for five configurations. Energies are given in two units, and the states are labeled with R denoting Rydberg, S singlet and T triplet, and S_0 the ground state.

In our fs studies of this reaction, as with pericyclic[15] and elimination[16] reactions, we initiate the motion with a fs laser pulse and detect with probe fs pulses, using multiphoton ionization/time-of-flight mass spectrometry. By probing a specific mass, parent acetone or intermediate acetyl, as a function of time, the real-time dynamics can be directly observed; see Fig. 1. We observe a buildup (50 fs) and decay (500 fs) of the transient intermediate, and the dynamical time scale for the secondary bond cleavage is found to be isotope and energy dependent (106 and 124 kcal/mol above dissociation). These results establish the nonconcertedness and the mechanism of the reaction, and are directly related to the electronic structure and vibrational motions.

II. EXPERIMENT

Figure 2 depicts a schematic of the experimental apparatus which combines a (skimmed) molecular beam and a fs laser system.[7] Two modes of detection were employed. In one mode, the evolution of all mass species was monitored at different time delays, while in the other mode, the transient for a specific mass was recorded. The latter was obtained by gating the mass signal as a function of the delay time between the first and second fs laser pulses.

The helium carrier gas was bubbled through the sample, acetone-h_6 (Mallinckrodt, 99.5%) or acetone-d_6 (CIL), 99.9% D, at ice or room temperature with a typical backing pressure of 20 psi. To reduce cluster formation, the pulsed nozzle was heated to 100 °C. The pressure in the TOF chamber was 3×10^{-6} Torr when the nozzle (0.3 mm diameter) was opened. The data were recorded, using a transient digitizer or a boxcar integrator, collected, and analyzed with a computer.

III. RESULTS AND DISCUSSION

The TOF mass spectra at different reaction times are shown in Fig. 3. The signals due to the parent [$(CH_3)_2CO^+$; 58 amu] and the reaction intermediate [(CH_3CO^+; 43 amu)] are both identified, but their evolution on the fs time scale is entirely different. The parent signal is strong at time zero and it completely disappears within a few hundred fs of the reaction time. Meanwhile, the intermediate signal increases in the first few hundred fs as the parent signal decreases, and then it decreases more slowly with increasing reaction time. This behavior indicates the presence of the intermediate, $CH_3CO^\dagger$, following the first α-cleavage of the C–C bond. From the observed power dependence of ~1.4 (two photons through intermediate), we can obtain the available energy of the reaction, as discussed below.

The transients of the parent and intermediate are shown in Fig. 3 together with the theoretical fits. The decay of the parent signal gives the lifetime (τ) of 50 ± 30 fs when the transient was fit to a single exponential decay including a convolution of the laser pulse width;[7] the cross-correlation HWHM was 75 ± 15 fs. The buildup and decay of the transient intermediate was also fit giving the τ_1 (buildup time) and τ_2 (decay time); τ_1 was found to correspond to the decay of the parent (50 fs), but τ_2 is much longer and depends on the total energy and isotopic composition.

For the 307 nm experiments (186 kcal/mol), $\tau_2 = 500 \pm 100$ fs for $CH_3CO^\dagger$ while for $CD_3CO^\dagger$ (see Fig. 3), $\tau_2 = 750 \pm 100$ fs. While the buildup time τ_1 is similar for both isotopic species, the decay time of $CD_3CO^\dagger$ is ~1.5 times longer than that of $CH_3CO^\dagger$. Moreover, the transients show a significant energy dependence in τ_2 of the acetyl intermediate. For the 280 nm experiments (204 kcal/mol), $\tau_2 = 180 \pm 50$ fs for the protonated species and $\tau_2 = 280 \pm 50$ fs for the deu-

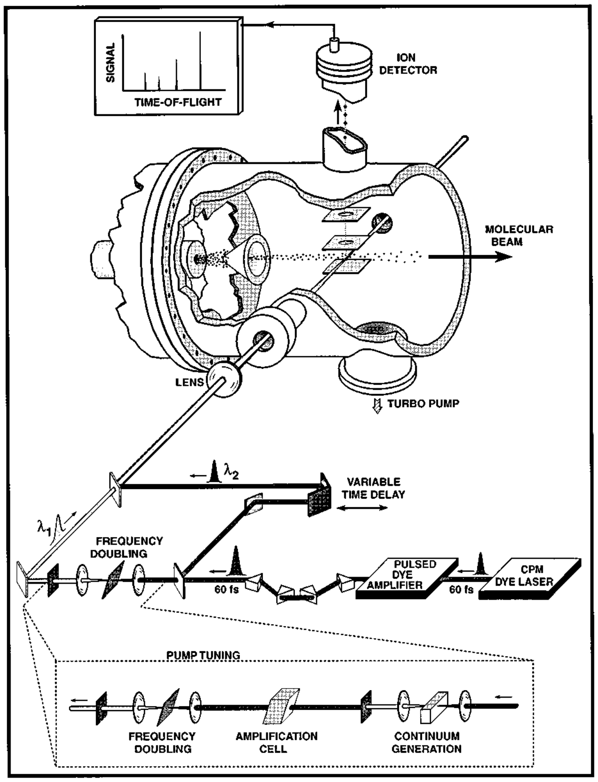

FIG. 2. Experimental apparatus showing the molecular beam, with the mass spectrometer, and the fs laser system. The white light generation for the 280 nm experiment is outlined in the dotted box.

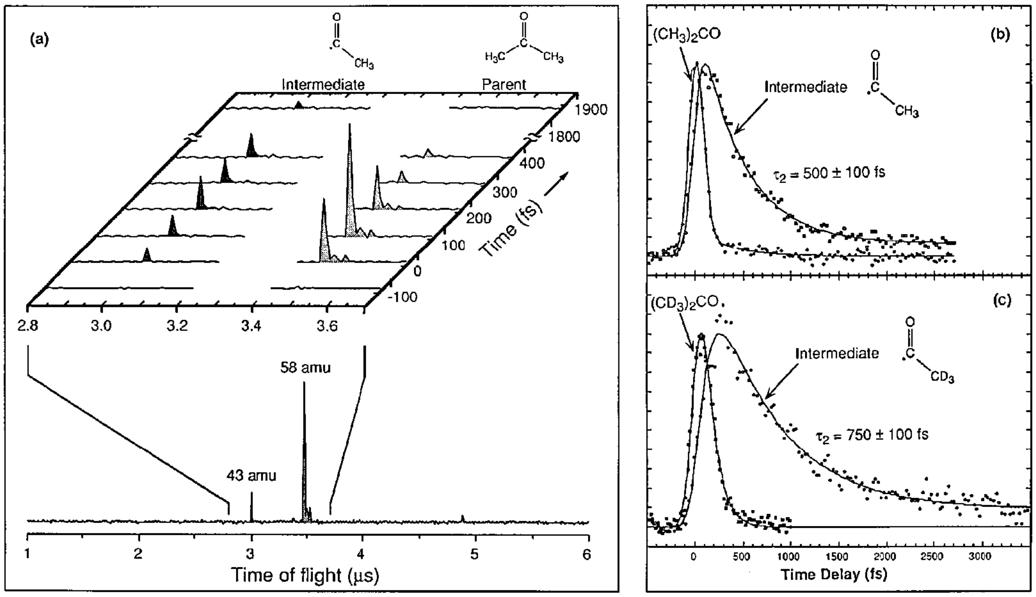

FIG. 3. Femtosecond mass spectra and transients for $(CH_3)_2CO$ and $(CD_3)_2CO$ reactions. (a) Time-of-flight mass spectra at different time delays. Notice the evolution of the parent signal (58 amu) and the longer decay of the intermediate (43 amu). Transients of (b) acetone and acetyl; (c) deuterated acetone and acetyl obtained at $\lambda_{pump}=307$ nm and $\lambda_{probe}=615$ nm. The theoretical fits are presented as solid lines (see the text for values). A less than 10% background, observed in the acetyl transient might be due to a small contribution from acetone dimers possible in the molecular beam (Ref. 11). Note that near time zero in (a) the signal is primarily that of the parent, indicating that the probed intermediate is ionized following neutral parent fragmentation. This is a key feature of the fs time resolution (Refs. 7 and 15).

terated species, both shorter than the values obtained in the 307 nm experiments.

The above results demonstrate that the reaction of acetone is nonconcerted and dynamically involves two steps. The first α-cleavage (50 fs) occurs on a time scale less or comparable to the vibrational period (essentially frozen nuclei), and the second cleavage involves the vibrational degrees of freedom, as evident by its longer time scale, isotope effect, and the energy dependence. These primary and secondary bond breakages must, therefore, be considered differently.

The fact that the primary C–C bond cleavage at these high energies is found to occur on a time scale shorter than 100 fs suggests that the potential energy surface is antibonding, repulsive along the reaction coordinate. The vibrational period of the C–C bond[17] is $\sim$43 fs and accordingly the σ^* promotion is prompted before any significant energy redistribution. This is consistent with the insignificant H/D isotope effect observed in the primary cleavage, and with the nature of the initial state. The excitation by two-photon absorption at 307 or 280 nm reaches the n-$4s$ Rydberg state which is broadened ($\sim$200 cm^{-1}, $\sim$30 fs)[18] by interaction with valence states. The *ab initio* calculation by the Bonn group[19] clearly identifies the states, and we have made symmetry correlations[20] for the reaction path which indicate σ^* repulsion in the C–C bond. This correlation is also consistent with Butler's analysis of nonadiabatic interactions in the dissociation of ketones studied by her group.[21]

The secondary C–C bond breakage is from the nascent hot acetyl intermediate. The breakage proceeds with a reaction barrier of 17 kcal/mol.[22,23] Because of this barrier, we consider the global PES and compare our results with the rate constants we calculate from the RRKM theory. The vibrational frequencies of CH_3CO, calculated by Hess and colleagues,[24] were used; for those of CD_3CO, a scaling, based on the ratios of vibrational frequencies of h_6 and d_6, was invoked. The rate constant is not strongly dependent on the angular momentum (J) for a reaction with a barrier, and the calculations were carried out for $J=0$ as a function of energy.

The available energy can be obtained from knowledge of the total deposited energy and product-state distributions. As discussed above, the primary α-cleavage occurs in 50 fs and this indicates that there is not enough time for the available energy to be redistributed among vibrational degrees of freedom, other than the motion along the reaction coordinate. An impulsive model (see Refs. 3 and 14), where all of the energy is in the C–C bond repulsion, predicts that 54% of the available energy goes into translational energy, 10% into the internal energy of CH_3, and 36% into the internal energy of CH_3CO. At 307 or 280 nm, the available energy to the CH_3CO and CH_3 products is $(186-80)=106$ or $(204-80)=124$ kcal/mol, respectively, since the bond energy is $\sim$80 kcal/mol (see Fig. 1).[25] Hence, the impulsive model predicts an internal energy of 38 or 45 kcal/mol for the acetyl intermediate at the two energies studied. The rotational energy of CH_3CO is taken to be $\sim$1 kcal/mol.[14]

For $E=37$ kcal/mol, our RRKM calculations give $\tau_2=375$ and 460 fs for $CH_3CO^\dagger$ and $CD_3CO^\dagger$, respectively. For $E=44$ kcal/mol, these values are $\tau_2=175$ and 200 fs. The theoretical values match well with the experimental results, not only qualitatively but also quantitatively in terms of the H/D isotope effect and energy dependence. However, it is questionable that one of the basic assumptions of a statistical rate theory, i.e., a complete randomization of the energy prior to reaction, will be satisfied for such a femtosecond reaction.

It seems that the first impulse of primary α-cleavage creates the needed vibrational distribution even on this short time scale. It is interesting to note that the translational energy distribution measured at 193 nm is broad and has a FWHM of $\sim$15 kcal/mol.[14] Not all modes of the phase space have to be involved, and the large isotope effect and energy dependence may have its origin in the dynamical motion of the wave packet on the PES, as observed before in the dissociation of methyl iodide.[26] Molecular dynamics will be part of our future work to unravel the extent of the vibrational motion in the secondary step.

IV. CONCLUSIONS

The elementary dynamics of the Norrish reaction in acetone were studied in real time. The primary and secondary C–C bond cleavage occur *nonconcertedly* on time scales one order of magnitude different. The intermediate lifetime at the energy studied here is shorter than its rotational period, which would mean a concerted mechanism if the internal molecular clock is used as the dividing line between the stepwise and concerted mechanisms, a criterion widely used. Therefore, the use of the rotational period of the intermediate or the rotation about a single bond is not indicative of true concertedness. Rather, the concertedness of the reaction should be judged from the comparison of the intermediate lifetime to the vibrational period along the reaction coordinate. Such a definition directly reflects concertedness and synchronicity, and describes the actual nuclear motions in the transition states.[27]

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