Direct femtosecond observation of the transient intermediate in the α-cleavage reaction of (CH$_3$)$_2$CO 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, $S_2$, 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. In contrast, a stepwise reaction involves two kinetically distinct steps via a stable intermediate. Houston and co-workers used the calculated molecular rotational time scale (~ps) of the intermediate as a dividing line between a concerted and a stepwise mechanism, defining concertededness 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$_3$)$_2$CO to CO and two CH$_3$ radicals. This two-bond (C–C) breakage is an ideal example for addressing the issue of concertededness and belongs to the general class of α-cleavage processes known as Norrish type-I reactions. 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. We use the fs mass spectrometry approach 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$_3$CO exist in a one-photon dissociation at 193 nm. Vaida and co-workers, from the absorption spectra, suggested a predissociative mechanism for the photolysis of acetone at around 193 nm. Leone and co-workers 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 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.

Later, Strauss and Houston 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. removed an approximation in the information-theoretic analysis 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 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.

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elimination reactions, we initiate the motion with a fs laser served; see Fig. 1. We observe a buildup function of time, the real-time dynamics can be directly ob-
specific mass, parent acetone or intermediate acetyl, as a
ionization/time-of-flight mass spectrometry. By probing a
pulse and detect with probe fs pulses, using multiphoton
gating the mass signal as a function of the delay time be-
for a specific mass was recorded. The latter was obtained by
different time delays, while in the other mode, the transient
one mode, the evolution of all mass species was monitored at
acetone-

III. RESULTS AND DISCUSSION

II. EXPERIMENT

Figure 2 depicts a schematic of the experimental appa-
ratus which combines a (skimmed) molecular beam and a fs
laser system. 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 be-
tween the first and second fs laser pulses.

The helium carrier gas was bubbled through the sample,
acetone-\textsuperscript{d\textsubscript{6}} (Mallinckrodt, 99.5\%) or acetone-\textsuperscript{d\textsubscript{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 cham-
ber was 3×10\textsuperscript{-6} Torr when the nozzle (0.3 mm diameter)
was opened. The data were recorded, using a transient digi-
tizer 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\textsubscript{3})\textsubscript{2}CO\textsuperscript{+};
58 amu] and the reaction intermediate [(CH\textsubscript{3}CO\textsuperscript{+}; 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 re-
action 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\textsubscript{2}CO\textsuperscript{+}, following the first \(\alpha\)-cleavage of the C–C bond.
From the observed power dependence of \(\sim 1.4\) (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 \(\tau\) of 50±30 fs when the
transient was fit to a single exponential decay including a
convolution of the laser pulse width;\textsuperscript{7} the cross-correlation
HWHM was 75±15 fs. The buildup and decay of the tran-
sient intermediate was also fit giving the \(\tau_1\) (buildup time)
and \(\tau_2\) (decay time): \(\tau_1\) was found to correspond to the decay
of the parent (50 fs), but \(\tau_2\) is much longer and depends on
the total energy and isotopic composition.

For the 307 nm experiments (186 kcal/mol),
\(\tau_2=500\pm100\) fs for CH\textsubscript{2}CO\textsuperscript{+} while for CD\textsubscript{2}CO\textsuperscript{+} (see Fig. 3),
\(\tau_2=750\pm100\) fs. While the buildup time \(\tau_1\) is similar for both
isotopic species, the decay time of CD\textsubscript{2}CO\textsuperscript{+} is \(\sim 1.5\) times
longer than that of CH\textsubscript{2}CO\textsuperscript{+}. Moreover, the transients show a
significant energy dependence in \(\tau_2\) of the acetyl interme-
diate. For the 280 nm experiments (204 kcal/mol), \(\tau_2=180\pm50\)
fs for the protonated species and \(\tau_2=280\pm50\) fs for the deu-
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 $\alpha$-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 in acetone is $\sim 43$ fs and accordingly the $\sigma^*$ 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 electronic excited state. The available energy can be obtained from knowledge of the total deposited energy and product-state distributions. As discussed above, the primary $\alpha$-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$_2$ and 36% into the internal energy of CH$_3$CO. At 307 or 280 nm, the available energy to the CH$_2$CO 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). 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$_3$CO is taken to be $\sim 1$ kcal/mol.

For $E=37$ kcal/mol, our RRKM calculations give $\tau_2=375$ and 460 fs for CH$_3$CO and CD$_3$CO, 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.

FIG. 3. Femtosecond mass spectra and transients for (CH$_3$)$_2$CO and (CD$_3$)$_2$CO 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 $\lambda_{\text{probe}}=307$ nm and $\lambda_{\text{probe}}=615$ 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).
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 ~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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¹² Contribution No. 9086.
⁴³ A. H. Zewail (to be published).