Femtosecond Chemically Activated Reactions: Concept of Nonstatistical Activation at High Thermal Energies

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Femtosecond chemical activation of reactions at very high thermal energies, much above the bond energy, is developed in this report. We address the concept of nonstatistical dynamics at such high energies. The approach offers a new direction for probing the dynamics of reactions in their ground state with unique activation, collision-free, and temporally and spatially defined.

Introduction

Since the work in the 1920s by Lindemann and Hinshelwood,[1,2] the issues of how energy flows in molecules and the influence on the outcome of reactions have been central to chemical kinetics and dynamics. Ideally, with lasers, one wishes to deposit a high energy in a complex molecule and observe the cleavage of a specific bond. However, in most cases, this ideal picture is not realized, and for energized polyatomic molecules the energy, which was initially concentrated in a specific vibrational motion, spreads out very rapidly into all modes of the molecule. This energy randomization, the phenomenon of intramolecular vibrational-energy redistribution (IVR), makes none of the vibrational modes specific, and therefore the reactions are said to be ergodic or statistical. In principle, however, the outcome of the reaction could be controlled if the breakage on a specific site or of a bond is induced by ultrafast impulses before the energy randomization is complete.[3] The dynamics of IVR in reactions therefore play a fundamental role in bond- or site-selective chemistry and in the description of rates and mechanism.

In a series of classic papers, Rabinovitch and co-workers[4] have addressed the relative importance of IVR in the chemical activation, with the addition of hydrogen atoms, of hydrocarbon molecules to form hot radicals. The effect of collisions on product yields was used to deduce the time scales of IVR (0.1−2 ps). With IR laser multiphoton excitation, reaching energies near and above dissociation, the role of IVR was examined by Letohkov and co-workers.[5] More recently, a variety of laser spectroscopic methods have been advanced to address the nature of IVR in different systems and at different energies (for reviews, see refs 6 and 7). Parmenter's group introduced the use of the collisional clock to examine changes in the spectra, at the single vibronic level, and deduced the time scales for IVR for the molecules in their excited states.[8]

With picosecond (ps) and femtosecond (fs) resolution, the nature and rates of IVR have been directly studied for excited molecules in molecular beams.[9] It was found that, depending on the coupling between modes and their density of states, well-defined regions of IVR can be observed, characterizing what is known as *restricted* and *dissipative* energy redistribution.[9] The latter represents the onset of the statistical behavior. However, in these studies the energy range covered is small relative to chemical binding energies. A central question relevant here is the following: What is the nature of IVR at energies much higher than chemical binding energies and how can IVR be probed directly? The statistical RRKM theory, which has been used to interpret the rates of unimolecular reactions, is based on the assumption that all energetically accessible states of the reactant are equally probable, i.e., a much faster IVR rate than the dissociation rate.[10] At such high energies, both IVR and dissociation take place competitively, and the applicability of the RRKM theory is questionable.[11]

With fs-resolved mass spectrometry, here we report on the development of an approach for studying the selectivity and nonstatistical behaviors of complex reactions, chemically activated at energies much above the bond energy. The concept behind the approach is simple. A fs pulse is used to initiate chemical activation by bond breakage after the energy is temporally and spatially deposited in one moiety of the molecule. The internally hot radicals in the ground electronic state, formed in a very short time (fs), are then monitored with a fs probe pulse in a mass spectrometer. This allows us to follow the reaction dynamics and IVR on the ground state of the radicals, but at very high energies above their bond energy for dissociation. Due to the ultrashort nature of the initial fs impulse, the internal energy of the nascent radical may at first be localized in a restricted number of vibrational modes. With time, both IVR and dissociation take place competitively and the dynamics can be monitored in real time.

Specifically, we consider systems of increasing carbon chain length, to increase the number of vibrational modes, and examine the selective bond breakage via Norrish type-I reactions (see below). We also use isotopic labeling to test the extent of IVR and the degree of spatial localization of energy. In structure, the analogy with the chemical activation approach of Rabinovitch[4] is evident, but with the fs initiation and resolution we are able to localize the energy temporally (and spatially) and to probe the dynamics directly in real time, without using collisional clocks.

Systems Studied

The systems studied here are the family of structures: acetone, CH_3COCH_3; diethyl ketone, $CH_3CH_2COCH_2CH_3$; and methyl ethyl ketone, $CH_3COCH_2CH_3$ (represented at the top of Figure 1), and its α-D and β-D isotopic analogues, $CD_3COCD_2CH_3$ and $CH_3COCH_2CD_3$. With the first fs pulse, this class of molecules undergoes Norrish type-I reactions on the fs time scale.[12] The two C−C bonds adjacent to the CO group (see Figure 1) are broken in a *stepwise* manner, with distinct time constants for the individual C−C bond cleavage. For

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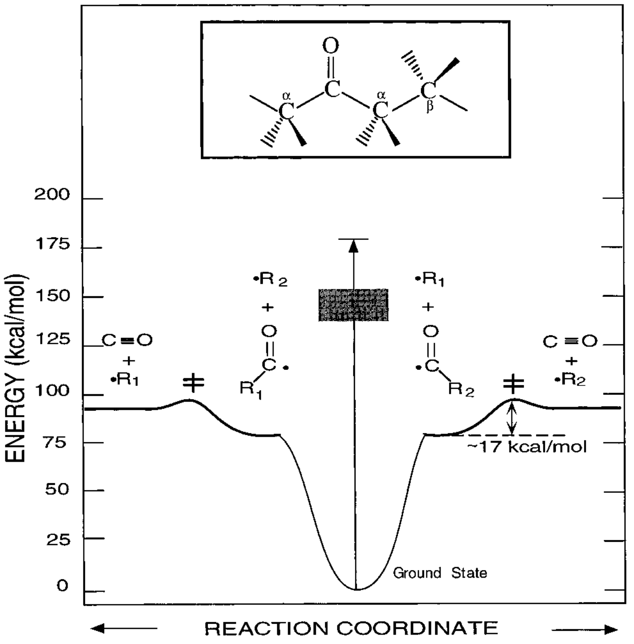

Figure 1. Reaction coordinates for the two channels in the α-cleavage of the class of molecules: R_1-CO-R_2, where R_1 and R_2 are either methyl (CH_3 or CD_3) or ethyl (CH_3CH_2, CH_3CD_2, CD_3CH_2) groups. For the asymmetric molecule shown in the inset, methyl ethyl ketone, the two channels are distinguishable. Similar coordinates can be drawn for the symmetric molecules. The intermediate reactant well between primary and secondary C−C bond cleavages is about 80 kcal/mol above the parent ground-state energy. The initial energy of 186 kcal/mol is indicated, and the shaded bar represents the estimated range of available energy for the secondary fragmentation. Transition states are labeled as ‡.

example, since the methyl ethyl ketone molecule has two inequivalent C−C bonds, there are two reaction channels which were both observed in our fs-resolved mass spectra (see Figure 2):

$$CH_3COCH_2CH_3^* \rightarrow CH_3\cdot + COCH_2CH_3^{\dagger}\cdot \quad (1)$$

$$CH_3COCH_2CH_3^* \rightarrow CH_3CO^{\dagger}\cdot + CH_2CH_3\cdot \quad (2)$$

In these primary reactions, or those of any of the parent molecules considered, the nascent $COCH_2CH_3$ (propionyl) and CH_3CO (acetyl) radicals are highly vibrationally excited, and thus dissociate further to give final products:

$$COCH_2CH_3^{\dagger}\cdot \rightarrow CO + CH_2CH_3\cdot \quad (3)$$

$$CH_3CO^{\dagger}\cdot \rightarrow CO + CH_3\cdot \quad (4)$$

Because the primary C−C bond cleavage in eqs 1 and 2 occurs on the fs time scale (see Figure 3a, for example), the radicals in eqs 3 and 4 are *temporally* clocked on the fs time scale, and the nascent radicals have specific *spatial* and *energetic* characteristics.[13]

Experimental and Results

The experimental setup has been detailed elsewhere.[14] The molecular beam was formed by a nozzle expansion and was skimmed in differentially pumped chambers. The fs laser pulses ($\lambda \sim 615$ nm, $\Delta t \sim 60$ fs) were generated from a colliding pulse, mode-locked (CPM) ring dye laser, pumped by an Ar^+ laser. These pulses were amplified in a four-stage pulsed dye amplifier, pumped by the second harmonic output of a Nd:YAG laser. The amplified pulses passed through four high-refractive-index prisms to be recompressed and divided into two parts. One part was frequency doubled and crossed the molecular beam

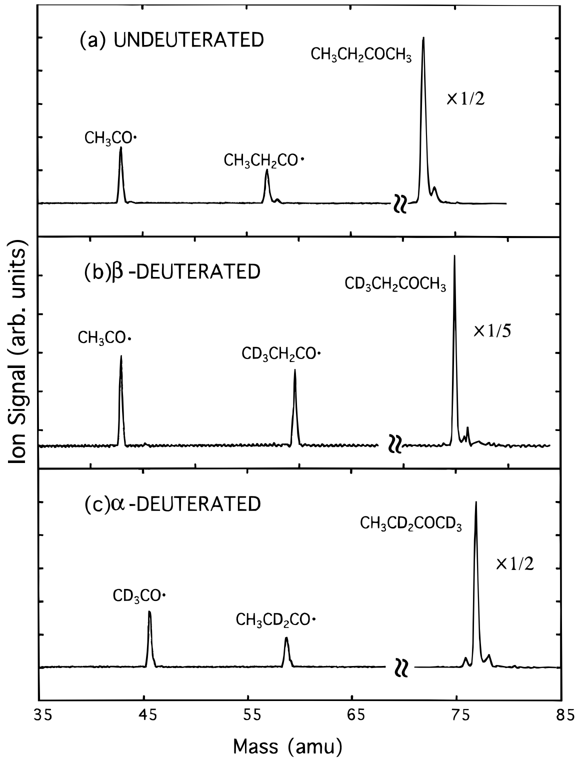

Figure 2. TOF mass spectra of (a) $CH_3CH_2COCH_3$, (b) $CD_3CH_2COCH_3$, and (c) $CH_3CD_2COCD_3$, taken at $t \sim 50$ fs. Two different intermediates, acetyl and propionyl radicals, are clearly present in the TOF mass spectra.

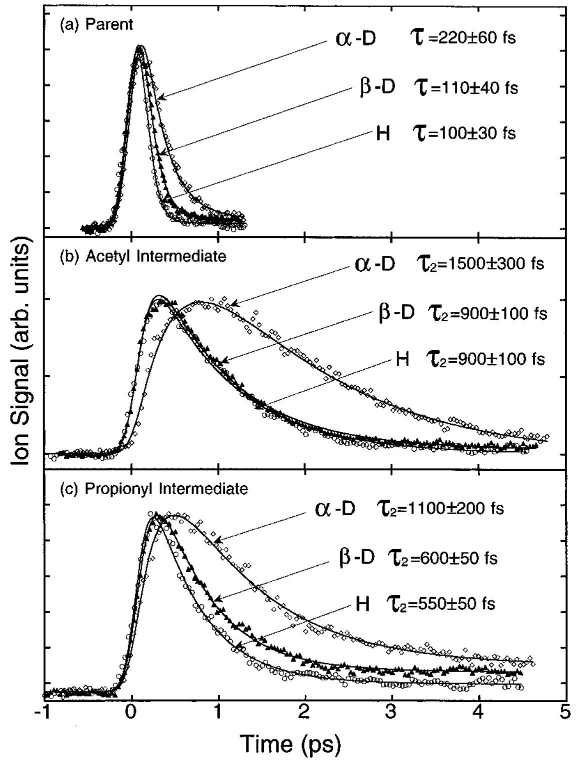

Figure 3. Femtosecond transients of (a) the parent, (b) the acetyl intermediate, and (c) the propionyl intermediate for the undeuterated (H), the α- (α-D) and β- (β-D) deuterated molecules (see Figures 1 and 2). The small long-lifetime component in some transients may have contributions from clusters as discussed in refs 12 and 17.

(initiation pulse). The other part was passed through a retroreflector on the computer-controlled translation stage and combined with the pump laser pulse to ionize the existing molecular species at any selected delay time (probe). For tuning of λ, we use continuum generation.[14] The ions were detected in the time-of-flight (TOF) mass spectrometer according to their mass-to-charge ratios. Transients were obtained by monitoring the specific ion signal as a function of the delay time between the clocking and probe laser pulses.

TOF mass spectra show the distribution of reactant, intermediate, and product species existing at the chosen delay. These are typified by the TOF mass spectra shown in Figure 2, recorded for excitation of methyl ethyl ketone and probing at 50 fs after the time zero. Transients were obtained for the parent molecules and show single-exponential decay (time constant τ). The transients for the propionyl and acetyl radicals from all parent molecules were fit by using a buildup-and-decay function as the molecular response function, $M(t) = A[\exp(-t/\tau_2) - \exp(-t/\tau_1)]$, giving time constants of buildup (τ_1) and decay (τ_2). The signals due to these intermediates grow with time constants similar to those of their parents, $\tau_1 \sim \tau$, and decay relatively slowly. Examples of transients and fits (for the methyl ethyl ketone experiments) are shown in Figure 3. For the acetyl radicals arising from acetone activation, $\tau_2 = 500 \pm 100$ fs; for the propionyl radicals from diethyl ketone, $\tau_2 = 750 \pm 100$ fs. For methy ethyl ketone $\tau_2 = 550 \pm 50$ (900 ± 100), 1100 ± 200 (1500 ± 300), and 600 ± 50 (900 ± 100) fs for unsubstituted, α-D, and β-D substituted propionyl (acetyl) radicals, respectively (see Figure 3).

Discussion

The primary C−C bond cleavage occurs in ~100 fs and is primarily due to σ^* repulsion.[12] Accordingly, we shall consider here only the secondary C−C bond dissociation shown in eqs 3 and 4, as our focus here is on the radical intermediates at high energies. The internal energies of these radicals are determined by the energy partitioning in the primary C−C bond cleavage. The reaction barrier for the secondary C−C bond breakage is $E_0 \sim 17$ kcal/mol and is similar for the CH_3CO and CH_3CH_2CO radicals.[15,16] Therefore, the radicals in the highly vibrationally excited state dissociate via the transition state defined at the saddle point on the potential energy surface along the reaction coordinate (see Figure 1). Now, the question is whether or not a complete energy randomization takes place prior to the dissociation of these vibrationally hot radicals.

First, we consider the acetone reaction, whose stepwise mechanism of dissociation has been established by this and the Castleman group.[12,17] The available experimental data allow us to derive 65 ± 10 kcal/mol as the range of vibrational energy content of the nascent acetyl radicals following excitation at 186 kcal/mol total energy.[18] Given the short time scale of radical formation, this energy may initially reside in a restricted subset of the total vibrational phase space. However, if the IVR rate is much faster than the dissociation rate, then the subsequent reaction would be statistical. To assess the statistical or nonstatistical nature of the acetyl decomposition reaction, the experimentally determined rate constant can be compared to the rate constant calculated by the RRKM theory: $k(E) = N^{\ddagger}(E - E_0)/h\rho(E)$, where $N^{\ddagger}$ is the number of states at the transition state and ρ is the density of reactant states.

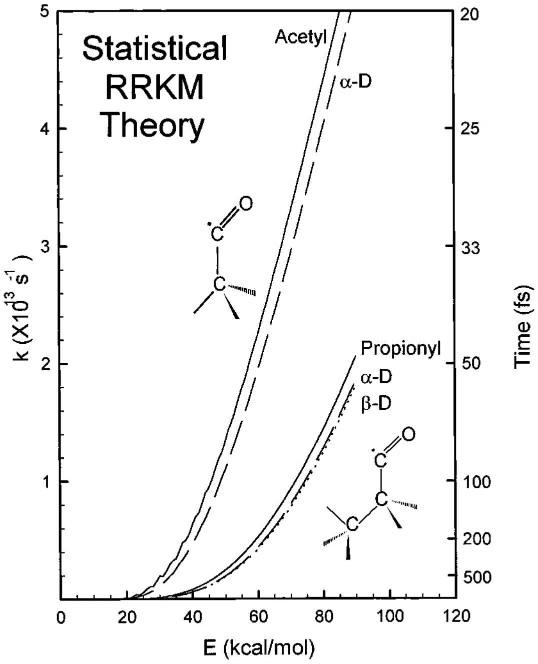

Figure 4. Theoretical RRKM rates and time constants as a function of vibrational energy for fragmentation of acetyl and propionyl radicals and their α- and β-deuterated forms. A barrier height of 17 kcal/mol is used for all species except α-D propionyl, for which 17.5 kcal/mol is used. The increase of 0.5 kcal/mol results from the change in zero-point energy between the reactant and transition state, which is minor compared to the total available energy.

The rate constant for the dissociation of the acetyl radical, $CH_3CO^{\dagger}\cdot \rightarrow CH_3\cdot + CO$, was obtained by using the RRKM theory based on the vibrational frequencies obtained from *ab initio* calculation.[21] As shown in Figure 4, for $E = 65 \pm 10$ kcal/mol, τ_2 ranges from 26 to 56 fs, which is ~10 times smaller than the experimental value of 500 fs.[22] This dramatic difference indicates that the vibrational energy of the acetyl is prevented from reaching the C−C stretch reaction coordinate by a slow or restricted IVR. The initial fs impulse, via the C−C coordinate, mostly affects the motion of the central carbon atom in the C−C−O moiety. The vibrational frequency of the C−C−O bend[21] corresponds to 70 fs, indicating ~7 periods before dissociation.

To investigate this behavior further, we consider the acetyl and propionyl radicals formed from the *same* molecule, methyl ethyl ketone. With primary cleavage energetics similar to those of acetone, the internal energy of each intermediate is also expected to fall in a similar range. Both radicals dissociate on a time scale similar to that of acetyl from acetone, with the decay of propionyl actually somewhat faster than that of acetyl from methyl ethyl ketone. As before, the discrepancy with the RRKM rate indicates a nonstatistical decomposition of acetyl. RRKM theory for the fragmentation of propionyl[23] at energies in the range 65 ± 10 kcal/mol also predicts rates faster than those measured, but the discrepancy is less pronounced than for acetyl (Figure 4). If the energy partitioning in the primary cleavage is different for methyl ethyl ketone than for acetone, the comparison between theory and experiment becomes more difficult.

For this reason, we studied the effect of *selective* isotopic labeling on the rates. The reaction of the propionyl radical was found to slow down by a factor of ~2 by the deuterium substitution on the α-carbon (see Figure 3). For β-D substitution, the rate is almost identical with that of the undeuterated molecule (a factor of ~ 1). For the propionyl radical, the RRKM theory predicts the isotopic rate ratio (k_H/k_D) to be only slightly above unity for both the α-D and the β-D substitution (1.18 and 1.21, respectively; see Figure 4). These theoretical predictions of similar rates independent of the position of D in the chain, keeping the same number of modes, are not consistent with the large difference observed experimentally between the α-D and *β*-D isotopic substitution effect (see Figure 3).

The above discrepancy is a strong indicator of nonstatistical behavior in the propionyl decomposition, as in the case of acetyl, and suggests that modes involving the motion of α-D atoms are primarily involved in the dissociation dynamics, while the modes involving the motion of *β*-D atoms have little involvement due to a slow IVR. Note, however, that if the available energy is restricted to modes of the O−C−C(α) moiety only but statistically distributed in that resticted phase space, one calculates a faster RRKM rate than that shown in Figure 4, which is clearly at odds with the experimental results. The values for the changes in $k(E)$ per hydrogen at our energies and their relationship to those of $k(T)$ expressed in the Bigeleisen's equation[25] will be treated elsewhere.

Conclusion

The approach presented in this contribution allows for the synthesis of chemically activated, thermally hot molecules in their ground states and with fs temporal clocking. Due to the nature of the first impulsive chemical activation, the vibrational excitation of the radical may be localized. Without the fs-resolved mass spectrometry, we would not have been able to observe the primary process of activation and the subsequent dynamics of the intermediates. The approach promises a new direction for studying unimolecular and also bimolecular[26] reactions. By activating with ultrafast pulses[3] and at high energies, the reactions may be controlled prior to the complete energy randomization. The full account of this work will be published in a series of papers.

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(13) As mentioned in the text, the preparation here of the vibrationally excited, ground-state radicals has an analogy with that of the chemical activation.[4] Instead of the H-atom addition to form a hot radical, here, as shown in eq 1, the CH_3 radical is ejected from the parent to excite vibrational modes of the propionyl radical, preferentially localized in the O−C−C(α) moiety. In chemical activation, there is no temporal resolution, the range of energies is wide and collisions are used to quench the reactions.

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(18) The acetyl vibrational energy content following acetone fragmentation is obtained by extrapolating from measured product translational, vibrational, and rotational energy distributions at 193 and 248 nm excitations.[15,19,20] The total available energies (E_{avl}) at those excitations are about 64 and 31 kcal/mol, respectively (see Figure 1). At both excitation energies, the translational energy of the nascent CH_3 is found to be ∼10 kcal/mol. Conservation of momentum then requires the total center of mass translational energy to be ∼13.5 kcal/mol. The CH_3 rotational energy is ∼1.5 kcal/mol,[19] and by conservation of angular momentum, the acetyl rotational energy is negligible. Experimental evaluations of the CH_3 vibrational energy content range from ∼1.5 kcal/mol[19] to many times higher.[20] These results have been modeled by a barrier impulsive model[15] and a double impulsive model[19] which give ∼17 and ∼3 kcal/mol for the total internal energy of CH_3 at 193 nm. Since there is some evidence to support each model, we have used both to extrapolate to 154 nm (E_{avl} = 102 kcal/mol) and derive internal energies of the acetyl radical of ∼56 and ∼76 kcal/mol, respectively, which gives roughly the range (65 ± 10 kcal/mol). It is interesting that this value is substantially higher than the 38 kcal/mol derived[12] from a *pure* C−C impulsive bond rupture.

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(22) The RRKM calculation gives $\tau_2 \sim 500$ fs if $E = 31$ kcal/mol.

(23) The vibrational frequencies of the propionyl radicals are estimated from experimental frequencies and assignments for methyl ethyl ketone vibrations.[24] Frequency changes at the transition state are estimated from the ab initio values for the acetyl radical[21] by assuming that the vibrational frequencies of the methyl group are not changed from the reactant to the transition state, since they are remote from the reaction center.

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