

- [8] Calculated from the thermodynamic data in ref. [14].
- [9] Calculated from the thermodynamic data in ref. [14]. The solubility of O₂ in benzene was taken to be $9.1 \times 10^{-3} \text{ M atm}^{-1}$, see ref. [29].
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Femtosecond Dynamics of Norrish Type-II Reactions: Nonconcerted Hydrogen-Transfer and Diradical Intermediacy**

Steven De Feyter, Eric W.-G. Diau, and Ahmed H. Zewail*

Herein we report our first real-time study of the dynamics of Norrish type-II reactions: the intramolecular hydrogen transfer and the reaction of the intermediate, diradical species. The nuclear motions associated with the breakage of C–H and C–C bonds and formation of O–H and C–C bonds are studied for the series 2-pentanone, 2-hexanone, and 5-methyl-2-hexanone, using femtosecond time-resolved mass spectrometry. The time scale for the ultrafast hydrogen atom transfer (70–90 fs) and diradical closure and cleavage (400–700 fs) are obtained from the time evolution of the mass-gated species—the observed and vastly different reaction times indicate the nonconcerted nature of the two steps. Density functional theory (DFT) calculations are also reported to elucidate the energetics along the reaction path, and we address the analogy with the McLafferty rearrangement in ion chemistry.

Norrish type-I^[1] and type-II^[2] reactions are of fundamental importance in photochemistry. The contrast between photochemical and thermal reactions of ketones has been of interest for more than 50 years. Elsewhere, the femtosecond (fs) dynamics of Norrish type-I reactions have been reported.^[3, 4] In these reactions the α -cleavage is the pathway for product formation. In contrast, in Norrish type-II reactions carbonyl compounds containing γ C–H bonds undergo a 1,5-hydrogen shift upon electronic excitation and yield new products by cleavage and cyclization processes. Figure 1 lists the molecular structures of the systems studied here; three have γ C–H bonds and for calibration purposes one does not.

The literature is rich with detailed studies in the solution and gas phases, with primary focus on the photochemistry of the first excited S₁ state.^[2] As noted in these studies the Norrish type-II reaction is deduced, from yield and quenching experiments, to be on the nanosecond time scale and competes with vibrational relaxation and intersystem crossing; there is a barrier for excited singlet reactions of about 4 kcal mol^{−1}. The studies reported here are at higher energy (see Figure 2) and are designed to address the primary ultrafast dynamics without complications from much slower relaxation processes. However, the Norrish type-II elementary processes discussed here are the two described in ref. [2] for the overall mechanism.

[*] Prof. A. H. Zewail, Dr. S. De Feyter, Dr. E. W.-G. Diau
Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology
Pasadena, CA 91125 (USA)
Fax: (+1) 626-792-8456
E-mail: zewail@caltech.edu

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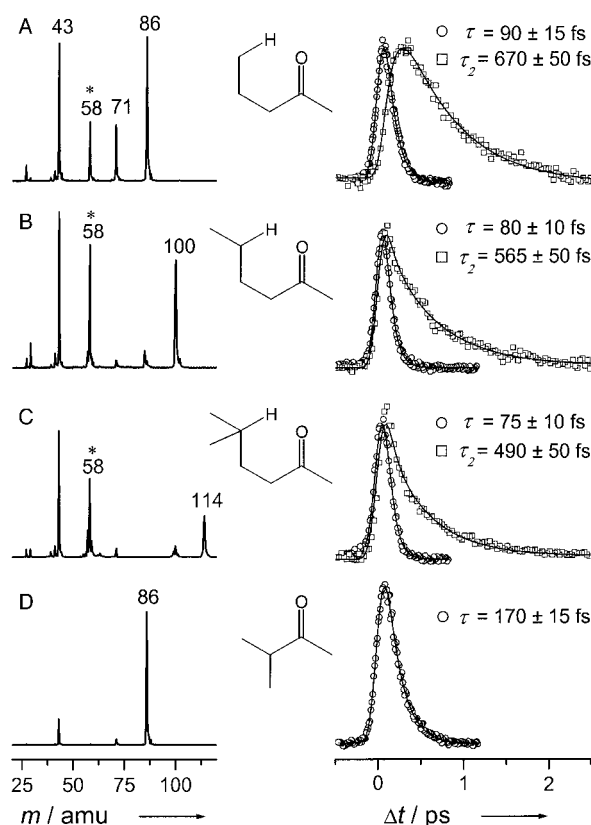


Figure 1. Femtosecond mass spectra (on the left) and transients (on the right): parent (○) and m/z 58 intermediate (□) of A) 2-pentanone, B) 2-hexanone, and C) 5-methyl-2-hexanone. D) is 3-methyl-2-butanone. The theoretical fits are represented as solid curves with the fitted time constant τ representing the decay time of the parent and τ_2 the decay time of the m/z 58 species. The other mass peaks are from the α -cleavage of C–C bonds (for further information see the text).

The fs laser and molecular beam apparatus have been described in detail elsewhere.^[5] Briefly, a fs laser system was integrated to a molecular beam apparatus with the capability of measuring the time-of-flight (TOF) mass spectra. The amplified pulses were typically about 80 fs and the energy was of the order of $150 \mu\text{J pulse}^{-1}$ at 615 nm. For the pump the 615 nm output was frequency doubled. The probe beam, which ionizes the transient species, was passed to a computer-controlled translation stage to generate the time delay. Both pump and probe beams were appropriately attenuated to minimize background signals.

Figure 1 displays the fs mass spectra and transients of A) 2-pentanone, B) 2-hexanone, C) 5-methyl-2-hexanone, and D) 3-methyl-2-butanone. The mass spectra of these molecules are characterized by their parent mass peak at m/z 86, 100, 114, and 86, respectively, and by additional peaks which are the radicals produced by α -cleavage of the C–C bonds. Our observation here of the additional peaks is entirely consistent with previous studies of α -cleavage in methyl alkyl ketones,^[3] in which the fs mass spectra contained a peak at m/z 43 corresponding to the acetyl radical and a peak at m/z ($M - 15$) corresponding to the alkyl carbonyl radical (Norrish type-I). However, all molecules studied here (A, B, and C) show a unique additional peak in the mass spectrum situated at m/z 58. This peak is only present when the molecular structure (A,

B, C) is poised for Norrish type-II reactions, as evident by the absence of the m/z 58 peak in the spectrum of 3-methyl-2-butanone (D), which lacks a hydrogen atom in the γ -position.

By gating the signal at the parent mass and m/z 58, we obtained the transient signals for the corresponding species. The results are shown to the right of Figure 1. A least-squares-fit with proper convolution gives the parent decay time $\tau = 90 \pm 15$ fs, 80 ± 10 fs, and 75 ± 10 fs for 2-pentanone, 2-hexanone, and 5-methyl-2-hexanone, respectively. The rise times of the intermediates are comparable to the decay times of their respective parents. The m/z 58 species decays in 670 ± 50 fs for 2-pentanone (A), 565 ± 50 fs for 2-hexanone (B), and 490 ± 50 fs for 5-methyl-2-hexanone (C).^[6] The decay of the α -cleavage intermediate is different. For example, for A, τ_2 (m/z 71) = 850 ± 50 fs and τ_2 (m/z 43) = 930 ± 50 fs.

The decay of the m/z 58 species is an order of magnitude different from that of the parent, which indicates that its origin is not from ion fragmentation of the parent. Accordingly, the 70–90 fs and 400–700 fs decay times, depending on the molecule, describe the two steps shown in Equation 1. Since the decay of the parent and the rise of the intermediate are similar, the hydrogen transfer, therefore, occurs in 70–90 fs. This is consistent with the time scale observed for intramolecular H-atom transfer (≈ 60 fs) observed in methyl salicylate.^[7]

Figure 2 depicts the reaction pathways of the 2-pentanone diradical intermediate formed after intramolecular hydrogen

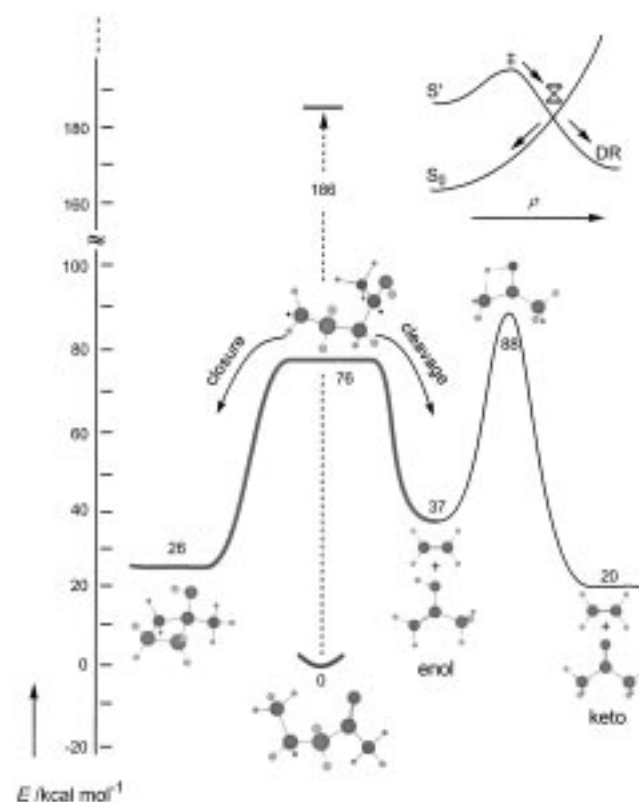
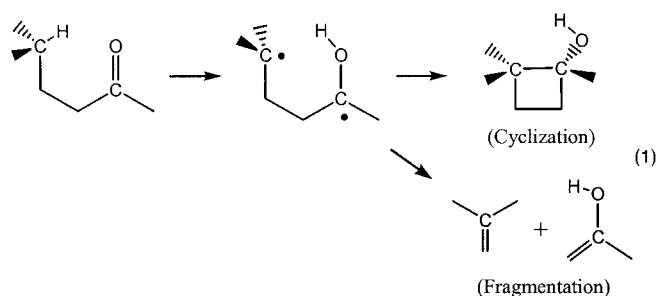


Figure 2. Ground-state potential-energy surface of 2-pentanone showing the possible reaction pathways of the diradical intermediate, which is formed after transfer of the hydrogen atom. The total experimental energy is also indicated.^[17] The structures and energies shown are from density functional theory calculations. The insert reflects the topology of the ground- and excited-state surfaces along the hydrogen transfer reaction coordinate (ρ , γ C–H distance, see text for further information).

transfer. The stationary points were calculated using the spin-unrestricted DFT method at the B3LYP/6-31G* level. As discussed elsewhere^[8, 9] the restricted method was used for all closed-shell species, whereas the unrestricted one was employed for open-shell species. Vibrational frequencies were calculated at the same level of theory in order to characterize the nature of the stationary points and to determine the zero-point energy correction. All calculations were carried out using the Gaussian package.^[10]

Our DFT calculations illuminate several points. First, the calculations show that the β C–C bond of the diradical intermediate is long (1.626 Å), that is, relatively weak. It is, therefore, anticipated that upon ionization the diradical species will easily undergo fragmentation to give the m/z 58 signal in the TOF mass spectrum. Second, once the diradical intermediate is formed, two reaction pathways are possible: the diradical can close the ring to form a cyclobutanol derivative, or it can break the C–C bond in the β position to yield an ethylene derivative and 2-propenol, the enol precursor of acetone [see Eq. (1)]. Third, the interconversion to the keto structure (acetone) involves a high energy barrier (Figure 2) and will not take place on these ultrafast time scales.



Although both cyclization and fragmentation are essentially barrierless (Figure 2), the cleavage of the diradical will be the dominant reaction channel as a consequence of entropy effects, that is, the conformational requirements for ring closure are more demanding than for fragmentation. The 1,4-diradical described above is similar to other diradicals, such as tetramethylene, studied in this laboratory.^[11] It is remarkable that the time scale for the decay is comparable (ca. 700 fs versus 400–700 fs) even though the precursors are entirely different. The entropic effects were shown to be very important; for tetramethylene, which forms ethylene and cyclobutane, fragmentation is a factor of two larger than cyclization.^[11b)]

The decay times (Figure 1) of the diradical intermediates show a systematic trend: the life time decreases with increasing number of alkyl substituents on the γ carbon atom. On the basis of the decrease in the γ C–H bond strength in going from 2-pentanone (98 kcal mol^{−1}) to 2-hexanone (94.5 kcal mol^{−1}), to 5-methyl-2-hexanone (92 kcal mol^{−1}),^[2b)] it is anticipated that the internal energy content of the diradical intermediates of 2-hexanone and 5-methyl-2-hexanone will be higher than in 2-pentanone,^[12] and hence result in somewhat faster dynamics. However, the change in bond energies is small and the potential of the diradical is essentially constant for small

energy changes to make a difference.^[11b)] Thus the increased number of degrees of freedom (18) when two methyl substituents are present and the increase in reaction rates suggest a highly nonstatistical behavior. Since the H-atom transfer is on the fs time scale, it is the reaction directionality that limits the phase space.

These intramolecular hydrogen transfer reactions, which are followed by cyclization or fragmentation, are quite common. In ion chemistry, the McLafferty rearrangement,^[13] as studied by mass spectrometry, is a direct analogue of Norrish type-II reactions. In fact, the electron impact mass spectra are very similar to our fs photoinduced mass spectra. Both the neutral channel (Norrish type-II reaction) and the ionic channel (McLafferty rearrangement: fragmentation of the parent ion) contribute to the overall m/z 58 signal. However, as discussed above, the fs resolution allows us to distinguish unambiguously between both processes: the contribution of the McLafferty rearrangement is reflected by a relatively short decay component, which, as expected, is identical to the neutral parent dynamics. On the other hand, the Norrish type-II reaction dynamics occur on the longer time scales reported in Figure 1. This observation is confirmed by the increase of the short decay component with increasing probe intensity. Moreover, the mass spectrum of 3-methyl-2-butanone, a structural isomer of 2-pentanone, lacks the m/z 58 peak, which is consistent with the fact that only ketones containing the γ C–H atom undergo the Norrish type-II reaction and McLafferty rearrangements, which are separated on the fs time scale.

Given the above experimental observations and theoretical studies, it is interesting to address the ultrafast population of the reaction intermediate (see insert Figure 2) and the nature of orbital correlations. The initial excitation of the ketones with a fs pulse populates a singlet excited surface (S'). Along the reaction coordinate (ρ), which involves the transfer of a γ -hydrogen atom, the molecule crosses a barrier. Based upon ab initio calculations of intermolecular hydrogen transfer reactions,^[14] it is suggested that intramolecular hydrogen transfer reactions of ketones also involve a conical intersection.^[15] The presence of such a conical intersection is consistent with the dominant deactivation path of excited ketones, that is, internal conversion to the ground state, and also with the ultrafast dynamics of the formation of the diradical reaction intermediate. The barrier on an adiabatic singlet excited surface (S') describes the hydrogen transfer when a C–H bond is broken and an O–H bond is formed, which is similar to the H-atom transfer process in malonaldehyde.^[16] Figure 3 gives a simple picture of orbital correlation, together with the calculated (DFT) highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

In conclusion, this contribution reports the fs dynamics of the elementary steps in Norrish type-II reactions, elucidating the nature of hydrogen atom transfer and the intermediate diradical species that undergoes closure and fragmentation. The energetics are obtained by density functional theory. Only with fs resolution can one dissect the two nonconcerted steps, and examine differences in Norrish type-II and McLafferty rearrangements, which are common in neutral and ion chemistry.

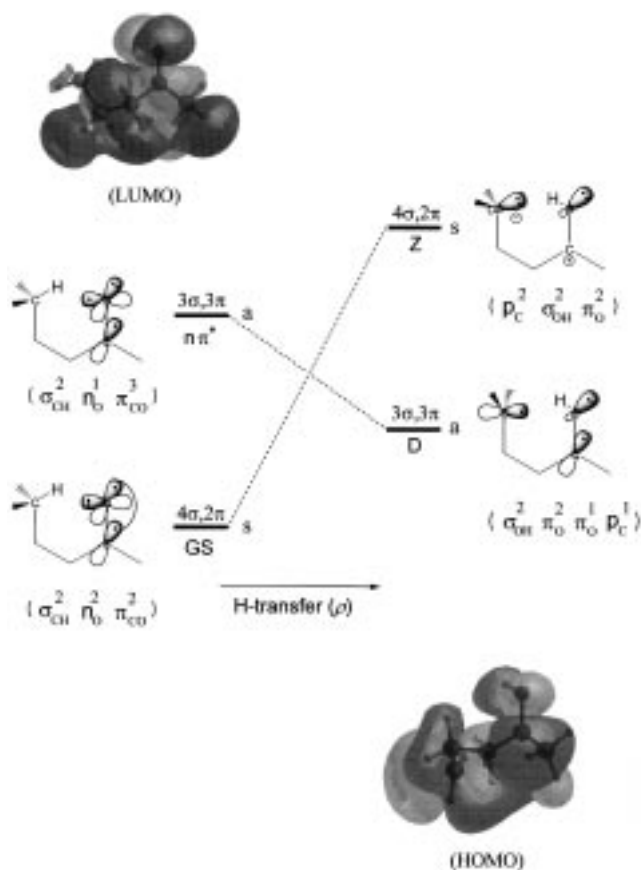


Figure 3. The HOMO and LUMO obtained from our density functional theory calculations, together with simple orbital correlations showing the direct formation of the diradical species. The correlation is with respect to the molecular plane of symmetry. Note that in the optimized geometry calculation of the HOMO and LUMO, this restriction is relaxed as the geometry is not planar.

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An EPR Investigation of the Kinetics of Inclusion of a Persistent Radical in Water-Soluble Calix[4]arenes

Paola Franchi, Marco Lucarini,* Gian Franco Pedulli,* and Domenico Sciotto

A voluminous literature reporting the synthesis and characterization of calixarenes behaving as highly selective receptors for metal cations and organic guest molecules has appeared during the last twenty years^[1]. These calixarenes are

[*] Dr. M. Lucarini, Prof. G. F. Pedulli, Dr. P. Franchi
Dipartimento di Chimica Organica "A. Mangini"
Università di Bologna, Via S. Donato 15
40127 Bologna (Italy)
Fax: (+39) 051-244064
E-mail: lucarini@alma.unibo.it, pedulli@alma.unibo.it
Prof. D. Sciotto
Dipartimento di Scienze Chimiche
Università di Catania, Viale A. Doria 6
95125 Catania (Italy)

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