J. Am. Chem. Soc. **1996,** *118,* 8755−8756 8755

Retro-Diels−Alder Femtosecond Reaction Dynamics

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Received June 20, 1996

In this communication, we present our first femtosecond (fs), real-time studies of the retro-Diels−Alder reactions of norbornene (NB) and norbornadiene (NBD), products of the cycloaddition of cyclopentadiene with ethylene and acetylene, respectively. The reaction path, together with transition state (TS) structures, is displayed in Figure 1 (bottom). The experiments were designed with the following considerations in mind. First, the reactions were studied in a molecular beam in order to isolate the elementary processes, free of solvent perturbations. Second, we examined the dynamics of the reaction from a well-defined initial geometry, a precursor of Diels−Alder products. Finally, with fs-resolved mass spectrometry we are able to study the transition of reactants to final products.

Since its discovery in the 1920s,[1] the nature of the TS and the mechanism of Diels−Alder reactions have remained the subject of intensive experimental and theoretical studies and heated debates.[2,3] In principle, there are two possible reaction mechanisms involving different TS structures:[4−11] a *concerted mechanism*, where the two bonds in the TS are formed in one step, at the same time (if at different times, then it is concerted asynchronous), or a *stepwise mechanism* with the formation of a diradical or a zwitterion intermediate as a first step (Figure 1).

The fundamental issue is, what is meant by concertedness of the reaction? As was pointed out elsewhere, for both Norrish[12] and pericyclic[13] reactions, the use of the molecular rotational time scale is not fundamental. Typically, a molecular rotation takes place in picoseconds or longer, but the dynamics of bond breakage/bond formation occur on the femtosecond time scale. Hence, the pertinent times for the dynamics are the actual TS time of passage, $\tau^{\ddagger}$ ("lifetime"), and the time of motion along the reaction coordinate, τ_{rxn}. Using internal rotations as a reference "clock", Berson and co-workers devised a clever kinetic approach to obtain the reaction time scales. By estimation of the rate of stereochemical change (through the internal rotation) and measurement of the degree of stereochemical retention, the rate of the reaction, $k_c(T)$, was deduced. They then compare $k_c(T)$ to the value derived from TS theory when $\Delta G^{\ddagger} \sim 0$; if the values are comparable, then there is no intermediate in the reaction path.[9,14]

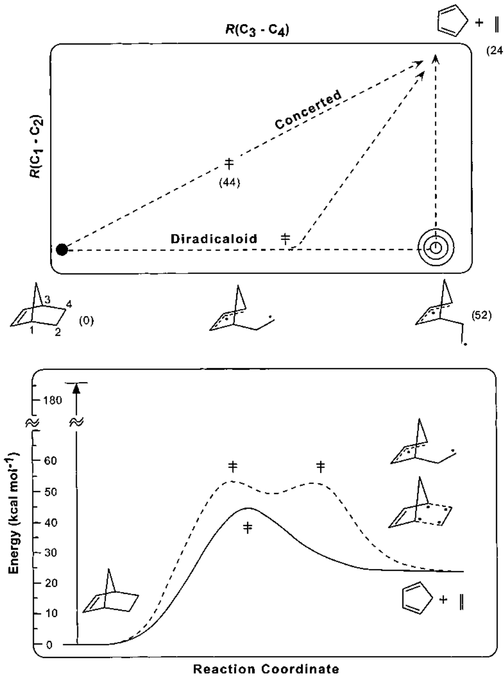

Figure 1. (top) Schematic of the reaction path as the length *R* of the two bonds changes in the Diels−Alder reaction or its reverse path. (bottom) Cut along the potential energy surface depicting the two reaction coordinates and their energetics. The energy of the diradical pathway (dashed) is adapted from ref 2.

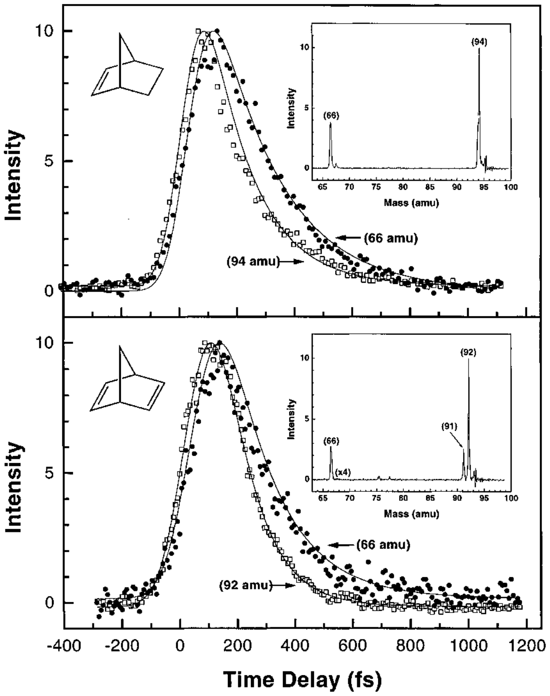

Figure 2. Femtosecond-resolved mass spectrometry of norbornene (top) and norbornadiene (bottom). The associated mass spectra are shown in the inserts.

Figure 2 shows the mass spectra obtained for NB and NBD in a molecular beam and with fs laser pulses.[15] For NB, there are only two peaks present: one at mass 94 amu corresponding to the precursor NB species and another at mass 66 amu corresponding to the "cyclopentadiene" intermediate. These observations are consistent with the retro-Diels−Alder products

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S0002-7863(96)02069-0 CCC: $12.00 © 1996 American Chemical Society

found in thermal,[16] photochemical,[17] and shock-wave[18] studies. For NBD, we observed three peaks, two representing the parent and intermediate and the third one for the parent minus 1 amu corresponding to the hydrogen elimination channel (see refs 16, 17, and 19). In the same figure, we display the fs transients.

For NB, at our total energy,[20] the precursor (94 amu) signal intensity rises with the fs pulses and decays exponentially back to its original intensity level; an exponential fit gives a decay time, τ, of 160 ± 15 fs. The signal from the intermediate rises and decays with different time constants; for the 66 amu, a biexponential function, convoluted with a Gaussian (pulse width ∼80 fs[15]), gave a rise time of $\tau_1 = 30 \pm 5$ fs and a decay time $\tau_2 = 220 \pm 20$ fs. (Similarly for NBD (Figure 2), $\tau \sim 110$ fs, $\tau_1 \sim 15$ fs, and $\tau_2 \sim 210$ fs.) When the energy was changed in NB to 137 kcal/mol, the analysis gave $\tau \sim 175$ fs, $\tau_1 \sim 40$ fs and $\tau_2 \sim 200$ fs.

The above results indicate that on the fs time scale we have observed an intermediate structure, the 66 amu fragment for both NB and NBD. The mass spectrum for NB only shows the two relevant masses, those of the precursor parent and the intermediate species. It is also evident that the breakage of the two C−C bonds occurs in 160 fs while the decay of the intermediate is in 220 fs. This difference in the decay excludes any production through the ionic channel of the reaction.[12,13] Furthermore, the fact that the 66 amu transient decays with time instead of building up indicates that it is an intermediate, *not* the final, stable cyclopentadiene product.

The observed dynamics bring to focus the following points. First, the fs time scale of the intermediates is longer than the vibrational period of the C−C bond, or the inverse rate value of TS theory for $\Delta G^{\ddagger} = 0$, indicating a true intermediate character on the reaction path. Second, the internal rotational period, given by the rate of stereochemical conversion, is about 1−10 ps,[21] longer than the reaction times. Given the reaction rates of the intermediates and these rates of stereochemical conversion, one deduces a very high degree of stereochemical retention (>90%), with the degree of stereorandomization reflecting the diradical presence. If the diradical species is not isolated in time, as in conventional studies of the whole product yields, then the stereochemical retention may be even higher, due to the concerted channel; the total yield will not indicate the critical role of the diradicaloid structure. In general, the precise value of the rotational rates cannot be determined for accurate clocking.

We have one more piece of information which helps us address the nature of the reaction path. When we carefully analyzed the buildup time τ_1 of the intermediate and compared it with the decay of the parent, we found that they do not match and in fact differ by a factor of 5. For this to occur, formation of the intermediate cannot be through one path only and must involve separate trajectories from the parent on the global potential energy surface (PES).

We suggest the following description. On the global PES both *symmetric* and *nonsymmetric* motions of the two C−C bonds are possible. The nonsymmetric motion will give rise to the *nonconcerted trajectories*, and in many ways is similar to the dynamical observations made in elementary reactions[22] and in double-proton transfer.[23] The symmetric motion will give rise to the *concerted trajectories*. Accordingly, the observed 160 fs is the time for the interconversion in the second step of the nonconcerted route through the diradicaloid structure. The implications to the Diels−Alder mechanism are of significance. *We suggest that both trajectories are present and that the asymmetry of the structure, the barrier height, and the available energy are the controlling elements for the formation of nonconcerted trajectories involving diradicaloid TS.* However, in both routes stereochemical retention is a consequence of the femtosecond C−C bond dynamical time scale.

The concerted trajectories produce the vibrationally-excited intermediate, cyclopent-2-ene-1,4-diyl, which then decays, after nuclear rearrangement and electronic hybridization, to form the products, cyclopentadiene and ethylene, in ∼200 fs.[24] The breakage of the two weakest C−C bonds[27] away from the initial fs excitation to the N → V and Rydberg states (for an excellent review, see ref 28) leads to the two types of trajectories of Figure 1 in ∼30 fs. This is consistent with the period of C−C stretch (∼40 fs).

We have made theoretical microcanonical RRKM and k(T) calculations. If NB is converting to products through the barrier on the ground state (Figure 1) and one concerted TS is invoked, the reaction times were found to be ∼5 ps, orders of magnitude slower than observed here. On the other hand, using the frequencies of modes given in ref 18, we obtained reaction times of ∼125 fs for the intermediates to transform to products, with an exit barrier of ∼5 kcal/mol, almost to the limit of $\Delta G^{\ddagger} \sim 0$. The diradical TS is expected to be at higher energy than the concerted TS by ∼8 kcal/mol,[2] and our measured reaction time of 160 fs is certainly of the correct order of magnitude. To connect with thermal $k(T)$ measurements we have used the $k(E)$ values and made a Boltzmann averaging at the internal temperature (1500 K) and obtained $k(T)$ of $\sim(300\ \mathrm{fs})^{-1}$, which is similar to that deduced for Cope rearrangement at relatively lower temperatures of ∼500 K.[14] For these reactions, we are currently studying the nature of the different channels and the molecular dynamics of different systems, including the isotopic species.

Acknowledgment. This work was supported by the NSF and by the AFOSR. We are grateful to Dr. J. S. Baskin for his effort on the RRKM calculations. We particularly acknowledge the stimulating discussions with and helpful suggestions from J. D. Roberts, J. Michl, K. N. Houk, and J. H. Kiefer. The discussions with Jerry Berson on the stereochemistry was paramount in clarifying several points and in kindling excitment about the organic world. We also thank Michael Machczynski for his experimental help and suggestions in the initial stage of the study.

JA9620696

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(20) The initial two-photon energy is 184 kcal/mol. Because the bond energy is ∼44 kcal/mol, the available energy is ∼140 kcal/mol.

(21) For a freely rotating methylene group, the inertial rotational time is 1.8 ps. For a rotation with a barrier, we used the Arrhenius equation to deduce the rotation rate, given E_0 of ∼1−3 kcal/mol and A (determined by the torsional motion, e.g., 290 cm^{-1} for ethane) of $8.7 \times 10^{12}\ \mathrm{s}^{-1}$.

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(24) It is known that these retro-Diels−Alder reactions proceed on the ground state PES. The reaction gives the same product whether activated thermally or photochemically,[16−19] implying ultrafast conversion to the ground state when photochemical activation is used. However, it should be noted that the breakage of a single bond by photochemical excitation leads to a diradical species in the ground state and the process of symmetry correlation is allowed as all states of diradical are degenerate. The breakage is also favorable because of the formation of the relatively stable allyl-type radical and the release of strain energy. For the concerted trajectories it is possible that, photochemically, the internal conversion occurrs at configurations far from equilibrium, utilizing a conical intersection[25] to convert cyclopentadiene species to the ground state. Excited-state correlation could lead to such state with subpicosecond lifetime.[26]

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