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Inertial Effects on the Intramolecular Vibrational Energy Redistribution and Nonadiabatic Photoisomerization of a 2,3-Substituted 1,3-Butadiene: A Quasi-Classical CASSCF Dynamics Study[†]

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Quasi-classical CASSCF trajectory calculations have been carried out on *s-cis*-1,3-butadiene and substituted 2,3-dideuterio-1,3-butadiene (DDB) to assess the inertial effect on the ultrafast nonadiabatic deactivation of their first singlet excited states. Calculations indicate that even this modest increase in the mass of the 2,3-substituents noticeably affects the photodynamics of *cis* → *trans* isomerization, by reducing the efficiency of the vibrational energy leakage between the initial relaxation and subsequent nonadiabatic decay modes. In qualitative agreement with experimental findings on related 1,3-dienes, the slowing down of the intramolecular vibrational energy redistribution (IVR) upon substitution results in extended excited-state lifetimes and reorients the photoregioselectivity toward *cis* rotamers and cyclic products.

Introduction

As is the case with thermal reactions, photochemical processes can be controlled by substitution through steric and electronic effects. For example, ring substituents can be employed to lock chromophores against isomerizations responsible for degrading the active species.[1] Electron donor or acceptor groups are capable of altering the topology of potential energy surfaces in a way that reinforces the desired behavior, such as the photochromic activity of fulgides or the emission of fluorophores.[2] In this work we explore a third approach that involves dynamically controlling photoregioselectivity using the inertial effects of substituents. To our knowledge, there have only been a few experimental studies investigating this effect,[3,4] and a single computational study which did not include dynamics calculations.[5] We present here the results of quasi-classical dynamics simulations on *s-cis*-1,3-butadiene and substituted 2,3-dideuterio-1,3-butadiene (DDB) illustrating inertial control of photoselectivity.

A schematic representation of the photodecay of *s-cis*-1,3-butadiene is shown in Figure 1.[6] The acyclic 1,3-diene absorbs a single photon at 254 nm and is promoted to the 1^1B_u ionic singlet excited state (S_2). After a few tens of femtoseconds this decays to the 2^1A_g covalent excited state (S_1) via an internal conversion process, and then propagates on S_1 for a few hundred femtoseconds before returning to the covalent 1^1A_g ground state (S_0) surface radiationlessly through an S_1/S_0 conical intersection (CI). Deactivation of *s-cis*-1,3-butadiene proceeds principally via an ultrafast (i.e., subpicosecond) nonadiabatic population transfer and yields a mixture of species: *cis* (**1c**) and *trans* (**1t**) single bond conformers, *E*/*Z* and *EE*/*ZZ* double bond conformers (**1c**$_{E\rightarrow Z}$ and **1c**$_{EE\rightarrow ZZ}$), and the cyclic products cyclobutene (**2**), methylenecyclopropyl diradical (**3**) and bicyclobutane (**4**). In previous computational work, minimum energy pathways were located for the disrotatory formation of **2**, and for **1c**$_{E\rightarrow Z}$, **3** and **4** following the photoexcitation of *s-cis*-butadiene, whereas *s-cis*/*s-trans* isomerization and concurrent double bond isomerization were attributed exclusively to dynamic pathways.[7b]

Numerous earlier theoretical studies, including some based on dynamics simulations, have provided considerable insight into the mechanism of diene deactivation.[7] It has been established that the system enters the S_1 surface with a molecular structure similar to the C_{2v} Franck−Condon (FC) geometry with some additional torsion of the terminal methylene groups and then relaxes adiabatically along the Q_{relax} nuclear coordinate toward a minimum on the surface.[8] Q_{relax} is dominated by in-plane conversion of the central single bond to a double bond, and the terminal double bonds to single bonds. In typically 1 ps or less, part of the nuclear kinetic energy initially accumulated in this high-energy vibrational mode flows to the lowest-energy nonadiabatic mode Q_{nonadia}, which is dominated by torsional motion, leading to rotation around the single bond that channels the system toward the conical intersection region where a nonadiabatic S_1/S_0 hop can occur. This crossing seam is known to extend over a large range of dihedral angles (θ):[5−7] nonadiabatic transitions at small torsional angles are expected to favor the formation of *cis* isomers and cyclic products over *trans* isomers, and vice versa for large values of θ. As heavier groups accelerate more slowly than lighter groups (inertial effect), classical mechanics would predict that 2,3-substitution of 1,3-dienes by groups or atoms heavier than hydrogen should slow down the $Q_{\mathrm{relax}} \rightarrow Q_{\mathrm{nonadia}}$ energy flow (IVR from stretch to torsion). This should lead to longer excited-state lifetimes, and decay to S_0 occurring at smaller angles of θ before IVR is complete, disfavoring the formation of *trans* products.

The few pertinent experimental studies of substituted dienes largely support the idea of a mechanistic scenario controlled by classical inertial effects.[9] Low-temperature spectroscopy experiments in an argon matrix carried out by Squillacote and co-workers demonstrated that 2,3-dimethyl substitution of s-*cis* 1,3-butadiene leads to a sharp decrease in the quantum yield of *trans* product and an increase in cyclobutene formation.[4b,c] At

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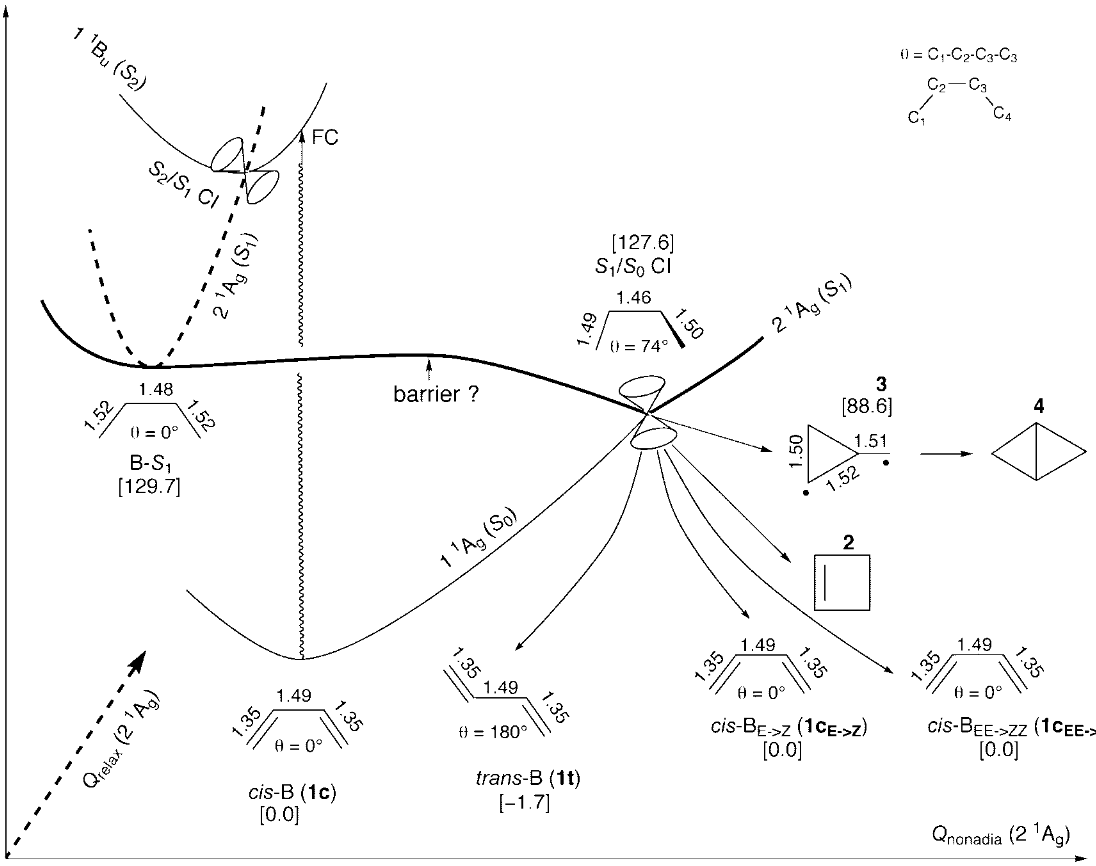

Figure 1. Representation of the potential energy surfaces and reaction pathways involved in the photoisomerization of *s-cis*-1,3-butadiene. Several distinct regions and critical points have previously been located on the S_1/S_0 conical intersection (CI) seam.[5-7] The CAS(4,4)/STO-3G energies (in kcal mol^{-1}) of the species observed during our simulations are given in square brackets, relative to the energy of *s-cis*-1,3-butadiene on S_0 (−153.101643 hartree). Bond lengths are given in Å. The trajectories are started on the covalent excited state (labeled S_1) where the Franck−Condon (FC) energy is +173.3 kcal mol^{-1}. The main topological features of the CAS(4,4)/STO-3G potential energy surfaces are identical to those computed at higher levels of theory and can be summarized as follows:[5-7,13] (i) at the FC geometry, the system is tens of kcal mol^{-1} above the minimum (or pseudominimum)[8] and this excess of energy can be used to overcome a barrier if it exists, (ii) the relaxation coordinate (Q_{relax}) on S_1 is dominated by single and double bond reversal, whereas the nonadiabatic coordinate (Q_{nonadia}) is mainly a twisting motion, and (iii) the S_1/S_0 seam is easily accessible over a large range of values of the C−C−C-C torsion angle θ.

15 K, deuteration of 2,3-dimethyl-1,3-butadiene (DMB) to the perdeuterated compound DMB-d_{10} stops *cis* → *trans* isomerization altogether.[4a] In contrast, singly substituted 1,3-dienes do not exhibit the expected trend and the related experimental findings are somewhat contradictory: the photoregioselectivities of 2-isopropyl-substituted[4d] and unsubstituted butadienes are identical but differ from that of 2-cyano-1,3-butadiene.[3] However, these two last experiments are less informative. From an inertial point of view, it is unclear how single substitution affects the ease of central bond isomerization, what the role of the solvent is, or if cyanide ligands have significant electronic effects.

In this study we compare the S_1 decay dynamics of *s-cis*-1,3-butadiene with 2,3-dideutero-1,3-butadiene (DDB). Deuterium atoms present the advantage of being electronically equivalent to hydrogen atoms; therefore, the simulations of 1,3-butadiene and DDB photodynamics can be performed using exactly the same potential energy surfaces, and the differences in their outcomes attributed solely to inertial effects. In addition to this, the relatively small increase in the mass of the substituent still confines the excited-state lifetime to the picosecond regime and makes the simulations computationally feasible. The main focus of the work is to see how deuterium substitution affects the geometry at which nonadiabatic decay to S_0 occurs, and what consequence this might have on the overall yield of the *trans* isomer. We stress that our primary interest is to test for the existence of an inertial effect, rather than attempting to quantitatively reproduce experimental data such as the yield of *trans* butadiene isomer as measured at room temperature and in solution. Similarly, we have not included an extensive mapping of the potential energy surfaces involved, as there are numerous studies in the literature describing these in greater detail.[7]

Computational Details

Quasi-classical CASSCF(4,4)/STO-3G trajectory calculations were carried out using the dynamics code implemented in the *Gaussian 03* package.[10] The nuclei were propagated using Newtonian Born−Oppenheimer dynamics with CASSCF gradients and Hessian-based trajectories for 2 ps, with a 0.5 fs integration time step. Microcanonical sampling of both velocities and coordinates was carried out on the ground-state surface. The initial conditions were determined by randomly distributing the ground-state zero point energy into potential and kinetic components with the help of the fixed normal-mode sampling procedure and then projected onto S_1 where the trajectories were initiated.[11] It has previously been shown that such sampling can accurately model the approach to a conical intersection.[12] The system was allowed to decay to S_0 via a trajectory surface hop algorithm implemented in Gaussian 03,[10] using the approach described by Groenhof and Robb.[13,14] Here, the CASSCF eigenvector at a point along the trajectory is compared with its previous value, and a large change in the eigenvector—together with a small energy gap between S_0 and S_1—is used to decide whether a crossing to S_0 should take place (i.e., that a region of strong nonadiabatic coupling has been encountered). State-averaged CASSCF was used throughout to ensure both potential energy surfaces were treated at the same level.

The trajectories were started directly on the dark covalent S_1 state (Figure 1) rather than on the absorbing S_2 state due to the methodological difficulty in describing the B_u ionic states of 1,3-dienes.[15] This is not expected to have a dramatic effect on the results, given the particularly short lifetime of the molecules on S_2 (see above), and the fact that the 1^1B_u and 2^1A_g states have previously been calculated to have similar energies at the Franck−Condon geometry using highly correlated post-CASSCF methods.[15]

All calculations were carried out with the minimal STO-3G basis set, due to the large number (0.8 million = 4000*100*2) of CAS energies, gradients and Hessians that needed to be evaluated. We believe that the use of the minimal STO-3G basis set should not affect the qualitative outcome of the simulations. First, the key topological features are identical to those previously determined from much higher-level calculations[5−7,15] (see Figure 1 caption). Second, for the *cis* → *trans* photoisomerization of a model chromophore of a protonated Schiff base, it was found that the use of a small basis set biases the dynamics toward longer excited-state lifetimes and lower conversion rates but does not alter the general mechanistic scenario. Finally, as we are testing for an inertial effect, we are only interested in how a change of mass affects the dynamics of a reaction given a common potential energy surface.

In this work the "product" was considered as being the first energy minimum reached on the S_0 surface after decay from S_1. Our simulations show that it is not uncommon for a vibrationally hot *trans* isomer that has just decayed to continue rotating around the central bond and to convert back to the *cis* isomer, and in some cases up to three successive rotations were observed within the ensemble of trajectories. In our view, defining the product in this way best reflects how the decay process is affected by substitution; i.e., we are not interested in the subsequent dynamics on the S_0 surface.

In agreement with a former computational study[7b] and experimental results,[3b,16] both $E \rightarrow Z$ and $EE \rightarrow ZZ$ isomerization occurring in the earliest stage of relaxation on the S_1 surface was observed for several trajectories. However, this conversion process was not monitored systematically as the resulting products are structurally equivalent. On the other hand, no trajectories led to the formation of cyclobutene,[17] contradicting results reported in a previous computational study using the MMVB method,[7b] and experimental work (where $\Phi = 0.12$ for cyclization was reported for 2,3-dimethylbutadiene in solution).[16] Reasons for the disagreement between the present and previous computational studies could include the following: (i) differences in the computed potential energy surfaces, (ii) solvent effects (a Stokes law viscosity term) were included in the previous study, and (iii) the dynamics in this study are stopped shortly after the hop has occurred.

Results and Discussion

Key results based on an ensemble of approximately 90 nonadiabatic trajectories for each butadiene and DDB system are presented in Table 1, and Figures 2 and 3 show the distribution of hops as function of torsional angle θ and time. The two sets of trajectories share common features. After 2 ps of simulation time, only *s-cis*-butadiene (**1c**), *s-trans*-butadiene (**1t**) and methylenecyclopropyl diradical (**3**) are observed. The average twist angle at the hopping geometry is quite large (∼80°) in both butadiene and DDB systems, which confirms that torsional motion is one of the main nuclear distortion coordinates associated with the nonadiabatic decay.

TABLE 1: Key Results of the Dynamics Study[a]

	butadiene	DDB
S_1 lifetime τ (fs)	989	1087
θ_{average} at the hopping geometry (deg)	82.1	79.8
% of *cis*-butadiene product (**1c**)[b]	56.7	63.9
% of *trans*-butadiene product (**1t**)[b]	41.1	30.2
% diradical cyclic product (**3**)[b]	2.2	5.8

[a] 100 trajectories in total were computed for butadiene and DDB. With hopping rates of 90% and 86% at the 2 ps cutoff time, the statistics include exactly 90 and 86 nonadiabatic trajectories for each system, respectively. [b] The nature of the product is determined just after decay when the system visits the first potential well on the S_0 surface.

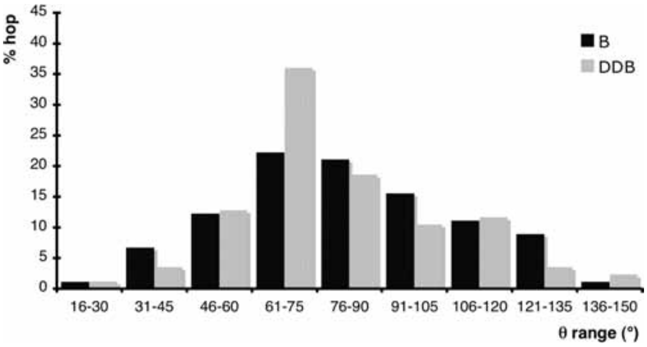

Figure 2. Distribution of hops (in %) occurring for a given range of twisting angle θ (in deg) for *s-cis*-1,3-butadiene (B) and DDB systems.

The differences between the two sets of simulations are subtle but fully consistent with the classical picture described above. Deuteration increases the average S_1 lifetime τ by approximately 98 fs (Table 1). The torsional mode is computed to be the lowest mode in the vibrational spectra of both S_1 and S_0 electronic states, although on S_1 it is shifted toward a higher frequency due to the central bond gaining some double bond character. Deuteration increases the period of vibration of this mode by approximately 7 fs on S_1; the remaining 91 fs difference is some indication of the extent to which deuteration slows down the IVR.

Deuteration is also associated with a 2° decrease in the average dihedral angle at the hopping geometry, although this reduction is sufficiently modest that it may not be statistically relevant. However, the distribution of θ at the hopping geometries indicates that deuteration has a strong impact on the propagation on S_1 and that butadiene hops over a much wider range of twisting angles θ compared to DDB. In other words, although the change in average hopping angle is modest, the spreading of the nuclear wavepacket over the S_1/S_0 seam has clearly been limited by deuteration. The results suggest that the overall effect on the photoregioselectivity is an 11% reduction in the quantum yield of *trans* isomers, and an increase in the formation of cyclic products (+4%) and unreactive (+7%) decay channels.

The differences in the distributions of θ, together with the changes in photoregioselectivities and S_1 excited-state lifetimes, are a strong indication that in the gas phase the inertial effect is taking place on the S_1 surface; i.e., the twisting mode is the

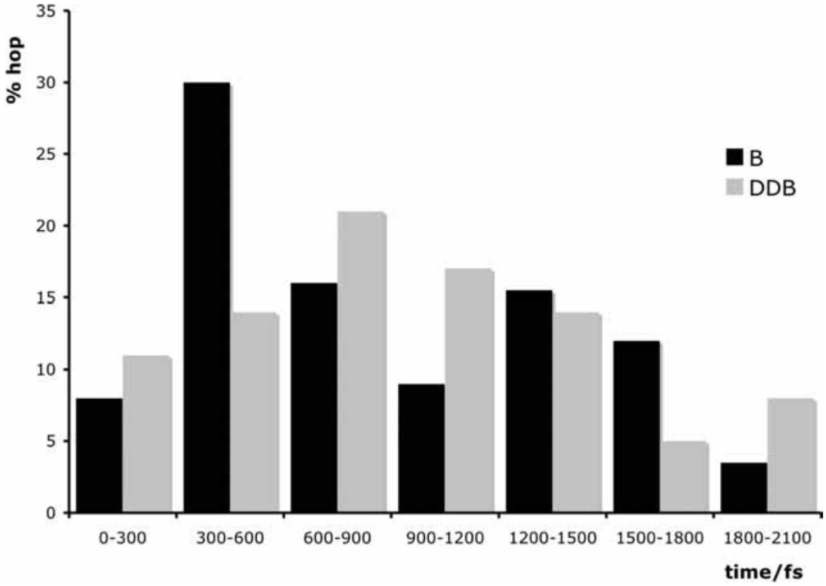

Figure 3. Distribution of hops (in %) as a function of time (in fs) for *s-cis*-1,3-butadiene (B) and DDB systems.

best acceptor of nuclear kinetic energy, not only on S_0 but also on S_1. This partly contradicts previous conclusions on related systems.[5] However, the latter were based on experiments conducted in solution where collisions with solvent molecules help to dissipate the thermal energy, and these are known[7b] to profoundly affect the photodynamics.

Conclusions

Quasi-classical CASSCF trajectory calculations have been carried out on *s-cis*-1,3-butadiene and substituted 2,3-dideuterio-1,3-butadiene (DDB) to assess the inertial (or "ponderal") effect on the ultrafast nonadiabatic deactivation of their first singlet excited states. The calculations indicate that a pure inertial effect does exist, and that even a modest increase in the mass of the 2,3-substituents noticeably affects the photodynamics of *cis* → *trans* isomerization. The increased inertial moments reduce both the efficiency of the vibrational energy leakage between the relaxation and nonadiabatic modes and the spreading of the wave packet on S_1. The results of the simulations suggest that the overall effect is to extend the excited-state lifetime of *s-cis*-butadiene (by nearly 100 fs), and to reduce the quantum yield of *trans* isomers (by up to 11%), in favor of *cis* isomers and cyclic products.

Several factors are known to influence the rate of IVR depending on the system in question and the timescales of the processes involved.[18] One is the density-of-states, derived from statistical mechanics: deuteration should increase the density of states that can be coupled and actually speed up IVR. However, previous experimental studies have shown that density of states is not necessarily a good predictor of vibrational lifetime for excited-state systems and tends only to be important on longer time scales.

This study provides an example of incomplete IVR affecting reactivity, because the reaction itself is ultrafast. Leitner and co-workers have also recently reported deuteration effects on IVR and *cis*−*trans* isomerization in stilbene. *Cis*−*trans* isomerization here was inhibited on deuteration, but this was predominantly due to the change in the S_1 barrier height due to zero point energy effects.[19] Such effects are unlikely to be important here, as the internal energy in the system is high, the excited-state lifetime is short, and the rate of reaction is dominated by nonadiabatic effects rather than a well-defined barrier on S_1.

Supporting Information Available: Representative Gaussian input files for the S_1 dynamics calculations. This information is available free of charge via the Internet at http://pubs.acs.org.

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