

Direct Dynamics Study of the Stereomutation of Cyclopropane

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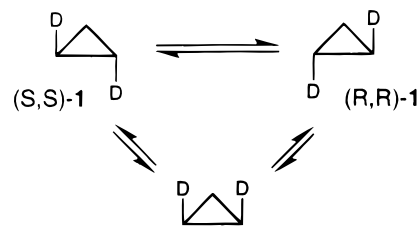
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In this paper we use classical trajectories to study the stereomutation of cyclopropane-1,2- d_2 .¹ We address two unsettled issues: the existence of trimethylene as a mechanistically significant intermediate, and the relative rates of double vs single rotation of the terminal methylene groups. These have been central issues for 3 decades, following theoretical work of Hoffmann^{1d} and Salem^{1e} and Benson's bond additivity model.^{1g} We also hope to examine nonstatistical effects that were not addressed in previous studies of small biradicals.^{2,3} In our recent direct dynamics study,⁴ we found that the decay of trimethylene is nonstatistical and intrinsically non-RRKM at low energy. Carpenter has presented substantial evidence that certain reactions proceeding via biradical structures show strong nonstatistical effects.⁵

The experimental situation is that two careful studies of isotopically substituted cyclopropanes have yielded different conclusions about the mechanism of stereomutation. The point of divergence is the double/single rotation ratio, k_{12}/k_1 , deduced from the relative rates of cis–trans equilibration and optical isomerization. In Berson's study of (S,S)-1 at 695 K (Scheme 1),⁶ the deduced value of k_{12}/k_1 depends strongly on the isotope effects (k_H/k_D) assumed for CHD–CHD vs CH₂–CHD cleavage. Berson's choice of k_H/k_D gave $k_{12}/k_1 = 50$, but other reasonable choices could bring this value down to about 5.^{6c} The collaboration of Baldwin, Lewis, Nafie, and Freedman⁷ reported $k_{12}/k_1 = 1.0 \pm 0.2$ from cyclopropane-1-¹³C-1,2,3- d_3 at 680 K, which required no assumption about k_H/k_D . The two pictures of stereomutation are very different. Berson's $k_{12}/k_1 = 5–50$ suggests a moderate to negligible stereorandom component and is consistent with predominant concerted double rotation. Baldwin's $k_{12}/k_1 = 1$ is consistent with a stereorandom

Scheme 1



intermediate or with competitive concerted single and double rotations.

At the outset, we can get a simple estimate for the time it takes a CHD group to rotate at 695 K. For a rotor with mean kinetic energy kT (the mean energy of a reaction coordinate⁸) the angular velocity, $(2kT/I)^{1/2}$, is 2.2×10^{13} radian s^{-1} for a CHD with a reduced moment of inertia I of 2.48 amu \AA^2 . The resulting mean time for a 180° CHD rotation is 140 fs, close to Zewail's 122 ± 8 fs lifetime for trimethylene- d_0 at high energy.^{9,10}

In the simulations reported here we use direct dynamics, in which trajectories are integrated using energies and derivatives obtained directly from semiempirical electronic structure theory without an analytic potential energy surface (PES).^{11,12} To do this we combined the general dynamics program VENUS¹³ with the MOPAC semiempirical package.¹⁴ Our PES, AM1-SRP (AM1¹⁵ with specific reaction parameters¹⁶), accounts for cyclization and propene formation and has been described in detail.⁴ Recent ab initio calculations on trimethylene^{2,10,17} predict a nearly flat PES in which conrotatory double rotation is favored over single rotation by about 1.5 kcal/mol and over disrotation by about 1 kcal/mol. AM1-SRP shows similar features. Three transition states govern conrotation, disrotation, and single rotation. There is a single broad, flat minimum along the conrotation path with a 0.4 kcal/mol cyclization barrier. The disrotation and single rotation barriers are 2.8 and 2.0 kcal/mol above the minimum, respectively. In a test of AM1-SRP,⁴ direct dynamics gave a trimethylene lifetime of 90 fs, close to experiment,^{9,10} and variational RRKM gave very similar results⁴ to variational RRKM on the ab initio PES.^{2a}

We examined two sampling schemes for generating a Boltzmann distribution for trimethylene at 695 K. With *barrier sampling*, we began at a transition structure and chose initial conditions by randomly perturbing that structure using quasi-classical normal mode sampling,¹⁸ then Boltzmann averaged the results from the three barriers. In *torsional Monte Carlo (MC) sampling*, we sampled the 19 nontorsional modes by normal

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Table 1. Effect of Initial Conditions on Product Distribution at a Fixed Energy of 4.39 kcal/mol above zpe, Initiated with Barrier Sampling at the Conrotatory Cyclization Barrier

n^a	E_{rc}^b	N_{tot}^c	N_{ct}^c	N_{con}^c	N_{dis}^c
0	4.39	104	0	100	0
1	3.77	100	1	91	1
3	2.56	114	21	71	1
7	0.13	101	34	12	22
3 ^d	2.56	109	0	108	0
3 ^e	2.56	124	68	15	7
3 ^e	2.56	126	0	8	0

^a Number of quanta initially placed into the lowest orthogonal mode (disrotation). ^b Initial kinetic energy of the conrotatory reaction coordinate in kcal/mol. ^c N_{tot} : total number of trajectories. N_{ct} : number of single rotation (cis→trans) trajectories. $N_{con(dis)}$: number of conrotatory (disrotatory) double rotation trajectories. ^d >95% of energy initially placed in mode 1 is potential energy. ^e >95% of energy in mode 1 is kinetic; rows 6 and 7 have mode 1 momenta of equal magnitude but opposite sign.

Table 2. k_{12}/k_1 Ratios as a Function of Sampling Scheme and C–C Cleavage Mode

sampling scheme	no. of traj	CHD–CHD	CHD–CH ₂
barrier	649	2.9	2.9
torsional MC	1219	3.5	4.1

mode sampling¹⁸ (using normal modes of a point near the conrotation barrier) and allowed the torsions to take on random values subject to thermal MC sampling.¹⁹ We integrated each trajectory forward and backward in time until a product was formed in each direction.

Table 1 shows results for *fixed energy* ensembles started at the conrotatory barrier with quasiclassical normal mode sampling.¹⁸ Here we examine the product distribution as a function of initial conditions, keeping the total energy at 4.39 kcal/mol above the zero point energy (zpe). If the dynamics were statistical, all conditions would yield the same product distribution. When all 4.39 kcal is in the conrotatory reaction coordinate, isomerization is exclusively conrotatory (row 1). If we remove energy from the reaction coordinate and place 1, 3, and 7 quanta into the lowest orthogonal mode (mode 1, disrotation), disrotation and single rotation increase. In rows 5–7, we put 3 quanta into mode 1 and control its initial phase (ratio of kinetic to potential energy). In row 5, >95% of the energy in mode 1 is potential energy. In rows 6 and 7, >95% is kinetic, with initial momentum of equal magnitude but opposite sign. Clearly the initial phase of mode 1 has a large effect on the ensuing dynamics. Overall, Table 1 shows very strong mode selectivity.

In the calculations at 695 K we computed the product distribution from the number of trajectories that connect each pair of isomers in Scheme 1. Table 2 shows the final k_{12}/k_1 ratios. Within a steady state kinetic description of trimethylene including cyclization via conrotation, disrotation, and single rotation, transition state theory (TST) predicts $k_{12}/k_1 = 1.5$, well below the values in Table 2. The difference is consistent with high mode selectivity in the trajectory results as documented in Table 1.

The lifetime distribution obtained with torsional MC sampling is strongly nonexponential.²⁰ Approximate time constants for trajectories initiated with CHD–CHD cleavage are $\tau \approx 60$ fs at times $t < 100$ fs, $\tau \approx 230$ fs for $100 < t < 550$ fs, and $\tau \approx 600$ fs for $t > 600$ fs. Seven percent of the trajectories last 1–4 ps. Figure 1 shows the survival probabilities for *reactive* trajectories (i.e., forward and backward propagation led to different cyclopropane isomers) initiated with torsional MC

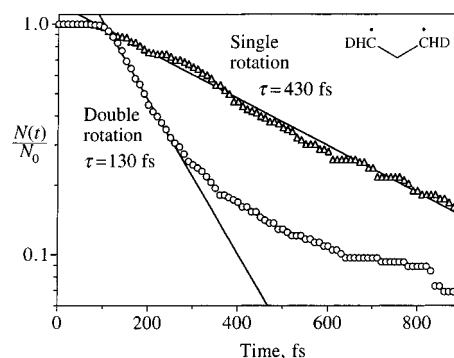


Figure 1. Semilog plot of survival probability $N(t)/N_0$ of reactive trajectories, where $N(t)$ is the number of trajectories that have not formed product at time t , and N_0 is the total number at $t = 0$. The abscissa is the time elapsed between entering the trimethylene PES through one cyclization transition state and leaving it through another. Triangles represent net single rotation ($N_0 = 142$) and circles represent net double rotation ($N_0 = 251$), including optical isomerization and cis-to-cis double rotation. Rotations of 2π are taken into account—e.g., a double $\pi, 2\pi$ rotation is counted as a single π rotation. Single exponential fits (straight lines) give the time constants τ .

sampling. The ratio of time constants, $430/130 = 3.3$, is essentially the same as the $k_{12}/k_1 = 3.5$ derived from product ratios. Most double rotation trajectories undergo a single set of 180° rotations and cyclize immediately. In the large majority of cases, the duration of a trajectory is the time it takes to achieve a (90,90) geometry (each methylene twisted 90° out of the CCC plane). The common feature of most long-lived trajectories is a mismatch of torsional phases that prolongs the trajectory. We base this on a survey of reactive and unreactive trajectories lasting >500 fs, 84% of which cyclize on the first approach to (90,90) even though they undergo many rotations.

In classifying the mechanism as concerted or nonconcerted, one could adopt the criterion that a species detectable by transient spectroscopy⁹ must be an intermediate. However, the majority of double rotation trajectories could hardly be more direct. It is legitimate to call these concerted. On the other hand, >400 fs is a time scale that accommodates multiple rotations and is more typical of an intermediate. Regardless of lifetime, nearly all share the property that the trajectory ends at the first approach to (90,90).

A kinematic model in which the lifetime is determined by the time it takes to reach (90,90) suggests a simple interpretation of Herek and Zewail's isotope effect.²¹ They measured $\tau = 122 \pm 8$ and 183 ± 14 fs for trimethylene- d_0 and $-1,1,3,3-d_4$, respectively. The kinematic model predicts a biradical decay rate proportional to the angular frequency, $(2E/I)^{1/2}$, where E is the energy. The ratio $[I(\text{CD}_2)/I(\text{CH}_2)]^{1/2} = 2^{1/2}$ predicts $\tau = 173$ fs for trimethylene- d_4 , within experimental error of the observed value.

In summary, classical trajectories on the AM1-SRP PES support a mechanistic continuum encompassing concerted and nonconcerted, in which nonstatistical effects are paramount. Our $k_{12}/k_1 = 2.9$ – 3.5 is not far from the 4.7 reported by Hrovat, Fang, Borden, and Carpenter²² on an analytical PES, which also showed nonstatistical character. The similarity of the two calculations suggests that these are robust features of trimethylene itself and are not strongly dependent on the subtle details of the PES.

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