10934 *J. Am. Chem. Soc.* **1996,** *118,* 10934−10935

Secondary Deuterium Kinetic Isotope Effects on the Isomerization of the Trimethylene Diradical to Cyclopropane

John E. Baldwin,*,† Teresa B. Freedman,†
Yukio Yamaguchi,‡ and Henry F. Schaefer III*,‡

Department of Chemistry, Syracuse University
Syracuse, New York 13244
Center for Computational Quantum Chemistry
University of Georgia, Athens, Georgia 30602

Received June 21, 1996

The trimethylene diradical (**1**-d_0) has long been considered a possible or even a likely short-lived reactive intermediate.[1−3] It has been frequently invoked heuristically in attempts to interpret the thermal isomerization of cyclopropane to propylene,[4] the photochemical decarbonylation of cyclobutanone,[5] loss of nitrogen from 1-pyrazoline[6] and from trimethylenediazene,[7,8] and the stereomutations of isotopically-labeled cyclopropanes.[3,9−12] Many different experimental and yet indirect approaches have provided ever more refined information bearing on the chemical propensities of the trimethylene diradical, and an equally extensive theoretical campaign has been waged to pin down its structural characteristics and modes of reactivity.[13−16]

$CH_2CH_2CH_2$

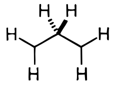
1-d$_0$

Late in 1994, Pedersen, Herek, and Zewail reported an experimental determination of the lifetime of the singlet trimethylene diradical generated photochemically from cyclobutanone.[17] Using femtosecond pump and probe pulses, and mass spectrometric and molecular beam techniques, they determined that the trimethylene intermediate formed from cyclobutanone decayed rapidly, with a lifetime of only 120 ± 20 fs. This real-time detection of the transient trimethylene diradical, a significant experimental achievement, validated the trimethylene diradical intermediate hypothesis and pointed toward fresh possibilities for bringing theory and experimental findings into closer dialogue. Related experimental and theoretical work on photochemical decarbonylations of ketones[18,19] and on tetramethylene diradical intermediates[20,21] soon followed.

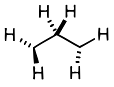
Relative lifetimes of three deuterium-labeled trimethylene diradicals, **1**-d_2, **1**-d_4, and **1**-d_6, have now been calculated; two of these relative lifetimes have been measured in recent experimental work. Comparisons between calculated and experimental relative lifetimes for deuterium-labeled trimethylenes provide a further test of the diradical intermediate hypothesis.

$CH_2CD_2CH_2$	$CD_2CH_2CD_2$	$CD_2CD_2CD_2$
1-d$_2$	**1**-d$_4$	**1**-d$_6$

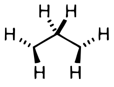
Published ab initio computations using DZP-TCSCF wave functions provided energies, molecular geometries, and vibrational force fields for the singlet trimethylene intermediate **1**-d_0-int (of C_s point-group and C_{2v} molecular symmetry[22]) and for the two transition structures leading from it to cyclopropane, one of C_1 point-group symmetry (for the conrotatory path) and one of C_s (for the disrotatory path).[13,14]



1-d$_0$-int



1-d$_0$-C_1(ts)



1-d$_0$-C_s(ts)

From these force fields were calculated the vibrational frequencies for the trimethylenes and the various deuterium-labeled trimethylenes. The frequencies were all scaled by a factor of 0.9 and then used to calculate k_H/k_D values over a range of temperatures for reactions proceeding from d_i-trimethylene intermediates to d_i-cyclopropane species using a conventional approach for the semiclassical rate constant ratios, with the aid the Bigeleisen−Mayer equation and the Teller−Redlich theorem.[23] These calculated k_H/k_D values are presented in Table 1. From them, the secondary deuterium isotope effects on overall relative isomerization rates and relative lifetimes were predicted through simple calculations involving no new parameters.

A kinetic model developed earlier for the thermal stereomutations of deuterium-labeled cyclopropanes by way of **1**-d_i intermediates as well as directly by way of "EF" transition structures[14] may be applied immediately to the paths leading from intermediates through conrotatory and disrotatory paths to cyclopropanes. For unlabeled trimethylene, 80% of the isomerization occurs by way of conrotatory motions through four equivalent versions of **1**-d_0-C_1(ts), while 20% takes place through disrotatory modes through two equivalent versions of **1**-d_0-C_s(ts), according to the results of quantum chemical calculations and the steady-state kinetic model employed.[14] The conrotatory paths are definitely favored, in agreement with the early theoretical findings of Hoffmann,[24] but the intermediate may also isomerize to cyclopropane through disrotatory ring closures. Recent calculations based on variational unimolecular rate theory[16] suggest that this balance is sensitive to the energy of the intermediate. At a total energy (E) that is 10 kcal/mol above the trimethylene intermediate, the conrotatory/disrotatory

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† Syracuse University.
‡ University of Georgia.

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S0002-7863(96)02083-5 CCC: $12.00

Table 1. Calculated k_H/k_D Ratios for Isomerizations of d_i-Trimethylene Diradical Intermediates (**1**-d_i-int) to d_i-Cyclopropanes by Way of Transition Structures **1**-d_i-C_1(ts) and **1**-d_i-C_s(ts)

	temp (K)			
trans. structure	500	700	900	1100
1-d_2-C_1(ts)	1.015	1.015	1.015	1.014
1-d_4-C_1(ts)	1.367	1.359	1.357	1.356
1-d_6-C_1(ts)	1.394	1.386	1.383	1.382
1-d_2-C_s(ts)	0.973	0.988	0.995	0.999
1-d_4-C_s(ts)	1.320	1.314	1.312	1.311
1-d_6-C_s(ts)	1.294	1.307	1.314	1.318

Table 2. Calculated k_H/k_D Ratios for Isomerizations of **1**-d_i-int to d_i-Cyclopropanes

	temp (K)			
intermed. diradical	500	700	900	1100
1-d_2-int	1.015	1.015	1.015	1.014
1-d_4-int	1.367	1.359	1.357	1.356
1-d_6-int	1.394	1.386	1.383	1.382

Table 3. Calculated and Observed Lifetime Ratios for d_i-Trimethylene Diradical Intermediates

intermed. compared	calcd	obsd[a]
τ(**1**-d_2-int)/τ(**1**-d_0-int)	1.01−1.02	1.06 ± 0.11
τ(**1**-d_4-int)/τ(**1**-d_0-int)	1.36−1.37	1.50 ± 0.14
τ(**1**-d_6-int)/τ(**1**-d_0-int)	1.38−1.39	

[a] For d_0-, d_2-, and d_6-trimethylene diradicals, experimental $\tau(d_i)$ values are 122 ± 8 fs, 129 ± 10 fs, and 183 ± 12 fs (Herek, J. L.; Zewail, A. H. California Institute of Technology, 1996, Unpublished results).

balance is computed to be 78:22; at higher energies, disrotatory paths increase in relative importance.

The kinetic model, then, together with the k_H/k_D values of Table 1, may be used to calculate overall k_H/k_D values for the isomerizations of d_i-trimethylenes to d_i-cyclopropanes, values which are directly proportional to relative lifetimes (Table 2). These calculated results may be compared with experimental results recently obtained by Herek and Zewail for three of the four trimethylenes in question, for d_0-, 2,2-d_2-, and 1,1,3,3-d_4-trimethylenes (Table 3).

The calculated relative lifetimes of Table 2 and the new femtosecond lifetime results cited in Table 3 are in very good agreement: **1**-d_0-int and **1**-d_2-int have essentially the same lifetimes, within experimental uncertainty, and the lifetime for **1**-d_4-int is substantially longer, as predicted from the calculated k_H/k_D ratios. The k_H/k_D ratios calculated from the theoretically based model for the isomerization of the trimethylene diradical intermediate to cyclopropane through multiple exit channels[14,16] and the Bigeleisen−Mayer semiclassical model for kinetic isotope effects are in evident accord with the experimentally determined relative lifetimes; this result leaves little role for a kinetically significant isomerization of the trimethylene intermediate to propylene, for this process should involve a substantial primary k_H/k_D effect,[25] one which is simply not in evidence.

Doubleday's calculations[16] again provide a telling additional perspective: at a total energy (E) that is 10 kcal/mol above the trimethylene intermediate, isomerization with formation of propylene is predicted to be a very minor contributor, less than 0.1% as significant as isomerization with formation of cyclopropane. Even when E is 30 kcal/mol above the trimethylene intermediate, the rate constant for propylene formation is calculated to be only 3% of the total rate constant for formation of cyclopropane through both conrotatory and disrotatory processes.[16]

The precise character of the trimethylene intermediate is of course not revealed unambiguously through the agreement between calculated relative lifetimes and measured lifetimes shown in Table 3. The local energetic minimum in the many-dimensional potential energy surface for the trimethylene intermediate is quite shallow, and the diradical may exist in a variety of conformational forms characterized by different C−C−C bond angles and H−C−C−H dihedral angles without any substantial variations in energy. For such a molecular entity, nearly a "twixtyl", "a molecule or a range of molecular conformations" having no minimum on a potential energy surface but "which operationally behaves as a true intermediate",[26] isomerization rates and lifetimes may be dictated more by the requirement that various vibrational modes must attain appropriate phase relationships with one another rather than by any all-important activation energy criterion.

Acknowledgment. We thank the National Science Foundation (CHE-9100246) and the National Institutes of Health (GM-23567) for support of this work at Syracuse University, the Department of Energy for support at the University of Georgia, and Dr. Jennifer L. Herek and Professor Ahmed H. Zewail of the California Institute of Technology for their indispensable encouragement and for permission to quote the unpublished lifetimes included in Table 3.

Supporting Information Available: Vibration frequencies calculated for d_i-trimethylene diradical intermediates and transition structures (1 page). See any current masthead page for ordering and Internet access instructions.

JA962083I

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