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The Di-π-methane Reaction of 3,3-Dimethyl-1,3-Diphenylpropene Revisited: Dynamics and Barriers for Competitive Singlet State Reactions

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The mechanism of the photochemical di-π-methane rearrangement of *trans*-3,3-dimethyl-1,3-diphenylpropene (DMPP) to *trans*-3,3-dimethyl-1,2-diphenylcyclopropane (DMCP) was investigated both by Hixson[1] and by Zimmerman[2] during the 1970s.[3] Direct irradiation results in the formation of DMCP in moderately high quantum yield ($\Phi \approx 0.40$) along with a small amount of *cis*-DMPP ($\Phi = 0.065$), whereas triplet sensitized irradiation yields only *cis*-DMPP.[2] A mechanism for decay of ^{1}DMPP* based on the studies of Hixson[1] and Zimmerman[2] is outlined in Scheme 1. According to this scheme there are four decay pathways for ^{1}DMPP*. Two of these, fluorescence and intersystem crossing (k_f and k_{isc}), are expected to be unactivated. The other two, phenyl-vinyl bridging and twisting about the C═C bond (k_{pv} and k_{twist}), are expected to be activated. Furthermore, phenyl−vinyl bridging is proposed to yield an intermediate I$_a$ that can either revert to ground-state DMPP (k_{nr}) or proceed to DMCP via the biradical intermediate I$_b$ ($k_{di\pi}$), depending upon which cyclopropane bond is cleaved (Scheme 1). This scheme is clearly too complex to permit assignment of rates and barriers by means of simple kinetic analysis. We report here the measurement of singlet lifetimes (τ) and quantum yields for fluorescence (Φ_f) and the formation of DMCP ($\Phi_{di\pi}$) and *cis*-DMPP (Φ_c) over a broad temperature range. Kinetic modeling provides conclusive evidence for the formation of *cis*-DMCP via both singlet and triplet pathways and for DMCP formation and nonradiative decay via a common intermediate. It further provides activation parameters for both of the activated primary photoprocesses and for the partitioning of the intermediate I$_a$.

Scheme 1

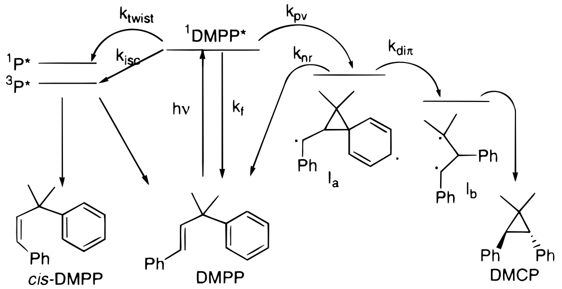

Table 1. Room Temperature Quantum Yields, Rate Constants (k_{rt}) and Activation Parameters for the Processes in Scheme 1

process	Φ[a]	k_{rt}, s^{-1} [b]	E_{act}, kcal/mol[c]	A[c]
k_f	0.041	6.4×10^7	*d*	*d*
k_{isc}	0.011[e]	3.1×10^7	*d*	*d*
k_{twist}	0.063[e]	1.7×10^8	6.6	1.3×10^{13}
k_{pv}	0.81[f]	1.4×10^9	2.0[g]	4.3×10^{10}[g]
$k_{di\pi}$	0.42	3.3×10^9	1.9	8.0×10^{10}
k_{nr}	0.39[h]	3.3×10^9	0.44	6.9×10^9

[a] Quantum yields are directly measured except as noted. [b] Rate constants obtained from the room-temperature quantum yields and lifetime. [c] Activation parameters obtained from kinetic modeling as described in text. [d] Unactivated processes. [e] The measured isomerization quantum yield is the sum of these values. [f] The quantum yield for phenyl-vinyl bridging is the sum of the quantum yields for di-π-methane rearrangement and nonradiative decay. [g] Values of $E_{pv} = 2.1$ and $A_{pv} = 3.0 \times 10^{10}$ are obtained from fitting the Φ_f data in Figure 1. [h] Quantum yield for nonradiative decay calculated using eq 1.

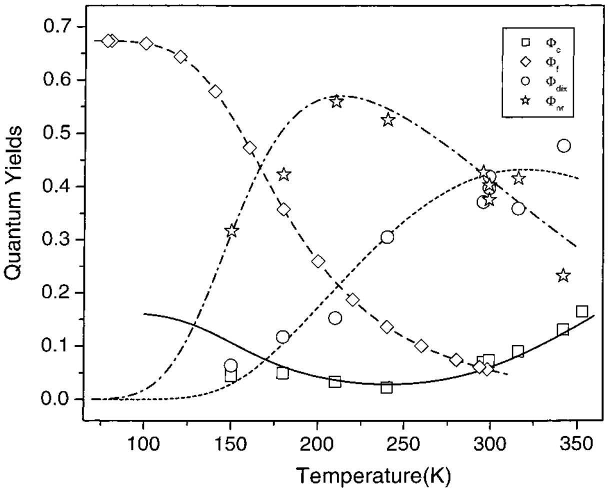

Figure 1. Temperature dependence of the quantum yields for trans,cis photoisomerization (Φ_c), fluorescence (Φ_f), di-π-methane rearrangement ($\Phi_{di\pi}$), and nonradiative decay (Φ_{nr}). Curve fitting is described in the text.

Values of Φ_f, $\Phi_{di\pi}$, Φ_c, and τ have been measured over the temperature range 150−352 K in deoxygenated methylcyclohexane solution. The data for 295.5 K is reported in Table 1 and is in good agreement with that reported by Hixson[1] for hexane solution and with Zimmerman[2] for *tert*-butyl alcohol solution at room temperature. Values of τ have also been measure below the solvent's glass transition temperature (~140 K) and are single exponential over the entire temperature range. The temperature dependence of Φ_f, $\Phi_{di\pi}$, and Φ_c is shown in Figure 1 and the temperature dependence of τ in Figure 2.[4] The values of Φ_f (Figure 1) and τ (Figure 2) increase with decreasing temperature, to limiting values of 0.66 and 10.1 ns, respectively, below 140 K. Also shown in Figure 1 is the temperature dependence of the quantum yield for nonradiative decay (Φ_{nr}) which is calculated

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(1) Hixson, S. S. *J. Am. Chem. Soc.* **1976**, *98*, 1271−1273.
(2) Zimmerman, H. E.; Steinmetz, M. G.; Kreil, C. L. *J. Am. Chem. Soc.* **1978**, *100*, 4146−4162.
(3) For a recent review, see: Zimmerman, H. E.; Armesto, D. *Chem. Rev.* **1996**, *96*, 3065−3112.
(4) Fluorescence decay times were measured using a PTI Timemaster apparatus capable of resolving decays ≥0.1 ns. The shortest decay time measured is that of DMPP at 352 K (0.29 ns). Low-temperature fluorescence quantum yield data is obtained by correcting the observed fluorescence intensities for the temperature dependence of the concentration and refractive index.

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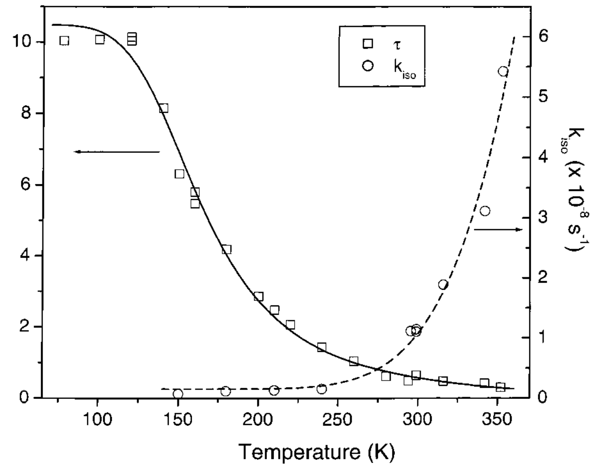

Figure 2. Temperature dependence of the singlet lifetime (τ) and the rate constant for trans,cis photoisomerization (k_{iso}). Curve fitting is described in the text.

using eq 1

$$\Phi_{nr} = 1 - (\Phi_f + \Phi_{di\pi} + 2\Phi_c) \qquad (1)$$

from the sum of the measured quantum yields at each temperature and the assumption that trans,cis isomerization via either a singlet or triplet mechanism occurs via a twisted intermediate that decays to a 1:1 mixture of trans and cis isomers ($\Phi_{twist} = 2\Phi_c$).[5] Unlike the values of $\Phi_{di\pi}$ which decrease with decreasing temperature, the values of Φ_{nr} display a maximum at ~200 K and decrease at either higher or lower temperature.

Rate constants for each of the primary processes in Scheme 1 can be calculated from the measured quantum yields and lifetimes at a given temperature. Values obtained at room temperature are reported in Table 1. The calculated fluorescence rate constant ($k_f = \Phi_f\tau^{-1}$) is independent of temperature. The calculated rate constant for trans,cis isomerization ($k_{iso} = 2\Phi_c\tau^{-1}$) is temperature-dependent (Figure 2). The isomerization data is bimodal, in accord with the occurrence of both triplet (unactivated) and singlet (activated) pathways.[5] Nonlinear data analysis provides a value of $k_{isc} = 3.1 \times 10^7$ s^{-1} for intersystem crossing, and values of $A_{twist} = 1.3 \times 10^{13}$ s^{-1} and $E_{twist} = 6.6 \pm 0.1$ kcal/mol for singlet state torsion. Since the values of k_f, k_{isc}, A_{twist}, and E_{twist} have been independently determined, fitting the temperature dependence of the lifetime (Figure 2) to eq 2 provides values of $A_{pv} = 4.3 \times 10^{10}$ s^{-1} and $E_{pv} = 2.0 \pm 0.1$ kcal/mol. Fitting the Φ_f data in Figure 1 to a modified form of eq 2 provides similar activation parameters for phenyl–vinyl bridging (Table 1). With kinetic data for all four of the primary photoprocess in hand it is possible to compare the experimental and calculated temperature dependence of Φ_c, as shown in Figure 1 (solid line). The good agreement between the experimental and calculated values provides support for the kinetic model.

$$\tau^{-1} = k_f + k_{isc} + A_{pv}\,e^{-\Delta E_{pv}/RT} + A_{twist}\,e^{-\Delta E_{twist}/RT} \qquad (2)$$

The temperature dependence of $\Phi_{di\pi}$ and Φ_{nr} is uniquely consistent with these processes occurring via a common intermediate formed from the singlet state of DMPP, in accord with the mechanism proposed by Hixson[1] and Zimmerman[2] (Scheme 1). These quantum yields are defined in eqs 3, 4 in terms of the probabilities of forming I_a from the singlet state ($P1$) and forming DMCP from I_b ($P2$). Simultaneous fitting of the values of $\Phi_{di\pi}$ and Φ_{nr} as shown in Figure 1 gives activation parameters for both $k_{di\pi}$ and k_{nr} (Table 1).

$$\Phi_{nr} = P1 \times P2 \qquad (3)$$

$$\Phi_{di\pi} = P1 \times (1 - P2) \qquad (4)$$

$$P1 = \frac{k_{pv}}{k_f + k_{isc} + k_{pv} + k_{twist}} \quad P2 = \frac{k_{nr}}{k_{nr} + k_{di\pi}}$$

Rate constants and activation parameters for all of the processes in Scheme 1 are summarized in Table 1. The rate constants for fluorescence and intersystem crossing are similar to the values previously reported for *trans*-1-phenylpropene ($k_f = 3.0 \times 10^7$ s^{-1}, $k_{isc} = 4.7 \times 10^7$ s^{-1}) as are the activation parameters for singlet state twisting about the C=C bond ($A_{twist} = 6.3 \times 10^{11}$ s^{-1} and $E_{twist} = 8.8$ kcal/mol).[5] The appearance of the absorption and fluorescence spectra of DMPP and 1-phenylpropene are also similar, in accord with the SCF-CI calculations of Zimmerman[2] which indicate that excitation in DMPP is localized on the styryl moiety. Both the value of A and E_{act} for pheny–vinyl bridging are smaller than those for trans,cis isomerization (Table 1). The smaller value of A_{pv} vs A_{twist} is consistent with a more ordered transition state for phenyl–vinyl bridging vs double bond torsion. However, the difference in activation energies for these processes is sufficiently large to render phenyl–vinyl bridging the dominant activated decay process at room temperature. Both at higher temperatures and very low temperatures trans,cis isomerization should become the dominant photoprocess due to the large preexponential for singlet isomerization and the unactivated nature of triplet isomerization. The two decay pathways for the intermediate I_a also have quite different activation parameters. The smaller value of A_{nr} vs $A_{di\pi}$ is consistent with a more ordered transition state for nonradiative decay, which requires overlap of the benzyl radical with the cyclopropyl bond undergoing fragmentation, and the smaller value of E_{nr} vs $E_{di\pi}$ is consistent with the more highly exergonic nature of the nonradiative decay process which leads to ground-state DMPP (k_{nr}) vs conversion of I_a to I_b ($k_{di\pi}$).

The results of this investigation provide a complete description of the competing reaction pathways for both the singlet state of DMPP and the first intermediate formed in the di-π-methane rearrangement. They are consistent with the stepwise mechanism for 1,2-phenyl migration[1,2] and not with a concerted 1,2-migration process as proposed by Robb et al.[6] for the di-π-methane rearrangement of 1,4-pentadiene. The Robb energy surface may be applicable to the truncated model but not to molecules with extended conjugation. The quantum yield for di-π-methane rearrangement is reported to be significantly lower for 1,3-diphenylpropene vs DMPP.[1] The effects of substituents at C-3 upon both phenyl-vinyl bridging and the behavior of the intermediate I_a will be the subject of a subsequent report.

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