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The T_1 $^3(\pi-\pi^*)/S_0$ Intersections and Triplet Lifetimes of Cyclic α,β-Enones

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The ground and triplet excited states of cycloheptenone, cyclohexenone, and cyclopentenone have been studied using CASSCF calculations. For these three molecules, the difference in energy (ΔE) between the twisted T_1 $^3(\pi-\pi^*)$ minimum and T_1 $^3(\pi-\pi^*)/S_0$ intersection increases as the flexibility of the ring decreases. A strong positive correlation between ΔE and the natural logarithm of the experimentally determined triplet lifetimes ($\ln \tau$) is found, suggesting that ΔE predominantly determines the relative radiationless decay rates of T_1.

Introduction

The photochemistry of cyclic enones has been studied extensively over the past 40 years, both mechanistically and synthetically. Classic sensitization and quenching experiments showed that the lowest-energy triplet state T_1 is responsible for a wide variety of enone photoreactions.[1] These transient triplets are twisted around the C═C bond at an angle that varies with the conformational rigidity of the enone chromophore.

The triplet lifetimes of several α,β-enones have been determined by Bonneau and Schuster et al.[2] These range from 8 ns for methyl vinyl ketone and 11 ns for cycloheptenone[2a] up to 185 ns for cyclopentenone.[2b,d] The short triplet lifetime of methyl vinyl ketone has been attributed to facile intersystem crossing near the twisted minimum on the T_1 $^3(\pi-\pi^*)$ potential energy surface to a maximum on the ground-state (S_0) surface.[3]

The photochemistry and photophysics of the simplest α,β-enone, acrolein, have recently been studied using CASSCF calculations.[4] After photoexcitation, *s-trans*-acrolein relaxes to the S_1 $^1(n-\pi^*)$ planar minimum **F** (Figure 1). From this point, the system can return to the ground state via two radiationless decay routes. The first involves intersystem crossing, leading eventually to the production of a twisted T_1 $^3(\pi-\pi^*)$ intermediate **B**. This intermediate subsequently decays to the ground state via a second intersystem crossing **I**, which can lead to isomerization of the C═C bond. The second radiationless decay route involves the singlet manifold only: relaxation to S_0 occurs in a single step via an S_1/S_0 conical intersection. This second route is not effective in conditions of low excess vibrational energy and will not be considered any further here.

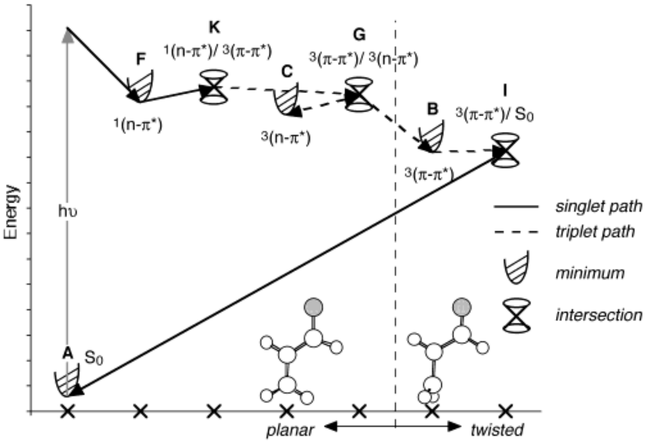

Figure 1. Outline of the triplet relaxation pathway of S_1 acrolein, based on ref 4. Critical points: S_0 planar minimum **A**; S_1 $^1(n-\pi^*)$ planar minimum **F**; S_1 $^1(n-\pi^*)/T_2$ $^3(\pi-\pi^*)$ crossing **K**; $^3(\pi-\pi^*)/^3(n-\pi^*)$ conical intersection **G**; T_1 $^3(n-\pi^*)$ planar minimum **C**; T_1 $^3(\pi-\pi^*)$ twisted minimum **B**; T_1 $^3(\pi-\pi^*)/S_0$ crossing **I**.

For acrolein, the lowest energy point on the T_1 $^3(\pi-\pi^*)/S_0$ intersection **I** (at which ISC from T_1 is expected to be most favorable[5]) is located only 0.31 kcal mol^{-1} above the twisted $^3(\pi-\pi^*)$ minimum **B** (Figure 1). As a consequence, the lifetime of this triplet is expected to be short.[6] This situation will be different for cyclic enones—such as cyclopentenone—where twisting around the C═C bond is constrained. In this paper, we report CASSCF calculations of the ground and triplet excited states of cyclopentenone, cyclohexenone, and cyclohep-

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[2] (a) Bonneau, R. *J. Am Chem. Soc.* **1980**, *102*, 3816−3822. (b) Schuster, D. I.; Dunn, D. A.; Heibel, G. E.; Brown, P. B.; Rao, J. M.; Woning, J.; Bonneau, R. *J. Am. Chem. Soc.* **1991**, *113*, 6245−6255. (c) Lifetimes used here from (a) and (b) were determined in cyclohexane solvent. (d) Cyclopentanone lifetime extrapolated to infinite dilution to avoid dimerization effects.

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[6] We have not found an experimental lifetime for the T_1 state of acrolein yet.

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Table 1. CASSCF/6-31G* Energies (kcal mol^{-1}) of Structures Involved in the Triplet Decay Pathway of α,*β*-Enones, Relative to B (Figure 1)

structure	cyclopentenone	cyclohexenone	cycloheptenone	methyl vinyl ketone	acrolein^a
A S_0 planar minimum	−71.06	−68.10	−57.56	−59.91	−60.18
G $^3(\pi-\pi^*)/^3(n-\pi^*)$ conical intersection	+8.79	+8.31	+17.12	+17.04	+14.12
C $^3(n-\pi^*)$ planar minimum	+3.95	+3.08	+11.38	+10.46	+9.16
B $^3(\pi-\pi^*)$ twisted minimum	0.00	0.00	0.00	0.00	0.00
ΔU^b	−28.74	−12.77	−1.01	+1.27	+1.19
I^c $^3(\pi-\pi^*)/S_0$ intersection	+6.64	+1.51	+0.16	+0.25	+0.31

^{a} Taken from ref 4. ^{b} ΔU is the energy difference between the $^3(\pi-\pi^*)$ and S_0 states at the geometry of the twisted $^3(\pi-\pi^*)$ minimum **B**. ^{c} The energy difference between **B** and **I** on the $^3(\pi-\pi^*)$ potential energy surface is referred to subsequently as ΔE.

tenone in order to understand the effect of geometry constraints on the triplet lifetimes. We show that there is a strong positive correlation between the energy difference ΔE between **B** and **I** and the natural logarithm of the experimentally determined T_1 lifetimes (ln τ). We have also considered methyl vinyl ketone as an example of an unconstrained acyclic α,*β*-enone with a known triplet lifetime.[6]

Computational Details

All critical points were optimized using the CASSCF procedure and standard 6-31G* basis set available in Gaussian 99.[7] The active space comprised six electrons in five orbitals, which included the *π*, *π** orbitals of the C═C fragment and the *π*, *π** and n orbitals of the C═O fragment. Equilibrium geometries were confirmed to be minima by analytical frequency computations. The lowest energy points of surface crossing[8] (T_1/S_0 and T_2/T_1) were optimized using the method previously described[9] with state-averaged orbitals. For the T_1/S_0 crossing, a weighting of 50%/50% was assigned to the triplet and singlet states in the state-averaging procedure; further details are given in ref 9a−d.

The CASSCF/6-31G* spin−orbit coupling was computed at the triplet/singlet crossing point **I** using a one-electron approximation with the effective charges on O (5.6) and C (3.6) determined by Koseki et al.[10]

Single-point triplet energies were also calculated using the B3LYP[11] and CCSD(T)[12] methods at the CASSCF/6-31G* geometries **B** and **I** to estimate the effect of dynamic electron correlation on the energy difference between these points. CASSCF geometries were used (an approximation) because neither B3LYP or CCSD(T) can be used to reoptimize the crossing.

Results and Discussion

Figure 1 shows the relaxation path for the S_1 $^1(n-\pi^*)$ state of acrolein that involves intersystem crossing between singlet and triplet potential energy surfaces.[4] It can be taken as a prototype for any α,*β*-enone.

Intersystem crossing from $^1(n-\pi^*)$ to $^3(\pi-\pi^*)$ states takes place in the region of the S_1/T_2 intersection **K** (Figure 1). This crossing is very favorable, as the spin−orbit coupling constant is large.[13] On the $^3(\pi-\pi^*)$ surface, the system can access a low-lying $^3(\pi-\pi^*)/^3(n-\pi^*)$ conical intersection **G** that provides a fast and efficient radiationless decay channel from T_2 to T_1. Because **K** and **G** are planar, the system can evolve from S_1 to T_1 without twisting.

Decay at the intersection point **G** can lead to two different T_1 minima: planar $^3(n-\pi^*)$, **C**, and twisted $^3(\pi-\pi^*)$, **B**. Because the initial relaxation has all taken place in the plane of the molecule, **C** can be populated.[4] However, **B** is the lowest energy point on T_1 overall and on the same $^3(\pi-\pi^*)$ surface that led to the intersection **G** from **K**. Population of **B** is therefore expected to be favored. From **B**, decay to the ground state via intersystem crossing occurs in the region of the T_1/S_0 intersection **I**. This is the rate-determining step in the relaxation process illustrated in Figure 1.

As the first steps of the relaxation path described above (via structures **F** and **K**) involve only in-plane deformations, cyclic enones are expected to exhibit the same behavior as acrolein. We have therefore ignored **F** and **K** in this investigation of the relaxation of cyclopentenone, cyclohexenone and cycloheptenone. The relative energies of the remaining optimized structures (**A**, **G**, **C**, **B**, and **I**) are shown in Table 1.

Table 1 shows that **B** is the lowest energy T_1 minimum for all of the systems considered here. None of them are so rigid that the $^3(n-\pi^*)$ minimum **C** is lower in energy,[14] which means that the relaxation mechanism via **B** and **I** shown in Figure 1 will operate in all of the systems studied here.

Table 1 also shows that the energy difference ΔE between **B** and **I** increases as the size (and flexibility) of the ring decreases, from 0.16 kcal mol^{-1} for cycloheptenone to 6.64 kcal mol^{-1} for cyclopentenone. This difference

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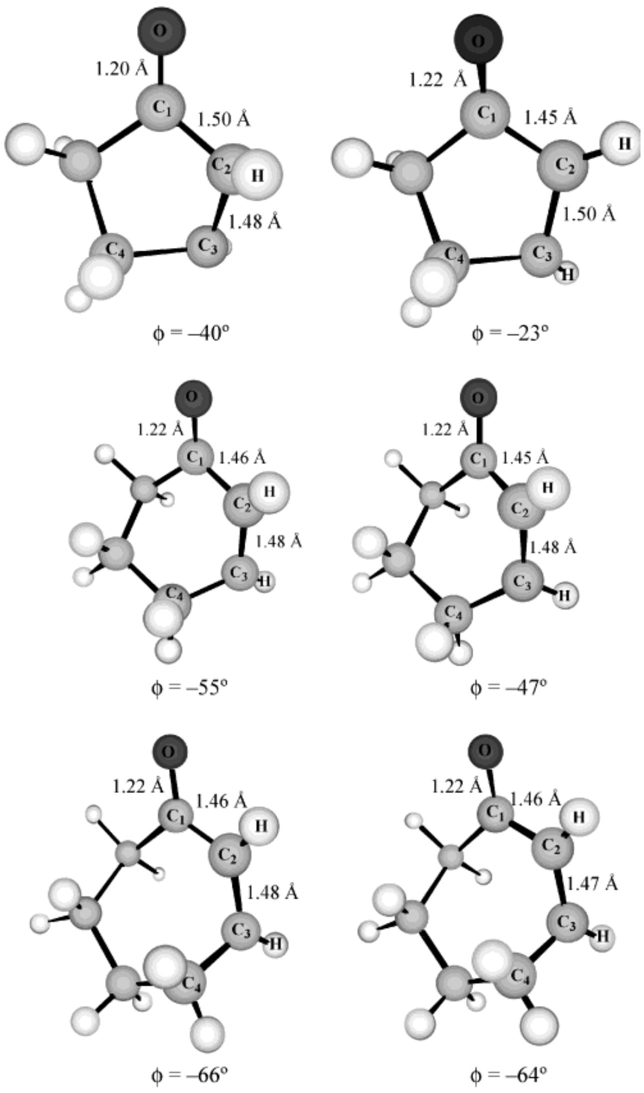

$T_1\ ^3(\pi\text{-}\pi^*)/S_0$ intersection
I

Twisted $T_1\ ^3(\pi\text{-}\pi^*)$ minimum
B

Figure 2. CASSCF/6-31G* geometries of the twisted $^3(\pi-\pi^*)$ minimum **B** and $^3(\pi-\pi^*)/S_0$ intersection **I** for cyclopentenone, cyclohexenone, and cycloheptenone. ϕ is the $C_4-C_3-C_2-C_1$ dihedral angle.

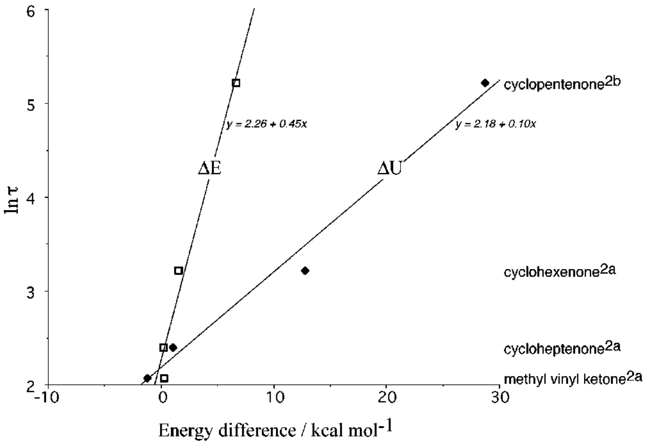

Figure 3. Experimental $^3(\pi-\pi^*)$ lifetimes (ln τ) of α,β-enones plotted against ΔE, the energy difference (Table 1) between the $^3(\pi-\pi^*)$ twisted minimum **B** and the $^3(\pi-\pi^*)/S_0$ intersection **I** (Figure 1), and ΔU, the energy difference between the $^3(\pi-\pi^*)$ and S_0 states at **B**. Lifetimes taken from ref 2, using cyclohexane as solvent.

Table 2. Spin−Orbit Coupling Constants Computed (CASSCF/6-31G*) for the $T_1\ ^3(\pi-\pi^*)/S_0$ Crossings I of the α,β-Enones Studied Here

	spin−orbit coupling constants (cm^{-1})
cyclopentenone	+0.5
cyclohexenone	+0.2
cycloheptenone	+0.1
methyl vinyl ketone	+0.3
acrolein	+0.3

can be understood by comparing the geometries of **B** and **I** for cyclopentenone, cyclohexenone, and cycloheptenone shown in Figure 2.

For the $^3(\pi-\pi^*)$ twisted minimum **B**, the $C_4-C_3-C_2-C_1$ dihedral angle ϕ varies from −23° for cyclopentenone to −64° for cycloheptenone. Thus, when the flexibility of the ring decreases, ϕ is forced to decrease. ($|\phi|$ for cycloheptenone is closer to the value of 90° for acrolein[4]). Figure 2 also shows that the $T_1\ ^3(\pi-\pi^*)/S_0$ intersections are more twisted than the respective $^3(\pi-\pi^*)$ minima: for cyclopentenone, ϕ has to increase by 17° to go from **B** to **I** but the increase is far smaller (2°) for cycloheptenone. Thus, when the flexibility of the ring decreases, more energy is required to reach the intersystem crossing point **I** from **B**, i.e., ΔE increases, as shown in Table 1.

Figure 3 shows the natural logarithm of the experimental triplet lifetimes[2] (ln τ) plotted against the computed energy difference ΔE between the $^3(\pi-\pi^*)$ twisted minimum **B** and the $T_1\ ^3(\pi-\pi^*)/S_0$ intersection **I**. A straight line for ln τ against ΔE would be expected for Arrhenius-like kinetics from

$$k = 1/\tau = A\ \exp(-\Delta E/RT)$$

Figure 3 shows that there is a strong positive correlation between ΔE and ln τ. However, the slope is found to be 0.45, a factor of 3.7 lower than the predicted value of 1.68 (i.e., $1/RT$, where $R = 1.986$ cal mol^{-1} and $T = 300$ K). We believe that this discrepancy is due to the combined lack of solvent and thermal effects in our calculations: these would reduce the energy difference between **B** and **I**, which is predominantly responsible for the difference in the observed lifetimes, as the rates of intersystem crossing (contained in A) are the same in each case.

Table 2 shows that the spin−orbit coupling constants at **I** are in fact all less than 1 cm^{-1} for the systems studied here, such that differences in spin−orbit coupling are unlikely to affect the $^3(\pi-\pi^*)$ lifetime. Variations in spin−orbit coupling constants with twist angle have been discussed for alkenes,[15] but there appears to be almost no such variation with the one-electron approximation used here for α,β-enones.

The inclusion of spin−orbit coupling (Table 2) makes the triplet/singlet crossing **I** weakly avoided. This leads to a barrier on the $^3(\pi-\pi^*)$ to S_0 pathway, for which the

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Arrhenius expression for the decay rate can be applied as described above. Here, instead of a single reaction at several temperatures, we have varied ΔE by studying a homologous series of reactions. In doing this, we have assumed that the system is fully equilibrated and that the rates of intersystem crossing (and, hence, the preexponential factors A) are constant. The temperature should also be constant: the experiments were not explicitly carried out at constant temperature, but the lifetimes were found to be insensitive to temperature changes from −30 to +30 °C.[2a]

It has also been suggested (by a reviewer, after Bonneau et al.) that the decrease of k_{isc} in small cyclic enones can be related to an increase in the energy splitting ΔU between the $^3(\pi-\pi^*)$ and ground states at the minimum **B** on $^3(\pi-\pi^*)$ (Table 1). ISC would then take place via a "vertical" nonradiative process. Although this decay cannot strictly be treated as an activated process as for ΔE above, we have also looked for a correlation between ΔU and ln τ. Figure 3 shows that the decrease of k_{isc} in small cycloalkenones does correlate with ΔU but that the slope (0.10) is further from the predicted value of 1.68 than was found for ΔE.

Finally, accurate values of reaction energy barriers often require a treatment of dynamic electron correlation, which CASSCF does not provide. For the enones studied here, we have estimated the effect of dynamic electron correlation on ΔE by recalculating the energies of **B** and **I** on the triplet surface using B3LYP and CCSD(T) at the CASSCF geometries. No significant differences between CASSCF and B3LYP or CCSD(T) were found (Table 3), suggesting that the CASSCF barrier heights are reliable.

Table 3. Energy Difference in kcal mol^{-1} between the $^3(\pi-\pi^*)$ Twisted Minimum B and the T$_1$ $^3(\pi-\pi^*)$/S$_0$ Intersection I, Calculated at the CASSCF/6-31G* Geometries with CASSCF/6-31G*, B3LYP/6-31G* and CCSD(T)/6-31G*

	CASSCF	B3LYP	CCSD(T)
acrolein	0.31	0.12	0.11
methyl vinyl ketone	0.25	0.13	0.13
cyclopentenone	6.64	8.49	6.99
cyclohexenone	1.51	1.44	1.35
cycloheptenone	0.16	0.10	-

Conclusions

We have calculated the ground and triplet excited states of cyclopentenone, cyclohexenone, and cycloheptenone using the CASSCF method. The torsional angle of the $^3(\pi-\pi^*)$ minimum is found to depend greatly on the rigidity of the system, ranging between −23° for cyclopentenone to −64° for cycloheptenone. The T$_1$ $^3(\pi-\pi^*)$/S$_0$ intersection geometries are more twisted than the respective $^3(\pi-\pi^*)$ minima. Thus, when the rigidity of the system is increased, more energy is required to reach the T$_1$/S$_0$ intersection and the $^3(\pi-\pi^*)$ minimum has a longer lifetime. The energy necessary to reach the T$_1$/S$_0$ intersection appears to determine the T$_1$ lifetime. Variations in spin−orbit coupling do not appear to be important for this decay process.

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Supporting Information Available: Energies and Cartesian coordinates of all optimized critical points. This material is available free of charge via the Internet at http://pubs.acs.org.

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