Computational Analysis of the Photoinitiation
Pathway of 2,2-Dimethoxy-2-Phenylacetopenone

**By Abby R. Moore and
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High-throughput screening based on computational methodologies has been used for many years in the pharmaceutical industry; however, its use for photoinitiator development has been very limited. The primary reason for this limitation has been due to lack of appropriately powerful modeling software. Fortunately, software has become available that will allow for modeling simple Type I photoinitiators such as 2,2-dimethoxy-2-phenylacetophenone (DMPA).

Introduction

The photochemical fate of DMPA is well known (Figure 1). The ground state species S_0 can absorb ultraviolet (UV) radiation to form the excited state singlet S_1^*. The S_1^* forms the excited state triplet T_1^* via intersystem crossing. The T_1^* then undergoes an alpha cleavage to produce free-radical species, a benzoyl radical and the 1, 1-dimethoxy-1-phenylmethyl radical. If a source of abstractable hydrogens (e.g., ether, thiol, amine) is available, both radicals could abstract a hydrogen. The benzoyl radical can add into an alkene (e.g., acrylate) and initiate polymerization whereas the 1, 1-dimethoxy-1-phenylmethyl radical probably inhibits initiation via combination with other radicals. This inhibition is exacerbated via inductive stabilization by the methoxy substituents and resonance stability of the phenyl group. However, the 1, 1-dimethoxy-1-phenylmethyl radical could undergo a rearrangement to form methyl benzoate and a methyl radical, which can subsequently initiate polymerization.

Results and Discussion

Use of the Spartan 2006 software (v.1.1.1), designed by Wavefunction, allowed the geometric analysis of DMPA as a model Type I photoinitiator. First, the molecular geometry was determined based on the Hartree-Fock 6-31G* permutations (Figure 1). This provided a base geometry on which to base the calculations performed using density functional theory (DFT). Close examination of the modeled S_0 of DMPA showed that the benzoyl moiety is not completely planar as measured by the dihedral angle comprising the carbonyl (169.54°).

Using DFT, specifically B3LYP, DMPA was modeled whereupon the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were determined (Figures 2 and 3). The HOMO was predominately located on the carbonyl with some electron density calculated on the phenyl and methoxy substituents. The LUMO

again is centered on the carbonyl and somewhat delocalized within the phenyl group bound to the carbonyl. This corroborates known photochemistry showing that the $\pi-\pi^*$ transition of DMPA occurs at the carbonyl.

Having been able to corroborate known photochemistry, the S_1^* of DMPA was calculated using DFT (B3LYP) including the HOMO and LUMO. Very little varied compared to the S_0 including the dihedral angle,

which was expected given that the excited electron originated at the carbonyl and indeed does go to the calculated LUMO of the S_0 DMPA.

An interesting fact about DMPA is that, after being excited into the S_1^* and undergoing the intersystem crossing to the T_1^*, the resulting excited state has an unexpectedly short lifetime before dissociating into the two radicals. Thus, when the T_1^* of DMPA was modeled using the same

parameters as before, the results were quite interesting. The geometry of the T_1^* should have a considerable sp^3 character where the bond angles should approximate 109.5° if the species exhibits di-radical character (i.e., tetrahedral conformation). This was observed in the modeling results (Figure 4). The bond angles centered on the "carbonyl" carbon were 113.43° and 112.77°. These values are within computational error of the tetrahedral bond angles. Furthermore, the phenyl group bound to the "carbonyl" carbon is now in an anti-planar conformation.

The HOMO (Figure 5) shows that the majority of the electron density is on the "carbonyl" carbon, specifically in the newly formed sp^3 orbital. The LUMO (Figure 6) is almost equally distributed in the phenyl rings indicating the π^* nature of this excited state.

It is well known that the T_1^* of DMPA quickly undergoes an alpha cleavage to form the benzoyl radical and the 1,1-dimethoxy-1-phenylmethyl radical. This can be explained using the computational output. Due to the anti-planarity of the phenyl group bound to the "carbonyl" carbon (dihedral angle = 36.44°), it is unlikely that the T_1^* of DMPA will undergo the intersystem crossing and relaxation back to the S_1^*; therefore, this modeling corroborates the forbidden nature of this transition. Thus, the only option for the T_1^* of DMPA is to undergo the alpha cleavage to form the stabilized radicals thereby providing evidence into the nature of the short lifetime of the T_1^* of DMPA. When modeled using DFT (B3LYP), the dissociation is demonstrated to be the favored process because of the resonance stabilization of the benzoyl radical and the inductive stabilization of the 1,1-dimethoxy-1-phenylmethyl
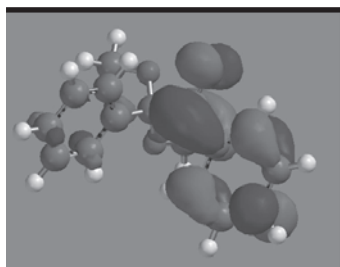
FIGURES 1-6
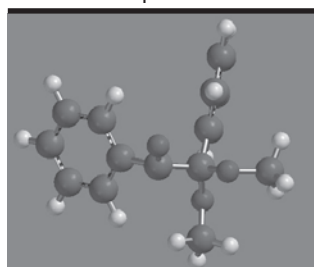
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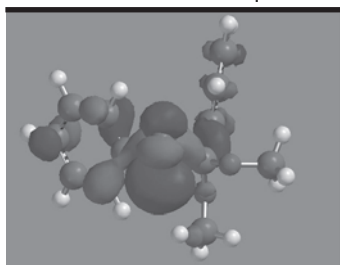**Molecular geometry of the S_0 DMPA**
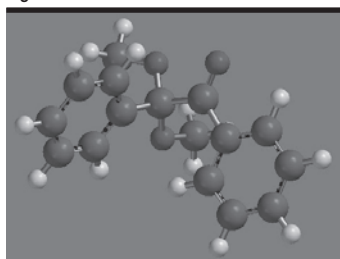
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Homo of the S_1^* DMPA
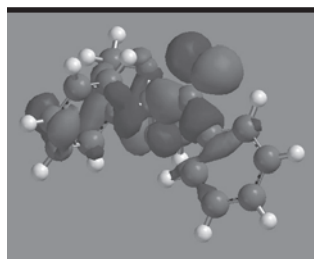
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LUMO of the S_1^* DMPA

4

Molecular geometry of the DMPA T_1^*

5

HOMO of the DMPA T_1^*

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LUMO of the DMPA T_1^*
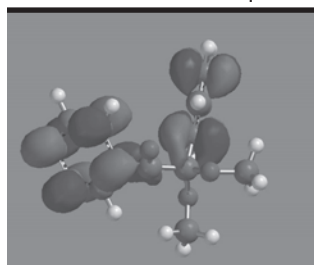
radical. The unpaired and localized radical on the "carbonyl" carbon (see Figure 5) is then delocalized thereby increasing the stability of the species upon dissociation.

Conclusions

The photochemical behavior of DMPA was modeled based on the ground state singlet S_0, the singlet excited state S_1^*, the triplet excited state T_1^*, and the radicals formed after alpha cleavage. The results corroborated the known photochemical behavior of each species based on the determination of the highest occupied molecular orbital and the lowest unoccupied molecular orbital (i.e. electron density). Furthermore, computational chemistry may be used as a high-throughput screening methodology to examine the potential viability of novel Type I photoinitiators prior to the pursuit of expensive syntheses and characterizations of these photoinitiators.

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Meet Our Rad Members

The RadTech Report *will feature a RadTech member in each issue. This special profile provides a snapshot of an individual member, allowing members to get to know each other and find out what each other thinks about the future outlook of UV&EB.*

This first issue highlights Allied PhotoChemical CEO & President Mike Kelly. Mike is a very active member of RadTech, serving on the Board of Directors and the RadTech Report *Editorial Board, and he co-chairs the Industrial Applications Focus Group.*

Mike Kelly, front row right, with some of his AlliedPhotoChemical staff.

Q Why is Allied Photochemical in the UV&EB business?

A Our founder was passionate about developing environmentally friendly UV&EB solutions and our investors wanted green technology—a perfect match.

Q How did you end up in the business?

A At first, I was a no-charge consultant to Allied assisting with the development and plan to drive UV&EB technology into the market-place. I was eventually invited to formally join the team. It's been an incredible experience and I have become very passionate about the potential for the UV&EB marketplace and Allied's position in the market.

Q Is there much difference between UV&EB and your other industry experiences?

A Yes. The market acceptance rate has been slower than other industries driven by several factors including a general lack of UV&EB process and equipment knowledge and other entrenched coating technologies.

Once a customer implements a successful system, two things happen. First, they start understanding the economic benefits and look for ways to further improve. Second, they start to realize the competitive advantage that UV&EB has provided them. As a result, they tend to keep a tight lid on the process details instead of advocating the technology to the market (i.e., competitors). While this is understandable, it makes it difficult for suppliers to build on previous wins.

Q Where do you see the UV&EB industry heading?

A I see the technology continuing to expand into new markets and continuing its growth in existing markets as suppliers of raw materials continue to produce more dynamic materials and technology.

Q RadTech sometimes gets asked why UV&EB is not bigger since it seems so good. What is your theory?

A I think there are several factors. Too often the qualification process is run exclusively by engineers (as a fellow engineer I am allowed to criticize). Engineers usually don't have the incentive to consider the full financial benefits of a new technology. They focus exclusively on the technical challenges and risks of switching technologies. When the (dramatic) financial benefits aren't fully considered the perceived "safe" choice is to stick with an older (less efficient) technology.

Often times UV&EB requires a top-down push. It's critical to get executive sponsorship at the customer.

To date, the industry has done a poor job presenting solutions to customers instead of individual pieces. Customers want to know that they have a complete team behind them when they switch to UV&EB. That means a formulator, equipment suppliers, an integrator, etc. It must be presented as a solution. You might even say as a "UV&EB Solutions Group," not as individual pieces.

Q Any message to your UV&EB suppliers, competitors?

A Keep diligent and keep pushing the UV&EB message. Support RadTech and related events. Keep focused on customer support and continually improving service.

Q How about you? What outside interests would you like to share?

A I have a 5-year-old son, Alex, and a 6-month old son, Jonathan. My favorite day of the week—Saturdays—is spent with "The Boys." I am also focused on making Allied a $100-300 million company.