

Elucidation of a Novel Photoproduct via Irradiation of Isopropylthioxanthone with Maleic Anhydride and its Effect on a Three-Component Photoinitiator

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Abstract

Isopropylthioxanthone (ITX) was shown via ultraviolet-visible (UV-Vis) spectroscopy to yield a single byproduct with maleic anhydride (MA) when irradiated ($\lambda \geq 350$ nm). Upon irradiation, the initial rate constant was determined using UV-Vis spectroscopy. The product was isolated and elucidated after obtaining the retention time and quantum yield from high performance liquid chromatography (HPLC). Finally, a proposed mechanism is included for the formation of the photoproduct which may reduce the initiation efficiency of photoinitiators incorporating ITX and a MA derivative.

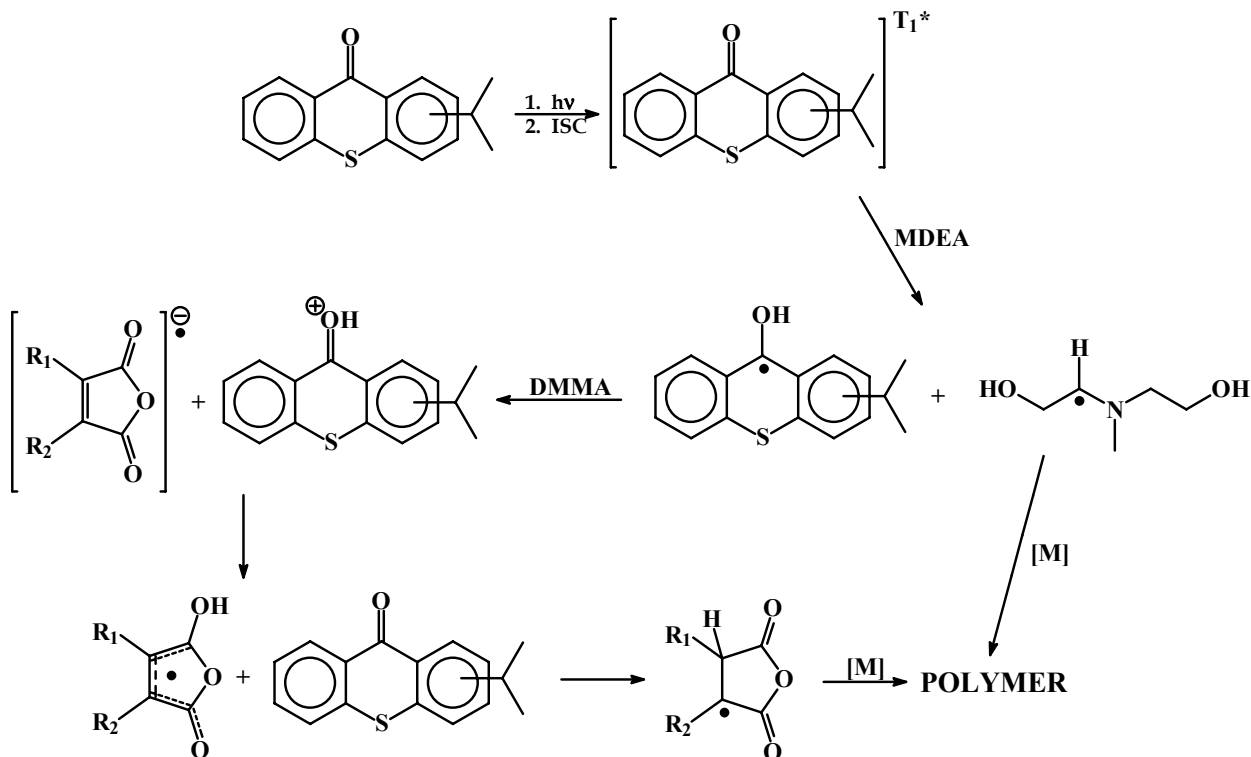
1. Introduction

All industries look for faster, cheaper, and more reliable ways to produce a product. The same is true in UV radiation curing; therefore, photoinitiating systems continue to be researched and developed. The UV curable coatings industry is reported to grow about seven percent in the next few years, much of which is due to research in *Type I* and *Type II* photoinitiators.¹ *Type I*, or cleavage, photoinitiators are efficient and use acetophenone derivatives to cleave a photoinitiator and produce two initiating radicals. *Type II*, or abstraction, photoinitiators are cheap and use benzophenone and tertiary amines in order to abstract a proton from a coinitiator to produce an initiating radical and a terminating radical. Developing a third type of initiator that combines efficiency and low cost would be ideal as both are desired features.² This third type of photoinitiator has been found for some systems and is referred to as a three-component photoinitiating system. Some of these systems use maleic anhydride (MA) derivatives or maleimides (made from maleic anhydrides), tertiary amines, and a cosynergist.³ A three-component photoinitiating system also offers two initiating radicals, similar to *Type I* photoinitiators, rather than one initiating and one terminating radical produced with *Type II* photoinitiators.⁴

One of these systems includes isopropylthioxanthone (ITX), 2,3-dimethyl maleic anhydride (DMMA), and N-methyl-N,N-diethanolamine (MDEA). A similar system that replaces DMMA with a maleimide gives a high rate of polymerization. However, DMMA, which is a better electron acceptor, should produce an even faster polymerization, but it does not.

In this system, two mechanistic pathways have been reported, chemical sensitization (Scheme 1) and photosensitization (Scheme 2).² However, there lies a discrepancy between the proposed photosensitization mechanism and kinetic rates determined via laser-flash photolysis.⁴ The reported mechanism shows an excited state triplet of ITX proceeding to be quenched via an energy transfer to yield an excited state

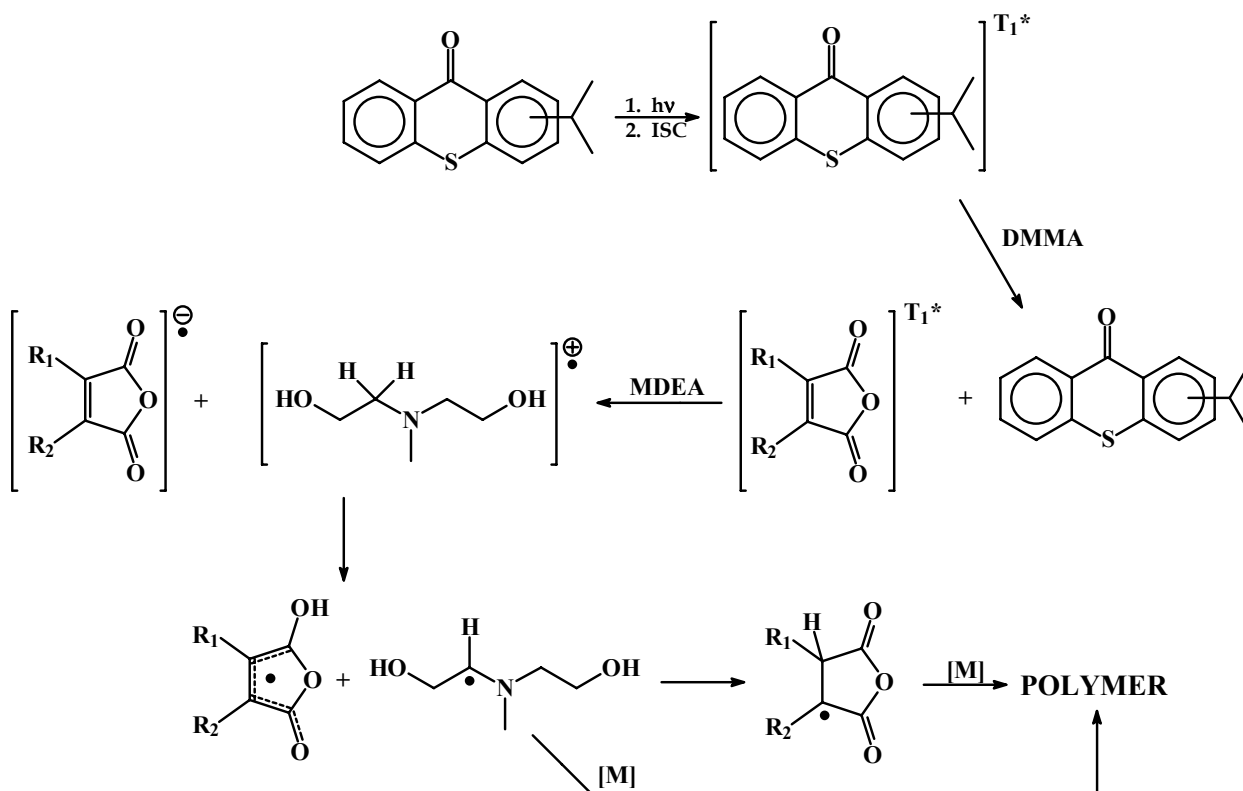
Scheme 1. Chemical sensitization of ITX/DMMA/MDEA system leading to polymer production.



of DMMA. The problem arises when the triplet energies (E_T) are considered. The triplet energy of ITX was found to be 64 kcal/mol while that of DMMA was estimated to be 72 kcal/mol.² An energy transfer from a lower energy to a higher energy is not thermodynamically favored and is thus unlikely. The laser-flash photolysis does show that a reaction is occurring on the order of $3.5 \times 10^9 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$. Either this energy transfer occurs despite thermodynamics or an electron/proton transfer occurs, yielding an unexpected side reaction which might explain the lack of rapidity with the overall polymerization. If this side reaction occurs, a photoproduct should be present.

Within this research MDEA is not used as it should not participate in a side reaction. MA was used as a model compound instead of DMMA since their photochemical properties should be very similar. UV-Vis was used to determine, first, if this possible side reaction was occurring. A disappearance of ITX was monitored, indicating ITX was reacting somehow. The UV-Vis helped lead to other discoveries mention herein. HPLC was essential to the discovery of a photoproduct.

Scheme 2. Photosensitization of ITX/DMMA/MDEA system leading to polymer production.



2. Experimental

2.1 Materials

Acetonitrile (ACN) of 99.5% purity was obtained from Sigma-Aldrich. MA of 99% purity was obtained from Acros Organics. ITX of an unknown purity was a donation from the Albemarle Corporation.

2.2 Irradiation

Procedure 1:

Approximately forty-four milligrams (44 mg) of MA and thirty-eight milligrams (38 mg) of ITX (3:1 molar ratio respectively) was weighed and diluted into 100 mL of ACN. This mixture was then transferred into a Pyrex brand 250 mL round bottom flask. Pyrex glassware was chosen as it absorbs UV radiation having wavelengths below 350 nm, therefore preventing MA from absorbing any UV radiation during irradiation. A nitrogen blanket was placed on the system to minimize the effects of oxygen quenching the excited state triplet of ITX. The solution was then placed under a Sylvania medium pressure mercury arc lamp (HPL80MDX(R) 80 Watt (R9) 0303 – outer casing removed) with stirring. A one (1) mL sample was taken every six (6) minutes, over the course of one hour, and diluted to ten (10) mL with ACN. An irradiation of ITX was also performed to verify that ITX was not reacting with itself.

Procedure 2:

Approximately 380 mg of MA and thirty-eight milligrams of ITX (25:1 Molar ratio respectively) was used in an irradiation described in *Procedure 1*. A one (1) mL sample was taken every minute for fifteen minutes and also at sixty minutes and diluted as described above.

Procedure 3:

Individual irradiations of ITX and MA by themselves were performed to verify that neither one was reacting with itself. Samples were prepared similarly as in *Procedure 2*, but samples were taken every two minutes between zero and fourteen minutes with a sixty minute sample also taken.

2.3 UV-Vis Spectroscopy

Absorption was measured at all wavelengths (250-450 nm) simultaneously with a Hewlett Packard Ultraviolet-Visible 8453 Photodiode Array. The desired solutions used ACN as the solvent.

2.4 HPLC

This was performed with a system by Shimadzu USA containing these components: SCL-10A VP System Controller, SPD-M10A VP Diode Array Detector, LC-10AT VP Liquid Chromatograph, FCV-10AL VP Pump. The system uses a Beckman Coulter Ultrasphere C18 High Performance Column. The column measures 250 x 4.6 mm and was purchased through Alltech. Absorption was again measured at all wavelengths (250-450 nm) simultaneously with this device; however, the HPLC chromatographically separated each species in the system providing a retention time and UV spectrum for each.

3. Results and Discussion

3.1 UV-Vis

UV-Vis is a simple and convenient method to watch the absorption of ITX decrease over time irradiated. *Figure 1* shows the peak of interest for ITX at 383 nm.

Figure 1. UV-Vis of ITX.

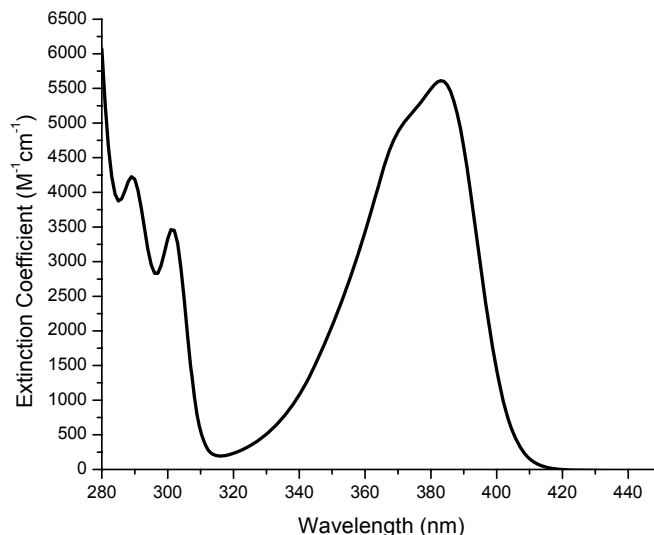
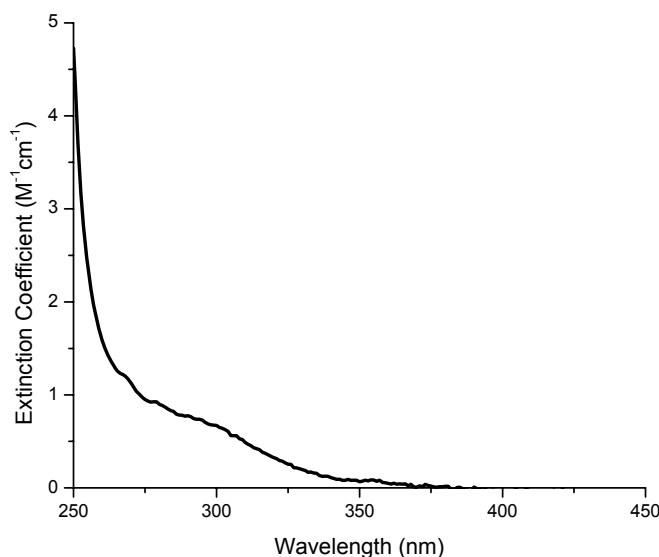


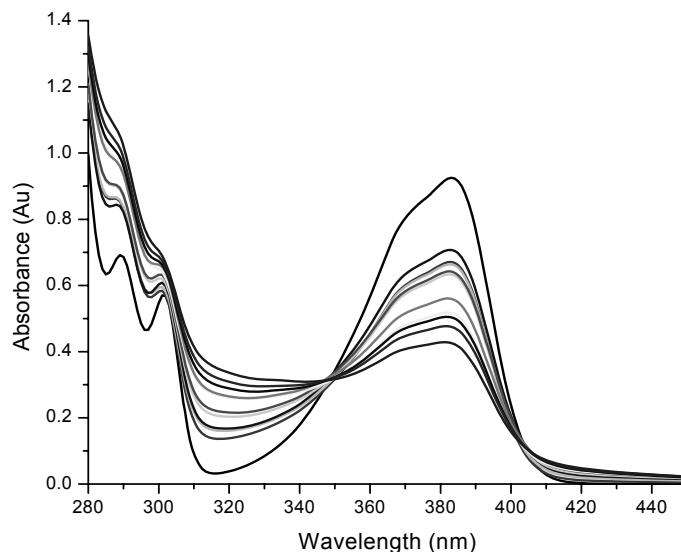
Figure 2 shows no significant absorbance above 350 nm for MA. Once the absorptions have been measured, Beer's law can be applied to determine the extinction coefficient

Figure 2: UV-Vis of MA.



since the path length and concentrations are already known. Over irradiation of the ITX and MA mixture, it was also found that a single isosbestic point occurs. *Figure 3* shows spectra of each sample taken between 0-60 minutes. All spectra meet at approximately 350 nm in an isosbestic point. Also significant is the decrease in the height of a 383 nm ITX peak. Since an isosbestic point means the entire system has an equivalent extinction coefficient at that point, a single photoproduct can then be assumed. ITX and

Figure 3. ITX/MA mixture after irradiation via Procedure 1.



ITX/MA samples were taken and diluted into ten different concentrations and run on the UV-Vis to calculate the extinction coefficient at 383 nm. The two runs gave extinction coefficients of $6357.7 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and $6346.1 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, respectively, giving an average of $6351.9 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.

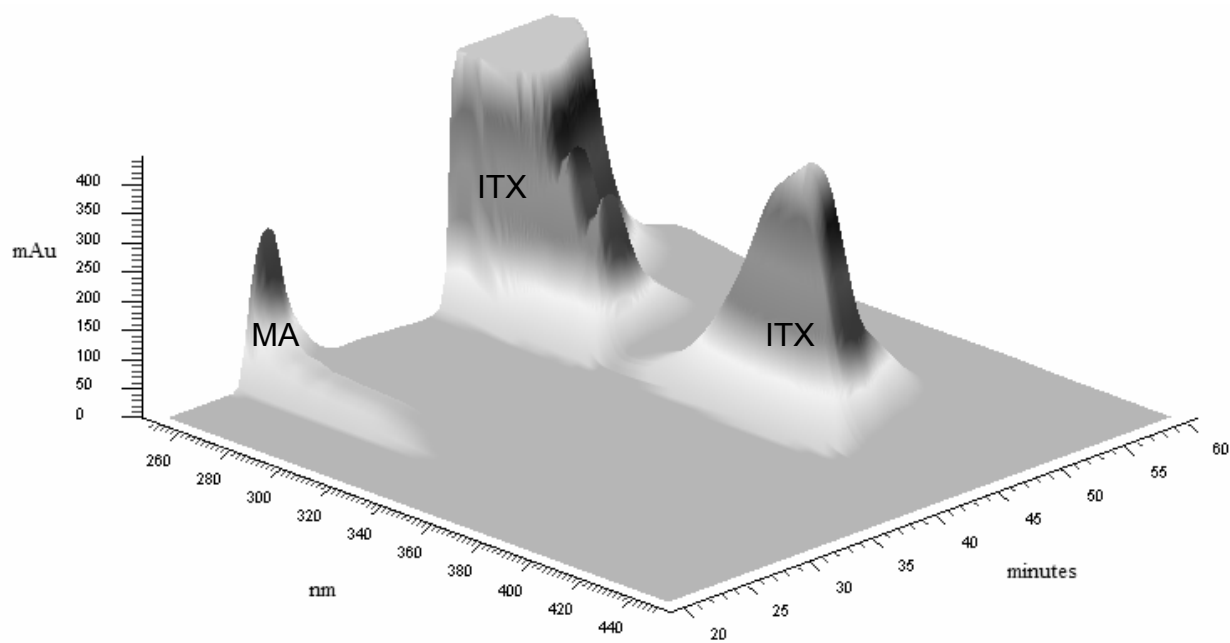
3.2 HPLC

Once an isosbestic point was elucidated, it became apparent that further UV-Vis work would not lead to any conclusion as a photoproduct was not visible and could be competitively absorbing. HPLC was then considered as an option as it separates all components out on its column. At first a 3:1 Molar ratio of MA to ITX, respectively; however, due to MA's low extinction coefficient, Beer's law indicates a higher concentration is needed to allow for the desired absorption. Therefore, Procedure 2 was introduced to give the 25:1 Molar ratio. It was discovered that a photoproduct developed steadily over the first seven minutes of irradiation. After the first seven minutes though, the system began to reach an equilibrium, and the system stayed fairly constant. It is believed the photoproduct only uses one molecule of MA to every one molecule of ITX; therefore a change in the peak height of MA is not as noticeable as it is for ITX.

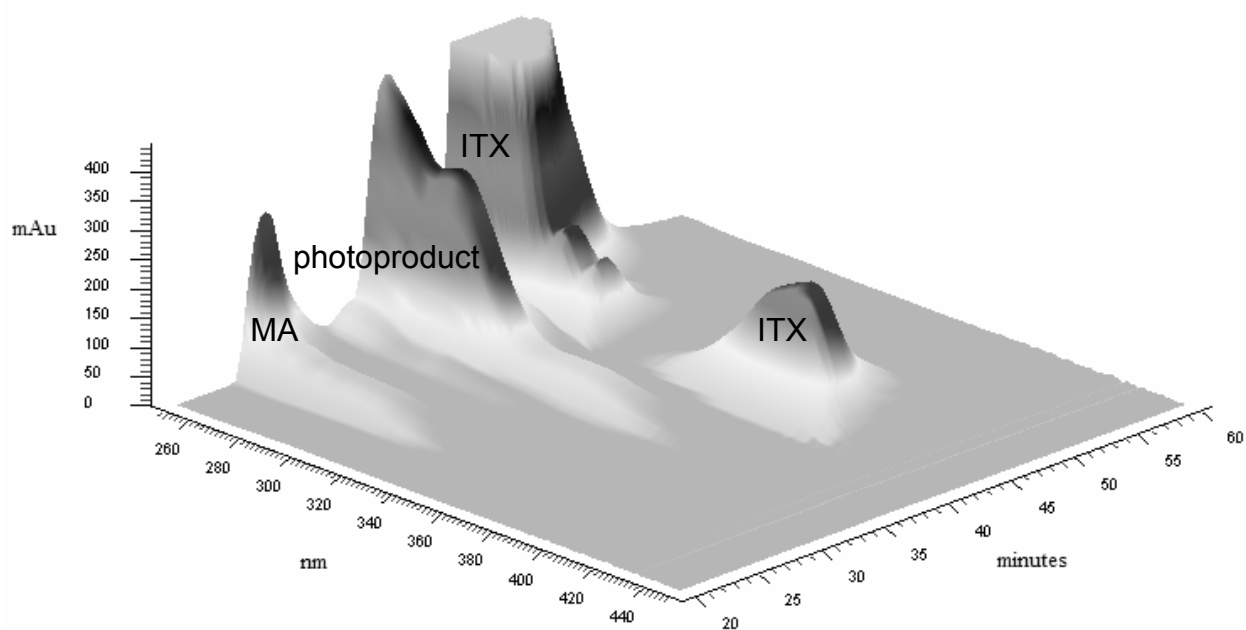
Also above was mentioned a possible degradation of ITX with long exposure to UV light. HPLC could possibly confer this with longer exposure; however, no significant change in ITX or MA is observed over a fourteen minute irradiation. The graphs in Figure 4 show a drastic change between a zero minute irradiation with ITX and MA peaks to a seven minute irradiation where the ITX peak diminishes and a photoproduct forms having a retention time of approximately thirty-five minutes. The weak absorbance near thirty minutes might be a second photoproduct. After seven minutes of irradiation, the system reaches equilibrium and very little change is observed.

Figure 4. HPLC of ITX/MA mixture on a 3D plot of Absorbance in milliabsorbance units (mAu) versus wavelength in nanometers (nm) versus retention time in minutes at zero and seven minutes of irradiation respectively.

Irradiation time: 0 min.



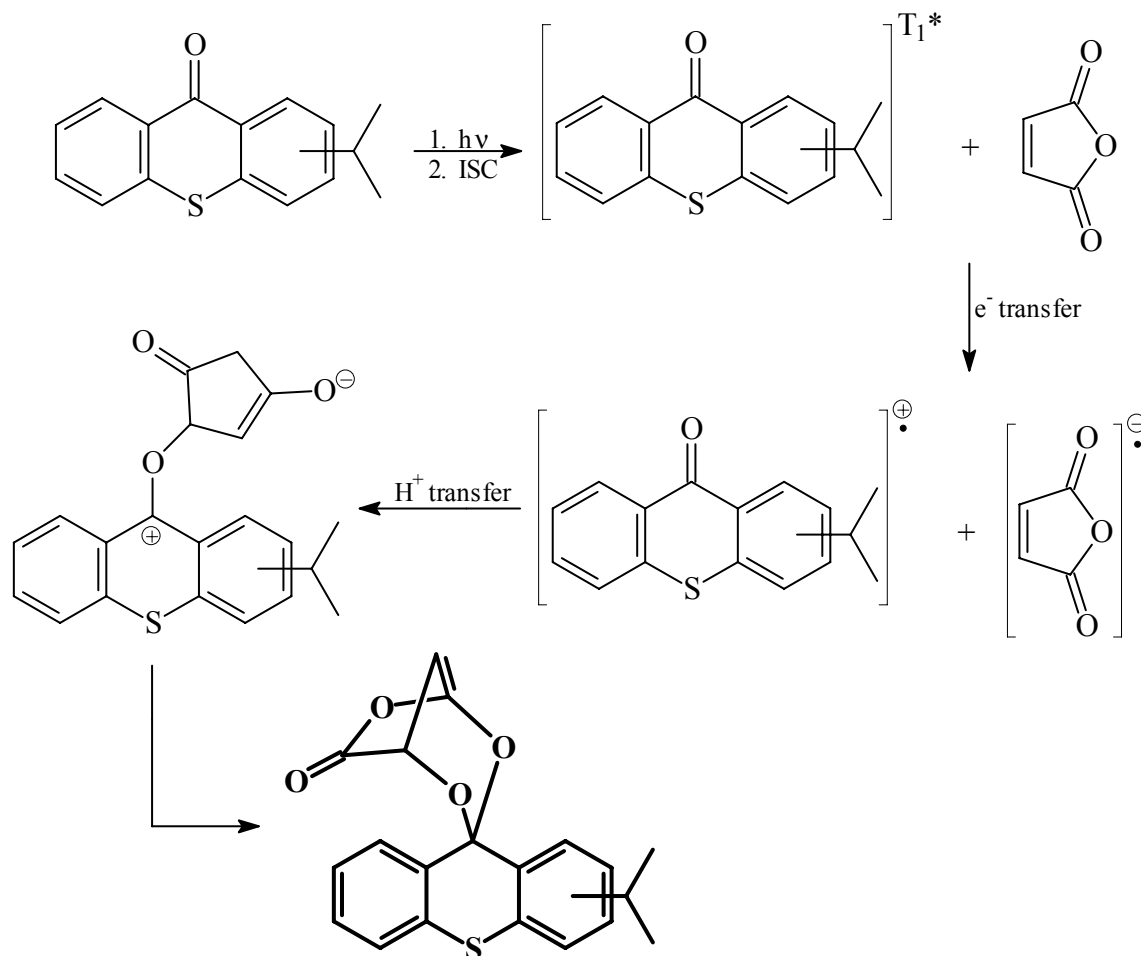
Irradiation time: 7 min.



3.3 A New Mechanism

With evidence that a side reaction occurs, a newly proposed mechanism is in order as the previously considered [2+2]-cycloaddition has a kinetic rate discrepancy.⁵ The reported rate of reaction is $3.5 \times 10^9 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, indicating an energy or electron/proton transfer. However, the [2+2]-cycloaddition suggests a chemical reaction which would occur on a rate of less than or equal to $10^5 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$. As this is a contradiction, a new mechanism was considered (Scheme 3). Though unlikely, if it were to occur, this mechanism would slow down the overall polymerization reaction, even with low quantum yields, by removing both ITX and MA from the photoinitiator system. With ITX often in concentrations less than 10^{-2} weight percent, the effect on photoinitiation efficiency could indeed be dramatic.

Scheme 3. Possible ITX/MA bicycloadduct formative mechanism.



4. Conclusions and Future Work

Elucidation of a photoproduct was shown through an isosbestic point on UV-Vis and through the absorbance of a photoproduct peak on the HPLC graphs. Discussion of a possible degradation of ITX with exposure to UV light over time offered a possible explanation of previous data being skewed from newly collected data. Finally, a revised mechanism consistent with reported rate constants was presented.

Some future work will be to calculate an initial rate constant with data obtain via HPLC and to calculate a quantum yield of the photoproduct. Isolation of the photoproduct for structural analysis will also be attempted. Corroboration of previously reported reaction rates will be considered. Finally, molecular modeling and/or computational analyses will allow for the mapping of the proposed mechanism to insure that it is thermodynamically feasible and, if so, will provide the enthalpies of formation (ΔH_f^\ddagger) for each reactant, transition state, intermediate, and product.

5. Acknowledgements

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6. References

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