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Time-Resolved Spectroscopic and Density Functional Theory Study of the Photochemistry of Irgacure-2959 in an Aqueous Solution

Mingyue Liu[†], Ming-De Li[*,†], Jiadan Xue[‡], and David Lee Phillips[*,†]

[†] Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong S.A.R., P. R. China
[‡] Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou 310018, China

KEYWORDS: Norrish Type I Reaction, Irgacure-2959, Photoinitiator, Time-resolved, Raman, DFT.

ABSTRACT: The photocleavage reaction mechanism of 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure-2959) was investigated using femtosecond (fs) and nanosecond (ns) transient absorption (-TA) spectroscopy and also picosecond (ps) and nanosecond (ns) time-resolved resonance Raman (-TR^3) spectroscopy experiments in a water-rich (volume ratio of acetonitrile:water=3:7) solution. TA spectroscopy was used to study the dynamics of the benzoyl radical growth and decay as well as to investigate the radical quenching process by the radical scavenger methyl acrylate. Ps- and ns-TR^3 spectroscopies were employed to monitor the formation of the benzoyl radical and also to characterize its electronic and structural properties. The fs-TA experiments results indicate that the Irgacure-2959 lowest lying excited singlet state S$_1$ underwent efficient intersystem crossing (ISC) to convert into its triplet state with a time constant of 4 ps. Subsequently, this triplet species dissociated into the benzoyl and alkyl radicals with a corresponding maximum absorption band at 415 nm. The TR^3 results in conjunction with results from DFT calculations confirmed that Irgacure-2959 cleaved into the benzoyl and alkyl radicals at a fast rate on the tens of picosecond timescale.

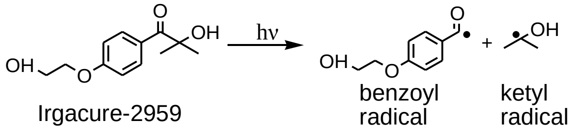
INTRODUCTION

The Norrish type I reaction has been known for over 70 years, and it can occur from either singlet or triplet states.[1-3] In recent years, 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure-2959) has received attention due to its applications in using its Norrish type I reaction as a convenient photocaged free radicals source for noble metal nanoparticles synthesis.[4 - 7] Irgacure-2959 is a typical member of highly efficient photoinitiators for photocleavage reactions that involves its excited states and dissociates into free radicals upon UV light irradiation through an α-cleavage reaction. A number of efforts have been devoted to metal nanoparticles synthesis by reducing metal ions using the radicals from the photocleavage reaction of Irgacure-2959. Yet the study of Irgacure-2959 itself and its related benzoyl radicals photochemistical properties remains limited with some laser flash photolysis and diode laser-based time-resolved infrared spectroscopy (TRIR) experiments reported for its photochemistry in acetonitrile solvent.[8-11]

Based on transient optical absorption experiments, Turro and co-workers reported that different substituents on the *para* position of the benzene ring play different roles on nature of the excited triplet state and the quantum yield of the α-cleavage reactions.[8] In their investigation, they employed 355 nm as the pump laser wavelength to excite the sample and pointed out that Irgacure-2959 with a HO(CH$_2$)O- substituent, has its triplet state involving a mixed n,π* and π,π* triplet character that leads to an intermediate level of photocleavage quantum yield of 0.29 that lies between the quantum yield of compounds with a *para* substituent of electron withdrawing groups of n,π* and electron donating groups of π,π* triplet characters. More recent work by Scaiano and co-workers found that Irgacure-2959 is a good photocaged radical source to reduce silver and gold nanoparticles in aqueous solutions. It was further confirmed that Irgacure-2959 underwent a cleavage reaction to produce benzoyl and ketyl radicals as shown in Scheme 1,[6] whose detailed mechanism of the cleavage process still remains open for investigation. It is thus important to assign the excited states and further work can be carried out to clearly identify the intermediate species and to elucidate an overall reaction pathway for Irgacure-2959 in an aqueous solution.

Direct information of reactive intermediates and their corresponding kinetics are of importance to better understand the related processes associated with the photochemical cleavage, which requires time-resolved techniques. Most of the previous time-resolved research work on this compound relied on laser flash photolysis (LFP) with a time resolution on the nanosecond timescale.[12,13] It would be useful to examine the reaction over a broader time scale and in particular the femtosecond to picosecond time scales to directly probe early time events in the reaction processes. Time-resolved Resonance Raman (TR^3) may obtain clear structural information from resonance Raman spectra that are convincing enough to provide direct pieces of evidence to distinguish among temporal and structurally similar reactive intermediates, especially, those that have overlapped absorption spectra in LFP measurements. Therefore, TR^3 is a powerful method to identify the intermediates generated and to monitor their corresponding kinetics of the short-lived species produced in the different time-scale processes.[14-20]

Scheme 1. Proposed photochemistry pathway of the benzoin Irgacure-2959 by Scaiano and co-workers



Time-resolved resonance Raman spectroscopy in combination with femtosecond to nanosecond transient absorption has been successfully used to study processes from a very early timescale to final products so as to analyze and characterize the nature and properties of the intermediates generated after irradiation.[21-25] In this paper, Irgacure-2959 was studied using fs-TA, ns-TA and time-resolved resonance Raman spectroscopy in an aqueous solution. These results found that the compound evolves from S_1 to T_1 through intersystem crossing and subsequently undergoes the photocleavage of the triplet state that is responsible for the generation of the benzoyl radical. In combination with results from density functional theory (DFT) calculations, the key species involved in the photocleavage of Irgacure-2959 are assigned using TR^3 spectra and a clear overall reaction mechanism is proposed. To our knowledge, this is the first time that time-resolved resonance Raman spectroscopy has been used to study the photocleavage reaction of Irgacure-2959.

RESULTS AND DISCUSSION

UV/Vis and fs-TA spectra of Irgacure-2959 in a water-rich solution. Figure 1 shows the UV/Vis spectra of Irgacure-2959 measured in pure MeCN and MeCN: H_2O=3:7 solutions. The most intense absorption band is located at 273 nm in MeCN which is associated with π,π* transition and this band is gradually red shifted to a longer absorption wavelength region at 279 nm as the concentration of water is increased in mixed aqueous solutions. Polarity of the solvent affects the absorption band position. In general, absorption bands associated with a π,π* transition shift to a longer absorption wavelength (redshift) when the solvent polarity is increased.

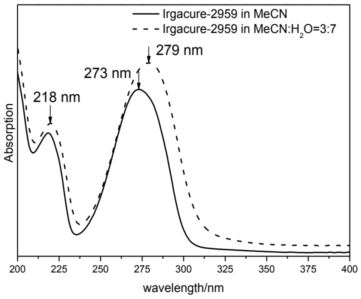


Figure 1. UV/Vis absorption spectra of Irgacure-2959 in MeCN and MeCN:H_2O=3:7 solvents with labels on the top right corner.

TD-DFT calculations were employed to simulate the UV/Vis absorption spectra (see results depicted in Figure 1S) and the frontier orbitals were also calculated from the B3LYP DFT calculations using a 6-311G** basis set (see results shown in Figure 2S) to examine the characteristics of the absorption transitions. The calculation results show that the absorption band at 273 nm arises mainly from the transition from the HOMO to the LUMO, and the band at 218 nm can be attributed to the HOMO to LUMO+1 transition. These two absorption bands are characteristic of π,π* absorption transitions. The pump laser wavelength employed in our fs-TA and ps-TR^3 experiments is 267 nm derived from the third harmonic of the fundamental 800 nm from the regenerative amplifier laser system.

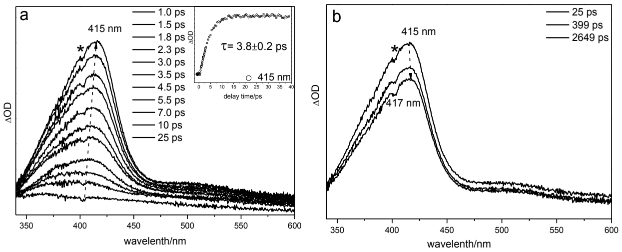


Figure 2a,b. Shown are fs-TA spectra of Irgacure-2959 at early time to later delay time recorded with 267 nm excitation in a MeCN:H2O=3:7 mixed solution. The asterisks (*) mark subtraction artifacts.

Figure 2a and 2b display the fs-TA spectra of Irgacure-2959 obtained in a MeCN:H_2O=3:7 mixed solvent from 0 to 2649 ps delay times. To better present the spectra with different time scales of these experimental results, two separated spectra with different time scales have been shown in Figure 2a (1-25 ps) and b (25-2649 ps) respectively. Figure 2a shows the temporal evolution of the early time spectra scale has a major strong absorption band growing in from 1 ps to 25 ps. At the beginning stage of 1 ps a broad absorption band at 410 nm evolves at a very fast rate up to 5 ps. Then, this absorption band grows relatively slowly and stops growing at about 14 ps. During this growth process, the maximum of the absorption band slightly shifts from 410 to 415 nm. The inset plot displays the kinetics of the transient absorption at 415 nm. The growth process is assigned to the S_1 to T_1 intersystem crossing process with a time constant of ~4 ps, which is assigned to the Irgacure-2959 triplet state growth for two reasons. First, an intermediate of Irgacure-2959 in neat acetonitrile with an absorption band at 390 nm was suggested to be assigned as the triplet in Turro and co-workers' publication,[8] although a slight redshift occurred from 390 nm to 410 nm which is affected by different polarity of the solvents. Secondly, a similar molecule (*p*-hydroxyphenacyl diethyl phosphate) also was observed to undergo an ISC process transforming its singlet state into its triplet state, where the transient absorptions of the singlet excited state and triplet state appeared around 320 nm and 400 nm respectively with an isobestic point around 330 nm.[26] Unfortunately, our current lowest wavelength of the white continued light (WCL) only could reach to 330 nm. Thus we did not obtain the transient absorption of Irgacure-2959 at wavelengths ≤330 nm. Even though, there is no obvious isobestic point in the spectra of Figure 2b, the spectral evolution is very similar with that reported for *p*-hydroxyphenacyl diethyl phosphate (HPDP)[26] and it is reasonable to attribute the growth of the 415 nm band to the formation of the triplet state.

Figure 2b displays the later time scale spectral changes of the fs-TA of Irgacure-2959. From 25 ps, it decays at a relatively fast rate to 400 ps and then it decays relatively slowly up to 2649 ps, with the maximum absorption slightly shifting to a longer wavelength absorption band at 417 nm. This may be associated with the cleavage of the triplet state of Irgacure-2959 into the benzoyl and ketyl radicals. It should be noted that the absorption band of the triplet species has a strongly overlapping absorption band with that of the benzoyl radical due to the triplet state of Irgacure-2959 and its benzoyl radical having the same basic chromophore of benzene and the HO(CH_2)O- substituent group. This makes it difficult to distinguish any reasonably distinct absorption bands between the Irgacure-2959's triplet and the benzyl radical from the TA spectra due to these two transient species being strongly overlapped with each other over an almost identical absorption region. The kinetics of the decay process is displayed in Figure 3.

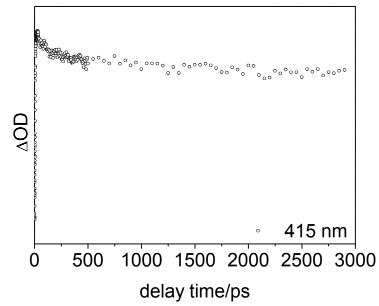


Figure 3. Temporal dependence of transient absorption spectrum at 415 nm for Irgacure-2959 recorded at later picosecond times.

Ps-TR^3 and ns-TR^3 experiments and results from DFT calculations.

As discussed in the preceding section, the TA spectra cannot clearly identify the triplet state of Irgacure-2959 and the benzyl radical owing to their very similar transient absorption. To investigate the nature and properties of the crucial intermediates generated from Irgacure-2959, time-resolved resonance Raman experiments were done in aqueous solutions. Figure 4a shows the overview of ps-TR^3 spectra of Irgacure-2959 in acetonitrile:water=3:7 mixed solution. One species has been observed from 0 ps to 4000 ps. This species appears at approximately 4 ps with the most intense bands at 934, 1157, 1319, 1447 and 1585 cm^{-1}. Initially, it grows in within 14 ps; later it grows more intense from 14 to 200 ps, and then slightly decays over the rest of delay time. According to the fs-TA spectra, the growing species obtained in the ps-TR^3 spectra after 14 ps can be assigned to the radical species of Irgacure-2959 due to the timescale of its growth after the observation of the formation of T_1 from S_1 by ISC with a 3.8 ps time constant. The triplet species is the precursor of its radical species. The growth kinetics of this species was fitted by the plotting the integrated area of the resonance Raman spectra at 1590 cm^{-1} versus the corresponding delay time as shown in Figure 5. Compared with kinetics of the fs-TA spectra in the inset plot of Figure 2a, the growth time constant is 21.7 ps, which is different from the one (3.8 ps) obtained by fs-TA experiment for the formation of the T_1 species of Irgacure-2959. From the temporal sequence, we propose that irradiation of Irgacure-2959 first converts fast into its triplet state through ISC with the time constant of 3.8 ps and then dissociates into two types of radicals with the time constant of 21.7 ps. Meanwhile, it is noted that in the early time scale (less than 14 ps) triplet state of Irgacure-2959 has not been easily observed by ps-TR^3 spectra, even though, triplet species and benzoyl radical have similar absorption bands centered around 415 nm. The 400 nm probe wavelength used in our ps-TR^3 experiments appears to be more sensitive to the benzoyl radical than the triplet state of Irgacure-2959 and suggests that the resonant enhancement at this wavelength is stronger for the benzoyl radical than for the T_1 species that is the precursor for the 21.7 ps time constant of formation of the benzoyl radical. Close inspection of the 0 ps, 10 ps and 14 ps TR3 spectra in Figure 4a shows that the Raman bands are significantly broader and appear to be sharper at longer delay times. This is likely due to vibrational cooling which typically occurs on the tens of ps time-scale. This suggests that the initial benzoyl radicals are formed vibrationally hot from the dissociation of the T_1 state of Irgacure 2959. Since the benzoyl radical and the T_1 state of Irgacure 2959 have the same basic chromophore of benzene and the HO(CH$_2$)O- substituent group and the vibrationally excited benzoyl radical at 0 ps and 10 ps have weak resonance Raman signals, a vibrationally excited T_1 state of Irgacure 2959 would also likely be very weakly resonantly enhanced using a 400 nm probe wavelength in the ps-TR^3 experiments. This suggests that the S_1 to T_1 ISC observed with a 3.8 ps time constant produces a vibrationally excited T_1 state that then readily dissociates to produce vibrationally excited benzoyl radicals. This is consistent with the behavior of the early time ps-TR3 spectra observed in Figure 4a where no obvious band are attributed to the T1 state and the initially produced benzoyl radical Raman bands are weak and very broad at early times but sharpen up on the tens of ps time scale typical of vibrationally cooling..

To better understand the later time scale reaction, ns-TR^3 experiments were also carried out in an aqueous solution. Figure 4b displays the ns-TR^3 spectra of 1mM Irgacure-2959 in open air in an acetonitrile:water=3:7 mixed solution from 0 to 1000 ns. One species is observed in the spectra. It decays gradually from the beginning spectrum with a strong vibrational bands located at 941, 1162, 1329 and 1590 cm^{-1}. Figure 3S shows the kinetics fitted by the integrated area of the strongest Raman band at 1590 cm^{-1} vs the delay time. This fit results in a decay time constant of 79 ns. The ns-TR^3 spectra clearly show that the species decays gradually until several hundreds of nanoseconds. Figure 4S displays the comparison of the resonance Raman spectrum of Irgacure-2959 obtained at a delay time of 10 ns with that from the ps-TR^3 spectra obtained with a delay time of 50 ps. Obviously, they have good agreement with each other. Hence, it is reasonable to deduce that these two spectra are contributed from the same species. The view of the TR^3 spectra from ps to ns timescale indicates that the benzoyl radical is generated from the triplet state of Irgacure-2959 and grows in at several hundred ps and decays gradually to 1000 ns with a time constant of 79 ns in an open air condition.

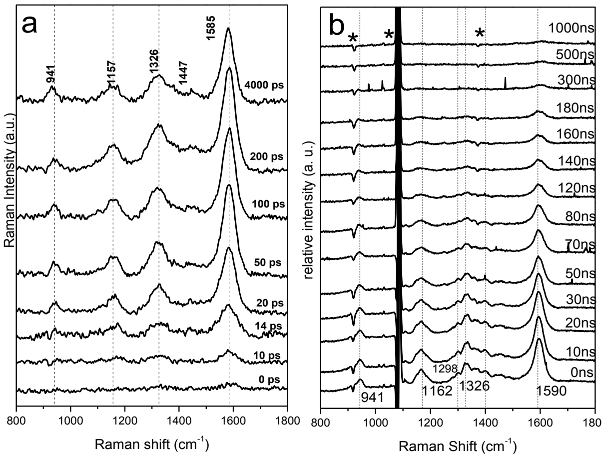


Figure 4a, b. ps-TR^3 and ns-TR^3 spectra of Irgacure-2959 in MeCN:H$_2$O=3:7 solvent obtained with 266 nm excitation wavelength and 400 nm (ps) and 416 nm (ns) probe wavelength at various delay times that inserted next to the spectra.

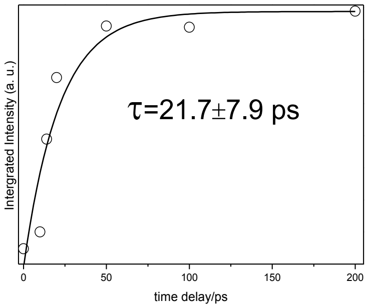


Figure 5. Time dependence of the resonance Raman band at 1585 cm^{-1} for Irgacure-2959 (open circle) in water:acetonitrile=3:7 mixed solution fit by an one exponential function with a ca. 21.7 ps growth time constant. The solid line indicates the kinetics fitting to the experimental data points.

To confirm the proposal that the major growth transient species in Figure 4a is the benzoyl radical, DFT calculations have been carried out to predict the Raman spectra of likely intermediates. Figure 6 displays a comparison of the experimental resonance Raman spectrum of Irgacure-2959 obtained at 50 ps and the DFT calculated Raman spectrum of the Irgacure-2959 benzoyl radical. The DFT calculation of the Raman spectrum vibrational bands of the benzoyl radical exhibits a good agreement with the experimental resonance Raman spectrum and this is the second piece of evidence that the species growing in after 14 ps can be reasonably assigned to the benzoyl radical of Irgacure-2959. Inspection of Figure 6 shows that most of the benzoyl radical Irgacure-2959 Raman bands observed in the ps-TR^3 are due to vibrations associated with the carbonyl C=O stretching vibration modes and ring breathing and stretching of the aromatic ring. According to the DFT results, the 941 cm^{-1} band is mainly due to the C-H bending modes. The 1157 cm^{-1} band is associated with the carbonyl C-C stretching mode located on C_4 and C_{11} (see Figure 7). The 1326 cm^{-1} band is contributed to by the ring C-C stretching mode. The most intense vibrational Raman band at 1585 cm^{-1} comes from the aromatic ring C-C stretching and carbonyl C=O stretching motions. Figure 7 shows the optimized structure of the Irgacure-2959 benzoyl radical. The corresponding bond lengths are labeled near the sides of each bond. The calculated benzoyl radical's Cartesian coordinates, sum of the electronic and thermal free energies for the optimized geometry obtained from the UB3LYP/6-311G** calculations are displayed in Figure 5S.

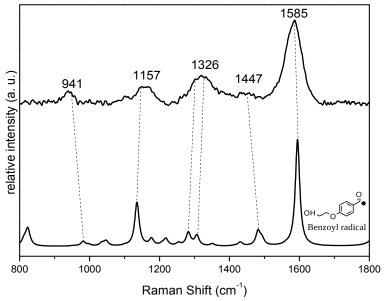


Figure 6. Comparison the experimental resonance Raman spectrum of Irgacure-2959 (top) obtained in the MeCN:H_2O=3:7 solvent at 50 ps delay time with the DFT calculated spectrum for the benzoyl radical species. Dotted lines display the correlation between the experimental and calculated Raman bands.

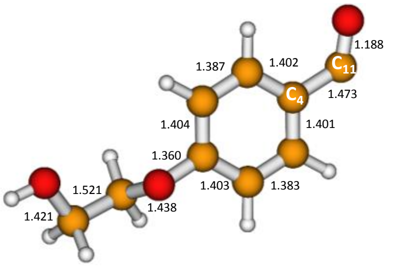


Figure 7. Optimized structure of the benzoyl radical of Igacure-2959 obtained from the UB3LYP/6-311G** calculations. Selected bond lengths are displayed in the structure.

Radical quenching experiments were carried out to confirm the hypothesis that the intermediate generated from the triplet is the benzoyl radical. Figure 8 displays the kinetics versus an increasing concentration of the carbon-centered radical quencher n-methylacrylate obtained by ns-TA spectra with an argon saturated solution condition in the sample cell. The results in Figure 8 clearly shows that the life-time of the radical decreased dramatically by increasing the concentration of the n-methylacrylate quencher. The related pseudo-first-order decay rate constant (k_{obs}) of the benzoyl radical versus the n-methylacrylate concentration spectrum is displayed in Figure 9. The data can be well fitted linearly which indicates that the transient species should be directly quenched by the radical-quencher under the argon saturated condition in the sample cell..

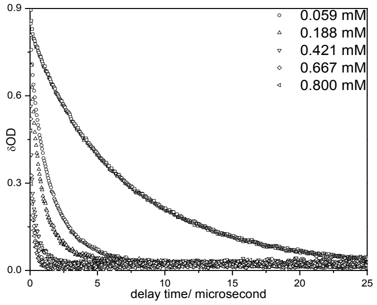


Figure 8. ns-TA kinetics of Irgacure-2959 at 410 nm by adding quencher with different concentrations normalized quenching delay time in an argon saturated condition.

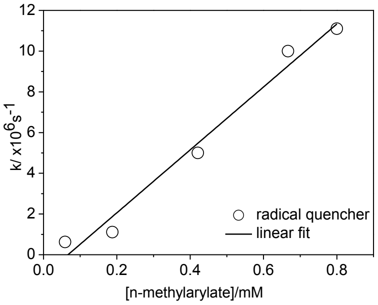


Figure 9. Pseudo-first-order decay rate constants (k_{obs}) of the benzoyl radical versus n-methylacrylate concentration, measured following laser flash photolysis (266 nm) of argon-saturated MeCN:H_2O=3:7 solution in the presence of different n-methylacrylate concentrations.

DFT calculations for the activation energy barrier To further verify that cleavage reaction takes place from the triplet state, DFT calculations were done to examine the activation energy barrier. The computations were performed at the (U)B3LYP/6-311G** level of theory. The optimized structures of the reactant complex (RC), the transition state (TS), and the product complex (PC) are shown in Figure 10, in which the cleaved C-C bond length is labeled. The reaction barrier was found to be 5.0 kcal/mol by the DFT calculations. The calculated relative energy profile for the cleavage reaction is shown in Figure 11. The cleavage reaction is initiated through the C-C bond as indicated by distance labeled in Figure 10. As the reaction goes from the TS to the PC, the C-C bond is completely cleaved. The reaction energy barrier is very small, which demonstrates that it is reasonable for Irgacure-2959 to undergo cleavage through its triplet state. This is consistent with the experimental results that the triplet state of Irgacure-2959 undergoes the cleavage reaction efficiently. The Cartesian coordinates, sum of the electronic and thermal free energies for the optimized geometry from the UB3LYP/6-311G** calculations for Irgacure-2959's transition state of interest in the paper are given in Figure 6S.

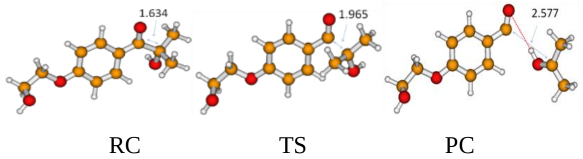


Figure 10. The optimized geometries of the RC, TS and PC calculated by B3LYP/6-311G(d,p) for the cleavage reaction of Irgacure-2959. Selected interatomic distances (in angstrom) are labeled in the structures.

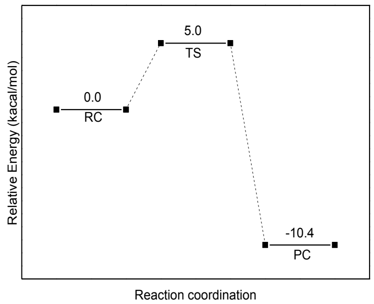
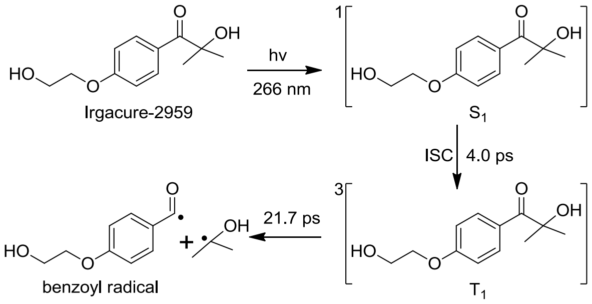


Figure 11. The reactive energy profile obtained from the DFT calculation for Irgacure-2959 photocleavage reaction.

For a clear view of the different species involved in the whole photochemical reaction process, Scheme 2 presents an overview of the mechanism that Irgacure-2959 evolves from ground state through singlet and triplet to cleave into the radical species after 266 nm laser irradiation. As depicted in Scheme 2, Irgacure-2959 was excited from ground state to its excited singlet state then converted into the triplet state which has an absorption band at 415 nm with a time constant of 4.0 ps. Then a homolysis cleavage reaction occurred resulting in the generation of benzoyl and ketyl radicals with a time constant of 27.1 ps.

This is the first time the benzoyl radical and its dynamics in water-rich solution was characterized by time resolved resonance Raman vibrational spectroscopy. The results show that in water, the benzoyl radicals are efficiently generated with a time constant of 21.7 ps. This provides significant information for the reactive intermediates with its corresponding kinetics involved in the photocleavage reaction of Irgacure-2959.



Scheme 2. Proposed Photocleavage Reaction Mechanism of I-2959 in water:acetonitrile mixed solution.

CONCLUSION

The photocleavage reaction mechanism of Irgacure-2959 was explored by using the fs-TA, ns-TA, ps-TR^3 and ns-TR^3 spectroscopies. In acetonitrile-water mixed solution, the singlet excited state converts into a triplet state through a highly efficient ISC process with a time constant of 4.0 ps. The triplet state of Irgacure-2959 has a strong absorption bands at 415 nm. The transient absorption band at 415 nm slightly decays and has a red-shift to 417 nm, this process is confirmed to be the photocleavage of the triplet state of Irgacure-2959 which results in the generation of benzoyl radicals that appear to be vibrationally excited when they are first produced. The comparison of the resonance Raman spectra from ps-TR^3 spectra and the DFT calculated Raman spectrum of the benzoyl radical further supports the assignment of the benzoyl radical in the aqueous solution. Radical quenching experiments done using ns-TA detection were also carried and these results also supported that Irgacure-2959 cleaves to produce a benzoyl radical. DFT calculations indicated that the activation energy barrier for the cleavage of Irgacure-2959 is 5.0 kcal/mol, this is complementary evidence to support that the triplet state of Irgacure-2959 undergoes the cleavage at an ultrafast rate consistent with experimental observations. The time-resolved spectroscopic study for Irgacure-2959 reported here presents a clear photochemical mechanism for Irgacure-2959 irradiated by UV light in water-rich solutions.

METHODS

Materials: The Irgacure-2959 (2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone) sample was commercially available and purchased from Sigma-Aldrich Company with 98% purity. It was used as received with acetonitrile and water to prepare a solution with a volume ratio of 3:7 for the experiments reported here. The sample solutions of Irgacure-2959 employed in the picosecond time-resolved resonance Raman (ps-TR^3) experiments were prepared at a concentration such that the absorbance was 2 using a 1 mm thickness quartz cell at the excitation wavelength of 266 nm.

Fs-TA experiments: The femtosecond time-resolved transient absorption (fs-TA) experiments were performed using a commercial femtosecond Ti: Sapphire regenerative amplified Ti: Sapphire laser system from Spectra Physics, Spitfire-Pro and an automated data acquisition system from Ultrafast System, Helios. The pump laser pulse wavelength is 267 nm, the third harmonic of the fundamental 800 nm from the regenerative amplifier. While the probe laser pulse was a white-light continuum from 350 nm to 800 nm generated in a CaF_2 crystal by using approximately 5% of the amplified 800 nm output from the Spitfire. The probe beam is split into two parts before passing through the sample: one goes through the sample, the other travels directly to the reference spectrometer that monitors the fluctuations in the probe beam intensity. The instrument response time is estimated to be 150 fs. At each of the temporal delay time, the data were averaged for 0.5 s. The maximum extent of the temporal delay time was 3300 ps for the optical stage used in the experiments. The detailed apparatus and methods for the fs-TA experiments have been discussed previously.[21]

Ps-TR^3 experiments: Picosecond time-resolved resonance Raman (ps-TR^3) experiments were done using an ultrafast system in our laboratory. The samples were pumped with a 267 nm laser pulse and probed with a 400 nm laser pulse. The durations of the pump and probe lasers were 1.5 ps and the pulse energies focused onto the sample was 5-10 μJ. The time resolution of the system was 2 ps and the time delay between the pump and probe pulses were adjusted using an optical delay line. A thin film stream of the sample was excited by the focused laser pulses of light and the signal of the Raman light was collected using a back-scattering configuration and detected by a liquid nitrogen cooled CCD. Detailed of the experimental apparatus and methods employed have been described previously.[26]

Ns-TR^3 experiments: Nanosecond time-resolved resonance Raman (ns-TR^3) measurements were performed using a pump-probe apparatus and methods described previously.[21] Concisely, the pump laser pulse wavelength of 266 nm was generated from the fourth harmonic of a Nd:YAG nanosecond pulsed laser. The probe laser pulse wavelengths of 354.7 nm for Irgacure-2959 in pure acetonitrile and 416 nm for Irgacure-2959 in acetonitrile:water with volume ration both 1:1 and 1:9 solutions were both generated from the third harmonic of the Nd:YAG nanosecond pulsed laser and the first Stokes hydrogen shifter laser line of the third harmonic. The energy of the laser used in the experiments was in a range from 2.5 to 3.5 mJ with a 10 Hz repetition rate. These two lasers were synchronized by a pulse delay generator to electronically control the pump and probe lasers time delay that was monitored by a fast photodiode and 500 MHz oscilloscope. The apparatus time resolution was about 10 ns. The pump and probe laser beams were optically aligned and focused onto a spot of a running sample solution stream so that these two laser pulses were spatially overlapped on the sample solution. The scattered Raman light was collected by using reflective optics into a spectrometer whose grating dispersed the light onto a charge-coupled device (CCD). The Raman signal was accumulated for 30 s by the CCD before being read out and stored to a computer. The spectra included here were obtained by the subtraction of a resonance Raman spectrum with a negative time delay of the probe before the pump -100 ns spectrum from the resonance Raman spectrum obtained with a positive time delay of pump before probe spectrum. The known acetonitrile solvent's Raman bands were used to calibrate Raman shifts with an approximate accuracy of 5 cm^{-1}.

Density Function Theory (DFT) computations were employed to study the properties of Irgacure-2959 for comparison purposes to make assignments of the intermediates generated in the excited states in various solvents. The optimized geometries, vibrational modes and the vibrational frequencies for the different species were obtained from DFT calculations that employed a (U)B3LYP/6-311G** basis set. No imaginary frequency modes were observed at the stationary states of the optimized structures presented here. The default G03 method was used to obtain the Raman spectra to determine the Raman intensity and shifts. A factor of 0.975 were used to scale the calculations of the Raman frequencies by the DFT calculations with (U)B3LYP/6-311G** basis set for comparison with the experimental Raman results in order to achieve a better understanding of the experimental data assignments. For the reaction energy profile for the Irgacure-2959 photocleavage reaction calculated from DFT computations, the sum of the electronic and thermal free energies of the TS (transition state) was subtracted from that of the RC (reactant complex) to obtain the energy barrier between the TS and the RC. We also obtained the energy barrier between the PC (product complex) and the RC in a similar manner. All of the calculations were done using the Gaussian 03 program suite.[27]

ASSOCIATED CONTENT

Supporting Information Available: The predicted absorption spectrum of singlet state of Irgacure-2959 is given. The DFT calculated frontier orbitals of Irgacure-2959 are provided. The Kinetic of Irgacure-2959 in MeCN:H_2O=3:7 solvent is given. Comparison the experimental resonance Raman spectrum of Irgacure-2959 obtained in the MeCN solvent with the experimental resonance Raman spectrum of Irgacure-2959 in the MeCN:H_2O=3:7 solvent are given. The Cartesian coordinates are provided. The Irgacure-2959 transition state Cartesian coordinates are given.

Corresponding Author

*Phone: +852-2859-2160. Fax: +852-2857-1586.
E-mail: phillips@hku.hk; mdli@hku.hk

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