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UNIVERSITY OF SOUTHERN CALIFORNIA LOS ANGELES  
A STUDY OF PHOTOPHYSICAL PROCESSES IN ORGANIC SYSTEMS.(U)  
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| Photophysical Processes      Glassy Media<br>Organic Systems      Photorotamerism<br>Aromatic Ketones      Diketones<br>Dioxetanes      Chemiexcitation                                                                                                                                                                                                                                                                            |                       |                                                             |
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| This report summarizes research results covering the topics: (a) the role of exciplexes in the photophysics of aromatic ketone triplets, (b) triplet-triplet annihilation of aromatic ketone triplets, (c) exploratory studies on photorotamerism in glassy media, (d) exploratory studies of the photophysics of rigid 1,2-diketones, and (e) elucidation of the chemiexcitation pathways in the decomposition of 1,2-dioxetanes. |                       |                                                             |

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**A STUDY OF PHOTOPHYSICAL PROCESSES IN ORGANIC SYSTEMS**

**FINAL REPORT**

**Lawrence A. Singer**

**October 24, 1978**

**U.S. ARMY RESEARCH OFFICE**

**RESEARCH TRIANGLE PARK**

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A) PUBLICATIONS

- 1) "Chemiluminescence from the reaction of singlet oxygen with 10,10'-dimethyl-9,9'-biacridylidene. A reactive 1,2-dioxetane." J. Org. Chem., 41, 2685 (1976), K-W Lee, L. A. Singer and K. D. Legg.
- 2) "Deactivation of benzophenone triplets via exciplex formation. Evidence for dual reaction pathways." J. Am. Chem. Soc., 99, 526 (1977), M.W. Wolf, R.E. Brown and L.A. Singer.
- 3) "Photostationary and transient studies of the phosphorescence from the benzil-anisole system. Direct evidence for reversible exciplex formation." Chem. Physics Letters, 51, 526 (1977), R. E. Brown, T-S Fang, C. L. Kwan and L. A. Singer.
- 4) "Triplet-triplet annihilation by diffusive encounter of benzophenone triplets in benzene solution." J. Phys. Chem., 82, 246 (1978), T-S Fang, R. Fukuda, R. E. Brown and L. A. Singer.
- 5) "Perturbation of the benzil ground and excited state geometries at low temperature in hydrocarbon glasses." J.C.S. Chem. Comm., 116 (1978), T-S Fang and L. A. Singer.
- 6) "Wavelength dependent photoprocesses in acenaphthaquinone." J. Am. Chem. Soc., 100, 6276 (1978), T-S Fang and L. A. Singer.
- 7) "Photophysical studies on benzil. Time-resolution of the prompt and delayed emissions and a photokinetic study indicating deactivation of the triplet by reversible exciplex formation." J. Phys. Chem., 82, in press, T-S Fang, R. E. Brown, C. L. Kwan and L. A. Singer.
- 8) "Variable temperature studies on the luminescence from benzil in a polymethylmethacrylate glass. An example of matrix controlled photorotamerism." Chem. Phys. Letters, in press, T-S Fang and L. A. Singer.

B) PERSONNEL SUPPORTED DURING GRANT PERIOD

Principal Investigator

Lawrence A. Singer: one summer month each year, 1975, 1976, 1977.

Postdoctoral Fellows:

Ronald E. Brown (part-time) 4/1/75 - 8/31/77  
Ken D. Legg summer only, 1975  
Chi Lup Kwan 7/1/76 - 2/28/78

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| <b>A</b>                        |                                                   |

B) PERSONNEL SUPPORTED: (Contd.)

Graduate Students:

Kyu-Wang Lee summer months, 1975 (Ph. D., 8/75)

Monte W. Wolf summer months, 1975, June, 1976 (Ph. D., 6/76)

Tai-Shan Fang summer months, 1975, 1976, 1977 (Ph. D., 6/78)

Samir Atik summer months, 1975, 1977

Chris Lee summer months, 1975, 1977

Undergraduate students:

Patrick Pakes 4/1/75

C) TECHNICAL REPORT

The work carried out during the period of the grant (1 April, 1975 - 30 September, 1978) covered the topics: (a) the role of exciplexes in the photo-physics of aromatic ketone triplets (publications 2,3 and 7), (b) triplet-triplet annihilation of aromatic ketone triplets (publications 4 and 7), (c) exploratory studies on photorotamerism in glassy media (publications 5 and 8), (d) exploratory studies of the photophysics of rigid 1,2-diketones (publication 6) and (e) elucidation of the chemiexcitation pathways in the decomposition of 1,2-dioxetanes (publication 1).

Studies under topic (a) were a continuation of earlier work carried out under the previous ARO grant (1 April, 1972 - 30 March, 1975). In studies during the more recent grant period, we elucidated the importance of charge transfer interaction in the exciplexes formed between benzophenone triplets ( $T_1$ ) and ground state substituted benzenes ( $S_0$ ). A key conclusion in that study (publication 2) was that two different transient exciplexes are formed that differ in the donor/acceptor roles assumed by the  $T_1$  and  $S_0$ . In following papers describing the deactivation of the benzil triplet by substituted

benzenes, we elucidated the kinetic scheme and showed that the transient exciplexes were reversibly formed in fluid media. We offered a kinetic methodology consistent with the observed nonlinear Stern-Volmer plots that provided estimates of several of the important kinetic parameters (publications 3 and 7).

Several years ago, we showed that triplet-triplet annihilation (topic (b)) of benzophenone triplets was an important pathway in fluid media (work done during previous grant period). We interpreted our results at that time in terms of diffusive encounter of the interacting triplets and the magnitude of the derived bimolecular rate constant ( $k_T$ ) implied a nearly diffusion limited reaction. The earlier study was not conclusive however, because the limited output of the nitrogen laser in our laboratory required that we use solutions  $< 1 \text{ M}$  in benzophenone in order to obtain sufficiently high  $[T_1]$  for triplet-triplet annihilation to compete favorably with the first-order decays. At such high concentrations of benzophenone, we could not exclude the possibility of the triplets encountering by a series of triplet-triplet energy transfers (hops) through the medium rather than by diffusion. We resolved this problem by studies on a neodymium laser where we were able to monitor triplet-triplet annihilation at concentrations of benzophenone approaching  $10^{-3} \text{ M}$  (the hopping mechanism is excluded at this concentration). We noted that  $k_T$  was invariant between  $0.015 - 0.0010 \text{ M}$  benzophenone ( $k_T \sim 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) and in excellent agreement with the earlier work done  $> 1 \text{ M}$  benzophenone. We concluded that the benzophenone triplets encounter by diffusion (publication 4).

A study of triplet-triplet annihilation of the benzil triplets was also carried out with the same results as with benzophenone. (Publication 7). In the latter work, we discuss the implication of the magnitude of  $k_T \approx 0.7 k_{\text{diffusion}}$  in terms of spin statistics.

In the course of our work on benzil, we noted unusual changes in the luminescences (fluorescence and phosphorescence) in low temperature glasses. (Topic (c)). After sorting out complications due to microcrystallization of the benzil in hydrocarbon glasses, we were able to show that in a methylcyclohexane glass, ground state benzil assume a geometry where the carbonyl groups are in a coplanar arrangement (probably trans-coplanar). Excitation of this geometry leads to a trans-coplanar excited state which eventually phosphoresces (long wavelength-580 nm). In an isopentane glass, the benzil ground state geometry is skewed (meaning that the carbonyl groups are in planes with a dihedral angle close to  $90^\circ$ ). Excitation of this ground state geometry leads to a skewed excited state which emits (phosphorescence near 530 nm). These observations mean that the isopentane glass inhibits the skewed to planar relaxation that is observed in fluid media and that the geometry of the benzil ground state depends on the hydrocarbon matrix (Publication 5). Additional evidence for restricted "phototorotamerism" in the excited state of benzil was obtained from a study in polymethylmethacrylate glass (Publication 8). In this study, the matrix barrier to excited state geometric relaxation was estimated from variable temperature studies. Further, discontinuities in temperature-luminescence profiles seem to correlate with known transition points in the polymer glass. Probes such as benzil may be useful for studying polymer glass transitions.

During the last two years, we extended our study of the photophysics of aromatic ketones to rigid 1,2-diketone systems such as acenaphthaquinone and phenanthraquinone (topic (d)). These systems introduce additional variations into the photophysical scheme of aromatic ketones. We noted a wavelength dependence in acenaphthaquinone with three separate photoprocesses: phosphorescence, a photocycloaddition reaction, and an interesting photooxidation reaction

(Publication 6) where in each case the efficiency of the process is greater with longer wavelength excitation such that  $\phi_{366}/\phi_{313} \sim 2.5$ . We speculate that shorter wavelength excitation leads to acyl carbon-acyl carbon bond scission that competes favorably with internal conversion to the photoreactive  $T_1$  state.

Our interest in the decomposition of 1,2-dioxetanes (topic (e)) has focused on elucidating the competition between chemiexcitation pathways that lead directly to the excited singlet and triplet states of the ketone products. In publication 1, we describe our results with the 1,2-dioxetane derived from 10,10'-dimethyl-9,9'-diacridylidene which upon decomposition yields two equivalents of N-methyl-acridone. The low lying excited states ( $S_1$  and  $T_1$ ) of this ketone have the  $\pi, \pi^*$  configuration. We observed that the excited singlet state of the acridone is populated with an efficiency of  $\sim 0.04$  as determined by measuring the chemiluminescence yield. The efficiency of formation of the acridone triplet state (using a chemical counting method) is  $\sim 0.04$  which is within experimental error of the value expected from intersystem crossing of the singlet state. We concluded that there is no evidence that the acridone triplet state is directly formed during decomposition of the dioxetane even though the triplet state is favored energetically by 15 or 20 kcal/mole. We suggest that spin conservation may be a key factor in controlling the competition between chemiexcitation paths into the singlet and triplet states with ketones having low lying  $\pi, \pi^*$  states.