Photodecarbonylation of α-Diketones: A Mechanistic Study of Reactions Leading to Acenes

*Rajib Mondal, Albert N. Okhrimenko, Bipin K. Shah, and Douglas C. Neckers**

Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH 43403

neckers@photo.bgsu.edu

Supporting Information

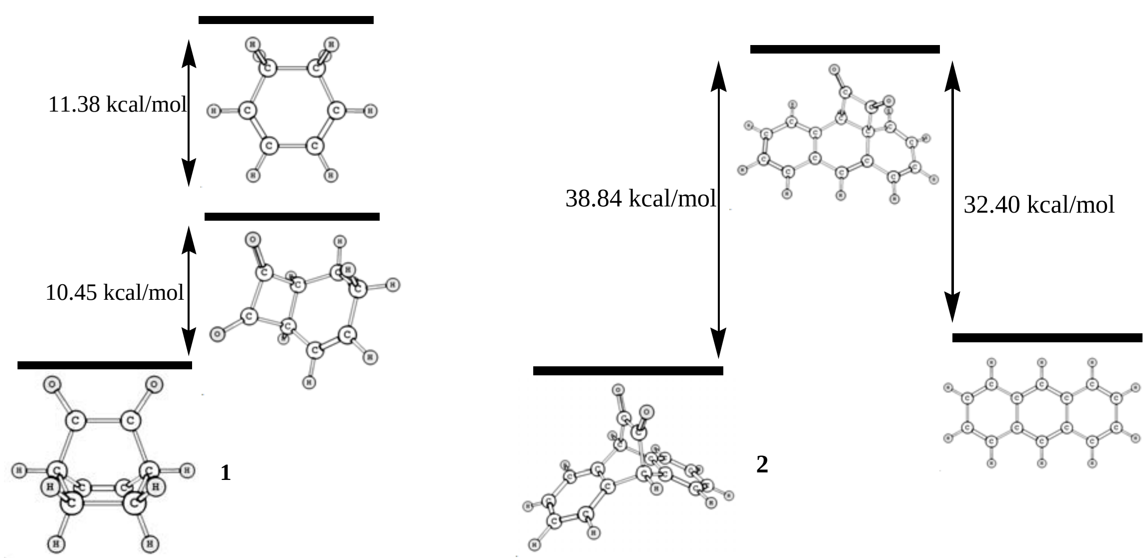


Figure S1. Energy differences of the ground state optimized structures of **1**, **2**, their isomers, and photodecarbonylated products; 1,3-cyclohexadiene and anthracene, respectively.

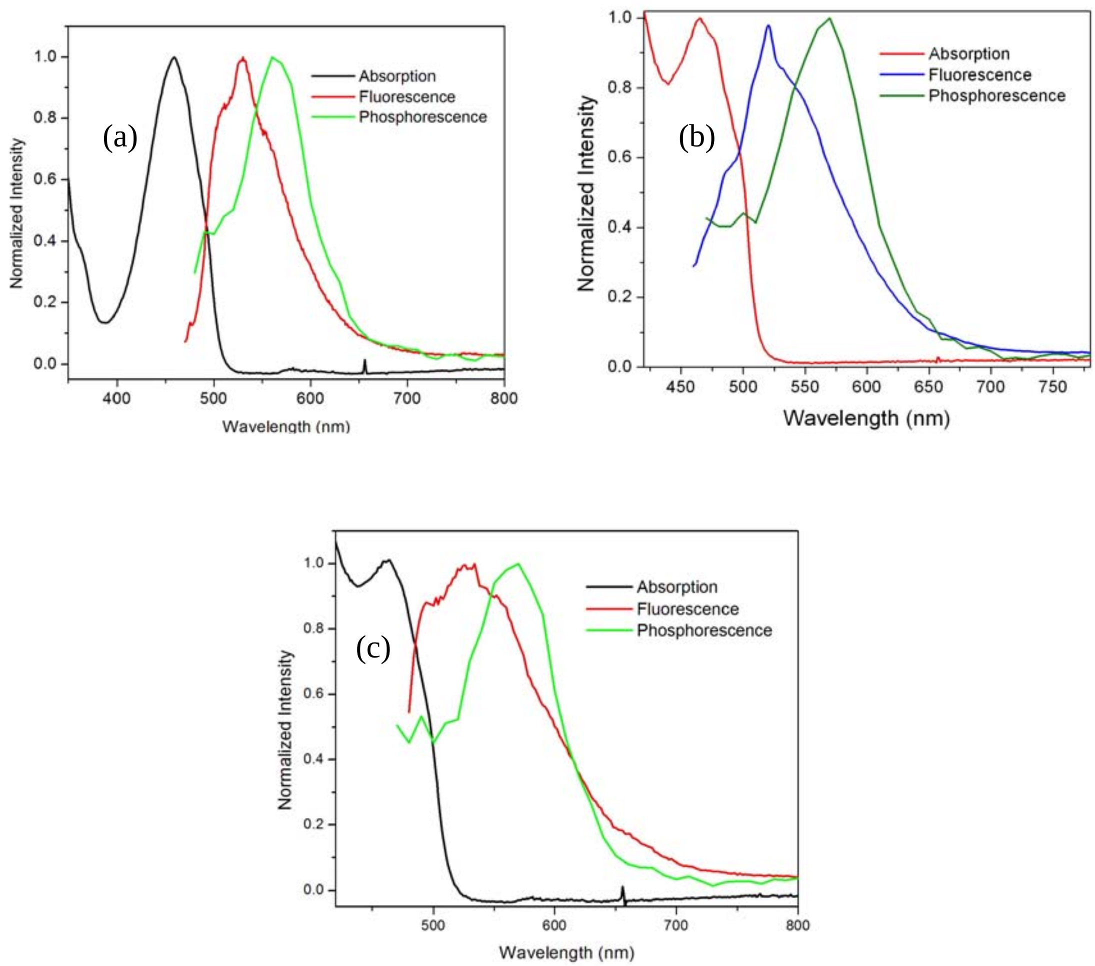


Figure S2. Normalized absorption, fluorescence, and phosphorescence spectra of (a) **2**, (b) **3**, and (c) **4**. (absorption and fluorescence spectra recorded in toluene at room temperature and phosphorescence spectra recorded in methanol/ethanol (1:4) matrix at 77 K).

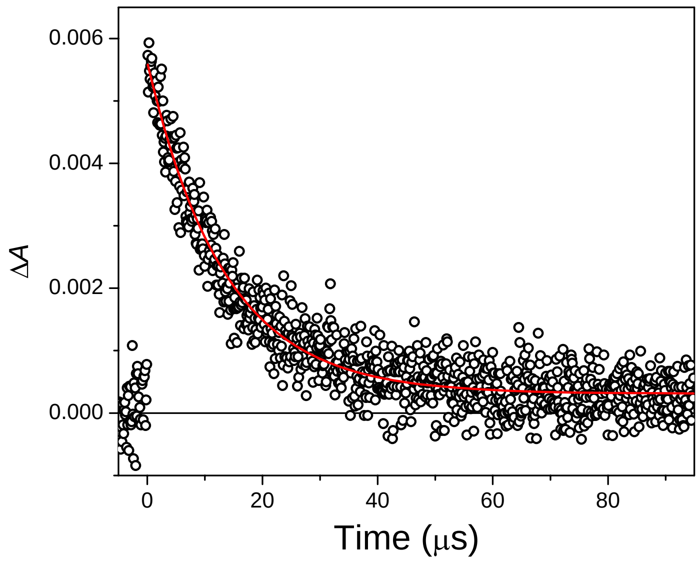


Figure S3. Nanosecond flash photolysis of **4** in toluene, argon-saturated (λ_{ex} = 460 nm): kinetic traces monitored at 500 nm (τ= 13.34 +/-0.27 μs) showing the lifetime of the triplet state of heptacene.

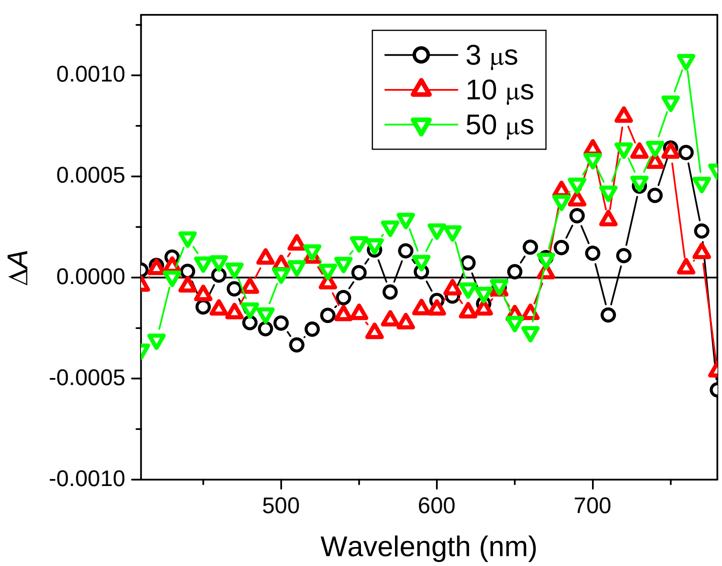


Figure S4. Absorption spectra obtained from the nanosecond laser flash photolyis of **4** in toluene (oxygen saturated), recorded (a) 3 μs (black), (b) 10 μs (red), and (c) 50 μs (green) after the laser pulse (λ_{ex} = 460 nm); the absorption in the 650-800 region is that of heptacene.

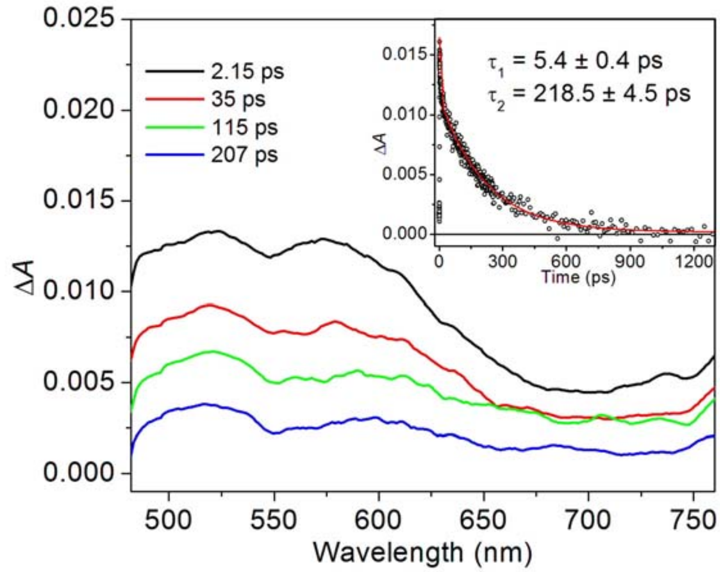
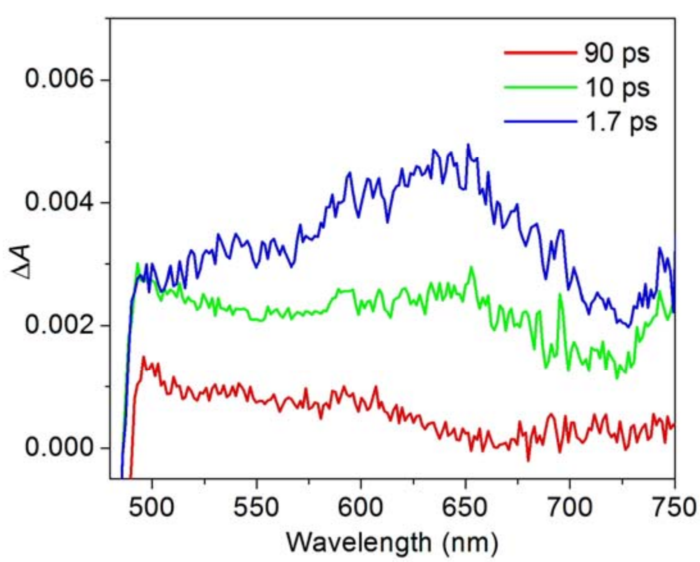


Figure S5. Absorbance difference spectra in the visible region of diketone **2** in toluene acquired following a 130 fs excitation pulse at 475 nm (pulse energy = 5 μJ). Inset: kinetic trace monitored at 550 nm.



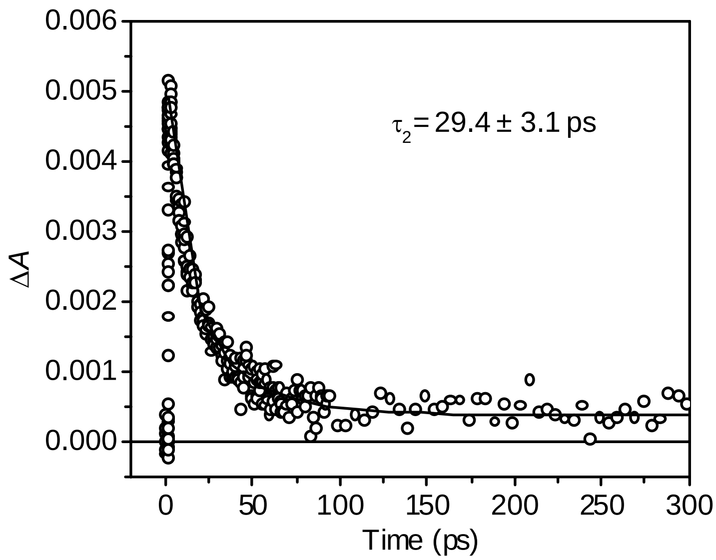


Figure S6. Absorbance difference spectra in the visible region of diketone **3** in toluene acquired following a 130 fs excitation pulse at 475 nm (pulse energy = 5 μJ) (topm). Kinetic traces monitored at 620 nm (bottom).

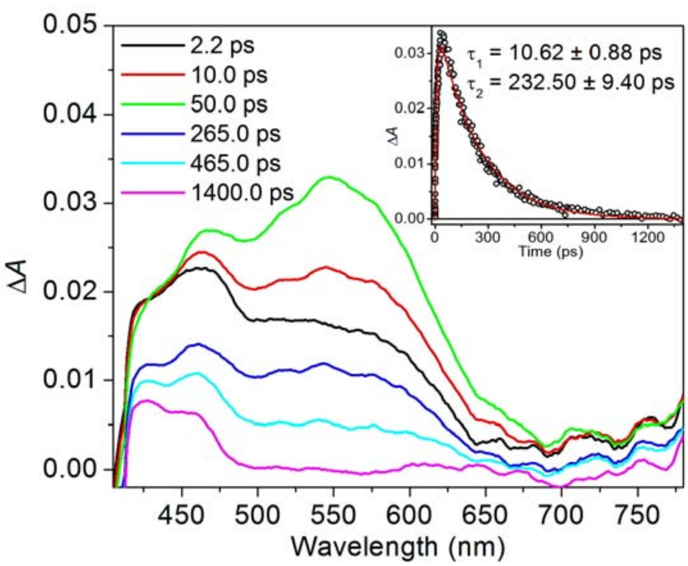


Figure S7. Absorbance difference spectra in the visible region of diketone **2** in toluene acquired following a 130 fs excitation pulse at 400 nm (pulse energy = 5 μJ). Inset: kinetic trace monitored at 550 nm.

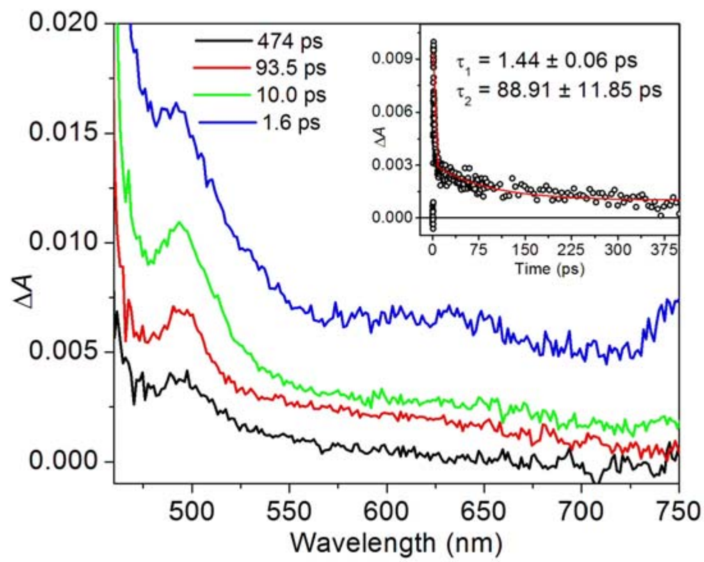


Figure S8. Absorbance difference spectra in the visible region of diketone **3** in toluene acquired following a 130 fs excitation pulse at 400 nm (pulse energy = 5 μJ). Inset: kinetic trace monitored at 620 nm.

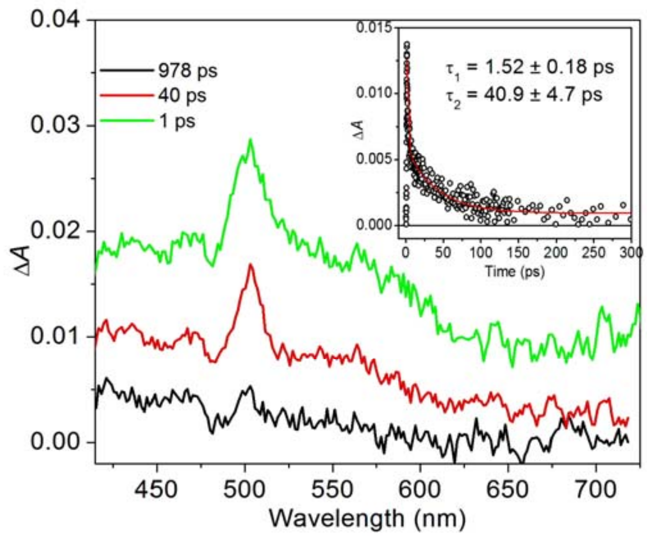


Figure S9. Absorbance difference spectra in the visible region of diketone **4** in toluene acquired following a 130 fs excitation pulse at 400 nm (pulse energy = 5 μJ). Inset: kinetic trace monitored at 620 nm.

Ref. 22. Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.