COMMUNICATION www.rsc.org/chemcomm | ChemComm

Two-photon induced photodecarbonylation reaction of cyclopropenones†

Nurtay K. Urdabayev, Andrei Poloukhtine and Vladimir V. Popik*

Received (in Cambridge, UK) 19th September 2005, Accepted 16th November 2005
First published as an Advance Article on the web 12th December 2005
DOI: 10.1039/b513248g

Irradiation of cyclopropenones (1a–c) with 800 nm pulses of ultrafast laser results in a photodecarbonylation reaction *via* nonresonant two-photon absorption of light.

UV photolysis of cyclopropenones often results in efficient decarbonylation and the formation of corresponding acetylenes in high yield (Scheme 1).[1] In the development of novel photonucleases, which is underway in our group, we employ the cyclopropenone photodecarbonylation for the *in situ* generation of reactive cyclic enediyne compounds.[2]

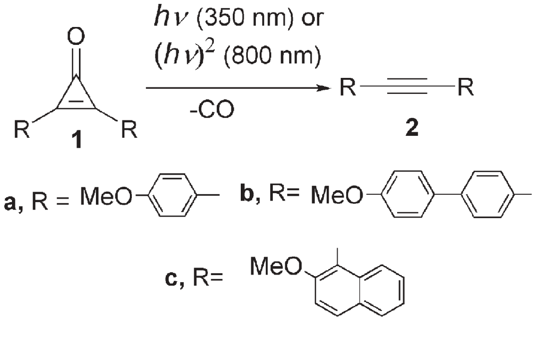
Decarbonylation of cyclopropenones is usually induced by UV irradiation. These conditions, however, are not compatible with many biomedical applications, which require use of light in a so-called "phototherapeutic window", a region of relative tissue transparency between 650 and 950 nm. One of the approaches allowing for the alleviation of this problem is to employ nonresonant two-photon excitation (2PE). At high light fluxes chromophores might simultaneously absorb two red/NIR photons producing excited states the same as or similar to ones accessible by excitation with UV light of twice the frequency.[3] Commercialization of ultrafast lasers has resulted in the development of numerous successful applications of the nonresonant two-photon excitation in fluorescent spectroscopy,[4] microscopy,[5] and photonics.[6] While many very efficient two-photon fluorophores have been reported,[7] the field of two-photon photochemistry[8] remains relatively unexplored. There are only a few examples of two-photon induced cycloaddition and cycloreversion reactions,[9] as well as the photo-Wolf rearrangement[10] and the uncaging of bioactive molecules[11] using two-photon excitation.

This communication describes for the first time the two-photon induced decarbonylation of cyclopropenones **1a–c**, as well as the direct determination of two-photon absorption cross-sections of these substrates.

Single-photon photochemistry of **1a–c**. The UV spectra of diaryl-substituted cyclopropenones **1a–c** in methanol show the longest wavelength band between 300 and 400 nm depending on substitution (**1a** λ_{max} = 341 nm, logε = 4.64; **1b** λ_{max} = 364 nm, logε = 4.19; **1c** λ_{max} = 390 nm, logε = 4.24, Fig. 1). We have not observed any absorption bands with $\lambda_{max} > 400$ nm even at very high substrate concentrations (up to 0.01 M).

While thermal decomposition of cyclopropenones **1a–c** requires temperatures in excess of 150 °C, the 350 nm irradiation of these compounds in methanol results in efficient decarbonylation and the quantitative formation of the corresponding acetylene (**2a–c**, Table 1, Scheme 1).

Two-photon induced decarbonylation of cyclopropenones (**1a–c**). The irradiation of **1a–c** in methanol with 800 nm ultrashort (*ca.* 95 fs) pulses from a Ti:sapphire laser results in the same process as the UV photolysis, *i.e.*, the loss of carbon monoxide and the formation of the corresponding acetylenes **2a–c**. The progress of this photoreaction was monitored by the formation of **2a–c** using HPLC (Fig. 2, Table S1).[12]



Scheme 1

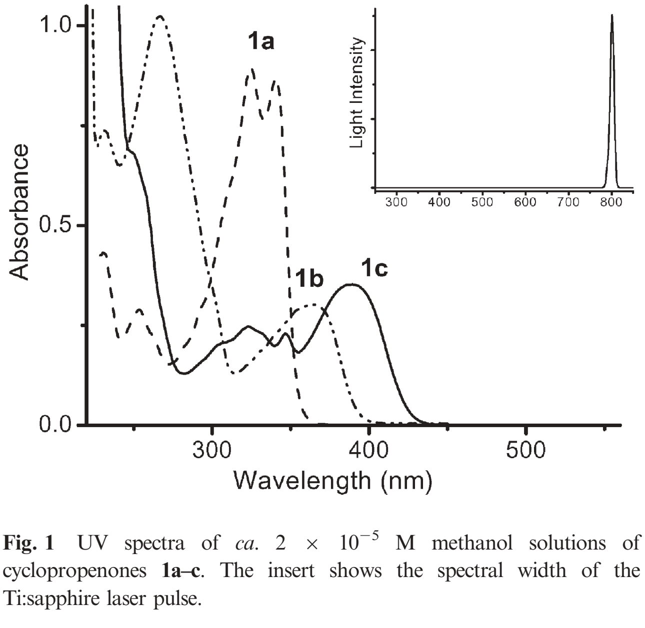


Fig. 1 UV spectra of *ca.* 2×10^{-5} M methanol solutions of cyclopropenones **1a–c**. The insert shows the spectral width of the Ti:sapphire laser pulse.

Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio, USA 43403. E-mail: vpopik@bgnet.bgsu.edu; Fax: +1 (419) 372-9809; Tel: +1 (419) 372-2470

† Electronic supplementary information (ESI) available: Derivation of eqn (1) and experimental details for 2PE and SPA photolyses. See DOI: 10.1039/b513248g

Table 1 Single- and two-photon photochemical properties of cyclopropenones **1a–c**

	Φ	$\sigma_{R(800)}$ (GM)[a]	$\sigma_{2PE(800)}$ (GM)[a]	ε_{400} (M^{-1} cm^{-1})
1a	0.26 ± 0.04[b]	0.0020 ± 0.0005 0.0019 ± 0.0004[c]	0.0077	4.6
1b	0.50 ± 0.01[b]	0.00796 ± 0.00007 0.0078 ± 0.0001[c]	0.016	292
1c	0.47 ± 0.06[b] 0.46 ± 0.06[d] 0.31 ± 0.04[e]	0.20 ± 0.04 0.18 ± 0.04[c] 0.17 ± 0.01[f]	0.42	14 550

[a] 1 GM = 10^{-50} cm^4 s $photon^{-1}$ $molecule^{-1}$. [b] At 350 nm. [c] Calculated from initial rates using zero-order approximation. [d] At 300 nm. [e] At 254 nm. [f] Calculated from the consumption of **1c**.

The spectral width of the Ti:sapphire laser used in this work is represented as an insert in Fig. 1. Evidently, there is no spectral overlap between the irradiation source and substrates **1a–c**, which is required for single-photon excitation. The conversion of the starting material by the two-photon induced photoreaction can be described by the equation [eqn (1)], which, in turn, has been derived from the differential form of Beer's law for the two-photon absorption.[13] In eqn (1) I^2 is the squared light flux ($photons^2$ cm^{-4} s^{-2}), which is integrated for the duration of the laser pulse, v represents the repetition rate, σ is the two-photon cross-section of the substrate (cm^4 s $photon^{-1}$ $molecule^{-1}$), Φ_{2PE} is the fraction of two-photon excited molecules that undergo chemical transformation, and C is the concentration of the substrate.

$$-\frac{dC}{dt} = \Phi_{2PE}\sigma \int_{pulse} I_0^2 dt \cdot v \cdot C \qquad (1)$$

Integration of equation [eqn (1)], the application of the 94 fs laser pulse width,[12] and the conversion to molar concentrations result in a kinetic equation [eqn (2)]. σ_R is the two-photon cross-section for the induction of the photodecarbonylation reaction and is a product of quantum efficiency and the two-photon absorption cross-section of the substrate, $\sigma_R = \Phi_{2PE}{*}\sigma$.

$$C = C_0 \cdot \exp\left(-\sigma_R \cdot \int_{-100\,fs}^{100\,fs} I_0^2 dt \cdot v \cdot t\right) \qquad (2)$$

$$\frac{\Delta C}{C_0} = -\sigma_R \cdot \int_{-100\,fs}^{100\,fs} I_0^2 dt \cdot v \cdot t \qquad (3)$$

Least-squares fitting of the experimental data to the equation [eqn (2)] allowed us to calculate values of σ_R (Fig. 2, Table 1). The two-photon induced decarbonylation of bis(2-methoxy-1-naphthyl)cyclopropenone (**1c**) was quite efficient and allowed us to calculate σ_R not only from the rate of product formation but also from the kinetic data on the consumption of **1c** (insert in Fig. 2). In addition to the use of the exponential equation [eqn (2)], we have applied a zero-order kinetic equation [eqn (3)] to calculate the two-photon cross-section for the induction of the decarbonylation reaction using data in the region of low conversion (Table 1). Values produced by all three calculations are in a very good agreement.

In order to verify that an observed reaction is, in fact, a two-photon process, we have analyzed the expected quadratic dependence of the rate of product formation on the light flux. Cyclopropenones **1b** and **1c** were irradiated for 25 min and 8 min correspondingly with laser pulses of variable energy.[14] Yields of acetylenes **2b** and **2c**, which were produced under these conditions, show quadratic dependence on laser power (Fig. 3, Table S2).[12]

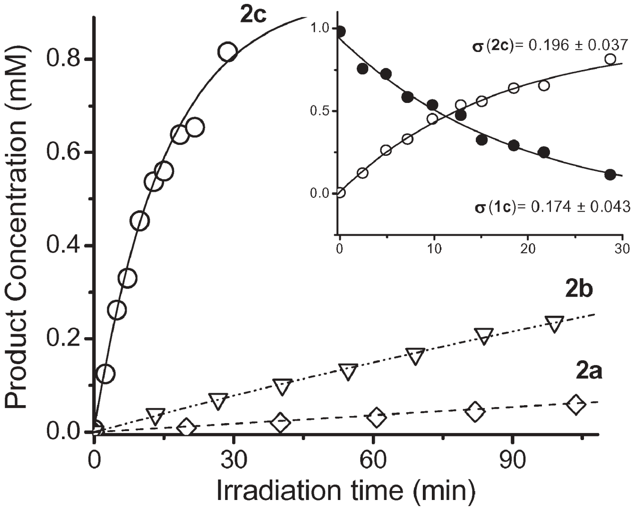


Fig. 2 Yields of acetylene **2a** (◇), **2b** (▽), and **2c** (○) formed in the two-photon induced decarbonylation of 1 mM methanol solutions of cyclopropenones **1a–c**. Lines shown were drawn using parameters obtained by least-squares fitting of eqn (2). The consumption of **1c** (●) and the formation of **2c** (○) are overlaid on the insert.

The logarithmic representations of the yield *versus* pulse energy dependences have slopes of 2.07 (**1b**) and 2.02 (**1c**), confirming the two-photon nature of the observed photodecarbonylation reaction.

To convert experimentally-determined two-photon cross-sections for the induction of the photodecarbonylation reactions, σ_R, into the two-photon absorption cross-sections of cyclopropenones **1a–c**, we need to know the fraction of two-photon excited molecules that undergo decarbonylation, Φ_{2PE}. The excited state initially populated upon two-photon excitation might be different from that initially populated upon single-photon excitation. However, according to Kasha's rule, photochemical reactions generally occur from the lowest singlet or triplet excited states

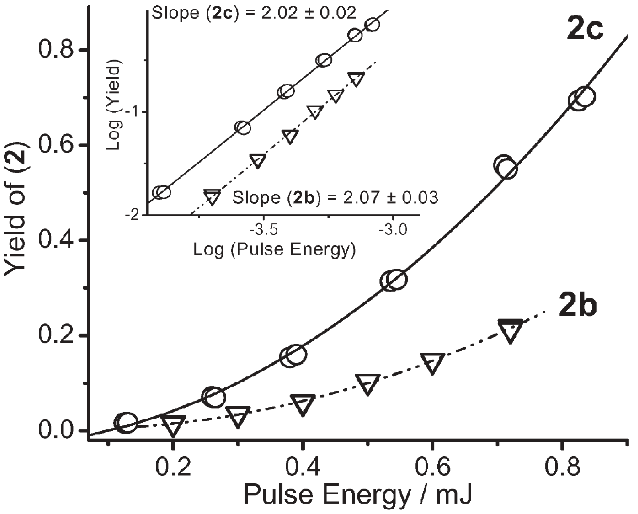


Fig. 3 Yield of acetylenes **2b** and **2c** formed on variable power 800 nm laser irradiation of cyclopropenones **1b** and **1c**.

regardless of the excitation method and the initial exited state.[15] Thus, we can assume that the quantum yield of the two-photon initiated process is equal to its single-photon counterpart, $\Phi_{2PE} = \Phi_{SPE}$. The latter values were determined by chemical actinometry at 350 nm (Table 1). To check the validity of Kasha's rule for excitation of cyclopropenones, we also measured the quantum yield for the decarbonylation reaction of **1c** at 254 nm and 300 nm, which showed very little variation from the 350 nm values (Table 1). The two-photon absorption cross-sections of cyclopropenones **1a–c** at 800 nm were calculated using single-photon quantum yields, $\sigma_{2PE(800)} = \sigma_{R(800)}/\Phi_{SPE}$, and are shown in Table 1.

The design of symmetric two-photon absorbing chromophores is usually based on the donor–π–acceptor–π–donor motif, where –π– is an extended conjugated π-system.[16] The very small two-photon cross-section of bis-*p*-anisylcyclopropenone (**1a**) is, therefore, not surprising since the π-system of this molecule is rather small (total area of a π-conjugated system is 305 $Å^2$). However, extension of the conjugation by the *p*-phenylene unit on both sides of the cyclopropenone in **1b** (area = 463 $Å^2$) does not bring much gain in the two-photon cross-section. The somewhat smaller bis(2-methoxy-1-naphthyl)cyclopropenone **1c** (area = 390 $Å^2$), on the other hand, shows a twenty six times larger two-photon absorption cross-section than **1b**. A much better correlation is observed between the two-photon absorption cross-sections and the extinction coefficients at 400 nm (Table 1). The fact that cyclopropenones **1a** and **1b** have very low absorption at 400 nm indicates that the energy of two 800 nm photons is insufficient to achieve excitation to the lowest SPE-accessible excited state. Apparently, there are no other lower lying states, which can be populated by 800 nm two-photon excitation.

In summary, we have shown the feasibility of the two-photon induced decarbonylation of cyclopropenones, which produces quantitative yields of the corresponding acetylenes. The two-photon absorption cross-sections of cyclopropenones **1a–c** were determined by the direct method based on the conversion of the substrate under irradiation with ultrashort pulses. The development of cyclopropenones with larger two-photon absorption cross-sections, as well as time-resolved investigation of the two-photon induced decarbonylation is underway in our group.

The authors thank the National Institutes of Health (grant CA91856-01A1) and the National Science Foundation (grant CHE-0449478) for the support of this project, as well as the Ohio Laboratory for Kinetic Spectroscopy for the use of instrumentation and technical assistance. A. P. thanks the McMaster Endowment for a research fellowship.

Notes and references

1 L. Agranat, A. Barak and M. P. Pick, *J. Org. Chem.*, 1973, **38**, 3064; C. H. Weidner, D. H. Wadsworth, C. S. Knop, A. I. Oyefesso, B. L. Hafer, R. J. Hartman, R. C. Mehlenbacher and S. C. Hogan, *J. Org. Chem.*, 1994, **59**, 4319; A. Poloukhtine and V. V. Popik, *J. Org. Chem.*, 2003, **68**, 7833.

2 A. Poloukhtine and V. V. Popik, *J. Org. Chem.*, 2005, **70**, 1297; A. Poloukhtine and V. V. Popik, *Chem. Commun.*, 2005, 617.

3 M. Göppert-Mayer, *Ann. Phys. (Leipzig)*, 1931, **9**, 273.

4 J. R. Lakowicz, *Two-Photon And Non-Linear Induced Fluorescence*, Plenum Press, New York, 1991; P. R. Callis, *Annu. Rev. Phys. Chem.*, 1997, **48**, 271; A. Becker, C. Hessenius, K. Licha, B. Ebert, U. Sukowski, W. Semmler, B. Wiedenmann and C. Grötzinger, *Nat. Biotechnol.*, 2001, **19**, 327.

5 M. Rubat, *Circ. Res.*, 2004, **95**, 1154; K. König, *J. Microsc. (Oxford)*, 2000, **200**, 2; R. Weissleder, *Nat. Biotechnol.*, 2001, **19**, 316.

6 H. B. Cumpston, S. P. Ananthadvel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I.-Y. S. Lee, D. Mcord-Maughon, J. Qin, H. Rockel, M. Rumi, X.-L. Wu, S. R. Marder and J. W. Perry, *Nature*, 1999, **398**, 51; S. Kawata and H.-B. Sun, *J. Photopolym. Sci. Technol.*, 2002, **15**, 471; K. D. Belfield and K. J. Schafer, *Chem. Mater.*, 2002, **9**, 3656.

7 S. Yao and K. D. Belfield, *J. Org. Chem.*, 2005, **70**, 5156; W. J. Yang, D. Y. Kim, M.-Y. Jeong, H. M. Kim, Y. K. Lee, X. Fang and S.-J. Jeon, *Chem.–Eur. J.*, 2005, **11**, 4198; M. Drobizhev, Y. Stepanenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Taylor and H. L. Anderson, *J. Am. Chem. Soc.*, 2004, **126**, 15352; S. J. K. Pond, O. Tsutsumi, M. Rumi, O. Kwon, E. Zojer, J.-L. Bredas, S. R. Marder and J. W. Perry, *J. Am. Chem. Soc.*, 2004, **126**, 9291; L. Beverina, J. Fu, A. Leclercq, E. Zojer, P. Pacher, S. Barlow, E. W. Van Stryland, D. J. Hagan, J.-L. Bredas and S. R. Marder, *J. Am. Chem. Soc.*, 2005, **127**, 7282.

8 K. D. Belfield, *Spectrum (Bowling Green, OH, U. S.)*, 2001, **14**, 1.

9 H.-C. Kim, S. Kreiling, A. Greiner and N. Hampp, *Chem. Phys. Lett.*, 2003, **372**, 899; K. D. Belfield, M. V. Bondar, Y. Liu and O. V. Przhonska, *J. Phys. Org. Chem.*, 2003, **16**, 69; A. S. Dvornikov, H. Bouas-Laurent, J.-P. Desvergne and P. M. Rentzepis, *J. Mater. Chem.*, 1999, **9**, 1081.

10 J. Dyer, S. Jockusch, V. Balsanek, D. Sames and N. J. Turro, *J. Org. Chem.*, 2005, **70**, 2143; A. P. Goodwin, J. L. Mynar, Y. Ma, G. R. Fleming and J. M. J. Frechet, *J. Am. Chem. Soc.*, 2005, **127**, 9952; N. K. Urdabayev and V. V. Popik, *J. Am. Chem. Soc.*, 2004, **126**, 4058.

11 V. Nikolenko, R. Yuste, L. Zayat, L. M. Baraldo and R. Etchenique, *Chem. Commun.*, 2005, 1752; O. D. Fedoryak, J.-Y. Sul, P. G. Haydon and G. C. R. Ellis-Davies, *Chem. Commun.*, 2005, 3664; Y. R. Zhao, Q. Zheng, K. Dankin, K. Xu, M. L. Martinez and W.-H. Li, *J. Am. Chem. Soc.*, 2004, **126**, 4653; M. Lu, O. D. Fedoryak, B. R. Moister and T. M. Dore, *Org. Lett.*, 2003, **5**, 2119; N. I. Kiskin, R. Chillingworth, J. A. McCray, D. Piston and D. Ogden, *Eur. Biophys. J.*, 2002, **30**, 588; T. Furuta, S. S. H. Wang, J. L. Dantzker, T. M. Dore, W. J. Bybee, E. M. Callaway, W. Denk and R. Y. Tsien, *Proc. Natl. Acad. Sci. U. S. A.*, 1999, **96**, 1193; E. B. Brown, J. B. Shear, S. R. Adams, R. Y. Tsien and W. W. Webb, *Biophys. J.*, 1999, **76**, 489; S. R. Adams, V. Lev-Ram and R. Y. Tsien, *Chem. Biol.*, 1997, **4**, 867.

12 See ESI†.

13 D. M. Friedrich, *J. Chem. Educ.*, 1982, **58**, 472.

14 The laser power output was attenuated using glass filters to achieve the intensity of the laser pulses in the range from 125 to 835 μJ pulse^{-1}.

15 N. J. Turro, *Modern Molecular Photochemistry*, University Science Books, Sausalito, 1991.

16 M. Rumi, J. E. Ehrlich, A. A. Heikal, J. W. Perry, S. Barlow, Z. Hu, D. McCord-Maughon, T. C. Parker, H. Rockel, S. Thayumanavan, S. R. Marder, D. Beljonne and J.-L. Bredas, *J. Am. Chem. Soc.*, 2000, **122**, 9500; S. J. K. Pond, M. Rumi, M. D. Levin, T. C. Parker, D. Beljonne, M. W. Day, J.-L. Bredas, S. R. Marder and J. W. Perry, *J. Phys. Chem. A*, 2002, **106**, 11470.