

Wolff Rearrangement of 2-Diazo-1(2*H*)-Naphthalenone Induced by Nonresonant Two-Photon Absorption of NIR Radiation

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The irradiation of α -diazoketones usually results in the Wolff Rearrangement and formation of ketenes.¹ The latter, in turn, reacts with nucleophiles to produce carboxylic acids or derivatives.² The most important industrial application of the Wolff rearrangement is found in photolithography, a process used in the production of electronic microchips and integrated circuit boards. The photoactive components of common Novolac-based positive photoresists are derivatives of 2-diazo-1(2*H*)-naphthalenone (2-diazo-1,2-naphthoquinone, **1**).³ The photodecomposition of **1** in the presence of water ultimately results in the formation of 1*H*-indene-3-carboxylic acid,^{3,4} which makes exposed areas of the resist soluble in the aqueous base.

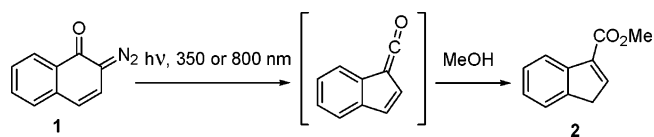
The Wolff Rearrangement of α -diazocarbonyl compounds is usually induced by UV radiation. The same excitation energy can be achieved by simultaneous absorbance of two red/NIR photons, a process that can take place at very high light fluxes.⁵ In recent years, ultrafast pulsed lasers capable of producing required light intensity became commercially available. This resulted in the development of many successful applications of nonresonant two-photon excitation (2PE) in fluorescent spectroscopy,⁶ microscopy,⁷ and photonics.⁸ The field of two-photon photochemistry⁹ remains relatively unexplored. There are few examples of cycloaddition and cycloreversion reactions¹⁰ or the uncaging of bioactive molecules¹¹ using 2PE.

This communication describes for the first time the two-photon induced Wolff rearrangement of 2-diazo-1,2-naphthoquinone (**1**).

Single-Photon Photochemistry of 1. The UV spectrum of the diazonaphthoquinone (**1**) in methanol shows a strong absorbance at 263 nm ($\log \epsilon = 4.56$) and a weaker band at 398 nm ($\log \epsilon = 3.92$), while the longest wavelength absorbance of methyl 1*H*-indene-3-carboxylate (**2**) is at 265 nm (Figure 1).

The 254, 300, and 350 nm irradiation of **1** in methanol results in the formation of methyl 1*H*-indene-3-carboxylate (**2**, Scheme 1), which was found to be identical to the independently prepared sample. It is interesting to note that the photolysis of **1** in an aqueous solution results in the formation of both isomeric acids, i.e., 1*H*-indene-1- and -3-carboxylic acids.¹² The former then undergoes a rearrangement into the more stable isomer. In our case, we observed the formation of only isomer **2**.

Scheme 1



The quantum yield of the photo-Wolff reaction of **1** in methanol is $\Phi_{254} = 0.33 \pm 0.04$ at 254 nm and decreases at longer wavelengths ($\Phi_{300} = 0.23 \pm 0.03$, $\Phi_{350} = 0.17 \pm 0.02$). A similar trend was reported for the photolysis of **1** in different solvents.¹³

Two-Photon-Induced Wolff Rearrangement of 2-Diazo-1,2-naphthoquinone (1). The irradiation of **1** in methanol with 800

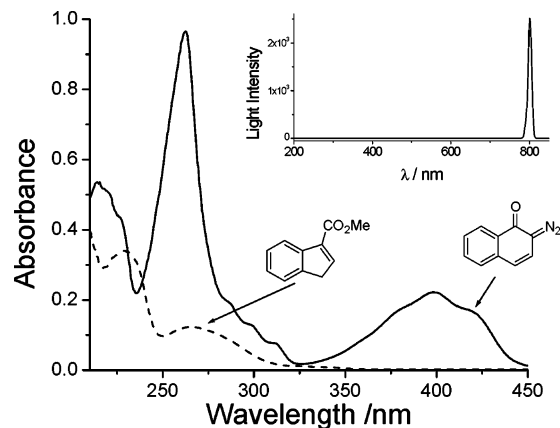


Figure 1. UV spectra of ca. 3×10^{-5} M methanol solutions of diazonaphthoquinone (**1**, solid line) and methyl 3-indenecarboxylate (**2**, dotted line). The insert shows the spectral width of the Ti:Sapphire laser pulse.

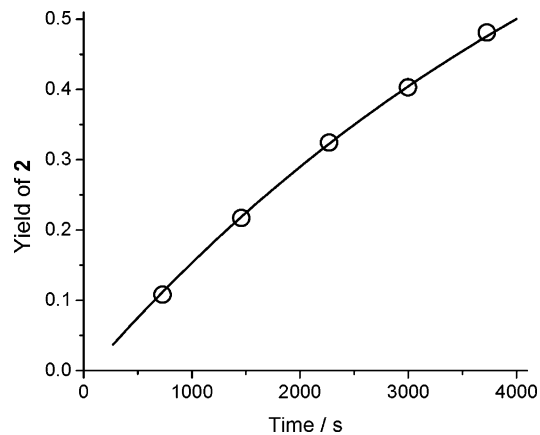


Figure 2. Yield of methyl 1*H*-Indene-3-carboxylate (**2**) formed in two-photon-induced Wolff rearrangement of 2-diazo-1,2-naphthoquinone (**1**). The line shown was drawn using parameters obtained by least-squares fitting of equation 4.

nm pulses from a Ti:Sapphire laser results in the same process as the UV photolysis, i.e., Wolff rearrangement. The progress of the photoreaction was monitored by the formation of methyl 3-indene-carboxylate (**2**, Figure 2, Table S1¹⁴ in Supporting Information).

The spectral width of the Ti:Sapphire laser used in this work is represented in the insert in Figure 1. Evidently, there is no spectral overlap between the irradiation source and the substrate **1**, which is required for single-photon excitation (SPE). The conversion of the starting material under two-photon-induced photoreaction can be discussed in terms of Beer's law for the two-photon absorbance, the differential form of which is represented by eq 1.1.¹⁵ I in eq 1.1 is the light flux (photons $\text{cm}^{-2} \text{s}^{-1}$), σ is a two-photon cross-section ($\text{cm}^4 \text{s photon}^{-1} \text{molecule}^{-1}$), N is the concentration of the substrate (molecules cm^{-3}), and x is the thickness of the sample (in cm).

$$-dI = 2\sigma I_0^2 N dx \quad (1.1)$$

$$-\Delta I = 2\sigma I_0^2 N x \quad (1.2)$$

As light intensity virtually does not change when passing through the sample due to the very low probability of two-photon absorption, we can rewrite eq 1.1 in a simplified form (eq 1.2), where ΔI represents the light flux absorbed by the sample.

The rate of photoreaction is equal to the absorbed light flux abated by the quantum yield of the reaction under 2PE conditions (Φ_{2PE}). The former is proportional to the squared light intensity (eq 2). The coefficient 1/2 in equation 2 reflects the two-photon nature of the process.

$$-\frac{dN}{dt} = \frac{1}{2} \frac{\Phi_{2PE} \Delta I}{x} = \Phi_{2PE} \sigma I_0^2 N \quad (2)$$

The pulsed source of irradiation should be taken into account and equation 2 is converted into 3, where squared light intensity is integrated for the duration of the laser pulse and ν represents repetition rate:

$$-\frac{dN}{dt} = \Phi_{2PE} \sigma \int_{\text{pulse}} I_0^2 dt \cdot \nu \cdot N \quad (3)$$

$$\frac{N}{N_0} = \exp\left[-\sigma_{WR} \cdot \int_{-100\text{fs}}^{100\text{fs}} I_0^2 dt \cdot \nu \cdot t\right] \quad (4)$$

Integration of eq 3 and the application of the 94 fs laser pulse width¹⁴ results in kinetic eq 4, where σ_{WR} is a two-photon cross-section for the induction of the Wolff reaction and is a product of quantum efficiency and the cross-section for the two-photon absorbance by the substrate, $\sigma_{WR} = \Phi_{2PE} \sigma$. Least-squares fitting of the experimental data represented in Figure 2 to eq 4 gives $\sigma_{WR} = (1.73 \pm 0.02)10^{-52} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ or $0.0173 \pm 0.0002 \text{ GM}^6$.

To verify that a two-photon reaction is observed, the expected quadratic dependence of the rate of methyl 3-indenecarboxylate formation on the irradiation power was analyzed. The yield of ester 2 formed in 970 s irradiation of 1 with laser pulses of variable energy is displayed in Figure 3 (Table S2 in Supporting Information).¹⁴ The laser power output was attenuated using glass filters to achieve the intensity of the laser pulses in the range from 245 to 939 $\mu\text{J pulse}^{-1}$.

Figure 3 illustrates the observed nonlinear dependence of the rate of photo-Wolff reaction on the pulse energy. The logarithmic representation of this dependence has a slope of 1.97 (inset in Figure 3), confirming the two-photon nature of the observed photochem-

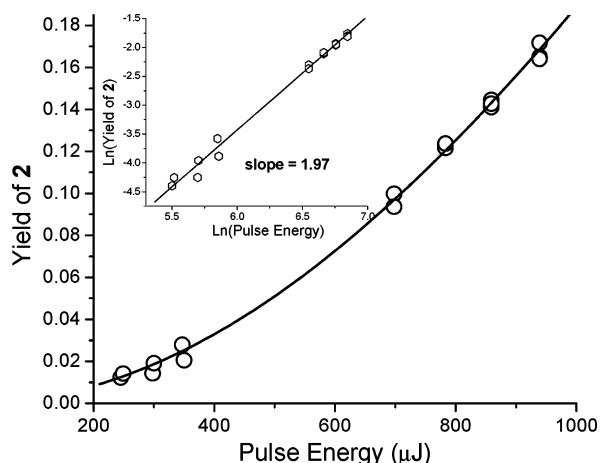


Figure 3. Variable-power photolysis of 1. The line shown was drawn using parameters obtained by least-squares fitting of eq 4.



Figure 4. Two-photon photolithography (800 nm) using Novolac-diazonaphthoquinone-based photoresist. The size of the image is $3 \times 2 \text{ mm}$.

istry. Least-squares fitting of the variable-power experimental data (Figure 3) to eq 4 gives $\sigma_{WR} = (1.667 \pm 0.011)10^{-52} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$, which is very close to the value obtained in variable-time of irradiation experiment.

The cross-section for the two-photon photo-Wolff reaction of 1 is a product of the two-photon absorption cross-section of 1 at 800 nm and the quantum yield of the photoreaction, $\sigma_{WR} = \sigma_{800} \Phi_{2PE}$. Photochemical reactions generally occur from the lowest singlet or triplet excited states regardless of the excitation wavelength. Thus, we can assume that $\Phi_{800} = \Phi_{400}$. The latter can be extrapolated from the SPE wavelength-quantum yield dependence¹⁴ to give $\Phi_{400} = 0.080$. The two-photon absorption cross-section of 1 at 800 nm is calculated to be $\sigma = (2.16 \pm 0.03)10^{-51} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$. The time-resolved investigation of the SPE- and 2PE-induced ketene formation is underway in our group.

To test the feasibility of two-photon photolithography we conducted 800 nm pulsed irradiation of the circuit board laminated with a diazonaphthoquinone-based photoresist through a chromium-coated glass mask. Conventional development in an aqueous base allowed us to pattern the image shown in Figure 4.

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Supporting Information Available: Experimental details on 2PE and SPA photolyses (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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