J. Am. Chem. Soc. **1996,** *118,* 1551−1552

Direct Observation of a Photoinduced Wolff Rearrangement in PMMA Using Ultrafast Infrared Spectroscopy

Thomas Lippert, Aaron Koskelo, and Page O. Stoutland*

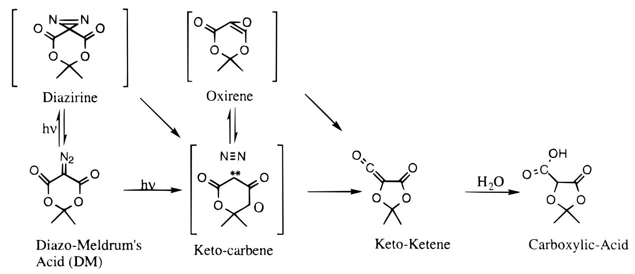
Division of Chemical Science and Technology
Mail Stop J-567, Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Received October 30, 1995

One of the most technologically important uses of organic photochemistry is in the imaging industry, where radiation-sensitive organic monomers and polymers are used in photoresists.[1] Common examples include systems in which photochemically formed acids become soluble in aqueous base (i.e., positive photoresists)[2] and where organic dopants sensitize a polymer toward ablation.[3] The chemistry which occurs in these systems is the basis for the manufacture of high-density electronic circuits, as well as for the production of printing plates.

One of the most widely used classes of compounds for imaging applications is diazoketones.[4] These compounds undergo a photoinduced Wolff[5] rearrangement to form a ketene intermediate, which subsequently hydrolyzes to a base-soluble carboxylic acid.[6] As part of a program to develop diagnostics for laser-driven reactions in polymer matrices,[7] we have investigated the photoinduced decomposition of 5-diazo-2,2-dimethyl-1,3-dioxane-4,6-dione (5-diazo Meldrum's acid, DM) in a PMMA matrix. This particular diazoketone is sensitive to deep UV (200−260 nm), making it suitable for high-resolution lithographic applications.[8] It has historically been difficult to study the chemistry of such resists as many of the intermediates are short-lived and absorb only in the UV. Recent advances in ultrafast infrared spectroscopy, however, now allow us to directly examine the initial steps occurring in UV photoresists with infrared spectroscopy. Herein, we describe the first room temperature observation of intermediates in the photochemistry of DM with ultrafast infrared spectroscopy.

Scheme 1



Shown in Scheme 1 is the generally accepted mechanism for the photodecomposition of diazo Meldrum's acid.[9] It is widely believed that the initial event is the loss of nitrogen and formation of a keto ketene, most likely through a short-lived carbene intermediate. This keto ketene is hydrolyzed by water present in the polymeric matrix to form a ketenehydrate[10] and finally a carboxylic acid. Various other intermediates have also been discussed. For example, it has been reported that isomerization to a diazirine may take place,[11] and that an oxirene[12] may also be present. For resist applications the key species is the carboxylic acid which results in the resist being base soluble.

For ablation applications, the ketene of DM (and its rate of formation and lifetime) is important as it has been reported to be involved in a multiple photon cyclic absorption process leading to heating and ultimately ablation.[9] Room temperature transient experiments have suggested that the keto ketene forms within 200 ns,[13] and is hydrolyzed on a ms to seconds time scale. Low-temperature experiments coupled with infrared spectroscopy have also identified the keto ketene intermediate ($\nu_{\text{ketene}} = 2143$ cm^{-1}).[14]

We have examined the photodecompositon of DM in a PMMA matrix[15] with picosecond infrared spectroscopy. The general experimental procedure has been described previously.[16] Briefly, our infrared probe pulse, tunable from 2900 to 1800 cm^{-1}, is generated by difference frequency mixing of a tunable amplified dye laser pulse (ca. 600 nm, 5 ps) with the doubled 532 nm output of a regenerative YAG amplifier. Our excitation pulse is the frequency-quadrupled output (266 nm, 60 ps) of the regenerative amplifier. Using conventional deconvolution techniques, we can typically resolve 20 ps events. Time resolution is obtained by optical delay and is variable from 0 to 6 ns. Samples consist of ∼3 μm thick coatings of PMMA

---

[1] (a) Bowden, M. J. *Materials for Microlithography*; Thompson, L. F., Willson, C. G., Frechet, J. M. J., Eds.; ACS Symposium Series 266; American Chemical Society: Washington, DC, 1984; 39. (b) Reichmanis, E.; Wilkins, C. W. *Microelectronic Polymers*; Htoo, M. S., Ed.; Marcel Dekker Inc.: New York, 1989; 1. (c) Soane, D. S.; Martynenko, Z. *Polymers in Microelectronics*; Elsevier: Amsterdam, 1989.

[2] (a) Pacansky, J.; Johnson, D. J. *J. Electrochem. Soc.* **1977**, *124*, 862. (b) Pacansky, J.; Lyerla, J. *IBM J. Res. Dev.* **1979**, *23*, 42. (c) Pacansky, J. *Polym. Eng. Sci.* **1980**, *20*, 1049.

[3] See, for example: (a) Lippert, T.; Stebani, J.; Ihlemann, J.; Nuyken, O.; Wokaun, A. *Angew. Makromol. Chem.* **1993**, *213*, 127. (b) Hiraoka, H.; Lazare, S. *Appl. Surf. Sci.* **1990**, *46*, 342. (c) Fukumura, H.; Mibuka, S.; Eura, S.; Masuhara, H.; Nishi, N. *J. Phys. Chem.* **1993**, *97*, 13761. (d) Srinivasan, R.; Braren, B. *Appl. Phys.* **1988**, *A45*, 289. (e) Davis, C. R.; Egitto, F. D.; Buchwalter, S. L. *Appl. Phys.* **1992**, *B54*, 227. (f) Kawamura, Y.; Toyoda, K.; Namba, S. *Appl. Phys. Lett.* **1982**, *40*, 374.

[4] Widely used in this regard are a variety of diazonaphthoquinones in Novalak resins, including the commercially available naphthoquinone diazides (Shipley-AZ1350J, Kodak-Photoresist 820, Hunt-HPR 204). See: Rabek, J. F. *Mechanism of Photophysical Processes and Photochemical Reactions in Polymers*; John Wiley & Sons: New York, 1987; p 446.

[5] Wolff rearrangements are widely used for various synthetic applications. See, for example: (a) Redmore, D.; Gutsche, C. D. *Adv. Alicyclic Chem.* **1971**, *3*, 125. (b) March, J. *Advanced Organic Chemistry*; McGraw-Hill: New York, 1985; p 974.

[6] (a) Delaire, J. A.; Faure, J.; Hassine-Renou, F.; Soreau, M.; Mayeaux, A. *Nouv. J. Chim.* **1987**, *11*, 15. (b) Vleggaar, J. J. M.; Huizer, A. H.; Kraakman, P. A.; Nijssen, W. P. M.; Visser, R. J.; Varma, C. A. G. O. *J. Am. Chem. Soc.* **1994**, *116*, 11754. (c) Tanigaki, K.; Ebbesen, T. W. *J. Phys. Chem.* **1989**, *93*, 4531.

[7] A key component of our program is to study reactions directly in the polymer matrix. In the case of diazoketones in particular, the reactivity can be completely different in solution. For example, in methanol the product after N$_2$ loss is Meldrum's acid: Hayashi, I.; Okada, T.; Kawanishi, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2506.

[8] (a) Willson, C. G.; Clecak, N. J.; Grant, B. D.; Twieg, R. J. *Electrochem. Soc. Prepr.* **1980**, 696. (b) Grant, B. D.; Clecak, N. J.; Twieg, R. J.; Willson, C. G. *IEEE Trans. Electron Devices* **1981**, *28*, 1300. (c) Willson, C. G.; Miller, R. D.; McKean, D. R.; Pederson, L. A.; Regitz, M. *Advances in Resist Technology and Processing IV*; Proceedings of SPIE 771; SPIE: Bellingham, WA, 1987; pp 2−10.

[9] Fujiwara, H.; Nakajima, Y.; Fukumura, H.; Masuhara, H. *J. Phys. Chem.* **1995**, *99*, 11481.

[10] (a) Andraos, J.; Chiang, Y.; Huang, C.-G.; Kresge A. J. Scaiano, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 10605. (b) Barra, M.; Fisher, T. A.; Cernigliaro, G. J.; Sinta, R.; Scaiano, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 2630.

[11] (a) Nikolaev, V. A.; Khimich, N. N. *Khim. Geterotsikl. Soedin.* **1985**, 321. (b) Livinghouse, T.; Stevens, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 6479. (c) Voigt, E.; Meier, H. *Chem. Ber.* **1975**, *108*, 3326.

[12] (a) Reference 6c. (b) Tanigaki, K.; Ebbesen, T. W. *J. Am. Chem. Soc.* **1987**, *109*, 5583. (c) Bouma, W. J.; Nobes, R. H.; Radom, L.; Woodward, C. E. *J. Org. Chem.* **1982**, *47*, 1869. (d) Tanaka, K.; Yoshimine, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 7655.

[13] Winnik, M. A.; Wang, F.; Nivaggioi, T.; Hruska, Z.; Fukumura, H.; Masuhara, H. *J. Am. Chem. Soc.* **1991**, *113*, 9702.

[14] Ulbricht, M.; Thurner, J.-U.; Siegmund, M.; Tomaschewski, G. *Z. Chem.* **1988**, *28*, 102.

[15] Commercial photoresists typically use Novolak resin as the polymer matrix. Here, we have choosen PMMA to avoid having the matrix absorb some of the UV excitation pulse. Later studies will examine the effect of different matrices.

[16]) (a) Doorn, S. K.; Dyer, R. B.; Stoutland, P. O.; Woodruff, W. H. *J. Am. Chem. Soc.* **1993**, *115*, 6398. (b) Stoutland, P. O.; Dyer, R. B.; Woodruff, W. H. *Science* **1992**, *257*, 1913.

0002-7863/96/1518-1551$12.00/0

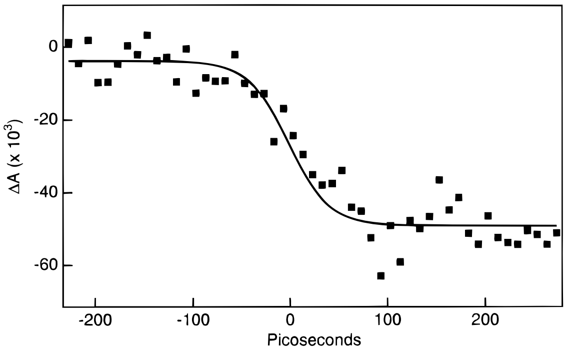


Figure 1. Change of absorbance as a function of time from −200 to 300 ps at 2190 cm^{-1}. The solid line is the instrument response.

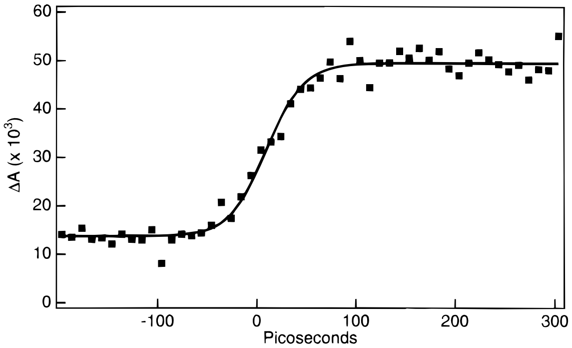


Figure 2. Change of absorbance as a function of time from −200 to 300 ps at 2150 cm^{-1}. The solid line is the instrument response. The small offset before the zero of time is due to a small pre(pump) pulse which is 7 ns before the primary pump pulse. Its presence does not affect the results in this case.

(Aldrich, $M_w = 120\,000$) doped with DM (TCI America, ca. 20% by weight) on polypropylene sheets.[17] The sheets are held taut with a metal frame and are translated with a computer-controlled stepper motor such that each location on the film is subjected to only a single laser shot. Both pump on and pump off data are taken which allow us to convert our data into ΔA units.

The change of the IR absorbance was monitored in the diazo/ketene region from 2120 to 2210 cm^{-1} at intervals of 10 cm^{-1}. Maximum changes in absorption occurred at 2190 cm^{-1}, where a decrease in absorbance was observed, and at 2150 cm^{-1}, where an increase in absorbance was observed. We assign the 2190 cm^{-1} change to the bleaching of the diazo Meldrum's acid and the 2150 cm^{-1} change to the appearance of the keto ketene intermediate.[18] The decrease in absorbance at 2190 cm^{-1} occurs within our instrument response and is constant for 6 ns as expected for the photodissociation (Figure 1). Similarly, the rise time of the 2150 cm^{-1} feature we assign to the keto ketene can also be described by our instrument response. Using deconvolution techniques we assign an upper limit on the appearance of the keto ketene of $\tau < 20$ ps (Figure 2); no change was seen out to 6 ns. The energy dependence of the signal intensities was linear, consistent with a single photon event. This was true both above and below the ablation threshold, suggesting that ablation is not important on this time scale. The quantum yield of decomposition was 0.8 ± 0.2.[20] In Figure 3 is shown the difference spectrum observed at 300−500 ps, generated by averaging the 300−500 ps data in each of the kinetic traces. As the bands due to the starting diazo compound and the keto ketene overlap significantly, we have fitted the difference spectrum to the difference of the DM infrared spectrum and a Gaussian function representing the keto ketene. The best fit yields a spectrum for the keto ketene centered at 2161 cm^{-1} and with a width (fwhm) of 29 cm^{-1}. Deviation from the experimental data at some wavelengths suggests that the spectrum is more complex than a single Gaussian as expected for dopants dispersed in polymeric matrices.[19]

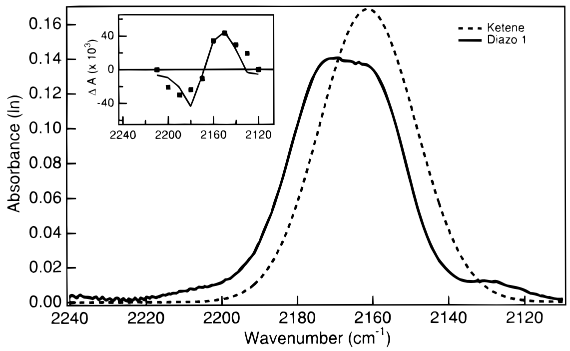


Figure 3. Spectra of DM (solid line) and the keto ketene (dashed line) at 300−500 ps calculated by fitting the difference spectrum (inset) to the difference of the DM spectra and a Gaussian function which best represents the ketene spectrum. The fit which results from the difference of the two spectra is shown in the inset.

The result that the keto ketene appears within 20 ps is significant in that a previous measurement was only able to determine that it appeared within 200 ns.[13] The observed rate is consistent with ultrafast absorption measurements by Vleggaar et al.,[6b] who found in the photofragmentation of the similar 2-diazonaphthoquinones that formation of the keto ketene in solution was complete within 8 ps, and with recent results of Wang et al.,[21] which show that Wolff rearrangements are accelerated for cyclic α-diazo ketones. Calculations suggest that the carbene or oxirene intermediates should also have low barriers to ketene formation.[22]

In summary, these experiments have provided the first example of how ultrafast infrared spectroscopy may be used to examine laser-driven reactions in polymeric matrices. We have determined that the photoinduced Wolff rearrangement of DM in a PMMA matrix is complete within 20 ps. The IR band assignable to the ketene is centered at 2161 cm^{-1} and has a width of 29 cm^{-1}. The rapid formation of the ketene is a key element of the high quantum yield of carboxylic acid formation and a key element as well for the use of DM as an ablation sensitizer. Future experiments will center on extending our wavelength range so that we may observe the ketone moieties, and hopefully the ketocarbene itself, and on examining the effect of different matrices. Finally, we will be extending our measurements to examine a variety of other processes (e.g., ablation, curing, etc.) for which detailed structural information on ultrafast timescales has technological importance.

JA9536429

---

(17) A typical film was prepared by dissolving 750 mg of PMMA and 200 mg of DM in 15 mL of THF. This was coated onto a polypropylene sheet (0.5−1.0 mm thick) with a #20 Mayer rod (wet thickness ≈ 50 μm). These were dried in air and stored in the dark. Monitoring the films with UV−vis and IR spectroscopy showed no decomposition over 2 weeks.

(18) Alternative possibilities including an oxirene intermediate or an electronically excited state were discounted. Previous studies have reported oxirenes to have much lower infrared oscillator strengths than we observe (Cársky, P.; Hess, B.A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 396. Torres, M.; Bourdelande, J. L.; Clement, A.; Strausz, O. P. *J. Am. Chem. Soc.* **1983**, *105*, 1698). With respect to the possibility of an electronically excited state, we feel that the infrared band position would be shifted dramatically from the ground state value (the observed shift is ∼10 cm^{-1}, *vide infra*). Additionally, an excited state which showed no decay over 6 ns and then exhibited a quantum yield of near unity for photodissociation would be unprecedented.

(19) In addition, the difference spectrum is minimally affected by a small artifact caused by a temperature-induced shift (ca. 5 cm^{-1}) in the spectrum of the residual ground state DM molecules.

(20) This agrees with the previously reported values of 0.6 and 1.0: refs 9 and 13.

(21) Wang, J.-L.; Toscano, J. P.; Platz, M. S.; Nikolaev, V.; Popik, V. *J. Am. Chem. Soc.* **1995**, *117*, 5477.

(22) (a) Lewars, E. G. *Chem. Rev.* **1983**, *83*, 519. (b) Harding, L. B. *J. Am. Chem. Soc.* **1981**, *103*, 7469. (c) Reference 12d.