

The Ultrafast Wolff Rearrangement in the Gas Phase

Andreas Steinbacher¹, Sebastian Roeding¹, Tobias Brixner¹, and Patrick Nuernberger^{1,2}

¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

²Physikalische Chemie II, Ruhr-Universität Bochum, Universitätsstraße 150, 44780 Bochum, Germany
andreas.steinbacher@phys-chemie.uni-wuerzburg.de

Abstract: The sub-picosecond Wolff rearrangement of gas-phase 5-diazo Meldrum's acid is disclosed with femtosecond ion spectroscopy. Distinct differences are found for 267 nm and 200 nm excitation, the latter leading to even two ultrafast rearrangement reactions.

OCIS codes: (300.6530) Spectroscopy, ultrafast; (260.5210) Photoionization; (320.7150) Ultrafast spectroscopy

1. Introduction

5-diazo Meldrum's acid (DMA), like other α -diazo carbonyls, can undergo a Wolff rearrangement (WR) reaction to form a ketene, the exact mechanism – stepwise or concerted – still being vividly discussed. While quantum-dynamical studies for similar compounds suggest a predominant stepwise mechanism [1], pyrolysis [2] and liquid-phase studies [3] of DMA could not infer the ultrafast timescale of the initial process because of a lack of time resolution or solvent effects, respectively. In order to determine how fast a WR can actually proceed, we investigate gas-phase DMA with femtosecond (fs) pump-probe photofragment ion spectroscopy. Besides corroborating the theoretically predicted stepwise reaction scheme, we elucidate the crucial role of excess energy introduced to the molecule by exciting not only with 267 nm but also with 200 nm pump pulses, which leads to a second WR.

2. Experimental Instrumentation

We use a Ti:Sa CPA system, delivering 35 fs pulses at 800 nm with 1 kHz repetition rate. The third (267 nm) or fourth (200 nm) harmonic are employed as pump pulses and recombined collinearly with the 800 nm probe (see sketch of the experimental scheme in the inset of Fig. 1). DMA molecules were purchased as crystals and are expanded effusively into the vacuum chamber at a temperature of 85 °C. The pump energies are adjusted so that molecules can be excited but no pump-only signal is generated. The ions are then generated by multiphoton ionization with the probe pulses and detected in a home-built reflectron time-of-flight (RETOF) mass spectrometer. The pump-probe delay τ is varied in steps of 35 fs up to 1 ps and in steps of 100 fs thereafter. For every value of τ , 10,000 subsequent laser shots are averaged and the final transient data is the sum of four single transients.

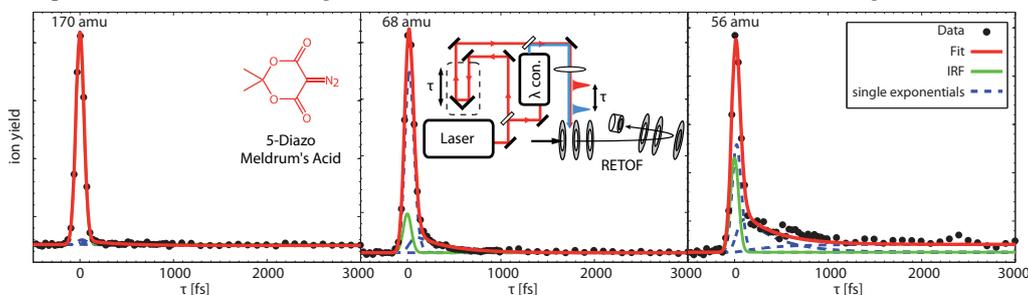


Fig. 1. Transient evolution of selected mass peaks after 267 nm excitation. The data points are shown as black dots and the result of the global fitting procedure are shown as solid red line. Also the single exponential contributions are presented as dashed blue lines and the IRF is plotted as solid green line. Left inset: Structure of DMA. Middle inset: Experimental apparatus. Pump pulses are generated from the 800 nm fundamental beam which itself is delayed. After recombination both pulses are focused into the vacuum chamber of the RETOF.

3. Results and Discussion

In Fig. 1 the transient evolution of ion signals at 170, 68, and 56 amu after 267 nm excitation is presented. Whereas 170 amu corresponds to ionized yet intact DMA, the ultrafast dynamics of the other ions provide information on the rearrangement and fragmentation processes. Prior to the WR in DMA, the diazo group is photolyzed off, which in theory could be traced by an ion signal at 142 amu corresponding to Carbene I and Ketene I (see inset in Fig. 2). Since this peak neither is present in the steady-state mass spectrum (not shown) nor in the pump-probe data due to fragmentation, the dynamics must be inferred from smaller fragment ions. In this context, the 68 amu fragment is of special interest since it originates from Carbene I and Ketene I, but not from further reaction products. Likewise, the fragment ion signals at 56 and 40 amu reflect the evolution of Carbene II and Ketene II (see inset in Fig. 2).

We fit the data of the 16 dominant mass peaks simultaneously with a sequential model consisting of three time constants, convolved with a Gaussian instrument response function (IRF) with a full width at half maximum of 104 fs, as obtained by a cross-correlation of pump and probe. The three time constants were determined to $\tau_1 = 27$ fs, $\tau_2 = 358$ fs, and $\tau_3 = \infty$, i.e. a permanent offset. The use of a time constant which is shorter than the IRF might seem arguable, but it has to be included to model our data appropriately.

As visible from the left panel in Fig. 1, the pump-probe signal of the parent ion peak at 170 amu follows the IRF, indicating that upon excitation, the DMA molecule is either instantly ionized or it loses the diazo group and hence no more ions at 170 amu are observable. The middle panel in Fig. 1 shows the evolution of the 68 amu mass peak, associated with the dynamics of Carbene I and Ketene I. The dashed blue lines disclose that in addition to a signal following the IRF, also ion signals decaying with τ_1 and τ_2 (rising with τ_1) contribute. The 27 fs time constant can be assigned to the WR from Carbene I to Ketene I. Corroborated by the evolution of the 56 amu peak shown in the right panel of Fig. 1 and associated to Carbene II, the lifetime of Ketene I can be inferred to be 358 fs. The 56 amu mass peak furthermore exhibits a permanent offset (τ_3). Hence, we conclude that Ketene I loses a CO on a sub-picosecond time scale to form Carbene II, a reaction already proposed in [2] (confer also the inset in Fig. 2).

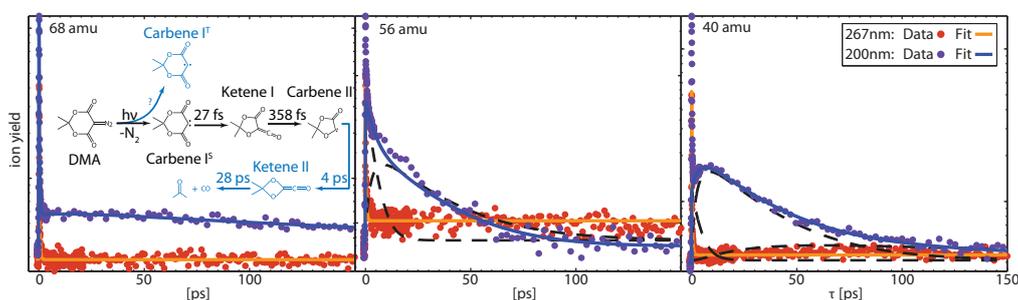


Fig. 2. Comparison of the transient evolution of selected mass peaks for 200 nm (violet dots) and 267 nm (red dots) excitation. The solid lines correspond to the result of the global fit approach, while the dashed black lines refer to the single exponential contributions. Inset: Schematic representation of the photochemical reactions with the corresponding time scales as inferred from our data. Reactions which were monitored with 267 nm are shown in black, while the additional pathways upon 200 nm excitation are shown in blue.

Theoretical studies reported [4] that higher-lying electronic states are involved in the WR of DMA. When exciting with 200 nm pulses, additional dynamics with time constants of $\tau_4 = 4$ ps and $\tau_5 = 28$ ps are observed. A comparison of the long-time behavior after 200 and 267 nm excitation is shown in Fig. 2. In the dynamics of the 68 amu ions (left panel of Fig. 2), a long-lasting contribution is present for 200 nm but not for 267 nm excitation, indicating a higher yield of Carbene I and possibly a subensemble of Carbene I being transferred to a triplet state. It is known that the latter hinders the rearrangement and thus the species is long-lived [4]. Furthermore, pumping at 200 nm leads to picosecond dynamics in the 56 and 40 amu mass peaks (middle and right panel of Fig. 2). As put forward by the pyrolysis study [2], Carbene I can further undergo a WR to Ketene II. The additional excess energy upon 200 nm excitation enables this reaction. Hence, within 4 ps Ketene II is formed, which then fragmentizes to CO and acetone within 28 ps.

4. Conclusion

A comparison of the ion signal after excitation of DMA with two different excitation wavelengths reveals that the WR in the gas phase is an ultrafast stepwise process towards a ketene. The latter is only stable on a sub-picosecond time scale and reacts on to a further carbene species. If enough excess energy is provided, the carbene performs a second WR before further fragmentation sets in.

[1] G. Cui and W. Thiel, "Photoinduced ultrafast Wolff rearrangement: a non-adiabatic dynamics perspective," *Angew. Chem. Int. Ed.* **52**, 433-436 (2013).

[2] S. L. Kammula, H. L. Tracer, P.B. Shevlin, and M. Jones, "Intramolecular decomposition of isopropylidene diazomalonalate (diazo Meldrum's acid)," *J. Org. Chem.* **42**, 2931-2932 (1977).

[3] P. Rudolf, J. Buback, J. Aulbach, P. Nuernberger, and T. Brixner, "Ultrafast multisequential photochemistry of 5-diazo Meldrum's acid," *J. Am. Chem. Soc.* **132**, 15213-15222 (2010).

[4] A. Bogdanova and V.V. Popik, "Experimental and theoretical investigation of reversible interconversion, thermal reactions, and wavelength-dependent photochemistry of diazo Meldrum's acid and its diazirine isomer, 6,6-dimethyl-5,7-dioxo-1,2-diaza-spiro[2,5]oct-1-ene-4,8-dione," *J. Am. Chem. Soc.* **125**, 14153-14162 (2003).