A Study of the Photochemistry of Diazo Meldrum's Acid by Ultrafast Time-Resolved Spectroscopies

Gotard Burdzinski,*,† Julien Réhault,§ Jin Wang,† and Matthew S. Platz*,‡

The Quantum Electronics Laboratory, Faculty of Physics, Adam Mickiewicz University, 85 Umultowska, Poznan 61-614, Poland, LASIR, CNRS, Centre d'Etude et de Recherches Lasers et Applications, bât. C5, Université de Lille 1, 59655 Villeneuve d'Ascq cedex, France, and Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio, 43210

Received: April 30, 2008; Revised Manuscript Received: June 24, 2008

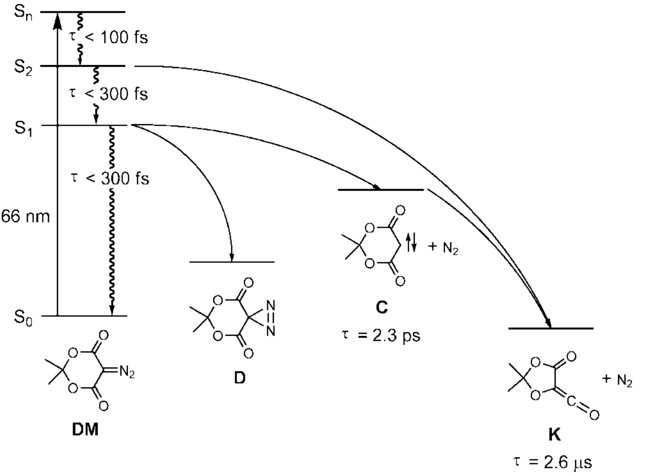
The photochemistry of Diazo Meldrum's acid (DM) was investigated by fs time-resolved UV−vis and IR spectroscopic methods. UV (266 nm) excitation of DM pumps the molecule to the S_5 and S_7 excited states. After fast internal conversion (IC), the S_2 state is formed, which will undergo Wolff rearrangement to form vibrationally excited ketene, which relaxes in 9 ps. The S_2 state will also relax to the S_1 state, which isomerizes to diazirine, fragments to form carbene, and relaxes further to the ground state of DM. The singlet carbene absorbs at 305 nm, is formed within 300 fs of the laser pulse, and has a lifetime of 2.3 ps in acetonitrile. The lifetime of DM in the S_2 and S_1 states is less than 300 fs. The quantum efficiency of DM decomposition is ~50% in chloroform with 266 nm excitation.

I. Introduction

Diazo carbonyl compounds undergo heat- and light-induced loss of nitrogen and rearrangement to form ketenes. This reaction was discovered at the beginning of the 20th century and is known as the Wolff rearrangement (WR).[1,2] The WR finds wide application in organic synthesis and photolithography and has been extensively studied by chemical, physical, and computational methods.[3] It is well-known that thermal decomposition of diazo carbonyl compounds constrained in the syn orientation by incorporation within a small ring leads to high yields of ketene and low yields of trappable carbonyl carbene.[4,5] This has led to speculation that nitrogen extrusion is concerted with carbon−carbon bond migration. It is also possible that a syn carbene is formed as a discrete intermediate but has an ultrashort lifetime that precludes any bimolecular chemistry. Acyclic singlet carbonyl carbenes prefer a conformation in which the carbonyl group is orthogonal to the plane defined by the carbene carbon and its two directly bonded substituent atoms to allow the filled hybrid orbital of the carbene to conjugate with the π system of the carbonyl group.[4] Popik and co-workers have pointed out that carbonyl carbenes incorporated within small rings struggle to achieve the preferred orthogonal orientation, are thereby destabilized, and are prone to ultrafast Wolff rearrangement.[4,5]

Diazo Meldrum's acid (DM) has been extensively studied by chemical, physical, and computational methods and conforms to the general pattern of the results. Jones and co-workers[6] found that UV photolysis of DM in neat alkenes leads to, at most, 1−2% formation of carbene adducts, whereas photolysis of its acyclic analogue, diazodimethylmalonate, leads to efficient trapping of dicarbomethoxycarbene. Similar results with UV photolysis of DM were later reported by Bogdanova and Popik[5] and by Nikolaev et al.,[7,8] who found efficient (quantum yield of 0.34, 254 nm) photolytic WR to form ketene lactone K (Scheme 1). The same two groups found that upon long wavelength photolysis of DM that WR is suppressed and that isomerization to the diazirine D (Scheme 1) becomes the dominant process, albeit in low quantum yield (0.024, 350 nm) along with a more modest yield of trappable carbene. Bogdanova and Popik concluded that WR and diazirine formation proceed in different excited states of DM and predicted that the lifetime of the upper excited state that directly forms ketene K is less than 1 ps.[5] Their calculations predicted that the singlet carbene derived from DM (C, Scheme 1) resides in a well with a depth of only 1 kcal/mol and, as a result, is predicted to have an ultrashort lifetime controlled by WR rather than by intermolecular reactions.

SCHEME 1



We have recently reported the use of ultrafast time-resolved UV−vis and IR spectroscopies to study the photochemistry of acyclic aryl diazo esters and ketones.[9,10] We found that ketene was formed in both a fast (less than 1 ps) process from the diazo ketone excited state (concerted WR) and in a slower process (700 ps) from the relaxed keto carbene. Photolysis of

---

* To whom correspondence should be addressed. E-mail: Gotardb@amu.edu.pl (G.B.); platz.1@osu.edu (M.S.P.).

† Adam Mickiewicz University.

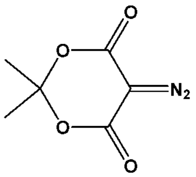
‡ The Ohio State University.

§ Université de Lille 1.

10.1021/jp803820c CCC: $40.75

an acyclic aryl diazo ester led only to the formation of relaxed carbene as there was no evidence of fast ketene formation in the diazo ester excited state.[10,11]

Time-resolved methods have been previously applied to study the photochemistry of DM in films[12] and in solution,[13] and an ultrafast IR study with 8 ps resolution was applied to the study of 2-diazo-1-naphthoquinones.[14] Stoutland and co-workers have previously studied the photochemistry of DM in a poly(methyl methacrylate) matrix with ps time-resolved IR techniques.[15,16] This group discovered that the ketene product was formed within 20 ps (the time resolution of their experiment) of excitation of DM. Stoutland's[15,16] study, Popik's work,[4,5] and our own studies of acyclic carbonyl carbenes[9] stimulated our interest in the photochemistry of a small ring diazo carbonyl compound. This led us to this study of the photochemistry of diazo Meldrum's acid with fs time-resolved UV−vis and IR spectroscopies to enable direct observation of diazo excited states and small ring carbonyl carbenes and to push the limits of observation of ketene formation.



Diazo Meldrum's Acid (DM)

II. Experimental Section

DM (5-diazo-2,2-dimethyl-1,3-dioxane-4,6-dione) was purchased from TCI America. The laser system consists of a short-pulse titanium−sapphire oscillator (Coherent, Mira) followed by a high-energy titanium−sapphire regenerative amplifier (Coherent, Positive Light, Legend HE USP). The beam is split into two beams to pump two OPAs (OPerA Coherent). The OPA with a SFG module generates an UV pump pulse (tunable from 240 to 310 nm), while the second OPA has a DFG module producing IR pulses (tunable from 2 to 10 μm). A Ge beam splitter splits the IR beam into reference and probe beams, and both are focused into the sample cell (Harrick Scientific), but only the probe beam overlaps with the pump beam in the sample. After passing through the sample, the probe and reference beams are spectrally dispersed in a grating spectrometer (Triax 320) and independently imaged on a liquid-nitrogen-cooled HgCdTe detector (2 × 32 elements) with 17 nm resolution. Every second UV pump pulse is blocked by a synchronized chopper to eliminate long-term drift effects. In both the IR and UV−vis experiments, the excitation wavelength is set to 266 nm and situated at the low-energy edge of the DM absorption band. The broad-band UV−vis femtosecond transient absorption system has been described elsewhere.[17] Solution concentrations were adjusted to an absorption of 0.7 in a 1 mm cell. The pump pulse energy was about 4 μJ at the sample position. The entire set of pump−probe delay positions (cycle) was repeated at least three times to observe data reproducibility from cycle to cycle. To avoid rotational diffusion effects, the angle between polarizations of the pump beam and the probe beam was set to the magic angle (54.7°). Kinetic traces were analyzed by fitting to a sum of exponential terms. Convolution with a Gaussian response function was included in the global fitting procedure. The instrument response was approximately 300 fs (fwhm). UV−vis transient absorption spectra were corrected for chirp in the probe continuum.[18] All experiments were performed at room temperature.

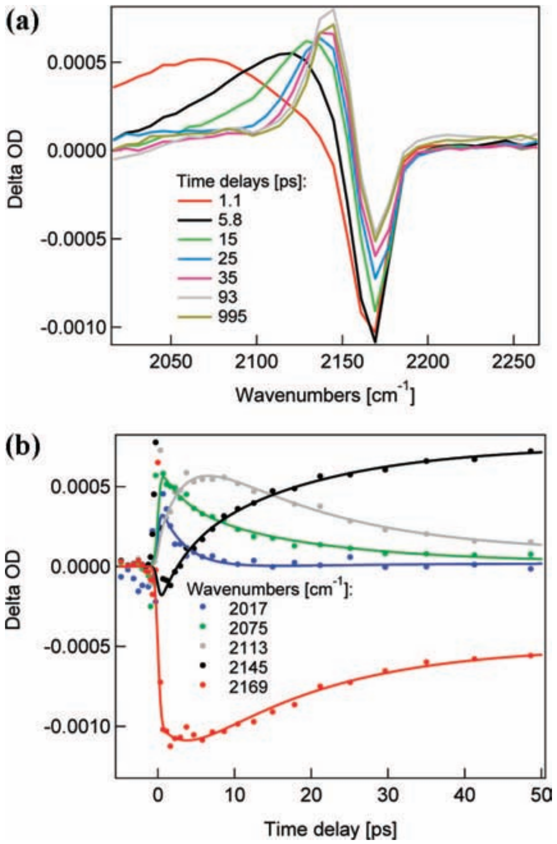


Figure 1. (a) Time-resolved infrared transient absorption spectra produced in chloroform after photoexcitation of DM at 266 nm. (b) Kinetic traces were recorded at 2017, 2075, 2113, 2145, and 2169 cm^{-1} (points) and fitted to a biexponential function (solid lines). Global fitting results in two characteristic time constants of 3.3 and 17.7 ps.

Calculations. DFT and TD-DFT calculations were performed using the Gaussian 03 suite of programs at The Ohio Supercomputer Center. Geometries were optimized at the B3LYP/6-31G(d) level of theory with single-point energies obtained at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory. Vibrational frequency analyses at the B3LYP/6-31G(d) level were utilized to verify that stationary points obtained corresponded to energy minima. The calculated frequencies were scaled by a factor of 0.9614.[19] The electronic spectra were computed using time-dependent density functional theory of Gaussian 03 at the B3LYP/6-311+G(d,p) level, and 20 allowed electronic transitions were calculated.

III. Results and Discussion

III.1. Ultrafast IR Spectroscopy. Time-resolved infrared spectra were obtained upon ultrafast photolysis (266 nm) of a solution of DM in chloroform over a spectral window of 2017−2263 cm^{-1} (Figure 1 a). Two distinctive spectral signatures were observed, the formation of a positive band peaking at 2160 cm^{-1} that corresponds to the ketene ($\nu_{C=C=O}$ stretching vibration[15]) and a negative band at 2169 cm^{-1} that can be assigned to diazo bleaching ($\nu_{-N=N}$ stretching vibration) caused by the concentration decrease of DM in the ground state due to the photoexcitation. The bleaching of the diazo band and the positive ketene absorption signal are present immediately (within the laser pulse, in less than 1 ps). The initially observed ketene band is very wide and red-shifted relative to the relaxed ketene.

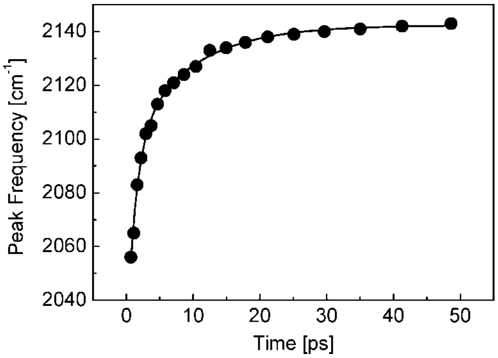


Figure 2. The time dependence of the ketene peak frequency. The solid line presents a biexponential fit giving 1.4 and 9 ps time constants.

At longer delay times, up to 50 ps, a frequency upshift to 2145 cm^{-1} is observed. This transient absorption band spectral evolution can be assigned to ketene vibrational cooling.[9,20]

This system can be analyzed more clearly than the data obtained upon ultrafast photolysis of a previously studied acyclic aryl diazo ketone. In contrast to the study of BpCN$_2$COCH$_3$,[9] the relaxed ketene band derived from DM is located at *lower* wavenumbers than the diazo depletion band, a fact noted by previous workers.[21] The absorption of the hot ketene and diazo depletion do not overlap, allowing clear observation of the initially born hot ketene band derived from DM. Our interpretation has precedent as vibrational cooling of a ketene intermediate has also been observed also in Glich and co-workers's IR studies of the photochemical transformation of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid.[22]

Figure 1b shows kinetic traces fitted with a biexponential function. A global fit results in two characteristic time constants, 3.7 and 17.7 ps, caused by vibrational relaxation.[23] A vibrational relaxation process is typically described by a peak frequency blue shift and band narrowing; in our case, the band maximum can be determined from the fitting of the positive ketene band to a skewed Gaussian shape.[24] Two characteristic time constants, 1.4 and 9 ps, are found upon fitting the time-dependent ketene peak frequency to a biexponential function (Figure 2). The first time constant is tentatively assigned to intramolecular vibrational redistribution,[24] while the second one is attributed to energy transfer from hot ketene to solvent. After this cooling process is complete (50 ps after the laser pulse), the ketene IR band persists without change up to 3 ns, which is the temporal limit of detection. The ketene lifetime is reported to be 2.6 μs in acetonitrile, determined from the growth of a ketene−pyridine ylide as a function of pyridine concentration using ns laser flash photolysis techniques.[13] The ketene UV absorption band is located below 300 nm,[12] which unfortunately is below our probe range in UV−vis femtosecond broad-band transient absorption measurements.

The diazo band of DM is bleached by photolysis due to the ultrafast decrease of the concentration of DM. The dynamics of the bleaching of the diazo band at around 2166 cm^{-1} (Figure 1a and b) might be affected by a contribution from both ketene formation and a ground-state DM recovery process. Nevertheless, it is clear that a large fraction of the excited DM molecules do not decompose and simply return to the ground state as manifested by the partial recovery from the initial, fast bleaching. On the basis of product studies, Bogdanova and Popik concluded that with 254 nm excitation of DM in methanol that the quantum yield of repopulation of the ground state of DM by internal conversion is about 60%.[5]

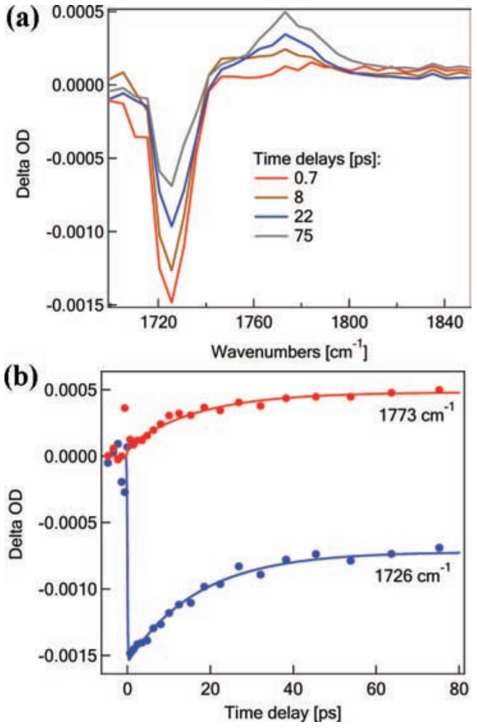


Figure 3. (a) Time-resolved infrared transient absorption spectra obtained in chloroform after photoexcitation of DM at 266 nm. (b) The kinetic traces at 1726 and 1773 cm^{-1} (points) were fitted to a monoexponential function (solid lines). Global fitting results in a 17 ps time constant.

To avoid the spectral overlap issue inherent with monitoring the diazo band of DM, we estimated the quantum yield of DM decomposition in chloroform with 266 nm light with the spectral probe range set at around 1744 cm^{-1} to monitor the bleaching of the ester $\nu_{C=O}$ stretching vibration (Figure 3a) of DM.[25] The negative ester bleaching band corresponds to the stationary IR spectrum (data not shown) of DM. The kinetic trace obtained at 1726 cm^{-1} (Figure 3b) indicates that about 50% of the instantaneously bleached signal recovers over 60 ps after the laser pulse. This means that ~50% of the photoexcited DM molecules return to the ground state in chloroform. A similar value can be estimated at frequencies slightly above 2170 cm^{-1} (Figure 1). The time constant of the recovery of the DM signal is 17 ps, which is much longer than the time constant of ketene formation. This is attributed to formation of hot, ground-state DM and its relaxation. Assuming that S_2 relaxes to S_1 and that S_1 then relaxes to hot DM by internal conversion, we can conclude that the lifetime of S_1 is less than or equal to 17 ps. Later we will conclude that the lifetime of S_1 is less than 300 fs.

Figure 3 also reveals the rise of a positive signal at 1773 cm^{-1} that can be assigned to the formation of a photoproduct. The isomeric diazirine $\nu_{C=O}$ stretching vibration is at 1799 cm^{-1},[26] in poor agreement with this result. Another reason we reject assigning this band to the diazirine D is that this molecule is only a minor product of 254 nm photolysis.[5] As the major product of 254 nm photolysis is ketene lactone K, the carrier of the 1773 cm^{-1} band is assigned to this species. This is in reasonable agreement with the predictions of DFT calculations (Supporting Information, Table S5). We also note that UV photolysis of DM in a cryogenic matrix produces a photoproduct at 1760 cm^{-1}, in fair agreement with this study.[27] This group assigned the 1760 cm^{-1} photoproduct to the lactone carbonyl moiety of ketene K.

The apparent formation of the relaxed ketene lactone K has a 17 ps time constant (Figure 3b) most likely due to vibrational cooling of the initially formed hot ketene lactone. This is the same as the time constant of the recovery of the DM signal monitored at the lactone vibration. Because the ketene lactone K is present within 1 ps of the laser pulse (monitored at the ketene band), there must be an ultrafast pathway from an excited state of DM to the ketene. It must be an upper excited state (S_2) as pumping DM to S_1 at 350 nm does not efficiently produce the ketene lactone.[5] However, the data obtained by monitoring the lactone vibration of K allows the possibility that some ketene lactone is formed in 17 ps from rearrangement of hot DM as it cools over 17 ps. Nevertheless, we feel that we can rule out a hot DM pathway to K because Bogdanova and Popik[5] calculated that the thermal barrier to decomposition of DM exceeds 50 kcal/mol, which seems far too high a barrier for the vibrationally excited DM of this study to overcome.

The data can be economically explained as shown in Scheme 1. Excitation of DM with 266 nm radiation pumps the diazo compound to the S_5 or S_7 excited singlet state as indicated by time-dependent density functional theory (TD DFT) calculations[28,29] (Table S2, Supporting Information), which predict that DM has two transitions with a large oscillator strength in the vicinity of 266 nm, at 238 nm ($S_0 \rightarrow S_5$, $f = 0.0291$) and 234 nm ($S_0 \rightarrow S_7$, $f = 0.0752$). Therefore, excitation at 266 nm results in the population of a set of highly excited singlet states. Decomposition in these states cannot be ruled out definitively, but a highly competitive ultrafast IC process likely leads DM to the dissociative S_2 state. The DM S_2 state must have a lifetime of less than 300 fs, as predicted,[5] and it decays by both ketene formation (growth time constant less than 0.4 ps) and internal conversion to S_1. The S_1 state isomerizes to the diazirine D,[5,8] forms carbene (as discussed later), and relaxes to the ground state. Our conclusions differ from those of Tanigaki and Ebbesen[21] who favor a slower, stepwise formation of ketene lactone and the presence of an oxirene intermediate.

III.2. Ultrafast UV−Vis Spectroscopy. The photochemistry of DM was also studied by femtosecond UV−vis transient absorption spectroscopy. The TD-DFT calculations (Table S1, Supporting Information) predict that the singlet carbene (Scheme 1) has electronic transitions with a significant oscillator strength above 300 nm (Figure 4a). Exposure of DM in acetonitrile to an ultrafast laser pulse at 266 nm produces the transient spectrum of Figure 4a. An absorption band with a maximum at 305 nm is formed within 300 fs of the laser pulse. Global fitting of the decay of transient absorption with a mono exponential function gives a 2.3 ps time constant (see Figure 4b). The same transient absorption spectra and kinetics are observed in chloroform; however, early delays are affected by solvent-related artifacts.

The carrier of the transient UV absorption spectrum can, in principle, be assigned to an excited state of DM or to the carbene dilactone. Several pieces of evidence persuade us that we have observed the transient absorption spectrum of the carbene. First, the decay of the UV absorbing transient is *slower* than the prompt growth of the hot ketene, and therefore, the carrier of transient UV−vis absorption cannot be the ketene precursor, an S_n ($n \geq 2$) excited state of DM. This is in line with previous reports that UV excitation of acyclic aryl diazo carbonyl compounds produce dissociative excited states such as $^1BpCN_2COCH_3^*$ with lifetimes less than 300 fs.[9]

TD-DFT calculations predict that the carbene dilactone absorbs broadly in the UV−vis region (black bars in Figure 4a and Table S1, Supporting Information), which is consistent with the experimentally observed transient absorption spectrum (Figure 4a). The short lifetime of 2.3 ps agrees with the predicted low (∼1 kcal/mol) barrier to rearrangement of this carbene.[4,5]

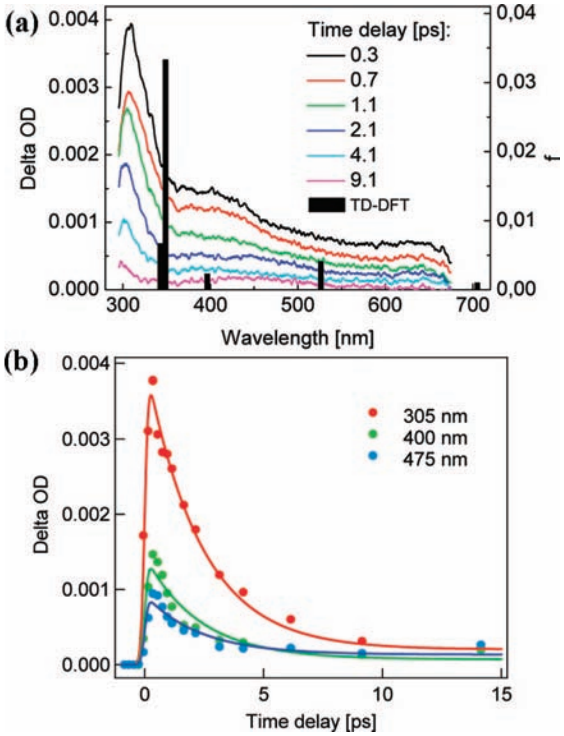


Figure 4. (a) Transient absorption spectra recorded over a 0.3−9.1 ps time window following photoexcitation of DM at 266 nm. The vertical bars indicate the positions and oscillator strength f of the electronic transitions calculated by TD-DFT for the carbene. (b) Kinetic traces at 305, 400, and 475 nm (points) fitted to a monoexponential function (solid lines). Global fitting yields a 2.3 ps time constant.

Bogdanova and Popik[4,5] have calculated the optimal gas-phase geometries of the singlet and triplet carbene and have predicted that the singlet has a boat-like structure and that the triplet is planar. The triplet was found to be lower in energy than the lowest singlet by 8.3 kcal/mol. This agreed with a study of Hutton and Roth[30] who detected the ESR spectrum of the triplet carbene in a low-temperature matrix. This led us to consider but ultimately reject assigning the transient spectra to a triplet diazo compound or carbene for the following reasons. First, Jones and co-workers[6] found that direct and benzophenone-sensitized photolysis of DM led to totally different (indeed largely orthogonal) products, which implies that direct photolysis does not form either a triplet diazo compound or carbene. Second, we have found that aryl ISC rates proceed on a time scale of tens to hundreds of picoseconds.[31] As the transients that we detect are formed within 1 ps, we think it highly unlikely they could be triplet carbenes.

Given the good agreement of the absorption spectrum and lifetime of the carrier of the transient spectrum with the predicted properties of singlet carbene C, and given that all previously detected diazo excited states have sub-ps lifetimes,[9] we assign the 305 nm absorbing transient to singlet carbene C. If the assignment is correct, then this is the shortest lifetime of any carbene observed to date. We have not observed a change of singlet carbene lifetime upon going from acetonitrile to chloroform, likely due to the fact that the carbene lifetime is too short (2.3 ps) to show sensitivity to solvent.

However, the carbene dilactone cannot be the main source of ketene as the IR experiments demonstrate that most of the ketene is formed in less than 1 ps (based on spectral integration of the peak area) and the carbene dilactone lifetime is 2.3 ps.

We expect that the singlet excited states (S_n, $n \geq 1$) of DM have very short lifetimes (less than 300 fs) and in this work are not detected by transient UV−vis spectroscopy due to the lack of a strong spectroscopic signature in our window of observation and/or a low instantaneous concentration.

It is not clear from our spectroscopic and kinetic data whether carbene C is formed from the S_2 or the S_1 excited state of DM or from both excited states. The product studies of Nikolaev et al. argue in favor of the formation of carbene C from S_1.[8] Assuming that the carbene is the carrier of the 305 nm band then requires that the lifetime of S_1 is the same as the growth time constant of the carbene (<300 fs).

A boat-like conformation of the singlet carbene has been calculated (see Table S1, Supporting Information). The calculations at the B3LYP/6-31G(d) level of theory suggest the singlet carbene is a real intermediate and it is a minimum on the potential energy surface. Bogdanova and Popik proposed that the boat-like conformation provides better overlap of the orbital containing the unshared pair of electrons localized on the carbene atom with the π-system of the carbonyl groups as in an enolate ion.[5]

Conclusions

UV photoexcitation of DM in chloroform at 266 nm produces a set of highly excited singlet states (S_5 and S_7). Internal conversion leads DM to the dissociative S_2 state. This state either decomposes by concerted Wolff rearrangement to form ketene or carbene dilactone or undergoes internal conversion to form S_1, which then re-forms DM or forms carbene. The product studies of Nikolaev et al. argue in favor of the formation of carbene C from the S_1 state.[8]

The carbene dilactone has a lifetime of 2.3 ps. This is the shortest lifetime of any carbene measured to date. The isomerization of the carbene dilactone to ketene is particularly rapid because it is forced into an unfavorable conformation by the small ring architecture. The stepwise (carbene) channel of ketene formation was found to be minor compared to the concerted Wolff rearrangement process in the DM excited states. The S_1 state of DM has a lifetime of less than or equal to 300 fs (the rise time of the carbene absorption at 305 nm), which is controlled by isomerization to the corresponding diazirine (minor) or carbene formation (minor) and by internal conversion to S_0 (major), consistent with the quantum yield of decomposition of DM at 350 nm of only 0.024.[5]

Approximately 50% of excited DM molecules return to the ground state upon 266 nm excitation, while the other excited DM molecules mainly undergo Wolff rearrangement.

Acknowledgment. This work was performed at The Ohio State University Center for Chemical and Biophysical Dynamics. Femtosecond UV−vis spectra were recorded at University in Lille 1. Support of this work by MF EOG is gratefully acknowledged. Gotard Burdzinski thanks the Foundation for Polish Science (FNP) for a “Homing” Grant in 2008. Jin Wang thanks the Ohio State University for a Presidential Fellowship. Support of this work by the US NSF and the Ohio Supercomputer Center is gratefully acknowledged.

Supporting Information Available: Details of calculations are in Tables S1−S6. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Wolff, L. *Justus Liebigs Ann. Chem.* **1902**, *325*, 129.
(2) Wolff, L. *Justus Liebigs Ann. Chem.* **1912**, *394*, 23.
(3) Kirmse, W. *Eur. J. Org. Chem.* **2002**, 2193.
(4) Popik, V. *Can. J. Chem.* **2005**, *83*, 1382.
(5) Bogdanova, A.; Popik, V. *J. Am. Chem. Soc.* **2003**, *125*, 14153.
(6) Jones, M.; Ando, W.; Hendrick, M.; Kulczycki, A.; Howley, P.; Hummel, K.; Malament, D. *J. Am. Chem. Soc.* **1972**, *94*, 7469.
(7) Nikolaev, V.; Khimich, N.; Korobitsyna, I. *Khim. Geterotsikl. Soedin.* **1985**, *3*, 321.
(8) Nikoloaev, V.; Shevchenko, V.; Platz, M.; Khimich, N. *Russ. J. Org. Chem.* **2006**, *42*, 815.
(9) Burdzinski, G.; Wang, J.; Gustafson, T.; Platz, M. *J. Am. Chem. Soc.* **2008**, *130*, 3746.
(10) Wang, J.; Burdzinski, G.; Kubicki, J.; Platz, M. *J. Am. Chem. Soc.* **2008**, *130*, 11195.
(11) Wang, Y.; Yuzawa, T.; Hamaguchi, H.; Toscano, J. *J. Am. Chem. Soc.* **1999**, *121*, 2875.
(12) Winnik, M.; Wang, F.; Nivaggioli, T.; Hruska, Z. *J. Am. Chem. Soc.* **1991**, *113*, 9702.
(13) Wang, J.; Toscano, J.; Platz, M.; Nikolaev, V.; Popik, V. *J. Am. Chem. Soc.* **1995**, *117*, 5477.
(14) Vleggaar, J.; Huizer, A.; Kraakman, P.; Nijssen, W.; Visser, R.; Varma, C. *J. Am. Chem. Soc.* **1994**, *116*, 11754.
(15) Lippert, T.; Koskelo, A.; Stoutland, P. *J. Am. Chem. Soc.* **1996**, *118*, 1551.
(16) Lippert, T.; Stoutland, P. *Appl. Surf. Sci.* **1997**, *109*, 43.
(17) Buntinx, G.; Naskrecki, R.; Poizat, O. *J. Phys. Chem.* **1996**, *100*, 19380.
(18) Nakayama, T.; Amijima, Y.; Ibuki, K.; Hamanoue, K. *Rev. Sci. Instrum.* **1997**, *68*, 4364.
(19) Scott, A.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.
(20) Burdzinski, G.; Middleton, C.; Gustafson, T.; Platz, M. *J. Am. Chem. Soc.* **2006**, *128*, 14804.
(21) Tanigaki, K.; Ebbsen, T. *J. Phys. Chem.* **1989**, *93*, 4531.
(22) Laimgruber, S.; Schreier, W.; Schrader, T.; Koller, F.; Zinth, W.; Gilch, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 7901.
(23) Hamm, P.; Ohline, S.; Zinth, W. *J. Chem. Phys.* **1997**, *106*, 519.
(24) Schrader, T.; Sieg, A.; Koller, F.; Schreier, W.; An, Q.; Zinth, W.; Gilch, P. *Chem. Phys. Lett.* **2004**, *392*, 358.
(25) Livinghouse, T.; Stevens, R. *J. Am. Chem. Soc.* **1978**, *100*, 6479.
(26) Shevchenko, V.; Khimich, N.; Platz, M.; Nikolaev, V. *Russ J. Org. Chem.* **2006**, *42*, 1213.
(27) Ulbricht, M.; Thurner, J.-U.; Siegmund, M.; Tomaschewski, G. *Z. Chem.* **1988**, *28*, 102.
(28) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. *J. Chem. Phys.* **1998**, *108*, 4439.
(29) Stratmann, R.; Scuseria, G.; Frish, M. *J. Chem. Phys.* **1998**, *8218*.
(30) Roth, H.; Hutton, R. *Tetrahedron* **1985**, *41*, 1567.
(31) Wang, J.; Kubicki, J.; Peng, H.; Platz, M. *J. Am. Chem. Soc.* **2008**, *130*, 6604.

JP803820C