Concerted Wolff Rearrangement in Two Simple Acyclic Diazocarbonyl Compounds

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The photochemistry of two simple acyclic diazo carbonyl compounds, azibenzil and diazoacetone, were studied using the tools of ultrafast time-resolved spectroscopy. In the former case, UV-vis detection allows observation of an absorption band of singlet benzoylphenylcarbene, decaying with a 740 \pm 150 ps time-constant in acetonitrile. IR detection shows that the ketene product of Wolff rearrangement (~2100 cm⁻¹) is formed by two parallel pathways: a stepwise mechanism with carbene intermediacy with a slow rise time-constant of 660 \pm 100 ps, and directly in the diazo excited state as confirmed by the immediate formation of an IR band of a nascent hot ketene species. Photolysis (270 nm) of diazoacetone in chloroform leads mainly to the ketene species through a concerted process, consistent with the predominance of the syn conformation in the diazoacetone electronic ground state and a zero quantum yield of the internal conversion process.

1. Introduction

Photolysis of diazo carbonyl compounds promotes the extrusion of molecular nitrogen and the formation of carbene, and in many cases the formation of a ketene. This reaction is known as the Wolff rearrangement (WR) and it has been extensively studied by stationary and time-resolved spectroscopic, chemical, and theoretical methods.¹ The data demonstrate that ketene formation can proceed directly in the excited diazo state in concert with molecular nitrogen extrusion. Ketene can also be produced in a stepwise process in which a carbene is first formed and then undergoes a subsequent isomerization.

Over 40 years ago, Kaplan and Meloy proposed that the concerted WR process is favored in the syn conformers of α -diazo carbonyl compounds, while the heat or light activation of anti conformers promotes the stepwise process, as demonstrated by the intermediacy of chemically trappable carbenes.² Time-resolved infrared experiments confirmed the validity of

SCHEME 1

this rule for acyclic diazo carbonyl compounds.^{3,4} Small cyclic diazo carbonyl compounds are structurally locked in a syn conformation and largely decompose and rearrange by a concerted mechanism, however, a stepwise pathway does still slightly contribute to the overall WR process.^{5,6} Since the typical lifetimes of the singlet excited states of the diazo precursors are less than 0.4 ps, the concerted process can be confirmed by a fast product rise (<0.4 ps).⁶ The stepwise process, which involves a carbene intermediate, results in a slower product rise (>1 ps) which is dependent on the carbene structure. The shortest lifetime of any carbene measured to date is 2.3 ps (a small ring carbene dilactone in acetonitrile).⁵

In a singlet carbene, the carbonyl group prefers to be orthogonal to the plane defined by the carbene carbon atom and the two atoms directly bonded to the carbene carbon.^{6,7} Incorporating a carbonyl carbene within a small ring enforces planarity (or near planarity), destabilizes the singlet carbene, and accelerates WR, thus the rigid enforcement of planarity (or



near planarity) of the molecule can be a major factor in ketene formation. $^{\rm 8,9}$

In acyclic diazo carbonyl compounds, the quantum yield of ketene formation depends upon substituents (R_1 and R_2 , Scheme 1). Other pathways in the diazo excited state that are competitive with WR include internal conversion to reform the diazo precursor in the ground state,⁶ cyclization when possible,¹⁰ or

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alkene formation by a 1,2-H shift process when R_1 is an alkyl group.¹¹ The WR quantum yield significantly decreases when the carbonyl unit is a part of an ester group as the rearrangement now requires loss of ester resonance energy.⁶ For diazo esters, Kaplan and Meloy's rule does not apply in force as it does with ketones. For example, the syn conformers of acyclic or macrocyclic diazomalonates do not undergo concerted WR upon photodecomposition and only carbene-derived products are formed.^{9,12}

Singlet carbenes are known to react rapidly with alcohol solvents or may undergo intersystem crossing to the triplet state, when the triplet carbene is the ground state.⁶ This test is used to assign putative singlet carbene absorption bands because if the carrier of the band is truly a carbene, then its lifetime will be dramatically shortened in alcohol relative to acetonitrile, halogenated, or hydrocarbon solvent.

In our previous ultrafast UV–vis and IR studies, we have focused on diazo carbonyl compounds containing aromatic chromophores because the diazo excited states and carbenes absorb at longer wavelengths than the smaller alkyl analogues.^{4,7,13} However, the photochemistry of a simple acyclic diazo ketone has not been previously subjected to ultrafast laser spectroscopic studies. Thus, the extent to which simple diazo ketone photochemistry resembles that of their aromatic analogues remains unclear. This motivated this study of diazoacetone ($R_1 = H, R_2$ = CH₃) and azibenzil ($R_1, R_2 = Ph$) for the sake of comparison.

2. Experimental Section

Azibenzil and diazoacetone were synthesized according to procedures described in the literature.^{14,15} The mid-IR and UV-vis femtosecond transient absorption systems have been previously described.^{7,16} Samples were prepared in 50 mL of solution with an absorption of ~1.0 at the excitation wavelength measured in a 1 mm optical flow cell. The entire set of pump-probe delay positions (cycle) is repeated at least three times, to ensure data reproducibility from cycle to cycle. To avoid rotational diffusion effects, the angle between the polarizations of the pump beam and the probe beam was set to the magic angle (54.7°). Kinetic traces are analyzed by fitting to a sum of exponential terms. Convolution with a Gaussian response function is included in the global fitting procedure. The instrument response was ~300 fs (fwhm). All experiments were performed at room temperature.

2.1. 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/6-31+G(d) level of theory with single-point energies obtained at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory. Vibrational frequency analyses at the B3LYP/6-31+G(d) level were utilized to verify that the stationary points obtained corresponded to energy minima. The calculated frequencies were then scaled by a factor of 0.9614.¹⁷ 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.

3. Results

3.1. Azibenzil. The photochemistry of azibenzil is amenable to study by both time-resolved UV-vis (over the spectral probe range 350-600 nm) and IR spectroscopy and the results obtained with this system will be detailed first. Ultrafast photolysis (307 nm) of azibenzil in acetonitrile produces the transient UV-vis spectra of Figure 1A. The initial broad band peaking at about 400 nm can be assigned to the diazo excited

state with a lifetime shorter than our instrumental response function (<0.3 ps). This short lifetime value is in line with our previous studies of other diazo compounds.⁶ Diazo excited state decay is followed by the formation of the vibrationally excited carbene species at shorter wavelength (370 nm). Subsequent vibrational relaxation leads to the thermalized carbene band observed after a delay time of 14 ps (Figure 1A). The UV spectrum observed is consistent with TD-DFT calculations of singlet benzoylphenylcarbene in the gas phase (Table S1 of the Supporting Information, SI) which predict significant carbene oscillator strength at 429 nm (f = 0.0275) and 333 nm (f =0.1298). Analysis of the transient absorption kinetic trace recorded at 370 nm (Figure 1B and S1 of the SI) results in 3 characteristic time-constants: < 0.1 ps (diazo excited state lifetime), 6 ± 1 ps (vibrational cooling) and 740 \pm 150 ps (carbene lifetime). The transient lifetime, as expected for a singlet carbene, was found to be significantly shorter in a reactive solvent such as methanol (140 \pm 20 ps).

According to Trozzolo and co-workers, photolysis of azibenzil in solution produces ketene as the major photoproduct (85%-90%).¹⁸ The rise of ketene could not be observed in the ultrafast UV-vis experiment, since its absorption band lies at about 313 nm.¹⁹ This is outside our detection window, in line with calculations (Table S2 of the SI) which predict ketene absorption at 283 nm (f = 0.1973). To observe the ketene rise ($\lambda_{ex} = 270$ nm), we used infrared detection (Figure 2) at ~2100 cm⁻¹ (calculations predict a strong ketene vibrational transition at 2088 cm⁻¹, Table S2 of the SI).²⁰ A positive ketene band rises at 2113 cm⁻¹ with two characteristic time constants: 45 \pm 10 ps (attributed to vibrational cooling of the hot ketene



Figure 1. Transient UV-vis spectra recorded for azibenzil in acetonitrile after excitation at 307 nm, (A). Kinetic traces selected at 370 nm (points) fitted with a 3-exponential function: < 0.1 ps, 6, and 740 ps (solid line), (B).



Figure 2. Transient IR spectra produced by ultrafast photolysis of azibenzil in acetonitrile ($\lambda_{exc} = 270 \text{ nm}$) (A). Kinetic trace at 2113 cm⁻¹ (points) fitted by a 2-exponential function with 45 and 660 ps components (solid line) (B).

formed in the concerted WR process) and 660 ± 100 ps (in agreement with the previously mentioned carbene lifetime of 740 ps).

Inspection of the transient absorption spectra in Figure 2A, at early delays, shows a negative band at 2090 cm⁻¹ caused by immediate bleaching of the diazo vibration and a broad positive band between 2030–2060 cm⁻¹ assigned tentatively to vibrationally excited ketene. The latter band might be slightly affected by overlap with the spectrum of a hot diazo species produced by internal conversion. The partial recovery of the ground state bleach takes place over a 100 ps time window indicating a reaction quantum yield, $\Phi_R = 0.5$, of diazo decomposition, in agreement with a previously reported value (0.5) in benzene solution upon irradiation with $\lambda = 313$ nm.¹⁹

3.2. Diazoacetone. Excitation (270 nm) of diazoacetone, in chloroform, generates the IR transient absorption spectra shown in Figure 3. At initial delays, a positive band is present at about 2020 cm⁻¹ and a negative band is seen at 2110 cm⁻¹. The initial positive band can be clearly assigned to the hot ketene species. An alternative attribution of this band to vibrationally hot diazoacetone in its electronic ground state (formed by internal conversion) can be ruled out, as the bleaching of the IR signature of the precursor is constant over a 2 ns time window, as deduced from $\nu_{C=0}$ recorded at about 1650 cm⁻¹ (Figure S2 of the SI).

Initially, the nascent ketene species undergoes vibrational relaxation as confirmed by band-narrowing and the spectral



Figure 3. Transient IR spectra produced by ultrafast photolysis of diazoacetone in chloroform ($\lambda_{exc} = 270 \text{ nm}$) (A). Kinetic trace selected at 2124 cm⁻¹ (points) approximated by a fit with 1-exponential function: $40 \pm 10 \text{ ps}$ (solid line) (B).

frequency upshift of the initial positive IR band over a 100 ps time window (Figure 3).⁵ The relaxed ketene band, at about 100 ps, strongly overlaps the $\nu_{N=N}$ bleaching band to a greater extent than is the case with azibenzil. The ketene infrared signal is constant up to 2 ns post excitation pulse (Figure 3B). Experiments performed in a carbene-trapping solvent, such as methanol, leads to very similar transient infrared spectra. Interestingly, the ratio of initial bleach amplitude to the relaxed ketene signal is the same in chloroform and methanol. Thus, little to no methanol trappable carbene is formed from diazoacetone with $\lambda_{ex} = 270$ nm, implying that all of the ketene is formed by the concerted WR process under these conditions.

4. Discussion

The transient spectra and kinetics obtained upon ultrafast photolysis of azibenzil in time-resolved IR and UV–vis studies are reminiscent of those with *p*-biphenyl methyldiazo ketone, BpCN₂COCH₃.⁴ However, in studies of BpCN₂COCH₃ the carbene band was better resolved spectroscopically than in this work. The maximum absorbance of the carbene was at 380 nm and a fast reaction pathway from hot carbene species to ketene could be ruled out based on the constant band area over 0.8-30 ps, indicating a constant carbene concentration.^{4,21}

In the case of azibenzil, calculations indicate that the dominant conformer is syn (62% in polar solvent estimated from Boltz-

TABLE 1: B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d)

Calculations of Gibbs Free Energy Differences (kcal·mol⁻¹) for Syn and Anti Conformers of Diazoacetone and Azibenzil in the Gas Phase, Cyclohexane, Chloroform, and Acetonitrile

$\begin{array}{c} N_2 & O \\ H & CH_3 \end{array} =$	— N₂ → H	CH ₃	N ₂ Ph	⊖ − Ph =	Ph	Ph
<i>s</i> -Z (syn)	<i>s</i> -E (anti)		<i>s</i> -Z (syn)		s-E (anti)	
	$\Delta G_{298\mathrm{K}}$	syn %	anti %	$\Delta G_{298\mathrm{K}}$	syn %	anti %
gas phase ^a	1.14	87.3	12.7	-0.21	41.2	58.8
cyclohexane ^b	1.05	85.5	14.5	0.00	50.0	50.0
chloroform ^b	1.10	86.5	13.5	0.17	57.1	42.9
acetonitrile ^b	1.21	88.5	11.5	0.28	61.6	38.4

^{*a*} The zero-point energy (ZPE) for the gas-phase calculations is corrected by a factor of 0.9806.¹⁷ ^{*b*} The solution-phase calculations used PCM models, and the geometries are from the gas-phase B3LYP/6-31+(d) calculations.

mann distribution at 293 K, Table 1). The short (less than 100 fs) lifetime of the diazo excited state indicates that the syn and anti forms produced with 270 nm light do not interconvert, thus the photochemistry proceeds from the Franck-Condon state. Our experimental observation that both concerted and stepwise paths are operative is in agreement with the presence of two diazo excited state conformers and with Kaplan and Meloy's rule, assuming that syn favors concerted WR and the anti conformer is disposed toward carbene formation. Calculations of diazoacetone predict that the electronic ground state exists mainly in the syn form (87%) in gas phase and in solution (Table 1) in agreement with the 90% value determined by NMR in acetone.22 Indeed time-resolved IR spectroscopy indicates that the majority of the ketene produced ($\lambda_{ex} = 270$ nm) arises through the concerted path as expected from the bias toward the syn form. The carbene lifetime is expected to be longer than 40 ps based on the results of pyridine ylide nanosecond laser flash photolysis studies.²² Note that these same ns LFP experiments ($\lambda_{ex} = 308$ nm) demonstrated that the yield of pyridine trappable carbene was relatively low. Thus, it seems clear that the contribution of the carbene pathway to ketene formation is minor ($\lambda_{ex} = 270$ nm), as demonstrated by (1) approximately the same amplitude of ketene signal in chloroform and in methanol, a carbene trapping solvent, (2) the failure to detect a carbene carbonyl infrared band at about 1563 cm⁻¹, Table S7 of the SI, (3) the failure to detect a slow rise of ketene signal in chloroform, and (4) the observed low yield of trappable carbene species reported earlier.²³

Another interesting experimental finding is the absence of the internal conversion process in the excited diazo state of diazoacetone, in contrast to larger diazo carbonyl molecules such as azibenzil and BpCN₂COCH₃ ($\Phi_{IC} \approx 0.5$).

Excitation of diazoacetone and azibenzil with 270 nm radiation pumps the diazo compound to the S_n ($n \ge 4$) state as indicated by time-dependent density functional theory (TD DFT) calculations (Tables S3–S6 of the SI).^{24,25} The initially excited diazo S_n ($n \ge 4$) state may undergo an ultrafast IC process to populate the S₁ state. Thus, we do not know from which singlet

diazo excited state nitrogen extrusion proceeds. From the ultrafast rise of ketene species (<0.4 ps time constant), we can deduce that the lifetime of the diazo excited state populated must be shorter than 0.4 ps.

Diazoacetone produces ketene with a large quantum yield upon UV excitation because the diazo carbonyl compound exists predominantly in the syn conformation favoring the concerted process (Kaplan and Meloy's rule) and its simple structure does not facilitate the internal conversion process $(S_1 \rightarrow S_0)$, and therefore, IC is not a competitive deactivation channel of the diazo excited state.

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Supporting Information Available: Spectra and kinetics of ultrafast studies, DFT, and TD-DFT calculations. This material is available free of charge via the Internet at http:// pubs.acs.org.

References and Notes

- (1) Krimse, W. Eur. J. Org. Chem. 2002, 2193.
- (2) Kaplan, F.; Meloy, G. K. J. Am. Chem. Soc. 1966, 88, 950.
- (3) Wang, Y.; Yuzawa, T.; Hamaguchi, H.; Toscano, J. J. Am. Chem. Soc. 1999, 121, 2875.

(4) Burdzinski, G.; Wang, J.; Gustafson, T. L.; Platz, M. S. J. Am. Chem. Soc. 2008, 130, 3746.

- (5) Burdzinski, G.; Rehault, J.; Wang, J.; Platz, M. S. J. Phys. Chem. A 2008, 112, 10108.
 - (6) Burdzinski, G.; Platz, M. S. J. Phys. Org. Chem. 2010, 23, 308.
 (7) Wang, J.; Burdzinski, G.; Kubicki, J.; Platz, M. S. J. Am. Chem.
- Soc. 2008, 130, 11195.
 - (8) Popik, V. V. Can. J. Chem. 2005, 83, 1382.
 - (9) Bogdanova, A.; Popik, V. V. J. Am. Chem. Soc. 2004, 126, 11293.
- (10) Zhang, Y.; Burdzinski, G.; Kubicki, J.; Platz, M. S. J. Am. Chem. Soc. 2009, 131, 9646.
- (11) Burdzinski, G.; Zhang, Y.; Selvaraj, P.; Sliwa, M.; Platz, M. S. J. Am. Chem. Soc. 2010, 132, 2126.
- (12) Bogdanova, A.; Perkovic, M. W.; Popik, V. V. J. Org. Chem. 2005, 70, 9867.
- (13) Wang, J.; Burdzinski, G.; Kubicki, J.; Gustafson, T. L.; Platz, M. S. J. Am. Chem. Soc. **2008**, 130, 5418.
 - (14) Nenitzescu, C. D.; Solomonica, E. Org. Synth. 1935, 15, 62.
 - (15) Arndt, F.; Amende, J. Chem. Ber. 1928, 61, 1122.
 - (16) Burdzinski, G.; Hackett, J. C.; Wang, J.; Gustafson, T.; Haddad,
- C.; Platz, M. J. Am. Chem. Soc. 2006, 128, 13402.
 (17) Scott, A.; Radom, L. J. Phys. Chem. 1996, 100, 16502.
 - (17) Scott, A., Kadolil, L. J. Phys. Chem. 1990, 100, 10
 - (18) Trozollo, A. M. Acc. Chem. Res. **1968**, 329.
- (19) Oncescu, T.; Contineanu, M.; Constatinescu, O. J. Photochem. 1976/ 1977, 6, 103.
- (20) Wagner, B. D.; Arnold, B. R.; Brown, G. S.; Lusztyk, J. J. Am. Chem. Soc. 1998, 120, 1827.
- (21) Kovalenko, S. A.; Schanz, R.; Farztdinov, V. M.; Henning, H.; Ernsting, N. P. *Chem. Phys. Lett.* **2000**, *323*, 312.
- (22) Toscano, J. P.; Platz, M. S. J. Am. Chem. Soc. 1995, 117, 4712.
 (23) Toscano, J. P.; Platz, M. S.; Nikolaev, V.; Cao, Y.; Zimmt, M. B.
- J. Am. Chem. Soc. 1996, 118, 3527. (24) Casida, M.; Jamorski, C.; Casida, K.; Salahub, D. J. Chem. Phys.
- (25) Stratmann, R.; Scuseria, G.; Frish, M. J. Chem. Phys. 1998, 8218.
- (25) Strathann, K., Seusena, G., Prisn, W. J. Chem. Phys. 1994 JP108690N