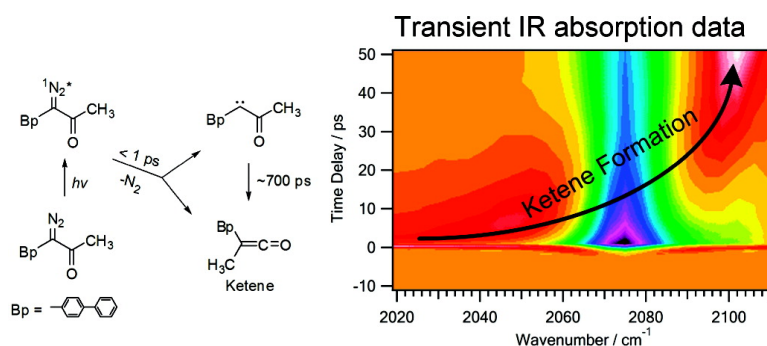


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J. Am. Chem. Soc., **2008**, 130 (12), 3746-3747 • DOI: 10.1021/ja711346z

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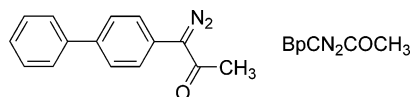
Study of Concerted and Sequential Photochemical Wolff Rearrangement by Femtosecond UV-vis and IR Spectroscopy

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The venerable Wolff Rearrangement (WR) was discovered over 100 years ago and has been thoroughly studied by chemical and physical methods.¹ Chemists have developed good intuition about the effect of the orientation of the diazo and carbonyl groups (syn favors rearrangement) and structure (WR is more common in diazo ketones than diazo esters) particularly in thermally activated processes. Yet there is still much to learn about the photochemically activated WR reaction. In principle, the photochemical Wolff Rearrangement may proceed in an excited state of the diazo precursor (in less than 1 ps), or from a vibrationally hot carbene (10–30 ps), or from a relaxed singlet carbene (100 ps–2 ns). Herein we report the use of ultrafast time-resolved UV-vis and IR spectroscopies to the study of a simple aryl diazo ketone to assess the relative importance of these processes to the light induced formation of ketenes from a diazo carbonyl precursor.



Ultrafast photolysis² (270 nm) of diazo ketone $\text{BpCN}_2\text{COCH}_3$ in acetonitrile (ACN) produces the transient UV-vis spectra of Figure 1. The first species detected is formed at 450 nm and decays within the laser pulse (300 fs). Based on our previous studies,^{3,4} this transient is assigned to a singlet excited state of the diazo ketone. As it decays, transient absorption attributed to the singlet keto-carbene grows at 380 nm. This assignment is consistent with our published studies of other singlet biphenylcarbenes^{3,4} and is in good agreement with TD-DFT calculations in the gas phase that predict that ${}^1\text{BpCCOCH}_3$ has its absorption maximum at 348 nm ($f = 0.5041$, Supporting Information, Table S1).

Between 1 and 30 ps after the laser pulse, the transient absorption band of ${}^1\text{BpCCOCH}_3$ grows and narrows, due to solvation⁴ and vibrational cooling^{2–5} of the carbene. The relaxed singlet carbene has a lifetime of 800 ± 100 ps in acetonitrile (Supporting Information, Figure S1). Similar results were observed in acetonitrile- d_3 which indicates that the singlet carbene lifetime is not limited by C–H(D) insertion into the solvent. The decay of the carbene is not accompanied by the growth of new transient absorption characteristics of a carbene-ACN ylide. Such an ylide is predicted by TD-DFT calculations to have its absorption maximum at 375 nm ($f = 0.3554$, Supporting Information, Table S2). The parent biphenyl carbene-ACN ylide absorbs at 370 nm.^{3a} These observations indicate that ${}^1\text{BpCCOCH}_3$ is consumed only by a unimolecular process, intersystem crossing (ISC, if the triplet is the ground state of the carbene), or Wolff Rearrangement, at ambient temperature. In a separate study,⁶ we concluded that carbene BpCCOCH_3 has a singlet ground state in acetonitrile. Thus, intersystem crossing does

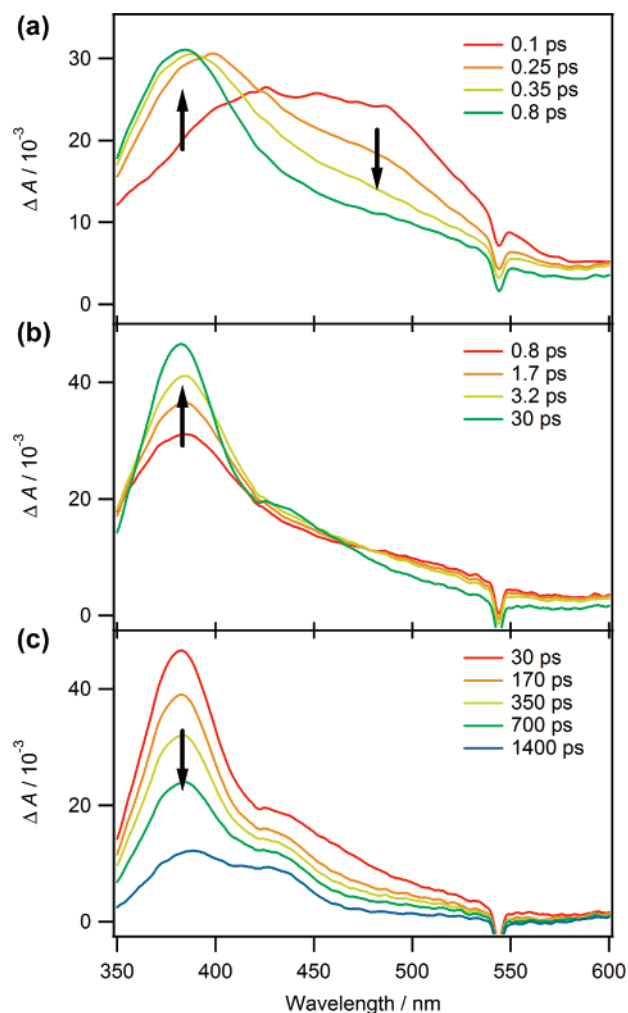


Figure 1. Transient spectra obtained by the photolysis of $\text{BpCN}_2\text{COCH}_3$ in acetonitrile. Spectra were generated by ultrafast LFP (270 nm) with time windows of (a) 0.01–0.8 ps, (b) 0.8–30 ps, and (c) 30–1400 ps.⁸

not contribute to the decay of ${}^1\text{BpCCOCH}_3$. Time-resolved IR studies to be discussed confirm that ${}^1\text{BpCCOCH}_3$ is consumed by WR.

The same system was studied by femtosecond IR transient absorption spectroscopy as shown in Figure 2. There is an immediate bleaching of the diazo vibration and the immediate (<1.3 ps) formation of a broad absorption band (positive) which straddles the diazo bleach (negative). The broad band is attributed to the prompt formation of vibrationally excited ketene. The ketene band narrowing and blue shift is observed over a 50 ps time window. The same type of blue shift of a ketene was observed by Glich and co-workers.⁷ After 50 ps, the ketene band continues to gain intensity

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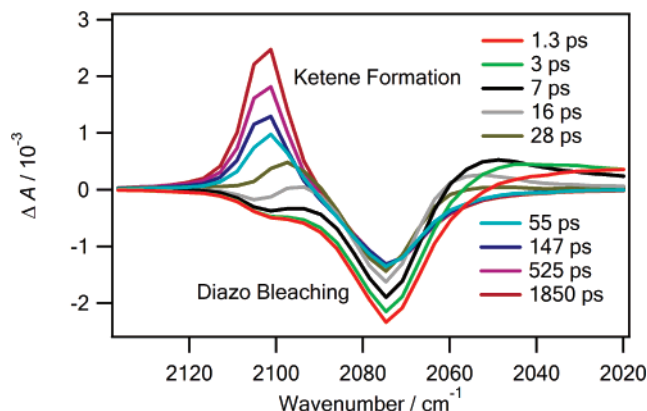
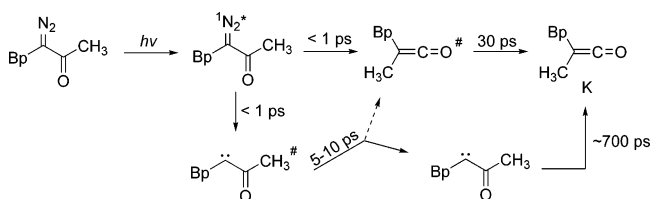


Figure 2. Ultrafast time-resolved IR data produced by the photolysis at 270 nm of $\text{BpCN}_2\text{COCH}_3$ in acetonitrile. Spectra were collected with a time window of 1.3–1850 ps.

Scheme 1



with a time constant of 700 ps (Supporting Information, Figure S2). We propose that the diazo excited state, $^1\text{BpCN}_2\text{COCH}_3^*$, decays in < 1 ps by both WR to form hot ketene and by the formation of ketocarbene. The data indicate that the relaxed ketocarbene undergoes WR in 700 ps in good agreement with the UV–vis study. It is possible that some vibrationally hot carbene is formed upon fragmentation of $^1\text{BpCN}_2\text{COCH}_3^*$ and undergoes WR on this time scale (30 ps), but the data are inconclusive on this point. The IR data obtained in chloroform are similar to those in acetonitrile (Supporting Information, Figure S3).

In summary, the ketene product (K) is clearly formed by two mechanisms (Scheme 1). The prompt WR process forms a hot ketene (#) in less than 1 ps, monitored around 2020 cm^{-1} , and this species undergoes vibrational cooling (VC) as manifested by a frequency upshift. Prompt formation of ketene is a concerted process; WR occurs in the diazo excited state from which hot ketene is formed directly. The slower 700 ps process is the rate of WR of a thermalized singlet carbene in acetonitrile in good agreement with

the results of ultrafast UV–vis spectroscopy. We speculate that photolysis of the syn conformer of the precursor leads to prompt formation of hot ketene from $^1\text{BpCN}_2\text{COCH}_3^*$ by WR in concert with nitrogen extrusion and that excitation of the anti conformer of $\text{BpCN}_2\text{COCH}_3$ promotes just nitrogen extrusion, carbene formation, and ultimately the formation of thermalized carbene.

Acknowledgment. This work was performed at The Ohio State University Center for Chemical and Biophysical Dynamics. Support of this work by the National Science Foundation and the OSU Supercomputer Center is gratefully acknowledged. G.B. thanks the Foundation for Polish Science (FNP) for a “Homing” Grant for the year 2007. J.W. thanks the Graduate School at the Ohio State University for a Presidential Fellowship.

Supporting Information Available: Details of calculations (Tables S1 and S2) and transient spectra and kinetic traces (Figures S1–S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA711346Z