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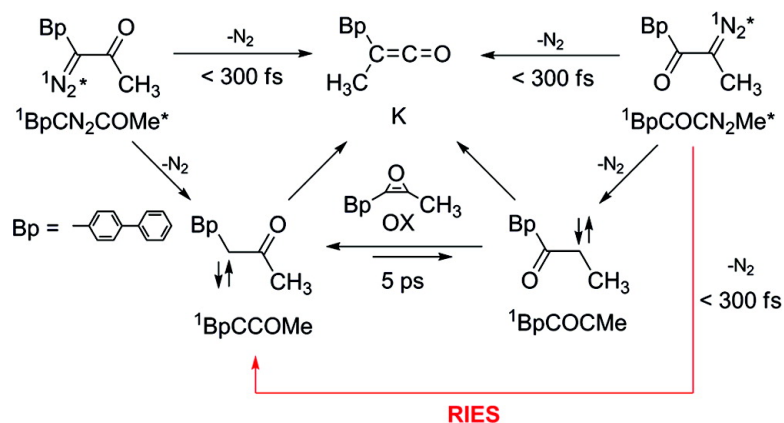
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## Ultrafast Carbene–Carbene Isomerization

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The conversion of  $\alpha$ -diazo ketones into ketenes (K) was discovered by Wolff in 1902.<sup>1</sup> This reaction, now known as the Wolff rearrangement (WR), has been extensively applied in synthetic chemistry, photolithography, and drug delivery.<sup>2</sup>

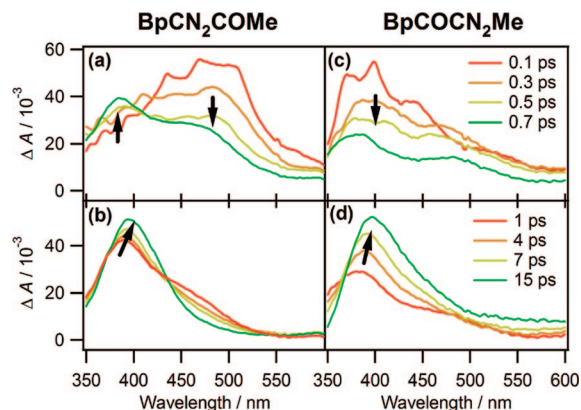
Two isomeric  $\alpha$ -diazo ketones,  $\text{PhCOCN}_2\text{Me}$  and  $\text{PhCN}_2\text{COMe}$ , afford the same mixture of stable products upon both direct and triplet-sensitized photolysis.<sup>3</sup> It was proposed that the two isomeric carbonyl carbenes rapidly interconvert through an oxirene (OX) intermediate or transition state.<sup>3</sup> Theory predicted that the potential energy surface (PES) connecting the carbene with the corresponding oxirene is very flat (0.2–0.5 kcal/mol) and that the oxirene can be a saddle point or a minimum on the PES depending on the theory used.<sup>4</sup> Low temperature photolysis experiments support this conclusion. Even at 77 K, the carbene–carbene interconversion ( $^1\text{PhCOCMe}$  to  $^1\text{PhCCOMe}$ ) cannot be suppressed.<sup>3</sup> The proposed mechanism is shown in Scheme 1, illustrated with the *para*-biphenyl analogs to be used in this study.

There are only two reports of the direct observations of oxirenes in cryogenic matrices,<sup>5</sup> and one of them was later disputed.<sup>6</sup>

Ultrafast photolysis<sup>7</sup> (308 nm) of  $\text{BpCN}_2\text{COMe}$  (Bp = *p*-biphenyl) in methanol produces the transient spectra shown in Figure 1a,b. A broadly absorbing transient, with absorption maximum at 475 nm, is formed within the laser pulse and decays in 300 fs. As this transient absorption decays, a new transient is observed with  $\lambda_{\text{max}} = 380$  nm. Following our previous studies, the former band is attributed to an excited state of the diazo precursor  $^1\text{BpCN}_2\text{COMe}^*$  and the latter to singlet ketocarbene  $^1\text{BpCCOMe}$ .<sup>8</sup> The assignment is in accord with TD-DFT calculations ( $\lambda_{\text{max}} = 348$  nm,  $f = 0.5041$ , Supporting Information (SI), Table S1). The maximum of the carbene transient absorption red shifts to 400 nm in a 1–15 ps time window. Following our studies of *p*-biphenyltrifluoromethylcarbene,<sup>9</sup> the red shifts are attributed to the dynamics of carbene solvation. Finally, the relaxed singlet carbene decays monoexponentially with a time constant of  $120 \pm 17$  ps in methanol, presumably by OH insertion to form an ether.<sup>10</sup>

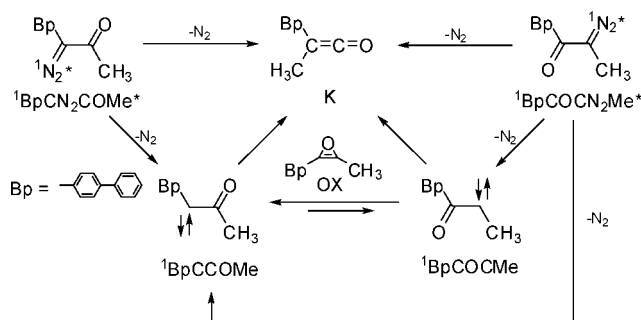
Ultrafast photolysis of the isomeric carbonyl diazo compound ( $\text{BpCOCN}_2\text{Me}$ ) in methanol produces a broad transient absorption centered at 400 nm, immediately after the laser pulse (300 fs), which is assigned to a diazo singlet excited state  $^1\text{BpCOCN}_2\text{Me}^*$ . The spectrum of this diazo excited state differs from that of  $^1\text{BpCN}_2\text{COMe}^*$ . Excitation of the two isomeric diazoketones does not produce a common excited-state species.

As the transient absorption of  $^1\text{BpCOCN}_2\text{Me}^*$  diminishes, the presence of a band at 380 nm can be observed. Between 1 and 15 ps after the laser pulse, the transient absorption maximum is also red-shifted to 400 nm, to yield a spectrum that is the same as that assigned to  $^1\text{BpCCOMe}$ . The lifetime of the 400 nm band is 110



**Figure 1.** Transient spectra of  $\text{BpCN}_2\text{COMe}$  (left) and  $\text{BpCOCN}_2\text{Me}$  (right) in methanol. Spectra were generated by ultrafast LFP (308 nm) with time windows of (a) and (c) 0.1–0.7 ps; and (b) and (d) 1–15 ps.

## Scheme 1



$\pm 5$  ps, the same as that of  $^1\text{BpCCOMe}$  (obtained from  $^1\text{BpCN}_2\text{COMe}^*$ ) in methanol within experimental error. TD-DFT calculations predict that  $^1\text{BpCOCMe}$  absorbs at 292 nm ( $f = 0.4980$ , SI, Table S2), which is outside of our detection window.<sup>10</sup> Thus, we conclude that the decay of  $^1\text{BpCOCN}_2\text{CH}_3^*$  in methanol eventually produces isomeric carbene  $^1\text{BpCCOMe}$  1–15 ps after the initial laser pulse. Similar results were obtained in acetonitrile and cyclohexane, although most notably,  $^1\text{BpCCOMe}$  has longer lifetimes in acetonitrile (Table 1).

Two mechanisms consistent with these results can be advanced, as shown in Scheme 1. The diazo excited state,  $^1\text{BpCOCN}_2\text{Me}^*$ , can decompose to form the corresponding carbene  $^1\text{BpCOCMe}^\#$  with substantial excess vibrational energy. Subsequently, this hot species can isomerize to  $^1\text{BpCCOMe}$ . Alternatively, a more economical explanation is possible; migration of the oxygen atom and loss of the  $\text{N}_2$  molecule could proceed in one step in the diazo excited state of  $^1\text{BpCOCN}_2\text{Me}^*$  to form the isomeric carbene  $^1\text{BpCCOMe}$  without intervention of hot or relaxed  $^1\text{BpCOCMe}$ . A related “Rearrangements in the Excited States (RIES)” mech-

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**Table 1.** Decay Time Constants of Singlet Carbene Formed upon Photoexcitation of BpCN<sub>2</sub>COME and BpCOCN<sub>2</sub>Me

|                      | BpCN <sub>2</sub> COME |                              | BpCOCN <sub>2</sub> Me |                              |
|----------------------|------------------------|------------------------------|------------------------|------------------------------|
|                      | $\tau$ /ps             | $\lambda_{\text{probe}}$ /nm | $\tau$ /ps             | $\lambda_{\text{probe}}$ /nm |
| methanol             | 120 $\pm$ 17           | 395                          | 110 $\pm$ 5            | 395                          |
| methanol- <i>O-d</i> | 130 $\pm$ 10           | 395                          | 110 $\pm$ 10           | 395                          |
| acetonitrile         | 700 $\pm$ 30           | 380                          | 720 $\pm$ 30           | 380                          |
| cyclohexane          | 180 $\pm$ 20           | 365                          | 140 $\pm$ 30           | 365                          |

anism has been proposed for 1,2-hydrogen shift<sup>11</sup> and Wolff rearrangements<sup>8</sup> in diazo excited states.

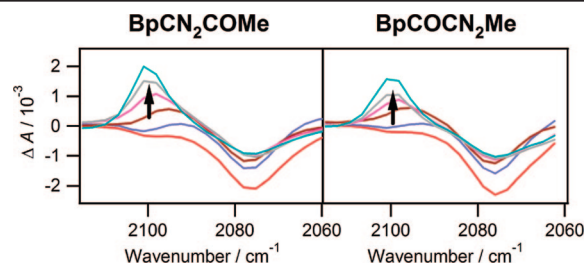
Upon ultrafast LFP of BpCN<sub>2</sub>COME, the growth of the carbene band is biexponential (SI, Figure S1a). The fast component, which is within our instrument response, is due to the instantaneous formation of the singlet carbene. The growth observed over a 1–15 ps time delay, whose amplitude is  $\sim 1/3$  of the instantaneous rise, is mainly due to band sharpening (vibrational cooling) and carbene solvation (Figure 1b).

Upon ultrafast LFP of isomeric diazo precursor, BpCOCN<sub>2</sub>Me, the carbene growth is also biexponential. However, due to the severe overlap of the <sup>1</sup>BpCOCN<sub>2</sub>Me\* and <sup>1</sup>BpCCOME transient absorptions, any fast growth of the carbene (if at all present) cannot be resolved. As shown in Figure 1d, however, a significant amount of the isomeric carbene is present 1 ps after the laser pulse. We propose that rearranged carbene formed in 1 ps is produced from the diazo excited state by the RIES mechanism. Between 1 and 15 ps, a more intense growth (50% of the total amplitude) is observed relative to BpCN<sub>2</sub>COME (33% of the total amplitude, compare Figure 1c and d) is recorded. We posit that the majority of the 1–15 ps growth of BpCOCN<sub>2</sub>Me is by conversion of “invisible” <sup>1</sup>BpCOCMe (or <sup>1</sup>BpCOCMe<sup>#</sup>), which absorbs outside of our detection window, to form its “visible” isomeric carbene <sup>1</sup>BpCCOME. Carbene solvation will also proceed but is a minor contributor of the intensity growth. The kinetic traces indicate that the time constant for the conversion from <sup>1</sup>BpCOCMe (or <sup>1</sup>BpCOCMe<sup>#</sup>) to <sup>1</sup>BpCCOME is 5 ps (SI, Figure S1b).

TD-DFT calculations predict the corresponding oxirene absorbs at 375 nm ( $f = 0.6307$ , SI, Table S3). We do not observe any spectral signatures for the oxirene in this study. It is possible that the oxirene absorbs at the same wavelength as <sup>1</sup>BpCCOME and if so then severe overlap of these two species may prevent us from confirming the existence of the oxirene. However, to be economical, we prefer to assign the 380–400 nm band solely to <sup>1</sup>BpCCOME. We conclude that the oxirene is either an undetectable transition state or is a true intermediate but given its very short lifetime, the resulting concentration of the oxirene is too low to detect.

Gas phase DFT calculations were performed on the two isomeric carbenes (SI, Table S4). <sup>1</sup>BpCCOME is 7.8 kcal/mol lower in energy than <sup>1</sup>BpCOCMe at 0 K. The transition state connecting the two isomeric carbenes was not located but the oxirene was located as a minimum, which is 0.7 kcal/mol higher in energy than <sup>1</sup>BpCOCMe. As found previously for formylcarbene, the PES connecting the oxirene and the carbene is flat,<sup>4</sup> thus the activation barrier for the conversion of <sup>1</sup>BpCOCMe to <sup>1</sup>BpCCOME should be close to 0.7 kcal/mol. This is in good agreement with the observation that some rearranged carbene is formed between 1 and 15 ps after excitation.

Ultrafast photolysis ( $\lambda_{\text{ex}} = 270$  nm) of the two isomeric diazo compounds was also performed with infrared detection, in acetonitrile, allowing us to observe the formation of the WR product ketene K (Figure 2). Very similar results were obtained for the two diazo compounds. In the region of 2060–2140 cm<sup>−1</sup>, diazo bleaching (2076 cm<sup>−1</sup>) is observed immediately after the laser pulse

**Figure 2.** Transient IR spectra produced by photolysis of BpCN<sub>2</sub>COME (left) and BpCOCN<sub>2</sub>Me (right) in acetonitrile. Spectra were generated by ultrafast LFP (270 nm) with time delays: 1 ps (red), 12 ps (purple), 28 ps (brown), 49 ps (pink), 110 ps (grey), and 2580 ps (blue).

(300 fs) and the ketene K-band (2100 cm<sup>−1</sup>) grows biexponentially, with time constants of 40–50 ps and 700–1000 ps. Following our previous ultrafast report of a WR,<sup>8</sup> the fast component is related to vibrational cooling of the ketene. Ketene, formed within 1 ps (by WR in the diazo excited states), is produced with excess vibrational energy, and the 40–50 ps process is related to vibrational cooling of the “hot” molecule. The slow (700–1000 ps) growth of the ketene band must be due to WR of the singlet carbene, which is in excellent agreement with the decay time constant of the relaxed carbene observed by UV–vis detection.

In summary, we propose that the diazo excited state, <sup>1</sup>BpCOCN<sub>2</sub>Me\*, decays by three processes in 300 fs. Concerted extrusion of nitrogen and WR to form ketene is one decay route. In the second route, the excited state will lose nitrogen to form either hot or relaxed <sup>1</sup>BpCOCMe, and in the third pathway, the excited state will lose nitrogen and undergo an oxygen migration to form rearranged carbene <sup>1</sup>BpCCOME in one step. The relatively unstable carbene, <sup>1</sup>BpCOCMe, isomerizes to the more stable carbene <sup>1</sup>BpCCOME with a time constant of 5 ps.

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**Supporting Information Available:** DFT and TD-DFT calculations, ultrafast kinetic traces, and syntheses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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