

Direct Observation of 1,2-Hydrogen Migration in the Excited States of Alkyl Diazo Esters by Ultrafast Time Resolved IR Spectroscopy

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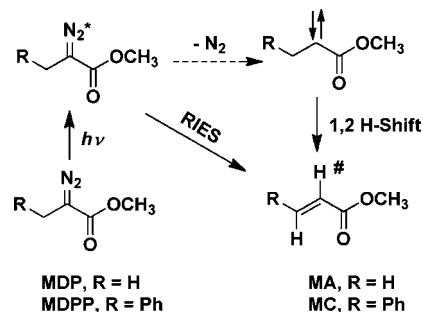
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The photochemistry of diazo compounds and diazirines has been extensively studied. It has been deduced that formal carbene rearrangement products can be formed via two pathways: directly from the excited state ("rearrangement in the excited state", named by Liu as RIES¹) or from a free carbene species.² Historically, the dual mechanisms were deduced from studies of photolyzed products. The support of RIES was provided by the observation of a "nontrappable carbene" route to rearranged products.² Recently an RIES process with diazo compounds was directly supported using ultrafast spectroscopy. The ultrafast formation of β - and γ -lactams was observed by time-resolved IR spectroscopy, likely from an excited diazoamide.³ Experimental observation of distinct carbonyl vibrations led to the conclusion that β -lactam is formed via RIES, while γ -lactam is produced by RIES as well as the intermediacy of relaxed singlet carbene. Another example of RIES studied recently is a Wolff rearrangement process in concert with nitrogen extrusion proceeding in photoexcited diazo carbonyl compounds. In these studies we found that ketenes can be formed by two mechanisms: in an RIES process proceeding in the diazo carbonyl excited state on a fast time scale (<0.3 ps), while the stepwise process involving a carbene intermediate proceeds with a time constant of 1–1000 ps depending on the carbene structure (cyclic versus acyclic).^{4–8}

Another intriguing process is the production of alkenes upon photolysis of alkyl diazo compounds. In this case an RIES process involves the 1,2 migration of hydrogen in concert with nitrogen extrusion.⁹ Recently we reported femtosecond time-resolved UV–vis transient absorption studies of *para*-biphenyldiazoethane (BpCN₂CH₃) and *para*-biphenyldiazomethane (BpCN₂H).¹⁰ The experimentally observed absorption bands were assigned to the diazo excited states (with $\lambda_{\text{max}} = 480$ nm and lifetimes less than 300 fs) and the singlet carbenes (with $\lambda_{\text{max}} = 360$ nm and lifetimes of from a few hundreds of picoseconds in acetonitrile to ~10 ps in a carbene scavenging solvent such as methanol). The observed quantum yield of formation of the carbene ¹BpCCH₃ is ~40% lower than that of ¹BpCH. This was rationalized as an example of an RIES process, which leads directly from the diazo excited state to *para*-vinylbiphenyl and consequently decreases the carbene yield. In these studies the rise of *para*-vinylbiphenyl has not been detected in the UV–vis region. Ultrafast IR spectroscopy is also not a promising tool based on calculations that predict weak C=C product bands (Table S1). Thus, we decided to choose other precursors, where the rearranged alkene product is conjugated with an ester group (Scheme 1). Even if the C=C vibration remains weak, the presence of the carbonyl group should facilitate observation of an alkene product by ultrafast IR spectroscopy. The quantum yield of

alkene formation is expected to be high as the Wolff rearrangement process of carbene esters is less than ketocarbenes.⁴ In this paper the mechanism leading excited diazo esters to alkene species will be constructed based on stationary and transient absorption IR spectroscopy and theoretical methods. Evidence will be presented in favor of the RIES mechanism.

Scheme 1. Reaction Pathways for Alkyl Diazo Ester Compounds upon UV Irradiation



Time-resolved infrared spectra were obtained upon ultrafast photolysis (266 nm) of a solution of methyl 2-diazopropionate (MDP, CH₃CN₂CO₂CH₃) in chloroform over a spectral window of 1750–1650 cm⁻¹ (Figure 1). Two distinctive spectral signatures were observed. A negative band at 1693 cm⁻¹ can be assigned to diazo bleaching (C=O stretching vibration according to calculations, Table S2) caused by the decreased concentration of MDP in the ground state due to the photoexcitation. Formation of a positive band peaking at 1733 cm⁻¹ corresponds to a C=O stretching vibration (Table S3) of methyl acrylate (MA, H₂C=CHCO₂CH₃). The bleaching of the diazo band and the positive absorption signal are present immediately (at delays shorter than 1 ps). Figure S1 shows that the diazo bleaching band observed at 2081 cm⁻¹ (N=N stretching vibration, Table S2) does not undergo any change over a 1–400 ps time window. On this basis we can deduce that the intensity of the C=O bleaching band in Figure 1 is constant, although the initially observed MA absorption band is very wide and is red-shifted relative to the thermalized species. At longer delay times, up to 70 ps, a frequency upshift to 1733 cm⁻¹ is observed. The evolution of this transient absorption band can be assigned to vibrational cooling.^{6,11} After the cooling process is complete (~70 ps after the laser pulse), the MA IR band persists without change up to 3 ns, the temporal limit of detection. The presence of wide alkene product carbonyl bands at short delays (~1 ps) indicates that the RIES process takes place on the ultrafast time scale. At longer delay times no rise of the band integration is observed (Figure S2); thus the ultrafast RIES process is the only pathway of alkene formation over a 3 ns time window under these conditions. The

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presence of **MA** is also confirmed by the stationary IR spectrum of the bleached solution and upon comparison with authentic **MA** sample in the same solvent (Figure S3).

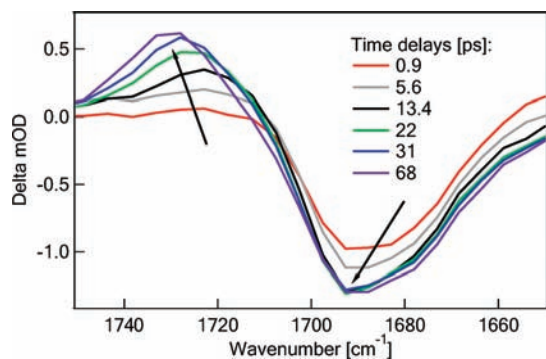


Figure 1. Time-resolved infrared transient absorption spectra produced in chloroform after photoexcitation of methyl 2-diazopropionate (**MDP**) at 266 nm.

The study of a second compound, methyl 2-diazo-3-phenyl propionate (**MDPP**, $\text{PhCH}_2\text{CN}_2\text{CO}_2\text{CH}_3$), in chloroform upon ultrafast photolysis (266 nm) reveals similar transient absorption infrared spectra (Figure S4). The only observed difference is the observation of two absorption bands of alkene product (methyl cinnamate, **MC**): the largely $\text{C}=\text{C}$ absorption band at 1635 cm^{-1} in addition to the $\text{C}=\text{O}$ absorption at 1723 cm^{-1} . Both IR bands are also present in the stationary IR spectrum of a bleached solution (Figure S5), in line with theoretical calculations (Table S4) and steady state FTIR spectra (Figure S5). Due to the lack of a diazo ground state recovery process over a 1 ns time window ($\text{N}=\text{N}$ stretching vibration at 2087 cm^{-1} , Figure S6, Table S5), again, we can deduce that the observed changes in Figure S4 are due solely to the formation of **MC**. Initially, the nascent hot **MC**, $\text{C}=\text{O}$ absorption band clearly undergoes narrowing and a frequency upshift to 1723 cm^{-1} over an 80 ps time window.

The mechanism of Scheme 1 also assumes that there are carbene intermediates leading to alkene species. We can assume that singlet carbene lifetimes are longer than 1 ps, since the shortest lifetime of any singlet carbene measured to date is 2.3 ps (produced from the photoexcited diazo Meldrum's acid⁶). Thus, carbene intermediacy should result in a slow (limited by carbene lifetime) rise of alkene product. However over a 1500 ps time window only an instantaneous product rise is observed (with a time constant less than 0.4 ps). The absence of carbene species is also confirmed by the failure to experimentally observe a distinct positive IR band, which can be assigned to singlet carbene, despite strong IR oscillator strength, predicted at 1606 cm^{-1} and 1607 cm^{-1} for $\text{CH}_3\text{CCO}_2\text{CH}_3$ and $\text{PhCH}_2\text{CCO}_2\text{CH}_3$, respectively (Tables S6 and S7). Also NMR and GC-MS analysis performed for a bleached solution of **MDP** and **MDPP** in methanol-*d*₄ does not indicate the formation of any product of insertion of singlet carbene into an OD bond. Based on these observations we can state that carbene species are not formed or must be formed with a very low quantum yield with these precursors under these conditions.

Excitation of **MDP** and **MDPP** with 266 nm radiation pumps the diazo compound to the S_2 state as indicated by time-dependent

density functional theory (TD DFT) calculations^{12–14} (Tables S8 and S9) which predict that $\text{S}_0 \rightarrow \text{S}_2$ transition has a large oscillator strength transition at 259.3 nm ($f = 0.0444$) and 291.9 nm ($f = 0.0242$) for **MDP** and **MDPP**, respectively. The initially excited diazo S_2 state may undergo an ultrafast IC process to populate the S_1 state, so we do not know from which singlet diazo excited state nitrogen extrusion proceeds. From the ultrafast rise of **MA** and **MC** (<0.4 ps time constant), we can deduce that the lifetime of the diazo excited state must be shorter than 0.4 ps. This agrees with observations made for other diazo excited states.⁴ Based on the absence of signal recovery in the bleached diazo vibrational band we can conclude that the diazo excited state does not return to the ground state in these two systems. The quantum yield of reaction leading to the diazo excited state to decomposition must be close to unity in chloroform with 266 nm light.

In summary, UV photoexcitation of **MDP** and **MDPP** in chloroform with 266 nm light produces the S_2 excited state. A diazo excited state undergoes rearrangement to produce **MA** and **MC** in concert with molecular nitrogen extrusion in less than 1 ps. This RIES process is confirmed by an instantaneous rise of IR transient absorption bands assigned to alkene products. Singlet carbene intermediacy in the alkene formation process is not experimentally observed with these two alkyl diazo esters and 266 nm excitation.

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Supporting Information Available: Figures S1–S6, Tables S1–S9, details of calculations, and complete citation of ref 14. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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