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Picosecond Optical Grating Calorimetry of Singlet Methylene in Benzene

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Many chemical reactions are believed to involve the initial formation of weak, highly reactive complexes. For example, several reactions of electrophilic carbenes with various nucleophiles are thought to involve π complexes.[1] However, while kinetic and product studies often suggest their existence, their direct detection is often quite difficult. In fact, no direct evidence for such complexes has been found to date. In this regard, we wish to now report the use of picosecond optical grating calorimetry to directly observe a highly reactive transient in the photochemical decomposition of diazomethane in benzene.[2,3] Based on the obtained kinetic and thermodynamic data, we believe this transient is a complex formed between singlet methylene and benzene.

Photochemical decomposition of diazomethane yields methylene, which reacts with benzene to form toluene and cycloheptatriene (via norcaradiene), Scheme 1.[4] Although concerted C=C and C—H insertion into benzene by methylene is possible, several experiments on the effect of various solvents on the product ratio suggest the intermediacy of a complex between methylene and benzene.[5]

The diffracted optical grating signals obtained following picosecond excitation (355 nm, 25 ps) of diazomethane and of a calibration compound copper(II) tetramethylheptanedionate in C_6H_6 are shown in Figure 1. Fast, radiationless decay of the calibration compound, <100 ps, yields a single heat deposition. In contrast, excitation of diazomethane results in two heat depositions, corresponding to a fast and a slow chemical process. Analysis of the experimental wave forms yields the ratio of the magnitude of the fast to the total heat deposition, $R = 0.39 \pm 0.02$, and the rate constant for the slow deposition, $k_2 = (2.4 \pm 0.3) \times 10^9\ s^{-1}$. The details of the analysis have been previously described.[2b,c] Excitation of diazomethane in pentane, ether, cyclohexene, hexafluorobenzene, and 2,3-dimethyl-2-butene all result in only a single, fast heat deposition.

The reaction enthalpies for the two processes can be determined if the total enthalpy change for the reaction of diazomethane with benzene is known. This value can be obtained by photoacoustic calorimetry.[6] Excitation of diazomethane in C_6H_6 (355 nm, 10 ns) results in only a single heat deposition. The experimental reaction enthalpy, ΔH_r, is −43.1 ± 1.5 kcal/mol, which is in good agreement with the calculated value of −43.3.[7] The reaction enthalpies for the fast, ΔH_1, and the slow, ΔH_2, heat depositions observed in the picosecond grating experiments can be calculated using the equations, $\Delta H_1 = E_{h\nu} - R(E_{h\nu} - \Delta H_r)$ and $\Delta H_2 = (\Delta H_r - E_{h\nu})(1 - R)$, where $E_{h\nu}$ is the photon energy, 80.6 kcal/mol. The calculated ΔH_1 and ΔH_2 values are +32.3 ± 3.1 and −75.4 ± 3.5 kcal/mol, respectively, Figure 2.[11]

The fast heat deposition corresponds to the formation of the transient, and the slow to its decay to products. The loss of

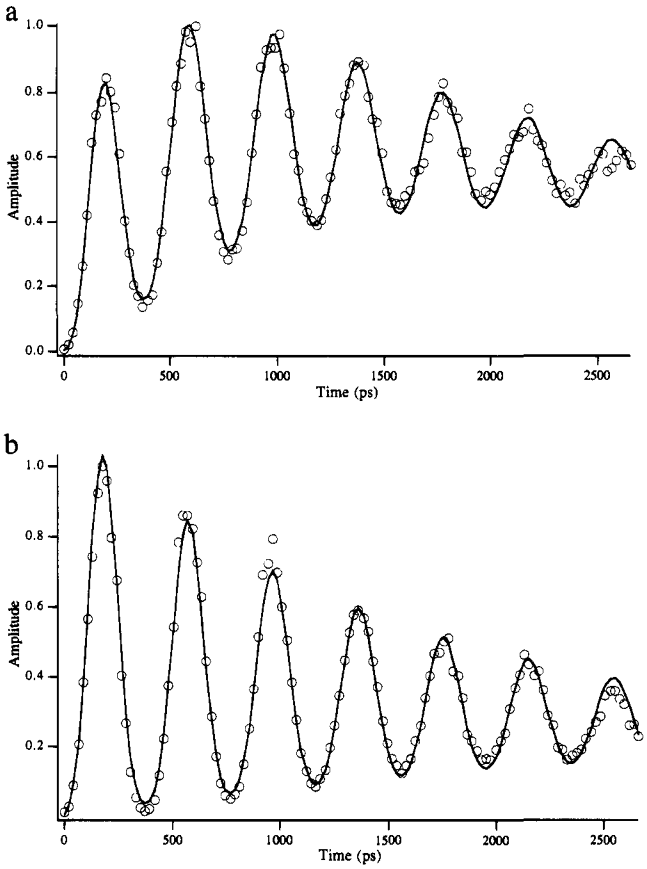
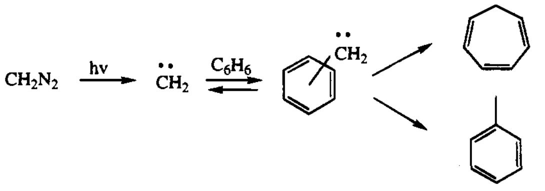


Figure 1. (a) Transient grating signal amplitude vs time following excitation of diazomethane (355 nm, 25 ps, <1 mJ) in C_6H_6. (b) Transient grating signal amplitude vs time following excitation of copper(II) tetramethylheptanedionate. The solid lines are the best fit to the experimental data.

Scheme 1



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(7) (a) Calculated using the 4.1:1 yield of cycloheptatriene:toluene and the ΔH_f values of benzene (19.8 kcal/mol),[8] toluene (12.0 kcal/mol),[8] cycloheptatriene (43.9 kcal/mol),[8] and diazomethane (61.0 kcal/mol, PM3).[9] (b) The rate of rearrangement of norcaradiene to cycloheptatriene is not known. However, the enthalpy change for the reaction is small, 4.1 kcal/mol,[10] and does not affect the overall reaction enthalpy significantly. (c) Several ΔH_f values have been suggested for CH_2N_2, see: Laufer, Okabe, H. *J. Am. Chem. Soc.* **1971**, *93*, 4137.

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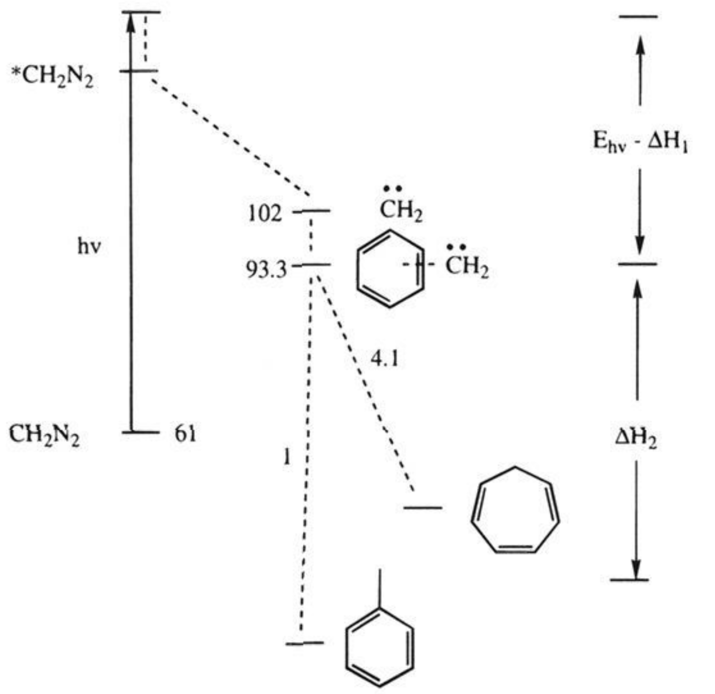
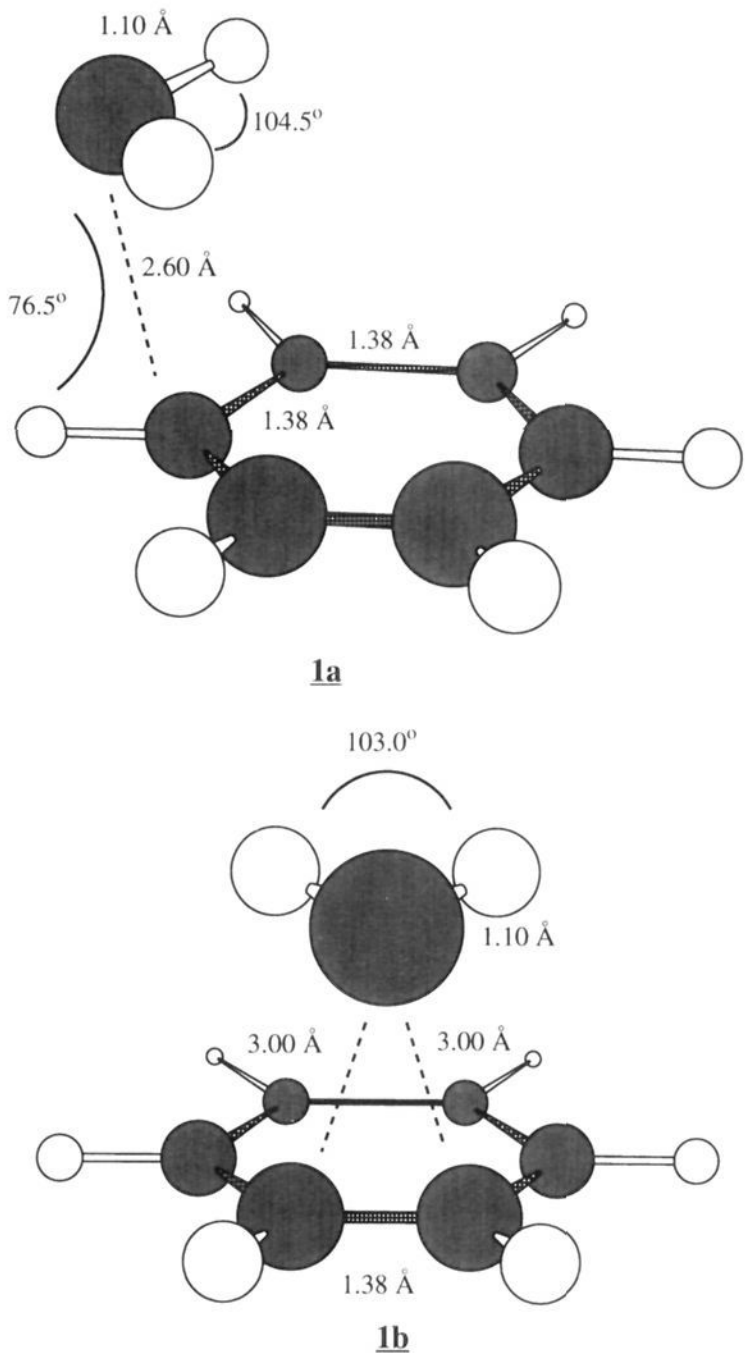


Figure 2. Energetics (kcal/mol) of the photochemical reaction of diazomethane in benzene as determined by transient grating optical calorimetry.

molecular nitrogen from diazomethane is highly efficient and rapid, so the formation of methylene, and possibly complexation with benzene, is included in the fast heat deposition. Importantly, the reaction enthalpies require that neither toluene nor cycloheptatriene be formed rapidly, but rather that *both* are formed from the transient.[12]

Possible candidates for the transient include singlet and triplet methylene and a methylene/benzene complex. Using ΔH_1 and the heat of formation of diazomethane, 61.0 kcal/mol,[9] the calculated experimental heat of formation of a CH_2 transient is 93.3 ± 3.1 kcal/mol, Figure 2. This value is significantly less than that of singlet methylene, 102 kcal/mol, but similar to that of triplet methylene, 93 kcal/mol.[13] However, previous studies have clearly indicated that direct irradiation of diazomethane yields products via the singlet state of methylene and not the triplet state.[5]

Consequently, we believe the transient is a weak complex between singlet methylene and benzene and is potentially responsible for the previously observed solvent effects on the chemistry of methylene.[5] Support for such a complex is obtained from *ab initio* calculations. Geometry optimization was performed at the RHF/6-31G* level, and electron correlation was included with second-order perturbation theory, using MP2 at these optimized geometries.[9] Two stationary points were located for weak π complexes, Figure 3. Their stability appears to result from weak electrostatic interactions between the electrophilic carbene and the π electrons of the benzene. The calculated dissociation energy of the more stable complex **1a**, 7.2 kcal/mol, is similar to the experimental dissociation energy of the complex, 8.7 ± 3.1 kcal/mol, obtained from the heats of formation of the complex, singlet methylene, and benzene.[14]



1a

1b

Figure 3. RHF/6-31G* optimized structures of methylene−benzene complexes **1a**,**b**.

In conclusion, picosecond optical grating calorimetry has been used to investigate the photochemical decomposition of diazomethane in benzene. The results indicate that a transient is formed in the reaction which we believe is a weak complex formed between singlet methylene and benzene.[15] We believe this technique is extremely useful in the calorimetric identification of such species in light of the inherent difficulties associated with most spectroscopic techniques. We hope to continue to investigate other such weak, reactive complexes using this technique.

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(11) The optoacoustic experiment measures density fluctuations which are due to both thermal expansion and reaction volume changes. Unfortunately, under the experimental conditions, we are unable to differentiate the two contributions. Consequently, our analysis neglects any reaction volume changes. Assuming that the loss of molecular nitrogen from diazomethane results in a positive reaction volume change and no complexation of the carbene occurs, the heat of reaction would be more endothermic than the calculated value of +32.3 kcal/mol. An estimated value of ~10 mL/mol for the reaction volume increase would increase the value by 2.9 to +35.2 kcal/mol. The heat of formation of the CH_2 transient would then be 96.2 kcal/mol, which is still less than that for singlet CH_2. However, if the reaction volume change is larger, the enthalpic criterion for distinguishing the complex from singlet CH_2 decreases.

(12) If either toluene or cycloheptatriene is formed rapidly and included in the fast heat deposition, the heat of formation of the transient would be greater than that of methylene. However, we cannot rule out the possibility that a fraction of either of these products is formed rapidly.

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(14) The energies (in hartrees) of methylene, benzene, and the complexes **1a**,**b** are −38.969 883, −231.456 4779, −270.437 846 and −270.435 592, respectively. The dissociation energy of complex **1b** is 5.8 kcal/mol.

(15) At present, we cannot experimentally distinguish between π and σ complexes. The σ-bonded biradical intermediate has been proposed and previously reported to be an intermediate in the isomerization of bicyclo-[2.2.1]hepta-2,6-diene to cycloheptatriene (via norcaradiene).[16] However, several experimental facts seem to suggest that it may not be the observed transient. First, the experimental heat of formation of a methylene−benzene complex is 113.1 ± 3.1 kcal/mol. Using the activation energy for the rearrangement, 50.6 kcal/mol,[16] and the diene heat of formation, 57.4 kcal/mol,[17] the heat of formation of the biradical can be estimated to be 108 kcal/mol, which is significantly less than that of the observed transient. Second, the predicted ratio of cycloheptatriene to toluene observed in the rearrangement of the diene at 25 °C is >150,[16] which is significantly larger than the observed value of 4. Third, previous calculations have failed to locate a σ complex.[5d]

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