PHOTODISSOCIATION OF DIPHENYLDIAZOMETHANE AND ENERGY RELAXATION IN THE DIPHENYLCARBENE FRAGMENT

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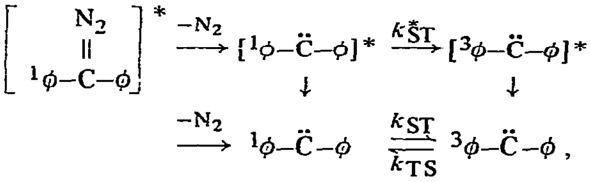
The dynamics of photodissociation of diphenyldiazomethane and energy relaxation in the diphenylcarbene fragment are investigated using picosecond laser methods. The equilibrium constant, free energy difference, and energy separation between the low-lying singlet and ground triplet states of the carbene are obtained.

1. Introduction

Although divalent carbon compounds (carbenes) $R'-\ddot{C}-R$ are an important class of short-lived and reactive intermediates, there is little known about the dynamics of their formation from photoexcited precursors or about the dynamics of energy relaxation in the carbene itself. There has been lively interest in the structural and chemical properties of these transient species for a considerable number of years [1–16]. Continuing experimental and theoretical [9,10] interest in carbenes derives from their novel reactions and their distinctive electronic structures. With the lowest-lying singlet and triplet states energetically near in the carbenes, the ground electronic state can be either a singlet or triplet depending upon the substituent groups (R, R′) [1,2]. This close proximity of singlet and triplet states, each with its characteristic chemistry, makes the kinetics of interconversion between them a key aspect of the properties of these important chemical intermediates.

In order to elucidate the dynamics of carbene formation, energy relaxation, and reaction, an ultraviolet picosecond laser pulse is used to generate the diphenylcarbene from a diphenyldiazomethane precursor. The sequence of energy decay steps following excitation of diphenyldiazomethane, ultimately leading to diphenylcarbene in its triplet ground state, can be written as.



$$\begin{tikzcd}
\left[\begin{matrix} N_2 \\ \| \\ {}^1\phi-C-\phi \end{matrix}\right]^* \arrow[r, "-N_2"] \arrow[dr, "-N_2"'] & {[{}^1\phi-\ddot{C}-\phi]^*} \arrow[r, "k_{ST}^*"] \arrow[d] & {[{}^3\phi-\ddot{C}-\phi]^*} \arrow[d] \\
 & {}^1\phi-\ddot{C}-\phi \arrow[r, shift left, "k_{ST}"] & {}^3\phi-\ddot{C}-\phi \arrow[l, shift left, "k_{TS}"]
\end{tikzcd}$$

where ϕ represents the phenyl group (C_6H_5) and the superscript * represents excited states. It has been shown in a pioneering investigation that there is a rapid equilibration between the low-lying singlet, ^{1}DPC, and triplet, ^{3}DPC, spin states [13]. Although the very fast intersystem crossing $^1\text{DPC} \xrightarrow{k_{ST}} {}^3\text{DPC}$ precluded measurement of this process, an estimated value of k_{ST} greater than $10^{10}\ s^{-1}$ was obtained [13]. In the present investigation the value of k_{ST} is obtained, which combined with the value of k_{TS} yields the equilibrium constant, free energy change, and energy separation of the low-lying ^{1}DPC and the ground-state ^{3}DPC. Results on the dynamics of the precursor photodissociation and the maximum energy of the carbon nitrogen bond in diphenyldiazomethane are also given.

2. Experimental

The ultraviolet excitation and probe pulses were generated by frequency quadrupling a single pulse from either a Nd YAG (266 nm) or Nd · phosphate glass (264 nm) laser. The pulse width of the Nd : YAG fundamental was ⩽25 ps and that of the phosphate between

4 and 8 ps. The fluorescence spectra were obtained using an OMA and $\frac{1}{4}$ m Jarrell–Ash monochromator. A picosecond streak camera–OMA system was used to observe the rise of the carbene fluorescence. In these latter experiments only an excitation pulse is used. On the other hand, in the laser-induced fluorescence measurements, which employs both an excitation and a probe pulse, a 1P21 photomultiplier and suitable interference filters centered at 500 nm were used. The various detection systems were computer interfaced to permit signal averaging and correction for the system response. The diphenyldiazomethane precursor was prepared in house [‡] and the solvent 3-methylpentane was purified before use. The solutions studied (5×10^{-4} M diphenyldiazomethane) were degassed and frequently changed to prevent product accumulation.

3. Discussion

Excitation of diphenyldiazomethane with a single pulse at 264 nm (Nd · phosphate) generated a weak fluorescence. The fluorescence signal varied linearly with pulse intensity (fig. 1) and exhibited a rise time of ≈15 ps. The spectrum (fig. 2) was measured and found to be identical with our measurements of the ^{3}DPC* fluorescence spectrum obtained on direct excitation of ^{3}DPC. This identity establishes that one of the photodissociative channels of diphenyldiazomethane leads to the excited triplet carbene ^{3}DPC*. Since ^{3}DPC* appears within 15 ps of photoexcitation, the carbon–nitrogen bond rupture step and the subsequent $^1\text{DPC}^* \rightarrow {}^3\text{DPC}^*$ intersystem crossing step cannot individually exceed 15 ps. Although ^{3}DPC* is produced rapidly, the quantum yield of ^{3}DPC* is small. The ^{3}DPC* is therefore not a major decay route of photoexcited diphenyldiazomethane, and, as we will discuss shortly, not an important pathway in producing the triplet ground-state carbene, ^{3}DPC.

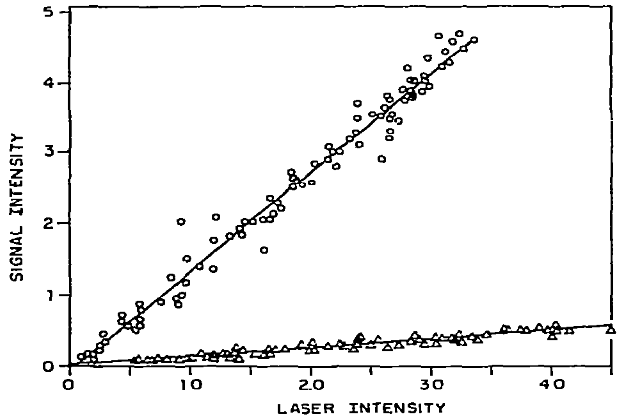


Fig. 1. ^{3}DPC fluorescence intensity versus laser intensity at 266 nm. The circles are ^{3}DPC fluorescence and the triangles are the solvent background. The solid lines are linear least-squares fits to the data.

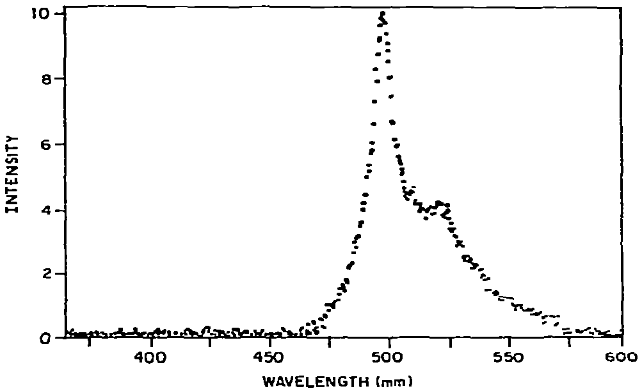


Fig. 2. Fluorescence spectrum of ^{3}DPC following excitation at 266 nm of 5×10^{-4} M diphenyldiazomethane in 3-methylpentane

The rate of formation of ^{3}DPC was determined using a laser-induced fluorescence method with 266 nm (Nd . YAG) excitation and probe pulses. Measurement of the triplet fluorescence intensity as a function of the time separation between the excitation and probe pulses yielded the kinetics of the triplet ground-state ^{3}DPC appearance. The fluorescences resulting from the excitation pulse alone and from the probe pulse alone were readily accounted for since they were small relative to the two-pulse laser-induced fluorescence signal. At the very low optical densities of the ^{3}DPC absorption the laser-induced fluorescence signal of ^{3}DPC* is proportional to the product of the excitation and probe pulse intensities. Since both pulses are at the same wavelength, their designation as probe or excitation pulses becomes arbitrary and the laser-induced fluorescence signal should be symmetric about

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[‡] Prepared by G. Hefferon and Professor N.J. Turro.

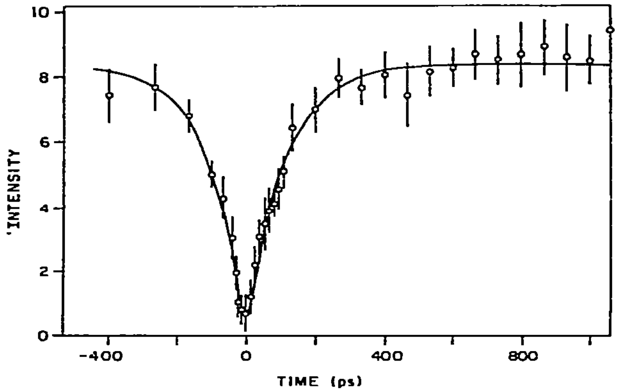

Fig. 3. Formation kinetics of ^{3}DPC The laser-induced fluorescence signal as a function of the time delay between excitation and probe pulses The solid curve is a calculated fit.

the origin ($t = 0$), as is found to be the case (fig. 3)[‡]. The rate of formation of ^{3}DPC obtained in these experiments was $(9.1 \pm 1) \times 10^9\ \mathrm{s}^{-1}$.

To determine if an important channel for the production of ^{3}DPC occurs via the decay of the excited carbene, $^3\mathrm{DPC}^* \rightarrow {}^3\mathrm{DPC}$, which we alluded to earlier, we measured the lifetime of ^{3}DPC*. From measurements of the ^{3}DPC* fluorescence decay we find its lifetime to be 4 ns. Since the laser-induced fluorescence results established that the ground-state triplet, ^{3}DPC, appears in 110 ps, we conclude that the primary source of the ^{3}DPC cannot be from the much more slowly decaying ^{3}DPC*. The dominant pathway for the production of ^{3}DPC is from the nearby ^{1}DPC state.

Although the key pathway for ^{3}DPC production does not proceed by the ^{3}DPC* route, the observation of fluorescence from the ^{3}DPC* on excitation of the parent diphenyldiazomethane molecule yields information on the energy of the carbon–nitrogen bond. By establishing that the ^{3}DPC* fluorescence varied linearly with the excitation intensity, we conclude that photodissociation results from the absorption of one photon at 266 nm (fig. 1). Knowing the energy of the exciting photon and the energy of the ^{3}DPC* thereby produced, we conclude that the energy of the carbon–nitrogen bond in diphenyldiazomethane is 2 eV or less.

Combining the singlet to triplet intersystem crossing value, k_{ST}, with that of the slower reverse process, k_{TS} [17], we find the equilibrium constant,

$$K = \frac{k_{\mathrm{ST}}}{k_{\mathrm{TS}}} = \frac{9.1 \times 10^9}{4.1 \times 10^6} = (2.2 \pm 0.6) \times 10^3 .$$

The free energy difference at 25°C is calculated to be 4.6 ± 0.2 kcal/mole. After correcting for the entropy difference arising from the different multiplicities of the singlet and triplet states, we obtain an energy separation between the ground triplet and neighboring singlet in diphenylcarbene of 3.9 ±0.2 kcal/mole.

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References

[1] R.A. Moss and M Jones Jr., Carbenes, Vol. 2 (Wiley, New York, 1975).
[2] W Kirmse, Carbene chemistry, Vol. 1, 2nd Ed. (Academic Press, New York, 1971).
[3] G. Herzberg and J W.C Johns, Proc. Roy. Soc. A295 (1966) 107.
[4] G Closs, C.A. Hutchison Jr. and B.E Kohler, J. Chem. Phys. 44 (1966) 413.
[5] I. Moritani, S.I. Murahashi, M. Nishino, K. Kimura and H. Tsubomura, Tetrahedron Letters (1966) 373.
[6] A.M. Trozzolo, Accounts Chem. Res. (1968) 329.
[7] W. Ware and P J. Sullivan, J. Chem. Phys. 49 (1968) 1445.
[8] P.F. Zittel, G.B. Ellison, S.V. O'Neil, E. Herbst, W.C Lineberger and W.P. Reinhardt, J. Am. Chem. Soc. 98 (1976) 3731.
[9] J. Metcalfe and E A. Halevi, J. Chem. Soc. Perkin II (1976) 634.
[10] J.F. Harrison, R.C. Liedtke and J.F. Liebman, J. Am. Chem. Soc. 101 (1979) 7162, and references therein.
[11] D. Bethell, G. Stevens and P. Tickle, J. Chem. Soc. Chem. Commun. (1970) 792.
[12] G.L. Closs, Topics Stereochem. 3 (1968) 193.
[13] G.L. Closs and B E. Rabinow, J. Am. Chem. Soc. 98 (1976) 8190.
[14] L.B. Harding and W.A. Goddard III, J. Chem. Phys 67 (1977) 1777.
[15] H.D. Roth, Accounts Chem. Res. 10 (1977) 85.
[16] R.K. Lengel and R.N. Zare, J. Am. Chem. Soc. 100 (1978) 7495.
[17] K B. Eisenthal, N J. Turro, M. Aikawa, J.A. Butcher Jr., C. Dupuy, G. Hefferon, W. Hetherington, G. Korenowski and M.J. McAuliffe, J. Am. Chem. Soc., to be published.

[‡] The best fit curve was obtained by convolution of an exponential rise with gaussian excitation and probe pulses.