SHORT COMMUNICATION

KINETICS AND SPECTROSCOPY OF 2-NAPHTHYLPHENYLCARBENE

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2-Naphthylphenylcarbene (2-NPC) was studied by low-temperature EPR spectroscopy and by solution-phase laser flash photolysis. 2-NPC was found to have a triplet ground state with two distinct rotomeric forms. The triplet carbene was found to react with methanol, 1,1-diphenylethylene, styrene, carbon tetrachloride, isoprene, toluene and 2-methyltetrahydrofuran.

INTRODUCTION

In recent years, aryl carbenes have been extensively probed by direct physical methods such as laser flash photolysis (LFP) and electron paramagnetic resonance (EPR) spectroscopy.[1] These studies demonstrated a large dependence of carbene reactivity on molecular structure. For example, both diphenylcarbene (DPC)[2] and 2-naphthylcarbene (2-NC)[3] have triplet ground states, but [3]DPC[1,4] generally reacts 100 times more slowly with typical quenchers then does triplet 1- or 2-naphthylcarbene.[1,5] Further, the pattern of stable products formed when 2-NC is generated in alkanes suggests that most of the chemistry of this carbene originates through its low-lying singlet state, whereas the chemistry of DPC in alkanes proceeds primarily through the ground triplet spin state.[6] To elucidate further the effect of structure on carbene reactivity, we studied 2-naphthylphenylcarbene (2-NPC), a species which shares structural features with both DPC and 2-NC. Our results are consistent with those recently reported by Fujiwara *et al.*[7] and indicate that the chemistry and kinetics 2-NPC more closely resemble those of DPC than those of 2-NC.


DPC   2-NC   2-NPC

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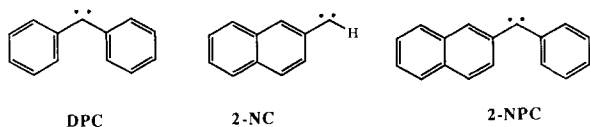
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RESULTS

Laser flash photolysis studies

Laser flash photolysis of dilute solutions of 2-naphthylphenyldiazomethane (2-NPDM) in deoxygenated cyclohexane produced a transient absorption band immediately after the flash which had a maximum at 385 nm. A shoulder appeared at 400 nm in the transient optical density spectrum $2 \cdot 0$ μs after the laser flash. At 20 μs after the laser flash, the absorption maximum had shifted to 405 nm. The growth of the 405 nm transient was concomitant with the disappearance of the 385 nm absorbing species.


NPDM   2-NPC   1
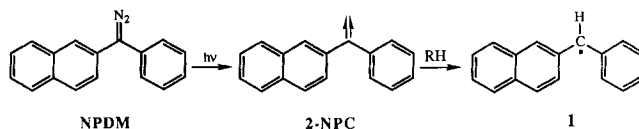
In a separate experiment, laser flash photolysis of 2-naphthylphenylmethane (2) in di-*tert*-butyl peroxide produced a transient with $\lambda_{max} = 405$ nm. The nature of the precursor to these transients, their order of appearance, EPR spectroscopy, chemical analysis and the absolute rate constant data (see below) suggest that the 385 nm transient can be assigned to triplet 2-naphthylphenylcarbene and the 405 nm absorbing species can be confidently assigned to the corresponding radical 1.

$$^tBuO-OBu^t \xrightarrow{h\nu} 2\,^tBuO\cdot$$
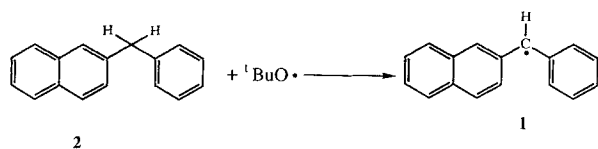
Our results are in good agreement with those of Fujiwara *et al.*,[7] who recently reported that $\lambda_{max} = 380$ nm for ^{3}2-NPC. This value is considerably red shifted relative to ^{3}DPC ($\lambda_{max} \approx 314$ nm)[4] and ^{3}2-NC ($\lambda_{max} \approx 362$ nm).[5] The 20 nm shift in the absorption maxima between ^{3}NPC and radical 1 is commonly observed between carbenes and their corresponding radicals (e.g. DPC and benzhydryl radical, $\lambda_{max} = 334$ nm).[8]

In an oxygen-saturated cyclohexane solution, a broad transient absorption ($\lambda_{max} = 435$ nm) was observed on laser flash photolysis of 2-NPDM. This new species, assigned to the carbonyl oxide 3, arises from the reaction of triplet NPC with O_2.[4d]
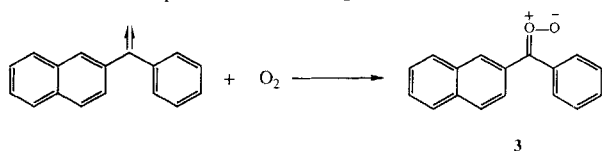
No ylids or complexes derived from 2-NPC were detected on LPF of 2-NPDM in acetone or acetonitrile. Conversely, 1- and 2-naphthylcarbene are known to form ylids in these solvents.[5]

EPR spectroscopy

The EPR spectrum of triplet 2-NPC was produced at 77 K in either 2-methyltetrahydrofuran (2-MTHF), toluene or carbon tetrachloride matrices by low-temperature photolysis of 2-NPDM. The spectrum in CCl_4 was particularly weak but qualitatively the same as that observed in either 2-MTHF or toluene. As with 1- and 2-NC, ^{3}2-NPC displays two sets of signals due to *syn* and *anti* rotomers:[3]

toluene matrix: $|D/hc|$ *anti* $= 0 \cdot 3889$ cm^{-1},
$|E/hc|$ *anti* $= 0 \cdot 01958$ cm^{-1};
$|D/hc|$ *syn* $= 0 \cdot 4034$ cm^{-1},
$|E/hc|$ *syn* $= 0 \cdot 0169$ cm^{-1};
2-MTHF matrix: $|D/hc|$ *anti* $= 0 \cdot 3898$ cm^{-1},
$|E/hc|$ *anti* $= 0 \cdot 0195$ cm^{-1};
$|D/hc|$ *syn* $= 0 \cdot 4044$ cm^{-1},
$|E/hc|$ *syn* $= 0 \cdot 0168$ cm^{-1}.

Fujiwara *et al.*[7] reported a low-temperature EPR spectrum of ^{3}2-NPC but they did not specifically address the presence of rotomeric forms, referring instead to average field parameters $|D/hc| = 0 \cdot 353$ cm^{-1} and $|E/hc| = 0 \cdot 016$ cm^{-1}. Assignment of zero field parameters to a specific conformer is made possible by simple PMO theory as detailed by Roth and

Hutton.[9] The $|D/hc|$ parameter is inversely proportional to r^3, the distance between the two unpaired electrons of the carbene. One unpaired electron of ^{3}2-NPC is localized in a σ-type orbital whereas the other is delocalized throughout the entire π system.

SYN   ANTI
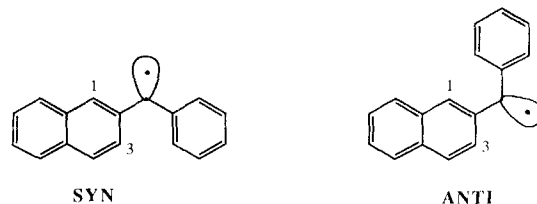
The major contributor to the zero field parameter in a carbene is the coupling between the unpaired electrons in the σ and π orbitals centered on the carbene carbon. An important secondary contribution to the $|D/hc|$ parameter is made by the coupling between the electron in the σ orbital and the π electron at C-1 of the *syn* rotamer. In the *anti* rotamer it is the interaction between the σ electron and the π electron density at C-3 that is crucial.

The distances between the σ orbital and the 1-position of the *syn* conformer and the σ orbital and the 3-position of the *anti* conformer are nearly the same. However, according to simple PMO theory,[10] the π electron density at the 1-position is twice that at the 3-position, which leads to a large σ electron–π electron coupling in the *syn* conformer. Hence the *syn* conformer would be expected to have the larger $|D/hc|$ value.

Absolute rate constants in solution

Bimolecular quenching rate constants for the reaction of triplet 2-NPC with various substrates were obtained (Table 1). Dilute solutions of 2-NPDM (10^{-3} M) in

Table 1. Comparative bimolecular quenching constants at ambient temperature

Substrate	$k_{obsd} \times 10^6$ (mol^{-1} s^{-1})		
	2-NPC	DPC[b]	2-NC[c]
Methanol	$29 \cdot 6 \pm 5 \cdot 5$[a]	$6 \cdot 8 \pm 2 \cdot 1$	$7 \cdot 25 \pm 0 \cdot 5$
Methanol-OD	$22 \cdot 4 \pm 2 \cdot 5$		
1,1-Diphenylethylene	$2 \cdot 04 \pm 0 \cdot 38$	$0 \cdot 48 \times 10^5$	
Styrene	$0 \cdot 64 \pm 0 \cdot 42$	$0 \cdot 38$	$43 \cdot 3 \pm 1$
Carbon tetrachloride	$1 \cdot 29 \pm 0 \cdot 42$	$2 \cdot 0$	$3 \cdot 35 \pm 0 \cdot 07$
Isoprene	$1 \cdot 39 \pm 0 \cdot 15$	$1 \cdot 36 \pm 0 \cdot 15$	
Cyclohexa-1,4-diene	$4 \cdot 6 \pm 0 \cdot 3$[d]		

[a] the quenching plot is curved, see text.
[b] see Ref. 4a and b.
[c] see Ref. 5d.
[d] see Ref. 7.

benzene were flash photolyzed at either 308 or 337 nm in the presence of suitable quenchers. A Lumonics TE-801 M-4 excimer laser (Xe–HCl–He, 308 nm, pulse width 8–10 ns; maximum pulse energy 110 mJ) and a Molectron UV-22 N_2 laser (337.1 nm, pulse width 5–10 ns, maximum pulse energy 6 mJ) were used. Bimolecular rate constants were obtained from the slope of plots of the observed rate constants of decay of ^{3}2-NPC versus quencher concentration. In benzene the carbene decay could be monitored free of overlapping absorptions of radical 1. Diethyl fumarate, *trans*-stilbene and tetramethylethylene reacted very sluggishly with ^{3}2-NPC, and therefore the bimolecular quenching rate constants of these substrates must be less than $10^5 \, l \, mol^{-1} \, s^{-1}$. These rate constants are much slower than those of ^{3}DPC or ^{3}2-NC with the same quenchers. A curved quenching plot was observed in the reaction of 2-NPC with methanol in a manner reminiscent of that observed in the reaction of phenylchlorocarbene and methanol.[11] This phenomenon was attributed to oligomerization of the alcohol. For the sake of comparison with other carbenes, the 'best' straight line fitted to the curved methanol quenching plot is reported in Table 1.

In toluene and 2-MTHF it was possible to monitor the growth of radical 1 at 405 nm. Owing to problems associated with spectral overlap, it was more reliable to monitor the growth of radical 1 than the decay of ^{3}2-NPC.[4] However, it was only possible to obtain pseudo-first-order growth rate constants in neat solvents owing to the sluggish nature of the hydrogen atom transfer. The temperature dependence of the pseudo-first-order growth rate constants were determined and yielded the following activation parameters: toluene, $E_a = 3 \cdot 2 \pm 0 \cdot 2 \, kcal \, mol^{-1}$, $A = 10^{7 \cdot 88 \pm 0 \cdot 05} \, s^{-1}$ (174–294 K); and 2-methyltetrahydrofuran, $E_a = 2 \cdot 8 \pm 0 \cdot 2 \, kcal \, mol^{-1}$, $A = 10^{8 \cdot 49 \pm 0 \cdot 11} \, s^{-1}$ (165–293 K). The activation energies and A factors observed are comparable to those for diphenylcarbene and, in the case of toluene, almost identical.

EPR kinetic studies

The decay kinetics of ^{3}2-NPC were monitored by EPR in 2-MTHF and toluene matrices. Non-exponential kinetics due to site problems were observed,[13,14] which limited the kinetic analysis to the initial 10% of the decay. The initial pseudo-first-order rate constants of decay triplet 2-NPC in frozen 2-MTHF and toluene were $(7 \cdot 07 \pm 1 \cdot 42) \times 10^{-4} \, s^{-1}$ and $(1 \cdot 65 \pm 0 \cdot 35) \times 10^{-5} \, s^{-1}$, respectively, at 77 K. However, extrapolation of the Arrhenius parameters obtained in solution phase predicts pseudo-first-order rate constants of $0 \cdot 167 \, s^{-1}$ (2-MTHF) and $4 \cdot 10 \times 10^{-2} \, s^{-1}$ (toluene) at 77 K. The predicted rate constants are several orders of magnitude larger than the measured values. Hence the assumption that

solution-phase parameters are valid for low-temperature matrices is clearly untenable.[12,13] It is apparent that the limited motion available to ^{3}2-NPC in a frozen glass or polycrystal retards its rate of reaction relative to its value in a mobile solution. The rigid phase may retard the rate of the classical hydrogen atom transfer to such an extent that another mechanism, such as quantum mechanical tunnelling, becomes operative.[13] Supporting evidence for this interpretation comes from the observation that ^{3}2-NPC did not react at an appreciable rate with CCl_4 at 77 K, even though in solution ^{3}2-NPC reacts more rapidly with CCl_4 than with toluene or 2-MTHF. The chlorine atom is too large for tunnelling and no reaction is observed under these conditions.

Product studies

Product studies indicate that diphenylcarbene[6] and 2-NPC react in a similar manner with hydrocarbons. Photolysis of 2-NPDM in cyclohexane produced 4, 5 and 6, products which are reasonably attributable to triplet processes (Scheme 1). Coinjection with authentic samples confirmed the presence of these products. 2-Naphthylphenylcyclohexylmethane (4) can in principle be formed either by radical abstraction–recombination processes or by a direct singlet C—H insertion reaction. The spin-state origin of this compound was demonstrated in an isotopic crossover experiment conducted in 1:1 (v/v) cyclohexane–cyclohexane-d_{12}. Analysis of the mass spectrum of 4 demonstrated that considerable amounts of crossover products $4d_1$ and $4d_{11}$ were formed in the mixed solvent system. These compounds cannot be formed in a concerted singlet C—H insertion reaction, thereby demonstrating a triplet carbene origin of this reaction product. Such crossover experiments have

NPDM

N_p= 2 Naphthyl

Ph= Phenyl

N_pCH_2Ph

5
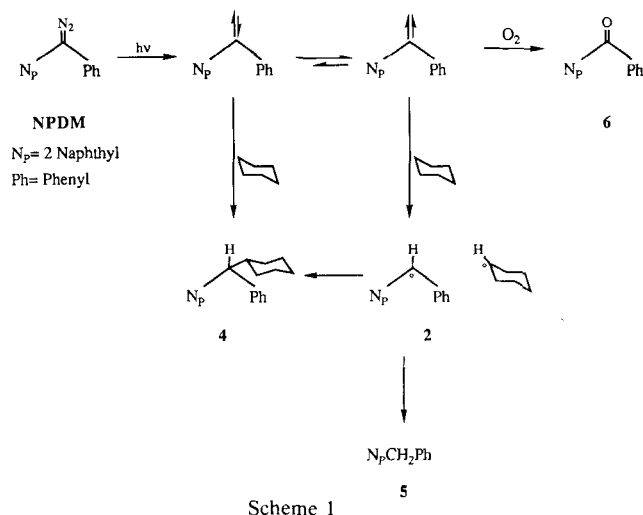
Scheme 1

shown that singlet C—H insertion is the main reaction pathway for fluorenylidene[6] and 1-naphthylcarbene in cyclohexane,[5a] but conversely, with diphenylcarbene,[6] the data indicate that as with [3]2-NPC, the carbene alkane adduct **4** arises via a triplet pathway.

CONCLUSION

The spectroscopic properties of 2-NPC resemble those of DPC and 2-NC. 2-NPC is a ground-state triplet species. It reacts in solution with hydrogen and chlorine atom donors and styrenes primarily through its ground triplet state. In this regard it resembles DPC rather than 2-NC, which reacts primarily through its low-lying singlet state. [3]2-NPC reacts faster with methanol than does either [3]DPC or [3]2-NC. The latter result implies that the singlet triplet energy gap in this carbene is smaller than that in DPC or 2-NC.[1] In this regard, benzannelation of DPC has an effect similar to that observed in fluorenylidene, where benzannelation increases the reactivity of the carbene to methanol, presumably by reducing the singlet triplet gap.[14] Despite the small singlet–triplett gap in 2-NPC this carbene reacts primarily through its ground triplet state in cyclohexane, as per diphenylcarbene.

REFERENCES

1. (a) G. B. Schuster, *Adv. Phys. Org. Chem.* **22**, 311 (1986); (b) M. S. Platz and V. M. Maloney in *Kinetics and Spectroscopy of Carbenes and Biradicals*, edited by M. S. Platz. Plenum, New York, (1990).
2. A. M. Trozzolo and E. Wasserman in *Carbenes*, Vol. 2, edited by R. A. Moss and M. Jones, Jr, Vol. 2, Wiley, New York, p. 185 (1975).
3. A. M. Trozzolo, E. Wasserman and W. A. Yager, *J. Am. Chem. Soc.*, **87**, 129 (1965).
4. (a) G. L. Closs and B. E. Rabinow *J. Am. Chem. Soc.*, **98**, 8190 (1976); (b) L. M. Hadel, M. S. Platz and J. C. Scaiano, *J. Am. Chem. Soc.*, **106**, 283 (1984); (c) L. M. Hadel, V. M. Maloney, M. S. Platz, W. G. McGimpsey and J. C. Scaiano, *J. Phys. Chem.*, **90**, 2488 (1986); (d) H. L. Casal, S. E. Sugamori and J. C. Scaiano, *J. Am. Chem. Soc.*, **106**, 7623 (1984).
5. (a) R. L. Barcus, L. M. Hadel, L. J. Johnston, M. S. Platz, T. G. Savino and J. C. Scaiano, *J. Am. Chem. Soc.* **108**, 3928 (1986); (b) L. M. Hadel, M. S. Platz and J. C. Scaiano, *Chem. Phys. Lett.* 446 (1983); (c) R. L. Barcus, B. B. Wright, M. S. Platz and J. C. Scaiano, *Tetrahedron Lett.*, **24**, 3955 (1983); (d) K. A. Horn and J. E. Chateanneuf, *Tetrahedron*, **41**, 1465 (1985); (e) G. W. Griffin and K. A. Horn, *J. Am. Chem. Soc.*, **109**, 4919 (1987); (f) P. C. Wong, D. Griller and J. C. Scaiano, *J. Am. Chem. Soc.*, **104**, 6631 (1982).
6. T. G. Savino, V. P. Senthilnathan and M. S. Platz, *Tetrahedron*, **42**, 2167 (1986).
7. Y. Fujiwara, M. Saski, Y. Tanimoto and M. Itoh, *Chem. Phys. Lett.*, **146**, 133 (1988).
8. (a) G. Porter and M. Windsor, *Nature (London)*, 180 (1957); (b) I. Norman and G. Porter, *Proc. R. Soc. London, Ser. A*, **230**, 399 (1955).
9. H. D. Roth and R. S. Hutton, *Tetrahedron*, **41**, 1567 (1985).
10. M. J. S. Dewar and R. C. Dougherty, *The PMO Theory of Organic Chemistry*. Plenum, New York (1975).
11. D. Griller, M. T. H. Liu and J. C. Scaiano, *J. Am. Chem. Soc.*, **104**, 5549 (1982).
12. B. B. Wright, K. Kanakarajan and M. S. Platz, *J. Phys. Chem.*, **89**, 3547 (1985).
13. (a) C.-T. Lin and P. P. Gaspar, *Tetrahedron Lett.*, **21**, 3553 (1980); (b) V. P. Senthilnathan, and M. S. Platz, *J. Am. Chem. Soc.*, **102**, 7637 (1980); (c) V. P. Senthilnathan and M. S. Platz, *J. Am. Chem. Soc.*, **103**, 5503 (1981); (d) B. Wright, V. P. Senthilnathan, M. S. Platz and C. W. McCurdy, Jr, *Tetrahedron Lett.* **23**, 833 (1982); (e) M. S. Platz, V. P. Senthilnathan, B. B. Wright and C. W. McCurdy, Jr, *J. Am. Chem. Soc.*, **104**, 6494 (1982); (f) M. S. Platz, *Acct. Chem. Res.*, **21**, 236 (1988).
14. P. B. Grasse, J. J. Zupancic, S. G. Lapin, M. P. Hendrich and G. B. Schuster, *J. Org. Chem.*, **50**, 2352 (1985).