

TRANSIENT SPECTRAL AND KINETIC BEHAVIORS OF CARBONYL YLIDE PHOTOGENERATED FROM 2,2-DICYANO-3-(2-NAPHTHYL)-OXIRANE

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Summary

On laser flash photolysis, by direct light absorption as well as under energy transfer sensitization by aromatic ketone triplets, 2,2-dicyano-3-(2-naphthyl)oxirane in fluid solutions forms an ylide characterized by broad and intense absorption spectra ($\lambda_{\text{max}} = 610 \text{ nm}$, $\epsilon_{\text{max}} = 2.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in benzene) and unusually long lifetimes in aprotic solvents ($\tau_{\text{Y}} = 130 \text{ } \mu\text{s}$ in benzene). The ylide reacts with water, alcohols and dipolarophiles with rate constants that are atypically low ($10^3 - 10^6 \text{ M}^{-1} \text{ s}^{-1}$). The reactivity follows a trend parallel to that of acidity of alcohols and opposite to that of electron-rich character of dipolarophiles.

1. Introduction

Although ylides characterized by dipolar structures are recognized [1] to be important intermediates in thermal and photochemical reactions of three-membered heterocyclic systems, very little spectral and kinetic data concerning their behaviors under fluid conditions are available. Many of the studies [2] for spectral characterization of carbonyl ylides derived from oxiranes have been confined to low temperature glassy matrices in which they are thermally stable. The intermediacy of ylides in reactions at room temperature has been established [3, 4] by intercepting them with suitable dipolarophiles (alkenes or alkynes) to give cyclic ethers and with alcohols to give ketals. Spectral observation and measurement of absolute rates of reactions of ylides at ambient temperature have become possible [5 - 8] by recent time-resolved techniques based on laser flash photolysis.

In this paper we are presenting some of our observations concerning the ylide photochemically generated from 2,2-dicyano-3-(2-naphthyl)oxirane (DCNO) by direct laser excitation at 337.1 and 248 nm as well as under

triplet energy transfer sensitization by aromatic ketone triplets. In particular, the studies under triplet sensitization enable us to measure the extinction coefficient of absorption of the ylide; to our best knowledge, this is the first time that the extinction coefficient data are being reported for an ylide. Our results show that the ylide from DCNO is a strongly absorbing oxygen-insensitive species ($\lambda_{\text{max}} = 610 \text{ nm}$, $\epsilon_{\text{max}} = 2.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in benzene) that is (i) unusually long lived ($\tau_Y \geq 65 \mu\text{s}$ in aprotic solvents) and (ii) relatively insensitive towards common dipolarophiles ($k_q^Y \leq 10^5 \text{ M}^{-1} \text{ s}^{-1}$), but (iii) moderately reactive towards water and alcohols ($k_q^Y = (1 - 8) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$).

2. Results and discussion

The absorption spectra of DCNO in methylcyclohexane (MCH) at 296 K and 77 K, presented in Fig. 1, curves A and B respectively, display the sharply defined 0-0 bands at 324 nm (at both temperatures). On steady state photolysis (313 nm) of DCNO in MCH glass at 77 K, a blue-colored species with a broad absorption spectrum ($\lambda_{\text{max}} = 590 \text{ nm}$ (Fig. 1, curve C)) is formed. The blue color disappears on further irradiation in the visible region, specifically at 577 nm; such a photobleaching phenomenon is characteristic of carbonyl ylides, as noted in earlier studies [2]. Laser flash photolysis of DCNO in cyclohexane, benzene or acetonitrile at 296 K using nitrogen laser pulses (337.1 nm, 8 ns, about 3 mJ) leads to the formation (within the laser pulse) of a long-lived transient species with an absorption spectrum (Fig. 1, curve D) very similar to that observed on steady state irradiation (313 nm) at 77 K. On the basis of spectral similarity as well as characteristic reactions (discussed later), we assign the carbonyl ylide

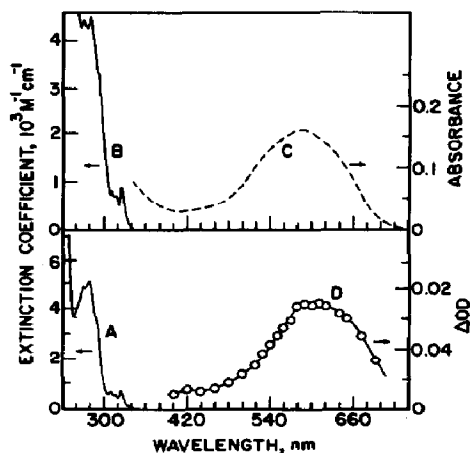


Fig. 1. Absorption spectra of DCNO ($8.1 \times 10^{-4} \text{ M}$) in MCH at 296 K (curve A) and 77 K (curve B) and of the ylide from DCNO in MCH glass at 77 K (curve C) and in cyclohexane at 296 K (curve D). The transient absorption spectrum (curve D) was obtained by direct 337.1 nm laser flash photolysis of a saturated solution of DCNO in cyclohexane (at 8 μs following laser flash).

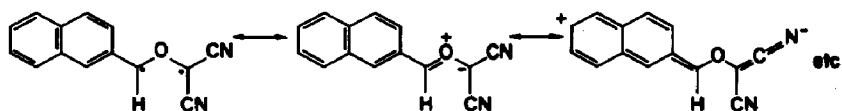


Fig. 2. Carbonyl ylide structures.

structures shown in Fig. 2 to the transient species. While two possible planar geometrical structures are possible for the ylide in which the 2-naphthyl group is in *endo* and *exo* orientations, we prefer the latter on the basis of adverse steric interactions present in the former.

Unfortunately, at 337.1 nm, the excitation occurs into the low energy weak tail ($\epsilon < 50 \text{ M}^{-1} \text{ cm}^{-1}$) of the (0-0) peak (probably "hot" band absorption) of DCNO. Experiments based on direct excitation at this wavelength require high concentrations ($5 \times 10^{-3} \text{ M}$ or more) and are fraught with complication from partial absorption of laser photons by impurities. However, the low intensity of absorption of DCNO at 337.1 nm enables us to study ylide formation, if any, from the oxirane through the intermediacy of its triplet [3], using suitable aromatic ketones as sensitizers. We have used benzophenone (BP) and *p*-methoxyacetophenone (PMA) for this purpose. On laser flash photolysis (337.1 nm) of 0.05 M BP (or PMA) in benzene containing $(1 - 4) \times 10^{-4} \text{ M}$ DCNO, ylide formation is observed at 560 - 650 nm on a time scale commensurate with the decay of the sensitizer triplet (${}^3\text{BP}^*$ monitored at 532 nm and ${}^3\text{PMA}^*$ monitored at 385 nm). The fact that the pseudo-first-order rate constant k_{obs} for the decay of the sensitizer triplet matches exactly with that for the formation of the ylide establishes that the latter is generated through a short-lived triplet of the oxirane and possibly a triplet diradical, the decays of which are too fast to be consequential in the kinetic analysis. The proposed steps involved in the triplet-sensitized ylide formation are shown below using BP as the energy donor ($Y \equiv$ ylide; ISC, intersystem crossing):



From the linear dependence of k_{obs} on [DCNO], the bimolecular rate constants k_q^T for triplet excitation transfer from ${}^3\text{BP}^*$ and ${}^3\text{PMA}^*$ to DCNO in benzene are found to be $4.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $5.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively. Assuming that the sole pathway for the decay of ${}^3\text{DCNO}^*$ is electrocyclic ring opening to the ylide, it becomes possible to determine the extinction coefficient ϵ_Y of absorption of the latter by comparative methods. The end-of-pulse absorbance ΔOD_0^T due to ${}^3\text{BP}^*$ (at 532 nm) measured in a solution containing BP alone was compared with the plateau absorbance

TABLE 1

Spectral and kinetic data for the ylide from 2,2-dicyano-3-(2-naphthyl)oxirane at room temperature

<i>Solvent</i>	λ_{\max}^a (nm)	τ_Y^b (μs)	<i>Quencher</i> ^c	k_q^{Yd} ($\text{M}^{-1} \text{s}^{-1}$)
Cyclohexane	590	90		
Carbon tetrachloride	600	130		
Benzene	610	130	MA (0.16)	1.0×10^5
			DMAD (1.4)	8.2×10^4
			DMM (1.9)	3.5×10^4
			DDF (2.4)	3.3×10^3
			Cyclohexene (3.7)	1.6×10^4
			TME (1.9)	7.4×10^3
			Methanol (3.2)	8.1×10^5
			Ethanol (1.6)	2.0×10^5
Acetonitrile	595	65	2-Propanol (4.1)	1.8×10^5
			Methanol (5.0)	3.3×10^5
			2-Propanol (3.0)	5.7×10^4
			H ₂ O (11.3)	1.4×10^5
			D ₂ O (11.0)	1.1×10^5
<i>tert</i> -Butanol	595	1.3		

^a ± 5 nm.

^b $\pm 15\%$.

^c MA, maleic anhydride; DMAD, dimethyl acetylene dicarboxylate; DMM, dimethyl maleate; DDF, 2,5-dimethoxy-2,5-dihydrofuran; TME, tetramethylethylene; the maximum molar concentrations of the quenchers used in the quenching studies are given in parentheses.

^d $\pm 20\%$.

$\Delta\text{OD}_{\infty}^Y$ due to the ylide (at 610 nm) following the completion of its formation in an optically matched solution containing both BP and DCNO. The equation

$$\epsilon_Y = \epsilon_T \frac{\Delta\text{OD}^Y}{\Delta\text{OD}_0^T} \frac{k_{\text{obs}}}{k_{\text{obs}} - \tau_T^{-1}} \quad (5)$$

was used to evaluate ϵ_Y , ϵ_T for ³BP* being $7.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ in benzene [9]. The value thus obtained in this manner for ϵ_Y in benzene is $(2.0 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. It should be noted that, if the efficiency of ylide formation from ³DCNO (eqn. (4)) is less than unity because of competitive decay(s) of the triplet oxirane (or subsequent triplet diradical intermediate), the actual value of ϵ_Y will be even higher.

When generated in low concentrations using reduced laser intensities ($0.2 \text{ mJ pulse}^{-1}$ or less at 337.1 nm), the ylide decays predominantly with first-order kinetics. The lifetimes τ_Y in different solvents are given in Table 1. It should be noted that τ_Y in acetonitrile is shorter than τ_Y in benzene or cyclohexane. This may be surprising in view of pronounced contributions expected from ionic configurations to the ylide structure (Fig. 2). However,

we should point out that although the acetonitrile used in this work was distilled before use, no special precaution was exercised to exclude moisture during the preparation of solutions; thus, the shortening of τ_Y in acetonitrile could in part be due to the quenching effect of water (see later) present in trace amounts in this solvent. The short τ_Y in *tert*-butanol (Table 1) is undoubtedly due to the reaction of the ylide with the alcohol (see later).

When produced in high concentrations, *e.g.* under direct excitation with Kr-F₂ excimer laser pulses (5 - 20 mJ at 248 nm) (as discussed below) or under triplet sensitization with tightly focused nitrogen laser pulses (2 - 3 mJ at 337.1 nm), the ylide decays with mixed kinetics; the second-order component in the decay manifests itself in the observed half-lives which become shorter at increasing laser intensities. This is illustrated by the experimental traces given in Fig. 3, insets. Such a kinetic behavior implies that bimolecular process(es)



contributes to ylide decay in addition to unimolecular ring closure or fragmentation

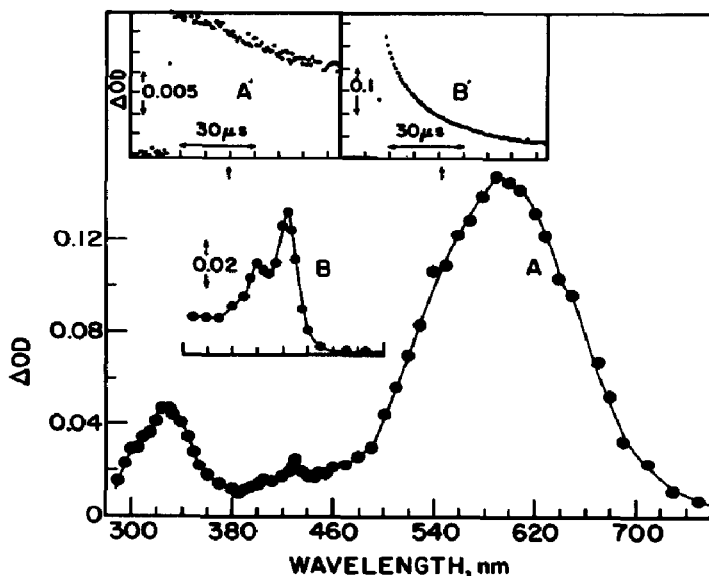


Fig. 3. End-of-pulse transient absorption spectra obtained by 248 nm laser flash photolysis of DCNO (3×10^{-4} M) in MCH at 296 K (curve A) and triplet-triplet absorption spectrum of 2-acetonaphthone in cyclohexane (obtained by direct 337.1 nm laser flash photolysis) (curve B). The insets show experimental traces at 600 nm observed by laser flash photolysis (337.1 nm) of a CCl₄ solution containing 0.05 M PMA and about 10^{-3} M DCNO at laser intensities of about 0.1 mJ pulse⁻¹ (curve A') and 3 mJ pulse⁻¹ (curve B').



or



From the best-fit of the decay profiles at high laser intensities into second-order equal-concentration kinetics, estimates of $4.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ are obtained for k_{2Y} in benzene and carbon tetrachloride respectively. Almost no change in τ_Y is observed on going from degassed to air-saturated solutions.

In addition to the ring opening to ylide, short wavelength (248 nm) laser excitation of *trans*-stilbene oxide is known [7] to lead to one-photon two-bond cleavage of the oxirane to phenyl carbene and benzaldehyde, part of the latter being observed in the triplet state. We have carried out a few laser flash photolysis experiments with DCNO in MCH and acetonitrile using 248 nm laser pulses (Kr-F₂ excimer, 20 ns, 5 - 20 mJ) for excitation. In these experiments, relatively dilute solutions ($(0.5 - 3) \times 10^{-4} \text{ M}$) were used and the transient phenomena could be monitored at short wavelengths (down to 290 nm). As shown in Fig. 3, curve A, the transient spectrum in MCH is dominated by the strong and broad absorption from the ylide (λ_{max} at 600 and 330 nm). In addition, two other transient phenomena are observed on a minor scale in the short wavelength spectral region. First, a relatively short-lived species ($\tau = 1.5 \mu\text{s}$) is formed with absorption maxima at 430 nm (major) and 405 nm (minor). The decay of this species is oxygen sensitive and the absorption spectrum is similar to the triplet-triplet spectrum of 2-acetonaphthone (Fig. 3, curve B), obtained on 337.1 nm laser excitation of this ketone in cyclohexane. Between the two plausible assignments of the 430 nm transient species, namely 2-naphthaldehyde triplet and dicyanocarbene, we prefer the former on the basis of the spectral similarity to 2-acetonaphthone triplet. Second, a "permanent" oxygen-insensitive photoproduct is formed (within the laser pulse), as evidenced by the lack of decay of the spectral absorption at 290 - 310 nm over about 100 μs . This appears to be due to 2-naphthaldehyde formed in the ground state as a result of direct photofragmentation of DCNO. Decreasing the laser intensity by 50% results in the lowering of the end-of-pulse absorbance changes at 590 nm, 430 nm and 295 nm by 50%, 65% and 60% respectively. Thus a small non-linear dependence on laser intensity is indicated for the species absorbing at 295 and 430 nm. This phenomenon may be trivial and arise from secondary absorption of laser photons by the ylide (leading to its decomposition) or by 2-naphthaldehyde (leading to its triplet formation), both species being photogenerated in the single exciting laser pulse. The observations concerning the transient phenomena and the laser intensity dependence in acetonitrile are very similar to those in MCH.

The reactivity of the ylide towards water, alcohols and various dipolarophiles was examined by monitoring its decay (at 580 - 610 nm) as a function

of the concentration of the reagents. The slopes of linear plots of pseudo-first-order rate constants k_{obs}^Y for ylide decay *versus* quencher concentrations gave the bimolecular rate constants k_q^Y for the reactions. A few such plots are shown in Fig. 4. The k_q^Y data are summarized in Table 1.

In summary, the lifetimes observed for the carbonyl ylide from DCNO in fluid solutions are significantly longer than those previously reported in the literature under comparable conditions, namely for carbonyl ylides from *trans*-stilbene oxide ($0.81 \mu\text{s}$ [7]), oxiranes bearing aryl, alkyl and fluorenylidene groups ($1 - 10 \mu\text{s}$ [5, 7]), pyrazolinone spirooxiranes ($0.3 - 11 \mu\text{s}$ [6]) and some aromatic ketoepoxides ($1 - 95 \mu\text{s}$ [8]). Furthermore, the rate constants for cycloaddition to dipolarophiles are smaller than those reported [7, 10] for related systems by one to three orders of magnitude. The behavior observed points to enhanced stabilization of the dipole via charge delocalization (as indicated in Fig. 2). Interestingly, because of the presence of cyano substituents, the ylide from DCNO would be expected to be more reactive towards electron-rich dipolarophiles (*e.g.* tetramethylethylene and 2,5-dimethoxy-2,5-dihydrofuran) than electron-poor counterparts (*e.g.* dimethyl acetylene dicarboxylate and maleic anhydride). In practice, as evident from the k_q^Y data in Table 1, an opposite trend is observed. Among the three alcohols, methanol is the most reactive; in addition, the k_q^Y values for alcohols in benzene are much higher than those in acetonitrile. These results suggest that protonation or hydrogen bond formation can be important at the initial stage of interaction of the ylide with hydroxylic molecules.

The absorption spectra and lifetimes of the carbonyl ylide from DCNO are similar to those of similarly structured zwitterionic intermediates formed

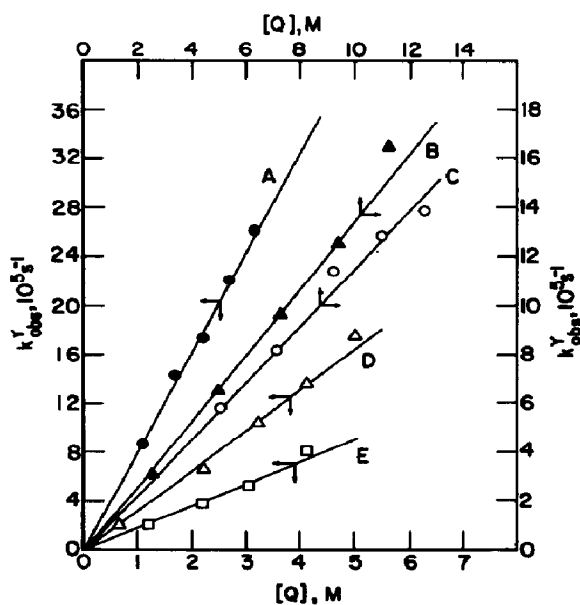


Fig. 4. Plots of observed pseudo-first-order rate constants k_{obs}^Y for ylide decay *versus* quencher concentrations: line A, methanol in benzene; line B, H_2O in acetonitrile; line C, D_2O in acetonitrile; line D, methanol in acetonitrile; line E, 2-propanol in benzene.

in the course of photochemical ring closure of aryl vinyl ethers [11], *N*-aryl enamines [12] and *S*-aryl vinyl sulfides [13] (cyclic carbonyl, azomethine and thiocarbonyl ylides respectively). Flash photolytic studies [11 - 13] have established that the latter intermediates are produced by triplet pathways. Furthermore, in terms of oxygen insensitivity and reactivity towards methanol, the carbonyl ylides from DCNO and some of the aryl vinyl ethers are comparable with one another.

3. Experimental details

DCNO was prepared by standard procedures described in the literature [14]. The sources and methods of purification of the solvents and reagents are given in previous publications [6, 8, 15]. For laser flash photolysis, use was made of either nitrogen laser pulses (337.1 nm, 8 ns, 2 - 3 mJ) from a Moletron UV-400 system or Kr-F₂ excimer laser pulses (248 nm, about 20 ns, 5 - 20 mJ) from a Tachisto gas excimer system. The description of the kinetic spectrophotometer and data processing system is available elsewhere [15, 16]. For transient spectra, a flow system was used to avoid accumulation of photoproducts. The kinetic measurements were performed using static cells of 2 - 3 mm path lengths. Deoxygenation of the solutions was effected by purging with oxygen-free argon. For the steady state photolysis a medium pressure mercury lamp (Bausch and Lomb SP-200) coupled with a Bausch and Lomb monochromator (33-86-07) was used as the excitation source. The absorption spectra were recorded on a Cary 219 spectrophotometer (1 nm bandpass).

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References

- 1 G. W. Griffin and A. Padwa, in O. Buchardt (ed.), *Photochemistry of Heterocyclic Compounds*, Wiley, New York, 1976, Chap. 2.
N. R. Bertoniere and G. W. Griffin, *Org. Photochem.*, 3 (1973) 1973.
- 2 R. S. Becker, R. O. Bost, J. Kolc, N. R. Bertoniere, R. L. Smith and G. W. Griffin, *J. Am. Chem. Soc.*, 92 (1970) 1302.
T. Do-Minh, A. M. Trozzolo and G. W. Griffin, *J. Am. Chem. Soc.*, 92 (1970) 1402.
- 3 I. J. Lev, K. Ishikawa, N. S. Bhacca and G. W. Griffin, *J. Org. Chem.*, 41 (1976) 2654.

- 4 G. A. Lee, *J. Org. Chem.*, **41** (1976) 2656.
G. A. Lee, *J. Org. Chem.*, **43** (1978) 4256.
J. P. K. Wong, A. A. Fahmi, G. W. Griffin and N. S. Bhacca, *Tetrahedron*, **37** (1981) 3345.
G. W. Griffin, K. Ishikawa and I. J. Lev, *J. Am. Chem. Soc.*, **98** (1976) 5697.
- 5 P. C. Wong, D. Griller and J. C. Scaiano, *J. Am. Chem. Soc.*, **104** (1982) 6631.
- 6 P. Umrigar, G. W. Griffin, B. A. Lindig, M. A. Fox, P. K. Das, T. M. Leslie, A. M. Trozzolo, S. N. Ege and A. Thomas, *J. Photochem.*, **22** (1983) 71.
- 7 A. M. Trozzolo and T. M. Leslie, *Bull. Soc. Chim. Belg.*, **91** (1982) 471.
T. M. Leslie, *Ph.D. Dissertation*, University of Notre Dame, Notre Dame, IN, 1980.
- 8 C. V. Kumar, P. K. Das, W. I. O'Sullivan, S. N. Ege and G. W. Griffin, *J. Chem. Soc., Perkin Trans. II*, in the press.
- 9 R. Bensasson and E. J. Land, *Photochem. Photobiol. Rev.*, **3** (1978) 163.
- 10 R. Huisgen and H. Mader, *Angew. Chem., Int. Edn. Engl.*, **8** (1969) 604.
R. Huisgen, *Angew. Chem., Int. Edn. Engl.*, **16** (1977) 572.
- 11 T. Wolff, *J. Org. Chem.*, **46** (1981) 978.
- 12 T. Wolff and R. Waffenschmidt, *J. Am. Chem. Soc.*, **102** (1980) 6098.
- 13 T. Wolff, *J. Am. Chem. Soc.*, **100** (1978) 6157.
- 14 A. Robert, J. J. Pommeret, E. Marchand and A. Fouchaud, *Tetrahedron*, **29** (1973) 463, and references cited therein.
- 15 S. K. Chattopadhyay, P. K. Das and G. L. Hug, *J. Am. Chem. Soc.*, **104** (1982) 4507.
- 16 P. K. Das, M. V. Encinas, R. D. Small, Jr., and J. C. Scaiano, *J. Am. Chem. Soc.*, **101** (1979) 6965.