Geminate Reverse Electron Transfer in a Photogenerated Ion-Pair. Mechanism of 1,4-Dicyanonaphthalene Sensitized Ylide Formation from Stilbene Oxides

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The 337.1 nm laser flash photolysis of 1,4-dicyanonaphthalene (sensitizer) in the presence of *cis* and *trans* stilbene oxides as quenchers (donors) shows the ready formation of mixtures of kinetically distinct isomeric carbonyl ylides on the time scale of sensitizer fluorescence quenching; geminate reverse electron transfer in photogenerated ion-pairs containing ring-opened radical-cations of oxiranes is responsible for the fast production of ylides.

Various methods have been recognized for ring-opening in aryloxiranes leading to the formation of 1,3-dipolar species, commonly known as carbonyl ylides. These include thermal activation,[1] direct photolysis,[2] triplet excitation transfer,[3] and electron-transfer (e.t.) photosensitization.[4] Stereochemical aspects of the various modes of ring-opening are of interest from the view point of symmetry control as implied in Woodward–Hoffman rules.[5] In this communication we present evidence (based on a nanosecond laser flash photolysis study) that the charge-transfer quenching of the 1,4-dicyanonaphthalene (DCN) singlet by *trans* or *cis* stilbene oxide results in the production of mixtures of kinetically distinct isomeric ylides. This occurs *via* fast back e.t. within the singlet-mediated e.t.-derived radical-ion pair in the solvent cage, rather than *via* back-donation of an electron from a solvated DCN radical anion to an oxirane-derived radical-cation. In fact, the solvated radical-ions are not produced to any significant extent even in polar solvents such as acetonitrile and methanol.

The transient absorption phenomena observed upon 337.1 nm laser flash photolysis of a deaerated MeCN solution of 0.5 mM DCN in the presence of 0.02—0.05 M *trans* or *cis* stilbene oxide are analysed in terms of contributions of three distinct species decaying on fairly well-separated time domains. The fastest component decays with a lifetime (τ) of 100 ± 10 ns and accounts for most of the transient absorption at 500—550 nm. The intermediate one, characterized by τ = 760 ± 20 ns, exhibits an absorption maximum ($\lambda_{max.}$) at 470 nm. Following the decay of these two transient species, a relatively weak residual absorption ($\tau > 10$ µs and $\lambda_{max.}$ = 455 nm) becomes apparent. These spectral and kinetic characteristics are illustrated in Figure 1, the insets of which show one experimental trace at 480 nm, comprising of both the 100 and 760 ns species (derived with *trans* stilbene oxide as

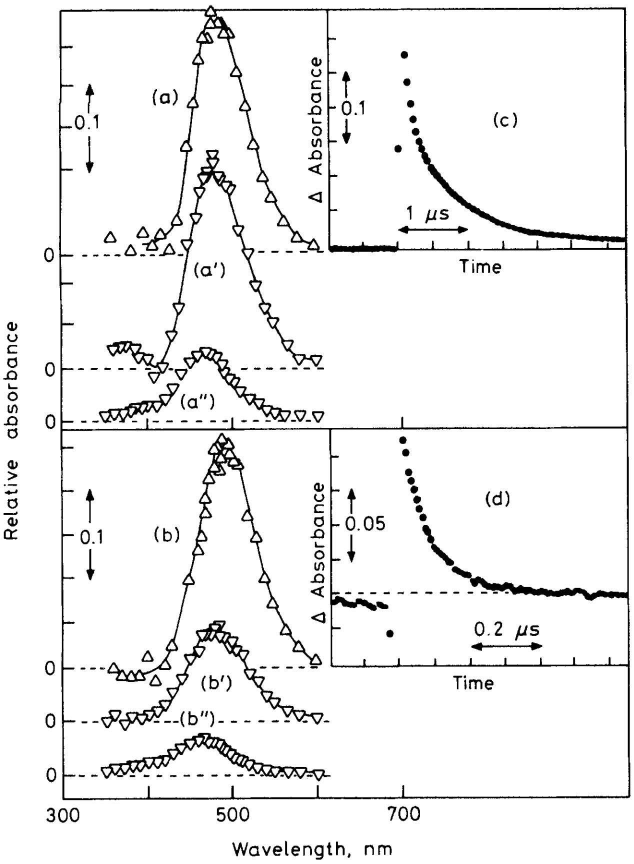
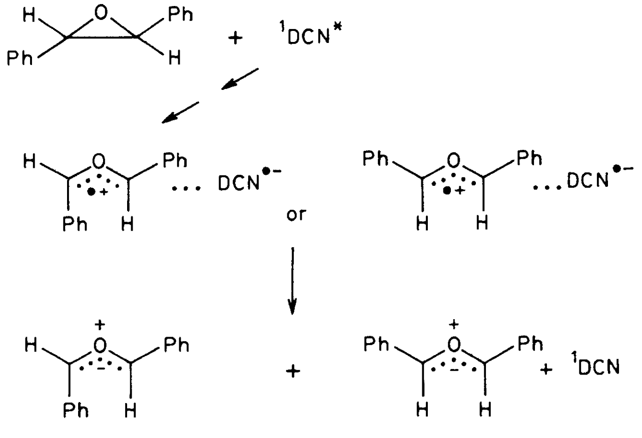


Figure 1. Time-resolved spectra of ylides formed upon 337.1 nm laser flash photolysis of 0.5 mM DCN in the presence of 0.025 M stilbene oxides [(a)—(a"), *trans* and (b)—(b"), *cis*] in Ar-saturated acetonitrile. The times in μs after laser flash to which the spectra correspond are: (a), 0.03; (a'), 0.08; (a"), 0.7; (b), 0.03; (b'), 0.15; (b"), 0.7. Insets: experimental traces at 480 (c) and 530 nm (d) observed upon laser flash photolysis of DCN in the presence of 0.025 M *trans* and *cis* stilbene oxides, respectively, in MeCN (deoxygenated).

substrate), and one at 530 nm comprising primarily of the 100 ns species (derived from *cis* stilbene oxide). Essentially similar results were obtained in tetrahydrofuran and methanol using relatively high concentrations ($\leqslant$0.05 M) of the stilbene oxides as quenchers for the DCN singlet.

An investigation, described in detail elsewhere,[6] and based on direct 266 nm laser flash photolysis of stilbene oxides in various solvents has established the formation of isomerically pure carbonyl ylides. In MeCN, the *trans-exo,endo* form photogenerated from *trans* stilbene oxide *via* symmetry-controlled disrotatory ring-opening is blue-shifted in absorption ($\lambda_{max.}$ = 470 nm) and enjoys a longer lifetime (760 ns) in comparison to the *cis-exo,exo* form ($\lambda_{max.}$ = 490 nm, τ = 100 ns) photogenerated from the *cis* oxirane. The unfailing similarity in terms of spectra and decay kinetics as well as insensitivity towards oxygen and efficient quenching by dipolarophiles (*e.g.*, maleic anhydride and dimethyl acetylenedicarboxylate) establishes that, under photosensitization by DCN, both *trans* and *cis* stilbene oxides give rise to mixtures of isomeric carbonyl ylides *via* relatively fast photochemical process(es) on the time-scale of the quenching of DCN fluorescence (τ_F = 9.5 ns in MeCN). The third transient (longest-lived, $\lambda_{max.}$ = 455 nm) observed under photosensitization is assigned to the triplet[7] of DCN since the spectrum, decay-behaviour, and oxygen-quenching are similar to those noted with DCN alone and with DCN in the presence of the stilbene oxides and an excess of a dipolarophile (to quench both of the 100 and 760 ns species). As expected, on the basis of unfavourable energy and electron transfer,[4] stilbene oxides show no quenching effect on the lifetime of the DCN triplet.



Scheme 1

The radical-anion of DCN in MeCN is characterized by a relatively sharp and intense absorption maximum at 390 nm (ε = 2.2 × 10^4 mol^{-1} dm^3 cm^{-1}).[7,8] Interestingly, very little absorbance change (Figure 1) at this wavelength is observed when DCN is flash-photolysed under extensive singlet quenching by stilbene oxides in any of the solvents examined, including the polar ones (MeOH and MeCN). This means that practically no solvated radical-ions are generated. Combining all the results, we conclude that under exothermic e.t.[4] quenching of DCN singlet by stilbene oxides in a polar solvent, the return of the electron in the photogenerated ion-pair results in the formation of open-ring, ground-state ylides as shown in Scheme 1 with *trans* stilbene oxide as the donor.†

Apparently, at some stage, the oxirane ring is ruptured in the radical-cation partner giving rise to at least two ring-opened forms. Evidence for ring-opened radical-cations of diarylcyclopropanes has been obtained recently from CIDNP studies.[9] Estimates based on the assumption that the *trans-exo,endo* and *cis-exo,exo* forms of the carbonyl ylides have equal extinction coefficients at 470 and 490 nm, respectively, give the molar ratio (in MeCN) of the two forms as 1 : 1.8 and 1 : 5 with the *trans* and the *cis* oxirane as the donors, respectively. In contrast to the photochemical ring-opening of isomeric oxiranes under direct photolysis,[6] where Woodward–Hoffman rules are well-maintained, the lack of isomeric purity of the ylides generated under e.t. photosensitization appears to be a reflection of relaxed symmetry-control in ring-opening *via* oxirane radical-cations. Furthermore, the fact that different molar ratios are obtained starting from the two oxirane isomers suggests the involvement of neither a common ring-opened structure nor an equilibrated mixture of two forms of radical-cation in the ion-pair.

In their pioneering work on steady-state e.t.-sensitized photoisomerization of stilbene oxides and dipolarophilic

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† The product of the fraction (δ_Y) of DCN singlet quenching events that give ylides (combined) and their maximum extinction coefficient (ε_Y, assumed to be same for the two forms) is estimated to be (2.6 ± 0.3) × 10^4 mol^{-1} dm^3 cm^{-1} for *trans* stilbene oxide as the quencher. Since ε_Y is not expected to be very different from that of the ylide from 2-(2-naphthyl)-3,3-dicyano-oxirane (2.0 × 10^4 mol^{-1} dm^3 cm^{-1}, P. K. Das and G. W. Griffin, *J. Photochem.*, in the press), this result indicates δ_Y to be close to unity.

interception of ylide intermediates, Albini and Arnold[4] proposed a mechanism in which the ylides are generated *via* back-donation of an electron from a sensitizer (acceptor) radical-anion to an open-ring oxirane radical-cation. Our results show that this back-donation is fast and occurs in the short-lived ion-pair in the solvent cage rather than following escape of the ions from it. Interestingly, the molar ratios of isomeric ylides observed by us under sensitization are in reasonable agreement with those estimable from the ratios of yields of stereoselective 1,3-cycloaddition products.[4] These point to a preference in the ring-opening of both oxirane radical-cations to the *cis-exo,exo* form.

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