1d, 1781-83-5; **1e**, 73223-32-2; **1f**, 4728-90-9; **2a**, 89789-35-5; **2b**, 89789-36-6; **2c**, 89789-37-7; **2d**, 89789-38-8; **2e**, 89789-39-9; **2f**, 89789-40-2; **2g**, 89789-41-3; **2h**, 89789-42-4; **2i**, 89789-43-5; **2j**, 89789-44-6; **3a**, 89789-45-7; **3b**, 89789-46-8; **3c**, 58564-79-7; **3d**, 89789-47-9; **3e**, 89789-48-0; **3f**, 89789-49-1; **3g**, 89789-50-4; **3h**, 89789-51-5; **3i**, 89789-52-6; CH_3CO_2H, 64-19-7; $CH_3CH_2CO_2H$, 79-09-4; $(CH_3)_2CHCO_2H$, 79-31-2; $CH_3(CH_2)_2CO_2H$, 107-92-6; $CH_3(CH_2)_3CO_2H$, 109-52-4.

Photoinduced Electron-Transfer Processes Involving Substituted Stilbene Oxides[1]

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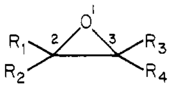
Electron-transfer interactions of several substituted stilbene oxides (oxiranes) containing cyano and carbomethoxy groups at 2,3-positions with the singlet and triplet states of 1,4-dicyanonaphthalene (DCN) and *N,N,N′,N′*-tetramethylbenzidine (TMB) have been investigated by steady-state fluorescence quenching, pulse radiolysis, and laser flash photolysis. The results are examined in the context of the behaviors of the oxiranes with respect to photosensitized isomerization and degradation under steady-state irradiation (350 nm). Transient spectra concerning radical ions and triplets of DCN and TMB as well as primary photoproducts observed in the photosensitization of some of the oxiranes are presented. Evidence for charge-transfer interaction with oxiranes in acetonitrile is obtained from transient-absorption spectral characterization of the radical anion of DCN and the radical cation of TMB; the efficiency of net electron transfer forming solvated radical ions is very small (0–0.3). No transient phenomena attributable to ylides formed via back electron transfer within an ion pair or between solvated radical ions are observed. With trans and cis forms of 2,3-dicarbomethoxy-2,3-bis(4-methoxyphenyl)oxirane, long-lived radical cations with dual absorption maxima at 400 and 580 nm are formed as a result of photosensitization by DCN in acetonitrile. The radical cation from the cis oxirane displays a relatively slow growth ($t_{1/2}$ = 350 ns) for its formation from a charge-transfer-derived precursor with a single absorption maximum at 460 nm; this transient behavior appears to be associated with either relatively slow ring opening of an initially formed, closed ring, radical cation of the cis oxirane via intramolecular electron transfer, or isomerization of an initially formed, open ring, strained configuration to a stable one derivable by electron transfer from the trans oxirane.

Introduction

Organic reactions mediated by charge-transfer interactions from electronically excited states are of current interest. Vicinal diaryl-substituted oxiranes undergo ring opening to carbonyl ylides[2] upon direct irradiation and our experience in this area provided the incentive for the present study[3] of the reactions of radical ions of such oxiranes presumably generated by photoinduced electron-transfer processes in solution. The importance of charge transfer has been recognized in the photochemical isomerization[4a,5] of arylcyclopropanes and in the photochemical addition[4b] of methanol to these systems; cyanoaromatics have been used as electron-transfer sensitizers (excited-state acceptors) in these studies. Albini and Arnold[6] have studied photosensitized isomerization of *cis*- and *trans*-2,3-diphenyloxiranes using a variety of acceptors and proposed a mechanism involving singlet-mediated formation and cleavage of oxirane radical cation followed by back electron transfer from the sensitizer radical anion to produce a carbonyl ylide. The intermediacy of the ylide was based on the results concerning its trapping by various dipolarophiles. More recently, Leslie and Trozzolo[7] observed that following laser excitation (337.1 nm) into a low-lying charge-transfer absorption band of the 1,4-dicyanobenzene and 2,3-diphenyloxirane system in acetonitrile the transient species characterized as a radical cation of the oxirane decayed much more rapidly than the radical anion of 1,4-dicyanobenzene (presumably to a ring closed form with the positive charge localized on oxygen or a phenyl ring).

In this paper we present the results of an investigation of electron-transfer interactions of several oxiranes with 1,4-dicyanonaphthalene (DCN) and *N,N,N′,N′*-tetramethylbenzidine (TMB), which play the roles of excited-

Chart I



1a, $R_1 = R_4 = CN; R_2 = R_3 = p\text{-}CH_3OC_6H_4$
1b, $R_1 = R_4 = CN; R_2 = R_3 = p\text{-}CH_3C_6H_4$
1c, $R_1 = R_4 = CN; R_2 = R_3 = C_6H_5$
2a, $R_1 = R_3 = COOMe; R_2 = R_4 = p\text{-}CH_3OC_6H_4$
2b, $R_1 = R_3 = COOMe; R_2 = R_4 = p\text{-}CH_3C_6H_4$
2c, $R_1 = R_3 = COOMe; R_2 = R_4 = C_6H_5$
3a, $R_1 = R_4 = COOMe; R_2 = R_3 = p\text{-}CH_3OC_6H_4$
3b, $R_1 = R_4 = COOMe; R_2 = R_3 = p\text{-}CH_3C_6H_4$

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(2) (a) Becker, R. S.; Bost, R. O.; Kolc, J.; Bertoniere, N. R.; Smith, R. L.; Griffin, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 1302–1311. (b) Do-Minh, T.; Trozzolo, A. M.; Griffin, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 1402–1403. (c) Wong, J. P. K.; Fahmi, A. A.; Griffin, G. W.; Bhacca, N. S. *Tetrahedron* **1981**, *37*, 3345–3355.

(3) Preliminary papers on part of this work were presented: (a) Griffin, G. W. 64th Chemical Conference and Exhibition, Chemical Institute of Canada, Halifax, Nova Scotia, May 31–June 3, 1982. (b) Griffin, G. W. 10th International Conference on Photochemistry, University of Crete, Crete, Greece, Sept. 6–12, 1982. (c) Griffin, G. W.; Muller, A. J.; Reichel, L. W.; Tamvakis, A. P.; Timpa, J. D. 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 28–April 2, 1982. (d) Griffin, G. W.; Muller, A. J.; Reichel, L. W.; Tamvakis, A. P.; Timpa, J. D. Symposium on Pure and Applied Photochemistry in conjunction with the 65th Annual Chemical Institute of Canada Meeting, Toronto, Canada, May 30–June 2, 1982. (e) Griffin, G. W.; Muller, A. J.; Reichel, L. W.; Tamvakis, A. P.; Timpa, J. D. IX IUPAC Symposium on Photochemistry, Pau, France, July 25–30, 1982. (f) Das, P. K.; Muller, A. J.; Griffin, G. W.; Gould, I. R.; Tung, C. H.; Turro, N. J. *Photochem. Photobiol.* **1984**, *39*, 281–285.

0022-3263/84/1949-1977$01.50/0

state acceptors and donors, respectively. The oxiranes bear electron-withdrawing groups, e.g., CN and COOMe, which make them suitable as acceptors for TMB excited states. On the other hand, the presence of CH_3 and OCH_3 substituents in the phenyl rings enhances their electron-donating capability for interaction with DCN excited states. Data have been obtained from laser flash photolysis, pulse radiolysis, and fluorescence measurements and examined in the context of the results concerning stereochemical change and degradation observed under steady-state photosensitization. No ylide formation has been observed in any case under conditions of electron-transfer sensitization; however, radical cations have been characterized for oxirane systems bearing carbomethoxy and *p*-methoxyphenyl groups. The efficiency of radical ion formation following escape from the solvent cage is found to be zero or small, suggesting that the isomerization via C–C bond rupture may occur in short-lived ion pairs, or short-lived ylides produced via back electron transfer.

The oxiranes under study are shown in Chart I.

Experimental Section

1,4-Dicyanonaphthalene (DCN) was prepared from 1,4-dibromonaphthalene by treatment with cuprous cyanide according to the procedures given in the literature.[8,9] The syntheses of the majority of the oxiranes employed in this study are described in a previous paper.[10] *N,N,N′,N′*-Tetramethylbenzidene (TMB), from Eastman, was purified by chromatography on alumina and recrystallization from ethanol. Spectral grade acetonitrile and methanol, both from Aldrich, were used as received. 2,5-Dimethyl-2,4-hexadiene (DMHD) and triethylamine (TEA), obtained from K and K and Baker Chemical Co., respectively, were passed through columns of silica gel and alumina (basic), respectively, prior to use. 1,2,4-Trimethoxybenzene (1,2,4-TMB), purchased from Fluka Chemical Co., was fractionally distilled under vacuum. Tetramethylethylene (TME), obtained from Aldrich, was used without further purification. Paraquat (PQ^{2+}), a Sigma Chemical Co. product, was dissolved in aqueous methanol and precipitated by adding a large volume of acetone. 1,2-Dichloroethane (Eastman, spectral grade) was distilled before use.

Steady-state fluorescence measurements were carried out by using an SLM photon-counting spectrofluorimeter,[11] and the determination of fluorescence lifetimes was based on the time-correlated photon-counting technique using equipment[11] available from Photochemical Research Associates. For laser flash photolysis experiments, nitrogen laser pulses (337.1 nm, 8 ns, 2–3 mJ) from a Molectron UV-400 system were generally used for excitation. In a few experiments (see Results section), the third harmonic at 355 nm (~6 ns, 2–6 mJ/pulse) from a Nd-YAG laser source (Quanta-Ray), and the output from a Kr–F_2 excimer system (Tachisto) at 248 nm (~20 ns, 10–20 mJ/pulse) were also used. A complete description of the flash photolysis apparatus is available in previous papers.[12] The actinometry for laser flash photolysis was performed using an acetonitrile solution of benzophenone optically matched with the sample solution. The benzophenone triplet was monitored at 520 nm (ϵ_{max} = 6500 M^{-1} cm^{-1})[13] and unit efficiency was assumed for the triplet yield (ϕ_T).[14] Spectrophotometric pulse radiolysis was conducted using the Notre Dame 7-MeV ARCO LP-7 linear accelerator as the source of electron pulses (5 ns, ~2 × 10^{16} eV/g per pulse). Details concerning the apparatus and the method are available elsewhere.[15a,b]

Table I. Kinetic Data for Quenching of Steady-State Fluorescence from DCN and TMB by Oxiranes and Other Quenchers in Acetonitrile

sensitizer	τ_F, ns	quencher	max [Q] used, mM	K_{SV}^F, M^{-1} [a]	k_q^s, 10^9 M^{-1} s^{-1} [b]
DCN	9.5	oxiranes			
		1a	8.2	146	15.4
		1b	11.9	21	2.2
		1c	15.2	48	5.1
		2a	4.0	105	11.1
		2b	16.2	~2	~0.2
		2c	16.3	~1	~0.1
		3a	9.6	108	11.4
		3b	8.4	7	0.7
		other quenchers			
		oxygen	2.9	127	13.4
		DMHD	17.6	180	19.0
		TEA	21.6	150	15.8
		TME	42.0	124	13.1
		1,2,4-TMB	6.0	180	19.0
TMB	11.1	oxiranes			
		1a	7.1	242	21.8
		1b	6.0	220	19.8
		1c	7.1	263	23.7
		2a	3.1	27	2.4
		2b	6.9	99	8.9
		2c	7.7	142	12.8
		other quenchers			
		oxygen	2.9	443	39.9
		DMHD	87.9	~0.4	~0.04
		TEA	180	<0.02	<0.002
		DCN	3.4	250	22.5

[a] ±10%. [b] From, $K_{sv}^F = k_q\tau_F$.

Results

Fluorescence Quenching: Stern–Volmer Constants. In deaerated acetonitrile strong fluorescence is exhibited by both TMB and DCN, λ_{max} = 404 and 380 nm (corrected), respectively. The measured fluorescence lifetimes, τ_F, are 11.1 and 9.5 ns for TMB and DCN, respectively. The fluorescence of both systems is quenched efficiently by several of the oxiranes studied. The Stern–Volmer constants (K_{sv}^F) for steady-state fluorescence quenching have been determined from standard linear plots for the relative decrease in fluorescence intensity at several quencher concentrations, [Q]. The data for the oxiranes and several other quenchers are given in Table I. While the behavior of the oxiranes toward singlet TMB and DCN will be discussed later, differences arising from the donor/acceptor properties of TMB ($E_{1/2}^{ox}$ = 0.32 V vs. SCE in 1:1 benzene:methanol mixture)[16] and DCN ($E_{1/2}^{red}$ = 1.67 V vs. Ag/0.1 M $AgNO_3$ in acetonitrile)[6] are evidenced by the bimolecular quenching rate constants (k_q^s) of such quenchers as oxygen, TEA, and DMHD (Table I).

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(4) (a) Hixson, S. S.; Boyer, J.; Gallucci, C. *J. Chem. Soc., Chem. Commun.* **1974**, 540–542. (b) Rao, V. R.; Hixson, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 6458–6459.

(5) Arnold, D. R.; Humphreys, R. W. R. *J. Am. Chem. Soc.* **1979**, *101*, 2743–2744.

(6) Albini, A.; Arnold, D. R. *Can. J. Chem.* **1978**, *56*, 2985–2993.

(7) Leslie, T. M. Ph.D. Dissertation, University of Notre Dame, 1980. Leslie, T. M.; Trozzolo, A. M., unpublished results.

(8) Hornung, E. C. In "Organic Syntheses"; Wiley: New York, 1965; Collect Vol. III, p 631.

(9) Arnold, D. R.; Maroulis, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5931–5937.

(10) Muller, A. J.; Nishiyama, K.; Griffin, G. W.; Ishikawa, K.; Gibson, D. M. *J. Org. Chem.* **1982**, *47*, 2342–2352.

(11) Chattopadhyay, S. K.; Das, P. K.; Hug, G. L. *J. Am. Chem. Soc.* **1982**, *104*, 4507–4514.

(12) Das, P. K.; Encinas, M. V.; Small, R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965–6970. Das, P. K.; Bhattacharyya, S. N. *J. Phys. Chem.* **1981**, *85*, 1391–1395.

(13) Bensasson, R. V.; Gramain, J-C. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1801–1810.

(14) Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* **1965**, *43*, 2129–2135.

(15) (a) Raghavan, N. V.; Das, P. K.; Bobrowski, K. *J. Am. Chem. Soc.* **1981**, *103*, 4569–4573. (b) Patterson, L. K.; Lilie, J. *Int. J. Radiat. Phys. Chem.* **1974**, *6*, 129–141. (c) Dorfman, L. M. *Acc. Chem. Res.* **1970**, *3*, 224–230.

(16) Horner, L.; Nickel, H. *Chem. Ber.* **1956**, *89*, 1681–1690.

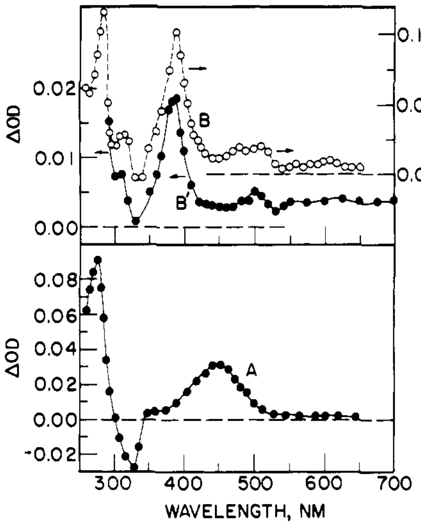

Figure 1. (A) Triplet–triplet absorption spectra of DCN in acetonitrile obtained by direct excitation (337.1 nm) of 3.5×10^{-4} M solution (at ~2 μs following laser flash). (B) Transient absorption spectrum of $DCN^{-}\cdot$ obtained by pulse radiolysis of 2.9×10^{-4} M DCN solution in 2-propanol at ~10 μs following the electron pulse. (B′) Transient absorption spectrum of $DCN^{-}\cdot$ observed by laser excitation of 3.5×10^{-4} M DCN solution in acetonitrile containing 70 mM TEA (at 3 μs following laser flash).

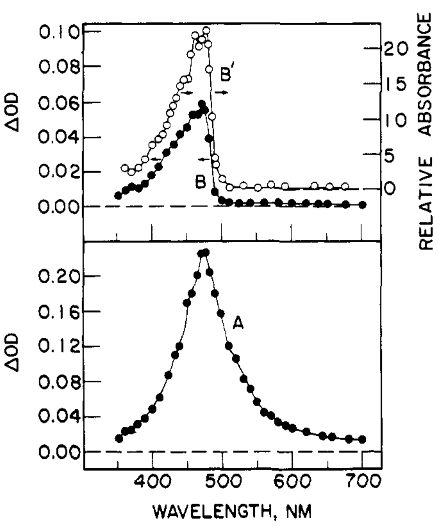

Figure 2. (A) Triplet–triplet absorption spectrum of TMB obtained by direct excitation of 9.0×10^{-5} M TMB solution in acetonitrile (0.2 μs following laser flash), corrected for the contribution of $TMB^{+}\cdot$ measured in a parallel experiment in the presence of 70 mM DMHD. (B) Transient absorption spectrum of $TMB^{+}\cdot$ in acetonitrile solution (9×10^{-5} M in TMB), obtained by photoionization in the presence of 70 mM DMHD (3 μs following laser flash). (B′) Absorption spectrum of $TMB^{+}\cdot$ obtained by pulse radiolysis of 5×10^{-4} M TMB solution in 1,2-dichloroethane (10 μs after the electron pulse).

Laser Flash Photolysis/Pulse Radiolysis. (i) Transient Processes Related with Triplets and Radical Ions of TMB and DCN. The direct laser excitation of DCN in deaerated acetonitrile leads to transient phenomena attributed solely to the triplet species ($^3DCN^*$). The triplet–triplet (T_1–T_n) absorption spectrum, shown in Figure 1A, exhibits maxima at 275 and 455 nm. Under conditions where the concentration of $^3DCN^*$ produced is low, that is, in optically dilute solutions (OD $\leq$ 0.1 in 3-mm cell at 337.1 nm) and at low laser intensities (~0.2 mJ/pulse at 337.1 nm), the triplet decay follows first-order kinetics and the lifetime approaches a value, ~40 μs. The maximum extinction coefficient ϵ_{max}^{TT}) of $^3DCN^*$ was determined by the triplet energy-transfer technique[17] using benzophenone as the donor preferentially excited at 355 nm (Nd-YAG laser). A comparison of observed ΔOD due to the benzophenone triplet at its maximum (520 nm in acetonitrile, ϵ_{max} = 6500 M^{-1} cm^{-1})[13] in a benzophenone solution (0.05 M) containing no quencher with that due to DCN triplet at 455 nm in solutions containing benzophenone (0.05 M) and DCN (0.005–0.01 M) gave a value of 7 (± 1) × 10^3 M^{-1} cm^{-1}[18] for ϵ_{max}^{TT} of DCN triplet at 455 nm. On the basis of these data, the triplet yield (ϕ_T) of DCN in deaerated acetonitrile was estimated to be 0.19 ± 0.03.

Pulse radiolysis[15a,c] of DCN in 2-propanol provided a convenient method of generating DCN radical anion ($DCN^{-}\cdot$) through attachment of solvated electron as well as electron transfer from the ketyl radical, $(CH_3)_2\dot{C}OH$. The spectrum of $DCN^{-}\cdot$ shown in Figure 1B is characterized by two sharp and intense peaks at 390 and 285 nm. A similar spectrum (Figure 1B′) assigned to $DCN^{-}\cdot$ was also observed upon laser excitation (337.1 nm) of DCN in acetonitrile containing 0.1–0.05 M TEA (quencher of $^1DCN^*$). Electron transfer from 1,2,4-TMB (a good electron donor, $E_{1/2}^{ox}$ = 1.12 V vs. SCE, in acetonitrile)[19] to $^1DCN^*$ (λ_{ex} = 337.1 nm, N_2 laser) as well as from $^1TMB^*$ (λ_{ex} = 355 nm, Nd-YAG laser) to DCN (ground state) was used for estimating the extinction coefficient of $DCN^{-}\cdot$. A comparison of the end-of-pulse absorbances (ΔOD's) at 390 nm (primarily due to $DCN^{-}\cdot$) with those due to 1,2,4-$TMB^{+}\cdot$ (450 nm, ϵ_{max} = 8.9×10^3 M^{-1} cm^{-1} in water)[20] and $TMB^{+}\cdot$ (470 nm, ϵ_{max} = 4.0×10^4 M^{-1} cm^{-1}, vide infra) gave (22 ± 3) × 10^3 M^{-1} cm^{-1} for the extinction coefficient of $DCN^{-}\cdot$.

Laser flash photolysis of TMB in acetonitrile leads to the formation of both the triplet ($^3TMB^*$) and the radical cation ($TMB^{+}\cdot$) whose absorption spectra overlap with each other very closely (λ_{max} = 470 nm for $TMB^{+}\cdot$ and 475 nm for $^3TMB^*$). Our observations in the course of the flash photolysis of TMB in acetonitrile parallel closely those reported in an analogous study[21] with methanol as the solvent. We have used the diene, DMHD (E_T = 58.7 kcal/mol)[22] to quench efficiently $^3TMB^*$ (E_T = 62.3 kcal/mol)[21] by energy transfer without quenching $TMB^{+}\cdot$ to any appreciable extent at the same time. Thus, in the presence of DMHD (0.05–0.07 M), the lifetime of $^3TMB^*$ becomes very short (18–25 ns) allowing us to monitor absorbances due to $TMB^{+}\cdot$ at an instant close to the laser pulse and hence, to estimate the yield of photoionization accurately. Also we have used paraquat (PQ^{2+}) in aqueous (5%, v/v) acetonitrile to quench $^1TMB^*$ and $^3TMB^*$ simultaneously and generate $TMB^{+}\cdot$ and $PQ^{+}\cdot$ in equimolar concentrations. From the extinction coefficients[23,24] of $PQ^{+}\cdot$ at its λ_{max}'s (605 and 395 nm) we obtained, ϵ_{max} = 40 (± 4) × 10^3 M^{-1} cm^{-1} for $TMB^{+}\cdot$; this is in good agreement with the values reported by other investigators.[21]

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[17] Bensasson, R.; Land, E. J. *Photochem. Photobiol. Rev.* **1978**, *3*, 161–191 and references therein.

[18] Using the technique[17] of triplet energy transfer from pulse radiolytically generated biphenyl triplet in benzene, ϵ_{max} values of (5.5 ± 0.5) × 10^3 and (3.3 ± 0.3) × 10^4 M^{-1} cm^{-1} have been measured for $^3DCN^*$ (at 455 nm) and $^3TMB^*$ (at 478 nm), respectively.

[19] Zweig, A.; Hodgson, W. C.; Jura, W. J. *J. Am. Chem. Soc.* **1964**, *86*, 4124–4129.

[20] O'Neill, P.; Steenken, S.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1975**, *79*, 2773–2779.

[21] Alkaitis, S. A.; Grätzel, M. *J. Am. Chem. Soc.* **1976**, *98*, 3549–3554.

[22] Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

[23] Farrington, J. A.; Ebert, M.; Land, E. J.; Fletcher, K. *Biochem. Biophys. Acta* **1973**, *314*, 372–381.

[24] Trudinger, P. A. *Anal. Biochim.* **1970**, *36*, 222–225.

Table II. Rate Constants for DCN and TMB Triplet Quenching by Oxiranes and Other Quenchers in Acetonitrile

triplet	T–T absorption maxima, nm (extinc tion coeff, 10^3 M^{-1} cm^{-1})	triplet[b] yield	quencher	max [Q] used, mM	k_q^T, M^{-1} s^{-1} [c]
DCN[a]	460 (7 ± 1)	0.19	oxiranes		
			1a	3	$<1 \times 10^6$
			3a	8	$<1 \times 10^6$
			other quenchers		
			oxygen	0.8	2.1×10^9
			DMHD	14.1	1.7×10^9
TMB[a]	470 (38 ± 4)	0.45	oxiranes		
			1a	4.3	2.8×10^8
			1b	7.3	7.9×10^8
			1c	5.6	1.8×10^9
			2c	6.4	5×10^6
			other quenchers		
			oxygen	0.8	2.2×10^{10}
			DMHD	21.1	9.5×10^8
			PQ^{2+} [d]	0.6	8.4×10^9

[a] Longest triplet lifetimes observed under low-intensity laser excitation are 40 and 10 μs for ^{3}DCN* and ^{3}TMB*, respectively. [b] ±20%. [c] ±10%. [d] In acetonitrile containing 5% water (v/v).

No apparent growth or decay at 470 nm is observed upon triplet quenching (>95%) of ^{3}TMB* by PQ^{2+} in aqueous acetonitrile; this implies that the extinction coefficient of $TMB^{+}\cdot$ at 470 nm is higher than or equal to that of ^{3}TMB* at the same wavelength. Comparison of ΔOD's due to ground-state depletion at 305–320 nm with those due to triplet at 470 nm produced by a 337.1 nm laser absorption gave a value of $36 \pm 4 \times 10^4$ M^{-1} cm^{-1}[18] for the maximum extinction coefficient of ^{3}TMB*. Figure 2A,B show the transient absorption spectra for ^{3}TMB* and $TMB^{+}\cdot$ obtained in acetonitrile by direct excitation at 337.1 nm. The radical cation, $TMB^{+}\cdot$, was also conveniently generated by pulse radiolysis in 1,2-dichloroethane[25] by way of charge transfer from solvent-derived radical cations (Figure 3A′). We could not detect transient absorption due to the solvated electron, e_{solv} (derived from photoionization of TMB), at 600–750 nm where a broad absorption band has been reportedly[26] observed in acetonitrile. The photoionization of TMB in acetonitrile (and reportedly methanol as well)[21] is found to be nearly monophotonic. It seems reasonable to consider the photoionization as a conventional process competing with the usual photophysical processes such as fluorescence, intersystem crossing and internal conversion, originating from the lowest singlet state. The quantum yields for photoionization and intersystem crossing (λ_{ex} = 337.1 nm) are 0.09 ± 0.02 and 0.45 ± 0.09, respectively. Data relating to DCN and TMB triplets and their quenching by various species are given in Table II.

(ii) Transient Phenomena in Singlet-Mediated Electron Processes with Oxiranes. Laser flash photolysis experiments were carried out using DCN and TMB as the excited-state acceptors and donors, respectively, for those oxiranes studied for which the singlet-mediated charge-transfer interaction was found to be the strongest as manifested in K_{sv}^F's (Table I). These oxiranes include the *p,p′*-dimethoxystilbene oxides (**1a**, **2a**, and **3a**) as donors for ^{1}DCN* and the *trans*-2,3-dicyano-substituted oxides (**1a–c**) and *cis*-2,3-dicarbomethoxystilbene oxide (**2c**) as acceptors for ^{1}TMB*. The oxiranes **2b** and **2c** undergo cis–trans photoequilibration under prolonged steady-state photosensitization by DCN. However, laser excitation of DCN in the presence of these oxiranes as well as **1b** and **1c** at concentrations 0.01–0.03 M does not show any significant transient phenomena other than that arising from ^{3}DCN*.

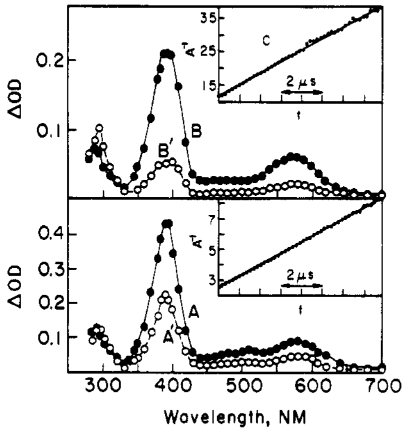

Figure 3. Transient absorption spectra observed at 50 ns (A,B) and 4 μs (A′,B′) following the laser flash in acetonitrile solutions of DCN (3.34×10^{-4} M) and oxirane **3a** (0.023 M). A,A′, deaerated; B,B′, air saturated. The insets, C and D, show the best fit of the decay profiles of spectral absorptions in the deaerated solution at 580 and 385 nm, respectively, into second-order equal-concentration kinetics.

The transient absorption spectra obtained as a result of laser flash photolysis of DCN in the presence of oxirane **3a** in deaerated and air-saturated acetonitrile solutions are shown in Figure 3. The experiment in the presence of air is informative. Although ^{1}DCN* is quenched by oxygen to the extent of about 20% in an air-saturated solution (based on K_{sv}^F of 127 M^{-1} for oxygen, Table I), the lifetimes of $DCN^{-}\cdot$ and ^{3}DCN* become considerably short (54 and 385 ns, respectively) under these conditions so that the contribution to the transient spectra of radical cations and other oxygen-insensitive photoproducts can be time resolved more effectively. The spectra in Figure 3A,A′ are characterized by a sharp peak at 390 nm (due to both $DCN^{-}\cdot$ and radical cation derived from the oxirane) and a broad, less intense peak at 580 nm (due solely to the radical cation). That the radical cation contributes strongly to the absorption at 380–420 nm is apparent from the spectra, Figures 3B,B′, in the presence of air. At ~2 μs following the laser flash, when virtually no $DCN^{-}\cdot$ or

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(25) Shank, N. E.; Dorfman, L. M. *J. Chem. Phys.* **1970**, *52*, 4441–4447. Arai, S.; Veda, H.; Firestone, R. F.; Dorfman, L. M. *Ibid.* **1969**, 1072–1077. Wang, Y.; Tria, J. J.; Dorfman, L. M. *J. Phys. Chem.* **1979**, *83*, 1946–1951.

(26) Singh, A.; Gesser, H. D.; Scott, A. R. *Chem. Phys. Lett.* **1968**, *2*, 271–273. See also: Bell, I. P.; Rodgers, A. J.; Burrows, H. D. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 315–326. Hayon, E. *J. Chem. Phys.* **1970**, *53*, 2353–2358. Truong, T. B. *Ibid.* **1982**, *77*, 5375–5378.

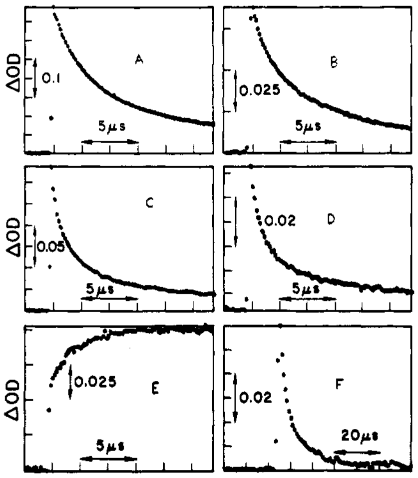

Figure 4. Representative experimental traces related with transient phenomena observed in 337.1 nm laser flash photolysis of deaerated (A,B,F) and aerated (C,D,E) solutions of DCN (3.3 × 10^{-4} M) and oxirane **3a** (0.023 M) in acetonitrile. A, 385 nm (degassed); B, 580 nm (degassed); C, 385 nm (air saturated); D, 580 nm (air saturated); E, (295 nm, air saturated); F, 580 nm (degassed).

^{3}DCN* exists, the spectrum exhibits a prominent peak at 400 nm with an intensity 2.4 times greater than that at 580 nm. It is also noted that a minor product, with absorption at 290–300 nm, grows in on the same time scale as that of the decay of the 580 nm (or 400 nm) species in both deaerated and air-saturated solutions.

Six representative experimental traces for the decay (or formation) of photoproducts observed for the (DCN + oxirane)-**3a** system are presented in Figure 4. The decay of the transient absorption at 390–400 nm and at 580 nm in deaerated solutions was found to fit well into second-order, equal-concentration kinetics (suggestive of back electron transfer between DCN$^{-\cdot}$ and the radical cation derived from the oxirane); the measured values for k/ϵ are 1.0 × 10^6 and 2.7 × 10^5 cm s^{-1} at 580 and 400 nm, respectively (k is the rate constant for second-order decay and ϵ is the extinction coefficient). Two such kinetic fits are shown in the insets of Figure 3. In air-saturated solution the initial portions of the decays of transient absorptions at both 400 and 580 nm regions become slightly faster (see Figure 4C,D). However, no reliable estimate for k_q by O_2 could be made because even in oxygen-saturated solutions the decay kinetics remain mixed (in fact, approach second-order more closely than first-order decay kinetics). Practically no quenching is observed for the 580 nm species by methanol (≤4 M) and TME (≤0.3 M), although bromide ion, added as tetrabutylammonium bromide, interacts with a bimolecular rate constant, 3 × 10^8 M^{-1} s^{-1}. The yields of transients absorbing at both 390 and 580 nm are reduced concomitantly to the same extents in the presence of varying concentrations of TME, understandably because of competitive quenching of ^{1}DCN* ($K_{sv}{}^F$ = 124 M^{-1}, Table I).

Laser flash photolysis of DCN in the presence of oxirane **2a** (cis isomer of **3a**) in deaerated or air-saturated acetonitrile shows a relatively slow step in the formation of the oxirane-derived radical cation. Transient spectra at the initial stage and after completion of this formation process in deaerated and air-saturated acetonitrile as well as two kinetic traces illustrating the slow growth at 405 and 580 nm are presented in Figure 5A,A′,B,B′ and their insets. The transient spectra (Figure 5A′,B′) in the case of oxirane **2a** following the completion of the initial formation process (over ~2 μs and during the subsequent decay (over ~70 μs) are identical with those observed with its trans counterpart (oxirane **3**) as the substrate (Figure 4). For both substrates in deaerated acetonitrile, the transient spectra at 350–650 nm can be analyzed in terms of contributions from DCN$^{-\cdot}$, oxirane-derived radical cation, and, to a small extent, ^{3}DCN*. In the presence of air, with both isomers, DCN$^{-\cdot}$ and ^{3}DCN* decay fast (vide supra) leaving behind the slowly decaying radical cation with maxima at 400 and 580 nm. The fact that the rate constant, (2.0 ± 0.2) × 10^6 s^{-1}, for the initial formation process of the radical cation of oxirane **2a** remains practically unchanged in the presence or absence of air rules out its origin from electron-transfer quenching of ^{3}DCN* by the cis oxirane. Plausible explanations for this process will be considered in the Discussion section.

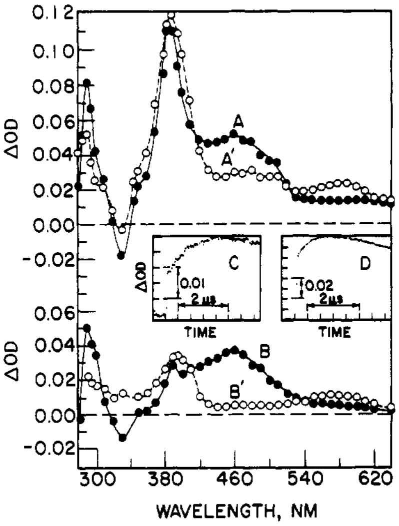

Figure 5. Absorption spectra of transients observed in 337.1 nm laser flash photolysis of 0.69 mM DCN and 2.7 mM oxirane **2a** in deaerated (A,A′) and air-saturated (B,B′) acetonitrile. A,B, 40 ns after the flash; A′,B′, 2 μs after the flash. Insets, experimental traces showing the growth of transient absorption at 580 nm (C) and 405 nm (D) in deaerated acetonitrile.

With oxirane **1a** as the quencher for ^{1}DCN*, the transient photoproduct spectra clearly show the formation of DCN$^{-\cdot}$, though in low yield, with the well-defined peak at 390 nm. The transient spectra in both aerated and deaerated solutions also show a broad absorption band at 400–500 nm (λ_{max} 455 nm), reminiscent of the spectrum of ^{3}DCN* (Figure 1A). We assign this transient absorption at 400–500 nm primarily to ^{3}DCN* on the basis of the spectral similarity and the fact that the rate constant for its decay in aerated solution is identical with that of ^{3}DCN*. The magnitude of the transient absorbance at 455 nm is much higher than the value expected after making allowance for ^{1}DCN* quenching by the oxirane (in competition with intrinsic intersystem crossing). This suggests that ^{3}DCN* is produced via the charge-transfer quenching of ^{1}DCN* by the oxirane. In an air-saturated solution, the transient spectrum after completion of ^{3}DCN* and DCN$^{-\cdot}$ decay shows a long-lived, weak, residual absorption at 300–390 nm rising in intensity at short wavelengths.

The transient spectra which develop upon laser flash photolysis of TMB in the presence of the oxiranes **1a–c** and **2c** are dominated by the strong absorption bands of TMB$^{+\cdot}$ and/or ^{3}TMB*; those obtained in the presence of DMHD (70 mM), which rendered ^{3}TMB* short-lived, allowed us to reveal absorptions due to TMB$^{+\cdot}$ and oxirane-derived photoproducts at a time close to the laser pulse without being obscured by the strong absorption of ^{3}TMB*. The spectra with oxiranes **1a–c** and **2c** as quenchers were, to all intents and purposes, identical with that of TMB$^{+\cdot}$, suggesting that the transient absorption due to the oxirane radical anions or related products are weak and featureless.

(iii) Triplet-Mediated Interactions with Oxiranes. Generation of ^{3}DCN* exclusively by energy transfer from triplet benzophenone produced by laser excitation at 355 nm in the presence of oxiranes **1a** and **2a** confirmed that the decay of ^{3}DCN* was not affected by the oxiranes (k_q^T < 10^6 M^{-1} s^{-1}). On the other hand, ^{3}TMB* was quenched to varying degrees by the oxiranes, particularly those with CN groups in 2,3-positions. k_q^T data are given in Table II.

(iv) Yields of Photoproduct(s) from Electron Transfer. Estimates were made regarding the fractions (ψ^S and ψ^T) of the singlet and triplet quenching events that result in ion formation. This was done in terms of yields (ϕ_{ion}) of DCN$^{-}\cdot$ and TMB$^{+}\cdot$ obtained from end-of-pulse absorbances (ΔOD) at 390 and 470 nm, respectively. For DCN sensitized reactions, the radical anion originated solely through singlet-mediated electron transfer. In this case, total ion yield (ϕ_{ion}^{tot}) was given by the following relationship. [OX] represents the oxirane concentration

$$\phi_{ion}^{tot} = (1 + K_{sv}^F[OX])^{-1}K_{sv}^F[OX]\psi^S \qquad (1)$$

used. With oxiranes **3a** and **2a**, the oxirane-derived radical cations contribution to ΔOD's at 390 nm was as strong as DCN$^{-}\cdot$ itself and therefore, it was necessary to isolate the contribution of DCN$^{-}\cdot$ so that ϕ_{ion}^{tot} could be calculated on the basis of its known extinction coefficient. The ratio (r) of ΔOD's (and hence extinction coefficients) at 390 and 580 nm was observed in air-saturated solutions at a time sufficiently delayed from the laser flash so that oxygen quenching precluded extensive accumulation of DCN$^{-}\cdot$ and ^{3}DCN*. The end-of-pulse ΔOD's at 580 nm in deaerated solutions were then multiplied by r and subtracted from the end-of-pulse ΔOD's at 390 nm to obtain ΔOD's due solely to DCN$^{-}\cdot$. Use of ϕ_{ion}^{tot} obtained in this manner and K_{sv}^F data (Table I) in eq 1 gave 0.3 ± 0.1 for ψ^S with oxirane **3a** as the substrate ([OX] = 0.01–0.02 M). The oxirane **1a** gave a much smaller value for ψ^S (<0.1 at [OX] = 0.025 M) based on the assumption that the end-of-pulse ΔOD at 390 nm was totally due to DCN$^{-}\cdot$.

Three pathways exist for the production of TMB$^{+}\cdot$, when TMB is used as the photosensitizer. These are (1) photoionization (presumably from ^{1}TMB*), (2) singlet-mediated quenching, and (3) triplet-mediated quenching. Assuming that electron-transfer quenching of ^{1}TMB* does not give ^{3}TMB*, one obtains eq 2 for ϕ_{ion}^{tot} in this case.

$$\phi_{ion}^{tot} = (1 + K_{sv}^F[OX])^{-1}[\phi_{ion} + K_{sv}^F[OX]\psi^S + \phi_T(1 + k_q^T\tau_T[OX])^{-1}k_q^T\tau_T[OX]\psi^T] \qquad (2)$$

Experiments were conducted with oxiranes in the presence of a sufficiently high concentration of DMHD to quench ^{3}TMB* by energy transfer (without quenching ^{1}TMB* appreciably) so that the triplet-mediated contribution to ϕ_{ion}^{tot} was negligible. Values for ψ^S in the range of 0.06–0.08 were obtained for **1a–c** and **2c** upon evaluation of ϕ_{ion}^{tot} at [OX] = 0.015–0.025 M. Furthermore, the quenching of ^{3}TMB* at 0.002–0.02 M concentrations of oxirane **2c** did not show any improvement in the ΔOD due to TMB$^{+}\cdot$ relative to the experiments where the diene was deliberately added to compete with ^{3}TMB* quenching by the oxirane. Our best estimates in this regard indicated that ψ^T was close to zero.

(v) Pulse Radiolysis and Direct Laser Flash Photolysis (248 nm) of Oxirane 3. It was important to establish the identity of the radical cation of oxirane **3a** by generating it under conditions where there was no complication from the contributions of ^{3}DCN* and DCN$^{-}\cdot$ to the transient absorption. This was accomplished by pulse radiolysis[25] in 1,2-dichloroethane wherein charge transfer occurred from solvent-derived cations to the substrate. Figure 6A shows the transient absorption spectrum obtained from oxirane **3a**. Note that the spectrum with maxima at 405 and 590 nm is almost identical with that observed under DCN sensitization (Figure 3B,B′) in air-saturated acetonitrile.

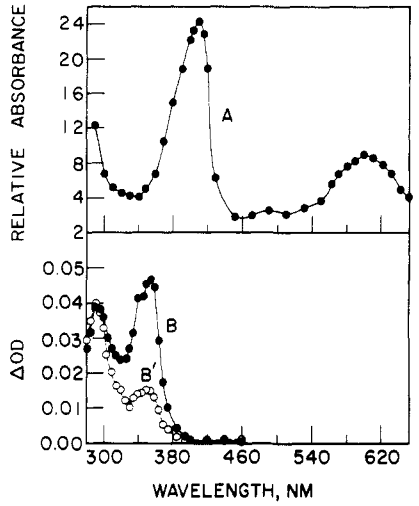

Figure 6. (A) Absorption spectrum of radical cation from oxirane **3a** generated by pulse radiolysis of 1.2 mM solution in air-saturated 1,2-dichloroethane (monitored at 1 μs following electron pulse). (B,B′) Transient absorption spectra monitored in 248 nm laser flash photolysis of 0.26 mM solution of oxirane in deaerated acetonitrile at 100 ns (B) and 1.5 μs (B′) after laser flash.

Question remains as to whether an open ring ylide is formed as a result of back electron transfer between the radical ions either in the solvent cage or after escape from it. To shed light on this, it is necessary to obtain information on the spectral and kinetic behavior of the ylide under conditions identical with those used for photosensitization by DCN. Oxirane **3a** was flash photolyzed directly in deaerated acetonitrile using laser pulses (248 nm) from a Kr–F$_2$ excimer laser system. The resulting transient absorption spectra, presented in Figure 6B,B′, indicates the formation of two distinct species with maxima at 355 and 295 nm, respectively. The former (λ_{max} 355 nm) decays with first-order kinetics; the rate constant for decay is 8.5 × 10^4 s^{-1} (not affected by the presence of oxygen). In the presence of H$_2$O and methanol the decay becomes considerably enhanced. Interestingly, the plots of the rate constant for decay (k_{obsd}) vs. [H$_2$O] or [MeOH] exhibit upward curvatures (see later); from the initial parts of these plots at low methanol (≤0.1 M) and H$_2$O (≤0.25 M) concentrations, values for rate constants for bimolecular quenching are estimated at 6.8 × 10^6 and 1.2 × 16^6 M^{-1} s^{-1}, respectively. The species with λ_{max} at 295 nm show no sign of decay over ~100 μs in the presence or absence of oxygen (≤2 mM), methanol (0.5 M), or water (0.56 M).

A study of laser intensity dependence shows that both of the species absorbing at 355 and 295 nm, respectively, are formed via monophotonic light absorption. Photolysis of oxirane **3a** is expected to give an ylide[2] (**4**) as well as a carbene (**5**) according to Scheme I. We assign the species with λ_{max} at 355 nm to the carbene **5**, most probably in the singlet form, on the basis of the similarity of the location of absorption maximum to that of (p-methoxyphenyl)-chlorocarbene (singlet)[27] as well as the similarity of be-

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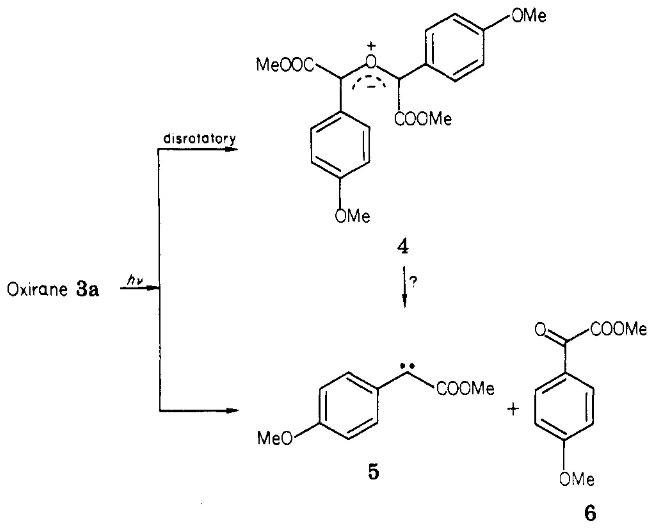
(27) Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5549–5551.

Scheme I



haviors in the quenching reactions by O_2, H_2O, and MeOH to those exhibited by related singlet carbenes.[27-29] The other possible assignment in terms of the carbonyl ylide,[30] 4, is ruled out on the basis of the lack of an absorption maximum at long wavelengths (400–700 nm) as expected for an ylide in which the charge separation would be large because of the presence of the methoxy substituents. The long-lived species with λ_{max} at 295 nm is most probably the carbonyl compound, 6, formed in the ground state. Extensive photolysis of a solution of oxirane **3a** in acetonitrile by 248 nm laser pulses does, in fact, show the development of an absorption band at 290–320 nm in the UV spectrum (to the red of the original absorption of the oxirane).

The lack of observation of an ylide in the direct photolysis of oxirane **3** can be explained by the instability imparted by the bulky substituents present in the system. Note that in the transient spectra (Figure 4) under photosensitization of oxirane **3** by DCN in aerated or deaerated acetonitrile, no absorption maximum is discernible at 355 nm either at a time close to the laser pulse or during the decay of the radical ion over ~80 μs. This means that the carbene (**5**) is not formed to any significant extent, either directly or via an ylide, as a result of back electron transfer between the radical ions. However, we cannot rule out the possibility of the recovery of the oxirane (original or isomeric) via fast ring closure of a short-lived ylide that might be produced in the course of the back electron transfer.

Discussion

It seems proper to present a summary of the results of photosensitization of the oxiranes by DCN and TMB under conditions of prolonged, steady-state photolysis at 350 nm. Unlike stilbene oxides[6] and 2,3-dimethylstilbene oxides,[2c] their 2,3-dicyano- and 2,3-dicarbomethoxy-substituted counterparts (**1c**, **2c**, and their cis–trans isomers) fail to undergo cis–trans isomerization and cycloaddition to various dipolarophiles under irradiation (350 nm) in acetonitrile containing DCN. On the other hand, the isomeric pairs of 2,3-dicarbomethoxy-*p*,*p*′-dimethoxystilbene oxides (**2a** and **3a**) and 2,3-dicarbomethoxy-*p*,*p*′-dimethylstilbene oxides (**2b** and **3b**) undergo photoequilibration under similar conditions providing isomeric mixtures favoring the trans isomers (**3a** and **3b**) in each case by a factor 9:1; however, attempts to intercept the ylide intermediates or their precursor radical ions by cycloaddition to various electron-rich or electron-poor dipolarophiles have been unsuccessful. While the oxirane **1b** is found to be virtually unreactive upon irradiation (350 nm) in an acetonitrile solution containing DCN, the oxirane **1a** containing *p*,*p*′-dimethoxy substituents undergoes facile photodegradation under these conditions producing a dark, intractable mixture from which *p*-methoxybenzoyl cyanide is isolated as a product upon fractional crystallization. With oxirane **1a**, no cycloadducts are detected in the product mixtures after irradiation in the presence of dipolarophiles. That a carbene intermediate is generated in this photosensitized reaction is proved by the isolation of methyl ether of *p*-methoxybenzaldehyde cyanohydrin as a photoproduct from a mixture containing methanol (trapping agent for (*p*-methoxyphenyl)cyanocarbene). Finally, oxiranes **1c** and **2c** as well as their cis/trans counterparts undergo cis–trans photoisomerization upon irradiation (350 nm) in acetonitrile in the presence of TMB (sensitizer); the composition in the photostationary mixtures corresponds to the molar ratio 9:1 in favor of the trans isomers.

The present results from fluorescence quenching and laser flash photolysis substantiate most of the findings from steady-state photolysis presented above. The photolability of oxiranes **1a**, **2a**, and **3a** as substrates in photosensitization by DCN is related with large K_{sv}^F values (Table I) which, in turn, are attributable to the lowering of oxidation potentials by *p*-methoxy substitution. By the same token, the inertness shown by oxiranes **2b** and **2c** in attempted photosensitization by DCN becomes understandable from very small K_{sv}^F values (Table I). Oxiranes **1b**, **1c**, and **3b** constitute intermediates cases (K_{sv}^F = 7–48). In spite of the fact that the rate constant for quenching by oxirane **1c** is higher than those by oxiranes **1b** and **3b**, the experimental finding that **1b** and **3b** undergo photoisomerization while **1a** does not remains less understood. Laser flash photolysis shows practically no formation of radical ions ($\psi^S \sim 0$) for any of these oxirane systems. It is possible that photoisomerization in the case of oxirane **1b** and **3b** occurs in the caged ion pair which is long-lived enough to allow the ring opening of the oxirane radical cation, while this is not the case with the ion pair derived from oxirane **1c** and ^{1}DCN*.

As expected, the rate constants (k_q^S) for the quenching of TMB fluorescence by oxiranes **2a–c** (Table I) follow an order opposite to that of the electron-releasing nature of para substituents in these systems. For oxiranes **1a–c**, k_q^S values are all in the limit of diffusion control. With these oxiranes the electron-releasing character of para substituents manifests itself in the quenching of TMB triplet (Table II).

The charge-transfer quenching[32] of a singlet or a triplet

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(28) Turro, N. J.; Butcher, Jr., J. A.; Moss, R. A.; Guo, W.; Munjal, R. C.; Fedorynski, M. *J. Am. Chem. Soc.* **1980**, *102*, 7576–7578.

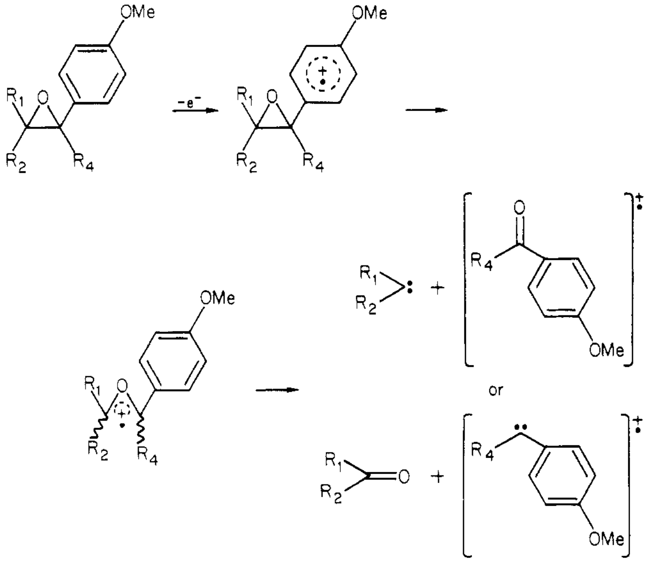
(29) The supralinear behavior in the plots for the quenching of (*p*-methoxyphenyl)carbomethoxycarbene (**6**) by water and methanol are very similar to that noted[27] for the quenching of singlet (*p*-methoxyphenyl)chlorocarbene by alcohols. In ref 27, this has been attributed to the participation of dimers and oligomers of alcohols in the quenching process.

(30) It should be noted that in reactions with O_2, water, TME, and alcohols, the behaviors of ylides, generated from related oxirane systems, namely, pyrazolinone spirooxiranes[31a] and 2,2-dicyano-3-(2-naphthyl)oxirane,[31b] are very similar to those of singlet carbenes. The assignment of the 355 nm species as the carbene, rather than an ylide, is based primarily on spectral similarity with (*p*-methoxyphenyl)chlorocarbene and lack of absorption in the visible region.

(31) (a) Umrigar, P.; Griffin, G. W.; Lindig, B. A.; Fox, M. A.; Das, P. K.; Leslie, T. M.; Trozzolo, A. M.; Eğe, S. N.; Thomas, A. *J. Photochem.* **1983**, *22*, 71–86. (b) Das, P. K.; Griffin, G. W., to be published.

(32) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271. Gordon, M. S.; Ware, W. R., Eds. "The Exciplex"; Academic Press: New York, 1975. Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834–839.

Scheme II



1a, $R_1 = R_4 = \mathrm{CN}; R_2 = p\text{-}\mathrm{CH_3OC_6H_4}$
2a, $R_2 = R_4 = \mathrm{COOMe}; R_1 = p\text{-}\mathrm{CH_3OC_6H_4}$
3a, $R_1 = R_4 = \mathrm{COOMe}; R_2 = p\text{-}\mathrm{CH_3OC_6H_4}$

in a polar solvent leads in general to the formation of a caged pair of radical ions which either dissociates into solvated radical ions or undergo back electron transfer in the cage producing the original substrates in the ground state. Conceivably, with oxiranes as the quenchers, the observed photoisomerization can take place either in the ion pairs or in the solvated radical ions, provided the rupture of the oxirane C–C bond occurs fast in these intermediates. Furthermore, as Albini and Arnold[6] suggested, the back electron transfer may result in the formation of an open ring ylide, a viable intermediate in which isomerization may occur. Our results show that the fractions (ψ^S or ψ^T) of singlet or triplet quenching events that give separated radical ions are very small (0–0.3). In particular, for the systems for which the separated ions via quenching of singlet and triplet photosensitizers are not observed at all, the intermediacy of ion pairs (singlet/triplet) and ylides,[6] both undetectable in our flash experiments because of short lifetimes, cannot be ruled out.

The fact that no cycloaddition products are formed when DCN photosensitization experiments are carried out in the presence of dipolarophiles can be explained as follows. As we have pointed out, even if an ylide is formed it may escape interception because of short intrinsic lifetimes. The possibility that the oxirane radical cation reacts with a dipolarophile forming the radical cation of the cycloadduct which subsequently accepts an electron from $\mathrm{DCN}^{-\cdot}$ is ruled out by our observation that the radical cation of oxirane **3a** displays no reactivity toward TME (an electron-rich dipolarophile). In addition, at very high concentrations of electron-rich dipolarophiles, the production of an ion pair or solvated radical ions would be suppressed because of competitive quenching of $^1\mathrm{DCN}^*$ by the dipolarophiles (olefins) themselves. Electron-poor dipolarophiles are expected to be unreactive toward the radical cation on the grounds that the latter is also electron deficient.

Our assignment of the transient species with absorption maxima at 400 and 580 nm (Figures 3 and 6A) as the radical cation derived from oxirane **3a** is well-established. The lack of resemblance of the transient spectrum with that of the radical cation[33] of *p*-methoxytoluene strongly suggests that the observed oxirane radical cation has an open-ring structure. Since the original site of the electron lost by the oxirane is most probably the *p*-methoxyphenyl moiety, the fast formation of open ring radical cation within the laser pulse would imply rapid intramolecular electron transfer from the ring to the aryl radical cation in oxirane **3a** (Scheme II). The dominant mode of the decay of the radical cation is back donation of an electron from $\mathrm{DCN}^{-\cdot}$ as evident from the second-order equal-concentration kinetics of its decay in deaerated solution. The concomitant small growth at 290–300 nm is possibly due to fragmentation of the cation to a minor extent forming the carbonyl compound.

Both laser-flash and steady-state photolysis data suggest that the photosensitization of oxirane **1a** by $^1\mathrm{DCN}^*$ leads to cleavage of the oxirane ring. No well-defined transient spectrum attributable to a relatively long-lived radical cation is observed in laser-flash photolysis, although long-lived absorption at 300–340 nm become noticeable in air-saturated acetonitrile following the decay of DCN triplet and concomitant recovery of DCN ground state. The latter spectral absorption appears to be associated with the fragments, namely, carbene and carbonyl compounds.

A very interesting finding in the present study is the growth of the transient absorption due to the radical cation of the cis oxirane (**2a**) at spectral regions 350–420 and 540–620 nm (Figure 5A,A′ and 5B,B′). This transient phenomenon is not observed with the trans isomer (**3a**). As evident from Figure 4A,B showing transient spectra close to the laser pulse, the precursor of the radical cation has a broad absorption maximum at 460 nm. Two alternative interpretations can be offered for the transient behavior observed with the cis oxirane on the short time scale. First, the precursor transient species with $\lambda_{\max}$ at 460 nm represents the initially produced, closed-ring form of oxirane **2a** radical cation, with the "hole" localized on one of the *p*-methoxyphenyl moieties. Intramolecular charge transfer ($\tau_{1/2}$ = 350 ns) occurs from the oxirane ring to the aryl radical cation; this is relatively slow because of small electronic overlap between an n orbital of the oxirane oxygen atom and the HOMO of the phenyl ring, and the latter can arise from strong steric interaction between the two *p*-methoxyphenyl groups in the cis isomer rendering the orientation of the phenyl rings normal to the plane of the oxirane ring. The other interpretation is that the slow growth represents the isomerization process whereby the open-ring radical cation initially produced from the cis oxirane changes to a more favorable configuration, i.e., the one in which the radical cation (open ring) is formed from the trans isomer. If this is the case, the large absorption spectral difference between the two radical-cation forms, namely, $\lambda_{\max}$ 460 nm for the one from the cis isomer and $\lambda_{\max}$'s 400 and 580 nm for the one from the trans isomer, is indicative of significant variance in their structures. Since very little is known about the role of steric factors in intramolecular charge transfer and about the rules (if any) that govern ring opening or closure in open-shell radical cations, both of the explanations given here are meant to be tentative.

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[33] The radical cation of *p*-methoxytoluene, generated by photoinduced electron transfer to $^1\mathrm{DCN}^*$ in acetonitrile, has a single absorption maximum at 435 nm in the spectral region 350–700 nm. Das, P. K., unpublished results.

J. Org. Chem. **1984**, *49*, 1985–1989 **1985**

Registry No. **1a**, 89909-33-1; **1b**, 89909-34-2; **1c**, 16801-14-2; **2a**, 81316-37-2; **2b**, 57699-36-2; **2c**, 57699-30-6; **3a**, 81316-44-1; **3b**, 81316-43-0; **5**, 89909-36-4; CuCN, 544-92-3; O_2, 7782-44-7; *p*-$MeOC_6H_4C(CH_3)(OH)CN$, 69813-75-8; MeOH, 67-56-1; *p*-$MeOC_6H_4\ddot{C}CN$, 89909-35-3; DCN, 3029-30-9; TMB, 366-29-0; TEA, 121-44-8; TME, 563-79-1; $DCN^{-}\cdot$, 68331-38-4; $TMB^{+}\cdot$, 21296-82-2; DMHD, 764-13-6; 1,2,4-trimethoxybenzene, 135-77-3; 1,4-dibromonaphthalene, 83-53-4.

Stereoselective Addition Reactions of Allylic Sulfides to Acetylenic Esters: *E*/*Z* Stereochemical Variations by Lewis Acid

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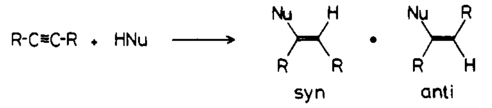
The Lewis acid catalyzed addition reactions of allylic sulfides to methyl propiolate (MP) and dimethyl acetylenedicarboxylate (DMAD) have been investigated. The stereochemical outcome is considerably influenced by the Lewis acid. While the $AlCl_3$-catalyzed reactions of MP afforded *E* adducts **2** as the major products, the use of $ZnCl_2$ resulted in the inversion of stereoselectivity to give *Z* adducts **3** mainly. The reactions of DMAD showed the similar change in the stereoselectivity, though these reactions had a higher trend of *E* selectivity. The stereochemical assignments of these adducts were made on the basis of the spectroscopic data as well as the chemical transformations. The reasonable reaction mechanism and the remarkable stereochemical effects of a Lewis acid are discussed in detail.

The stereochemistry of nucleophilic additions to acetylenic compounds is an object of current attention.[1] The theoretical studies by Houk et al.[2] and Dykstra et al.[3] have predicted on the basis of ab initio calculations that nucleophilic additions to unactivated acetylenes proceed via a single transition state to give anti products, and this is observed experimentally.[4] In contrast, nucleophilic additions to activated acetylenes are known to give variable stereochemical results, i.e., syn and anti adducts (eq 1),



(1)

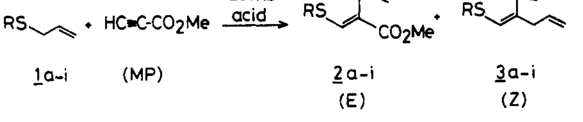
depending on the substituents, nucleophiles, and reaction media.[1,4–8] These are also compatible with the recent ab initio calculations by Caramella and Houk,[9] which indicate that the vinyl anions formed by nucleophilic addition to acetylenes are bent but the barrier to inversion is considerably lowered by electron-withdrawing substituents. On the other hand, less attention has been paid to the stereochemical effect of the Lewis acids, whereas the Lewis acids have been often employed to activate the acetylenic esters in their addition reactions.[10,11]

Table I. Lewis Acid Catalyzed Addition Reaction of Allylic Sulfides 1 with Methyl Propiolate (MP)[a]

entry	allylic sulfide 1, R =	Lewis acid	% yield[b] 2 + 3	*E*:*Z* ratio[c] (2:3)
1	**1a**, C_6H_5	$AlCl_3$	71	72:28
2		$FeCl_3$	45	80:20
3		$TiCl_4$	69	80:20
4		$EtAlCl_2$	51	67:33
5		$BF_3\cdot Et_2O$	77	65:35
6		$SnCl_4$	20[d]	50:50
7		$ZnCl_2$	92	3:97
8	**1b**, cyclohexyl	$AlCl_3$	80	90:10
9		$ZnCl_2$	94	29:71
10	**1c**, $CH_2CH{=}CH_2$	$AlCl_3$	73	78:22
11		$ZnCl_2$	95	10:90
12	**1d**, $CH_2CO_2CH_3$	$AlCl_3$	71	77:23
13		$ZnCl_2$	80	>98Z
14	**1e**, *n*-C_5H_{11}	$AlCl_3$	77	80:20
15	**1f**, CH_2Ph	$AlCl_3$	73	86:14
16	**1g**, CH_2CH_2OH	$AlCl_3$	complex mixture	
17	**1h**, CH_2CH_2OAc	$AlCl_3$	41	71:29
18	**1i**, $CH_2CH_2CH_2Br$	$AlCl_3$	83	79:21

[a] All reactions were carried out at 25 °C in methylene chloride by using 1.0 equiv of allylic sulfide 1, 1.2 equiv of methyl propiolate, and 1.1 equiv of the Lewis acid. Reactions using $ZnCl_2$ were carried out without the solvent. [b] Isolated yields. [c] The olefin ratio was determined by a combination of GLC and ^1H NMR analyses. [d] The deallylation products (7) were also isolated in 23% yield.

We previously reported a novel $AlCl_3$-catalyzed reaction of methyl propiolate and allylic sulfides to produce the 1:1 adducts with syn (i.e., *E*) stereoselectivity (see eq 2).[12] It



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(1) Houk, K. N.; Strozier, R. W.; Rozeboom, M. D.; Nagase, S. *J. Am. Chem. Soc.* **1982**, *104*, 323 and references cited therein.
(2) Strozier, R. W.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 1340.
(3) Dykstra, C. E.; Arduengo, J. E.; Fukunaga, T. *J. Am. Chem. Soc.* **1978**, *100*, 6007.
(4) Dickstein, J. I.; Miller, S. I. "Chemistry of the Carbon-Carbon Triple Bond"; Patai, S., Ed.; Wiley: New York, 1978.
(5) Winterfeldt, E.; Krohn, W.; Preuss, H. *Chem. Ber.* **1966**, *99*, 2572.
(6) Herbig, K.; Huisgen, R.; Huber, H. *Chem. Ber.* **1966**, *99*, 2546.
(7) Huisgen, R.; Giese, B.; Huber, H. *Tetrahedron Lett.* **1967**, *1883*.
(8) Truce, W. E.; Tichenor, G. J. W. *J. Org. Chem.* **1972**, *37*, 2391.
(9) Caramella, P.; Houk, K. N. *Tetrahedron Lett.* **1981**, *22*, 819.
(10) Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426.
(11) Medici, A.; Fogagnolo, M.; Pedrini, P.; Dondoni, A. *J. Org. Chem.* **1982**, *47*, 3844.

0022-3263/84/1949-1985$01.50/0