## Naphthalene Derivative Sensitized Photosolvolysis of Oxiranes via Electron-Transfer Mechanisms

Summary: Sensitized photosolvolysis of cyclohexene and styrene oxide by the singlet excited states of naphthalene derivatives occurs through the oxide anion radical intermediate by electron transfer.

Sir: In contrast to the photochemical formation of carbonyl ylides from diaryl (or more substituted) oxiranes,<sup>1-3</sup> simple alkyl- and phenyl-substituted oxiranes undergo light-induced solvolysis in alcohols to give the diol monomethyl ethers.<sup>4,5</sup> The original claim<sup>4a</sup> of photosolvolysis of oxiranes was later shown to be incorrect but arising from dark reactions initiated by "photogenerated acids".4b,5 More recently, it was demonstrated that a trace amount of a metal ion, such as  $Fe^{3+}$ , will act as a catalyst to pro-mote the photosolvolysis.<sup>6</sup> This communication describes sensitized photosolvolysis of cyclohexene oxide and styrene oxide by unexpected singlet excited state naphthalene derivatives through electron transfer to generate oxirane anion-radical intermediates. The results dramatically contrast to the photosensitized (electron transfer) formation of oxirane cation radicals<sup>7</sup> followed by the C-C bond scission.

In order to eliminate these intruding catalytic effects,<sup>4-6</sup> the solvents were distilled from ethylenediamine tetraacetic acid and photolysates were analyzed without delay. Irradiation of a methanol solution containing a sensitizer  $(2-3 \times 10^{-3} \text{ M})$  and styrene oxide  $(10^{-3}-10^{-1} \text{ M})$  or cyclohexene oxide  $(10^{-2}-10^{-1} \text{ M})$  at room temperature under nitrogen through a Pyrex filter caused solvolysis, giving 2-phenyl-2-methoxyethanol and trans-2-methoxycyclohexanol, respectively, in addition to trace amounts of other compounds in each case as shown by capillary GC analysis.<sup>8a</sup> For 1-naphthol-sensitized photolysis, the disappearance of oxides and the formation of the methyl ethers were shown to follow zero-order kinetics. The diols corresponding to hydrolysis of the oxides were also formed in small amounts in aqueous (>20%) methanol solution. For a fixed concentration of oxides, the quantum yields are the same within  $\pm 10\%$  at various stages of measurements up to 45% conversion. Therefore, the photo-

(2) (a) Lev, I. J.; Ishikawa, K.; Bhacca, N. S.; Griffin, G. W. J. Org. Chem. 1976, 41, 2654. (b) Lee, G. A. Ibid. 1976, 41, 2656. (c) Arnold, D.

solvolysis is genuine and their quantum yields are shown in Table I.

Triplet-state sensitizations were excluded by the failure of either benzophenone alone or a benzophenone (0.08)M)-1-naphthol (0.021 M) couple to sensitize the photosolvolysis when benzophenone was selectively photoexcited (>350 nm). Nor were the triplet signals of these naphthalene derivatives generated by flash photolysis quenched by styrene oxide.<sup>8b</sup> Fluorescence of the naphthalene derivatives was quenched by styrene oxide, but the rate constants from Stern-Volmer plots  $(1-7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1})$ varied, depending on excitation wavelengths and were smaller than those obtained by the kinetic analysis of the photosolvolysis (see Table I). The intensity of the fluorescence ( $\lambda_{max}$  353 nm) spectra of 1-naphthol in benzene was increased, and their  $\lambda_{max}$  shifted to longer wavelengths (356 nm) when cyclohexene oxide was added; under similar conditions the absorption spectra also showed a small but finite  $\lambda_{max}$  at 325 nm. In methanol, these spectral effects could not be detected unambiguously. It was concluded that a ground-state complex might be formed even in polar-protic solvent which interfered in fluorescence quenching calculations. The involvement of the singlet states of the naphthalene derivatives was established by the competitive quenching of the sensitized solvolysis with N-nitrosodimethylamine ( $E_{\rm S}$  78 kcal/mol) which had been shown to quench fluorescence of these naphthalene derivatives in methanol with diffusion-controlled rate constants<sup>9</sup>  $(10^{10}-10^{11} \text{ M}^{-1} \text{ s}^{-1})$ .

Assuming a generalized sensitization mechanism shown in Scheme I, the quenching rate constants (Table I) were obtained by plotting  $1/\Phi$  vs. 1/[oxide] according to the common Stern-Volmer equation

$$\frac{1}{\Phi} = \frac{1}{\beta} + \frac{1}{\beta k_q \tau \text{[oxide]}}$$

where

$$\beta = \frac{k_6}{k_6 + k_7}$$

The sensitization pattern shown in Table I indicates that the heightened acidity of singlet excited state naphthols<sup>10,11</sup> does not play any role in the photosolvolysis. The solvolysis appears to be initiated by electron transfer as shown in eq 1 and 3 (Scheme I), where NP are naphthalene derivatives. While the contributions of the two pathways cannot be easily assessed, in polar protic solvent, e.g., water and methanol, photosolvolysis originated from a groundstate complex (eq 1) may be small, and electron transfer via the dynamic exciplex formation (eq 3) dominates the reaction. Regardless of this uncertainty, the proposal is supported by two observations. The quenching rate constants vary by more than 2 orders of magnitude and cor-

<sup>(1)</sup> Griffin, G. W. Angew. Chem., Int. Ed. Engl. 1971, 10, 537.

R.; Karnischky, L. A. J. Am. Chem. Soc. 1970, 92, 1404. (d) Ullman, E. F.; Milks, J. E. Ibid. 1964, 86, 3814.

<sup>(3)</sup> Griffin, G. W.; Padwa, A. In "Photochemistry of Heterocyclic Compounds"; Buchardt, O., Ed.; Wiley: New York, 1976; p 41.

<sup>(4) (</sup>a) Tokumaru, K. Bull. Soc. Chem. Jpn. 1963, 40, 242. (b) Hisaoka, M.; Tokumaru, K. Chem. Lett. 1973, 251.

<sup>(5)</sup> Roussi, G.; Beugelmans, R. Tetrahedron Lett. 1972, 1333.
(6) Kagan, J.; Juang, P. Y.; Firth, B. E.; Przybtytek, J. T.; Singh, S. P. Tetrahedron Lett. 1977, 4289.
(7) Albini, A.; Arnold, D. R. Can. J. Chem. 1978, 56, 2985.

<sup>(8) (</sup>a) In a typical preparative run, a methanol (200 mL) solution containing cyclohexene oxide (4 mL, 3.86 g) and 1-naphthol (190 mg, 6.5  $\times$  10<sup>-3</sup> M) was irradiated through a Pyrex filter for 15 h. The crude oil exhibited the NMR signals of 1-naphthol and trans-2-methoxycyclohexanol, and a small portion was separated by preparative GC on a SE-30 column to give these two products in >90% yields. (b) We are indebted to Dr. J. C. Scaiano, National Research Council of Canada, for this unpublished information.

<sup>(9)</sup> Chow, Y. L. Acc. Chem. Res. 1973, 6, 354 and unpublished results. (10) Weller, A. In "Progress in Reaction Kinetics"; Porter, G., Ed.;

Pergamon Press: Oxford, England, 1961; Vol. 1, p 189. (11) Ireland, J. F.; Wyatt, P. A. H. In "Advances in Physical Organic Chemistry"; Gold, V., Bethell, D., Eds.; Academic Press: London, 1973; Vol. 12, p 18.

lable I.	Naphthalene	Derivative Sensitiz	ed Photosolvolysis	i of	Oxiranes in	Methanol
----------	-------------	---------------------	--------------------	------	-------------	----------

	naphthalenes	$E_{(\mathbf{D}/\mathbf{D}^{*})},^{a}$ eV	$E_{\rm S}, ^b$ eV	$\tau, c$ ns	cyclohexene oxide		styrene oxide	
					$\Phi^{d}$	$10^{-9}k_{q}, M^{-1} s^{-1}$	$\Phi^{d}$	$10^{-9}k_{\rm q},{\rm M}^{-1}{\rm s}^{-1}$
	1-OH	0.63	3.84	7.5	0.32	1.1	0.38	1.4
	2-OH	1.07	3.76	8.9	0.16	0.38	0.21	0.51
	$1 \cdot OCH_3$	1.38	3.86	49	0.33	0.18	0.40	0.23
	Н	1.54	3.87	96	0.11	0.022	0.21	0.047
	1-CN	>2	3.86	26	< 0.01	< 0.007	< 0.01	< 0.007

<sup>a</sup> The oxidation potentials are taken from ref 16-18. <sup>b</sup> The lowest singlet-state energies are taken from ref 19 except 1-naphthol,  $E_S$  of which was calculated from the 0-0 transition band at 323 nm in methanol. <sup>c</sup> The singlet-state lifetimes are taken from ref 20 and 21. <sup>d</sup> The quantum yields of the epoxide disappearance determined by GC analysis on a SE-30 capillary column: solutions containing 0.058 M of cyclohexene oxide or styrene oxide and ca. 10<sup>3</sup> M of a sensitizer were irradiated with a Pyrex filter for 6 h and 1 h, respectively.

Scheme I  
NP + CH<sub>2</sub>CH<sub>2</sub>O 
$$\rightleftharpoons$$
 [NP---CH<sub>2</sub>CH<sub>2</sub>O]  $\xrightarrow{h\nu}$   
[NP+.---CH<sub>2</sub>CH<sub>2</sub>O<sup>-</sup>.] (1)

$$NP \xrightarrow{h\nu} *NP \tag{2}$$

\*NP + 
$$\underset{\square}{\operatorname{CH}_2\operatorname{CH}_2\operatorname{O}} \xrightarrow{\mathcal{R}_q} [\operatorname{NP}^+ \cdot - - - \underset{\square}{\operatorname{CH}_2\operatorname{CH}_2\operatorname{O}^-} \cdot] \rightarrow$$

 $CH_{2}CH_{$ (3)

$$\cdot \operatorname{CH}_{2}\operatorname{CH}_{2}\operatorname{O}^{-} + \operatorname{CH}_{3}\operatorname{OH} \not\approx \cdot \operatorname{CH}_{2}\operatorname{CH}_{2}\operatorname{OH} + \operatorname{CH}_{3}\operatorname{O}^{-} \cdot$$
(4)

$$\cdot CH_2CH_2OH + NP^+ \cdot \rightarrow NP + {}^+CH_2CH_2OH$$
(5)

$$^{+}CH_{2}CH_{2}OH + CH_{3}OH(CH_{3}O^{-}) \xrightarrow{\kappa_{6}} CH_{3}OCH_{2}CH_{2}OH$$
(6)

$$^{+}CH_{2}CH_{2}OH + CH_{3}OH(CH_{3}O^{-}) \xrightarrow{H_{7}} CH_{2}CH_{2}O + CH_{3}OH$$

$$(7)$$

$$NP^{+} \cdot + CH_{3}CO_{2}^{-} \rightarrow NP + CH_{3}CO_{2}^{-} \rightarrow CH_{4} + CO_{2}$$
(8)

$$^{+}CH_{2}CH_{2}OH + CH_{3}CO_{2}^{-} \rightarrow CH_{2}CH_{2}O + CH_{3}CO_{2}H$$
(9)

relate reasonably linearly with  $E_{D/D^+} - E_S$  (Table I); if one uses the recently published reduction potential of styrene oxide  $(E^0 = 2.30 \text{ eV})$  determined by cathodic redox catalysis,<sup>12</sup> electron transfer from the singlet excited naphthalene derivatives to the oxide is thermodynamically feasible, except 1-cyanonaphthalene, according to the Weller's equation.<sup>13</sup> It may be noted that the lowest singlet level energies for the sensitizers are within 3 kcal/mol of one another, supporting the absence of an energy transfer mechanism, in spite of the fact that styrene oxide, having fluorescence<sup>14</sup> at 280-360 nm, should possess a state low enough to participate in energy transfer.

Secondly, sodium acetate at  $1 \times 10^{-3}$  M quenched photosolvolysis sensitized by 1-naphthol or its methyl ether; the gas samples were chromatographically analyzed to show the presence of small amounts of  $CO_2$  and  $CH_4$ . These products could be obtained by a competitive electron-transfer reaction as shown in eq 8. Among other possibilities, acetate may also quench the photosolvolysis according to reaction 9. Thus, acetate participates in quenching after the completion of the excited-state interaction as in eq 3. This is supported by the observations that, while the methyl ether sensitized solvolysis of styrene oxide is guenched by the acetate ion, its fluorescence intensity is not affected under the same conditions. The anion radicals of oxiranes proposed in eq 3 have been generated by cathodic reduction mediated by redox catalysis and are shown to open the ring very fast, leading to the solvolysis product.<sup>12,15</sup>

Acknowledgment. We are grateful to the National Sciences and Engineering Research Council of Canada for generous financial support of this project. B.M. thanks the University Council, Universytet im. Adama Mickiewicza, Poznan, for study leave.

Registry No. Cyclohexene oxide, 286-20-4; styrene oxide, 96-09-3; 1-naphthol, 90-15-3; 2-naphthol, 135-19-3; 1-methoxynaphthalene, 2216-69-5; naphthalene, 91-20-3; 1-cyanonaphthalene, 86-53-3.

(15) Boujlel, K.; Simonet, J. J. Electrochem. Acta 1979, 24, 481. (16) Meites, L.; Zuman, P. In "Electrochemical Data"; Wiley: New York, 1974; Vol. A, Part 1.

(17) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley: New York, 1970; p 459.

- (18) Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. J. Am. Chem. Soc. 1978, 100, 535.
- (19) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

(20) Berlman, I. B. "Handbook of Fluorescence Spectra of Aromatic Molecules"; Academic Press: New York, 1965. (21) Solomon, B. S.; Steel, C.; Weller, A. J. Chem. Soc. D 1969, 927.

## Yuan L. Chow,\* Bronislaw Marciniak Pratiba Mishra

Department of Chemistry Simon Fraser University Burnaby, British Columbia, Canada V5A 1S6 Received June 24, 1983

## A Novel Catalytic Synthesis of Carbamates by the Oxidative Alkoxycarbonylation of Amines in the Presence of Platinum Group Metal and Alkali Metal Halide or Onium Halide

Summary: Carbamates are prepared in good yields from amines, alcohols, CO, and oxygen in the presence of a novel catalyst system comprising platinum group metal and iodide.

Sir: Carbamates are important as precursors for preparing organic isocyanates without using dangerous phosgene, since they are thermally dissociated to give isocyanates and alcohols in good yields. Thus, the effective catalyst system for preparing them has been desired. We have now found that the catalyst system comprising platinum group metal and alkali metal halide or onium halide is very effective for the oxidative alkoxycarbonylation of amines by CO and oxygen (eq 1).

$$\frac{\text{RNH}_2 + \text{CO} + \text{R'OH} + \frac{1}{2}\text{O}_2 \rightarrow \text{RNHCOOR'} + \text{H}_2\text{O}}{2}$$
(1)

<sup>(12)</sup> Boujlel, K.; Martigny, P.; Simonet, J. J. Electroanal. Chem. 1983, 144, 437

<sup>(13)</sup> Rehm, D.; Weller, A. Ber. Bunsenges. 1969, 73, 834.
(14) Becker, R. S.; Bost, R. O.; Kolc, J.; Bertoniere, N. R.; Smith, R. L.; Griffin, G. W. J. Am. Chem. Soc. 1970, 92, 1302.