112 *Bull. Korean Chem. Soc., Vol. 9, No. 2, 1988*

Communications to the Editor

jima, I. *Tet. Lett.* 1986, 4025, 4029.

4. Evans, D. A. Asymmetric Synthesis Vol. 3, p. 2, Ed. Morrison, J. D. Academic Press, New York, 1983.

5. Ireland, R. E.; muller, R. H.; Willard A. K. *J. Am. Chem. Soc.* 1976, 98, 2868

6. Schlosser, M. *Top. Stereochem.* 1970, 5, 1.

Salt Effects in Electron-Transfer Induced Photooxygenation of 1,1-Diphenyl-2-Vinylcyclopropane; in the Presence of LiClO₄ NaClO₄, and (n-Bu)₄NClO₄

Sang Chul Shim* and Hyung Jae Lee

Department of Chemistry, The Korea Advanced Institute of Science and Technology Seoul 130-650. Received December 18, 1987

The influence of alkali cation on the photoreaction of organic compounds has been the subject of extensive investigation in recent years.[1] The effect of alkali cations on the photoreduction of carbonyl compound has been recently examined by picosecond transient laser spectroscopy and the interactions between the solvent and the salts have been probed by Raman spectroscopy.[2] These interactions between the molecules of solvent and the cations constitute the driving force for the formation of the solvent separated ion pairs. The main factors affecting the interactions between the solvent and the cations at any temperature and pressure are the ionic size, charge, and the solvent size, viscosity, and dielectric constant.[3]

In an attempt to elucidate the role of cation-solvent interactions in the exchange mechanism, we now report the salt effect on a novel photooxygenation of 1,1-diphenyl-2-vinylcyclopropane (VCP-DPh, **1**) cosensitized by 9,10-dicyanoanthracene (DCA) and biphenyl (BP).[4] Photooxygenation of **1**(10^{-1}M) DCA(10^{-4} M) and BP(10^{-2}M) in the presence of LiClO₄, NaClO₄ and (n-Bu)₄NClO₄ in dry acetonitrile solution was carried out. The solution was irradiated at 10°C under oxygen with a 450-W medium-pressure mercury arc lamp through a CuSO₄-filter soluton. The reaction was monitored by HPLC.

In a given temperature, pressure, solvent, and ionic charge of salt cation, each salt of different cation influences the VCP-DPh photooxygenation quantum yield differently. The quantum yield of VCP-DPh photooxygenation increased in the order of LiClO₄ < NaClO₄<(n-Bu)₄NClO₄, as shown in Figure 1.

For alkaline salts, this observation may be explained as the following. A small ion, like Li,+ binds with acetonitrile more strongly than larger ions, like Na+[5,6], suggesting that the effective ionic radius of solvated Li+ could be larger than that of Na+ because the smaller ions carry the thicker solvent sphere. Consequently, an increase in the size of Stoke's radius results in the lower mobility of alkali cations and causes the quantum yield to increase less effectively.[7,8]

In addition, the strong solvent-cation interaction formed by the smaller alkali cations such as Li+ relative to Na+ and the polar solvent such as acetonitrile results in an increase in the thermodynamic barrier for exchange process. For ion-pair exchange between salt and radical ions to occur, these ion-dipolar forces must be overcome. Thus, a high barrier as-
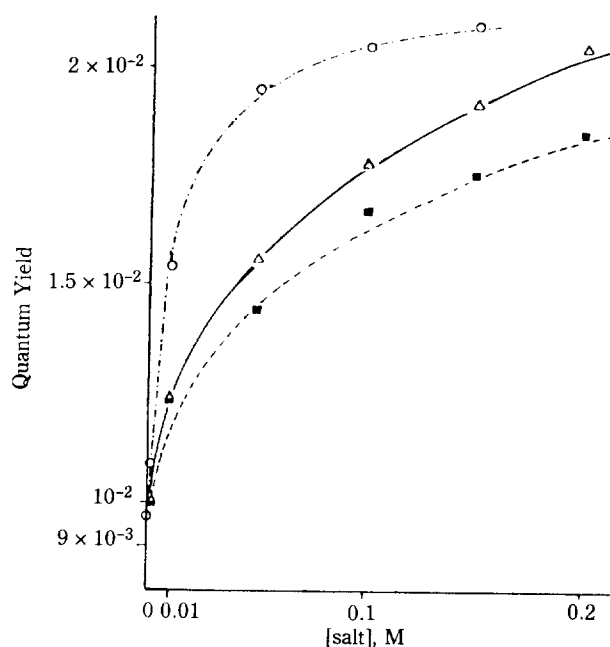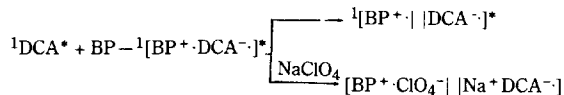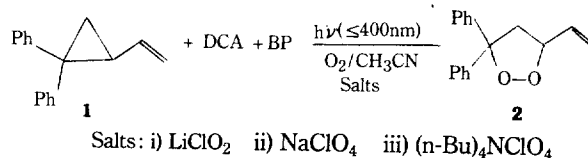

Figure 1. Salt effect on the Photooxygenation of 10^{-2}M VCP-DPh, 10^{-4}M DCA, and 10^{-2}M BP; LiClO₄(■), NaClO₄(△), and (n-Bu)₄NClO₄(○).

Salts: i) LiClO₂ ii) NaClO₄ iii) (n-Bu)₄NClO₄

$$^1DCA^* + BP \rightarrow {}^1[BP^+ \cdot DCA^-]^* \begin{cases} \longrightarrow {}^1[BP^+ \cdot | \; |DCA^- \cdot]^* \\ \xrightarrow{NaClO_4} [BP^+ \cdot ClO_4^- | \; |Na^+ DCA^-] \end{cases}$$
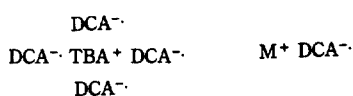
Scheme 1

sociated with the desolvation of alkali metal cation cuases the formation of solvent separated ion pairs to decrease. The difference in overall rates of ion-pair exchange reaction for NaClO₄ and LiClO₄ was demonstrated by the Raman analysis of acetonitrile-salt solutions in recent years.[2] The larger alkali cation in acetonitrile increases the formation of solvent

separated ion pairs due to the higher mobility and the weaker solvent-cation interaction.

For (n-Bu)$_4$NClO$_4$, the quantum yield shows the same tendency as alkali metal salts but is nearly constant at salt concentration over the range of 0.05 to 0.15 M. Tetra-n-butylammonium perchlorate is a phase transfer catalyst of the bulky group of which little association has been detected in acetonitrile.[9] A strong interaction between the salt and solvent at infinite dilution arises due to the long-range charge solvent polarization effect for acetonitrile[9] and results in the smaller ionic mobility relative to those of alkali metal salts.[10] However, it is assumed that ion-pair exchange reactions between salt and radical ions take place at the solvent separated ion pair stage resulting in the larger quantum yield due to the more efficient formation of the ion-pair complexes of tetra-n-butylammonium cations surrounded by more radical ions relative to alkali metal cations (Scheme 2).

DCA$^-$·

DCA$^-$· TBA$^+$ DCA$^-$·   M$^+$ DCA$^-$·

DCA$^-$·

Scheme 2. Ion pair complexes

Quadrupolar or aggregated salts formed between two or more salts of tetra-n-butylammonium perchrolate by the solophobic interaction at the higher concentration also causes the nicely constant pattern.[11]

Based on these results, we suggest that solvent-cation interaction constitutes the driving force for the formation of solvent separated ion pairs and inhibits back electron-transfer increasing the oxygenation quantum yields in the photooxygenation reaction of VCP-DPh.

References and Notes

1. J. M. Lefour, A. Loupy, Tetrahedron, **34,** 2597 (1978); H. C. Brown, K. Ichikawa, *J. Am. Chem. Soc.,* **83,** 4372 (1961); E. C. Ashby, J. R. Boone, *ibid.,* **98,** 5524 (1976).

2. J. D. Simon, K. S. Peters, *J. Am. Chem. Soc.,* **105,** 4875 (1983).

3. J. F. Coetzee, C. D. Ritchie, "Solute-Solvent Interaction"; Marcel-Dekker: New York, 1976, Vol. 2; P. C. Jordan, "Chemical Kinetic and Transport"; Plenum: New York & London, 1979.

4. S. C. Shim, J. S. Song, *J. Org. Chem.,* **51,** 2817 (1986).

5. R. L. Kay, J. L. Hawes, *J. Phys. Chem.,* **69,** 2420, 2787 (1965); T. L. Fabry, R. M. Fuoss, *ibid.,* **68,** 971 (1964).

6. Pauling crystal radii are 0.6Å for Li$^+$ and 0.95Å for Na$^+$· Pauling L. "Nature of the Chemical Bond and the Structure of Molecules and Crystals"; 3rd ed., Cornell University Press, New York, 1960.

7. (a) Cation Conductances in acetonitrile at 25°C are 69.2 for Li$^+$, 76.6 for Na$^+$, and 61.93 ohm^{-1}m^{2}eq^{-1} for (n-Bu)$_4$N$^+$; (b) Stokes ion radii $r_s = \dfrac{0.82 \times |Z|}{\lambda_0 + \eta}$ are 3.44 Å for Li,$^+$ 3.10 Å for Na$^+$. F. Accascina, *Ric. Sci. Rend.,* **7,** 556 (1966); R. L. Kay, B. J. Hales, G. P. Cunningham, *J. Phys. Chem.,* **71,** 3925 (1967).

8. Solvation number in acetonitrile at 25°C surrounded the cation by solvents are 9 for Li$^+$ and 6 for Na$^+$. E. S. Amis, J. F. Hinton, "Solvent Effects of Chemical Phenomena" Academic Press, New York & London, 1973, Vol. 1; E. Hirsch, R. M. Fuoss, *J. Am. Chem. Soc.,* **82,** 1013; 1018 (1960).

9. B. E. Conway, "Ionic Hydration in Chemistry and Biophysics"; Elsevier, Amsterdam-Oxford-New York, 1981, Vol. 12.

10. Crystal ion radius by Pauling scale and Stokes ion radius estimated from Fisher-Hirschfelder model are 3.75Å and 3.83Å for (n-Bu)$_4$N$^+$, respectively. D. S. Berns, R. M. Fuoss, *J. Am. Chem. Soc.,* **82,** 5585 (1960); J. F. Coetzee, G. P. Cunningham, *ibid.,* **87,** 2529 (1965).

11. R. Zwanzig, *J. Chem. Phys.,* **38,** 1603, 1605 (1963); **52,** 3625 (1970).