

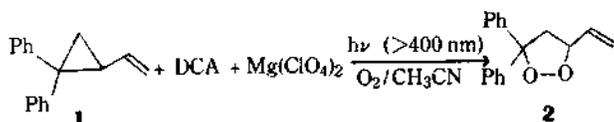
Salt Effects in Electron-Transfer Induced Photooxygenation of 1,1-Diphenyl-2-Vinylcyclopropane

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Electron-transfer mediated photoreactions are very much affected by added salts. The important reactions reported until now are electron-transfer mediated photoisomerization and photooxygenation of olefins¹, 1,2-diarylcyclopropane², and aromatic hydrocarbon compounds³, electron-transfer mediated photoreduction of carbonyl compounds⁴, and fluorescence quenching of exciplexes.⁵



- i) in the absence of BP
ii) in the presence of BP

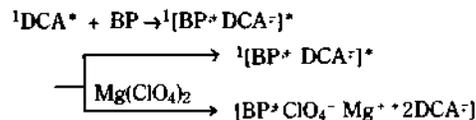
The role of salts in ion-pairs formed as an intermediate for the photoreactions has been extensively studied and recently probed by picosecond absorption spectroscopy.^{1,4} The salt might enhance the efficiency of the formation of solvent separated ion pairs and increase the lifetime of the reactive radical ions after they are formed.

In an attempt to elucidate the role of salts in the ion-pair intermediates, we now report the salt effects on a novel pho-

toxygenation of 1,1-diphenyl-2-vinylcyclopropane (VCP-DPh, **1**) which is cosensitized by 9,10-dicyanoanthracene (DCA) and biphenyl (BP).⁶ Irradiation of a dry acetonitrile solution of 10^{-2} M **1**, 10^{-4} M DCA, and 10^{-2} M BP in the presence of $\text{Mg}(\text{ClO}_4)_2$ at 10°C under oxygen bubbling gave dioxolane (**2**) as a major product. A 450-W medium-pressure mercury arc lamp and a CuSO_4 -filter solution were used and the reaction was monitored by HPLC.

The quantum yield of **2** increased dramatically in the presence of $\text{Mg}(\text{ClO}_4)_2$ (Figure 1). It is shown that the salt effect has the steep pattern at the lower concentration and develops the gradual pattern at the higher concentration of salt. The initial quantum yield increase cannot be explained solely in terms of an ionic strength effect as Winstein has proposed.⁷ The steep pattern at the concentration of $\text{Mg}(\text{ClO}_4)_2$ up to 0.01M is probably due to the special salt effect⁸, that is, ion-pair exchange reactions between salt and radical ions take place and then ion-pair complexes formed result in the suppression of the back electron transfer process because they accelerate the formation of solvent separated ion pairs. The facts that salts increase the lifetime of solvent separated ion pair and accelerate the rate of ion pair separation relative to that of the back electron transfer process were demonstrated by picosecond absorption spectroscopy in recent years.^{2a}

These observations of the steep pattern at the lower concentration of salt, therefore, indicate that the addition of salt results in the inhibition of back electron transfer in the contact ion pair in the solvent cage formed between biphenyl cosensitizer and singlet excited DCA (Scheme 1).



Scheme 1

However, the gradual pattern at the higher concentration of $\text{Mg}(\text{ClO}_4)_2$ over the range of 0.01 to 0.2 M is due to the normal salt effect, that is, as the concentration of salt increases at equilibrium, the radical ions in solution are surrounded by a spherical distribution of counter-ions of salt and then the ionic atmosphere is formed. When the ionic atmosphere formed by the salt ion cloud is large, it may move as if it were a charged colloidal particle aggregate and consequently the ionic strength is increased but the remaining salt ions not forming salt aggregates exist as the common ions. The addition of salt consequently accelerates the formation of solvent separated ion pair because of the ionic strength but decreases the ion pair separation due to the common ion effect⁹, so that the salt effect shows the gradual pattern.

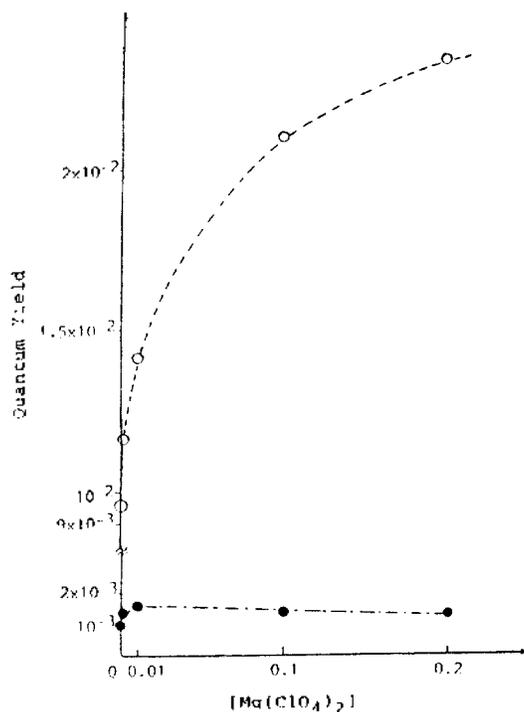
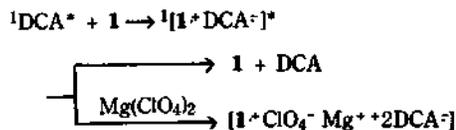


Figure 1. Salt effects on the photooxygenation of 10^{-2} M VCP-DPh and 10^{-4} M DCA in the presence of $\text{Mg}(\text{ClO}_4)_2$: in the presence of 10^{-2} M BP and in the absence of BP (●).

The photooxygenation reaction in the absence of biphenyl as a cosensitizer takes place in only a little amount and the addition of salt does not greatly affect the radical ion pairs formed in the solvent cage (Figure 1) probably due to a strong interaction between two radical ions in the contact ion pair formed between VCP-DPh and $^1\text{DCA}^*$, $^1[\text{VCP-DPh}^+ \text{DCA}^-]^*$, indicating that back electron transfer is faster relative to the ion-pair separation in the absence of biphenyl as a cosensitizer (Scheme 2).



Scheme 2

The absence of biphenyl causes the formation of solvent separated ion pair to decrease about tenfold because the stronger interaction between two radical ions in the contact ion pair formed between VCP-DPh and $^1\text{DCA}^*$ relative to that formed between BP and $^1\text{DCA}^*$ results in the faster back electron transfer (Figure 1).

The fluorescence of DCA in acetonitrile is rapidly and irreversibly quenched by the addition of VCP-DPh and BP respectively, while it is unaffected by the addition of salts indicating that salt does not affect the singlet excited DCA but influences ion pairs formed in the solvent cage.

These results support the proposition that salts suppress the back electron transfer in the contact ion pair formed between BP cosensitizer and $^1\text{DCA}^*$ in the photooxygenation reaction of VCP-DPh.

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