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SALT EFFECTS IN PHOTOINDUCED ELECTRON TRANSFER REACTIONS

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Summary: Metal salts and oxygen react synergistically to inhibit back-electron-transfer in photoinduced reactions.

The upsurge of interest in electron-transfer mediated photoreactions of organic compounds[1] has engendered new efforts to control the outcome of these processes. One of the more significant results is the discovery that added salts can greatly affect the products of these reactions. In one of the most striking examples of this phenomenon, Mizuno, Otsuji, and coworkers[2] recently reported that the photooxidation of several biphenyl derivatives is enhanced by the addition of $Mg(ClO_4)_2$. Other, perhaps related, effects of added salts have been reported by several other groups[3] including our own.[4] Herein we describe experiments that identify the root cause of some salt effects as the dramatic increase in the lifetime of free radical cations as a consequence of the inhibition of back electron transfer.

There are two distinct roles that salts might play in the enhancement of electron-transfer mediated photoreactions. The salt might increase the efficiency for formation of free radical ions after the initial electron transfer event. Or, the salt could act to increase the lifetime of the reactive radical ions after they are formed. These two possibilities can be easily distinguished with the laser techniques we have developed.[5]

The fluorescence of 1,4-dicyanonaphthalene (**DCN**) in acetonitrile solution is quenched by trans-stilbene (**TS**) or by 4,4'-dimethoxybiphenyl (**DMB**) at the diffusion limited rate. This is not a surprise since the Weller approach[6] predicts that electron transfer in these examples will be exothermic by 12.9 and 17.8 kcal/mol respectively. Operation of the electron transfer scenario is confirmed with the observation of the expected radical ions by laser transient absorption spectroscopy. Figure 1 shows the absorption spectrum recorded ca. 500 ns after irradiation of **DCN** in acetonitrile containing **TS**. The absorption with an apparent maximum at 390 nm is assigned to the dicyanonaphthalene radical anion ($\mathbf{DCN}^{\bar{\cdot}}$)[7] and that at 470 nm to the trans-stilbene radical cation ($\mathbf{TS}^{\dot{+}}$).[8] When **DMB** is employed as the electron donor, its radical cation ($\mathbf{DMB}^{\dot{+}}$) is observed at 430 nm.[9] The relative yields of these radical ions is readily estimated from their characteristic absorbances at early time in the experiment (<200 nsec) when their formation is complete, but no significant consumption has occured.

The lifetimes of the **DCN**$^{-\cdot}$ and **TS**$^{+\cdot}$ (or **DMB**$^{+\cdot}$) in the absence of an added trapping agent are apparently limited by back-electron-transfer. This is evidenced by the clean second-order reaction kinetics exhibited for consumption of these ions. A typical curve is shown on Figure 2, and the data are summarized in the Table.

Table: Relative Yields and Lifetimes of Radical Ions with Various Additives

Additives		ΔOD^a				k_2/ε(cm/sec)^b		
1	**2**	**DCN**$^{-\cdot}$	**TS**$^{+\cdot}$	**DCN**$^{-\cdot}$	**DMB**$^{+\cdot}$	**DCN**$^{-\cdot}$	**TS**$^{+\cdot}$	**DMB**$^{+\cdot}$
--	--	0.057	0.057	0.10	0.25	$(1.31\pm.18)\times10^6$	9.28×10^5	$(1.13\pm.05)\times10^6$
O_2	--	ND^e	0.042	ND	0.16	ND	$(2.68\pm1.1)\times10^5$	$(1.83\pm.16)\times10^4$
$Mg(ClO_4)_2$, .001 M	--	--	--	--	--	3.82×10^5	--	4.47×10^5
$Mg(ClO_4)_2$, .01 M	--	--	--	--	--	1.42×10^5	--	1.78×10^5
$Mg(ClO_4)_2$, .3 M	--	0.097	0.084	0.14	0.36	$(4.53\pm3.1)\times10^4$	$(1.99\pm.99)\times10^5$	$(9.34\pm.37)\times10^4$
$TBAClO_4$^{d}	--	0.093	0.085	0.21	0.37	$(6.24\pm1.8)\times10^5$	6.39×10^5	5.78×10^5
$Mg(ClO_4)_2$, .3 M	O_2	ND	0.066	ND	0.27	ND	$(2.92\pm1.1)\times10^4$	$(2.42\pm.74)\times10^3$
$TBAClO_4$	O_2	ND	0.058	ND	0.13	ND	1.22×10^6	$(9.46\pm.58)\times10^5$

a) Change in absorbance at wavelength characteristic of the radical ion, proportional to its initial yield.

b) Bimolecular rate constant for consumption of the radical ion divided by the extinction coefficient of the ion (generally unknown) at the monitored wavelength. Values without standard deviations are from single measurements.

c) Solutions were saturated with O_2 by bubbling for 2 minutes.

d) 0.3 M tetra-n-butylammonium perchlorate.

e) Not detected because of the rapid quenching of **DCN**$^{-\cdot}$ by O_2.

Examination of the Table reveals three significant points concerning the influence of salts and oxygen as additives on the behavior of the radical ions. First, addition of the salt ($Mg(ClO_4)_2$ or $TBAClO_4$[10]) does not result in an increase in the yield of radical ions (compare ΔODs). Second, addition of $Mg(ClO_4)_2$, but not $TBAClO_4$, causes the lifetime of **TS**$^{+\cdot}$ (or **TMB**$^{+\cdot}$) to increase ca. tenfold. Third, when the solution contains both O_2 and $Mg(ClO_4)_2$, the lifetime of **TS**$^{+\cdot}$ (or **TMB**$^{+\cdot}$) increases another 10-100 fold. These effects can be easily rationalized.

We propose that Mg^{+2}, but not TBA^+, forms a complex with **DCN**$^{-\cdot}$ that slows the rate of back electron transfer between **DCN**$^{-\cdot}$ and **TS**$^{+\cdot}$ (or **DMB**$^{+\cdot}$). This, of course, increases the lifetime of the radical cation. The greatest increase in the radical cation lifetime is observed when both $Mg(ClO_4)_2$ and O_2 are present. We suggest that this is a consequence of two reactions: first, electron transfer from **DCN**$^{-\cdot}$ to O_2 to form $O_2^{-\cdot}$, and then complexation of Mg^{+2} with superoxide. The magnesium superoxide thus formed must be an especially ineffective electron donor to **TS**$^{+\cdot}$ (or **DMB**$^{+\cdot}$).

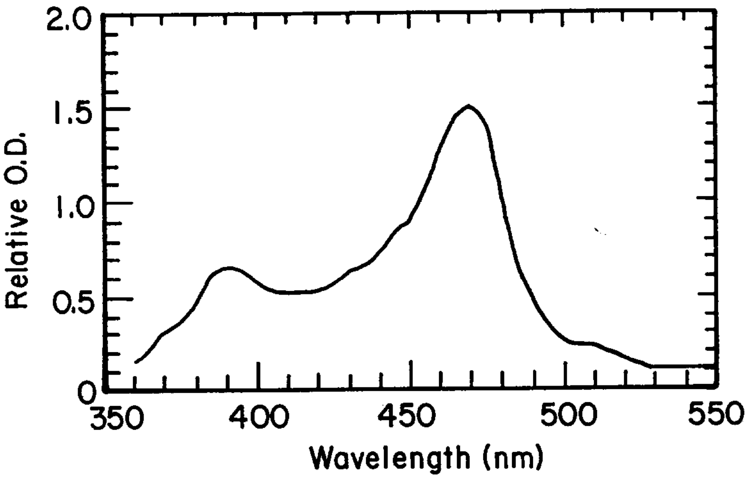

Figure 1. Transient absorption spectrum following laser flash photolysis of a system containing 1x10^{-5} M **DCN** and 2x10^{-2} M **TS** in CH_3CN.

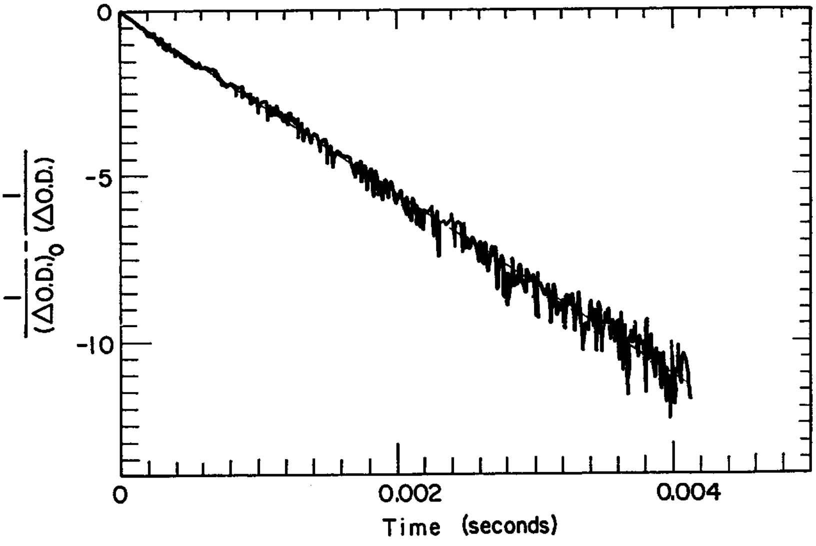

Figure 2. Plot of second-order fit of absorption decay of **DMB**$^{+\cdot}$ (generated by laser photolysis of an O_2-saturated solution containing 1x10^{-5} M **DCN**, 2x10^{-2} M **DMB**, and 0.3 M $Mg(ClO_4)_2$ in acetonitrile.

In summary, our data reveal that added salts do not significantly increase the yield of ions formed in photo-induced electron transfer reactions in polar (CH_3CN) solvent. The salt effect, and the synergistic O_2 effect,[2] operates through inhibition of back-electron-transfer. A related phenomenon has been reported for protic acids by Mattes and Farid.[11]

REFERENCES AND NOTES

1) S. L. Mattes and S. Farid, "Organic Photochemistry", Ed. A. Padwa, Dekker, New York (1983). R. S. Davidson, Adv. Phys. Org. Chem., **19**, 1 (1983).

2) K. Mizuno, N. Ichinose, T. Tamai, and Y. Otsuji, Tetrahedron Lett., **26**, 5823 (1985). K. Mizuno, N. Ichinose, and Y. Otsuji, Chem. Lett. (Japan), 455 (1985).

3) T. R. Evans, R. W. Wake, and M. M. Sifain, Tetrahedron Lett., 701 (1973). K. Kalyanasundaram and M. Neumann-Spallart, Chem. Phys. Lett., **88**, 7 (1982). N. Kitamura, S.-i. Imabayashi, and S. Tazuke, Chem. Lett. (Japan), 455 (1983). J. J. McCullough and S. Yeroushalmi, J. Chem. Soc., Chem. Commun., 254 (1983). F. D. Lewis, J. R. Petisce, J. D. Oxman, and M. J. Nepras, J. Am. Chem. Soc., **107**, 203 (1985). J. M. Masnovi, A. Levine, and J. K. Kochi, J. Am. Chem. Soc., 107, 4356 (1985). J. L. Goodman and K. S. Peters, J. Am. Chem. Soc., **107**, 6459 (1985). R. J. Hartley and L. R. Faulkner, J. Am. Chem. Soc., **107**, 3436 (1985).

4) B. E. Goodson and G. B. Schuster, J. Am. Chem. Soc., **106**, 7254 (1984).

5) K. A. Horn and G. B. Schuster, Tetrahedron, **38**, 1095 (1982).

6) D. Rehm and A. Weller, Isr. J. Chem., **8**, 259 (1970).

7) N. J. Peacock and G. B. Schuster, J. Am. Chem. Soc., **105**, 3632 (1983).

8) L. T. Spada and C. S. Foote, J. Am. Chem. Soc., **102**, 391 (1980).

9) B. Grant, N. J. Clecak, M. Oxsen, A. Jaffe, and G. S. Keller, J. Org. Chem., **45**, 702 (1980).

10) Tetra-n-butylammonium perchlorate.

11) S. L. Mattes and S. Farid, J. Chem. Soc. Chem. Commun., 457 (1980).

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