THE IMPORTANCE OF ALCOHOL NUCLEOPHILICITY IN THE TRAPPING OF THE PHOTOCHEMICALLY GENERATED RADICAL ION PAIR FROM N-METHYLPHTHALIMIDE AND α-METHYLSTYRENE

Paul H. Mazzocchi*, David Shook, and Leslie Liu, Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, U. S. A.

Abstract- The efficiency of alcohol trapping of the N-methylphthalimide-alkene radical ion pair has been shown to be a function of both solvent polarity and alcohol nucleophilicity.

The electron transfer photochemistry of aromatic imides has been the subject of continued and intensive investigation over the past several years. Of particular importance with respect to the electron transfer process is the effect of the solvent polarity which can dramatically affect the E_{ox} and E_{red} and the "dipole interaction term," C, in the Weller equation[1].

$$\Delta G_{ET} = E_{ox} - E_{red} - E_{oo} - C$$

In the case of the phthalimide-alkene system the electron transfer generated radical ion pair can be intercepted by nucleophiles, in most cases alcohols, to give the trapped product 2. In a study of the reaction of N-methylphthalimide (NMP) and alkenes with a series of alcohols, Maruyama and co-workers[2] ascribed differences in reactivity of the various alcohols to differences in their polarities (Table 1) since the reactions were run in pure alcohol.
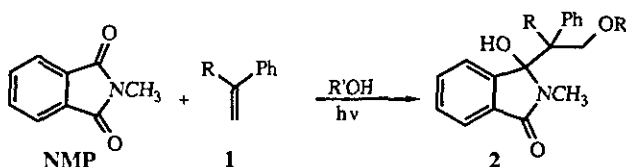

Table 1

		2 Yield(%)	Dielectric Constant
a	R=H,R' = Me	74	32.6
b	R=H,R' = Et	69	24.3
c	R=H,R' = i-C$_3$H$_7$	57	18.3
d	R=H,R' = t-C$_4$H$_9$	54	10.9

However, we recognized that the fact that alcohol addition to 3 always gave the most stable radical 5[3] might mean that the transition state for the production of 5 was late and that the nucleophilicity of the alcohol might also be an important factor since alcohol addition would compete with reverse electron transfer (Scheme 1).

Scheme 1

$$NMP + 1 \xrightleftharpoons[K_{-et}]{h\nu, K_{et}} NMP + 3 \xrightarrow[R'OH]{K_1} 4 + 5 \longrightarrow 2$$
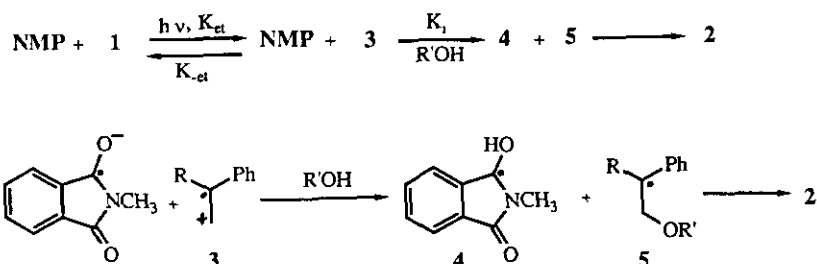
We decided to examine the solvent polarity and nucleophilicity effects of a series of alcohols on the ion pair trapping reaction of NMP and 1. Our approach was to look at relative quantum yields for product formation under conditions where the nucleophile (alcohol) concentration was kept constant but the solvent polarity was varied. This was accomplished by using mixtures of alcohol in acetonitrile and methyl acetate. Our preliminary studies made it clear that dielecrtic constant, which is a bulk solvent property, was a poor predictor of the actual solvent polarity in our system where hydrogen bonding to the carbonyl oxygen by the alcohols is likely to make the microscopic solvent polarity significantly different than the macroscopic polarity. It seemed to us that the Z value scale developed by Kosower[4] would be a better measure of the microscopic solvent polarity in our system. Thus we measured the Z values of a number of acetonitrile-methyl acetate-0.3 M alcohol mixtures and determined the relative quantum yields of product 2 under these conditions where the solvent polarity value changed but alcohol molarity was kept at a constant value.

The results are shown in Figure 1. Examination of the line for 2e is instructive. It reaches its highest value at the Z value of 72 but the straight line extrapolates back to $\Phi = 0$ at a Z value of 62, a value that is expected for pure hydrocarbons in which neither our reaction or the Z value measurement can be accomplished. Suffice it to say that no radical ion formation and therefore no product should be obtained under these conditions. Clearly this plot establishes the already conceded fact that solvent polarity is a key determinant in the reactivity of this radical ion pair. However the individual plots (2e-2i) for each of the alcohols (MeOH, EtOH, i-PrOH, t-BuOH, CF_3CH_2OH, respectively) also establishes that nucleophile reactivity is also an important consideration in this reaction and is a key contributor in the determination of the overall quantum yield for production of 2 along with solvent polarity[5]. These data, along with the linear Stern-Volmer plots determined for the production of 2a according to the relationship

$$1/\Phi_2 = K_{et}/K_1[ROH] + 1$$

establishes that Scheme 1 accurately describes the photochemistry of this system.
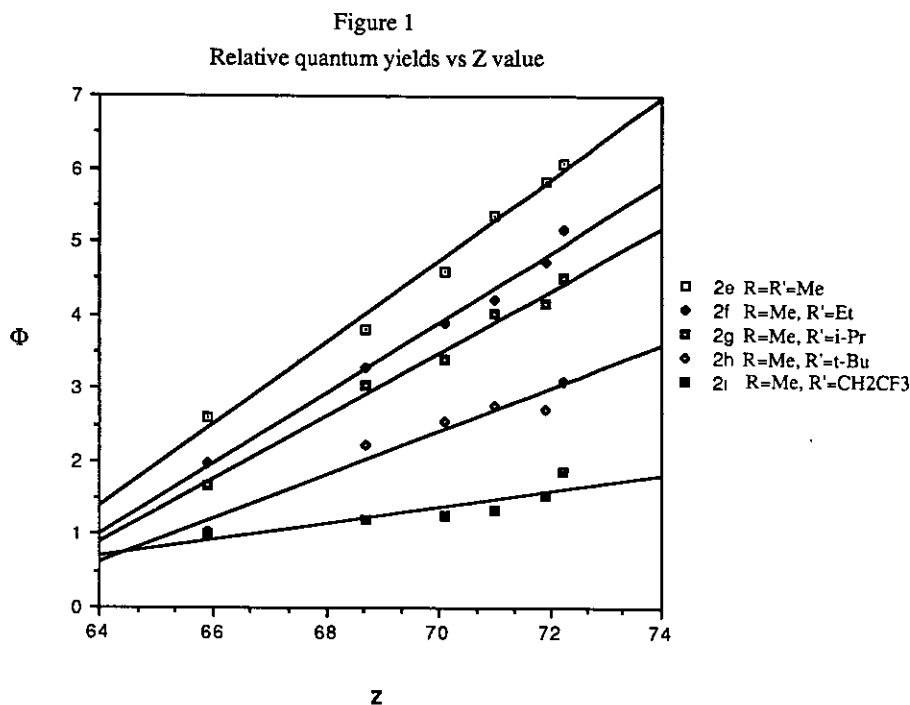
Figure 1
Relative quantum yields vs Z value

ACKNOWLEDGEMENT

REFERENCES

1. D. Rehm and A. Weller, *Israel J. Chem.* **1970**, *8*, 259.

2. K. Maruyama and Y. Kubo, *Chemistry Letters* **1978**, 851.

3. (a)K. Maruyama and Y. Kubo, *Chem. Lett.* **1978**, 851.(b)P. H. Mazzocchi and F. Khachik, *Tetrahedron Letters* **1981**, 4189. (c)H. Hoyashi, S. Nagakwa, Y. Kubo and K. Maruyama, *Chem. Phys. Lett.* **1980**, *72*, 291. (d)P. H. Mazzocchi, S. Minamikawa and P. Wilson, *Tetrahedron Letters* **1978**, 4361.

4. E. M. Kosower, *J. Am. Chem. Soc.* **1958** *80*, 3253.

5. The low reactivity of trifluoroethanol, which is a poor nucleophile but a strong acid, establishes the alcohol addition to **3** , not protonation of NMP·is the key step.

Received, 15th December, 1986