Tetrahedron Letters, Vol. 33, No. 38, pp. 5529-5532, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

# Electron Transfer between Neutral Radicals Generated from Photolysis of Diphenylmethyl 1-Naphthalenecarboxylate in Polar Solvents

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*Key Words:* Diphenylmethyl naphthalenecarboxylate; photolysis; radical pair; electron transfer

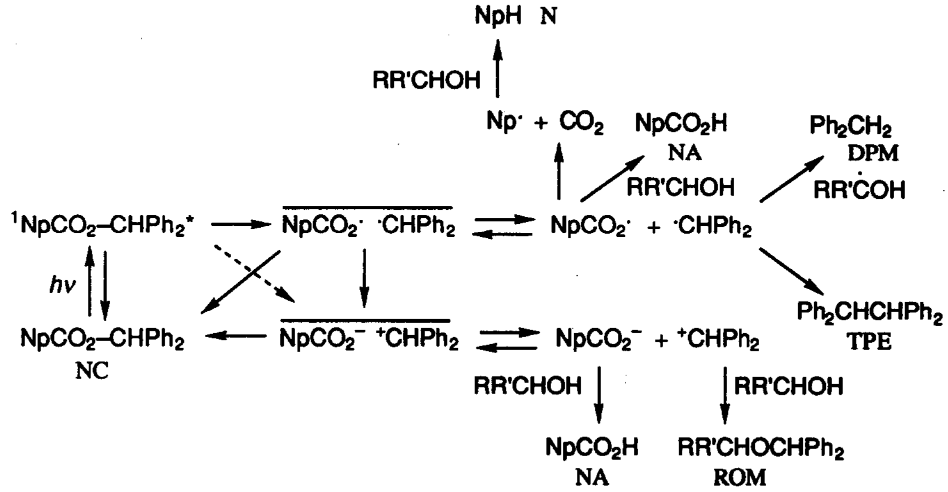
***Abstract:*** *From the fact that photolysis of diphenylmethyl 1-naphthalenecarboxylate in methanol, ethanol, and 2-propanol afforded the corresponding alkoxydiphenylmethanes in addition to 1,1,2,2,-tetraphenylethane and other products, it is proposed that the radical pairs of* $Ph_2CH\cdot$ *and* $ArCO_2\cdot$ *resulting from the photolysis undergo electron transfer to give* $Ph_2CH^+$ *and* $ArCO_2^-$ *with a rate constant comparable to radical recombination in the solvent cage.*

In spite of recent extensive attention to electron transfer from various aspects,[1] few attempts have been made in the electron transfer between neutral free radicals probably because of a difficulty in working with appropriate reactions. Photochemistry of carboxylic esters has been investigated mostly to follow the behavior of the resulting free radicals.[2] However, recently Pincock and his coworkers reported that photolysis of 1-naphthylmethyl phenylacetates in methanol gave ionic products in addition to homolytic products.[3] This work has prompted us to report our own findings on the effects of alcoholic solvents on product distribution and efficiency in photolysis of diphenylmethyl 1-naphthalenecarboxylate (NC).

Irradiation of NC (0.01 mol $dm^{-3}$) was carried out with 313-nm light from a high-pressure mercury lamp in deaerated acetonitrile and alcohols such as methanol, ethanol, and 2-propanol. Table 1 lists the products determined in these solvents. The photolysis of NC in acetonitrile gave 1-naphthalenecarboxylic acid (NA), naphthalene (N), 1,1,2,2,-tetraphenylethane (TPE), diphenylmethane (DPM), and small amounts of diphenylmethanol and benzophenone. Furthermore, in alcohols the corresponding alkoxydiphenylmethanes (ROM) were also produced. TPE clearly results from dimerization of diphenylmethyl radicals produced from photolysis of NC. Production of ROM in alcohols undoubtedly shows the formation of a diphenylmethyl cation as an intermediate.[4]

Photolysis of NC was also carried out in acetonitrile containing varying amounts of methanol. Figure 1 shows plots of the product yields as a function of methanol concentration. This figure shows that addition of methanol increases the yield of methoxydiphenylmethane (MeOM) and also the yield of NA at the expense of N; however, the yield of TPE was not affected by the amount of methanol. Another remarkable feature is an increase of NC conversion with increasing concentration of methanol, although the quantum yields for NC disappearance were as low as $3\times10^{-4}$ in acetonitrile, $6\times10^{-4}$ in 2-propanol, and $1\times10^{-3}$ in methanol.[5]

These results clearly demonstrate that in the alcoholic solvents the reaction proceeds through both free radicals and ions as depicted in Scheme 1. The ion pairs of $Ph_2CH^+$ and $ArCO_2^-$ might result mostly from electron transfer in radical pairs[6] of $Ph_2CH\cdot$ and $ArCO_2\cdot$.[7] Recent photolytic studies of diphenylmethyl derivatives in acetonitrile show that the halides give both $Ph_2CH\cdot$ and $Ph_2CH^+$, but that the acetate and trifluoroacetate afford only $Ph_2CH\cdot$ accompanied by a very small amount of $Ph_2CH^+$ in the latter case.[8]



Scheme 1.

The bond cleavage of NC takes place in the excited singlet state; triplet sensitization with aromatic ketones did not cause the reaction. The electron transfer between component radicals in the generated radical pairs should proceed with a rate constant competing with those of their recombination in the cage and escape from the cage. The rate constants for cage escape are estimated to be $3.5\times10^{9}\ s^{-1}$ in methanol[3b] and $6.7\times10^{8}\ s^{-1}$ in more viscous 2-propanol.[9] For the electron transfer in the pair of 4-methoxy-1-naphthylmethyl and phenylacetoxyl radicals a rate constant of $1.5\times10^{10}\ s^{-1}$ is estimated in methanol.[3b] The reported oxidation potentials of $Ph_2CH\cdot$ (0.35 V vs. SCE)[10] and $NpCH_2\cdot$ (0.47 V vs. SCE)[3b] in acetonitrile give, when combined with the electrochemical potentials of acyloxyl radical, 0.86[11] and 1.46 V[11] vs. SCE for $PhCO_2\cdot/PhCO_2^-$ and $RCO_2\cdot/RCO_2^-$ ($R=C_2H_5$, $C_3H_7$), respectively, the free energy change, $\Delta G°$, for electron transfer of $-0.51$ and $-0.99$ eV for $Ph_2CH\cdot\cdot\cdot OCONp$ and $NpCH_2\cdot\cdot\cdot OCOCH_2Ph$ pairs, respectively. Judging from these data,[12] the rate constant for electron transfer in the present system might be in the order of $10^{9}$ to $10^{10}\ s^{-1}$.

The resulting diphenylmethyl cation will react with alcohols competing with its recombination with a naphthalenecarboxylate anion. As mentioned above, both of the conversion of NC and the yield of MeOM increase with increasing methanol concentration. The increase of methanol concentration elevates the portion of $Ph_2CH^+$ to be trapped by methanol prior to its recombination with naphthalenecarboxylate anions. Furthermore, the increase in the yield of ROM in the order of 2-propanol, ethanol, and methanol reflects the increasing reactivity of $Ph_2CH^+$ with these alcohols in this sequence.[13]

Table 1. Products in Photolysis of Diphenylmethyl 1-Naphthalenecarboxylate (NC) in Polar Solvents

| Solvent | Irradiation time /h | Conversion /% | Product/% | | | | |
|---|---|---|---|---|---|---|---|
| | | | 1-$NpCO_2H$ (NA) | NpH (N) | $(Ph_2CH)_2$ (TPE) | $Ph_2CH_2$ (DPM) | $ROCHPh_2$ (ROM) |
| $CH_3CN$ a) | 65 | 40 | 9 | 38 | 8 | 6 | – |
| 2-PrOH | 24 | 60 | 67 | | 20 | 8 | 6 |
| EtOH | 20 | 83 | 70 | | 20 | 5 | 17 |
| MeOH | 16 | 79 | 66 | | 18 | 4 | 27 |

a) $Ph_2CO$ (1%) and $Ph_2CHOH$ (5%) were also produced in $CH_3CN$.

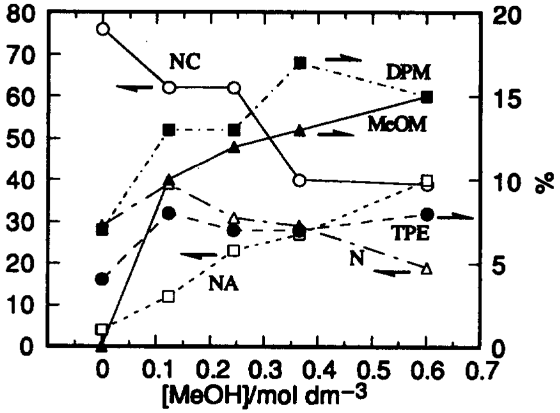


Fig. 1. Plots of Product Yields as a Function of Methanol Concentration in Photolysis of Diphenylmethyl 1-Naphthalenecarboxylate (NC) in Acetonitrile Containing Varying Amounts of Methanol. The yields of NC (○), NA (□), and N (△) are plotted along the left ordinate, and those of TPE (●), DPM (■), and MeOM (▲) along the right ordinate.

The NC exhibits a fluorescence spectrum similar to that from the corresponding methyl ester,[14,15] and the red shift was observed in polar solvents such as alcohols and acetonitrile. The fluorescence quantum yield ($\phi_f$) was determined to be higher in alcoholic solvents compared to those in acetonitrile and hexane; $\phi_f = 0.05, 0.28, 0.38, 0.41$, and 0.46 in hexane, acetonitrile, 2-propanol, ethanol, and methanol, respectively. The fluorescence lifetimes was also changed from 0.2 ns in hexane to 1.4 ns in 2-propanol, as determined by single photon counting technique.[16] This spectral behavior indicates that the excited singlet state is stabilized in polar solvents, particularly in protic solvents like alcohols. Intersystem crossing of the present ester might take place through the $n,\pi^*$ $T_2$ state. In polar solvents, however, the stabilization of the $\pi,\pi^*$ $S_1$ state results in a change of the relative positions of $T_2$ and $S_1$ states, leading to decrease in intersystem crossing efficiency.[13,14] Thus, the quantum efficiency of bond cleavage might increase with increasing population in the $S_1$ state.

In conclusion, the present results indicate that the electron transfer surely takes place in polar solvents between neutral radicals of sufficiently different electrochemical potentials with a rate constant comparable with that for radical recombination in solvent cage.

The authors thank University of Tsukuba for partial support of this work by President's Special Grant for Education and Research (K.T.).

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(Received in Japan 1 June 1992)