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A Novel Role of Methanol in In-Cage Reaction of Radical Cations During Photosensitized C–C Bond Cleavage of 1,1,2,2-Tetraphenylethane[†]

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The C-C bond cleavage in the photosensitized one-electron oxidation of 1,1,2,2-tetraphenylethane in MeCN was significantly reduced by the addition of MeOH. A laser flash study revealed that protic solvents suppressed the formation of dissociated cation radicals but not that of sensitizer anions. A novel synergistic oxidation of solvent methanol with ion pairs is suggested.

Recently, much attention has been focussed on C-C bond cleavages via photoinduced electron transfer.[1)] As a typical case, the photochemical cleavage of 1,1,2,2-tetraphenylethane (**1**) with 1,4-dicyanonaphthalene (DCN) as a photo-sensitizer (Eq. 1) has been intensively studied.[2-4)] Arnold et al. reported that the fragment cation (**2**) was trapped by methanol to afford diphenylmethyl methyl ether (**4**) and that the counterpart radical (**3**) was reduced by DCN$^{-\bullet}$ to the corresponding anion which was protonated to give diphenylmethane (**5**).[2)] The net efficiency of the reaction was temperature dependent, which was attributed to the activation energy of C-C cleavage step, i.e., the bond energy of the radical cation. This proposal is based on an assumption that the overall efficiency was determined by the rate of C-C cleavage. However, this was inconsistent with a laser flash photolysis study, reported by Das et al.,[3)] exibiting that the C-C cleavage was much faster than the back electron transfer from DCN$^{-\bullet}$; i.e., the overall quantum yield was not controlled by the C-C cleavage rate. Thus, the true factor determining the cleavage efficiency is not clear. We wish to report here a mechanistic study on the photosensitized C-C fission of **1**, revealing an unusual effect of protic solvents to suppress the formation of free radical cation (**1**$^{+\bullet}$). This result seems to suggest a novel synergistic electron transfer in solvent-separated ion pairs.

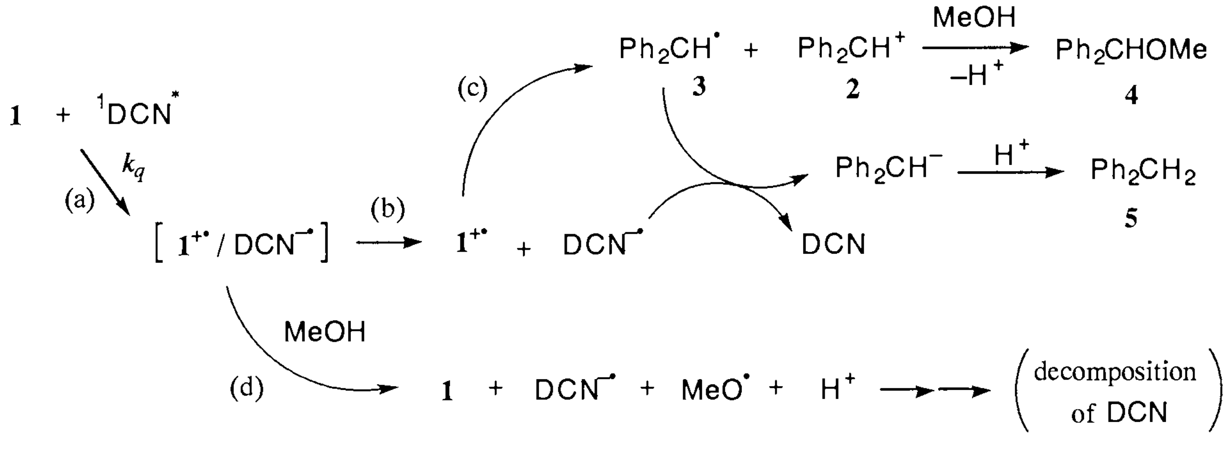
$$\underset{\mathbf{1}}{Ph_2CH\text{–}CHPh_2} \xrightarrow[-\,DCN^{-\bullet}]{DCN\,/h\nu} \mathbf{1}^{+\bullet} \longrightarrow \underset{\mathbf{2}}{Ph_2CH^{+}} + \underset{\mathbf{3}}{Ph_2CH^{\bullet}} \qquad (1)$$

[†] Dedicated to Professor Emeritus Osamu Simamura, The University of Tokyo, for the celebration of his 80th Birthday.

Irradiation of **1** (10 mmol dm^{-3}) and DCN (3.0 mmol dm^{-3}) in MeCN containing 0.3–25 vol % MeOH under argon at 20 °C yielded Ph_2CHOMe (**4**) and Ph_2CH_2 (**5**) as reported.[2)] At low conversion (< 40%), the product ratios of **4**/**5** were approximately unity with over 95% selectivities, not affording other products such as a coupling product with DCN.[4)] However, substantial amounts of the sensitizer DCN were consumed, yielding a complex mixture of non-volatile products.[5)] The effect of methanol on quantum yields for the conversions of **1** and DCN is shown in Fig. 1. With increasing volumes of methanol, the conversion of **1** decreased dramatically while the consumption of DCN became the major process. Similar results were obtained for the cases of H_2O and EtOH in place of MeOH, but not for the case of ethyl ether. Then, it is apparent that protic solvents retard the C-C fragmentation from $\mathbf{1}^{+\bullet}$.

The quenching of DCN fluorescence with **1** showed that the slopes (i.e., $k_q\tau$) of the Stern-Volmer plot, I/I_0 vs [**1**], decreased only slightly with increasing % volumes of methanol; i.e., 75, 59, 64, 57, and 55 mol^{-1}dm^3 for 0, 1, 3, 10, and 20 vol % MeOH, respectively.[6)] However, in the present experiments with [**1**] = 10 mmol dm^{-3}, the quantum yields for the electron transfer (step (a) in Scheme 1) were in the range from 0.43 to 0.36 and were not affected by the methanol concentrations. It is notable that the quantum yields for the formation of ion pairs are practically identical to the net quantum yield of 0.41 at 0.3% methanol, suggesting that the conversion of generated $\mathbf{1}^{+\bullet}$ to **4** and **5** is almost quantitative when the concentration of methanol is relatively low.

Laser flash photolysis (XeCl, 308 nm, 15 ns) of **1** (10 mmol dm^{-3}) and DCN (0.2 mmol dm^{-3}) in MeCN-MeOH (0 to 20 vol %) showed an absorption of DCN$^{-\bullet}$ (λ_{max} = 390 nm) immediately after the laser pulse, followed by the formation of fragment radical $Ph_2CH^\bullet$ (λ_{max} = 325 nm), as reported by Das et al.[3)] The first order rate constants for the C-C cleavage (step (c) in Scheme 1) determined from the build-up of $Ph_2CH^\bullet$ were $(7\pm1) \times 10^6$ s^{-1} and were independent of methanol % volume. However, as shown in Fig. 2, the relative intensities of the $Ph_2CH^\bullet$ after the completion of fragmentation (i.e., 1.5 μs after the laser pulse) were decreased considerably with increasing MeOH vol %, while those of DCN$^{-\bullet}$ (390 nm) remained unchanged. Since the C-C cleavage (step (c)) is so fast and **3** is generated quantitatively, the observed decrease in the yields of **3** indicates the significant reduction in the formation of $\mathbf{1}^{+\bullet}$. In other words, the overall efficiency is determined by the quantum



Scheme 1.

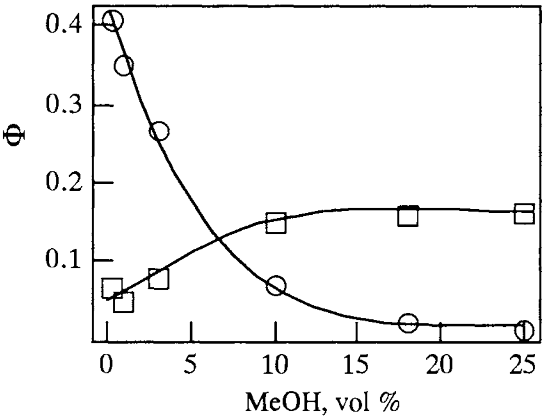


Fig. 1. Effect of MeOH on the net quantum yields for the conversions of **1** (○) and DCN (□).

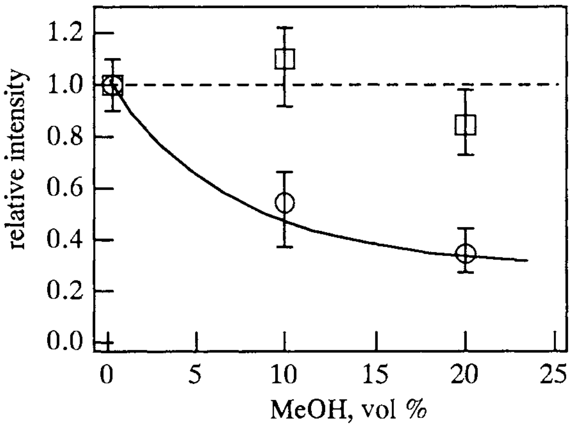


Fig. 2. Effect of MeOH on the relative intensities of transient absorptions of $Ph_2CH^{\bullet}$ (○) and $DCN^{-\bullet}$ (□).

yield of the dissociated $\mathbf{1}^{+\bullet}$. Therefore, the temperature dependence at high methanol concentrations should be explained by a known temperature effect on the dissociation of ion pairs (i.e., step (b) in Scheme 1).[7]

It is noted that protic solvents may accelerate back electron transfers within geminate ion pairs.[8] A notable point in the present study is that the amount of free $\mathbf{1}^{+\bullet}$ is not equivalent to that of $DCN^{-\bullet}$ (Fig. 2), suggesting an alternative consumption of radical cation species. In addition, the high selectivity in the production of **4** and **5** indicates that **1** is recovered from $\mathbf{1}^{+\bullet}$. Thus, a plausible pathway for the consumption of DCN is a one-electron transfer from methanol to $\mathbf{1}^{+\bullet}$ as pathway (d) in Scheme 1. The electron transfer is to occur in geminate ion pairs $[\mathbf{1}^{+\bullet}/DCN^{-\bullet}]$ before their dissociation, since the observed lifetimes of free $\mathbf{1}^{+\bullet}$ are unaffected by methanol. The one-electron oxidation of methanol is usually difficult because of its high ionization potential[9] and has been given little attention in electron transfer reactions.[10] Such an oxidation of methanol might be achievable within ion pairs as discussed in the following. The photochemical electron transfers are known to occur via "contact ion pair" (CIP) or "solvent-separated ion pair" (SSIP).[11] In SSIP, solvent molecules around ion pairs are strongly polarized due to the electric field. For the present case of methanol, the separated charges may induce a strong hydrogen bonding with the anion radical as envisioned in Fig. 3. The removal of one-electron from the polarized or dissociated methanol by donor cation radicals may be attainable within the SSIP.[12] Thus, a novel synergistic one-electron oxidation is exemplified.[13]

In summary, the present study revealed that the addition of MeOH in photoinduced electron transfer reactions might suppress the formation of free ions probably by a novel synergistic electron-transfer in radical ion pairs.

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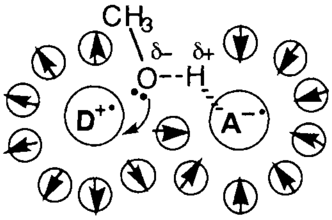

Fig. 3. A schematic drawing of the cooperative oxidation of methanol in solvent-separated ion pair.

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6) The k_q values could not be evaluated since the lifetimes of $^1DCN^*$ in mixed solvents of MeOH-MeCN were not known: In MeCN, $k_q = 7.9 \times 10^9$ mol^{-1}dm^{3}s^{-1} was determined from the reported lifetime of 9.5 ns; P. K. Das, A. J. Muller, and G. W. Griffin, *J. Org. Chem.*, **49**, 1977 (1984).

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