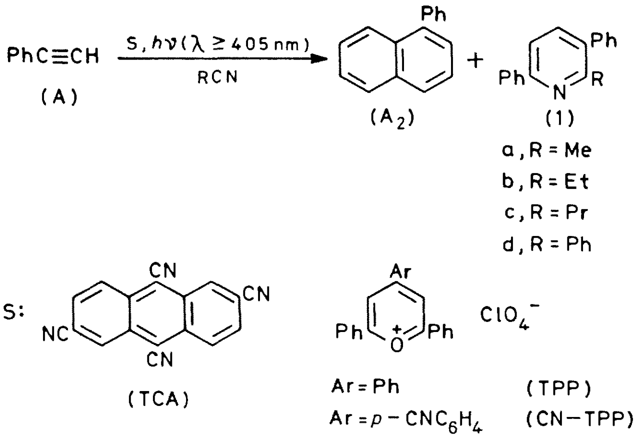
Photosensitized Electron-transfer Reactions of Phenylacetylene

By SUSAN L. MATTES and SAMIR FARID*
(*Research Laboratories, Eastman Kodak Company, Rochester, New York* 14650)

Summary Phenylacetylene (A) reacts with excited sensitizers (S) to produce radical ions (S)$^{\cdot -}$, (A)$^{\cdot +}$, which react as geminate or separated pairs with (A) to give a dimeric radical cation (A^{+}–$^{\cdot}$A), the latter reacts with nitriles to give pyridines (**1**) or with nitromethane leading to an oxidation product (**2**) and a dimer (1-phenylnaphthalene) is also formed *via* the geminate pair.

IN a preliminary investigation[1] it was found that phenylacetylene (A) reacts with photoexcited 2,4,6-triphenylpyrylium (TPP) fluoroborate in acetonitrile to give a dimer, 1-phenylnaphthalene[2] (A_2), and a solvent-incorporated product, 2-methyl-3,6-diphenylpyridine (**1a**). This report deals with the mechanism of this and other novel photosensitized electron-transfer reactions of phenylacetylene.

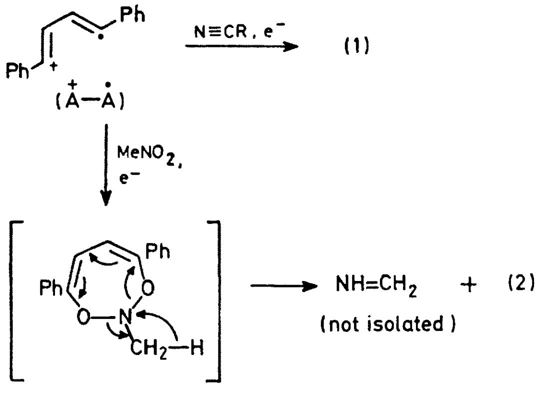
9,10-Dicyanoanthracene (DCA), which has been used as a sensitizer to study the electron-transfer photochemistry of several olefins, does not sensitize this reaction because electron transfer from ^{1}(DCA)* to (A) is an endothermic process. However, 2,6,9,10-tetracyanoanthracene (TCA), which is more readily reduced [$E^{\text{red}} = -0.45$ V *vs.* S.C.E. (standard calomel electrode)] but has similar singlet excitation energy ($\Delta E_{00} = 2.90$ eV) to that of (DCA) ($E^{\text{red}} = -0.88$ V *vs.* S.C.E., $\Delta E_{00} = 2.94$ eV), sensitizes the above-mentioned reactions of (A) in several nitriles and was used for most of this study.



Unexpectedly, we found that irradiation ($\lambda \geqslant 405$ nm) of (TCA) and (A) in nitromethane produces dibenzoylethylene (**2**) besides phenylnaphthalene (A_2). Compound (**2**) corresponds to a combination of two molecules of (A) and two oxygen atoms, which come from the solvent ($MeNO_2$, under degassed conditions), and its formation represents a novel photochemical reaction.[3]

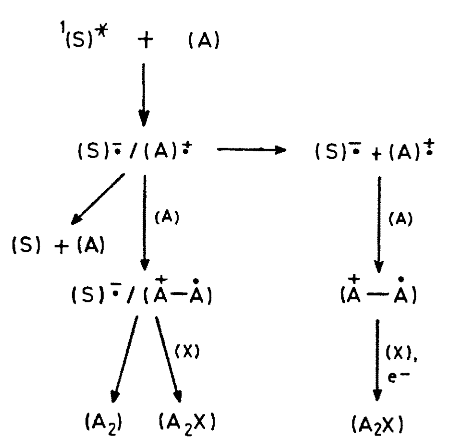
$$(A) \xrightarrow[\text{MeNO}_2\ \text{degassed}]{S,\,h\nu} (A_2) + PhCO{-}CH{=}CH{-}COPh \quad (2)$$

The formation of the solvent-incorporated products (**1**) and (**2**) can be rationalized in terms of nucleophilic addition of the nitrile or the nitro group to the 1,4 radical cation ($A^{+}\!\!-\!\cdot A$) to give the pyridine (**1**) or a seven-membered heterocyclic compound as a precursor to (**2**), respectively (*cf.* Scheme 1). In the following discussions the solvent-incorporated products (**1**) and (**2**) will be referred to as (A_2X).



Scheme 1

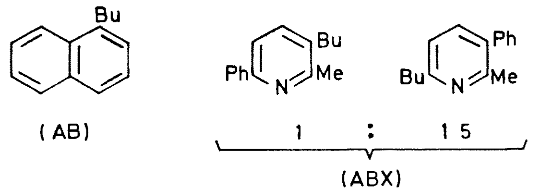
We found that the product distribution (A_2X)/(A_2) is strongly dependent on the concentration of (A). A plot of (A_2X)/(A_2) against $[(A)]^{-1}$, using acetonitrile as a solvent, gives a straight line with a slope of 1·15 mol/l and an intercept of 1·4. This change in ratio is compounded by an increase in the yield of (A_2) and a decrease in that of (A_2X) with increasing [(A)]. These data can be best explained in terms of a mechanism involving two consecutive intermediates: a primary intermediate, which reacts with (A) leading ultimately to both products or, in a competing reaction, is converted into a secondary intermediate which yields only (A_2X). We propose that these intermediates are the geminate (or contact) ion pair $(S)^{\cdot-}/(A)^{\cdot+}$ and the separated (or out-of-cage) radical cation of phenylacetylene $(A)^{\cdot+}$, respectively (Scheme 2). This is the first example in such photoinduced electron-transfer reactions where there is evidence for trapping the geminate ion pair prior to its dissociation.†



Scheme 2. (X): RCN or RNO_2; (A_2X): addition product (**1**) or (**2**).

As would be expected from such a mechanism, the product distribution depends on the sensitizer used. For example, at 0·4 M phenylacetylene in acetonitrile, the ratio of (A_2X)/(A_2) changes from 4·3 with (TCA) as a sensitizer to 12 and 16 when the pyrylium salts (TPP) and (CN-TPP) are used, respectively.

Support for some aspects of the proposed mechanism is obtained from a mixed acetylene reaction. Sensitized irradiation (in MeCN) of (A) in the presence of hexyne (B), which has a higher oxidation potential than that of (A) and does not react with the excited sensitizer, leads to a mixture of (A_2) and the mixed dimer, 1-butylnaphthalene (AB), as well as (A_2X) and the two isomeric pyridines (ABX). The sequence of the addition reactions leading to the pyridines is evident from the stereochemistry of the (ABX) isomer which has the butyl group *ortho* to the nitrogen. This compound can be formed only through nucleophilic addition of the nitrile to the dimeric, and not the monomeric, radical cation.



Kinetic studies, which will be discussed in a detailed publication, showed that both monomeric radical cation intermediates $(S)^{\cdot-}/(A)^{\cdot+}$ and $(A)^{\cdot+}$ have, as expected, similar relative affinities towards different acetylenes.

---

† From quenching experiments, using 1,4-dimethoxybenzene, a bimolecular reaction constant of *ca.* 5×10^9 l mol^{-1} s^{-1} is estimated for the addition of (A) to the geminate pair. From this and other kinetic data a reaction constant for the separation of the geminate pair of *ca.* 10^9 to 5×10^8 s^{-1} is estimated. These values are very close to those measured in other systems using different techniques (A. Weller, Presentation at the American Chemical Society Meeting, Washington, D.C., September 10—14, 1979).

This is also the case with the dimeric radical cation intermediates $(\mathrm{S})^{\overline{\cdot}}/(\mathrm{A}^{+}\text{–}{}^{\cdot}\mathrm{A})$ and $(\mathrm{A}^{+}\text{–}{}^{\cdot}\mathrm{A})$ in their reactions with nucleophiles.

One possible explanation for why the geminate pair leads to (A_2) whereas the separated radical cation does not is that the formation of (A_2) is preceded by an electron transfer $(\mathrm{S})^{\overline{\cdot}}/(\mathrm{A}^{+}\text{–}{}^{\cdot}\mathrm{A}) \rightarrow (\mathrm{S}) + (\mathrm{A}^{\cdot}\text{–}{}^{\cdot}\mathrm{A})$ giving a biradical, which undergoes cyclization.

(*Received*, 11*th October* 1979; *Com.* 1079.)

---

[1] S. Farid, K. A. Brown, J. C. Doty, S. E. Hartman, and J. L. R. Williams, Abstract Y1, Book of Abstracts of the VIII International Conference on Photochemistry, Edmonton, Canada, 1975.

[2] Direct irradiation of phenylacetylene in cyclohexane gives a 5 : 1 mixture of 1-phenylazulene and 1-phenylnaphthalene; D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, **1963**, 695.

[3] This photosensitized electron-transfer reaction is mechanistically different from the addition of directly excited nitrobenzene to alkenes; G. Büchi and D. E. Ayer, *J. Amer. Chem. Soc.*, 1956, **78**, 689; J. L. Charlton, C. C. Liao, and P. De Mayo, *ibid.*, 1971, **93**, **2463.**

Printed by Heffers Printers Ltd Cambridge England