

PHOTOCHEMICAL REACTION OF 5-DIAZODIBENZO(a,d)CYCLOHEPTENE WITH TCNE LEADING TO CYCLOPROPANE DERIVATIVE. ELECTRON TRANSFER FROM CARBENE TO TCNE

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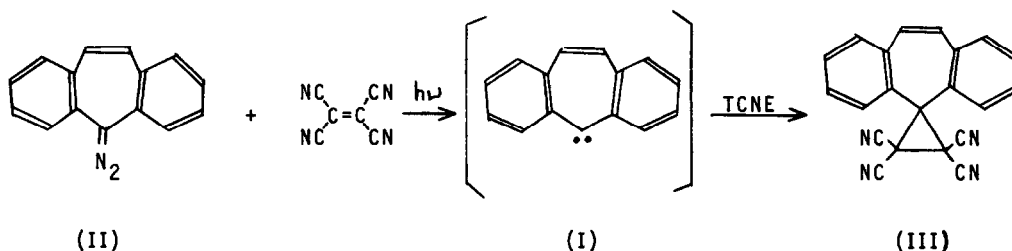
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We wish to report a first example for direct observation of an electron transfer from dibenzo(a,d)cycloheptenylidene(I) to tetracyanoethylene(TCNE).

A mixture of 5-diazodibenzo(a,d)cycloheptene(II)(0.2g) and TCNE(0.12g) in ethyl acetate(20ml) was irradiated at 20° using a Hg lamp equipped with NaNO₂ filter solution¹ to isolate 436nm region. After evolution of an essentially quantitative amount of nitrogen had ceased, separation and purification of the product with a silica gel chromatography gave 0.33g(60%) of spirocyclopropane derivative(III); mp 230-231°, pmr(CD₃CN,TMS)δ8.05-7.35(multiplet), UV(CH₂Cl₂)₂₃₃, 268,292nm(ε×10⁴,3.7,1.4,1.7), m/e(parent)318, Anal. Calcd for C₂₁H₁₀N₄:C,79.23; H,3.17;N,16.99. Found:C,79.27;H,3.26;N,17.05.

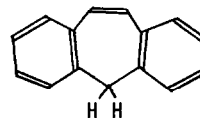


This reaction can be easily understood as the simple addition of (I) to TCNE. We previously proposed that a charge transfer complex plays an important role in the transition state of the addition reaction of (I) to olefins.² The present system is ideal for study of electronic interaction between carbene and olefin, because TCNE has an electron withdrawing nature and cycloheptatrienylidene has an electron releasing character.³ Accordingly, electronic spectra

of (I)⁴ in the presence of TCNE were investigated to elucidate the precise feature of the addition reaction.

Surprisingly, the spectrum of the anion radical of TCNE (TCNE⁻) was observed when a rigid matrix of (II) ($6 \times 10^{-4} \text{M}$) and TCNE ($5 \times 10^{-2} \text{M}$) in 2-methyltetrahydrofuran (2-MTHF) was photolyzed at 77°K for 1 min using UV35 filter (>350nm). The spectrum is shown in Fig I with curve a (—), which has the same vibrational structure as free TCNE⁻.⁵ Increase of the absorption intensity with shorter wavelength must be due to overlapping of the absorption of (I), (II), or other species.⁶

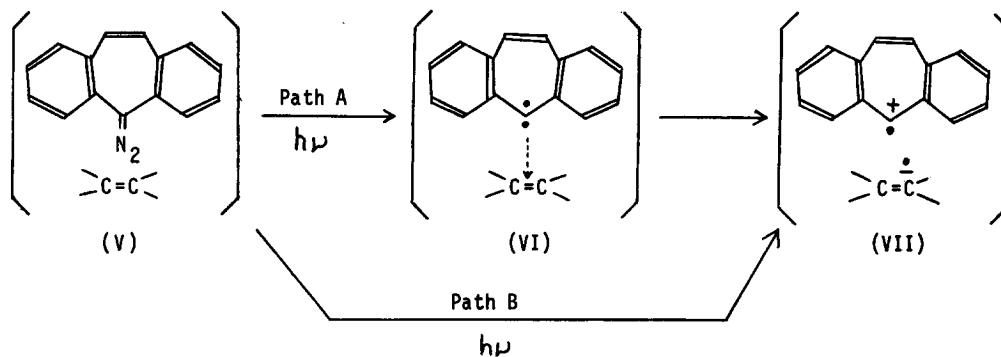
To clarify what species transferred an electron to TCNE, we undertook following controlled experiments. As it had been reported that TCNE⁻ is produced from photolysis of a solution of TCNE in tetrahydrofuran,⁵ we first explored this possibility. When a rigid matrix of TCNE in 2-MTHF was photolyzed under the same condition, TCNE⁻ with relatively weak intensity was observed as shown in Fig I (curve b ·····). A rigid matrix of TCNE and 5H-dibenzo(a,d)cycloheptene (IV) in 2-MTHF was also photolyzed under the identical condition. TCNE⁻ with almost same intensity as b was produced (Fig I, curve c ———). Obviously, the intensity of TCNE⁻ is greatly enhanced when the solution of TCNE in the presence of (II) is irradiated. These results indicate that electron transfer either from the solvent or the dibenzo(a,d)cycloheptenyl structure is minor.



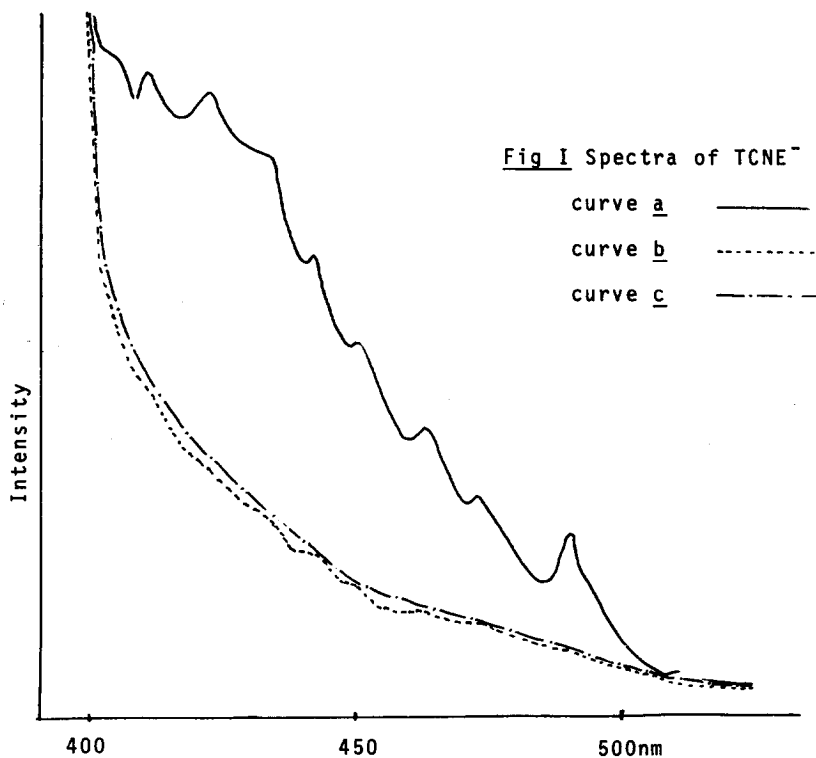
(IV)

A possibility remains that an electron transfer occurs directly from (II) without via (I). Irradiation of a matrix of (II) ($6 \times 10^{-3} \text{M}$) and TCNE ($1 \times 10^{-2} \text{M}$) in 2-MTHF with UV43 (>430nm) produced only the absorption spectrum of (I) without forming TCNE⁻. Prolonged irradiation increased the intensity of the spectrum, which soon reached to saturation. Subsequent irradiation with UV35 (>350nm) produced absorption spectrum of TCNE⁻ and decreased the intensity of carbene (I). Consequently, it is now apparent that an electron transfer occurs from carbene (I) to TCNE.

Although the charge transfer state (VI) we proposed previously² is not detected, we believe that electron transfer (II)⁷ occurs via (VI) (path A) rather



than directly from (V)(path B). The reasons are as follows. 1) Weak interaction between (II) and TCNE in the ground state (V) was detected by the electronic spectrum. Therefore, TCNE locates close enough to interact with (I) in the rigid matrix. 2) Esr spectrum of (I) in the presence of TCNE was investigated. While the D value of free (I) was found to be 0.3841cm^{-1} , that of (I) in the



presence of TCNE was observed to be 0.3827cm^{-1} (experimental error, $\pm 0.0005\text{cm}^{-1}$). Consequently, electron on the divalent carbon is much delocalized in the presence of TCNE. 3) Photolysis of (II) in the presence of biphenyl instead of TCNE did not produce the anion radical of biphenyl. Biphenyl is an excellent electron acceptor.⁸ Therefore, if the electron transfer proceeds through path B, biphenyl anion radical must be produced. Presumably, in the case of TCNE, CT state (VI) makes it easy to form (VII).

References

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- 3) W. M. Jones, C. L. Ennis, J. Amer. Chem. Soc., 91, 6391 (1969)
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- 5) Y. Achiba, S. Katsumata, K. Kimura, Bull. Chem. Soc. Jap., 45, 1272 (1971); Chem. Phys. Lett., 13, 213 (1972)
- 6) There is an absorption of dibenzo(a,d)cycloheptenyl cation in this region (400-500nm). The absorption near 500nm belongs to the carbene (I)⁴
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- 8) G. B. Gallivan, W. H. Hamill, J. Chem. Phys., 44, 1279 (1966)