Table I. Results from Long-Term Operation of Surface-Modified p-Si Electrodes for the Photoassisted Evolution of H_2

E_{appl}	$i_{photo_{max}}$, mA/cm²	stability
−0.1 V vs. SSCE	0.1	10% decay in 3 h
−0.175 V vs. SSCE	2.6	50% decay in 3 h 90% decay in 8 h
−0.1 V vs. SSCE	1.1	50% decay in 2 h

the reversible potential for hydrogen evolution at this pH can be achieved, but the electrodes degrade upon long-term operation. After long-term irradiation, all electrodes were coated with a black film. A similar black film was found on electrodes modified only with the PBV (lacking Pt). This decomposition of the viologen polymer probably occurs either by hydrogenation[17] (as reported in previous studies[13,18,19]) or to reaction with trace O_2.[31] The viologen polymer coated Pt electrodes can be cycled repetitively with very small decrease in current (<5% after 3 h). This result suggests that the polymer itself is chemically robust. That a black film is formed on the coated p-Si electrodes in the presence or absence of Pt would imply that a process other than hydrogenation may be responsible, at least in part, for the decomposition; this could very well be due to reactions with trace O_2. Reactions at the silicon/polymer interface may also account for the decrease in photocurrent.

Conclusions

Coating of a p-Si electrode with a thin film of poly(benzyl viologen) and Pt promotes the photoevolution of hydrogen. Although the system is stable at low light intensities for several hours, the film eventually degrades with a decrease in photocurrent. The results of a number of studies of semiconductor electrodes and powders with the purpose of driving desired chemical reactions (e.g., H_2 or O_2 evolution) under illumination have shown that one requires not only the semiconductor system, whch provides for photon capture and electron–hole pair separation, but also catalysts. Polymer films provide a useful approach to incorporation of such catalyst systems on a semiconductor surface. Poly(benzyl viologen) films may also be useful in electrochromic (EC) displays.[32] Those on p-Si (or other p-type semiconductor) electrodes are examples of photoaddressable EC displays, as described earlier for heptylviologen bromide on p-GaAs.[33]

Acknowledgment. Helpful conversations with H. White and F.-R. F. Fan are gratefully acknowledged. This work was supported by the National Science Foundation (CHE 8000682) and the Robert A. Welch Foundation.

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Photocatalysis. 6.[1] On the Mechanism of the Cyclotrimerization of *trans*-Cycloheptene, Catalyzed by Copper(I) Triflate

Ton Spee and Adri Mackor*

Contribution from the Institute for Organic Chemistry TNO, 3502 JA Utrecht, The Netherlands.

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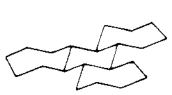
Abstract: The *trans*-cycloheptene ligand in the copper(I) triflate–*trans*-cycloheptene complex cyclotrimerizes at 60 °C in the presence of *cis*-cycloheptene. With use of cycloheptene-d_4 or *trans*-cyclooctene it was established that cyclotrimerization is a process involving *trans*-cycloheptene molecules only. No *cis*-cycloheptene or *trans*-cyclooctene molecules are incorporated into the trimer. However, *cis*-cycloheptene exerts an accelerating effect on this reaction by replacing the reacted *trans*-cycloheptene at copper(I). The most likely explanation of these results is a concerted "template" cyclotrimerization process of either three (*R*)- or three (*S*)-*trans*-cycloheptene molecules around copper. Another possibility would be a two-step mechanism, involving a cupracyclopentane intermediate, irreversibly formed from two *trans*-cycloheptene molecules. No evidence for such an intermediate has been found so far.

Salomon and Kochi et al.[2] have reported on the photochemical formation of a cycloheptene dimer, catalyzed by copper(I) trifluoromethanesulfonate (triflate). Reinvestigation of this reaction by Evers and Mackor[1] showed that dimerization is only a minor reaction and that a cyclic trimer is formed in over 80% yield. This is essentially a two-step process. First, a photochemical cis → trans isomerization of cycloheptene coordinated to copper takes place. A copper(I) triflate–*trans*-cycloheptene complex, having a 1/1 Cu/olefin ratio, has been isolated as a stable colorless crystalline solid, and it has been characterized.[3] Then, under the conditions of the photocatalytic process or in the dark at slightly elevated temperatures (50–60 °C), a cyclotrimerization occurs to give the trimer **1** with an all-trans structure,[4] in essentially a quantitative yield.



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Transition-metal-catalyzed cyclotrimerization reactions, common for alkynes, are very rare for alkenes. To our knowledge,

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[4] According to IUPAC nomenclature, **1** is *trans-anti-trans-anti-trans*-tetracyclo[14.5.0.0^{2,8},0^{9,15}]heneicosane or perhydrocyclohexa[1,2:3,4:5,6]tricycloheptene.

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Table I. ^{1}H and ^{13}C NMR Spectral Data for Trimers 1 and 1-d_{12}, in CDCl$_3$[a]

	^{1}H NMR spectrum[b]				^{13}C NMR spectrum			
trimer	δ_{H_1}	δ_{H_2}	δ_{H_3}	δ_{H_4}	δ_{C_1}	δ_{C_2}	δ_{C_3}	δ_{C_4}
1	0.83 (6 H)	1.18 (6 H) 1.84 (6 H)	1.40 (6 H) 1.62 (6 H)	1.55 (6 H)	48.25 (2 C)	33.76 (2 C)	26.08 (2 C)	28.26 (1 C)
1-d_{12}		1.18 (3 H) 1.84 (3 H)	1.40 (6 H) 1.62 (6 H)	1.55 (6 H)	≈48 (br)	33.80 (1 C) ≈33 (br)	26.08 (1 C) 25.85 (1 C)	28.26 (1 C)

[a] Chemical shifts in δ with respect to Me$_4$Si. [b] Assignment as confirmed by decoupling experiments, yielding also the following coupling constants: $J(2,2') = J(3,3') = 14$ Hz; $J(2,3) = 3$ Hz; $J(2,3') = 11$ Hz; $J(2',3) = J(3,4) = J(3',4) = 6$ Hz.

there is only one other example of a cyclotrimer, which is also formed from a strained cycloalkene, viz. cyclopropene, under the influence of a Pd(0) catalyst.[5] It appears that the driving force for the cyclotrimerization of cycloalkenes is the release of ring strain.

In order to better understand the factors governing the process, we have started an investigation into the mechanism of this thermal cyclotrimerization of cycloheptene, starting from the CuOTf·*trans*-C$_7$ complex.

Results

When CuOTf·*trans*-C$_7$ is heated in neat cyclopentene, cyclohexene, or cyclooctene, it can be concluded from GC MS analyses that **1** is the only trimer formed and that no mixed trimers are present in the reaction mixture. Similarly, even 1-methylcycloheptene does not cotrimerize with CuOTf·*trans*-C$_7$. To preclude steric hindrance at the double bond, we prepared also 5-(methoxymethyl)cycloheptene (**2**) and irradiated it in the presence of its CuOTf complex. A mixture of products was obtained, among which a trimer (parent peak *m/e* 420) was identified by GC MS. When CuOTf·*trans*-C$_7$ was trimerized in the presence of a large excess of **2**, no mixed trimer was found, **1** being the only trimerization product. This was not considered as final evidence, since **2** does not give a clean trimerization reaction. Therefore, we synthesized 1,2,3,3-tetradeuteriocycloheptene, having 95% ^{2}H at each position. From this material the corresponding complex CuOTf·*trans*-C$_7$-d_4 was prepared in the same way as described before for the undeuterated compound,[3] and the trimer was obtained from the complex by a thermal reaction in cycloheptene as the solvent. By careful GC MS analysis it was shown that this trimer was **1**-d_{12}, having the same deuterium content (95%) as the starting material. Trimers **1**-d_4 or **1**-d_8 could not be detected above the level of detection, which is 0.5%.

From this experiment we conclude that **1** is formed from three molecules of *trans*-cycloheptene only, no incorporation of the cis compound taking place. However, the presence in solution of a coordinating compound, like cycloheptene or *p*-dioxane, exerts an accelerating effect on the rate of formation of the trimer. E.g., in the weakly coordinating solvent benzene, at 60 °C, CuOTf·*trans*-C$_7$ does not trimerize in 1 h, while the addition of 2 equiv of cycloheptene leads to the disappearance of more than 50% of the complex within the same period.

As a further result of these experiments, ^{1}H and ^{13}C NMR spectra of trimer d_{12} were obtained, which support its structure as **1**. These spectra also allow a definite assignment of the NMR signals to the various positions, cf. Figures 1 and 2 and Table I. Due to its D_3 symmetry, **1** shows four different carbon resonances and it has six magnetically distinguishable hydrogen resonances.

Further insight into the mechanism of the cyclotrimerization was obtained from experiments with *trans*-cyclooctene.[6] This is the smallest *trans*-cycloalkene, which is stable as a free compound. Although *trans*-cyclooctene is less strained than *trans*-cycloheptene, one might envisage that a mixed trimerization, e.g. with two *trans*-cycloheptene molecules and one *trans*-cyclooctene molecule, would have sufficient driving force to occur, if the *trans*-configuration of the reacting cycloalkene is a stereochemical prerequisite. However, no mixed trimers were observed by GC MS after a trimerization of CuOTf·*trans*-C$_7$ in *trans*-C$_8$ as the solvent at 60 °C or at 80 °C, using in the latter case a very low concentration of the complex. A comparison of the coordination and reaction behavior of *trans*-cycloheptene with that of *trans*-cyclooctene is especially relevant, since Kochi et al.[7] have isolated

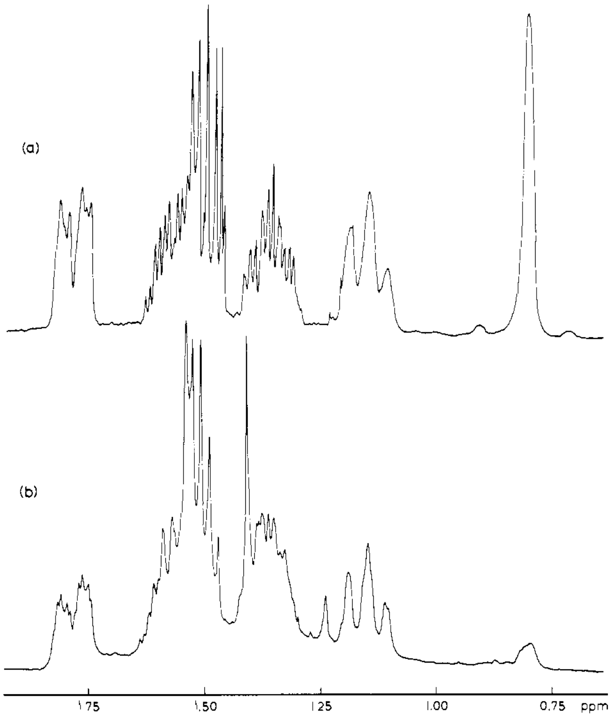

Figure 1. 300-MHz ^{1}H NMR spectra of **1** (a) and **1**-d_{12} (b), in CDCl$_3$.

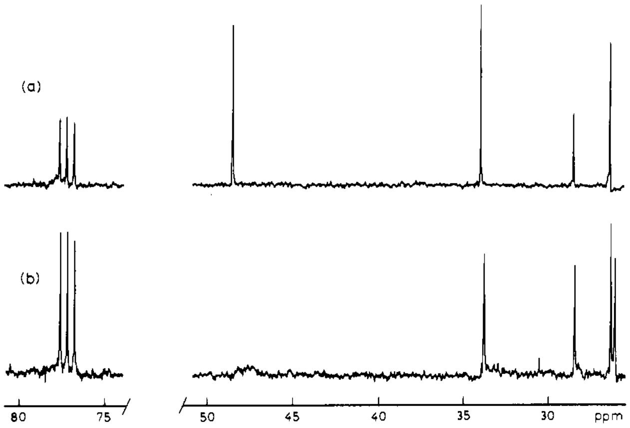

Figure 2. 75.5-MHz ^{13}C NMR spectra of **1** (a) and **1**-d_{12} (b), in CDCl$_3$.

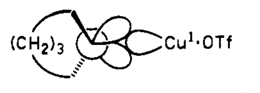

Figure 3. σ-Bonding in CuOTf·(*R*)-*trans*-cycloheptene.

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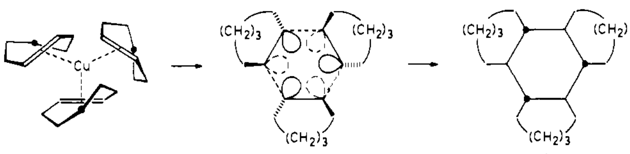

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Figure 4. Cyclotrimerization of (*R*)-*trans*-cycloheptene to give trimer **1**, having all carbon atoms at the central ring with *S* chirality.[10]

a CuOTf·tris(*trans*-cyclooctene) complex. For comparison with the reactivity of CuOTf·*trans*-C_7, we have prepared a CuOTf·*trans*-C_8 (1/1) complex and have heated it in neat cycloheptene, up to 80 °C. No cyclic trimers of cycloheptene and/or cyclooctene were obtained.

Discussion

For the cyclotrimerization of cycloheptene to occur, it seems that not only the trans structure, but also a ring-strain, higher than that in *trans*-cyclooctene is required. One should realize, that the trans double bond in *trans*-cycloheptene is strongly twisted,[3] as shown in a Newman projection, thereby weakening its double-bond character and increasing its coordinating power as a ligand for copper(I).

A reasonable explanation of our results is a concerted cyclotrimerization of three *trans*-cycloheptene ligands around a central copper ion, in a "template" reaction. The feasibility of a CuOTf·tris(olefin) complex is evident from the isolation of such a complex of *trans*-cyclooctene and the symmetrical structure of the CuOTf·1,5,9-cyclododecatriene complexes.[7a] Moreover, Evers[8] found a change in the chemical shift of the *trans*-cycloheptene olefinic hydrogen signal $\Delta(\delta_H)$, upon addition of *cis*-cycloheptene to a solution of CuOTf·*trans*-C_7. When $\Delta(\delta_H)$ was plotted against the molar ratio $x = [cis\text{-}C_7]/[\text{CuOTf}\cdot trans\text{-}C_7]$, straight lines were observed with different slopes for $x < 2$ and $x > 2$. These measurements suggest the existence in solution of a complex CuOTf·*trans*-C_7·(*cis*-C_7)$_2$. We have also isolated this complex, as shown by elemental analysis. It easily loses *cis*-C_7 in vacuum or in an atmosphere of inert gas.

The following mechanism accounts for the nonreactivity of *cis*-cycloheptene and for its accelerating influence on the formation of the trimer of *trans*-cycloheptene.

$$\text{CuOTf}\cdot trans\text{-}C_7 + 2cis\text{-}C_7 \rightleftarrows \text{CuOTf}\cdot trans\text{-}C_7\cdot(cis\text{-}C_7)_2 \quad (1)$$

$$2\text{CuOTf}\cdot trans\text{-}C_7\cdot(cis\text{-}C_7)_2 \rightleftarrows \text{CuOTf}\cdot(trans\text{-}C_7)_2\cdot cis\text{-}C_7 + \text{CuOTf}\cdot(cis\text{-}C_7)_3 \quad (2)$$

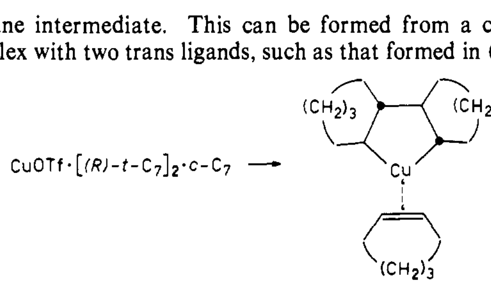
$$\text{CuOTf}\cdot(trans\text{-}C_7)_2\cdot cis\text{-}C_7 + \text{CuOTf}\cdot trans\text{-}C_7(cis\text{-}C_7)_2 \rightleftarrows \text{CuOTf}\cdot(trans\text{-}C_7)_3 + \text{CuOTf}\cdot(cis\text{-}C_7)_3 \quad (3)$$

$$\text{CuOTf}\cdot(trans\text{-}C_7)_3 + 3cis\text{-}C_7 \rightarrow \mathbf{1} + \text{CuOTf}\cdot(cis\text{-}C_7)_3 \quad (4)$$

In this mechanism, it is the function of the cis compound to assist in establishing the equilibria 1–3, leading to the CuOTf·(*trans*-C_7)$_3$ complex, by coordinating to those copper ions, which have transferred their trans ligand to another molecule of copper complex and which would be left otherwise with an empty coordination shell. In the cyclotrimerization step (4) the reacting species is CuOTf·(*trans*-C_7)$_3$, albeit present in a very low concentration. The trimer **1** may be formed in a concerted process, as depicted below.

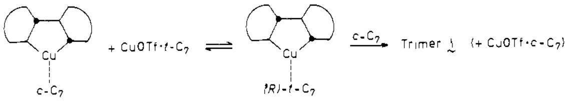
The D_3 symmetry of trimer **1** shows that it is a racemic mixture of molecules, formed from either three (*R*)- or three (*S*)-*trans*-cycloheptene molecules.[9,10] Apparently, the reaction is highly stereospecific. All three *trans*-cycloheptene ligands in one reacting molecule of the complex CuOTf·(*trans*-C_7)$_3$ are of the same chirality.

A reasonable alternative to a concerted process would be a two-step mechanism, as in (5) and (6), involving a cupracyclopentane intermediate. This can be formed from a copper(I) complex with two trans ligands, such as that formed in (2). We



(5)

may assume that such a process is irreversible, the driving force being the release of the ring strain of two *trans*-cycloheptene molecules. For agreement with the experiment, the cis ligand has to be exchanged for a *trans*-cycloheptene with the same chirality as the two trans molecules incorporated into the metallacyclopentane ring.



(6)

Direct evidence for such a two-step mechanism would be the capturing of the cupracyclopentane intermediate in another process than (6), via., cyclodimerization or a mixed cyclotrimerization with *cis*-cycloheptene or *trans*-cyclooctene. Such products have not been observed. If any dimers are formed, they remain below the 0.5% level.

In another attempt to divert an intermediate cupracyclopentane, we have added up to 2 equiv of the powerful ligand triphenylphosphine[11] in order to block one or two coordination sites at copper. No other products than the trimer **1** were observed by GC MS analysis. Both triphenylphosphine and *trans*-cycloheptene are strong ligands for Cu(I) and they compete for coordination sites. The result apparently is that in solution a range of Cu(I) complexes is present, varying in composition between CuOTf·(PPh$_3$)$_3$[11] and CuOTf·(*trans*-C_7)$_3$. Finally, purging the solution with CO during the cyclotrimerization in cycloheptene or in benzene (a slow reaction occurring at 70 °C) does not lead to carbonyl insertion products. Thus, we have no evidence for the intermediacy of a cupracyclopentane compound, and we therefore favor a concerted mechanism. We are presently giving further attention to this question and that of photochemical vs. thermal processes in the cyclodimerization and -trimerization reactions of cycloheptene.

Experimental Section

Nuclear magnetic resonance spectra were recorded on a Varian SC-300 spectrometer, at the Central Laboratory TNO, Delft, and on a Bruker WH-90 spectrometer. GC MS analyses were performed on a Finnigan-3100 D mass spectrometer, coupled to a Finnigan-6100 MS data system, using the following column: OV-1 (3%) on Chrom-WHP 100–120, 80-cm glass, $^1/_4$-in. o.d. 2-mm i.d.; on column injection, carrier gas He, 30 mL/min; temperatures, injection 250 °C, column 100–200 °C (15 °/min) and 200–250 °C (15 °/min).

Elemental analyses were carried out under supervision of Mr. W. J. Buis. All complexes were prepared and kept in a nitrogen atmosphere in closed systems.

Cycloheptene-*1,2,3,3-d$_4$* 3 was prepared from cycloheptanone by exchange with D_2O, catalyzed by K_2CO_3 in the presence of NaCl, to give cycloheptanone-*2,2,7,7-d$_4$*. This compound was reduced to cycloheptanol-*1,2,2,7,7-d$_5$* by reduction with $LiAlD_4$. Elimination of HDO with pentachlorophenol[12] yielded the cycloheptene-*d$_4$* without migration of the double bond, having a degree of deuteration at all deuterated positions of 95% (NMR analysis).

Copper(I) Triflate-*trans*-Cycloheptene-*1,2,3,3-d$_4$* Complex. (CuOTf)$_2$·benzene complex[13] was dissolved in hexane, containing an excess of **3**. Subsequently the solvent was cooled to −20 °C and the solvent was decanted to leave a white crystalline complex with the composition CuOTf·**3** (correct elemental analysis for C, H, Cu, and F, with

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deviations ≤0.2%).[7] From this complex the CuOTf·*trans*-cycloheptene-d_4 complex was prepared photochemically.[3]

Copper(I) triflate–*trans*-cycloheptene–bis(*cis*-cycloheptene) complex was prepared as a colorless crystalline solid by dissolving copper(I) triflate–*trans*-cycloheptene in *cis*-cycloheptene and evaporating the solvent, followed by dissolution of the crystalline residue in hexane and evaporation to dryness. This compound was analyzed at the same day of the preparation to give the following results:

Anal. Calcd for $C_{22}H_{36}CuF_3O_3S$: C, 52.72; H, 7.25; Cu, 12.68; F, 11.37; S, 6.40. Found: C, 50.94; H, 6.91; Cu, 12.26; F, 11.54; S, 6.37. It easily loses cycloheptene ligands, and after 2 weeks, the analysis corresponds approximately to CuOTf·*trans*-cycloheptene·(*cis*-cycloheptene)$_{0.8}$ (^{1}H NMR and elemental analysis). A CuOTf·*cis*-cycloheptene complex, having a ligand/metal ratio not exceeding 1.0, was prepared similarly.

Copper(I) triflate·*trans*-cyclooctene complex[7a] was prepared similarly by ligand exchange. Three milliliters of *trans*-cyclooctene was refluxed with 3.5 g of $(CuOTf)_2$·benzene in 150 mL of hexane for 5 min, and subsequently the mixture was cooled to -20 °C. The supernatant was removed, and the remaining crystals were washed twice with 10 mL of hexane. The yield was 3.27 g (73%). NMR analysis showed that the product was free from benzene. Elemental analysis demonstrated the loss of some ligand, as was easily observable by its smell.

Anal. Calcd for $C_9H_{14}CuF_3O_3S$: C, 33.48; H, 4.54; Cu, 19.69; F, 17.67. Found: C, 29.02; H, 3.59; Cu, 20.50; F, 19.06.

Influence of Cycloheptene on the Cyclotrimerization in Benzene. A 58.1-mg (0.19-mmol) sample of CuOTf·*trans*-C_7 was dissolved in 2.5 mL of C_6D_6. Two 0.5-mL portions of this solution were transferred to NMR tubes, one containing 2 equiv of cycloheptene, as shown in the ^{1}H NMR spectrum from the 2/1 ratio of cis/trans olefinic hydrogens. With use of *p*-xylene as an internal standard, both samples were heated to 59.5 °C for 45 min and they were analyzed afterward. The decrease of the *trans*-cycloheptene signal in the solution, containing extra cycloheptene, was approximately 50%. In the other solution the trans olefinic H signal had not decreased significantly. Further heating of the solutions at 70 °C for 10 min did not affect the blank solution, while in the solution, containing cycloheptene, a further 10% decrease of the trans signal was observed.

Cyclotrimerization of CuOTf·*trans*-C_7 in the Presence of *cis*-C_7, *trans*-C_8, or Triphenylphosphine. A solution of approximately 1 mmol of CuOTf·*trans*-C_7 was heated to 60 °C for 2 h in the presence of 4 mL of cycloolefin. The complex was destroyed afterward by pouring out the solution into 5 mL of concentrated aqueous ammonia. The ammonia layer was extracted twice with 4 mL of diethyl ether. The combined organic layers were dried with $MgSO_4$. Subsequently the solution was concentrated by distillation to approximately 1 mL and then analyzed on GC MS.

For the experiment with PPh_3 0.64 mmol of CuOTf·*trans*-C_7 was dissolved in 8 mL of cycloheptene. This solution was divided into four equal portions, to which increasing amounts of PPh_3 were added (0, 1.0, 1.5, 2.0 equiv). The cyclotrimerization was performed as before. No other product than trimer **1** was found by GC MS analysis.

Acknowledgment. We thank Professors W. Drenth and H. J. T. Bos for helpful discussions and our TNO colleagues in the Department of Physical Organic and Analytical Chemstry for their cooperation, in particular Mrs. G. G. Versluis-de Haan. The hospitality (T.S.) of the Department of Organic Chemistry of the State University at Utrecht is gratefully acknowledged.

Locally Excited Triplet State Production from Excited Charge-Transfer Complexes

Bobby K. Adams and William R. Cherry*

Contribution from the Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506. *Received April 13, 1981*

Abstract: The photochemistry and photophysics of a series of homologous charge-transfer complexes, involving substituted stilbenes and fumaronitrile, have been examined. The rate constants for fluorescence (k_f), production of the stilbene triplet state (k_T), and decay back to the ground state (k_d) have been determined. The values of k_T for the complexes were found to be logarithmically related to the energy gap between the initial and final states. In contrast, k_f and k_d are independent of the identity of the substituted stilbene. These results verify the previously proposed mechanism of stilbene isomerization in the parent system.

The decay of an exciplex or excited charge-transfer complex (CTC) to a locally excited triplet state has been extensively studied.[1-12] Early work on excited CTC demonstrated that phosphorescence could be observed from the species with the lowest triplet energy. For example, phosphorescence from the 1,2,4,5-tetracyanobenzene/hexamethylbenzene complex is observed because the triplet state of the complex is energetically below both locally excited triplet states of the components.[3] On the other hand, the triplet state of naphthalene is energetically below the triplet state of the complex formed with 1,2,4,5-tetracyanobenzene with the result that only naphthalene phosphorescence is observed.[4]

Luminescence is not the only indication of triplet state formation. Reactions typical of locally excited triplet states of either the donor or acceptor have been observed. For instance, Aloisi et al.[5] reported that the formation of the exciplexes between styrylnaphthalene and various amines results in isomerization of the styrylnaphthalene. Similarly, Hayashi and Nagakura[6] found that exciplexes formed between fumaronitrile and several singlet aromatic hydrocarbons decayed with concomitant formation of maleonitrile. Both of these isomerizations have been attributed to formation of the locally excited triplet state of the acceptors.

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* Address correspondence to this author at the Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803.

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