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Photochemical Electron-Transfer Reactions: Effect of Ring Opening of the Cyclobutane Radical Cation on the Dimerization of Phenyl Vinyl Ether

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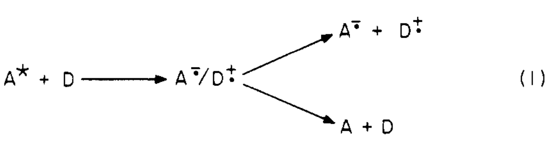
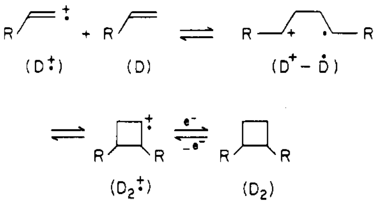
The photosensitized electron-transfer dimerization of olefins proceeds via several reversible steps. Limited kinetic data on some of these processes have been reported. We used the dependence of the product distribution in the electron-transfer-sensitized dimerization of phenyl vinyl ether (PVE) to determine some of the otherwise not readily accessible rate constants. Ring opening of the radical cation of one of the dimers of PVE, *cis*-1,2-diphenoxycyclobutane (C), proceeds in acetonitrile at room temperature at a rate constant of ca. 1.8×10^6 s^{-1}. The reaction constant of electron transfer from PVE to $C^{+\cdot}$, the chain propagation reaction, is ca. 1.5×10^8 M^{-1} s^{-1}. The role of the ratio of these two competing reactions on the course of such dimerizations is discussed.

The 2 + 2 cyclodimerization of olefins via the radical cation, produced by electron-transfer photosensitization (eq 1), has been recognized to involve several reversible



A: electron acceptor
D: olefinic electron donor

steps (eq 2).[1,2] These dimerizations are likely to proceed



(2)

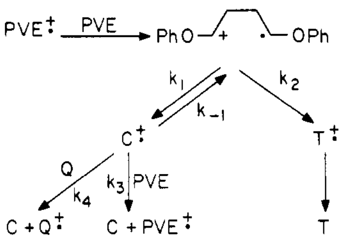
via a chain mechanism, as electron transfer from the neutral olefin to the radical cation of the dimer (eq 3) in most cases is energetically feasible.[1-3]

$$D_2^{+\cdot} + D \rightarrow D_2 + D^{+\cdot} \qquad (3)$$

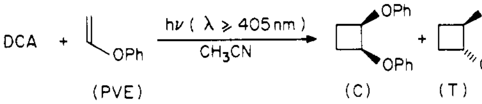
These dimerization reactions are controlled primarily by a number of competing processes:[4] (1) the energy-wasting, reverse electron transfer in the geminate pair, which competes with the separation of the radical ions (eq 1), and possible interception of the radical ion pair, (2) the competition between addition of the radical cation ($D^{+\cdot}$) to a neutral olefin to form the dimeric 1,4 radical cation (D^+–$D\cdot$) and the reduction of $D^{+\cdot}$ by the acceptor radical anion or by impurities in the system, (3) the competition between the cyclization of D^+–$D\cdot$ to give the cyclobutane radical cation ($D_2^{+\cdot}$) and the cleavage to its components, (4) the reduction of the cyclobutane radical cation to give the final product by electron transfer from $A^{-\cdot}$ or from a neutral olefin (the chain propagation step), which competes with the ring opening.

Although some kinetic studies on these processes have been reported,[4] data about the rate constants for ring opening of the cyclobutane radical cation ($D_2^{+\cdot}$) are scarce.[5] This Letter deals with the determination of the rate constant of such a ring-cleavage reaction in the dimerization of phenyl vinyl ether (PVE) and its effect on the product distribution.

Scheme I



The electron-transfer-sensitized photodimerization of PVE has been the subject of several publications.[3,6-10] At concentrations of PVE ≳ 0.1 M two isomeric cyclobutanes are formed in the ratio of ca. 60:40 (eq 4). Contradictory stereochemical assignments of these dimers have been made.[11] We established, by X-ray analysis, that the minor isomer has the trans configuration (T)[12] (cf. Figure 1).



(4)

DCA = 9,10-dicyanoanthracene

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[1] Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133.

[2] Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80.

[3] Evans, T. R.; Wake, R. W.; Jaenicke, O. In "The Exciplex"; Gordon, M.; Ware, W. R., Ed.; Academic Press: New York, 1975; p 345.

[4] Mattes, S. L.; Farid, S. "Organic Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233, and references therein.

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[6] Kuwata, S.; Shigemitsu, Y.; Odaira, Y. *J. Chem. Soc. D* **1972**, 2. *J. Org. Chem.* **1973**, *38*, 3803.

[7] Farid, S.; Hartman, S. E.; Evans, T. R. In "The Exciplex"; Gordon, M.; Ware, W. R., Ed..; Academic Press: New York, 1975; p 327.

[8] Mizuno, K.; Ogawa, J.; Kamura, M.; Otsugi, Y. *Chem. Lett.* **1979**, 731.

[9] Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1980**, *102*, 4303.

[10] Mizuno, K.; Kagano, H.; Kasuga, T.; Otsuji, Y. *Chem. Lett.* **1983**, 133.

[11] The original stereochemical assignments of C and T made by Shigemitsu[6] are correct and were confirmed by X-ray analysis of T.[12] T (mp 67–68 °C; lit.[6] mp 66–68 °C) has shorter retention time than C when analyzed on a 6 ft × 1/8 in. gas chromatography column of 1.5% Dexsil 300 on 80/100 Chrom W set at 150 °C.

[12] Clear, tabular single crystals were obtained from methanol. The crystal data are as follows: $a = 14.085$ (3), $b = 16.572$ (2), $c = 5.721$ (3) Å, $\alpha = 91.12$ (2), $\beta = 99.15$ (3), $\gamma = 95.95$ (1), space group $P\bar{1}$, $Z = 4$ (2 molecules per asymmetric unit), $D_c = 1.218$ g cm^{-3}. Intensity data were collected by the $\omega - 2\theta$ scan method on an Enraf-Nonius CAD4 diffractometer with monochromated Mo Kα radiation. The structure was solved by direct methods and refined by the full-matrix least-squares method to $R = 0.063$. Of the 4601 independent intensities measured ($2\theta \leq 50°$), 2515 had $I > \sigma(I)$ and were used in the refinement. Bond distances averaged over equivalent bonds in the two independent molecules (labeled A and B in the supplementary material) are given in Figure 1.

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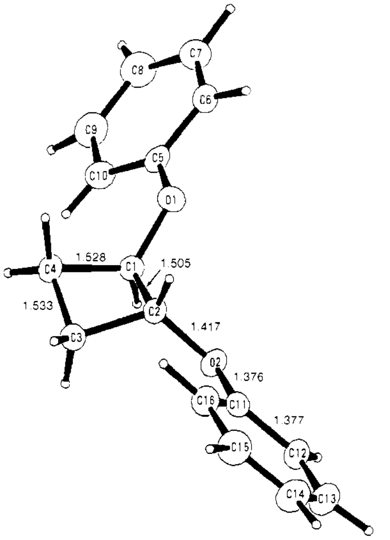

Figure 1. Molecular structure of the trans dimer (T). The given bond lengths are average values from equivalent bonds in two independent molecules.[12] The cyclobutane rings are puckered by 32° and 33°.

Recently, Mizuno et al.[10] made the interesting observation that the ratio of the dimers C:T, to which they assigned the opposite stereochemistry, decreases precipitously from the ca. 60:40 ratio to predominantly T when the concentration of PVE is decreased below ca. 0.03 M. To account for this effect the authors proposed a mechanism based on two intermediates, the geminate pair and the separated radical cation of PVE, which lead to different product distributions. Although interception of the geminate pair is important in other electron-transfer photoreactions,[5,13] as shown below, this mechanism cannot adequately explain the kinetic data in PVE dimerization.

The data, however, are readily explained in terms of dimerization via the separated radical cation involving a chain mechanism,[3,7] taking into account the reversible formation of the *cis*-cyclobutane (C) reported by Evans et al.[3] Moreover, we used this varying product distribution to determine the kinetics of the ring opening of $C^{+\cdot}$ and that of the chain-propagation step (eq 3).

Ring opening of $C^{+\cdot}$ is evident from the isomerization of C to T when C is irradiated in the presence of DCA.[3] Under these conditions the trans isomer T is stable. The increase in the [T]/[C] ratio at low [PVE] can result from the decrease in the rate of electron transfer to $C^{+\cdot}$, which competes with the ring cleavage to the 1,4 radical cation (Scheme I). Recyclization of the latter to both $C^{+\cdot}$ and $T^{+\cdot}$ changes the dimer ratio according to eq 5.

$$\frac{[\mathrm{T}]}{[\mathrm{C}]} = \frac{k_2}{k_1} + \frac{k_2}{k_1}\frac{k_{-1}}{k_3}\frac{1}{[\mathrm{PVE}]} \tag{5}$$

A plot of [T]/[C] vs. 1/[PVE] from irradiations to very low conversion[14] gave a straight line with an intercept of 0.64 and a slope of 0.0075 M, which corresponds to k_{-1}/k_3 of 1.17×10^{-2} M. The linearity of this plot justifies the assumption made in deriving eq 5 that the reduction of $C^{+\cdot}$ to C is primarily through electron transfer from PVE or from impurities in this compound.[15]

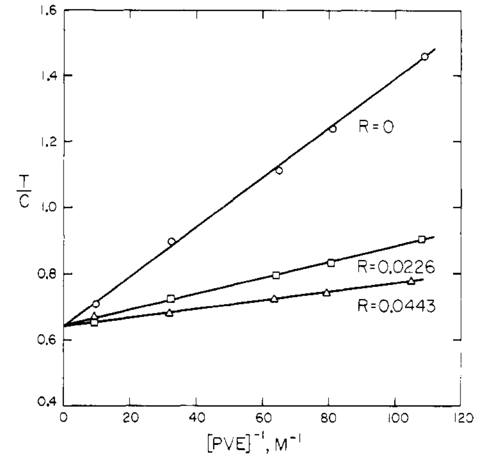

Figure 2. Plot of the product ratio [T]/[C] vs. $[\mathrm{PVE}]^{-1}$ from irradiations of degassed CH_3CN solutions saturated with DCA (~0.55 mM) in the absence ($R = 0$) and in the presence of 1,2,4-trimethoxybenzene at constant molar ratio to [PVE] of 0.0226 and 0.0443.

According to the mechanism of Scheme I, [T]/[C] should decrease when the irradiation is carried out in the presence of another electron donor (Q) until a value close to the ratio of $k_2{:}k_1$ of 0.64 is reached. In fact, at [PVE] = 1.23×10^{-2} M, [T]/[C] decreases from 1.24 in the absence of other electron donors to 0.83 in the presence of 2.82×10^{-4} M 1,2,4-trimethoxybenzene as Q, and further increases in [Q] to 6.4×10^{-3} and 1.3×10^{-2} M give the expected minimum value for [T]/[C] of 0.64.

It can be shown that irradiation at a constant [Q]/[PVE] ratio R will yield the product ratio expressed by eq 6.

$$\frac{[\mathrm{T}]}{[\mathrm{C}]} = \frac{k_2}{k_1} + \frac{k_2}{k_1}\frac{k_{-1}}{k_3 + Rk_4}\frac{1}{[\mathrm{PVE}]} \tag{6}$$

Indeed, plots of [T]/[C] vs. 1/[PVE], at $R = 0.0226$ and 0.0443, are linear and have lower slopes, 0.0024 and 0.0013 M, respectively, than that obtained in the absence of Q (Figure 2). From these slopes it follows that k_4/k_3 is ca. 100 ± 7. If we assume that k_4 is 1.5×10^{10} $M^{-1}\ s^{-1}$, the diffusion-controlled rate, as justified by the strong exothermicity of this reaction, values for k_3 of ca. 1.5×10^{8} $M^{-1}\ s^{-1}$ and for k_{-1} of ca. 1.8×10^{6} s^{-1} are obtained. Previously, using a different approach, we estimated[16] k_3 to be 2.1×10^{8} $M^{-1}\ s^{-1}$, which is in good agreement with the value from the present work.

The fact that the trans isomer T does not undergo photosensitized electron-transfer isomerization shows that the reaction constant for ring opening of $T^{+\cdot}$ is substantially lower than 1.8×10^{6} s^{-1}, the corresponding reaction constant of $C^{+\cdot}$. The steric hindrance in C is probably the reason for the lower stability of its radical cation. In agreement with that, the rate contant for ring opening of the radical cation of the strongly sterically hindered dimer of diphenylethylene, 1,1,2,2-tetraphenylcyclobutane, is about two orders of magnitude higher than that for $C^{+\cdot}$.[5]

For the dimerization to be efficient, the rate constant of electron transfer to the cyclobutane radical cation must compete favorably with the ring cleavage. In spite of the

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[13] Mattes, S. L.; Farid, S. *J. Chem. Soc., Chem. Commun.* **1980**, 126.

[14] The isomerization of C to T, reported in ref 3, was confirmed through reaction of the former with selectively excited DCA. Because the reaction constant for quenching DCA^{*1} with C is similar to that with PVE,[3] the conversion at low [PVE] had to be kept very low to avoid altering the primary product ratio. In the early stages of these reactions T/C remained almost constant. As expected, however, this ratio increased with the degree of conversion, contrary to statements made in ref 10. At PVE concentrations substantially lower than 0.01 M, this effect was too pronounced to allow accurate determination of the primary ratio.

[15] The slope/intercept ratio of this plot represents a minimum value for k_{-1}/k_3. If there were electron-donor impurities in PVE, this ratio would be equal to $k_{-1}/k_3(1 + \rho)$, where $\rho = k_i/k_3 \times$ (molar fraction of the impurity) and k_i is the reaction constant for electron transfer from the impurity to $C^{+\cdot}$.

[16] In ref 7, this rate constant was estimated to be 1.4×10^{8} $M^{-1}\ s^{-1}$ on the basis that the diffusion rate constant is 1×10^{10} $M^{-1}\ s^{-1}$. On the more likely assumption made in the present work that the latter is 1.5×10^{10} $M^{-1}\ s^{-1}$, the value of k_3 would be 2.1×10^{8} $M^{-1}\ s^{-1}$.

two orders of magnitude difference in the reactivities of the radical cations of tetraphenylcyclobutane and of C, both dimerization reactions show similar dependence on the olefin concentration because k_3 is also two orders of magnitude slower than the corresponding reaction in the dimerization of diphenylethylene. These differences result from the fact that PVE and C have similar oxidation potentials, whereas diphenylethylene is much more readily oxidized than its cyclobutane dimer.[5]

The mechanism proposed by Mizuno,[10] which involves interception of the geminate ion pair, can be ruled out for the dimerization of PVE for several reasons. The near constant value of [T]/[C] when the concentration of PVE is ca. 0.1 M and higher would require that almost all the dimer is formed via the intercepted geminate pair even at 0.1 M PVE. Since the reaction constant[5,13,17] for the separation of geminate radical ion pairs in acetonitrile at room temperature is ca. 5×10^8 s^{-1}, the reaction constant for interception of the pair would have to be higher than the diffusion-controlled rate. On the other hand, the efficient quenching[7] at low ratios of quencher to PVE means that the dimerization is one to two orders of magnitude slower than the diffusion-controlled rate. Furthermore, if most of the product is formed via the intercepted pair at [PVE] > 0.1 M, then no chain reaction can take place, contrary to the findings reported earlier.[18]

Registry No. *cis*-1,2-Diphenoxycyclobutane radical cation, 87638-53-7; phenyl vinyl ether, 766-94-9; *trans*-1,2-diphenoxycyclobutane, 35370-70-8.

Supplementary Material Available: X-ray data of the *trans*-cyclobutane derivative (T): bond lengths, interatomic angles, positional and thermal parameters, observed and calculated structure factor amplitudes (32 pages). Ordering information is available on any current masthead page.

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[17] Schulten, K.; Staerk, H.; Weller, A.; Werner, J. J.; Nickel, B. *Z. Phys. Chem.* (*Frankfurt am Main*) **1976**, *101*, 371. Weller, A. *Ibid.* **1982**, *130*, 129.

[18] The chain reaction reported in ref 3 and 7 was confirmed again by measuring quantum yields of dimerization of 0.84 and 1.24 in acetonitrile at PVE concentrations of 0.102 and 0.508 M, respectively. As shown in ref 7, the quantum yields and their dependence on [PVE] are very sensitive to traces of impurities in PVE and/or in the solvent. This is particularly so because of the small rate constant of the chain-propagation step (cf. text).

Direct Excitation of Triplet States in Supersonic Jets. Rotationally Resolved $^3A_u \leftarrow {}^1A_g$ Laser-Induced Phosphorescence Spectrum of Glyoxal

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By combining the techniques of free-jet expansion, high-power laser excitation, and phosphorescence detection, we have observed a rotationally resolved spectrum of the 0_0^0 band in the spin-forbidden $^3A_u \leftarrow {}^1A_g$ transition of glyoxal. A preliminary analysis of this spectrum is given, together with a brief discussion of the advantages of this approach for the study of the static and dynamic properties of triplet states under collision-free conditions.

Introduction

Laser spectroscopy, particularly in combination with supersonic jets, is a very powerful tool for the study of electronically excited states of polyatomic molecules. In most applications reported to date, the focus has been on excited *singlet* states, or at least on states which are connected to the ground state by spin-allowed transitions. But many photophysical processes that occur following the absorption of light depend, as well, on the properties of metastable, "dark" states. Chief among these are excited *triplet* states, the object of much attention since their existence was first demonstrated by Lewis and Kasha[1] nearly 40 years ago. Owing to their low oscillator strengths to the ground state, such states are usually accessed only indirectly.[2] In this report, we show that triplet states of polyatomic molecules can also be prepared, with rotational state selection, by *direct* excitation of the spin-forbidden $T_1 \leftarrow S_0$ transition and detection of the resulting phosphorescence in a supersonic jet.

Experimental Section

The free jet was formed by expansion of helium through a 1-mm pulsed nozzle into a chamber evacuated by a 25-cm oil diffusion pump backed by a large mechanical pump. The carrier gas (P_0 = 1–5 atm) was saturated with glyoxal contained in a steel bottle maintained at 273 K. *trans*-Glyoxal was prepared by gently heating a mixture of the glyoxal trimer dihydrate, obtained from Aldrich, and P_2O_5 under vacuum. The seeded jet was crossed 2 cm downstream of the nozzle by a Nd^{3+}:YAG pumped Coumarin 500 dye laser which delivered ~25-mJ pulses of 10-ns duration at a 10-Hz repetition rate. The overall spectral width was 0.03 cm^{-1} with an etalon in the laser cavity. The laser was pressure tuned over 10-cm^{-1} intervals by introducing N_2 into the cavity through a regulated flow valve. Phosphorescence was collected by f/1.2 optics and imaged on a filtered photomultiplier tube. The detection system was coaxial with the jet, the first lens being located 7 cm downstream of the nozzle. Under these conditions, molecules spend about 10 μs in the viewing region. Signals were detected with a boxcar integrator with a delayed gate of 1-μs duration. Relative line positions were determined

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[1] G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944).

[2] Important exceptions do, of course, occur, both in the condensed phase and in the gas phase. See, for example, C. Michel and C. Tric, *Chem. Phys.*, **50**, 341 (1980); G. ter Horst, Ph.D. Thesis, R. U. Groningen, 1982.

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