

BENZENE PHOTOSENSITIZED DEPOLYMERIZATION OF α -TRUXILLIC ACID

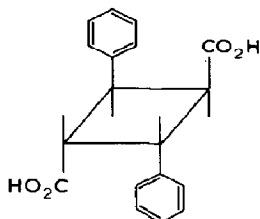
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(Received February 12, 1974)

Summary

α -Truxillic acid,



in aerated methanol solution excited in the phenyl absorption band ($\sim 1/4 \mu\text{m}$) was reported earlier to photolyze 18% more efficiently than in deoxygenated solution concomitant with a 17% attenuation of fluorescence emission. The oxygen clearly facilitated intersystem crossing to another reactive excited state. Thus, the reaction rate of forming the scission product cinnamic acid from the non-fluorescent excited triplet state is larger than its excited precursor. The scission of the cinnamic acid dimer in the present investigation was effected by benzene photosensitization. Although both the first excited singlet and triplet states of the donor lie roughly 2 kcal/mol higher than the respective acceptor states the experiments presented here indicate that the photosensitized reaction proceeds by triplet energy transfer.

Introduction

The photochemical decomposition of α -truxillic acid to *trans*-cinnamic first reported by Stoermer and Foerster [1] was effected six years later in benzene suspension [2]. Absorption and luminescence spectra [3] of the cinnamic acid photodimers made it quite apparent that some of the scission reaction in benzene obtained by irradiation could be due to energy transfer from benzene to the diphenylcyclobutane-dicarboxylic acid since both the first excited singlet and triplet states of benzene were about 2 kcal/mol more energetic than either excited state in α -truxillic acid. In order to determine if

such energy transfer was involved it was decided to test this assumption with α -truxillic acid and to elucidate the multiplicity of the excited state.

Experimental

The benzene used in this investigation was J. T. Baker "Intra-Analyzed" gas chromatographed spectrophotometric grade. Experimental details in all other respects were the same as described earlier [3].

Results

Benzene sensitization of α -truxillic acid scission

Quantum yields of sensitized scission, defined as molecules of dimer splitting per quantum of radiation absorbed by the benzene, were determined in aerated and deoxygenated methanol solutions as a function of donor and acceptor concentrations (Table 1). Correction is made in the calculations for the small amount of dimer scission produced by radiation directly absorbed by the dimers. This occurs with a quantum efficiency of 0.12. An irradiation wavelength of 248 nm was chosen for this experiment to maximize the relative absorptivity of the benzene compared to that of the α -truxillic acid. This, together with the use of large excesses of benzene in the mixtures insured that most of the incident radiation was absorbed by benzene.

TABLE 1

Summary of benzene sensitized quantum yields of scission for α -truxillic acid/MeOH

[Benzene] 2 α -truxillic acid	[Benzene] (mM)	[α -truxillic acid] (mM)	$\Phi_{\text{Sens.}}$ (air saturated)	$\Phi_{\text{Sens.}}$ (degassed)	$\frac{\Phi_{\text{degassed}}}{\Phi_{\text{air. sat.}}}$
22.5	2.25	0.050	0.031	0.160	5.1
84.7	22.5	0.133	0.031	0.150	4.8
225	22.5	0.050	0.022	0.079	3.6
562	56.2	0.050	0.021	—	—
847	22.5	0.0133	0.015	0.055	3.7

The benzene sensitized scission quantum yield, $\Phi_{\text{sens.}}$, was found to increase with increase in α -truxillic acid concentration at a constant benzene concentration of 22.5 mM.

On the other hand, at a constant 0.050 mM α -truxillic acid concentration, the sensitized quantum yield decreased as the benzene concentration was increased from 2.25 to 50.0 mM. The observed decrease is attributed to self-quenching of excited benzene molecules by unexcited benzene molecules. Such self-quenching is competitive with energy transfer [4], and thus reduces the yield of sensitized scission.

Data in Table 1 are arranged in order of increasing mole ratio of benzene to α -truxillic acid. They show that $\Phi_{\text{sens.}}$ decreases with increasing benzene/ α -truxillic acid ratio.

Sensitized quantum yields for air equilibrated solutions ($[\text{O}_2] = 2.12 \text{ mM}$) exhibit scission rates which are from 3 to 5 times smaller than those for the corresponding deoxygenated solutions. This attenuation of the sensitized scission in the presence of oxygen is in marked contrast to the effect of oxygen on the direct photochemical scission reaction. The direct photochemical scission quantum yield was found to be 18% larger for the aerated solution than in the absence of oxygen.

Special note should also be taken of the fact that for two of the degassed solutions tested the benzene sensitized quantum yield actually exceeds the direct photolysis quantum yield ($\Phi_r^0 = 0.12$) for deoxygenated α -truxillic acid in methanol. It is quite conceivable that even higher sensitized quantum split to cinnamic acid with higher efficiency than do molecules in the exciplex concentrations.

These observations can be accounted for most plausibly by a mechanism involving triplet energy transfer from benzene to α -truxillic acid, coupled with the earlier results [3] which indicate that α -truxillic acid triplets splits to cinnamic acid with higher efficiency than do molecules in the excited singlet state.

The susceptibility to oxygen quenching also indicates that a species of relatively long lifetime is involved in the chain of events leading to sensitized scission. This quenchable species is presumably the benzene triplet. The lifetime of triplet benzene in solution was found to be concentration dependent and a value of $\sim 1 \mu\text{s}$ for 10^{-2} M benzene in cyclohexane was determined by Lipsky [5].

The demonstrated occurrence of triplet-triplet energy transfer from benzene to dimer does not rule out the possibility that singlet-singlet energy transfer could also take place in the same solution, considering that either process is exothermic by about 2 kcal/mol. If any singlet energy transfer were to take place, it would be evidenced by a simultaneous quenching of benzene fluorescence and sensitization of dimer fluorescence.

Discussion

The results of the benzene sensitized scission experiment are strongly suggestive of a triplet-triplet energy transfer process, from benzene to α -truxillic acid, resulting in the cleavage of the dimer triplets. It is necessary to assume that the benzene triplet is involved in this sensitization in order to account for: (1) a high degree of susceptibility of the sensitized photolysis yield to oxygen quenching, inasmuch as the presence of oxygen actually enhances the direct photolysis rate; and (2) a higher yield for sensitized scission (at low ratios of benzene/ α -truxillic acid) than that obtained by direct irradiation of α -truxillic acid.

The maximum value of $\Phi_{\text{sens.}} = 0.16$, obtained with 2.2 mM benzene plus 0.050 mM α -truxillic acid, is of interest in estimating the fraction, γ , of dimer triplets which cleave to product. If every excited benzene molecule were to intersystem cross to a triplet, and then transfer energy to an α -truxillic acid molecule, the fraction of dimer triplets splitting would have to be at least 0.16. Actually, reported triplet yields for benzene in solution range from $\Phi_{\text{ISC}} = 0.24$ [6] to $\Phi_{\text{ISC}} = 0.42$ [7]. Then, assuming 100% efficient energy transfer of 42% of the excited benzene molecules to give dimer triplets, and of 58% of the excited benzene molecules to give dimer singlets ($\Phi_r^0 = 0.12$), the lower limit yield of scission from dimer triplets to give an overall scission yield of 0.16 is $\gamma = 0.19$.

The value of γ could be considerably higher than this to the extent that the energy transfer steps are less than 100% efficient. In addition, it is likely that the sensitized quantum yield of 0.16 is not the maximum obtainable for all possible combinations of donor and acceptor concentrations.

At this point, we have additional evidence from benzene sensitization, that dimer triplets can undergo scission more efficiently than dimer singlets, and at the same time, from piperylene quenching, that most if not all of the product formation in the direct photolysis actually come from scission of excited singlets.

It necessarily follows from this that the intersystem crossing yield for excited α -truxillic acid singlets must be quite low, and furthermore that any perturbation which tends to increase the intersystem crossing yield should cause an increase in the observed yield of scission. The effects observed upon addition of oxygen to α -truxillic acid solutions can be accounted for in just this way.

References

- 1 R. Stoermer and G. Foerster, Ber., 52 (1919) 1555.
- 2 H. Stobbe and A. Lehfeldt, Ber., 58 (1925) 2415.
- 3 J. Rennert and D. Grossman, J. Photochem., 3 (1974/75) 000.
- 4 E. K. C. Lee, J. Phys. Chem., 71 (1967) 2804.
- 5 S. Lipsky, J. Chem. Phys., 28 (1963) 2786.
- 6 A. A. Lamola, Ph. D. Thesis, California Institute of Technology, Pasadena, 1965.
- 7 H. Morrison and R. Peiffer, J. Am. Chem. Soc., 90 (1968) 3428.