

QUANTUM YIELDS OF THE MERCURY PHOTOSENSITIZED CIS-TRANS
ISOMERIZATION OF 1,3-PENTADIENE

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Received March 10, 1975

The quantum yields of the cis→trans and trans→cis Hg $6(^3P_1)$ photosensitized isomerizations of 1,3-pentadiene at 100 Torr and 22 °C are 0.54 ± 0.02 and 0.42 ± 0.02 , respectively. The steady state ratio ($[\text{trans}] / [\text{cis}]$)_{ss} is 1.27 ± 0.05 which is almost identical with the ratio of the quantum yields, $\Phi(c \rightarrow t) / \Phi(t \rightarrow c) = 1.29 \pm 0.10$. The cis→trans isomerization is suggested as a useful actinometer for mercury sensitized reactions.

Квантовые выходы Hg $6(^3P_1)$ фотосенсибилизированный цис → транс и транс → цис изомеризации 1,3-пентадиена при давлении 100 торр и температуре 22°C равны $0,54 \pm 0,02$ и $0,42 \pm 0,02$, соответственно. Отношение ($[\text{транс}] / [\text{цис}]$)_{сс} в стационарном состоянии равно $1,27 \pm 0,05$, что почти идентично с отношением квантовых выходов $\Phi(\text{ц} \rightarrow \text{т}) / \Phi(\text{т} \rightarrow \text{ц}) = 1,29 \pm 0,10$. Изомеризация цис → транс предлагается в качестве удобного актинометра для реакций, сенсбилизированных ртутной лампой.

INTRODUCTION

The cis→trans and trans→cis isomerizations of 1,3-pentadienes (piperlyenes) have been widely used as sensitive probes for the participation of triplet species in photochemical reactions, especially in the liquid phase /1/. Whereas the cis→trans

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isomerization of butene-2 has been proposed and used as an actinometer for Hg $6(^3P_1)$ reactions in the gas phase /2,3/, mercury sensitization of the piperylenes seems to have been subjected only to qualitative or semi-quantitative investigations /4-6/. We have therefore undertaken the determination of the quantum yields of the triplet mercury photosensitized cis \rightleftharpoons trans isomerizations of piperylene, partly because of our interest in the sensitized isomerizations of the piperylenes /7/ and partly in view of their possible use as actinometers for Hg $6(^3P_1)$ sensitized reactions.

EXPERIMENTAL

Cis-piperylene (Fluka, AG, purum) contained about 0.3% trans-piperylene. Trans-piperylene (Fluka, AG, purum) was 99% pure, it contained only about 0.1% of the cis-isomer and 0.9% cyclopentene.

The light source for measuring the steady-state ratio ($[\text{trans}] / [\text{cis}]$)_{ss} = R_{ss}, was an "Original Hanau" NN 15/44 low pressure Hg lamp and the reaction cell was a cylindrical quartz tube. A 4 mm thick Vycor plate was used to cut-off light with wavelengths of $\lambda < 220$ nm.

The light source for the quantum yield measurements was a UVSL-15 Minera-light lamp, the intensity at 253.7 nm, $8.07 \pm 0.10 \times 10^{13}$ photons/sec, was determined by butene-2 (100 Torr) actinometry /3/. All of these experiments were performed in a cylindrical cell, 2 cm long and 5 cm in diameter, fitted with Vycor windows.

The cis- and trans-piperylenes were analyzed either on an 8 m column containing 20 wt% silicone oil (SISS, SI-710) on 45-60 mesh chromosorb (F. &

M. Scientific Corp.) or on an 8.6 m column containing 30% propylene carbonate on 60-80 mesh chromosorb P. The butene-2 isomers were separated on the latter column.

RESULTS AND DISCUSSION

Reaction products

Meinwald and Smith /4/ observed no significant reaction other than very slow polymer formation upon mercury photosensitization of a mixture of cis- and trans-piperylene. Srinivasan and Boué /5/ found however that both piperylenes yield 1,3-dimethylcyclopropene at the same rate when photosensitized by $\text{Hg } 6(^3\text{P}_1)$. They also reported /6/ that cis-piperylene forms two other minor products while the most important reaction is cis-trans isomerization, being about 25 - 50 times faster than 1,3-dimethylcyclopropene formation.

The above results are in general qualitative agreement with those of the present study. We find that geometrical cis-trans isomerization is the only major reaction. Polymerization occurs, with $\Phi(-\text{piperylene}) < 0.15$. Also, only three minor gaseous products ($\Phi < 10^{-2}$) are observed at medium irradiation times. Under very prolonged irradiation a host of products, at least 20, can be discerned by gas chromatography. In spite of the low absorption coefficients for piperylene ($\epsilon_{\text{cis}} = 31$ and $\epsilon_{\text{trans}} = 50.6$ in cyclohexane solution /8/) relative to the absorption coefficient for mercury at 253.7 nm, some of these products could be formed via relatively unimportant competitive direct photolysis of the piperylenes /5, 8, 9/.

Cis-trans isomerization

The quantum yields were determined at 22 ± 1 °C and at 100 ± 2 Torr under initial conditions (less than 5% conversion). $\Phi(c \rightarrow t) = 0.54 \pm 0.02$ and $\Phi(t \rightarrow c) = 0.42 \pm$

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± 0.02 giving $\Phi(\text{total}) = 0.96 \pm 0.04$. These isomerization quantum yields are about five times higher than those obtained in the direct photolysis of piperylene at 253.7 nm in dilute cyclohexane solution /5, 8/.

The photostationary state, R_{ss} , was determined by long irradiations of both isomers under saturating mercury conditions and was found to be 1.27 ± 0.05 at 100 Torr. This result is at variance with the observation by Meinwald and Smith /4/ that the ratio of cis to trans isomer (30% cis, 70% trans) does not vary over 16 hrs of irradiation. Under their experimental conditions, this period of irradiation was more than twice that necessary to entirely convert 100 Torr of 1,4-pentadiene to polymer and other products. There is no obvious explanation for this discrepancy. It is clear however that R_{ss} determined in the present study is in line with that expected for a high energy sensitizer /1(b), 7/. It is also strikingly close to the ratio observed in prolonged sensitizations of 3-methylcyclohexene ($R_{ss} = 1.29$ /10/) where the product piperylene competes efficiently with the substrate for the excited mercury atoms.

The ratio of the initial rates of isomerization (equal to the ratio of the initial quantum yields) is 1.29 ± 0.10 which is almost identical with the stationary state ratio of 1.27. The results can therefore be explained by a simple mechanism involving excitation of both isomers at the same rate and the formation of a single triplet common to both piperylene isomers /1(b)/. Thus at 100 Torr piperylene, there is no evidence for the formation of a complex between a vibrationally excited triplet and a ground state piperylene molecule. Such a complex has been invoked /11/ to explain high cis-trans quantum yields upon irradiation of benzophenone in pure cis-piperylene /11, 12/. The phenomenon may result from a pre-existing alignment of the cis-piperylene molecules around the benzophenone molecule. This type of alignment, due to solvation of the benzophenone, cannot exist in the gas phase.

CONCLUSIONS

The higher quantum yield of the cis-trans isomerization as well as the elution of trans-piperylene first on the g. c. columns ordinarily used, favour the use of the cis-trans isomerization as an actinometer for Hg $6(^3P_1)$ sensitized reactions. If the lamp has a non-negligible output of radiation at $\lambda < 254$ nm, butene-2 actinometry /3/ should be used. Under normal circumstances, piperylene actinometry should be preferable to butene-2 /2, 3/ and propane /13/ actinometry, especially if gas handling facilities are not available.

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The authors gratefully acknowledge financial support from the F. N. R. S.

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