

PHOTOSENSITIZATION OF THE 1,3-PENTADIENES AND THE 1,2-DICHLOROETHYLENES BY BENZALDEHYDE IN THE GAS PHASE*

G. R. DE MARÉ, M-C. FONTAINE, G. HUYBRECHTS** and M. TERMONIA

Service de Chimie Physique I, Faculté de Science, Université Libre de Bruxelles, 50 Av. F.-D. Roosevelt, B-1050 Brussels (Belgium)

(Received July 26, 1972)

SUMMARY

The sum of the quantum yields of the benzaldehyde photosensitized *cis* → *trans* and *trans* → *cis* isomerizations for both the 1,3-pentadienes (over the pressure range studied: 50–400 Torr) and the 1,2-dichloroethylenes (for substrate pressures ≥ 100 Torr) is near unity, indicating that the quantum yield for intersystem crossing in benzaldehyde irradiated at 365.5 nm is also near unity. Energy transfer from triplet benzaldehyde to *cis*-1,2-dichloroethylene, requiring an average of ~10⁴ collisions, proceeds at about 1/40 the rate of energy transfer to *trans*-1,3-pentadiene. Preliminary experiments show that energy transfer to both *cis*- and *trans*-2-butene proceeds at about 1/35 the rate of energy transfer to *trans*-1,3-pentadiene.

INTRODUCTION

Photosensitization of 1,3-cyclohexadiene (CHD) by benzaldehyde (BzH) in the gas phase has been shown to yield CHD dimers in the ratio typical of triplet photosensitization of the diene¹. The rate of dimer formation decreased with decreasing CHD pressure, presumably because either the initially formed dimers require collisional stabilization or the transfer of triplet energy from BzH to CHD is inefficient. We therefore undertook the study of the *cis* ⇌ *trans* photosensitized isomerizations of the 1,3-pentadienes² and the 1,2-dichloroethylenes³ to determine the efficiency of energy transfer from benzaldehyde in the gas phase to known triplet energy acceptors. The present paper reviews the results of these studies^{2,3} and gives some new results on the dichloroethylene photosensitization. Preliminary

* Paper presented at the tenth Informal Conference on Photochemistry, Stillwater, Oklahoma, May 14–18, 1972.

** Present address: Vrije Universiteit Brussel, Laboratorium voor Fysische Scheikunde, Faculteit der Toegepaste Wetenschappen, 105 Ad. Buyllaan, B-1050 Brussels, (Belgium).

data on the competitive photosensitization of the 2-butenes and *trans*-1,3-pentadiene are also given.

The experimental details have already been described^{2,3}.

1,3-PENTADIENE (PD)

Sensitization of *cis*- and *trans*-PD by BzH at 365.5 nm ($I_0 = 3.91 \pm 0.09 \times 10^{-9}$ einstein $\text{cm}^{-2} \text{sec}^{-1}$) leads only to *cis* \rightleftharpoons *trans* isomerization². No extraneous gas chromatographic peaks were observed and no measurable pressure changes were detected. The rates of the *cis* \rightarrow *trans* [$v(c \rightarrow t)$] and *trans* \rightarrow *cis* [$v(t \rightarrow c)$] isomerizations at constant PD pressure of 51 ± 2 Torr are linear functions of BzH pressure (Fig. 1).

The quantum yields $\Phi(c \rightarrow t)$ and $\Phi(t \rightarrow c)$ were determined under initial conditions (less than 3% conversion) at constant BzH pressure of 7.4 ± 0.1 Torr. They are independent of PD pressure and of added N_2 or CO_2 (Fig. 2). The straight lines in Fig. 2 are weighted averages of the experimental points. The results can be explained by a mechanism similar to those proposed for triplet photosensitized isomerizations in solution⁴ and for the crossphase photosensitization of PD⁵:

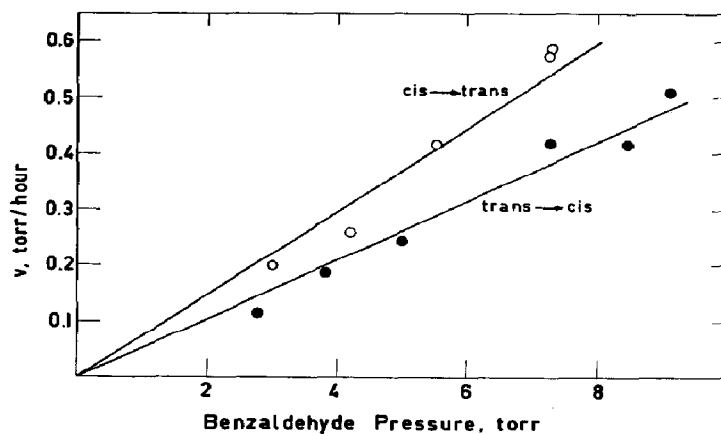
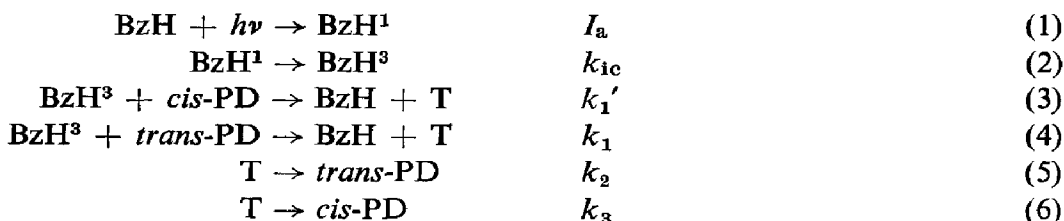


Fig. 1. Rate of the photosensitized isomerization of the 1,3-pentadienes at 51 ± 2 Torr and $60.0 \pm 0.5^\circ \text{C}$ as a function of benzaldehyde pressure. $I_0 = 3.91 \pm 0.09 \times 10^{-9}$ einstein $\text{cm}^{-2} \text{sec}^{-1}$. (From ref. 2.)

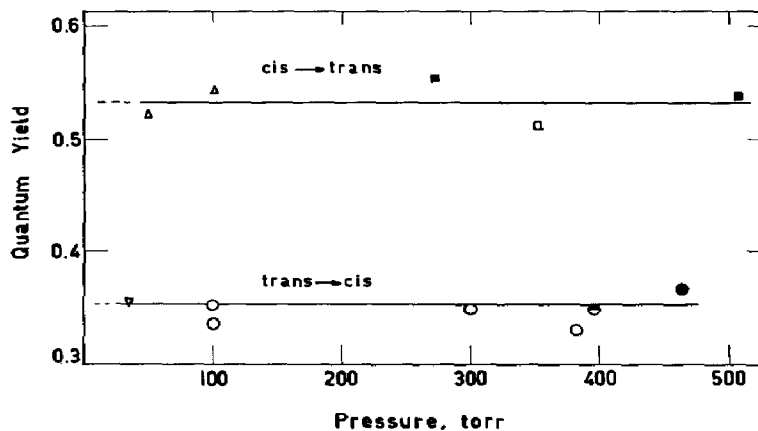


Fig. 2. Quantum yields of the photosensitized isomerization of 1,3-pentadiene at $60.0 \pm 0.5^\circ\text{C}$ as a function of 1,3-pentadiene or 1,3-pentadiene + added gas pressure. Benzaldehyde pressure = 7.4 ± 0.1 Torr. (Δ , ∇), mean of several experimental points; (\blacksquare), *cis*-1,3-pentadiene = 91.6 Torr, CO_2 = 178.8 Torr; (\blacksquare), *cis*-1,3-pentadiene = 95.4 Torr, N_2 = 411.5 Torr; (\odot), *trans*-1,3-pentadiene = 93.7 Torr, CO_2 = 302.6 Torr; (\bullet), *trans*-1,3-pentadiene = 91.2 Torr, N_2 = 372 Torr. $I_0 = 3.91 \pm 0.09 \times 10^{-9}$ einstein $\text{cm}^{-2} \text{sec}^{-1}$. (From ref. 2.)

where BzH^1 and BzH^3 are benzaldehyde in the electronically excited singlet and first triplet state, respectively and T is the normal or "phantom" triplet of PD⁴. According to this mechanism the rates of isomerization are given by:

$$v(c \rightarrow t) = [k_2 / (k_2 + k_3)] I_a = \Phi(c \rightarrow t) I_a \quad (7)$$

and

$$v(t \rightarrow c) = [k_3 / (k_2 + k_3)] I_a = \Phi(t \rightarrow c) I_a \quad (8)$$

and the photostationary state by:

$$\alpha_s = \{(trans\text{-PD}) / (cis\text{-PD})\}_s = k_2 k_1' / k_3 k_1 \quad (9)$$

Under initial conditions, the ratio of the rates, $v(c \rightarrow t) / v(t \rightarrow c)$, and of the quantum yields, $\Phi(c \rightarrow t) / \Phi(t \rightarrow c)$, should be equal to k_2 / k_3 , the natural decay ratio of T. From Figs. 1 and 2 one calculates $k_2 / k_3 = 1.5 \pm 0.2$ at 60°C . Neglecting any effect due to the difference in temperature, this value is in good agreement with $k_2 / k_3 = 1.4$ determined previously at 50°C ⁵. The photostationary state was approached from both sides at 50°C and was found to be 1.38 ± 0.05 , indicating that $k_1 \approx k_1'$, i.e. that BzH transfers its energy at the same rate to both *cis*- and *trans*-PD.

The sum of the quantum yields, $\Phi(\text{tot}) = \Phi(c \rightarrow t) + \Phi(t \rightarrow c)$, is 0.9 ± 0.2 , thus showing that triplet energy transfer from BzH to PD in the gas phase is an efficient process (quantum yield near unity; the number of collisions required for energy transfer to occur cannot be determined from the above data). The data also indicate that $\Phi(S_1 \rightarrow T_1)$ for BzH must be near unity at 365.5 nm.

1,2-DICHLOROETHYLENE (DCE)*

Sensitization of DCE by BzH at 365.5 nm (61°C , $I_0 = 2.73 \pm 0.09 \times 10^{-9}$ einstein $\text{cm}^{-2} \text{sec}^{-1}$) does not give rise to atom "scrambling" to form 1,1-dichloroethylene. The quantum yields of *cis* \rightleftharpoons *trans* isomerization (Fig. 3) increase with increasing DCE pressure up to about 100 Torr and then level off. The sum $\Phi(\text{tot}) = \Phi(c \rightarrow t) + \Phi(t \rightarrow c)$ is 1.02 ± 0.10 for experiments performed at DCE pressures above 100 Torr, indicating that there is only one vibrationally relaxed triplet state (with the CHCl groups at about 90° to each other) which is common to both isomers⁶. This triplet state decays to the ground state isomers in the ratio *cis*/*trans* = $\{\Phi(t \rightarrow c)/\Phi(c \rightarrow t)\} = 1.5$. These results can be compared directly with those of Grabowski and Bylina⁶ who used oxygen at high pressure to induce $T_1 \leftarrow S_0$ absorption by DCE isomers in the liquid phase. They found $\Phi(t \rightarrow c) = 0.61 \pm 0.07$, $\Phi(c \rightarrow t) = 0.45 \pm 0.06$ and $\Phi(\text{tot}) = 1.06 \pm 0.13$ which is in good agreement with the present work [$\Phi(t \rightarrow c) = 0.62 \pm 0.07$, $\Phi(c \rightarrow t) = 0.40 \pm 0.03$ and $\Phi(\text{tot}) = 1.02 \pm 0.10$ for pressures ≥ 100 Torr]. The ratio $\{\Phi(t \rightarrow c)/\Phi(c \rightarrow t)\}$ is 1.3 in their work, well within the combined experimental errors of 1.5. This indicates that, as in the case of PD, the phase (liquid or gas) has little effect on the decay ratio of triplet DCE.

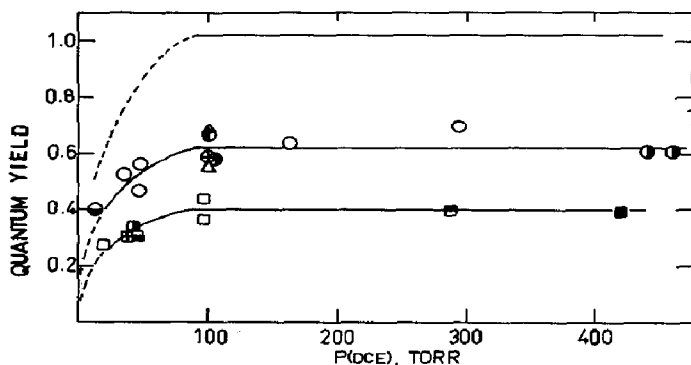


Fig. 3. Quantum yields for the benzaldehyde photosensitized *cis* \rightarrow *trans* ($\square, \boxplus, \blacksquare, \square, \blacksquare, \blacksquare$) and *trans* \rightarrow *cis* ($\circ, \ominus, \odot, \oplus, \oplus, \triangle$) isomerizations of 1,2-dichloroethylene (DCE) as a function of DCE pressure at 61°C . The benzaldehyde pressures used were (in Torr): \triangle , 3.0; \odot , 4.8; \ominus , 5.6; $\odot, \boxplus, \blacksquare$, 6.6; \circ, \square , 7.4; \blacksquare , 8.0; \square , 8.8; \oplus , 9.1; \blacksquare , 10.4. (From ref. 3.)

The fall-off in the isomerization quantum yields as the DCE pressure is reduced below 100 Torr (Fig. 3) reflects either the competition of other steps with the energy transfer process or loss of excited dichloroethylene molecules, for instance by decomposition. The first possibility is believed to be the correct one since no decomposition products were observed and a new series of experiments

* The experiments reported in ref. 3, as well as the determination of I_a/I_0 reported in ref. 2, were inadvertently performed at 61°C rather than at 60°C .

showed that addition of up to 300 Torr of CO₂ at a DCE pressure of 20 Torr does not affect the isomerization quantum yield. Using a simple mechanism for the photosensitization and a value of 10⁴ sec⁻¹ for the sum of the monomolecular deactivation constants for BzH³, one calculates that energy transfer from BzH to DCE occurs on the average only every 10⁴ collisions. Since there is presumably little energy difference between the first triplet states of BzH and DCE (see ref. 3), this low frequency for the energy transfer is not unexpected.

COMPETITIVE EXPERIMENTS

Hammond *et al.*⁷ concluded from their results on photosensitization in solution, that transfer of energy probably occurs on every collision between a triplet and a second molecule if the transfer is exothermic. Since energy transfer from BzH³ (energy 71.9 kcal/mole⁸) to PD is very exothermic, competitive BzH photosensitizations of *cis*-DCE and *trans*-PD (triplet energy = 59 kcal/mole⁹) were performed and the rates of isomerization were determined by gas chromatography. *Trans*-PD was found to be only about 40 times more efficient than *cis*-DCE in accepting energy from BzH³; this relative efficiency is very close to those reported in the literature for PD and DCE isomers deactivating triplet energy donors in solution (see Table 1). Thus even with an exothermicity of ~20 kcal/mole, an average of about 250 collisions is required for the transfer of triplet energy from BzH³ to *trans*-PD. The possibility that PD could accept energy from BzH³ and then transfer it to DCE (thus increasing its relative efficiency) is considered improbable: the total quantum yield of isomerization does not exceed the value expected.

Competitive experiments under the same conditions as those used for the *cis*-DCE and *trans*-PD pair³ were performed using the *cis*- and *trans*-2-butenes and *trans*-PD. These preliminary experiments show that energy transfer from BzH³ to the butenes proceeds at about 1/35 the rate of energy transfer to *trans*-PD.

TABLE I

RELATIVE EFFICIENCY OF 1,3-PENTADIENE (PD) COMPARED TO 1,2-DICHLOROETHYLENE (DCE) AND 2-BUTENE (B) IN QUENCHING TRIPLETS

Donor	E_T (kcal/mole)	Phase	$T(^{\circ}\text{C})$	Quencher isomer		$\left(\frac{k_q(\text{PD})^b}{k_q(\text{a})}\right)$	Ref.
				PD	a		
2-Octanone	c	Liquid	1.5-3.5	d	<i>cis</i> -DCE	~60	10
Butyrophenone	74.6 ¹¹	Solution	d	d	<i>trans</i> -DCE	50	12
Butyrophenone	74.6 ¹¹	Solution	25	d	<i>cis</i> -DCE	~30	13
Benzaldehyde	71.9 ⁸	Gas	61	<i>trans</i>	<i>cis</i> -DCE	~40	3
Benzaldehyde	71.9 ⁸	Gas	60	<i>trans</i>	<i>cis</i> -B	~35	This work
Benzaldehyde	71.9 ⁸	Gas	60	<i>trans</i>	<i>trans</i> -B	~35	This work

^a Molecule in competition with PD for triplet energy.

^b Ratio of the quenching efficiencies.

^c Probably about 75 kcal/mole.

^d Not specified.

ACKNOWLEDGEMENTS

The authors thank Dr. T. Lehman and Dr. J. Olbregts for helpful discussions and one of us (M.T.) wishes to thank the I.R.S.I.A. for a scholarship.

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