PHOTOCHEMICAL ISOMERIZATION OF 1,3-BIS(4-NITROPHENYL)-1-BUTENE

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Photoisomerization of 1,3-bis(4-nitrophenyl)-1-butene was investigated. The quantum-yield value of photoisomerization depends on the nature of the solvent and on the wavelength of the excitation radiation. The photoisomerization velocity in alcohols is oxygen independent. 1,3-Bis(4-nitrophenyl)-1-butene reveals a phosphorescence spectrum with a triplet energy 19 600 cm^{-1} (234·42 kJ mol^{-1}). The quantum yield of phosphorescence reaches values 10^{-3} up to 10^{-2}.

Our preceding papers concerned the preparation of *trans* and *cis* derivatives of 1,3-bis(4-nitrophenyl)-1-butene[1] and its photolysis by polychromatic radiation both in acetonitrile and 2-propanol[2]. This paper presents results obtained when examining the photochemical isomerization of 1,3-bis(4-nitrophenyl)-1-butene in alcohols, n-heptane and acetonitrile.

Photochemical *trans-cis* isomerization of olefins with aromatic substituents can proceed either through an S_1 (*e.g.* with 1,3-diphenylpropene[3]), or a T state (*e.g.* with 1-phenyl-1-propene[4]). The measured phosphorescence spectrum (77 K) of *trans*-1,3-bis(4-nitrophenyl)-1-butene is plotted in Fig. 1. The character of the spectrum did not change in relation to the solvent. Energy of the triplet in ethanol is 19 600 cm^{-1}; in methylcyclohexane a minute increase to 20 000 cm^{-1} was observed. The phosphorescence life-time τ_{ph} in ethanol is 80 ms, in methylcyclohexane 98 ms. The quantum yield of phosphorescence φ_{ph} in 95%-ethanol varied within 10^{-3} to 10^{-2}. The phosphorescence spectrum of the *cis* form differed from that of the *trans* form in the intensity values ($\tau_{ph}^{cis} = 78$ ms) only.

These data entitled us to presume that photoisomerization proceeds preferentialy through the T state. The fact that aromatic nitrocompounds revealed no fluorescence could be likely due to an $S_{n,\pi^*} \rightsquigarrow T_{\pi,\pi^*} \rightsquigarrow T_{n,\pi^*}$ conversion[5]. The triplet energy of our compound is close to E_T of nitrobenzene (21 000 cm^{-1}, ref.[6]), the lowest T level of which is of an $n\pi^*$ nature[5]. Considering this argument we postulate the same presumption, which is also backed by a very low value of the phosphorescence yield. On the other hand, the relatively high life-time of phosphorescence (by 10^{-1} s^{-1}) could be ascribed to a considerable interference effect of the π,π^*-state.

As known[7], nitroderivatives related to benzene achieve high yields of triplets, *e.g.* φ_{ST} for benzene is approximately 0·7, (ref.[7]). Were our presumption correct, the photoisomerization velocity should not be influenced by the presence of oxygen in solution. Value for $k_T \rightsquigarrow S_0$ is reported[7] to be 10^9 s^{-1}. Since the $\varphi_{t\to c}$ value in our case is great, the rate constant (velocity constant) of isomerization shall achieve high $k_{t\to c}$ values, as well ($\geqq 10^9 \text{ s}^{-1}$). The constant of quenching by oxygen equals $k_q \,.\, [O_2]$; *e.g.* for alcohols the value $k_q = k_{dif} \approx 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ (ref.[8]), and at an approximately $10^{-2} \text{ mol l}^{-1}$ concentration of oxygen, the value was reported to be of the 10^8 s^{-1} order (ref.[9]). The presented presumption was also experimental-

TABLE I

Quantum yields of *trans-cis* photoisomerization of 1,3-bis(4-nitrophenyl)-1-butene in various solvents: $\lambda_{exc} = 313$ nm, $I = 8{\cdot}8 \,.\, 10^{16}$ qu. s^{-1}

Solvent	Viscosity η, cP	$\varphi_{t\to c}$
Methanol	0·547	0·70
95% Ethanol	1·092	0·65
2-Propanol	2·06	0·56
Tert-butanol	3·30	0·35
Acetonitrile	0·34	0·31
n-Heptane	0·39	0·42

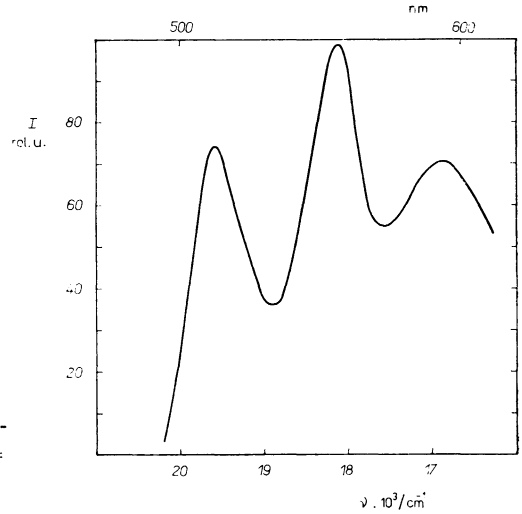


FIG. 1

Phosphorescence spectrum of 1,3-bis(4-nitrophenyl)-1-butene in ethanol (77 K), λ_{exc} = = 313 nm ly verified. The photoisomerization rate ($\lambda_{exc} = 313$ nm) in oxygen saturated 2-propanol solution virtually equaled that observed in the same solution, but argon saturated.

The quantum yields of *trans-cis* isomerization in various solvents are presented in Table I. Values given in Table II were employed for calculations. The relationship between the magnitude of quantum yield of isomerization and wavelength of the excitation radiation is summarized in Table III. As seen, the quantum yield of photoisomerization reaches its maximum at 313 nm. The drop of quantum yield value at 253·7 nm might be due to reabsorption by the inactive chromophore *B*. Lowering

TABLE II

Spectral data of 1,3-bis(4-nitrophenyl)-1-butene in various solvents

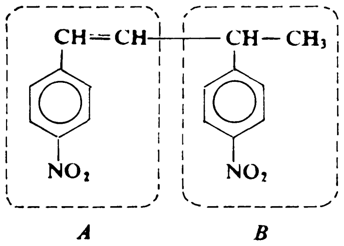
Solvent	$\lambda\varepsilon$, 10^{-4} l mol^{-1} cm^{-1}	
	trans	*cis*
Methanol	313 (1·95) 320 (1·83)	295 (1·81) 320 (1·37)
95% Ethanol	313 (1·95) 320 (1·83)	295 (1·81) 320 (1·37)
2-Propanol	310 (2·04) 320 (1·81)	295 (1·79) 320 (1·27)
Tert-butanol	307 (2·26) 320 (1·99)	290 (2·09) 320 (1·31)
n-Heptane	295 (2·26) 310 (1·91)	280 (1·97) 310 (1·07)
Acetonitrile	310 (2·12) 320 (2·05)	295 (1·73) 320 (1·22)

TABLE III

Relationship of $\varphi_{t \to c}$ on λ_{exc} in 95% ethanol and 2-propanol, $I = 4 \sim 8 \cdot 10^{16}$ qu s^{-1}

Solvent	λ_{exc}, nm		
	253·7	313	334
95% Ethanol	0·34	0·65	0·45
2-Propanol	0·31	0·56	0·37

of the $\varphi_{t \to c}$ value at 334 nm can be associated with the existence of an energy barrier at transition from state S_1 to the reactive state T. Effect of the solvent viscosity can be ascribed to an enhancement of molecular volume during the isomerization, what has already been observed[10]. On the other hand, it could not be excluded that even in the isomerization course photoreactions are taking place; these are known with aromatic nitro compounds. *E.g.*, abstraction of hydrogen from the solvent can be considered when reacting alcohols[7,11].



SCHEME 1

EXPERIMENTAL

1,3-Bis(4-nitrophenyl)-1-butene was prepared and chromatographically purified according to[1]. Apparatus for photochemical measurements was described in[12]. Ferrioxalate actinometer[8] was employed for determination of the quantum yield. Relative error of $\varphi_{t \to c}$ was found to be ±0·15%. Apparatus and method described in[13] were used for luminiscence measurements. The absorption spectra were recorded with an SF-8 (USSR) spectrophotometer at a 1 cm-cell length.

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