PHOTODECOMPOSITION OF TETRAZENES

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Photodecomposition of tetraaryltetrazenes, 1,4-diaryl-1,4-diethyl-2-tetrazenes and 1,4-diphenyl-1,4-dialkyl-2-tetrazenes in the UV region was studied. The activation energy of the decomposition of the tetrazenes is lower than the energy of light absorbed. The results allowed a conclusion about a high quantum yield and a fast course of the decomposition reaction.

When investigating reactive radicals, some authors also studied radicals having an unpaired electron on the nitrogen atom. Investigations were made of thermal decompositions of tetrazenes and of the effects of the medium on decomposition[1–3]. The effects of light on the N—N=N—N system were observed in the case of tetramethyl-2-tetrazene[4,5] and some 1,4-dialkyl-1,4-diphenyl-2-tetrazenes[6]. Similarly to the decomposition reactions of analogous azo compounds, nitrogen and the corresponding radicals capable of secondary reactions are the primary reaction products.

This paper has been devoted to a study of the effects of light radiation upon aryl and alkyl substituted 2-tetrazenes of various structures. Tetraaryltetrazenes, 1,4-diaryl-1,4-diethyl-2-tetrazenes and 1,4-diphenyl-1,4-dialkyl-2-tetrazenes were synthesized by a procedure commonly used[7]: The corresponding secondary amines were nitrosated, reduced to hydrazines, and oxidized to tetrazenes (Table I).

The absorption maxima of the characteristic chromophore vary within the region 300—375 nm. To check the possibility of investigation of the decomposition by means of spectroscopy, solutions of an appropriate concentration were subjected to a radiation lasting 50 hours from a low-pressure mercury discharge tube. The absorption spectra of irradiated samples are represented in an uncorrected form in Fig. 1. A complete disappearance of the characteristic light absorption azochromophore has been observed only in the case of tetraphenyl-2-tetrazene and 1,4-diphenyl-1,4-diethyl-2-tetrazene. 1,4-Dimesityl-1,4-diethyl-2-tetrazene and 1,4-diphenyl-1,4-ditert-butyl-2-tetrazene do not enable an exact quantitative investigation of the decomposition course to be made, owing to a small difference between the wavelengths of the absorption maxima of tetrazenes and the decomposition products. Similarly, tetrazenes substituted with 2-naphthyl, and also 1,4-diphenyl-1,4-dibenzyl-2-tetrazene exhibit residue absorptions within the region 350—360 nm, thus reducing the exactitude of the quantitative determination of the course of photodecomposition.

The time course of photodecomposition was followed in monochromatic radiation 360 nm (spectral band width 11 nm). A high-pressure mercury discharge tube HQE Osram (40 W) and the grating monochromator of a Spekol-Zeiss apparatus were used in the measurements. The intensity of light leading to decomposition was determined by calibration with a ferrioxalate actinometer[8]; its value was $1·6 . 10^{16}$ q l^{-1} s^{-1}. A decrease of the characteristic absorption at 360 nm

was measured by means of a photomultiplier. A constant amount of solutions was used, and the contents of the cell were stirred. The course of the decomposition reactions is shown in Fig. 2.

TABLE I

Characteristics of 1,1,4,4-Tetrasubstituted 2-Tetrazenes

2-Tetrazene	M.P., °C	λ_{max}, nm		$a \cdot 10^{-4}$, mol^{-1} cm^{-1}	
		A[a]	B[b]	A[a]	B[b]
Tetraphenyl	123—124[c]	357	360	2·05	2·06
Tetra-2-naphthyl-	145—147[c]	352	—	4·03	—
1,4-Diphenyl-1,4-diethyl-	113—114	355	353	3·32	3·17
1,4-Diphenyl-1,4-dibenzyl-	145·5[c]	352	347	3·74	3·96
1,4-Diphenyl-1,4-di-t-butyl-	115·5[c]	312	312	0·72	0·63
1,4-Dimesityl-1,4-diethyl-	101—101·5	305	305	1·78	1·76
1,4-Di(2-naphthyl)-1,4-diethyl-	160[c]	352	353	4·46	5·14

[a],[b]Solution: [a]in tetrahydrofuran, [b]in cyclohexane. [c]Under decomposition.
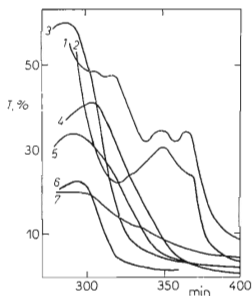

FIG. 1

Absorption Spectra of the Decomposition Products of 2-Tetrazenes

1 Tetra(2-naphthyl)-, 2 1,4-(2-naphthyl)-1,4-diethyl-, 3 tetraphenyl-, 4 1,4-diphenyl-1,4-di-tert-butyl, 5 1,4-dimesityl-1,4-diethyl-, 6 1,4-diphenyl-1,4-diethyl-, 7 1,4-dibenzyl-1,4-diphenyl-.
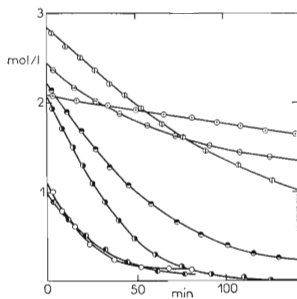

FIG. 2

Time Course of the Light Decomposition of 2-Tetrazenes in Tetrahydrofuran

⊙ Tetra(2-naphthyl)-, ○ 1,4-di(2-naphthyl)-1,4-diethyl-(in cyclohexane), ◑ 1,4-di-(2-naphthyl)-1,4-diethyl-, ◐ tetraphenyl-(in cyclohexane), ⊖ tetraphenyl-, ◗ 1,4-diphenyl-1,4-diethyl-, ◓ 1,4-dibenzyl-1,4-diethyl-.

The values were used to calculate the quantum yields of decomposition (Table II). An experiment was carried out under the same experimental conditions in order to investigate the photodecomposition of tetrazenes in chloroform solution. In this case, the reaction mechanism is not a simple one, and the UV spectra do not allow an exact analysis of the process. Only the initial course of the reaction was studied; it occurred at a rate which was approximately twice as high as that in cyclohexane or tetrahydrofuran and the quantum yield of the process was higher than unity (1,2—1,4).

TABLE II

Quantum Yields of Decomposition (φ) of 1,1,4,4-Tetrasubstituted 2-Tetrazenes in Tetrahydrofuran

2-Tetrazene	φ
Tetraphenyl-	0·10; 0·14[a]
1,4-Di(2-naphthyl)-1,4-diethyl-	0·24; 0·24[a]
1,4-Dibenzyl-1,4-diphenyl-	0·15
1,4-Diphenyl-1,4-diethyl-	0·32
Tetra(2-naphthyl)-	0·02

[a] In cyclohexane.

It follows from the values obtained that there exists an effective photodecomposition of the tetrazenes under study. If compared with tetraaryltetrazenes, the aromatic aliphatic tetrazenes exhibit a higher quantum yield and a faster course of the decomposition reaction. The reaction rate is governed by the laws of a strong homogeneous light absorption, and at each moment it is described by a relationship depending on the amount of the light energy absorbed. The energy absorbed in the decomposition of the tetrazenes varies within the limits of 80—95 kcal mol^{-1}. This energy is more than twofold the activation energy of the thermal process. If we compare this finding with the state of similar azo compounds, we can see that in this case, too, the absorbed energy is approximately twice as high as the activation energy, but the rates and quantum yields of the decomposition of the azo compounds are lower.

An attempt at using the radicals formed by photodecomposition of tetrazenes in the initiation of the radical polymerization of methyl methacrylate did not lead to satisfactory results. No measurable rate of photopolymerization could be established, with the exception of tetrazenes substituted with 2-naphthyl. At a concentration of photoinitiator, 1,4-di(2-naphthyl)-1,4-diethyl-2-tetrazene, $2 . 10^{-4}$ mol l^{-1}, the polymerization rate was $5 . 10^{-5}$ mol l^{-1} s^{-1}. The quantum yield of the polymerization reaction is of an order of 10^2. A comparable polymerization rate was established for the thermal polymerizations of methyl methacrylate initiated with tetrazenes at temperatures 60—75°C and concentrations of initiator of $2 . 10^{-2}$—$4 . 10^{-2}$ mol l^{-1}. The initiation activity is also low, being about 0·1 for 1,4-dimesityl-1,4-diethyl-tetrazene.

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