# **PHOTOCHEMISTRY** =

# Sensitized Photolysis of Stearic Acid Azide

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**Abstract**—In an IR-spectroscopic study of the sensitized photolysis of stearic acid azide in a solution of benzene, it was found that the introduction of Michler's ketone into the system decreased the efficiency of isocyanate formation by a factor of about 10. It was hypothesized that the azide photolysis in the presence of Michler's ketone can be explained by the formation of a complex of the acyl azide with the ketone in a triplet excited state, a displacement of electron density from the acyl azide group, and its degradation with the formation of a triplet acylnitrene, which is incapable of rearranging into isocyanate.

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In the study of the photorearrangement of azides into isocyanates (Curtius rearrangement), three possible reaction paths should be considered. First, this is a reaction path without the participation of nitrene; in this case, the rearrangement occurs simultaneously with the degradation of the azide group without the intermediate formation of nitrene. In the course of a radical mechanism, an azide decomposes with the formation of acylnitrene; then, the nitrene is rearranged into isocyanate from a triplet (second reaction path) or singlet state (third reaction path). There is evidence for the occurrence of each of these mechanisms. Acyl azides are rearranged into isocyanates both upon photolysis and upon thermolysis [1-3]. The yield of isocyanates upon thermolysis is nearly quantitative [4], whereas it is most frequently no higher than 40% upon photolysis regardless of the nature of the solvent [5]. The absence of a solvent effect on the yield of isocyanates can be explained by the reaction path without the participation of nitrene [6-8]. However, acylnitrenes and their reaction products were detected along with isocyanates upon the photolysis of acyl azides [9]; this fact is evidence in favor of the radical paths of this reaction (Scheme 1).



Scheme 1. Reaction paths in the photolysis of acylazides

Sensitizer	$E_t$ , kJ/mol [14, 15]	$k_{\rm NCO}/k_{\rm azide}$	
		FS-7	UFS-1
Anthracene	178	0.845	_
Benzanthrone	193	0.939	0.900
Benzyl	222	1.025	_
Naphthalene	253	0.746	_
Anthraquinone	261	_	0.703
Biphenyl	274	0.958	_
Michler's ketone	275	0.134	0.083
DMPA	278 [16]	_	0.775
Benzophenone	287	1.027	0.692
Acetophenone	310	0.973	_
Acetone	335	0.788	0.689
_	353	0.849	0.673

Ratio of the rate constant of isocyanate formation to the rate constant of azide degradation

The rearrangement of acyl azides into isocyanates is a convenient method for the preparation of carbamic acids, urethanes, ureas, and primary amines. The photochemical method of the synthesis of isocyanates can make it possible to use acyl azides as photochemical modifiers for the surfaces of polymers, including biopolymers. However, the photochemical method of the synthesis of isocyanates is ineffective because of a low yield of this reaction (as compared with that of thermolysis) [10].

On the other hand, the control of the photochemical generation of acylnitrenes, which are capable of inserting into ordinary and multiple bonds, can also allow one to use them as photoaffinity labels. Therefore, the study of the mechanism of photolysis of acyl azides for controlling the conditions of formation of both isocyanates and acylnitrenes is of considerable current interest.

Sensitized photolysis will make it possible to convert acyl azide into a triplet excited state and to obtain triplet nitrene or isocyanate escaping a singlet excited state and, thus, to exclude or confirm a singlet reaction path of the formation of isocyanate, to define the reaction scheme of photolysis and, possibly, to choose a method for controlling this reaction.

The aim of this work was to study the effect of energy transfer from the triplet states of sensitizers on the yields of acyl azide photolysis products.

The test material was stearic acid azide with an absorption maximum at 225 nm, which is transparent

in the absorption ranges of the test sensitizers. The sensitizers were 11 substances with triplet level energies from 176 to 356 kJ/mol (see the table).

#### **EXPERIMENTAL**

To study the sensitized photolysis of azide, a benzene solution of stearic acid azide (concentration of  $5 \times 10^{-2}$  mol/l) with a sensitizer (azide : sensitizer molar ratios of 1 : 1 and 1 : 2) was irradiated with light from a DRK-120 mercury quartz lamp through UFS-1 or FS-7 light filters in an IR-spectroscopic cell of KBr with an optical path length of 0.539 mm at a distance of 28 cm. The photolysis and measurement of spectra were conducted at room temperature.

The IR spectra of solutions were measured on a Shimadzu IRPrestige-21 spectrophotometer ( $4000-400 \text{ cm}^{-1}$ ).

Stearic acid azide was synthesized by the diazotization of stearic acid hydrazide.

Synthesis of stearic acid azide. Dioxane (80 ml) was added to 3 g of stearic acid hydrazide, and the mixture was heated in a water bath until the complete dissolution of the sediment. Then, 25 ml of HCl (conc) was added to the solution. The solution with the precipitated hydrazide hydrochloride was cooled in an ice bath to  $0-5^{\circ}$ C, and a solution of 5 g of NaNO<sub>2</sub> in 20 ml of water was gradually added with stirring. After the addition of the solution, the mixture was stirred for 20 min. The precipitate was filtered off, reprecipitated from dioxane with water, and dried in a vacuum.

## **RESULTS AND DISCUSSION**

Changes in the concentrations of the azide and its photolysis products were monitored by measuring the absorption of analytical absorption bands in the IR spectra of the solutions before and in the course of irradiation. The absorption band of the asymmetric stretching vibration of the azide group ( $v_{as}$  N<sub>3</sub>) at 2134.7 cm<sup>-1</sup> was chosen as the analytical absorption band of the azide. An absorption band due to the asymmetric stretching vibration of the isocyanate group ( $v_{as}$  NCO) at 2257.2 cm<sup>-1</sup> was chosen for heptadecyl isocyanate, whereas the stretching vibration of the amide carbonyl group (v CO) at 1646.25 cm<sup>-1</sup> was used for amides.

The photolysis of azide solutions both in the presence and in the absence of sensitizers decreased the absorbance of absorption bands due to the asymmetric stretching vibrations of the azide group and the stretching vibrations of the carbonyl group of acyl azide (1720 cm<sup>-1</sup>). Simultaneously, absorption bands due to the asymmetric stretching vibrations of the isocyanate group and several weak absorption bands in the range of 1650-1615 cm<sup>-1</sup>, which were attributed to the carbonyl groups of the resulting amides, appeared. That is, under the described conditions, the azide decomposed with the formation of isocyanate and primary or second amides as in the direct photolysis of the azide.

We did not detect qualitative changes in the IR spectra of irradiated solutions upon changing a sensitizer. Only the rates of formation and the ratios between of reaction products changed.

Changes in the absorbance of analytical absorption bands in the azide photolysis were measured to conversions of about 10%. The kinetics of the azide photolysis and the formation of isocyanate and amides were described by a straight line with a correlation coefficient of about 0.98.

The efficiency of the formation of isocyanate and amides with different sensitizers was judged from the ratios of the rate constants of formation of the photolysis products to the rate constant of azide decomposition.

The table summarizes the experimental data. The figure shows the dependence of the ratio between rate constants on the triplet state energy of the sensitizers.

In the photolysis of solutions through a UFS-1 light filter, which passes light in the range of 250–400 nm, the ratio of the rate constant of isocyanate formation to the rate constant of azide degradation was  $0.74 \pm 0.10$  for the majority of the test sensitizers. However, in the photolysis in the presence of Michler's ketone ( $E_T = 275$  kJ/mol), the ratio between the constants was  $0.08 \pm 0.10$ , that is, lower by an order of magnitude.

Upon the replacement of the light filter by FS-7, which is transparent in the range of 290–450 nm, the average ratio of the rate constants of isocyanate formation to the rate constants of azide degradation was  $0.91 \pm 0.10$  for all of the sensitizers other than Michler's ketone, for which this ratio was  $0.13 \pm 0.10$ .

After excluding Michler's ketone from the consideration, the average rate constants of azide degradation were  $1.8 \times 10^{-3}$  and  $8.7 \times 10^{-4}$  for UFS-1 and FS-7 light filters, respectively, and they did not depend on the presence of a sensitizer in solution. That is, with the use of the UFS-1 light filter, the azide decomposed more rapidly than with FS-7 by a factor of 2; this fact can be explained by a shift of the transmission cutoff of light filters from 250 to 290 nm and, as a result, a decrease in the portion of radiation directly absorbed by the azide.

Thus, in the cases under consideration, isocyanate was formed without the participation of sensitizers only in the direct photolysis of the azide, which cannot be completely excluded. The sensitizers introduced into the system did not participate in energy transfer, and they cannot be called, strictly speaking, sensitizers in this case.

The sensitizers used are, for the most part, ketones or other carbonyl compounds. Therefore, the region of the absorption of the carbonyl groups of amides



Dependence of the ratios of the isocyanate formation to the .azide degradation rate constants upon the triplet state energies of sensitizers during irradiation through (I) FS-7 and (2) UFS-1 light filters.

overlaps with the absorption of the carbonyl groups of the sensitizers; this fact made the analysis of IR-spectroscopic data difficult to perform.

Among a number of absorption bands in the region of  $1650-1615 \text{ cm}^{-1}$ , we recognized a band at  $1646.25 \text{ cm}^{-1}$ , which appeared in all of the test systems, and attributed it to the stretching vibration of the carbonyl group of amide.

The found ratios of the rate constants of amide formation to the rate constants of azide photolysis in the photolysis with both UFS-1 and FS-7 light filters differed only slightly from each other for all of the test sensitizers. The ratio between the rate constants increased by a factor of about 2 for sensitizers with an energy difference between the ground and triplet excited states in the range of 222–302 kJ/mol. However, with consideration for a small change in the absorbance of the chosen band, the above data did not allow us to reliably state that the sensitizers transfer energy to the azide molecule and lead to an increase in the efficiency of amide formation.

It is unlikely that the decrease in the efficiency of isocyanate formation in the azide photolysis sensitized by Michler's ketone can be explained only by energy transfer from the ketone in a triplet excited state to the azide and by a change from a singlet to a triplet reaction path. In this case, sensitizers with close energies between the ground and triplet excited states should behave analogously; however, this was not observed experimentally.

It is believed that Michler's ketone, which transferred to a triplet excited state upon the absorption of a light photon, removed hydrogen from the aliphatic tail of an azide or isocyanate; thus, it became reduced to 4,4'-(dimethylamino)diphenyl-substituted methanol or substituted pinacol, respectively [11]. The resulting alcohols interacted with isocyanate to decrease its concentration in the solution. In this case, it is impossible to understand why an analogous behavior was not observed with other ketones capable of forming an alcohol upon photoreduction, for example, benzophenone.



Scheme 2. Hypothetical mechanism of the photolysis of stearic acid azide sensitized by Michler's ketone.

It is likely that the azide photolysis in the presence Michler's ketone [12, 13] can be explained by its ability to coordinate stearic acid azide with the formation of a triplet exciplex (Scheme 2).

Upon the absorption of a light photon, the ketone transferred to a singlet and then to a triplet excited state. In the course of the relaxation of the triplet state, electron density was displaced from the N, N-dimeth-ylamine and phenylene groups to the carbonyl group with the formation of a quinone-like structure. This structure served as an acceptor in the formation of a complex with the azide to cause the displacement of electron density from the acyl azide group of stearic acid azide and its degradation to triplet acylnitrene. It is likely that the resulting triplet acylnitrene cannot be rearranged into isocyanate, and it reacted with the formation of primary and secondary amides.

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