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REVERSIBLE PHOTOISOMERIZATION OF BENZYL THIOCYANATE AND ISOTHIOCYANATE

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Aryl and alkyl thiocyanates are known to isomerize to isothiocyanates through an ionization path [1]. For the benzyl derivative the reaction does not take place in mild conditions (unless electrophilic catalysts [1b] or an ionic thiocyanate are present: in this last case a direct nucleophilic displacement by the nitrogen end of SCN^- ion is operative [2]); on the other hand under drastic temperature conditions the isomerization is accompanied by extensive decomposition.

It was interesting to examine the possibility of obtaining the isomerization by a photochemical way.

Benzyl thiocyanate was then irradiated with a low pressure mercury arc, using the 2537 Å line, in n-hexane solutions $\sim 10^{-4}$ M at room temperature; the changes in the system were followed with an Optica CF4 grating spectrophotometer.

By irradiation in the presence of oxygen the initial spectrum of thiocyanate (λ_{max} = 260 mμ, ε_{max} = 470) evolves regularly towards a spectrum showing a principal intense absorption peak at 241 mμ; this spectrum, by prolonged irradiation, moves again indicating successive photoreactions and/or degradation.

The same spectral behaviour is obtained by irradiation of benzyl isothiocyanate, benzyl thiol, benzyl disulfide and of cyclic trithiobenzaldehyde.

UV and IR analysis of the main photoproduct have led to its identification as benzaldehyde (stretching $\nu_{C=O}$ = 1715 cm^{-1}, in n-hexane; λ_{max} = 241 mμ).

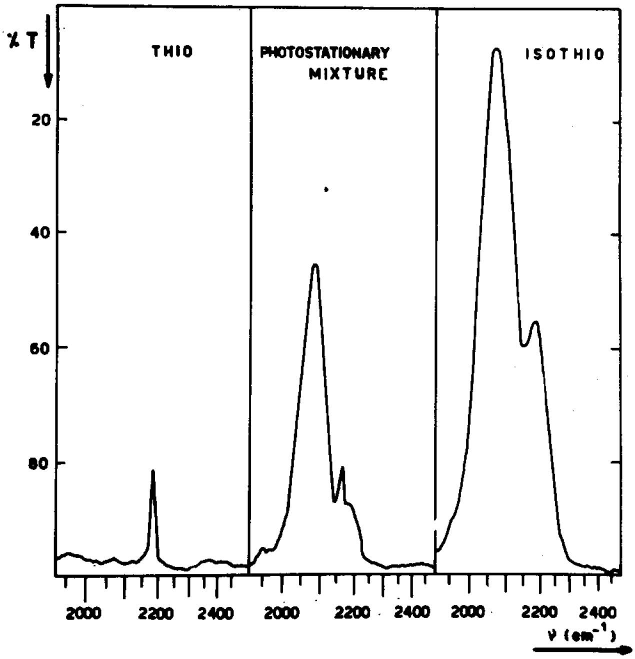
It is to be noted that in the first stages of irradiation the spectrum of the isothio-derivative (λ_{max} = 251.5 mμ, ε_{max} = 1520) moves towards that of thiocyanate before giving the photo-oxidation product.

We then studied the photochemical behaviour of the thio-isothio system in the absence of oxygen, being able to show a reversible photoconversion of both isomeric compounds.

$$C_6H_5CH_2\text{-}S\text{-}C\equiv N \xleftrightarrow{h\nu} C_6H_5CH_2\text{-}N{=}C{=}S$$

Due to the high extinction coefficients of benzaldehyde (ε_{max} = 13500) and the consequent strong disturbance of oxygen traces in the UV analysis, the photoequilibrium mixture has been analyzed by IR spectrophotometry using a Perkin Elmer mod. 21 instrument with NaCl optics. In these experiments the concentration was about 10^{-2} M in n-hexane. The irradiation was accomplished in a quartz 1 mm path cell and the solution transferred to a 1 mm IR cell for the analysis. As to the determination of the photoequilibrium composition, an approximate estimation was made in preliminary experiments, starting from the pure isomers. A series of solutions were then prepared, with a thio-isothio ratio varying near the presumed equilibrium from either sides, and shortly irradiated until no further changes in spectrum occurred. In this way it was possible, observing the entity and the direction of changes, to estimate the precise photostationary ratio neglecting the photodecomposition and photochemical side reactions [3, 4].

The figure shows the spectrum of the photoequilibrium mixture (total concentration $\sim 2\cdot 10^{-2}$ M) compared to the spectra of the pure isomers at the same concentration in the region of the pseudo-asymmetrical stretching absorption ($\nu_{S-C\equiv N} = 2178$ cm^{-1}, $\nu_{N=C=S} = 2088$ cm^{-1}).



The ratio is sensitive to variations in experimental conditions (mainly concentration); anyway in the cited conditions a stationary mixture of 70% thio - 30% isothio has been found.

The photoreaction is probably proceeding by a radical-chain mechanism with benzyl and resonance stabilized NCS radicals as intermediates.

Bacon and Irwin have studied the photo-initiated thiocyanation of arylalkyl-hydrocarbons by thiocyanogen [5]: the homolytic thiocyanogen radical (N≡C-S• <---> •N=C=S) gives the thiocyanate by substitution at the α-position of hydrocarbon. Similar reaction may occur in our case where both benzyl and NCS radicals can react with the initial thio or/and isothiocyanate leading to isomerization.

To demonstrate the homolytic photolysis of the substrate, some experiments have been accomplished in E.P.A. (ether-isopentane--ethanol 5:5:2) solutions at liquid nitrogen temperature, using a procedure elsewhere described [6]. Profiting by the sensitivity of the luminescence technique in detecting trapped free radicals produced by low temperature photolysis [7], we succeeded in detecting the fluorescence emission of benzyl radical in the 460-530 mμ region, by starting both from benzyl thio and benzyl isothiocyanate. In this way we have direct evidence of the existence of the intermediate arylalkyl radical. The increase of the photoconversion rate with concentration indicates that this radical reacts with a second molecule of thiocyanate as supposed.

Similar results have been obtained in preliminary experiments on benzhydryl derivatives, although in this case care must be taken to avoid concurrent thermal isomerization.

The photoequilibrium is here much more displaced towards isothiocyanate and photooxidation, which accompanies extensively the isomerization when oxygen is not eliminated, leads to benzophenone.

More detailed experiments are in progress on benzyl and other arylalkyl thio and isothiocyanates both on the conversion kinetics and on the photochemical behaviour at 77°K in order to obtain kinetic and mechanistic informations on the structural effects on quantum yields and photoequilibria.

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