

## PHOTOLYSIS STUDIES OF *p*-ISOTHIOCYANATOBENZALDEHYDE IN SOLUTION

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### Summary

The reactivity of *p*-isothiocyanatobenzaldehyde in a neutral solvent (*n*-heptane) as well as in methanol, ethanol and isopropanol was studied under conditions of excitation by a polychromatic beam from a high pressure mercury lamp. Photooxidation of *p*-isothiocyanatobenzaldehyde in these solvents occurs in the form of consecutive first order reactions. Basic data for the formal reaction kinetics are presented.

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### 1. Introduction

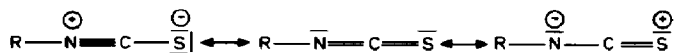
During the entire existence of photochemistry as a science, extensive studies of the photooxidation of benzaldehyde have been made [1], the first reports appearing as far back as the 1890s. Less attention, however, has been devoted to its derivatives. With respect to the utility potential of *p*-isothiocyanatobenzaldehyde (*p*-ITKB) in chemical synthesis, its reactivity with alcohols (methanol, ethanol and isopropanol) as well as its photolysis in a neutral non-polar solvent (*n*-heptane) were studied in this research. Recently, there has been increasing interest in the photochemical properties of this type of compound, particularly with regard to the possibilities offered in complex system syntheses, with subsequent investigation of their impact upon live biological systems [2].

### 2. Theoretical background

Isothiocyanates are heterocumulenes of the type  $X=C=Y$  containing carbon atoms as part of the accumulated system [3]. The chemical reactivity of heterocumulenes varies very widely between extremely reactive compounds and almost inert compounds. Some heterocumulenes can be prepared in reaction mixtures only, while others are stable at room temperature. Thus heterocumulenes have a broad reactivity spectrum, and their

functional group is always polar and ready to react with electrophilic and nucleophilic reagents. However, they often undergo reactions of the cycloaddition type.

When investigating the reactivity characteristics of heterocumulenes, their electronic structure must be taken into consideration. Thus, the resonance structures shown in Scheme 1 are possible for isothiocyanates.

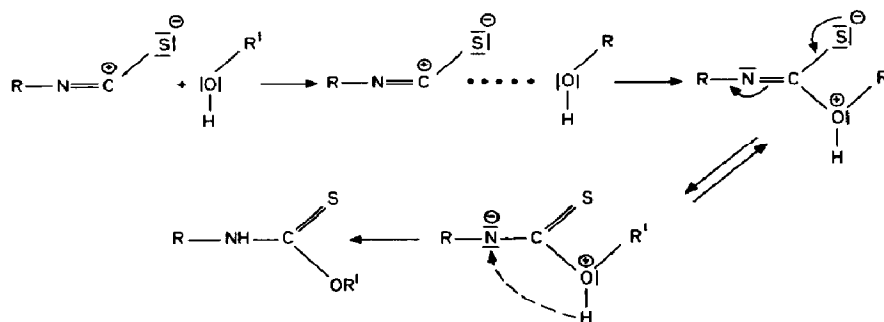


Scheme 1.

With changes in the R substituent and thus the polarity, the statistical participation of these structures may also change, hence changing the reactivity of the system.

Based on experimental data we can conclude that (1) electron-acceptor substituents decrease the reactivity of heterocumulenes and electron-donor substituents increase it and (2) steric effects are frequently found in the course of cycloaddition reactions.

The reaction scheme shown in Scheme 2 between isothiocyanates and alcohols might be expected.



Scheme 2.

Although this reaction proceeds rather slowly with alcohols [4], it can be accelerated by increasing the nucleophilic character of the oxygen by converting the alcohol to an alcoholate which, with an isothiocyanate, gives a monothiourethane. In our case, with respect to the experimental conditions selected, the isothiocyanate group can be presumed to be inactive [5].

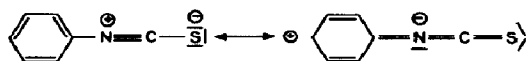
Several workers have studied the IR spectra of isothiocyanates, particularly the wide and complex absorption band between  $2000$  and  $2100\text{ cm}^{-1}$  which is characteristic of these compounds and can be explained as being a result of asymmetric valency vibrations of the  $-\text{NCS}$  group. Since vibrational interactions take place, this band is very wide and somewhat displaced towards higher wavelengths compared with the vibrations of the  $\text{C}=\text{S}$  and  $\text{C}=\text{N}$  bonds. Ham and Willis [6] have determined three basic bands which are characteristic of all aromatic isothiocyanates:

(1) a strong and complex absorption band at  $2100\text{ cm}^{-1}$  which is present in both the IR and Raman spectra and is attributable to asymmetric vibrations of the NCS group;

(2) a strong Raman but very weak absorption IR band at  $1243\text{ cm}^{-1}$ ;

(3) a strong IR band at  $927\text{ cm}^{-1}$  which is practically non-existent in the Raman spectra and is attributable to vibrations of the NCS group.

The UV spectrum of phenylisothiocyanate shows two characteristic absorption maxima:  $\lambda = 277\text{ nm}$ ,  $\log \epsilon = 4.04$ ;  $\lambda = 218\text{ nm}$ ,  $\log \epsilon = 4.25$ . Both can be attributed to  $\pi-\pi^*$  transitions, the higher wavelength band being due to electron charge transfer effects (see Scheme 3).



Scheme 3.

The intensity and position of these UV absorption spectral bands are little affected by solvents.

Previous photochemical investigations of isothiocyanates include the photoisomerization of thiocyanates to isothiocyanates and the process of atomic sulphur elimination [5].

From a comparison of the reactivity of aldehydic and isothiocyanate groups it can be expected that the  $-\text{OH}$  group in alcohols will react preferentially with the excited  $-\text{CHO}$  group.

### 3. Experimental

*p*-ITKB was prepared by the following method. 14 g (0.12 mol) of *p*-aminobenzaldehyde was dissolved in 1 l of 10% hydrochloric acid in a 2 l single-necked flask. 15 g (0.12 mol) of thiophosgene was added to the solution in a time span of 2 h at room temperature. The total mixing time was 10 h. The *p*-ITKB precipitated was then filtered, desiccated and extracted using light naphtha (boiling point range,  $80 - 100\text{ }^\circ\text{C}$ ). After all the extracts had been collected, they were condensed in a rotary vacuum evaporator and the raw *p*-ITKB was subsequently purified by crystallization from petroleum ether. The resulting yellow crystalline plates had a melting point of  $71\text{ }^\circ\text{C}$ .

The solvents used were methanol pro UV (Lachema, Brno), ethanol pro UV (Lachema, Brno), isopropanol pro UV (Lachema, Brno), *n*-heptane pro UV (Lachema, Brno), tetrahydrofuran (Germed, VEB Jenapharm, G.D.R.) refluxed with KOH and distilled in the absence of direct light (the fraction taken had a boiling point of  $64.5 - 66\text{ }^\circ\text{C}$ ), petroleum ether p.a. (Lachema, Brno) and KOH p.a. (Lachema, Brno).

The solutions were subjected to UV irradiation in quartz measuring cells of internal diameter 1 cm and approximately 10 ml in volume; polymeric matrices in adapted metallic holders were used. A high pressure mercury lamp (HBO-500, Narwa, BGW Berlin, G.D.R.) behind a quartz condensing lens was

used as the source of UV radiation. The lamp was connected to a TPC 63 source. A mixing bath with a stirrer was used to maintain a constant temperature in the cell holder.

UV absorption spectra of the solutions were measured using a Specord UV VIS recording spectrophotometer (Zeiss, Jena, G.D.R.) and quartz cells of diameter 0.992 cm and approximately 2 ml in volume.

IR spectra were measured using a Specord 71 IR recording spectrophotometer (Zeiss, Jena, G.D.R.) and IR spectrometric cells of the KRS-5 type; the sample diameter (fluid thickness between internal walls) was 0.272 mm.

Mass spectra of the samples studied were measured using an MS-902-S mass spectrometer (AEI, Manchester) under the following conditions: emission, 100  $\mu$ A; electron energy, 70 eV; temperature of the ion chamber, 20 °C.

#### 4. Discussion

UV spectra of *p*-ITKB in *n*-heptane obtained after various periods of photolysis are shown in Fig. 1. Three basic absorption bands were found

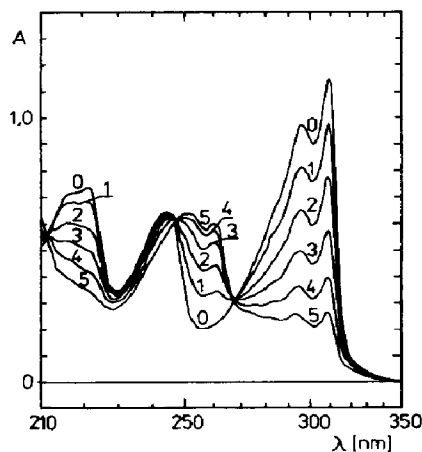
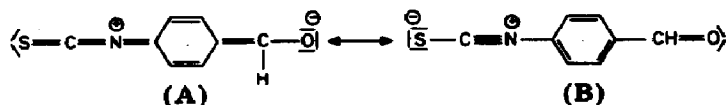


Fig. 1. UV absorption spectra of *p*-ITKB in *n*-heptane (concentration  $c_0 = 4.067 \times 10^{-5} \text{ mol l}^{-1}$ ) after various exposure times: 0, 0 s; 1, 180 s; 2, 360 s; 3, 540 s; 4, 720 s; 5, 900 s.

(at 220, 250 and 300 - 310 nm) each of which consisted of two overlapping internal peaks. The cumulated spectrum was then broken down using numerical methods to the respective characteristic components.

The absorption maximum at 220 nm is attributed to the excited aromatic system [7]. The extent of conjugation depends on the momentary polarization condition of the molecules and is generally explained using the equilibrium shown in Scheme 4.



Scheme 4.

Thus, all three absorption bands will be split into two individual components. The absorption band at 250 nm is attributed to the  $n-\pi^*$  transition of the  $-\text{CHO}$  group; this is confirmed by the UV spectrum of benzaldehyde taken under identical conditions (Fig. 2). There is also an interesting bathochromic

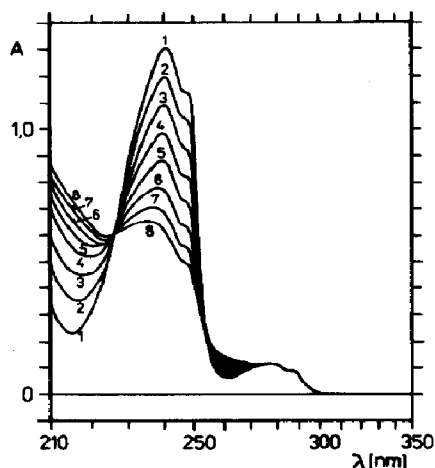


Fig. 2. The UV absorption spectrum of benzaldehyde in *n*-heptane after a maximum exposure time of 230 min [8].

shift of this band (see Fig. 1) with an increase in the exposure time. This may be explained by increased conjugation of the molecule. The absorption maxima at 300 and 310 nm are due to  $n-\pi^*$  excitations of the electron pair on the nitrogen atom in the  $-\text{NCS}$  group. These maxima show a decrease with increasing exposure time, probably due to a decrease in conjugation in accordance with the equilibrium shown in Scheme 4.

A survey of the experimental data from the formal kinetic mechanism viewpoint (Scheme 4) is given in Table 1. The rate of decrease of the initial concentration indicates a first order kinetic equation. Assuming that Scheme 4 is valid, then the kinetics for a first order reaction may be determined from the following expression:

$$\frac{A_B}{A_A} = e^{kt} - 1 \quad (1)$$

where  $A_A$  and  $A_B$  are the absorbances of the structures A and B. Equality of the molar extinction coefficients of the A and B structures is assumed. From eqn. (1) an increase in the absorption bands (*i.e.* of the structures present) may be expected. Thus it can be assumed that the photon absorp-

TABLE 1  
Kinetic data for the photolysis of *p*-ITKB in *n*-heptane

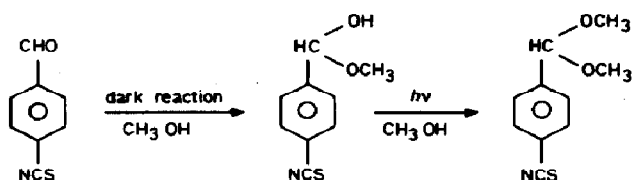
Exposure time (s)	Absorbance <i>A</i>				<i>c</i> (mol l <sup>-1</sup> )	log <i>c</i>
	λ = 222 nm	λ = 260 nm	λ = 296 nm	λ = 309 nm		
0	0.755	0.21	0.97	1.15	4.067 × 10 <sup>-5</sup>	-4.39
180	0.705	0.34	0.81	0.97	3.481 × 10 <sup>-5</sup>	-4.46
360	0.615	0.44	0.65	0.77	2.723 × 10 <sup>-5</sup>	-4.56
540	0.525	0.53	0.50	0.57	2.016 × 10 <sup>-5</sup>	-4.70
720	0.435	0.57	0.36	0.40	1.415 × 10 <sup>-5</sup>	-4.85
900	0.365	0.60	0.24	0.27	1.023 × 10 <sup>-5</sup>	-4.98

The photolysis rate constant ( $1.376 \times 10^{-3} \text{ s}^{-1}$ ) is expressed as the apparent rate constant of the pseudo-unimolecular reaction between *p*-ITKB and excess solvent (or eventually further solution components, e.g. O<sub>2</sub>) under the conditions given (exposure to polychromatic UV light).

tion causes the equilibrium shown in Scheme 4 to shift to a structure with a shorter length of conjugation, and causes a decrease in the number of *n* electrons on the oxygen atom of the -CHO group. The specific reaction rate under the conditions shown is — in agreement with literature data of similar systems [9] — characterized by a formal rate constant of  $k = 1.376 \times 10^{-3} \text{ s}^{-1}$ .

As evidence for the validity of the assumption that the system does not undergo molecular changes during the UV radiation, a mass spectrum of *p*-ITKB in *n*-heptane after a maximum exposure of 30 min was measured and was compared with that of untreated *p*-ITKB; both spectra were found to be identical. We further show mass spectra taken using different energy levels; they confirm the existence of only molecular ions with  $m/e = 163$ . It is evident from Fig. 3 that energy levels of approximately 14 eV are necessary to cause fragmentation of *p*-ITKB in *n*-heptane.

Similar to *p*-ITKB in *n*-heptane, *p*-ITKB in methanol before photolysis also exhibits three absorption bands corresponding to group absorptions: λ = 227 nm for the π-π\* transitions of the aromatic system; λ = 240 nm for the n-π\* transitions of the acetal group (HO-CH(OCH<sub>3</sub>)); λ ≈ 316 nm for the transitions of the -NCS group (Fig. 4). Figure 5 shows the UV spectrum of benzaldehyde in methanol after 4200 s of exposure. Only single bands can be seen for *p*-ITKB in methanol. This can be explained by a more pronounced conjugation in *p*-ITKB molecules in this solvent because of its higher polarity, and also because of the prior dark reaction which leads to hemiacetal formation. Similar observations have been made with *o*-nitrobenzaldehyde [10]. The total reaction scheme can be represented as shown in Scheme 5. The formation of methylacetal in *p*-ITKB was confirmed by mass spectral measurements of methanolic *p*-ITKB solutions after an exposure of 30 min (Fig. 6).



Scheme 5.

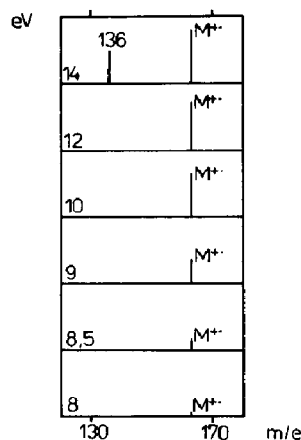
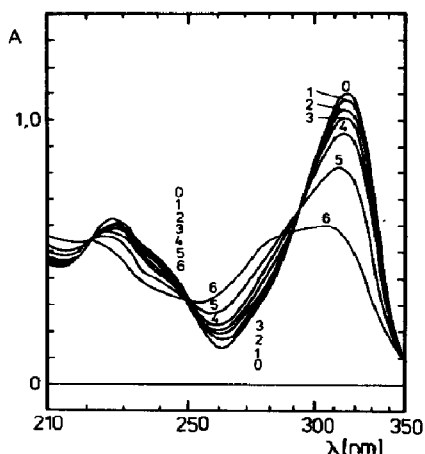
Fig. 3. Mass spectra of *p*-ITKB in *n*-heptane.

Fig. 4. UV absorption spectra of *p*-ITKB in methanol (concentration  $c_0 = 4.159 \times 10^{-5} \text{ mol l}^{-1}$ ) after various exposure times: 0, 0 s; 1, 60 s; 2, 240 s; 3, 480 s; 4, 900 s; 5, 1800 s; 6, 3600 s.

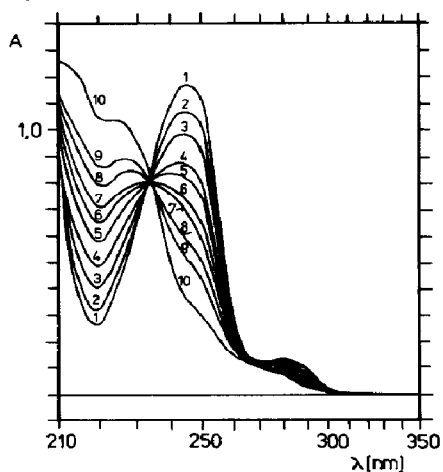


Fig. 5. The UV absorption spectrum of benzaldehyde in methanol after a maximum exposure time of 4200 s [10].

The kinetics are shown in Table 2; Fig. 7 presents graphically the dependence of the concentration decrease on exposure time; this corresponds to a unimolecular mechanism since one of the reactants (methanol) is in excess by  $10^3$ . This means that this is a pseudo-unimolecular reaction, having a rate constant of  $k = 1.789 \times 10^{-4} \text{ s}^{-1}$ , again in good agreement with the available literature data [9].

As found for *n*-heptane and methanol, the UV spectra of *p*-ITKB in ethanol are composed of three characteristic absorption bands (Fig. 8) which can be interpreted in a similar way to the methanol system.

TABLE 2

Kinetic data for the photolysis of *p*-ITKB in methanol

Exposure time (s)	Absorbance <i>A</i>				<i>c</i> (mol l <sup>-1</sup> )	log <i>c</i>
	λ = 213 nm	λ = 227 nm	λ = 262 nm	λ = 317 nm		
0	0.40	0.62	0.14	1.10	4.159 × 10 <sup>-5</sup>	-4.38
60	0.41	0.61	0.15	1.08	4.084 × 10 <sup>-5</sup>	-4.39
240	0.42	0.60	0.19	1.04	3.932 × 10 <sup>-5</sup>	-4.41
480	0.43	0.59	0.20	1.01	3.819 × 10 <sup>-5</sup>	-4.42
900	0.45	0.58	0.22	0.95	3.592 × 10 <sup>-5</sup>	-4.44
1800	0.48	0.56	0.28	0.82	3.100 × 10 <sup>-5</sup>	-4.51
3600	0.52	0.50	0.36	0.54	2.042 × 10 <sup>-5</sup>	-4.69

The rate constant of the photolysis is  $1.789 \times 10^{-4} \text{ s}^{-1}$ .

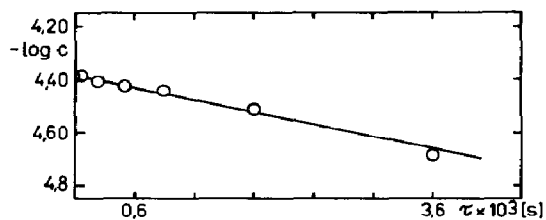
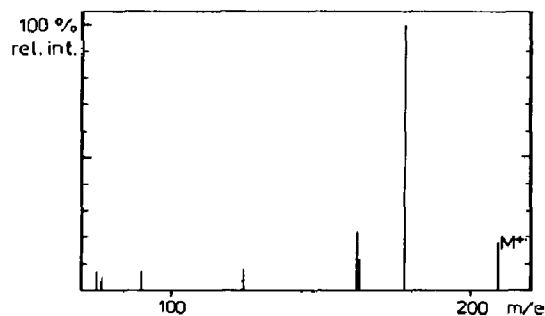


Fig. 6. The mass spectrum of *p*-ITKB in methanol.

Fig. 7. The change with time of the initial *p*-ITKB concentration in methanol.

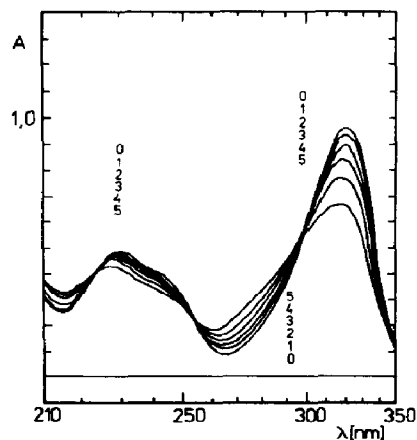
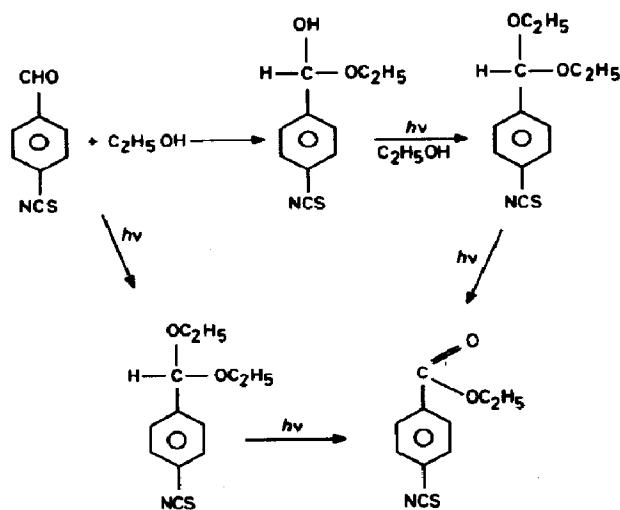


Fig. 8. UV absorption spectra of *p*-ITKB in ethanol (concentration  $c_0 = 3.9032 \times 10^{-5} \text{ mol l}^{-1}$ ) after various exposure times: 0, 0 s; 1, 120 s; 2, 240 s; 3, 420 s; 4, 660 s; 5, 1020 s.



According to other workers [11] ethanol forms hemiacetals by dark reactions to a lesser degree than methanol; hence the slower reaction process, the smaller decrease of the  $-NCS$  group absorption band ( $\lambda_{max}$  at 320 nm) and the smaller decrease of the concentration of the initial component with exposure time are not surprising. The apparent rate constant value of  $k_1 = 3.22 \times 10^{-4} \text{ s}^{-1}$  agrees, with respect to magnitude, with that of the measurements in methanol.

Based on these results the photolysis mechanism of *p*-ITKB in ethanol can be described as shown in Scheme 6.



Scheme 6.

The results of UV absorption spectral measurements of the photolysis of *p*-ITKB in isopropanol are shown in Fig. 9. With increasing photolysis

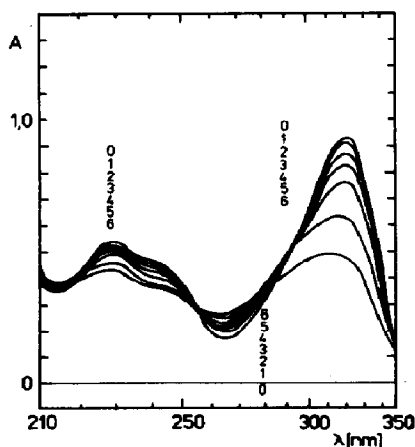
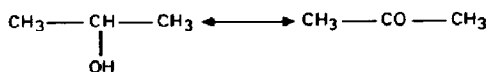


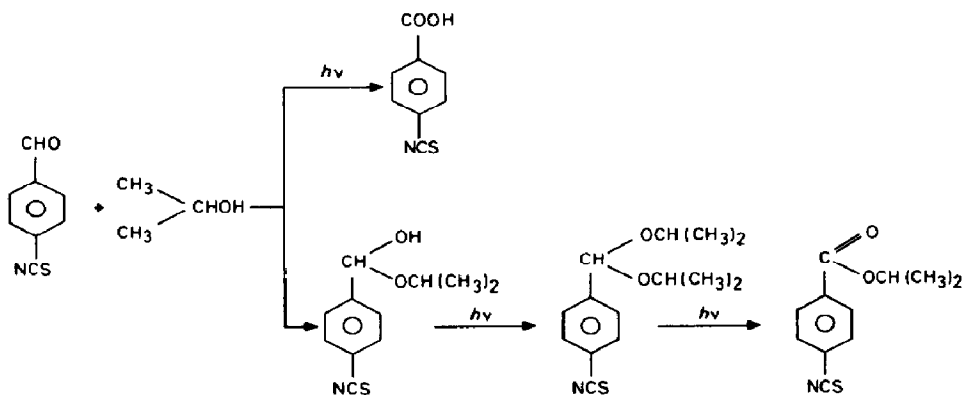
Fig. 9. UV absorption spectra of *p*-ITKB in isopropanol (concentration  $c_0 = 4.242 \times 10^{-5} \text{ mol l}^{-1}$ ) after various exposure times: 0, 0 s; 1, 60 s; 2, 240 s; 3, 420 s; 4, 720 s; 5, 1200 s; 6, 2400 s.

time the absorption band of the  $\text{-NCS}$  group ( $\lambda_{\text{max}} = 320 \text{ nm}$ ) decreases continuously as a result of new chromophore formation by a parallel reaction [12] (see Scheme 7).



Scheme 7.

Based on analogy with the nitrobenzaldehyde photolysis, the formation of free *p*-isothiocyanatobenzoic acid together with a certain amount of its isopropyl ester can be predicted with great certainty (see Scheme 8).



Scheme 8.

The apparent rate constant  $k_1 = 1.917 \times 10^{-4} \text{ s}^{-1}$  is, with respect to the reaction order, in accordance with the constants found for the other solvents.

## 5. Conclusions

It has been shown experimentally that, during the photolysis of *p*-isothiocyanatobenzaldehyde in *n*-heptane solution with polychromatic light, no decomposition reactions occur. Only a shortening of the system conjugation appears to take place.

Under identical conditions, but in the polar solvents methanol, ethanol and isopropanol, hemiacetal forms are identified. In isopropanol the photolytic process has been found to be connected with a decrease in the absorption maximum of the  $\text{-NCS}$  group, probably as a result of oxidation of isopropanol to acetone [8]. Moreover, absorption changes during exposure in these systems will also occur because, apart from the hemiacetals, certain amounts of *p*-isothiocyanatobenzoic acid are also formed. The apparent rate constants during photolysis in the polar solvent systems are ten times smaller than those in *n*-heptane as is the rate constant for the isomerization reaction in non-polar *n*-heptane; rate constants in the range  $10^{-4} \text{ s}^{-1}$  are found.

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