

SHORT COMMUNICATION

Photochemical Reactions of 1,3-Diphenyl-1-propen-2,3-one in Polystyrene Solutions

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α,β -Enone compounds were found among the carbonyl products of polystyrene photooxidation. In our previous papers,¹⁻³ numerous model impurities have been used for elucidating their possible role in actual polymer degradation. The choice of model compounds was based on the identification of products from polystyrene photooxidation. Each of these products was incorporated into a polystyrene sample, and the photochemical processes in such systems were investigated. In this way, it was possible to determine their individual influence on the polymer photooxidation.

α,β -Enones should be taken into account when the mechanism of polystyrene deterioration is considered as being able to absorb efficiently the near UV radiation.

1,3-Diphenyl-1-propen-2,3-one (chalcone) was chosen as a simple model compound, representing the α,β -enone products of polystyrene photooxidation. Chalcone *trans*→*cis* photoisomerization and thermally initiated *cis*→*trans* isomerization have been studied by several authors.⁴⁻⁷

In previous papers^{8,9} the kinetic courses of *trans*-chalcone photochemical reactions in various solvents were studied. The following processes were found to occur: 1) *trans*→*cis* photoisomerization, 2) intermolecular hydrogen abstraction, and 3) reaction between chalcone and singlet oxygen generated in the system. The relative quantum yields depend on the nature of the solvent. These three photochemical processes lead to the consumption of *trans*-chalcone.

The aim of this paper is to evaluate the

photochemical reactivity of *trans*-chalcone in the presence of polystyrene in CH₂Cl₂ and toluene solutions.

Because of the high extinction coefficient of *trans*-chalcone and the relatively low extinction coefficients of photochemical reaction products in the spectral range investigated, UV spectrophotometry made possible the monitoring of the *trans*-chalcone consumption process.

EXPERIMENTAL

1,3-Diphenyl-1-propen-2,3-one was prepared and purified for spectral analysis in the organic chemistry laboratory at the Jagiellonian University.

Polystyrene was prepared by the thermal polymerization of styrene at 80°C for 450 h. The weight-average molecular weight of this polymer, determined viscometrically, was 462 000.

Toluene and methyl chloride of special grade for spectroscopy were used as solvents.

Chalcone solutions were irradiated with light at $\lambda > 305$ nm. An ASH 400 medium pressure Hg lamp and a phthalate liquid filter¹⁰ were used. The incident radiation intensity at 313 nm was 2.3×10^{-9} Einstein s⁻¹ cm⁻² as determined by ferrioxalate actinometry.¹¹

Photochemical experiments were carried out in cylindrical quartz cells of 0.5 cm thickness in the presence of air at atmospheric pressure.

Polystyrene films of 2×10^{-3} cm in thickness, containing chalcone, were prepared as described in a previous paper.²

The UV absorption spectra of the solutions and polystyrene films were recorded with a Zeiss Specord UV-VIS spectrophotometer.

RESULTS AND DISCUSSION

The near UV ($\lambda > 305$ nm) irradiation of chalcone solutions in CH_2Cl_2 and toluene with the addition of polystyrene at a concentration of 10^{-4} to 10^{-1} mol dm^{-3} results in a decrease in chalcone absorption ($\lambda_{\text{max}}^{\text{ch}} = 307$ nm). These absorption changes occur very rapidly. For the toluene solution ($c_{\text{ch}}, 3.5 \times 10^{-5}$ mol dm^{-3} ; $c_{\text{PS}}, 7.8 \times 10^{-3}$ mol dm^{-3}), the value of absorption at $\lambda_{\text{max}}^{\text{ch}}$ is halved after 25 s of irradiation.

During the same time interval, an increase in absorption at $\lambda = 262$ nm could be observed, thus indicating the formation of *cis*-chalcone in the *trans* \rightarrow *cis* photoisomerization process.⁵

Lutz and Jordan⁴ observed thermally initiated *cis* \rightarrow *trans* isomerization of chalcone in the presence of H^+ ions in an isooctane solution.

Similar results were obtained for CH_2Cl_2 solutions of chalcone containing polystyrene at various concentrations, as shown in Figure 1.

It can be noticed that the heating of a solution results in reincrease in absorption in the range of the *trans*-chalcone absorption. It may thus be con-

cluded that *trans* \rightarrow *cis* isomerization is the main photochemical process occurring during the early stages of the near UV irradiation of a chalcone + polystyrene solution.

The experiments carried out for solutions at various polystyrene concentrations indicate that an increase in the polystyrene concentration is followed by a decrease in the rate of chalcone consumption process. In general, the rate of *trans*-chalcone consumption is given by the equation,

$$-\frac{dc_{\text{ch}}}{dt} = I_a \phi_{\text{ISC}} \phi_{\text{cons}} \quad (1)$$

where,

I_a is the rate of light-absorption process (Einstein $\text{dm}^{-3} \text{s}^{-1}$),

ϕ_{ISC} is the quantum efficiency of *trans*-chalcone excited triplet-state formation,

ϕ_{cons} is the quantum efficiency of *trans*-chalcone consumption process.

Dissolving eq 1 leads to,

$$\phi = \phi_{\text{ISC}} \phi_{\text{cons}} = \frac{\Delta c + \frac{1}{\epsilon l} \ln \frac{1 - e^{-A_0}}{1 - e^{-A_t}}}{I_0 \Delta t} \quad (2)$$

where,

Δc is the change in the *trans*-chalcone con-

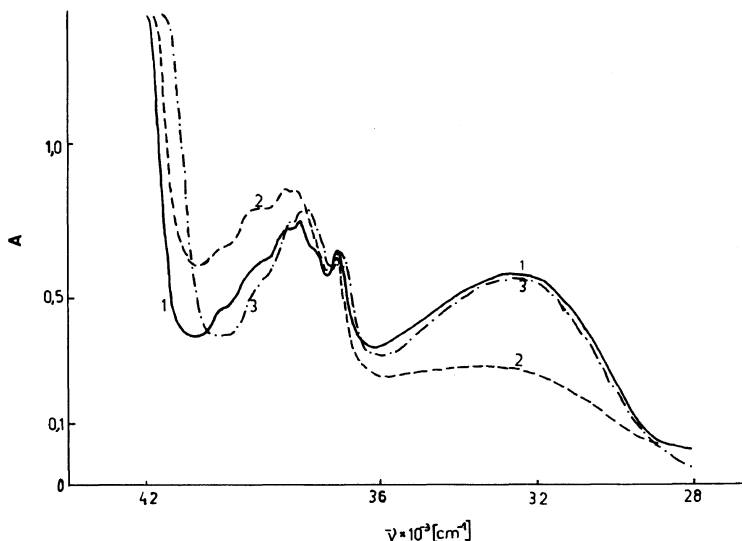


Figure 1. UV absorption spectra of chalcone + polystyrene in CH_2Cl_2 ($c_{\text{ch}}, 2 \times 10^{-5}$ mol dm^{-3} ; $c_{\text{PS}}, 2 \times 10^{-3}$ mol dm^{-3}): 1, before irradiation; 2, after irradiation with light at $\lambda > 305$ nm for 60 s; 3, after heating at the boiling point of CH_2Cl_2 for 5 min at the presence of HCl.

centration corresponding to the irradiation time Δt ,

ε is the molar extinction coefficient at $\lambda_{\text{max}}^{\text{ch}} = 307 \text{ nm}$,

l is the thickness of solution layer,

A_0 is the initial sample absorbance at $\lambda_{\text{max}}^{\text{ch}} = 307 \text{ nm}$,

A_t is the sample absorbance after irradiation time Δt ,

I_0 is the incident light intensity (Einstein $\text{dm}^{-3} \text{s}^{-1}$).

Figure 2 shows the inter-dependence of the ratio φ_0/φ and polystyrene concentration, where φ_0 and φ are the quantum efficiencies of the *trans*-chalcone consumption process in a toluene solution with and without the presence of polystyrene, respectively.

The experimental data presented in Figure 2 show that the quantum efficiency of the *trans*-chalcone consumption process decreases as the polystyrene concentration increases.

Trans→*cis* chalcone photoisomerization could also be observed when *trans*-chalcone was incorporated into the polystyrene film but the rate and quantum efficiency of this process were considerably reduced ($\varphi_0/\varphi \approx 10^2$), owing perhaps to the increase in the viscosity of the system.

The results obtained here indicate that in the initial period of the irradiation of PS+chalcone samples (solutions, films), the photooxidation of polystyrene does not occur because of *trans*→*cis* photoisomerization of chalcone, which is the predominant process in the system. It was noticed, however, that the photoisomerization was followed by much slower secondary processes in which chalcone was also consumed. The sensitized photooxidation of polystyrene films connected with the second step of the chalcone consumption process is the subject of present investigation.

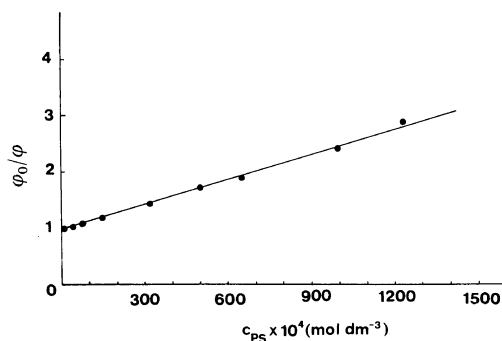


Figure 2. Dependence of φ_0/φ (φ_0 , quantum efficiency of the *trans*-chalcone consumption process in the absence of polystyrene; φ , quantum efficiency of *trans*-chalcone consumption in the presence of polystyrene) on the polystyrene concentration.

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