

PHOTOISOMERIZATION OF CHALCONE: WAVELENGTH DEPENDENCE

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Summary

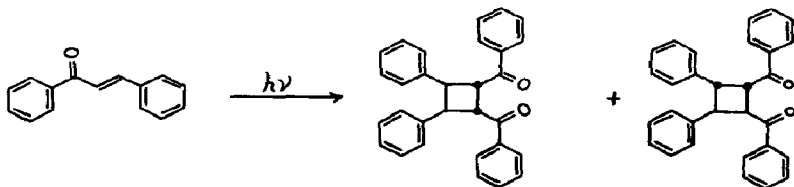
The quantum yield for the *cis-trans* photoisomerization of chalcone (1,3-diphenylpropen-3-one) is wavelength dependent. At 313 nm the *trans-to-cis* quantum yield is 0.36 and the *cis-to-trans* quantum yield is 0.135. At 366 nm the *trans-to-cis* quantum yield is 0.48 and the *cis-to-trans* quantum yield is 0.23. These values were not affected by changes in the concentration of chalcone or by the presence of oxygen. A comparison with the literature data is made and reasons for the quantum inefficiency and the wavelength dependence are discussed.

1. Introduction

The photochemistry of cyclic enones has been studied extensively [1] and there is considerable interest in the photochemistry of acyclic aliphatic enones [2]; however, the aromatic enones have been neglected. This is somewhat surprising considering the work that has been expended on the photochemistry of stilbene [3]. Chalcone (1,3-diphenylpropen-3-one), which is the simplest enone analogue to stilbene, has received very little attention in the literature.

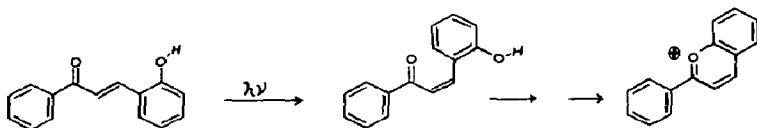
The increasing use of chalcones as photostabilizers of polymers [4], in sun screen lotion [5] and in colour photography [6] indicates that their photochemistry deserves more attention.

When we began our study it was known [7] that *trans*-chalcone photodimerizes in an analogous manner to cinnamic acid [8] to give two dimers as shown in Scheme 1. This dimerization occurs even in solution [9]



Scheme 1. The dimerization of *trans*-chalcone.

but with a low quantum yield. The principal reaction has been reported [10] to be *cis-trans* isomerization. In the case of *trans*-2-hydroxychalcones the *cis* isomer can cyclize to form chromanones [11] in a process that may also occur in nature (Scheme 2).



Scheme 2. The isomerization and cyclization of 2-hydroxychalcone.

We decided to examine the photochemical isomerization of chalcone by measuring quantum yields for the *trans-to-cis* and *cis-to-trans* isomerizations using light of wavelength 366 nm. While our study was in progress Mitina *et al.* [12] reported on studies carried out at 313 nm. Since our results at 366 nm were different, we repeated our studies using the 313 nm mercury line.

2. Experimental

trans-Chalcone was purified by repeated recrystallization first from ethanol and then from hexane. *cis*-Chalcone was prepared from the *trans* isomer by photoisomerization using sunlight [10] and was purified while protected from light by recrystallization from hexane and pentane. It was shown to be pure by a combination of techniques including UV absorption spectra, nuclear magnetic resonance spectra, the melting point range and thin-layer chromatography. The cyclohexane and hexane used as solvents for the photolysis were purified [13] and did not absorb at wavelengths longer than 230 nm. All samples were irradiated in Pyrex test tubes which were soaked in detergent and then repeatedly rinsed with distilled water. Solutions of both *cis*- and *trans*-chalcone which were subjected to the same treatment as the irradiated samples, but which were not irradiated, showed no changes in absorbance.

Solutions of pure *cis*- or *trans*-chalcone in cyclohexane were oxygenated by passing dry oxygen for 30 min or were degassed through four freeze-pump-thaw cycles. The samples were protected from exposure to room light during preparation, degassing and storage. The irradiations used the light of a 450 W Hanovia medium pressure lamp filtered by passage either through Corning filters 0-52 and 7-37 to isolate the 366 nm emission line or through a K_2CrO_4 filter solution and a Corning 7-54 filter to isolate the 313 nm mercury emission line. A merry-go-round apparatus [14] was used for all irradiations. The actinometer used was potassium ferrioxalate of concentration either 0.15 M [15] or 0.006 M [16].

Analysis of the irradiated solutions was by UV absorption using a Perkin-Elmer-Coleman 139 spectrophotometer with measurements at 262 nm (isosbestic point), 240 nm (maximum for *cis*-chalcone) and 300 nm (maximum for *trans*-chalcone) [17].

In all experiments reported the absorbance at 262 nm remained constant and independent of conversion, showing that chalcone dimers were not formed. Emission spectra were sought using a Hitachi-Perkin-Elmer MPF-3A spectrofluorimeter with 3-methylpentane as solvent but no emission was observed either from fluid solution or at low temperature in the glass.

3. Results

Photostationary state concentrations of *cis*- and *trans*-chalcone were found by monitoring the concentration of both *cis*- and *trans*-chalcone as a function of time and the photolysis was continued until the ratio of *cis* to *trans* remained constant.

As shown in Table 1, irradiation at 366 nm in cyclohexane gave the same photostationary state ratio regardless of the identity of the starting chalcone (*cis* or *trans*), the initial concentration of chalcone or the concentration of oxygen. A different photostationary state was found using 313 nm irradiation, but this was also independent of oxygen concentration.

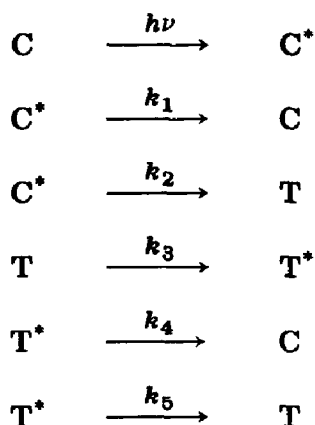
TABLE 1

Photostationary state concentration of *cis*-chalcone

Starting isomer	Initial concentration (M)	Oxygen	Irradiation wavelength λ (nm)	% <i>cis</i> (measured)	% <i>cis</i> (calculated) ^a
<i>trans</i>	5×10^{-5}	None	313	85 ± 8	88
<i>trans</i>	5×10^{-5}	Saturated	313	88 ± 9	88
<i>trans</i>	5×10^{-3}	None	366	69 ± 7	70
<i>trans</i>	5×10^{-3}	Saturated	366	68 ± 7	70
<i>trans</i>	5×10^{-5}	None	366	69 ± 7	70
<i>trans</i>	5×10^{-5}	Saturated	366	69 ± 7	70
<i>cis</i>	5×10^{-5}	None	366	69 ± 7	70
<i>cis</i>	5×10^{-5}	Saturated	366	71 ± 7	70

^aSee text.

Initial quantum yields for the isomerization of *trans* to *cis* and of *cis* to *trans* were found by curve fitting the experimental quantum yields using an equation derived from the following general kinetic scheme:



(C, *cis*-chalcone; C*, *cis*-chalcone in an excited state; T, *trans*-chalcone; T*, *trans*-chalcone in an excited state).

The nature of the excited state was not specified but it was assumed that there was no energy transfer from the excited state(s) of *cis* to the ground state of *trans* or vice versa. The final expression depends only on the following variables of which the first seven are independent variables and the last two are dependent variables: K , the initial concentration of *cis*- or *trans*-chalcone; C , the final concentration of *cis*-chalcone (chosen); T , the final concentration of *trans*-chalcone (chosen); ϵ_c , the molar absorptivity of *cis*-chalcone at the wavelength irradiated (6700 at 313 nm, 256 at 366 nm); ϵ_t , the molar absorptivity of *trans*-chalcone at the wavelength irradiated (19000 at 313 nm, 284 at 366 nm); ϕ_{TC}° , the initial quantum yield for the transformation of *trans*-chalcone to *cis*-chalcone; ϕ_{CT}° , the initial quantum yield for the transformation of *cis*-chalcone to *trans*-chalcone; ϕ_{TC} , the quantity of *cis*-chalcone formed in moles divided by the number of einsteins of radiation absorbed; ϕ_{CT} , the quantity of *trans*-chalcone formed in moles divided by the number of einsteins of radiation absorbed; I , the intensity of the light absorbed by the sample.

The differential equations relating the rate of formation of *cis*-chalcone or *trans*-chalcone to the variables were generated using the steady state approximation; the equations obtained were

$$\frac{dC}{I dt} = \frac{k_1 \epsilon_c C}{(\epsilon_c C + \epsilon_t T)(k_1 + k_2)} + \frac{k_3 \epsilon_t T}{(\epsilon_c C + \epsilon_t T)(k_3 + k_4)} - \frac{\epsilon_c C}{\epsilon_c C + \epsilon_t T}$$

and

$$\frac{dT}{I dt} = \frac{k_2 \epsilon_c C}{(\epsilon_c C + \epsilon_t T)(k_1 + k_2)} + \frac{k_4 \epsilon_t T}{(\epsilon_c C + \epsilon_t T)(k_3 + k_4)} - \frac{\epsilon_t T}{\epsilon_c C + \epsilon_t T}$$

Integration then gave the following expressions:

$$\phi_{TC} = \frac{C(\phi_{TC}^\circ \epsilon_T + \phi_{CT}^\circ \epsilon_C)^2}{C(\epsilon_T - \epsilon_C)(\phi_{TC}^\circ \epsilon_T + \phi_{CT}^\circ \epsilon_C) + \epsilon_T \epsilon_C K(\phi_{CT}^\circ + \phi_{TC}^\circ) \ln X_C}$$

$$\phi_{CT} = \frac{T(\phi_{TC}^{\circ}\epsilon_T + \phi_{CT}^{\circ}\epsilon_C)^2}{T(\epsilon_C - \epsilon_T)(\phi_{TC}^{\circ}\epsilon_T + \phi_{CT}^{\circ}\epsilon_C) + \epsilon_T\epsilon_C K(\phi_{CT}^{\circ} + \phi_{TC}^{\circ}) \ln X_T}$$

where

$$X_C \equiv \frac{\phi_{TC}^{\circ}\epsilon_T K}{\phi_{TC}^{\circ}\epsilon_T K - C(\phi_{TC}^{\circ}\epsilon_T + \phi_{CT}^{\circ}\epsilon_C)}$$

$$X_T \equiv \frac{\phi_{CT}^{\circ}\epsilon_C K}{\phi_{CT}^{\circ}\epsilon_C K - T(\phi_{TC}^{\circ}\epsilon_T + \phi_{CT}^{\circ}\epsilon_C)}$$

In the special case where $\epsilon_C = \epsilon_T$ these expressions reduce to the formula used by Figuera and Serrano [18].

Using experimental values of K and C , values of ϕ_{TC}° and ϕ_{CT}° were chosen and were used to calculate ϕ_{TC} . The calculated values of ϕ_{TC} were then compared with the experimental values and the square of the residuals was summed for all experiments performed at 366 nm starting from *trans*-chalcone. The values of ϕ_{TC}° and ϕ_{CT}° were then adjusted and the calculation was repeated. It was found that when starting from *trans*-chalcone changes in ϕ_{CT}° had little effect on the calculated values, but a best value of ϕ_{TC}° was found by the method of least squares. The calculations were repeated in the same way using values of K and T to calculate ϕ_{CT} for the isomerization starting with *cis*-chalcone and values of ϕ_{CT}° were found. Here again it was found that the calculated values of ϕ_{CT} were insensitive to the value of ϕ_{TC}° used in the calculations. In the same way values of ϕ_{CT}° and ϕ_{TC}° were found for irradiations performed at 313 nm. The results are shown in Figs. 1 - 6 with the calculated lines of best fit shown as full lines. The initial quantum yields found by this method of curve fitting are given in Table 2. The

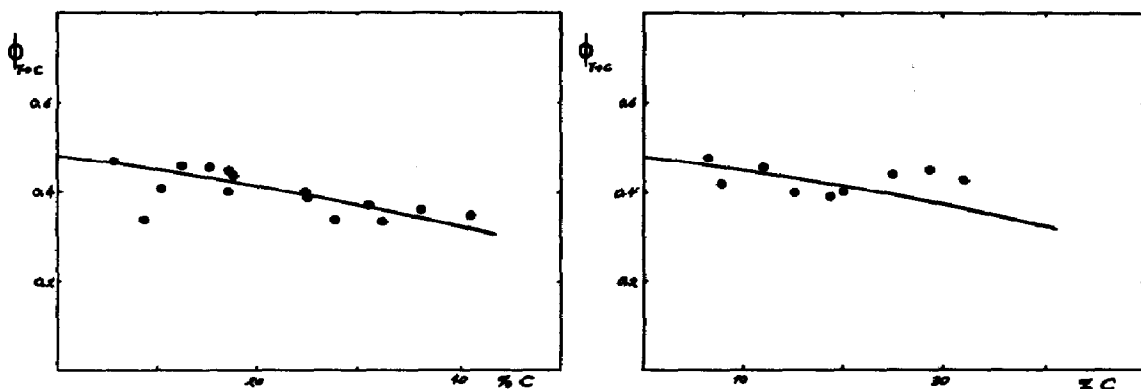


Fig. 1. Quantum yields for the isomerization of *trans*-chalcone to *cis*-chalcone at 366 nm in hexane: initial concentration of *trans*-chalcone, 5.10×10^{-3} M; samples degassed.

Fig. 2. Quantum yields for the isomerization of *trans*-chalcone to *cis*-chalcone at 366 nm in hexane: initial concentration of *trans*-chalcone, 5.25×10^{-3} M; samples oxygen saturated.

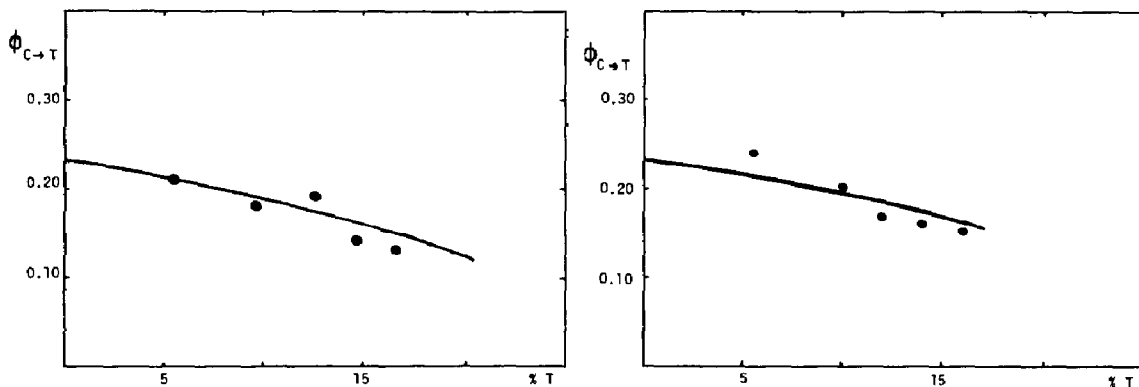


Fig. 3. Quantum yields for the isomerization of *cis*-chalcone to *trans*-chalcone at 366 nm in hexane: initial concentration of *cis*-chalcone, 4.9×10^{-3} M; samples degassed.

Fig. 4. Quantum yields for the isomerization of *cis*-chalcone to *trans*-chalcone at 366 nm in hexane: initial concentration of *cis*-chalcone, 5.35×10^{-3} M; samples oxygen saturated.

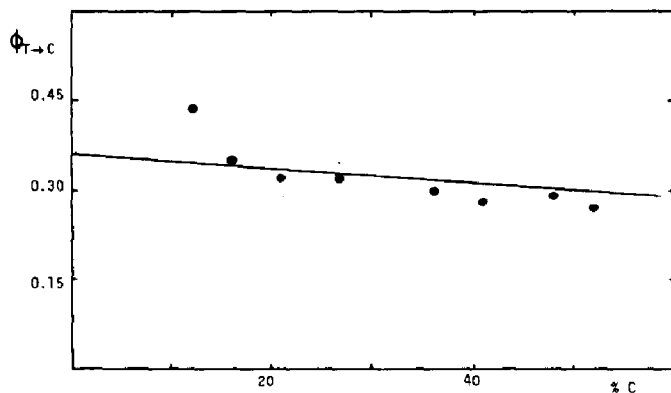


Fig. 5. Quantum yields for the isomerization of *trans*-chalcone to *cis*-chalcone at 313 nm in hexane: initial concentration of *trans*-chalcone, 2.2×10^{-4} M; samples degassed.

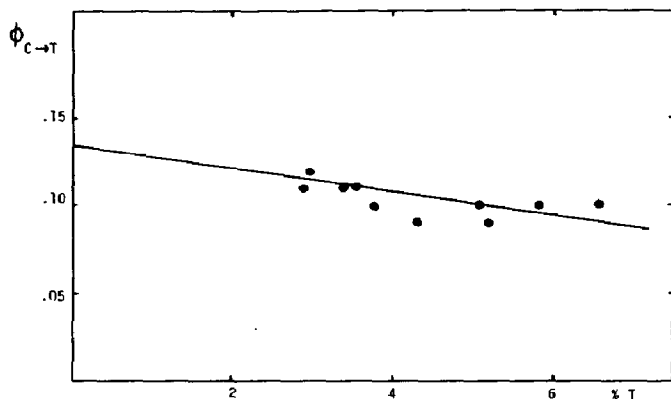


Fig. 6. Quantum yields for the isomerization of *cis*-chalcone to *trans*-chalcone at 313 nm in hexane: initial concentration of *cis*-chalcone, 3.4×10^{-4} M; samples degassed.

TABLE 2
Initial quantum yields

λ (nm)	ϕ_{TC}°	ϕ_{CT}°
313	0.36 ± 0.01	0.135 ± 0.01
366	0.48 ± 0.01	0.23 ± 0.01

agreement between the calculated and the experimental quantum yields are within the experimental error of the data. The calculated initial quantum yields were used to calculate the photostationary state concentration of *cis*-chalcone from the following equation:

$$\frac{C}{T} = \frac{\phi_{TC}^{\circ} \epsilon_T}{\phi_{CT}^{\circ} \epsilon_C}$$

The results are shown in Table 1. The agreement between the experimental and the calculated values is very good.

4. Discussion

It can be seen from Table 1 that the photostationary state composition (PSC) does not depend on the chalcone concentration or on the presence or absence of oxygen. At 366 nm the same PSC is reached starting from either the *cis* isomer or the *trans* isomer and there is an excellent agreement between the PSC values calculated from initial quantum yields and the experimental values. At 313 nm the calculated and experimental values also show excellent agreement. From this we conclude that there is no energy transfer between *cis*-chalcone and *trans*-chalcone under the conditions of our experiments. This and the good agreement between the calculated and observed quantum yields shown in Figs. 1 - 6 indicate that the general model used is adequate to account for the results.

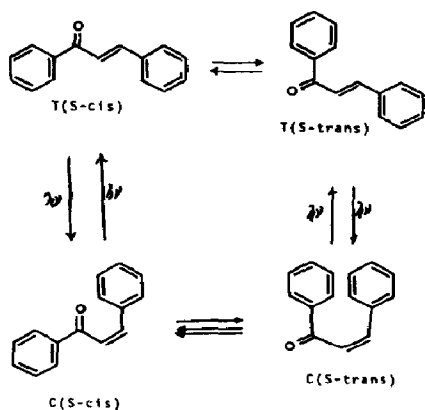
Our results at 313 nm are different from those obtained by Mitina *et al.* [12]. They obtained a percentage concentration of *cis*-chalcone at the PSC of 80% compared with our value of 88%; they obtained values for the initial quantum yields of $\phi_{TC}^{\circ} = 0.54$ and $\phi_{CT}^{\circ} = 0.38$ with the value of ϕ_{CT}° being derived from the PSC and the measured value of ϕ_{TC}° . Our values are $\phi_{TC}^{\circ} = 0.36$ and $\phi_{CT}^{\circ} = 0.135$. It appears that they did not actually reach the PSC. A small change in the value at the PSC would produce a large change in the value of ϕ_{CT}° . We are not able to account for the difference between our value of ϕ_{TC}° and their value. Mitina *et al.* [12] indicate that the reaction is quenched by naphthalene and is sensitized by acetophenone; however, we were unable to check these results as these additives absorb in the UV where our analyses were performed and attempts at separation prior to analysis resulted (in our hands) in partial thermal isomerization of the chalcone

mixture, thus invalidating the analyses. Since Mitina *et al.* [12] also followed isomerization by UV spectral changes it would have been necessary for them to remove the sensitizer or quencher without changing the *cis*-to-*trans* ratio prior to analysis. Further, under the conditions used naphthalene absorbs a reasonable fraction of the light, making analysis of the quenching more difficult. Unfortunately experimental details of this part of their work are not given. We attempted to suppress the photoisomerization using 1,3-cyclohexadiene but adducts were formed which interfered with the analysis. From our own results we conclude that if a triplet state is involved it is short lived, as there is neither apparent quenching by oxygen nor phosphorescence emission.

We found that at both wavelengths studied the sum of the initial *cis*-to-*trans* quantum yields with the *trans*-to-*cis* quantum yields ($\phi_{CT}^{\circ} + \phi_{TC}^{\circ}$) is appreciably less than unity, even though isomerization is the only photo-reaction observable.

The model used by Mitina *et al.* is based on their finding that the quantum yields for *trans*-to-*cis* and *cis*-to-*trans* isomerizations sum nearly to unity (0.94) and that the isomerization is quenched by naphthalene and not by anthraquinone. They postulate that the isomerization occurs through the triplet state and involves a twisted triplet biradical. Their model does not explain the wavelength dependence of the isomerization or the lack of quenching by oxygen. Although the triplet state may well be involved we do not consider this to have been proved.

The data available are not sufficient to distinguish between possible mechanisms but the wavelength dependence indicates either that two (or more) excited states are involved or that the photochemistry is conformer dependent. One possibility is that the conformations *S-trans* and *S-cis* of both *cis*- and *trans*-chalcone result in different photochemistry. The wavelength dependence would then result from different absorptions of the various conformers.



Scheme 3. The possible photochemistry of various chalcone conformers.

A second possibility (among many) is that the intersystem crossing quantum yields of both *cis*-chalcone and *trans*-chalcone are wavelength dependent with the reaction occurring from the triplet state.

Whatever the cause, the most interesting result of our work was the finding that the isomerization quantum yields are wavelength dependent. This, coupled with the known wavelength dependence for aliphatic enones [19], may indicate that the phenomenon is general.

We are continuing our studies of this system in order to discover the cause of the quantum inefficiency and the wavelength dependence.

After this work had been completed and prepared for publication some related work came to our attention [20, 21].

Acknowledgments

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