

PHOTOCHEMISTRY OF SUBSTITUTED CYCLOHEPTATRIENES XIII: THE DEPENDENCE OF QUANTUM YIELDS FOR SIGMATROPIC HYDROGEN SHIFTS ON THE EXCITATION ENERGY*

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Summary

The partial quantum yields in a substituted cycloheptatriene reversible system were measured to determine the dependence on the excitation energy. The quantum yields decrease significantly with increasing excitation wavelength. This is in accordance with the prediction from orbital symmetry considerations for a sigmatropic hydrogen shift.

The chemical deactivation from higher excited states is able to compete with internal conversion processes. Furthermore the wavelength dependence of the partial quantum yields is interpreted with two different pericyclic minima in the excited state. The participation of conformers as a possible origin for the wavelength dependence of quantum yields is excluded.

1. Introduction

A useful generalization in solution phase photochemistry implies that the photoreactions occur from the lowest excited singlet or triplet state. In the field of luminescence this generalization has led to the rules of Vavilov and Kasha [2]. Recently a number of exceptions to these rules have become known both in the field of photochemistry and in the field of emission [3].

The investigations of the photochemical and photophysical deactivation behaviour of arylcycloheptatrienes have shown that this class of compounds also exhibits a different behaviour from the cited rules [4, 5]. Thus, in the 1-(*p*-dimethylaminophenyl)-4-aryl cycloheptatrienes the sigmatropic hydrogen shift can compete successfully with the internal conversion from higher excited states [6]. The orbital symmetry analysis of the photoreactivity for cycloheptatriene itself and its derivatives suggests that the mechanism

*For Part XII, see ref. 1.

of the sigmatropic 1,7 hydrogen shift is by excitation into higher electronic states [7].

A general experimental manifestation of higher excited state photochemistry is wavelength-dependent quantum yields. It is therefore the purpose in this paper to discuss the photochemical quantum yields in the reversible system $1 \rightleftharpoons 2$ (Fig. 1) at different wavelengths of the excitation light.

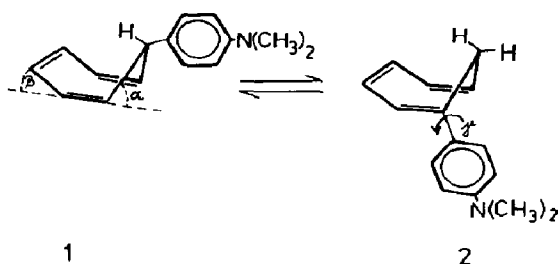


Fig. 1. The substituted cycloheptatriene reversible system.

2. Experimental procedure

The compounds 1 and 2 (Fig. 1) were available from earlier work [5]. The photoreactions were carried out in ethanolic solutions (about 10^{-5} mol l^{-1}). The excitation source was a high intensity monochromator (Bausch and Lomb 1350) with a 175 W xenon lamp. The slit width varied from 1 to 5 mm (half-bandwidth, 6 - 30 nm).

TABLE 1

Partial quantum yields, molar extinction coefficients and mole fractions for the photoequilibrium of the isomers 1 and 2 (Fig. 1) at different excitation wavelengths

| λ_{exc} (nm) | x_2 | ϵ_1 ($m^2 mol^{-1}$) | ϵ_2 ($m^2 mol^{-1}$) | $\varphi_{1 \rightarrow 2}$ | $\varphi_{2 \rightarrow 1}^a$ | $\varphi_{12}/\varphi_{21}$ |
|-------------------------|-------------------|------------------------------------|------------------------------------|-----------------------------|-------------------------------|-----------------------------|
| 254 | 0.928 ± 0.007 | 1887 | 735 | 0.583 ± 0.032 | 0.116 ± 0.015 | 5.1 ± 0.6 |
| 267 | 0.882 ± 0.010 | 1108 | 656 | 0.508 ± 0.024 | 0.115 ± 0.014 | 4.5 ± 0.5 |
| 275 | 0.855 ± 0.011 | 597 | 603 | 0.501 ± 0.017 | 0.083 ± 0.006 | 6.0 ± 0.5 |
| 285 | 0.879 ± 0.017 | 385 | 580 | 0.512 ± 0.020 | 0.047 ± 0.008 | 10.9 ± 2.0 |
| 290 | 0.893 ± 0.012 | 337 | 618 | 0.544 ± 0.012 | 0.035 ± 0.004 | 15.5 ± 2.0 |
| 313 | 0.730 ± 0.019 | 210 | 1229 | 0.452 ± 0.011 | 0.029 ± 0.003 | 15.9 ± 1.5 |
| 330 | 0.388 ± 0.028 | 65 | 1708 | 0.285 ± 0.005 | 0.017 ± 0.002 | 16.8 ± 2.0 |
| 365 | 0.025 | 10 | 1210 | — ^b | 0.009 ^c | — ^b |

^a Calculated from the photoequilibrium composition. The values agree satisfactorily with those from direct measurements.

^b Not measured.

^c Directly measured.

The absorbance–time functions for the kinetic analysis were measured with an automatic apparatus [8]. The calculations of the quantum yields were carried out with a procedure that is analogous to a modified Zimmermann procedure [9, 10].

The composition of the photoequilibrium mixture had to be determined carefully for the investigation of the dependence of the quantum yields on the excitation energy. This was achieved with molar extinction coefficients (error, less than or equal to 1%) and with the absorbance of the solution of the photoequilibrium mixture obtained from an iterative procedure [9] (Table 1). A secondary actinometer [10] calibrated with the ferrioxalate actinometer was used to measure the intensity of the exciting light. The low temperature absorption spectra were measured with a commercial cuvette (Oxford Instruments) and a UV spectrometer (Specord, VEB Carl Zeiss, Jena).

3. Results and discussion

The absorption spectrum of 7-(*p*-dimethylaminophenyl)cycloheptatriene 1 is the sum of the dimethylaniline and cycloheptatriene spectra [4]. Therefore the lowest excited state in this molecule is localized in the dimethylaniline chromophore.

In contrast with this the S_1 state of the isomeric derivative 2 is determined by π delocalization, which is marked by charge transfer from the dimethylaniline group to the seven-membered ring [7] (Fig. 2). Although, as a result of the different molar extinction coefficients of dimethylaniline and cycloheptatriene, the light is mainly absorbed by the dimethylaniline chromophore in compound 1 at all excitation wavelengths, the sigmatropic hydrogen shift in the seven-membered ring nevertheless takes place very effectively (Table 1). Even for excitation of molecule 1 with 330 or 365 nm light, which cannot excite the cycloheptatriene chromophore, the photo-reaction takes place. Indeed the quantum yields decrease significantly in this excitation region (Table 1). The decrease in the quantum yields cannot be interpreted by an inner filter effect of the dimethylaniline chromophore as the analysis of the absorption spectra shows. The quantum yield of the sigmatropic hydrogen shift from molecule 2 to molecule 1 decreases in an analogous fashion to that in the process 1 \rightarrow 2, but more distinctly (see Table 1).

The effect of the wavelength dependence of the partial quantum yield can be assigned generally to two different origins.

(1) Different conformers of the compounds studied exist which differ both in absorption and in the quantum yield of the same photoreaction.

(2) Higher excited electronic and/or vibrational (hot) states are involved.

The evidence for conformers is very difficult to prove and the assumption that the deactivation processes are not equally effective in this mechanism is a postulate in most cases (see, for example, ref. 11).

In the arylcycloheptatrienes 1 and 2 studied, the conformers are probably those which differ in the boat-like shape (angles α and β) or in the torsional

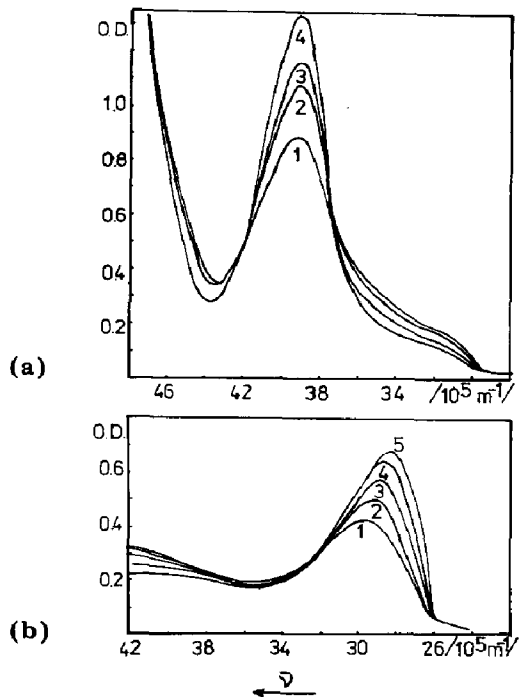
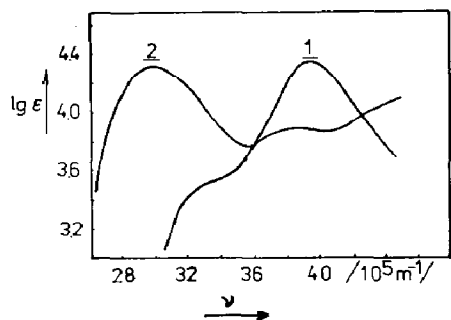


Fig. 2. Absorption spectra of the compounds 1 and 2 in ethanol.

Fig. 3. The effect of temperature on the absorption spectra (uncorrected) in 4:1 ethanol:methanol mixtures. (a) Compound 1: curve 1, 290 K; curve 2, 170 K; curve 3, 160 K; curve 4, 90 K. (b) Compound 2: curve 1, 290 K; curve 2, 210 K; curve 3, 160 K; curve 4, 120 K; curve 5, 100 K.

angle γ between the planes of the seven-membered ring and the arene substituent. The low temperature spectra (Fig. 3) support this assumption. Also similar to acyclic polyenes [12] the intensity (molecules 1 and 2) and the position (molecule 2) of the absorption bands are influenced hyperchromically and bathochromically respectively by decreasing the temperature. Such effects can be interpreted in terms of a distortion of the molecular fragments from near coplanarity at room temperature [12].

The absorption band positions of the conformers must differ considerably to give the observed wavelength-dependent quantum yields because the different conformers can be excited separately only in this case. From Fig. 3 it can be seen that the absorption properties of the postulated conformers of molecules 1 and 2 differ only slightly in the band position in the long wavelength region but not in that short wavelength region in which the quantum yields decrease significantly (Table 1). Therefore a mixture of such conformers cannot be the origin of the wavelength dependence of the reaction quantum yields in this case. Hence case (2) can be taken into consideration.

The wavelength dependence of the quantum yield discovered for the reaction $2 \rightarrow 1$ confirms the assumption in the three-centre bond model for

the transition state of the sigmatropic 1,7 hydrogen shift [7] that this photo-reaction should preferably take place in higher excited electronic states. This means that the photoreaction is able to compete with internal conversion processes from these states. The situation is similar for isomer 1.

The excitation of the S_1 state in molecule 2 also leads to a sigmatropic hydrogen shift. This is in contrast with the situation in the 1-(*p*-dimethylaminophenyl)-4-aryl cycloheptatrienes (see Section 1). There is no evidence for intramolecular cyclization in compound 2 or in compound 1.

Earlier investigations of the sigmatropic hydrogen shift suggest a common pericyclic minimum for the reactions in the reversible system $1 \rightleftharpoons 2$ [13]. In this connection it is interesting to note that two exciting wavelength regions exist in which the partial quantum yield ratio is nearly constant (Table 1). This ratio is determined by the special deactivation rates from the minimum in the hypersurface of the excited state to the ground states of molecule 1 and molecule 2. Consequently the two different quantum yield ratios mean that, in the dependence on excitation conditions, different pericyclic minima for the sigmatropic hydrogen shift are achieved (Fig. 4).

The decreasing population of the lower energy minimum in the dependence on the exciting light is very similar for isomers 1 and 2. Obviously the deactivation process leading to a diminished population of the pericyclic minimum from the Franck–Condon excited state is connected in both isomers. This can be due to a common property of the seven-membered ring, for instance a vibrational mode of the cycloheptatriene ring. Such a behaviour can be explained by assuming that the rate of the internal conversion process in S_1 is dependent on the vibronic level. This hypothesis cannot be checked at present but it is clear that different excited states are involved in the chemical deactivation of excited arylcycloheptatrienes and lead to different reaction products [5] and different rates.

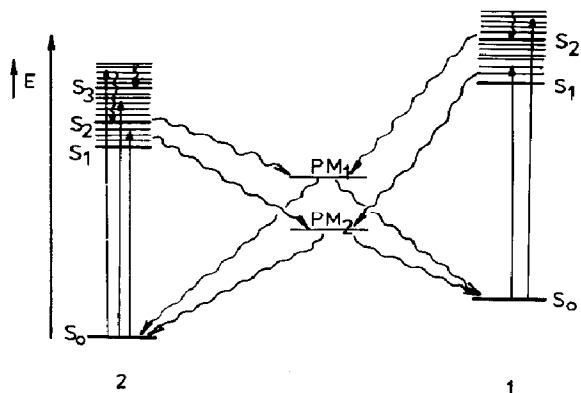


Fig. 4. A scheme for the pericyclic reaction $1 \rightleftharpoons 2$: PM, pericyclic minimum in the excited state hypersurface.

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