TRIPLET STATE PROPERTIES OF DICHLOROBENZENES

Z. B. ALFASSI[†] and C. M. PREVITALI[‡]

Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556 (U.S.A.)

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Summary

The triplet–triplet absorption spectra have been determined by laser flash photolysis for ortho, meta and para dichlorobenzene. The wavelength of maximum absorption λ_{max} was 290 nm for both the ortho and meta isomers and was 310 nm for the para isomer. The triplet decay was studied in cyclohexane and in methanol. It was found to be a function of the initial triplet concentration and the rate constants for triplet–triplet annihilation and the first-order decay were obtained. The relative triplet yields in methanol were determined by energy transfer to anthracene, and absolute quantum yields were estimated. From this and comparison with literature data for the photodecomposition quantum yields, it was concluded that the photochemically active state in methanol is the excited singlet.

1. Introduction

The photochemistry of aryl halides has been the subject of numerous papers during the last twenty years [1]. At present the main interest comes from the potential applications to synthesis and because of the importance of halogenated materials as environmental pollutants. In the case of aryl chlorides little agreement is found in the literature about the excited states involved and the detailed mechanism of the photoreactions. This is mainly due to the presence of parallel photolysis pathways which are dependent on the solvent composition [2] and to the lack of photophysical studies in different media.

In previous studies on the photolysis of dichlorobenzenes [3 - 5] the photodecomposition quantum yields were found to be strongly influenced by the position of the chlorine atoms; the ortho isomer being the most photolabile. In cyclohexane, Bunce *et al.* [5] suggest that the triplet state is

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predominantly involved in the photolysis of the meta and para derivatives. However in the case of *ortho*-dichlorobenzene a dual mechanism, singlet and triplet, seems to be operating. In order to get a further understanding of the photochemical mechanism we have undertaken a laser flash photolysis study of the three isomers of dichlorobenzene in cyclohexane and in methanol.

2. Experimental details

1,2-dichlorobenzene (Aldrich), 1,3-dichlorobenzene and 1,4-dichlorobenzene (Matheson or Fluka) were of the highest quality commercially available and were used without further purification. Cyclohexane and methanol were spectrophotometric grade and anthracene was Aldrich (purity, 99.9%). The dichlorobenzenes concentrations were in the range 0.004 - 0.02 M. Unless otherwise stated, all the solutions were deaerated by purging with oxygen-free argon.

The laser flash photolysis facility has been described elsewhere [6]. The excitation source was a Quanta Ray Nd:YAG laser with frequency quadruplication (266 nm). The excitation was at 90° to the analyzing beam and the laser beam was defocused over the ground face of 2 or 10 mm absorption cells in order to eliminate hot spots in the beam. Fresh solutions were used for each laser pulse.

Actinometry was performed with a standard solution of naphthalene in cyclohexane. The absorption of naphthalene triplet was monitored at 414 nm with narrow slits in the monochromator. A quantum yield of 0.75 and extinction coefficient of 24 500 M^{-1} cm^{-1} were taken for the naphthalene triplet [7].

3. Results and discussion

When excited at 266 nm the dichlorobenzenes show transients formed immediately after the laser flash, with a broad absorption with maxima near 300 nm (Fig. 1). The ortho and meta isomers have peaks around 290 nm and the para isomer around 310 nm. These bands are very similar to the triplet–triplet absorption of chlorobenzene [8, 9]. Only small variations which are within the experimental error were found between the spectra in cyclohexane and in methanol. The transient was diffusionally quenched by oxygen and anthracene. In the latter case the growth of the triplet of anthracene could be observed. So it can be concluded that the absorption is due to the triplet state of the dichlorobenzenes. The triplet absorption intensities were directly proportional to the laser pulse energy and decayed by a first-order process over a period of a few microseconds.

In both solvents, cyclohexane and methanol, the observed first-order rate constant of decay was found to be a function of the initial triplet
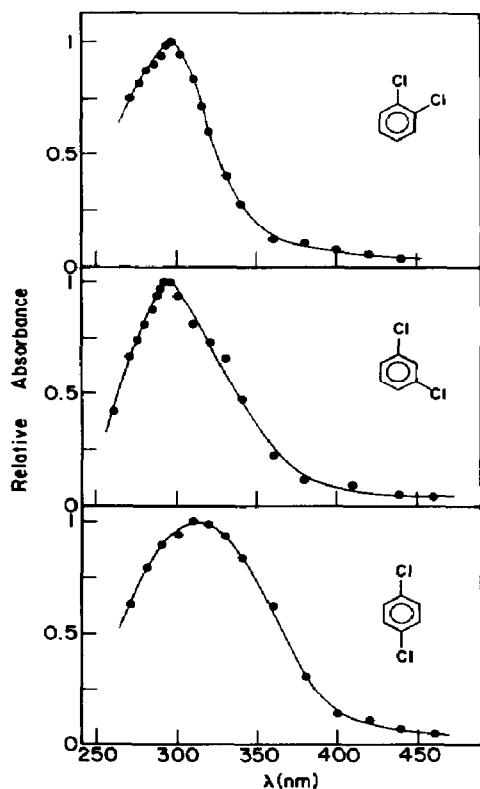
Fig. 1. Triplet–triplet absorption spectra in cyclohexane of ortho, meta and para dichlorobenzenes excited at 266 nm.

concentration. Accordingly, a kinetic analysis based on a triplet–triplet annihilation process was used. The following deactivation reactions were considered:

$$Cl_2Ph^T \xrightarrow{k_1} Cl_2Ph \qquad (1)$$

$$2Cl_2Ph^T \xrightarrow{k_2} 2Cl_2Ph \qquad (2)$$

$$Cl_2Ph^T + Cl_2Ph \xrightarrow{k_3} 2Cl_2Ph \qquad (3)$$

where Cl_2Ph^T and Cl_2Ph stand for the triplet and ground state of the dichlorobenzenes respectively. From plots of the observed initial first-order rate constant *versus* maximum absorbance k_1 and k_2/ϵ_T could be obtained [9, 10], ϵ_T being the molar extinction coefficient of the triplet state at the absorption maximum wavelengths. The k_2/ϵ_T were about the same for all three dichlorobenzenes within experimental error and the following values were obtained in both solvents:

$k_2/\epsilon_T = (1.1 \pm 0.3) \times 10^6 \text{ s}^{-1}$ cm (cyclohexane)

$k_2/\epsilon_T = (2.0 \pm 0.7) \times 10^6 \text{ s}^{-1}$ cm (methanol)

TABLE 1

First-order decay and yields of triplet states of dichlorobenzenes

	$k_1 \times 10^{-5}$ (s^{-1})		$\phi_T \epsilon_T$ (M^{-1} cm^{-1})	
	Cyclohexane	*Methanol*	*Cyclohexane*	*Methanol*
1,2-Dichlorobenzene	4.6 ± 0.5	3.6 ± 1.0	3000 ± 500	600 ± 250
1,3-Dichlorobenzene	3.7 ± 0.5	5.1 ± 0.5	3800 ± 600	2800 ± 400
1,4-Dichlorobenzene	2.3 ± 0.2	3.0 ± 0.4	4000 ± 700	3500 ± 500

The errors quoted are the standard deviations of three different measurements.

The values of k_1 are collected in Table 1. These rate constants are not much influenced by the solvent polarity. This fact contrasts with the finding for chlorobenzene, where the first-order decay is solvent dependent [11]. Within the error margin of k_1 we were not able to observe any dependence of k_1 on the dichlorobenzenes concentrations, so it can be concluded that $k_3 < 10^7$ M^{-1} s^{-1}.

The products $\phi_T \epsilon_T$, where ϕ_T is the triplet quantum yield, were determined by naphthalene actinometry. They are also shown in Table 1. In cyclohexane there is not much variation in the values and they follow the trend found by Bunce *et al.* [5] for the intersystem crossing quantum yield in this solvent.

A striking result is the low value of $\phi_T \epsilon_T$ for 1,2-dichlorobenzene in methanol. Since k_2/ϵ_T was nearly the same for the three isomers, assuming k_2 to be diffusion controlled a large variation in the ϵ_T is not to be expected. So the difference in $\phi_T \epsilon_T$ is most probably due to a much lower triplet quantum yield. In order to check this hypothesis we measured the relative triplet yields and the approximate extinction coefficients by energy transfer to anthracene.

Using anthracene concentrations in methanol in the range 10^{-4} - 10^{-5} M most of the light at 266 nm was found to be absorbed by the dichlorobenzenes. The small fraction of direct excitation was measured by blank experiments and subtracted from the experimental results.

The triplet absorption spectrum of anthracene in methanol was determined and a sharp maximum was found at 420 nm. From the growth of the absorbance of the anthracene triplet A^T at this wavelength, the rate constant for energy transfer k_4 could be obtained:

$$Cl_2Ph^T + A \xrightarrow{k_4} Cl_2Ph + A^T \tag{4}$$
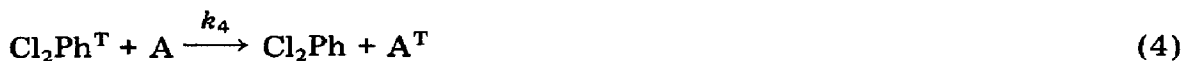
k_4 was the same for all three isomers within experimental error, with a value in agreement with that expected for a diffusion-controlled process in methanol $((2.0 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1}). The relative yields of the dichlorobenzene triplets were obtained from the following equation:

TABLE 2

Triplet yields and extinction coefficients of dichlorobenzenes in methanol as determined by energy transfer to anthracene

	Relative triplet yield	ϵ_T (M^{-1} cm^{-1})	ϕ_T	ϕ_{HCl} [a]
1,2-Dichlorobenzene	0.10	3100 ± 600	0.2 ± 0.1	0.81
1,3-Dichlorobenzene	0.65	3400 ± 400	0.8 ± 0.2	0.33
1,4-Dichlorobenzene	1.0	3800 ± 400	$0.95^{+0.05}_{-0.15}$	0.04

[a]From ref. 3.

$$[Cl_2Ph^T]_0 = \frac{OD^{\infty}_{420}}{\epsilon_A^T} \frac{k_4[A] + k_1}{k_4[A]} \tag{I}$$

where $[Cl_2Ph^T]_0$ is the initial concentration ($t = 0$) and OD^{∞}_{420} is the absorbance of the anthracene triplet at the plateau reached after the growth. From eqn. (I), even if ϵ_A^T is not accurately known, the relative yields of Cl_2Ph^T can be obtained. These relative yields are shown in Table 2. It can be seen that they confirmed that the low value of $\phi_T \epsilon_T$ in Table 1 for 1,2-dichlorobenzene is due to the low intersystem crossing and not to a low extinction coefficient.

Assuming that the extinction coefficient of A^T in methanol is the same as that in ethanol (($5.0 ± 0.5$) × 10^4 M^{-1} cm^{-1} [10]) we obtained through the use of this value for ϵ_A^T and eqn. (I) the extinction coefficients and quantum yields for the triplet states of the three isomers (Table 2).

In the last column in Table 2 we give the results of Basinski and Latowska [3] for the quantum yield of HCl formation when the three isomers are irradiated in methanol at 254 nm.

Even although the margin of error in the intersystem crossing quantum yields is high, owing to the assumptions involved, it can be seen that ϕ_T + ϕ_{HCl} is nearly unity in all three cases. This strongly suggests that the photochemically active state for producing HCl is the excited singlet for the dichlorobenzenes in methanol.

In cyclohexane Bunce et al. [5] reported a dependence of the photodecomposition quantum yields on the dichlorobenzenes concentrations. Assuming that this is due to a deactivation process of the triplet state (reaction 2), from their data and the lifetimes in Table 1, we can estimate values for k_3 of $3 × 10^6$ and $7 × 10^6$ M^{-1} s^{-1} for ortho- and meta-dichlorobenzene respectively, in agreement with our findings ($k_3 < 10^7$ M^{-1} s^{-1}). However from their value for para-dichlorobenzene, the value $4 × 10^7$ M^{-1} s^{-1} is obtained for k_3. This is beyond the margin of error of our results and the discrepancy may be due to some quenching of the singlet state in this case.

Acknowledgments

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