PHOTOPHYSICS OF CHLOROBENZENE IN CYCLOHEXANE

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Summary

The photophysical parameters of chlorobenzene in cyclohexane were determined. The fluorescence quantum yield was found to be 0.007 ± 0.0005 and the fluorescence lifetime was 0.74 ± 0.09 ns independent of the chlorobenzene concentration. The triplet state properties were studied by laser flash photolysis at an excitation wavelength of 265 or 248.8 nm. The triplet–triplet absorption spectrum with $\lambda_{max} = 300$ nm ($\epsilon_{300} = (6250 \pm 300)$ M^{-1} cm^{-1}) was obtained. The triplet decay was found to be a function of the laser intensity and a rate constant of $(7.8 \pm 1.5) \times 10^9$ M^{-1} s^{-1} was obtained for a triplet–triplet annihilation process. The triplet lifetime extrapolated at zero triplet concentration was 1.6 ± 0.1 μs independent of the chlorobenzene concentration within the experimental error. At low laser intensities and high chlorobenzene concentrations a second maximum appears at 365 nm in the transient absorption spectrum. The species responsible for this band is present immediately after the laser pulse and is very much longer lived than the triplet state. The implications of these results for the continuous photolysis mechanism of chlorobenzene are discussed.

1. Introduction

The photochemistry of chlorobenzene has been the subject of many studies, in part because of the importance of chloroaromatic compounds as environmental pollutants. However, there has been little consensus on the mechanism and nature of the excited states involved. In the gas phase photolysis [1] the excited singlet state was considered to decompose to phenyl radicals and chlorine atoms with a quantum yield of 0.4 at 253.7 nm. In contrast, the homolysis of the aryl—Cl bond in alkane solvents was proposed to occur via the triplet state [2].

The photodecomposition quantum yield in cyclohexane was found to decrease as the chlorobenzene concentration increased [2]. This was explained by a self-quenching process of the excited singlet state, which competes with intersystem crossing.

To understand the photolysis mechanism fully it is desirable to have a clear knowledge of the photophysical processes of chlorobenzene. Nevertheless, very few data concerning the primary processes in solution are found in the literature.

In a laser flash photolysis study by Lindqvist and coworkers [3] the triplet-triplet absorption spectrum and lifetime in cyclohexane were determined. A roughly first-order decay with a rate constant of 2×10^6 s^{-1} was reported. Recently Leismann et al. [4] determined the fluorescence lifetime as 0.786 ± 0.012 ns in acetonitrile. This short lifetime makes it difficult to sustain an excited singlet self-quenching mechanism in order to explain the continuous photolysis results of Bunce et al. [2].

In this paper we wish to present results on the determination of the photophysical parameters in cyclohexane which show that the excited singlet is not affected by the ground state chlorobenzene concentration and also afford a reinterpretation of the triplet state properties.

2. Experimental details

Chlorobenzene (Baker Analyzed) was further purified by fractional distillation. Cyclohexane (Fisher Spectranalyzed) was passed through an activated alumina column. Unless otherwise mentioned, all the solutions were deaerated by purging with oxygen-free nitrogen.

Fluorescence spectra were determined with a photon counting spectrofluorometer (SLM Instruments). As a result of the low fluorescence yield of chlorobenzene and the proximity of absorption and emission, the solvent Raman scattering had to be taken into account and it was eliminated by the storage and automatic subtraction of background spectra. The areas under the spectra were directly determined by addition in the photon counting mode. Corrected excitation spectra were obtained using Rhodamine B as the quantum counter. Fluorescence lifetimes were determined with a single-photon counting set-up (Photochemical Research Associates) interfaced with a PDP 11/55 multiuser computer system for deconvolution, storage and hard-copy graphics of the acquired data. Front surface excitation was employed for the more concentrated samples. The computer-controlled laser flash photolysis system has been described elsewhere [5]. For excitation at 265 nm the fourth harmonic of an Nd-YAG laser was used (Quanta Ray). Excitation at 248.8 nm was accomplished with a Kr-F$_2$ excimer laser (Tachisto). The analyzing light path was 2 mm. All experiments were carried out at room temperature.

3. Results

The fluorescence emission and excitation spectra can be seen in Fig. 1. The excitation spectrum is the same as the absorption spectrum for the band

between 275 and 240 nm, so it can be concluded that there is no wavelength effect on the fluorescence quantum yield in that area of the spectrum. In the same region the fluorescence quantum yield was found to decrease in the gas phase with decreasing excitation wavelength [6]. It was suggested that this effect could be due to non-radiative processes from various vibrational levels. In solution these states should be rapidly depopulated and therefore no such effect is observed. In addition a coarse vibrational structure of the emission spectrum is observed in cyclohexane. This is only slightly present in the gas phase spectrum [6].

We determined the fluorescence quantum yield in cyclohexane as 0.0070 ± 0.0005. Benzene was used as the standard with a quantum yield of 0.060 in cyclohexane ($\phi_F = 0.07$ [7]; $\phi_F = 0.053 \pm 0.008$ in hexane [8]). The fluorescence decay was found to be monoexponential with a lifetime value of 0.74 ± 0.09 ns. The fluorescence lifetime was independent of the chlorobenzene concentration within the experimental error quoted, for the range 0.005 - 0.04 M.

Laser pulsed excitation at 248.8 or 265 nm of chlorobenzene in deoxygenated cyclohexane produced transient absorptions with maxima at 300 and 365 nm (Fig. 2). The second maximum at 365 ns was found to increase with increasing chlorobenzene concentration and it disappears at high laser intensities (Fig. 3). Also in Fig. 3 it can be seen that the maximum at 365 nm corresponds to a much longer-lived intermediate.

The species absorbing at 300 nm corresponds to the triplet state, previously described by Lindqvist and coworkers [3]. We confirmed that it is
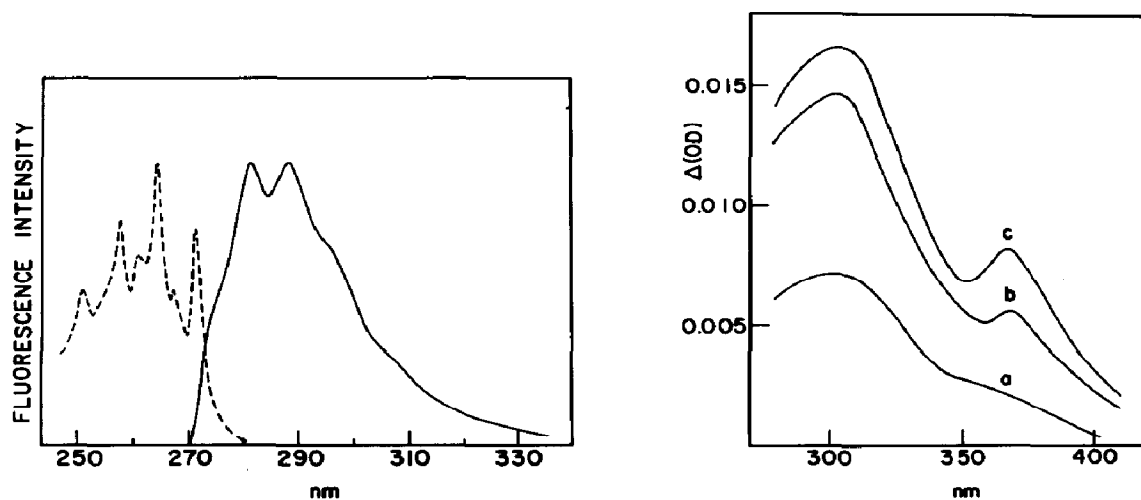

Fig. 1. Fluorescence of chlorobenzene 4×10^{-4} M in cyclohexane: — — —, excitation spectrum (spectral resolution, 1 nm; emission wavelength, 300 nm); ———, emission spectrum (spectral resolution, 2 nm; excitation wavelength, 263 nm).

Fig. 2. Transient absorption spectra (end of pulse) of chlorobenzene excited at 248.8 or 265 nm in cyclohexane at room temperature: curve a, 0.004 M; curve b, 0.01 M; curve c, 0.02 M. (The spectra have not been normalized to the number of photons absorbed.)

quenched by oxygen with a diffusional rate constant. The maximum at 365 nm is not present in the spectra taken with aerated solutions.

We obtained the extinction coefficient of the triplet at the maximum at 300 nm using naphthalene in cyclohexane as the reference. It was first established that the triplet yield was a linear function of the number of photons absorbed. Naphthalene triplet absorption was monitored at 414 nm. A value of 24 500 M^{-1} cm^{-1} was taken for the extinction coefficient at that wavelength [9]. The triplet quantum yield of naphthalene being 0.75 [9], we obtained 4000 ± 200 M^{-1} cm^{-1} for the product $\phi_T \epsilon_T$, where ϕ_T is the triplet quantum yield and ϵ_T is the triplet extinction coefficient at 300 nm for chlorobenzene in cyclohexane.

The intersystem crossing quantum yield was measured by Bunce *et al.* [2] by the sensitized biacetyl phosphorescence technique. They obtained a value of 0.64; this gives $\epsilon_T = 6250 \pm 300 \, M^{-1} \, cm^{-1}$.

The rate constants for the decay of the chlorobenzene triplet were determined for different laser intensities and different chlorobenzene concentrations. The higher the initial concentration of triplets, the higher is the initial observed rate constant. The same results were obtained by excitation at 248.8 or 265 nm. This suggests that a triplet–triplet annihilation process is taking place. Accordingly a bimolecular rate constant can be determined for this process by the method of Bensasson and Gramain [10], *i.e.* by plotting the initial observed rate constant of the triplet decay against the initial triplet T concentration:
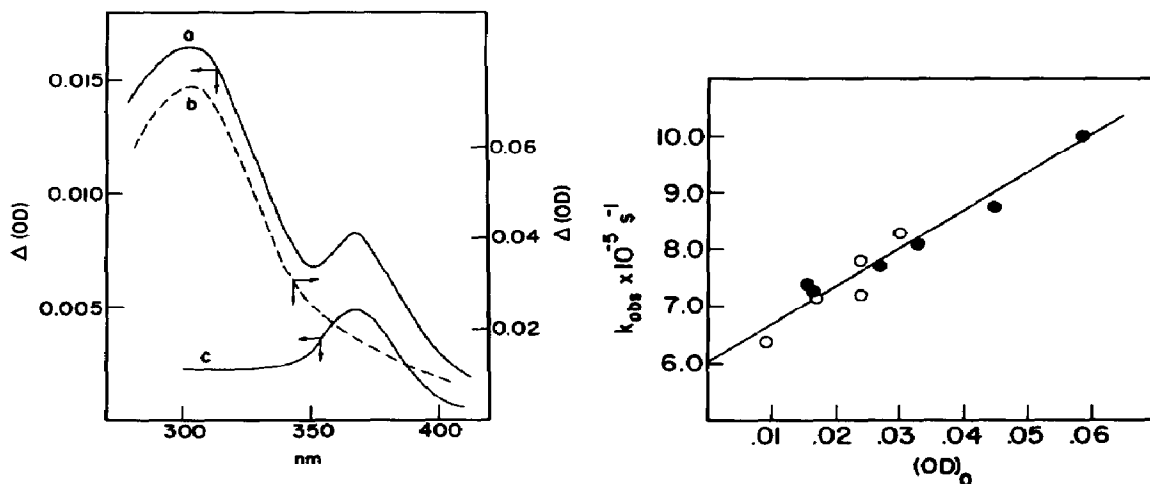

Fig. 3. Transient absorption spectra: curve a, measured immediately after the laser pulse for a 0.02 M chlorobenzene solution; curve b, obtained with the same solution but at a laser intensity about four times higher; curve c, residual of the spectrum shown in curve a measured 3 μs after the pulse.

Fig. 4. Initial rate constants for chlorobenzene triplet decay *vs.* the absorbance at the end of the laser pulse at 300 nm for chlorobenzene concentrations of 0.0043 M (○) and 0.01 M (●).

$$\left(\frac{d}{dt} \ln[T] \right)_{t \to 0} = k_1 + k_2[T]_0 \tag{1}$$

where k_1 is the rate constant for decay of the triplet chlorobenzene at a given chlorobenzene concentration and k_2 is the bimolecular rate constant for triplet–triplet annihilation. A plot in the form of the initial decay rate constant k_{obs} *versus* the end of pulse optical density OD at 300 nm can be seen in Fig. 4. Similar plots were obtained for other concentrations of chlorobenzene and, from a least-squares treatment for all of them, we found that

$$k_{obs} \ (s^{-1}) = (6.1 \pm 0.3) \times 10^5 + (6.2 \pm 1.1) \times 10^6 (OD)_0 \tag{2}$$

in the concentration range 0.004 - 0.02 M.

From the slope, using the extinction coefficient at 300 nm (optical path, 2 mm), we obtained $k_2 = (7.8 \pm 1.5) \times 10^9 \ M^{-1} \ s^{-1}$, a typical value for triplet–triplet annihilation.

4. Discussion

The primary photochemical process of chlorobenzene in cyclohexane has been established to be simple homolysis of the Cl—phenyl bond [11]. Bunce *et al.* [2] found that the quantum yield ϕ_r depends on the chlorobenzene concentration, according to the equation

$$\phi_r^{-1} = (1.94 \pm 0.08) + (21.5 \pm 2.2)[ClPh] \tag{3}$$

where ClPh stands for chlorobenzene. They suggested that the excited state from which the bond splitting occurs is the triplet state and ascribed the self-quenching process to a singlet state excimer formation.

Our value for the singlet lifetime, 0.74 ns, agrees well with that of 0.79 ns determined in acetonitrile [4]. Within our experimental error we do not find any concentration effect on the lifetime up to 0.04 M chlorobenzene. Since according to eqn. (3) we should expect a change of at least 40% in the lifetime within our concentration range, we think that the quenching of the singlet state is most improbable. However, a process involving the quenching of the triplet by the ground state is more likely.

If our value of 1.6 μs for the triplet lifetime extrapolated at zero laser intensity is used, eqn. (3) would require a quenching rate constant of 6.5 $\times$ $10^6 \ M^{-1} \ s^{-1}$. The introduction of a self-quenching process for the triplet state would render k_1 in eqn. (1) dependent on the chlorobenzene concentration:

$$k_1 = k_1^1 + k_3[ClPh] \tag{4}$$

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TABLE 1

Rate constants for excited state processes of chlorobenzene in cyclohexane

Process	Rate constant
S $\rightarrow$ ClPh + $h\nu_F$	$k_F = 9.5 \times 10^6$ s^{-1}
S $\rightarrow$ ClPh or products	$k_d = 4.9 \times 10^8$ s^{-1}
S $\rightarrow$ T	$k_{isc} = 8.6 \times 10^8$ s^{-1}
T $\rightarrow$ decay or reaction	$k_1 = 6.1 \times 10^5$ s^{-1}
T + T $\rightarrow$ 2ClPh	$k_2 = 7.8 \times 10^9$ M^{-1} s^{-1}
T + ClPh $\rightarrow$ 2ClPh	$k_3 \leqslant 6.5 \times 10^6$ M^{-1} s^{-1}

ClPh, ground state chlorobenzene; S, first excited singlet state; T, triplet state.

where $k_1{}^1$ is the unimolecular decay rate constant. A value of $k_3 = 6.5 \times 10^6$ M^{-1} s^{-1} gives a variation in k_1 of 20% in the concentration range of the laser flash experiments. We do not observe such an effect but our experimental error of at least 10% does not preclude this process from taking place.

Our results for the triplet state properties although coincident in the main features are not the same as those of Lindqvist and coworkers [3]. The differences, the failure to notice the band at 365 nm and the much shorter lifetimes, are probably due to the higher laser intensity used by these researchers.

The photophysical parameters determined in this work allow us to calculate the rate constants shown in Table 1. The low value of k_F is in agreement with the forbidden nature of the first absorption band of chlorobenzene ($\epsilon = 281$ M^{-1} s^{-1} at 264 nm in cyclohexane). We do not exclude the possibility that some photochemical process can take place from the singlet state. Especially since the second maximum shown in the spectra in Fig. 2 is already present immediately after the laser pulse, it is highly improbable that it could arise from a reaction of the triplet state. One possibility is that some product originating from the singlet state reacts with the ground state of chlorobenzene. Further work is necessary to clarify this point. The dependence of the 365 nm maximum on the laser intensity also remains to be explained.

Acknowledgments

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