VIBRATIONAL RELAXATION OF TRIPLET DICHLOROBENZENES STUDIED BY PHOTOSENSITIZED PHOSPHORESCENCE OF BIACETYL

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Summary

The photosensitized phosphorescence of biacetyl by dichlorobenzene vapour has been investigated under stationary conditions. The quantum yields of stable triplet formation for dichlorobenzenes increased with an increase in the pressure of a foreign gas (ethane or butane), suggesting that the vibrational relaxation of initially formed triplet molecules is competitive with the photodissociation of the C—Cl bond. The effect of the foreign gas pressure on the yield of stabilized triplet formation by 0—0 excitation has led to photodecomposition rate constants of dichlorobenzenes of about 10^8 s^{-1}. Step-ladder collisional relaxation processes have been postulated for the excitation at shorter wavelengths.

1. Introduction

A recent study of the 253.7 nm photolysis of chlorotoluene vapour indicated that the quantum yield of photodecomposition decreases with the pressure of ethane above 150 Torr [1]. However, the photodecomposition of monochlorobenzene vapour at 253.7 nm was insensitive to the presence of foreign gases at a pressure ranging from about 50 Torr up to 760 Torr [2]. This difference in the pressure dependence for chlorotoluene is caused by the methyl group substitution on the monochlorobenzene ring. This result suggests that an increase in the degree of internal freedom resulting from methyl substitution gives rise to the longer lifetime for the excited chlorotoluene molecules. The small value (10^{-2}) of the fluorescence quantum yield is independent of the foreign gas (ethane) pressure up to 760 Torr and the fluorescence lifetime is approximately 1 ns for excitation at a wavelength longer than 255 nm [3].

The photosensitized phosphorescence of biacetyl by triplet chlorotoluene molecules observed in the vapour phase [4, 5] suggested that the quantum yield of triplet formation is close to unity in the presence of

ethane at the limiting high pressure. These results indicate that excited singlet chlorotoluene molecules probably undergo intersystem crossing to excited triplet levels within a time of about 1 ns. The decomposition process, therefore, should compete with the relaxation of vibrationally excited triplet molecules to stable triplet molecules in the lowest vibrational level of the $\pi^*-\pi$ triplet state.

Small fluorescence quantum yields (10^{-3}) and pressure-independent fluorescence lifetimes (less than 1 ns) for dichlorobenzene vapour also indicate that the excited singlet dichlorobenzene molecules should undergo intersystem crossing to triplet levels within 1 ns [6]. A recent study on the photolyses of o- and m-dichlorobenzene at 253.7 nm has revealed that the photodecomposition quantum yields are almost independent of the ethane pressure [7]. p-Dichlorobenzene showed a different sensitivity for the pressure of a foreign gas: an increase in the photodecomposition quantum yield with an increase in the pressure of the foreign gas [8]. Time-resolved measurements of biacetyl phosphorescence sensitized by dichlorobenzene vapour excited at 266 nm along with stationary measurements of the sensitized phosphorescence intensity excited at various wavelengths have revealed that thermalized triplet molecules of dichlorobenzenes have lifetimes sufficiently long to be detected by sensitized phosphorescence [9]. In this paper we describe an investigation of the collisional relaxation of vibrationally excited dichlorobenzene molecules in the triplet state by the measurement of the phosphorescence intensity of biacetyl photosensitized by dichlorobenzene.

2. Experimental details

A conventional system was used for the observation of the phosphorescence of biacetyl photosensitized by dichlorobenzene vapour and this has been described in detail elsewhere [4, 5]. The light source for 253.7 nm excitation was a low pressure mercury lamp. The reaction cell had two flat fused silica windows and the phosphorescence was observed at right angles to the incident excitation light flux by using a monochromator-photomultiplier combination. The excitation spectra of sensitized phosphorescence were measured using a monochromatized xenon lamp for the irradiation. The relative monochromatic light intensity (half-band width, 0.2 nm) was measured over the wavelength region 280 - 250 nm to correct the excitation spectrum. Sample vapours and foreign gases (ethane and butane) were handled using a grease-free vacuum line. The pressures of the sample vapours and foreign gases were measured using a capacitance manometer. After the introduction of the sample and the foreign gas the mixture was stirred by a glass circulator for a suitable time (about 1 h). The irradiation was carried out at room temperature. Samples were renewed frequently in order to eliminate interference by photoproducts.

o- and m-Dichlorobenzene (Tokyo Kasei) were purified by repeated vacuum distillation. p-Dichlorobenzene (Tokyo Kasei) was purified by

repeated recrystallization from methanol solution. Ethane and butane (stated purity, 99.9%) were commercially available from Takachiho and were used without further purification. Biacetyl was obtained from Tokyo Kasei; it was distilled under vacuum and the middle fraction was stored in the dark at 24 °C.

The quantum yield for stable triplet formation of dichlorobenzene was determined relative to that of benzene. The experiments indicated that the phosphorescence intensity of biacetyl (0.2 Torr) photosensitized by benzene (0.97 Torr) at 253.7 nm was constant for the addition of ethane at various pressures up to 50 Torr. For the fixed pressures of benzene (0.97 Torr) and of ethane (30 Torr), the photosensitized phosphorescence intensity of biacetyl was extrapolated to the limiting high biacetyl pressure from those at low biacetyl pressures on the assumption that self-quenching effects by biacetyl are not important. The ratio of the sensitized phosphorescence intensity at the limiting high biacetyl pressure to that at the biacetyl pressure of 0.2 Torr was found to be 1.07 ± 0.04.

Similarly, for the phosphorescence sensitized by benzene, the intensity ratio of the dichlorobenzene-sensitized phosphorescence of biacetyl at the limiting high biacetyl pressure to that at the biacetyl pressure of 0.2 Torr was determined to be 2.80 ± 0.05 for o-dichlorobenzene, 1.50 ± 0.02 for m-dichlorobenzene and 1.41 ± 0.02 for p-dichlorobenzene, independent of the pressure of ethane. The ratio was also independent of the pressure of dichlorobenzene up to 2.0 Torr.

Thus, the formation quantum yield of stable triplet molecules of dichlorobenzene excited at 253.7 nm could be determined from the relative intensities of the phosphorescence of biacetyl photosensitized by benzene (0.97 Torr) and by dichlorobenzene (about 0.8 Torr), on the assumption that at the limiting high biacetyl pressure the stabilized triplet molecules transfer their excitation energy to biacetyl molecules with the same efficiency as benzene. Normally, pressures of sensitizers and biacetyl were maintained at constant values: benzene, 0.97 Torr; o-dichlorobenzene, 0.54 Torr; m-dichlorobenzene, 0.97 Torr; p-dichlorobenzene, 0.69 Torr; biacetyl, 0.2 Torr. The absorption intensities of these sensitizers at 253.7 nm were 0.006 cm^{-1} for benzene, 0.0038 cm^{-1} for o-dichlorobenzene, 0.0058 cm^{-1} for m-dichlorobenzene and 0.0045 cm^{-1} for p-dichlorobenzene. The formation quantum yield of thermalized triplet benzene is assumed to be 0.74 from the value of the fluorescence quantum yield (0.26) [10].

3. Results

3.1. Quantum yield of triplet formation of dichlorobenzene

253.7 nm irradiation of a mixture of biacetyl (0.20 Torr) and p-dichlorobenzene (0.69 Torr) in the presence of ethane (760 Torr) caused an intense phosphorescence emission from biacetyl with three vibrational peaks at 512 nm, 561 nm and 613 nm [11]. Since biacetyl vapour itself absorbs

radiation at 253.7 nm, a control experiment was performed for a mixture of suitable pressures of biacetyl and ethane. Biacetyl phosphorescence was not detectable. Therefore, the phosphorescence emission was caused by energy transfer from the excited p-dichlorobenzene molecules. This phosphorescence intensity sensitized by dichlorobenzenes varied with the pressure of added ethane. However, the intensity of the phosphorescence of biacetyl sensitized by benzene (0.97 Torr) irradiated at 253.7 nm remained constant on varying the ethane pressure from 5 to 50 Torr.

The quantum yields QY_T of triplet formation for photoexcited p-dichlorobenzene molecules can be determined relatively from a comparison of the biacetyl phosphorescence intensity sensitized by p-dichlorobenzene with that sensitized by benzene. The efficiency of energy transfer from the stable triplet sensitizer to biacetyl was assumed to be unity. Typical sensitized phosphorescence excitation and absorption spectra for dichlorobenzenes are shown in Fig. 1. Various factors, such as the excitation light
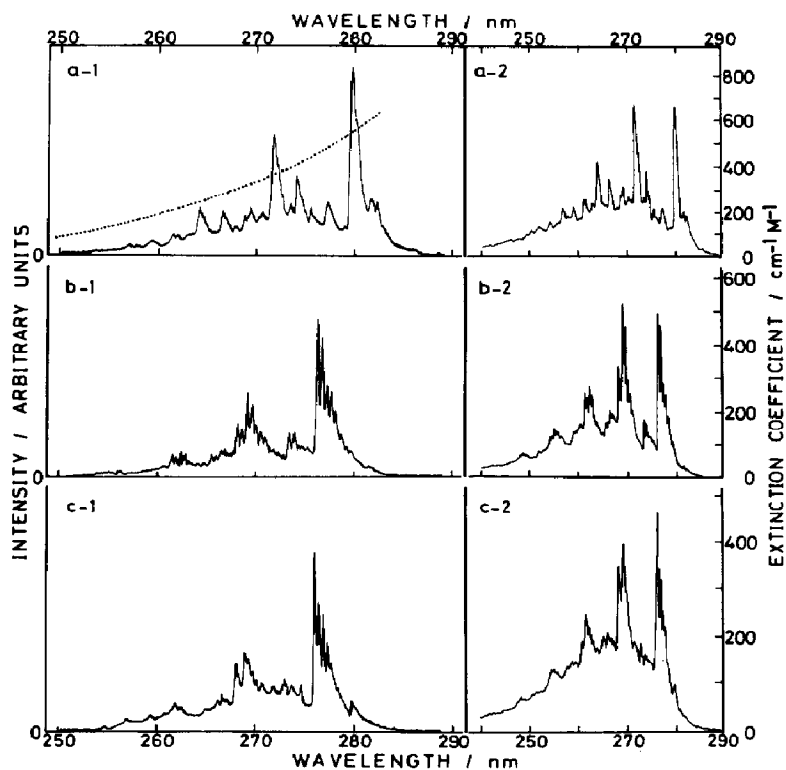

Fig. 1. Absorption spectra (curves 2) and photosensitized phosphorescence excitation spectra (curves 1) of dichlorobenzenes: curves a, p-dichlorobenzene; curves b, m-dichlorobenzene; curves c, o-dichlorobenzene. The spectral resolutions of the absorption spectra of the dichlorobenzene vapour are 0.2 nm and the intensities of the absorption spectra are normalized. The excitation band widths for the photosensitized phosphorescence excitation spectra are also 0.2 nm and the excitation spectral intensities can be normalized by using the spectral profile shown by the broken line shown with curve a-1 which was obtained from the fluorescence observed for p-terphenyl.

intensity, the absorbance of a sample or benzene vapour and the biacetyl pressure (usually 0.2 Torr) mentioned in Section 2 were taken into account for the estimation of the triplet formation quantum yield.

The value of QY_T varies with the pressure of added ethane and the wavelength of excitation. The sensitized phosphorescence excitation spectra of p-dichlorobenzene vapour were measured for various pressures of ethane. The QY_T values thus obtained are plotted against the pressure of ethane for some excitation wavelengths in Fig. 2. When the pressure of ethane increased to 760 Torr, the value of QY_T for p-dichlorobenzene excited at 279.6 nm (0−0 transition) reached a value of about 0.7.
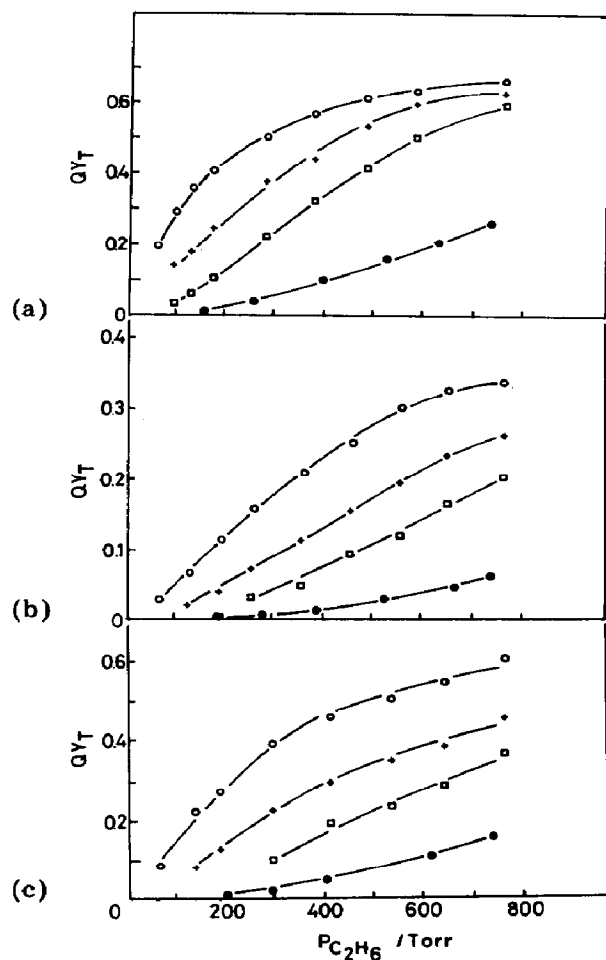

Fig. 2. Plots of stable triplet formation quantum yields QY_T against the pressure of ethane at various excitation wavelengths. (a) p-Dichlorobenzene (0.57 Torr) + biacetyl (0.20 Torr): ○, 279.6 nm (0−0 transition); +, 275.6 nm; □, 264.2 nm; ●, 253.7 nm. (b) m-Dichlorobenzene (0.93 Torr) + biacetyl (0.20 Torr): ○, 276.3 nm (0−0 transition); +, 269.1 nm; □, 262.3 nm; ●, 253.7 nm. (c) o-Dichlorobenzene (0.89 Torr) + biacetyl (0.20 Torr): ○, 275.9 nm (0−0 transition); +, 271.5 nm; □, 261.2 nm; ●, 253.7 nm. The data at 253.7 nm excitation were obtained from a measurement of dichlorobenzene-photosensitized phosphorescence emission excited by a resonance line of the low pressure mercury lamp.

A similar pressure dependence of QY_T was observed for various excitation wavelengths. Results for m- and o-dichlorobenzenes are also shown in Fig. 2. The values of QY_T for m-dichlorobenzene (Fig. 2(b)) are relatively smaller than those for p- and o-dichlorobenzene. In the excitation at shorter wavelengths, the collisional relaxation of vibrationally hot triplet molecules seems to be incomplete and the value of QY_T still shows a tendency to increase even in the presence of ethane at 760 Torr.

3.2. Photodecomposition rate of triplet dichlorobenzene molecules

The inverse of the QY_T values shown in Fig. 2 was plotted against the inverse of the ethane pressure. The plots give a straight line for those QY_T
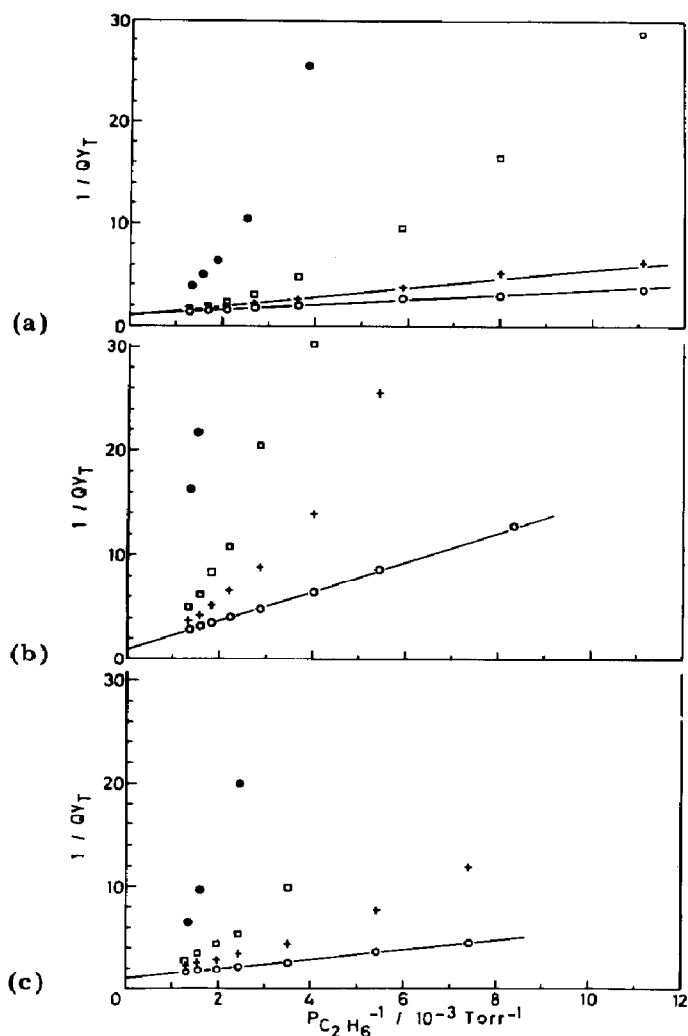

Fig. 3. Plots of the inverse of QY_T against the inverse of the ethane pressure: (a) p-dichlorobenzene; (b) m-dichlorobenzene; (c) o-dichlorobenzene. The data plotted are from the results shown in Fig. 2. The plots for 0–0 transitions and some lower excitation energies give straight lines.

values for 0–0 excitation as shown in Fig. 3. In the case of p-dichlorobenzene molecules excited at wavelengths shorter than the 0–0 transition the plots also give the linear relation. The straight line in Fig. 3 implies the validity of the relation

$$\frac{1}{QY_T} = \frac{k_d}{k_{X2}QY_{T\dagger}[X]} + \frac{1}{QY_{T\dagger}} \tag{I}$$

which can be obtained from a single-step relaxation mechanism, omitting reactions (1) and (2) from the scheme given in Section 4.1.

The intercept and the slope of this straight line lead to the value of the ratio k_d/k_{X2}. The value of k_d may be obtained as shown in Table 1 if we assume the deactivation collision frequency k_{X2} by ethane to be the same as that by propane [5] which has been derived from the collisional deactivation of the triplet benzyl chloride molecule [12]. From the straight lines in Fig. 3, single-step collisional deactivation of vibrationally hot triplet molecules of o- or m-dichlorobenzene is also expected for the 0–0 band excitation. Analogously to p-dichlorobenzene, values of k_d were estimated for m-dichlorobenzene and o-dichlorobenzene and these are listed in Table 1. The value of k_d for m-dichlorobenzene is the largest of the three isomers and the p-isomer has the smallest value.

Values of $QY_{T\dagger}$ for the 0–0 excitation are also obtained from the plots in Fig. 3 and are listed in Table 2 along with results for butane as another collision partner. The values obtained are close to unity within experimental error for all isomers.

TABLE 1

Summary of k_d/k_{X2}, k_{X2} and k_d for dichlorobenzenes in the presence of ethane

Molecule	Excitation wavelength (nm)	k_d/k_{X2} ($\times 10^{-2}$ M)	k_{X2} [a] ($\times 10^9$ M^{-1} s^{-1})	k_d ($\times 10^8$ s^{-1})
p-Dichlorobenzene	279.6	1.2	8.5	1.0
	277.2	1.9	8.5	1.6
	275.6	2.3	8.5	2.0
m-Dichlorobenzene	276.3	6.0	8.5	5.1
o-Dichlorobenzene	275.9	2.6	8.5	2.2

[a]The value of k_{X2} is assumed to be the same as the collisional quenching rate constant of propane for triplet benzyl chloride molecules. The rise time of the absorption of benzyl radicals formed by the 266 nm picosecond laser pulse photolysis in the presence of propane (120 Torr) is 4.5 ns, while the value is 6.0 ns in the absence of propane [12]. This result leads to a value of the collisional quenching rate constant for propane of 8.5×10^9 M^{-1} s^{-1}, which is smaller by a factor of 0.04 than the hard-sphere collision number of propane (2.1×10^{11} M^{-1} s^{-1}).

TABLE 2

Values of QY_T† at 0–0 excitation

Molecule	Foreign gas	
	C_2H_6	C_4H_{10}
p-Dichlorobenzene	0.91	1.0
m-Dichlorobenzene	0.91	0.98
o-Dichlorobenzene	0.96	1.0

4. Discussion

4.1. Reaction mechanism

Triplet (T*) molecules initially formed by the 253.7 nm excitation (excitation energy, 112.6 kcal mol⁻¹) have an energy of 15 kcal mol⁻¹ in excess of the C—Cl bond dissociation energy (97 kcal mol⁻¹ [13]). Even with the 0–0 excitation, p-dichlorobenzene has an excess energy of about 5 kcal mol⁻¹. Thus initially formed T* molecules can give rise to dissociation of the C—Cl bond which is competitive with non-radiative processes to the ground singlet state (S_0) or collisional relaxation to lower vibrational levels (T†). The thermalized triplet (T) molecules, stable against dissociation, presumably have longer lifetimes than vibrationally excited triplet molecules. The stable triplet state, presumably a π^*–π state, is situated at about 82 kcal mol⁻¹ above the ground state [14].

Molecules stabilized to stable triplet levels undergo either energy transfer to biacetyl or non-radiative transitions to the ground state (S_0). The self-quenching of triplet molecules by ground state dichlorobenzene molecules (M) seems to be slow and unimportant compared with the other decay processes of triplet molecules under the present experimental conditions. In the case of triplet chlorotoluene molecules the self-quenching rate is also negligible compared with the rates of energy transfer and non-radiative transitions [4].

The mechanism of the reaction of vibrationally hot triplet molecules of dichlorobenzene that are initially formed by intersystem crossing from the excited singlet state can be expressed as follows:

$$M(T^*) \xrightarrow{k_d} \text{chlorophenyl radical} + Cl \tag{1}$$

$$M(T^*) + X \xrightarrow{k_{X1}} M(T†) + X \tag{2}$$

$$M(T†) \xrightarrow{k_d} \text{chlorophenyl radical} + Cl \tag{3}$$

$$M(T†) + X \xrightarrow{k_{X2}} M(T) + X \tag{4}$$

$$M(T) + Bi(S_0) \xrightarrow{k_{ET}} M(S_0) + Bi(T) \tag{5}$$

$$M(T) \xrightarrow{k_{nr}} M(S_0) \tag{6}$$

$$Bi(T) \xrightarrow{k_p} Bi(S_0) + h\nu \tag{7}$$

For processes (5), (6) and (7) the rate constants k_{ET} and k_{nr} have been measured and this has been discussed previously [9] and $1/k_p$ has already been reported to be 1.8 ms [15]. Two-step relaxation of vibrationally hot triplet dichlorobenzene molecules has been assumed for a simplification of the reaction scheme for triplet levels of high excitation energy though there must be various step-ladder collisional relaxation processes. (Multistep collisional relaxation processes have been successfully applied to vibrationally highly excited toluene molecules in their electronic ground state [16].) The rate constants of the two collisional relaxation processes of vibrationally hot molecules should have different values but are assumed to be equal since in the present qualitative reaction scheme these values cannot be determined in a unique manner.

4.2. Vibrational relaxation of triplet dichlorobenzene molecules

From the two-step mechanism described above, a steady-state treatment gives the relation

$$QY_T = \frac{QY_{T^*}k_{X1}[X]k_{X2}[X]}{(k_d + k_{X1}[X])(k_d + k_{X2}[X])} \tag{II}$$

for QY_T. Taking the reciprocal of QY_T leads to

$$\frac{1}{QY_T} = \frac{k_d^2}{QY_{T^*}k_{X1}k_{X2}[X]^2} + \frac{k_d(1/k_{X1} + 1/k_{X2})}{QY_{T^*}[X]} + \frac{1}{QY_{T^*}} \tag{III}$$

where QY_{T^*} denotes the quantum yield of T^* formation. This quadratic equation can reproduce the relation between $1/QY_T$ and $1/[X]$. A typical example for 253.7 nm irradiation is shown in Fig. 4, but this cannot give the true rate constants. However, this fit only shows that a step-ladder collisional relaxation mechanism of T^* can qualitatively explain the relation between QY_T and $[X]$.

The results for the pressure dependence of QY_T (Fig. 2) are explained by the collisional relaxation of vibrationally excited triplet p-dichlorobenzene molecules and the increase in the population of thermalized triplet p-dichlorobenzene, whose lifetime is sufficiently long for the energy to be transferred to biacetyl [9]. Non-thermalized triplet molecules should undergo photodissociation or intersystem crossing to the ground singlet state. The derived values of the photodecomposition rate constant in Table 1 are very similar to the relative photodecomposition rate constants of chlorotoluenes. p-Chlorotoluene has the longest lifetime in the excited triplet state [1, 5].
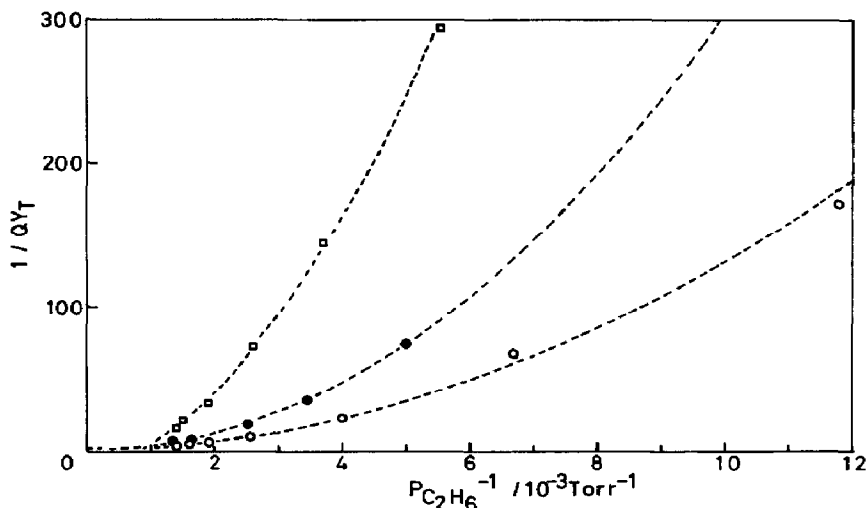
Fig. 4. Plots of the inverse of QY_T against the inverse of the ethane pressure at 253.7 nm excitation for (a) p-dichlorobenzene, (b) m-dichlorobenzene and (c) o-dichlorobenzene, all in the presence of biacetyl (0.20 Torr). The broken lines show the best fit of the quadratic function which is given by eqn. (III) in the text.

This may be explained by molecular symmetry. The longest lifetime has been also observed for the triplet state of dimethylbenzene or trimethylbenzene of highest molecular symmetry [17].

4.3. Effects of the ethane pressure on the quantum yields of photodecomposition and triplet formation

Photodecomposition quantum yields QY_d of dichlorobenzenes at 253.7 nm have been measured previously [7, 8] and are shown in Fig. 5 (broken line) together with the QY_T obtained in the present work. The value of QY_T for p-dichlorobenzene at 253.7 nm was about 0.2 in the presence of 760 Torr ethane, while QY_d had a maximum value of about 0.9 at ethane pressures higher than 200 Torr. The gradual increase in the values of the C_6H_5Cl formation quantum yield at lower ethane pressures has been interpreted as resulting from collision-induced decomposition. Thus QY_T is expected to decrease gradually with the increase in the ethane pressure up to 200 Torr if vibrationally hot triplet molecules are relaxed to the stable triplet levels with a constant probability. The value of QY_T, however, is very small (shown in Fig. 5(a)) and a quantitative comparison of the QY_T with the QY_d is not possible for these pressure ranges.

The tendency of QY_T to increase with ethane pressures higher than 200 Torr and the pressure independence of QY_d may indicate that collisional stabilization of vibrationally excited triplet dichlorobenzene molecules formed by 253.7 nm irradiation is competitive with non-radiative transitions to the ground electronic state and decomposition. The excited dichlorobenzene molecules which undergo decomposition cannot be singlet because the fluorescence quantum yields of dichlorobenzene excited at 253.7 nm
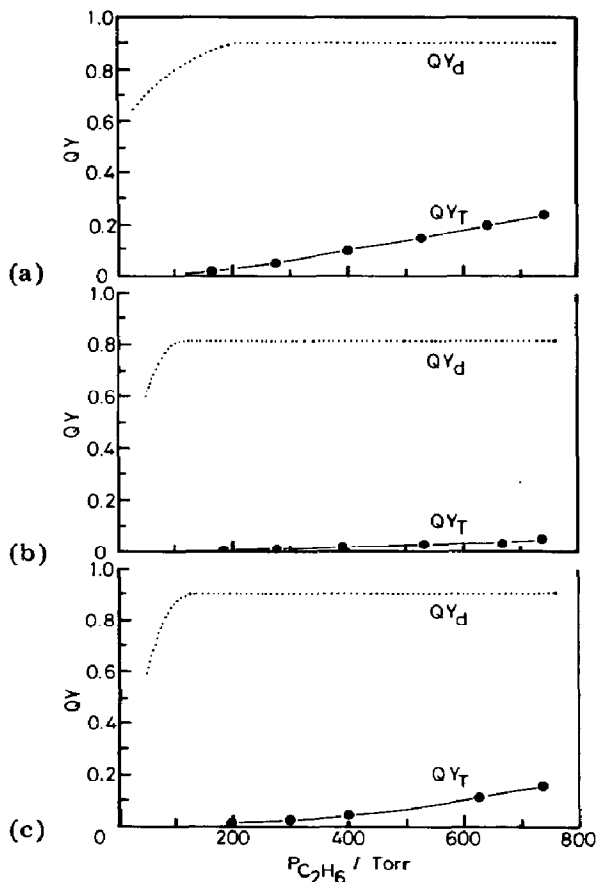
Fig. 5. Plots of quantum yields against ethane pressure at 253.7 nm excitation for (a) *p*-dichlorobenzene, (b) *m*-dichlorobenzene and (c) *o*-dichlorobenzene. QY_d, photodecomposition quantum yields taken from previous work [7, 8]. The values of QY_T were taken from the results in Fig. 2.

were very small and increase very slightly with the pressure of ethane [6]. Therefore, the increase in QY_T suggests the collisional deactivation of vibrationally excited triplet dichlorobenzene molecules that are formed by intersystem crossing from the optically excited singlet level. Values of QY_d close to unity were obtained for *o*-, *m*- and *p*-dichlorobenzene excited at 253.7 nm. Also, in Section 3.2, the quantum yields QY_T of triplet formation were shown to be near unity at the limiting high ethane pressure for all the dichlorobenzene isomers excited at 0–0 transitions. Therefore, the excited molecules at 253.7 nm mostly undergo intersystem crossing to triplet levels and then decompose to related fragments or are collisionally relaxed to lower triplet levels. The small increase in QY_T at higher ethane pressures may be involved in the large experimental errors for QY_d.

In Fig. 3, as the pressure of ethane increases, the values of $1/QY_T$ obtained with shorter wavelength excitations gradually approach the linear plots of $1/QY_T$ for the 0–0 excitation. This is indicative of values of QY_T close to unity at the limiting high ethane pressure for every dichlorobenzene

isomer and also indicates a high efficiency of intersystem crossing from the initially excited singlet state even for the excitation at shorter wavelengths. The fact that there seems to be no apparent decrease in the formation of T* with shorter wavelength excitation indicates the absence of any fast non-radiative decay channel of the photoexcited singlet state that is competitive with the intersystem crossing.

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