Photodechlorination of octachlorodibenzo-*p*-dioxin and octachlorodibenzofuran in alkane solvents in the absence and presence of triethylamine ☆

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Abstract

Octachlorodibenzo-*p*-dioxin and octachlorodibenzofuran undergo reductive photodechlorination in hexane with low chemical yield and moderate ($\phi \approx 0.01$) quantum yield. A homolytic reaction is indicated both by deuterium incorporation experiments and by kinetic studies which exclude the intermediacy of excimers. Quenching experiments suggest the involvement of both singlet and triplet reactive excited states. Photodechlorination is strongly accelerated by triethylamine (Et$_3$N), but curved plots of ϕ^{-1} vs. [Et$_3$N]$^{-1}$ imply that two reactive excited states are involved. Deuterium incorporation experiments indicate that the major reaction pathway entails partial electron transfer to form an exciplex, followed by proton transfer within the exciplex.

Keywords: Photodechlorination; Alkane solvents; Deuterium solvents; Triethylamine
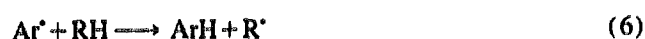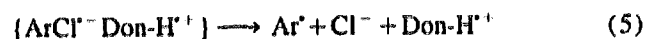
1. Introduction

The photodehalogenation of aryl halides can occur by homolysis, electron transfer or photonucleophilic substitution [1]. Homolysis, when thermodynamically favourable, affords radical intermediates which yield dehalogenation products in hydrogen donor solvents or arylation products in aromatic solvents [2] (Scheme 1).

$$Ar–Cl + h\nu \longrightarrow Ar–Cl^* \tag{1}$$

$$Ar–Cl^* \longrightarrow Ar^* + Cl^* \tag{2}$$

$$Ar^* + R–H \longrightarrow Ar–H + R^* \tag{3}$$
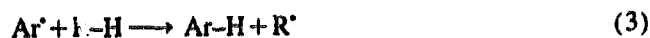
<div align="center">Scheme 1.</div>

Dechlorination can also occur by bimolecular mechanisms involving excimers [3,4] or electron donors (Don-H) such as amines [5], dienes [6,7], sulphides [8] and sodium borohydride [9]. These reactions may be initiated by photoexcitation of either the aryl halide or the electron donor [7,10] and lead to radical ions in polar solvents or to an exciplex in non-polar solvents (Eq. (4)). Dehalogenation is completed upon the loss of halide ion from the radical-anion-like partner and hydrogen abstraction by the resulting aryl

radical (Eqs. (5) and (6)) or by proton transfer and loss of a chlorine atom (Eq. (7)).

$$ArCl + Don-H \longrightarrow \{ArCl^{\cdot-} Don-H^{\cdot+}\} \tag{4}$$

$$\{ArCl^{\cdot-} Don-H^{\cdot+}\} \longrightarrow Ar^* + Cl^- + Don-H^{\cdot+} \tag{5}$$

$$Ar^* + RH \longrightarrow ArH + R^* \tag{6}$$

$$\{ArCl^{\cdot-} Don-H^{\cdot+}\} \longrightarrow \{ArClH^{\cdot}Don^{\cdot}\} \longrightarrow$$
$$ArH + Cl^- + Don^* \tag{7}$$

<div align="center">Scheme 2.</div>

The electron transfer mechanism can be distinguished from homolysis by dependence of the quantum yield of reaction on the concentration of the electron donor and often by a change in regioselectivity of dechlorination of polyhalogenated systems [11].

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are widespread and persistent environmental pollutants for which photodegradation (in the atmosphere, in water and on surfaces) has been claimed to be an important environmental sink [12]. Irradiation of octachlorodibenzo-*p*-dioxin (OCDD, 1) and octachlorodibenzofuran (OCDF, 2) in benzene–hexane (5:95 v/v) led to dechlorination [13], mainly at the lateral (2,3,7,8) positions, although a somewhat different regio-

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☆ Taken from the M.Sc. thesis of A.K.

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selectivity was observed when 1 was photolysed on surfaces [14]. The regiochemistry of dechlorination is important because it determines whether the photolysis of highly chlorinated congeners such as OCDD is likely to produce significant quantities of laterally substituted, toxic congeners such as 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD).

Less is known about the photochemistry of PCDFs. Photolysis of 2,7-dichlorodibenzofuran in methanol and hexane gave 2-chlorodibenzofuran and the parent heterocycle, along with unidentified resinous products [15]. The higher photolability of OCDF compared with less chlorinated congeners [12] was attributed to the steric hindrance of chlorines at the positions 1 and 9 of the aromatic rings, similar to that in ortho-substituted polychlorobiphenyls [16].

The goals of our research were to study photoreactions of OCDD (1) and OCDF (2) in organic solvents in the absence and presence of electron donors, principally triethylamine. This paper deals with the following issues: the material balance from OCDD under homolytic conditions; quantum efficiency and excited state multiplicity of photolysis of 1 and 2; and characterization of the electron transfer reactions of OCDD and OCDF.

2. Experimental details

High performance liquid chromatography (HPLC) grade iso-octane, methanol and dichloromethane and Spectranalysed grade cyclohexane and tetrahydrofuran (THF) were obtained from Fisher. All solvents were used as received, with the exception that THF was purified by keeping it overnight over sodium hydroxide pellets, followed by distillation in a flame-dried apparatus over sodium metal under argon. Triethylamine (Et$_3$N) was obtained from Eastman and furan from Aldrich Co. OCDD, OCDF and 1,2,4,7,8-PeCDD were purchased from Accu-Standard Co.

The light source was a Rayonet RPR photochemical reactor equipped with 16 RPR-3000 low pressure mercury lamps which emit a band at 300 nm with a bandwidth of 25 nm at half-intensity.

The products of reductive dechlorination of OCDD and OCDF were quantitated using gas chromatography–ECD (GC-ECD) equipped with J&W DB-5 capillary columns. Calibration curves were prepared for 1,2,4,7,8-PeCDD, 1,2,3,6,7,9-HeCDD, 1,2,3,4,6,7,9-HpCDD (3), 1,2,3,4,6,7,9-HpCDD (4), OCDD, 1,2,3,7,8-PeCDF, 1,2,3, 4,7,8-HeCDF, 1,2,3,4,6,7,8-HpCDF and OCDF. Similar response ratios were observed for 3 and 4 and it was assumed that other isomeric congeners had equal response ratios. 2,2',4,4'-Tetrachlorobiphenyl was used as a standard for calibration and for analysis of the photoproducts. The GC-ECD peaks were identified by gas chromatography–mass spectrometry (GC-MS) (Hewlett-Packard 5890 Series II gas chromatograph interfaced to a Hewlett-Packard model 5971 mass-selective detector).

Quantum yields of substrate disappearance (ϕ_r) were measured by potassium ferrioxalate actinometry [17] using solutions of potassium chromate and nickel sulphate [18] as a filter. The actinometer in water ($n_D = 1.33$) and the test solution in hexane ($n_D = 1.37$) were placed in 8 mm o.d. Pyrex test tubes which were placed coaxially in 25 mm o.d. Pyrex test tubes containing the optical filter. The filter transmitted in the 285–335 nm region, with maximum transmittance of approximately 20% at 313 nm. The actinometer and test solutions were irradiated simultaneously in the photoreactor using a merry-go-round to assure equal light intensity incident on all solutions. All the light was absorbed by the actinometer; the intensity absorbed by the test solution was determined in a separate experiment.

Quantum yields of intersystem crossing of 1 and 2 in cyclohexane were measured by the method of Sandros [19], in which one compares the intensity of phosphorescence of biacetyl, sensitized by either the test compound or a reference sensitizer (we used benzophenone, $\phi_{isc} = 1.00$), after correction for phosphorescence due to direct excitation of biacetyl. Measurements were made at a series of concentration of biacetyl), with the concentration of the sensitizers kept constant through the series, and adjusted so that both sensitizers absorbed the same fraction of the incident light at the excitation wavelength.

3. Results and discussion

3.1. Products and material balance

Dechlorinated congeners were the only identified products of photolysis of OCDD and OCDF (Tables 1 and 2). As found previously [20–22], the material balance from OCDD was low and decreased at higher conversion, because the further dechlorination of the primary products also occurs in low yield. No products resulting from coupling with solvent or from C–O bond cleavage were detected. The latter process had been suggested to rationalize the low product yields [23].

Several experiments were carried out to account for the low material balance upon homolysis of 1 and 2. Adsorption of product to the glass walls of the reaction ampoules was ruled out by the observation that the UV absorbance of the photolyte was associated with the solution rather than with the empty ampoule.

The possible formation of a benzyne intermediate through vicinal loss of two chlorines was explored by attempting to trap the putative benzyne with furan. Small quantities of two furan adducts were obtained. One, with m/z 488, had a pattern of seven chlorine atoms in its mass spectrum, consistent with a furan-substituted heptachlorodibenzo-*p*-dioxin. The second had m/z 454 and a pattern of six chlorine atoms in the molecular ion cluster; it might therefore represent either a benzyne intermediate trapped by furan through Diels–Alder addition (5) or an adduct of furan and the aryl radical formed by

Table 1
Material balance on photolysis of 1 (8.1 μM) in degassed hexane

	Time (min)				
	5	15	25	45	80
ΣPeCDD (10^{-7} M)		0.195		0.18	2.01
ΣHeCDD (10^{-7} M)			0.12		
3 (10^{-7} M)	0.99	2.20	2.84	2.50	1.19
4 (10^{-7} M)	0.47	0.85	0.95	0.45	0.62
1 (10^{-7} M)	76.42	56.37	34.74	16.32	4.91
Total (10^{-7} M)	77.87	59.56	38.46	19.45	8.73
Conversion (%)	5.6	30.4	57.1	79.8	93.9
Yield of reduction products (%)	32	13	8	5	5

Table 2
Material balance of photolysis of 2 (9.3 μM) in degassed hexane

	Time (min)				
	2.5	5	15	20	40
ΣPeCDF (10^{-7} M)				1.13	1.05
ΣHeCDF (10^{-7} M)	0.31	0.40	3.74	8.02	6.45
ΣHpCDF (10^{-7} M)	12.75	18.20	24.89	24.46	16.28
2 (10^{-7} M)	71.99	65.33	44.18	21.03	8.71
Total (10^{-7} M)	85.05	83.85	72.53	54.66	32.49
Conversion of 2 (%)	22.3	29.4	52.3	77.0	90.6
Yield of reduction products (%)	63	68	58	46	28

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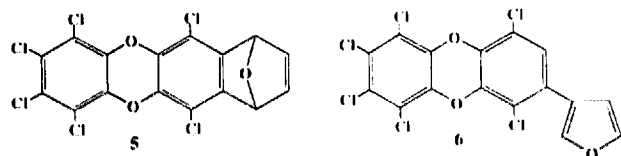
photolysis of a heptachlorodibenzo-*p*-dioxin (6). The latter structure appeared more likely, because reflux in EtOH–HCl of an isolated sample (0.2 mg) followed by treatment with diazomethane failed to give any sign of methylation product of the phenol to which 5 would rearrange, while overnight reflux in absolute ethanol–concentrated sulphuric acid (10:1) resulted in decomposition, consistent with the instability of furans in acid.

The observation of furan adducts as well as dechlorination products suggested that the aryl radicals from 1 and 2 might have an unusually high propensity to arylate rather than abstract hydrogen. Arylation of starting material could cause the apparent material balance to be low, because a dimeric product would be too involatile to observe by GC–MS (and possibly also by direct probe MS, a technique which we also tried). However, the proportions of dechlorination and phenylation upon irradiation of 1 in mixtures of benzene and cyclohexane were normal (Fig. 1), thus excluding this possibility.
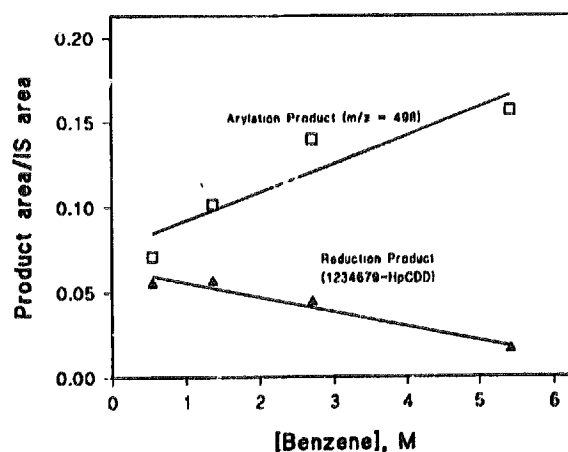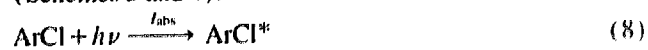

Fig. 1. Relative yields of arylation and reduction products of 1 at different concentrations of benzene.

An excimer mechanism was tested by studying the dependence of ϕ_r for 1 on the initial substrate concentration (Schemes 3 and 4).
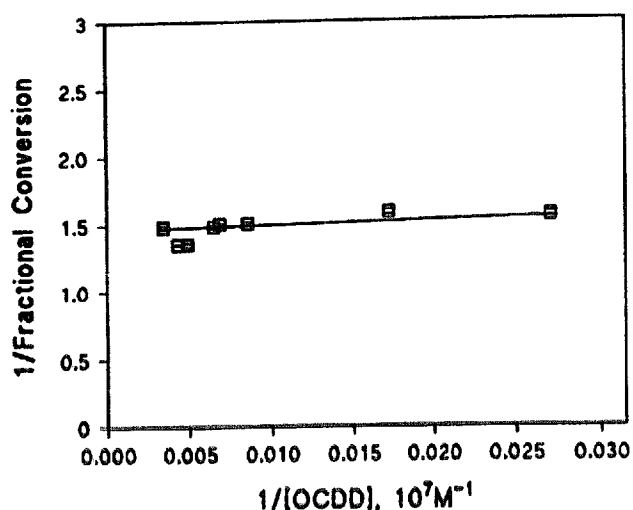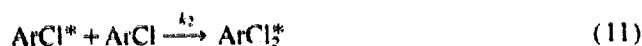
$$ArCl + h\nu \xrightarrow{I_{abs}} ArCl^* \qquad (8)$$

$$ArCl^* \xrightarrow{k_1} ArCl \qquad (9)$$

$$ArCl^* \xrightarrow{k_2} products \qquad (10)$$

Scheme 3 (homolysis).

Fig. 2. Plot of the inverse of the conversion of OCDD vs. the inverse of concentration.

$$ArCl + h\nu \xrightarrow{I_{abs}} ArCl^* \tag{8}$$

$$ArCl^* \xrightarrow{k_1} ArCl \tag{9}$$

$$ArCl^* + ArCl \xrightarrow{k_2} ArCl_2^* \tag{11}$$

$$ArCl_2^* \xrightarrow{k_3} products \tag{12}$$

$$ArCl_2^* \xrightarrow{k_4} ArCl + ArCl \tag{13}$$

Scheme 4 (excimer).

Under the conditions of low concentration necessitated by the insolubility of 1, $I_{abs} = I_0(1 - 10^{-A}) \approx 2.3I_0\epsilon l\,|ArCl|l$ and the rate of reaction by homolysis is predicted to be concentration dependent (Eq. (14)) but the fractional loss of 1 to be independent of substrate concentration (Eq. (15)).

$$\frac{-d[ArCl]}{dt} = \frac{k_2}{k_1 + k_2} 2.3I_0\epsilon l[ArCl] \tag{14}$$

$$\frac{-d[ArCl]}{[ArCl]} \Big/ dt = \frac{k_2}{k_1 + k_2} 2.3I_0\epsilon l \tag{15}$$

The analogous treatment of Scheme 4 affords Eq. (16), whose rearranged form (Eq. (17)) predicts the inverse of the fractional conversion of 1 to be proportional to the inverse of OCDD concentration.

$$\frac{-d[ArCl]}{dt} = 2\frac{k_4}{k_3 + k_4} \cdot \frac{k_2[ArCl]}{k_1 + k_2[ArCl]} 2.3I_0\epsilon l[ArCl] \tag{16}$$

$$\frac{1}{\dfrac{-d[ArCl]}{[ArCl]} \Big/ dt} = \left(1 + \frac{k_3}{k_4}\right)\left(1 + \frac{k_1}{k_2[ArCl]}\right)\frac{1}{4.6I_0\epsilon l} \tag{17}$$
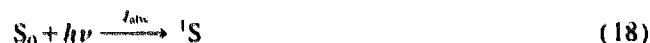
The experimental result was that the fractional conversion of 1 at constant irradiation time was independent of substrate concentration (Fig. 2), thereby excluding an excimer mechanism.

3.2. Quantum yields of reaction under homolytic conditions

Quantum yields of disappearance of 1 and 2 in degassed solutions were 0.012 ± 0.001 and 0.018 ± 0.001 respectively and decreased somewhat in the presence of air (Table 3). (This contrasts with the work of Hung and Ingram [13], who did not observe any effect of dissolved oxygen on the rate of disappearance of 1.) Our value of ϕ_r for 1 is much larger than those reported previously in water–acetonitrile (about 10^{-5} [2,13,24]) or hexane $(1.3 \times 10^{-3}$ [13]), although it is unclear from these previous reports whether the quantum yield was computed with allowance made for incomplete light absorption by 1. Higher quantum yields of dechlorination have been observed for TCDD in hexane (0.04 [25] and 0.05 [26]). To our knowledge the quantum yield of photolysis of 2 has not been previously reported.

3.3. Quantum yields of intersystem crossing

Quantum yields of intersystem crossing of 1 and 2 in cyclohexane were measured by the method of Sandros [19]. Steady state analysis of the kinetic scheme (Eqs. (18)–(24)) for sensitizing phosphorescence of biacetyl (B) by a sensitizer (S) (or equivalently by the reference sensitizer R) gave the expression for the quantum yield of phosphorescence, which for convenience is presented in reciprocal form (Eq. (25)). The ratio of the quantum yield of biacetyl phosphorescence from benzophenone (ϕ_p^R) to that from OCDD (ϕ_p^S) is given in Eq. (26).

$$S_0 + h\nu \xrightarrow{I_{abs}} {}^1S \tag{18}$$

$${}^1S \xrightarrow{k_1} S_0 \tag{19}$$

$${}^1S \xrightarrow{k_2} {}^3S \tag{20}$$

$${}^3S \xrightarrow{k_3} S_0 \tag{21}$$

$${}^3S + B \xrightarrow{k_4} S_0 + {}^3B \tag{22}$$

$${}^3B \xrightarrow{k_5} B + h\nu' \tag{23}$$

$${}^3B \xrightarrow{k_6} B \tag{24}$$

Scheme 5.

Table 3
Quantum yields of 1 and 2 in absence and presence of air

Substance	Quantum yield		
	Aerated solution	Solution degassed by N_2 bubbling	Solution degassed on a vacuum line
OCDD (1)	0.0069	0.0093	0.012
OCDF (2)	0.0062	0.0098	0.018

$$\frac{1}{\phi_p} = \left(1 + \frac{k_6}{k_5}\right)\frac{1}{\phi_{isc}}\left(1 + \frac{k_3}{k_3[B]}\right) \quad (25)$$

$$\frac{\phi_p^S}{\phi_p^R} = \frac{\phi_{isc}^S}{\phi_{isc}^R}\cdot\frac{k_4^R[B]+k_3^R}{k_4^R}\cdot\frac{k_4^S}{k_4^S[B]+k_3^S} \quad (26)$$
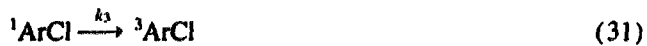
At high concentrations of biacetyl, $k_4^i[B] \gg k_3^i$ and the ratio of quantum yields (intensities) of phosphorescence is directly proportional to the ratio of quantum yields of inter-system crossing (Eq. (27)).

$$\frac{\phi_p^S}{\phi_p^R} = \frac{I_p^S}{I_p^R} = \frac{\phi_{isc}^S}{\phi_{isc}^R} \quad (27)$$

The measured values of ϕ_{isc} were 0.8 ± 0.1 for both 1 and 2, but because the reaction quantum yields are low (0.01), the photon balance does not allow us to reach a definite conclusion about the multiplicity of the reactive excited state.

3.4. Quenching experiments

Oxygen quenches most triplet excited states at close to the diffusion-controlled rate. At the equilibrium concentration of oxygen in solvents such as iso-octane and hexane, about 10^{-3} M [27], strong oxygen quenching is expected for all but the shortest-lived triplet states. In the case of 1 and 2 the quantum yields of reactions decreased only twofold to threefold when O_2 was present, suggesting either a very short-lived triplet or reaction from both singlet and triplet states. Quenching experiments with ferrocene ($E_T = 41$ kcal mol^{-1} [28]) favour the second explanation, in that the plot of ϕ_0/ϕ_q vs. [ferrocene] was curved (Eqs. (28)–(35) and Fig. 3). At 300 nm the absorbance of ferrocene was negligible at the concentration selected.

$$ArCl + h\nu \xrightarrow{I_{abs}} {}^1ArCl \quad (28)$$

$${}^1ArCl \xrightarrow{k} ArCl \quad (29)$$

$${}^1ArCl \xrightarrow{k_2} products \quad (30)$$

$${}^1ArCl \xrightarrow{k_3} {}^3ArCl \quad (31)$$

$${}^1ArCl + Q \xrightarrow{k_4} ArCl + Q^* \quad (32)$$

$${}^3ArCl \xrightarrow{k_5} ArCl \quad (33)$$

$${}^3ArCl \xrightarrow{k_6} products \quad (34)$$

$${}^3ArCl + Q \xrightarrow{k_7} ArCl + Q^* \quad (35)$$

Scheme 6.

Application of steady state kinetics gave the ratio ϕ_r^0/ϕ_r^q for 1 in the absence and presence of quencher (Eq. (36)), where $\tau^1 = (k_1 + k_2 + k_3)^{-1}$ and $\tau^3 = (k_5 + k_6)^{-1}$.

$$\frac{\phi_r^0}{\phi_r^q} = \frac{(1 + k_4[Q]\tau^1)(1 + k_7[Q]\tau^3)}{1 + \frac{k_2k_7[Q]\tau^3}{k_2 + k_3k_6\tau^3}} \quad (36)$$
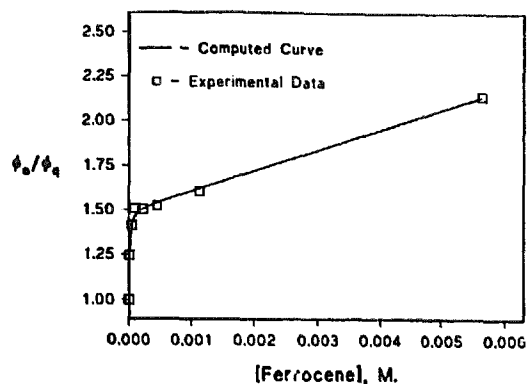

Fig. 3. Curve-fitting of the data of quenching experiment to Eq. (37).

Eq. (36) has the form of Eq. (37), where $y = \phi^0/\phi^q$, $a = k_4\tau^1$, $b = k_7\tau^3$ and c corresponds to constants in the denominator of Eq. (36).

$$y = \frac{(1 + a[Q])(1 + b[Q])}{1 + c[Q]} \quad (37)$$

Curve fitting using the modelling software package FIGURE-P afforded the coefficients $a = 76 \pm 3$, $b = 169\,200 \pm 32\,000$ and $c = 113\,000 \pm 22\,000$, $r = 0.998$, consistent with two reactive excited states, and the plausible hypothesis that one (the triplet) is much longer-lived than the other. Note that a triplet-only reaction ($k_2 = 0$), but with quenching of both ^{1}ArCl and ^{3}ArCl, would give an upward-curving parabola in place of Eq. (36); this does not fit the experimental data. At high concentration of quencher, efficient quenching of the singlet state prevents population of the triplet and an excellent fit to a straight line was observed (slope 116 M^{-1} $= ab/c$, $r = 0.999$).

Excited state lifetimes of PCDDs and PCDFs have not yet been reported experimentally, although the triplet lifetime of the parent dibenzo-p-dioxin was claimed to be very short (less than 1 ns [29]). Evidence for a relatively long triplet lifetime for 1 was obtained in the course of measuring ϕ_{isc}, when it was found that at low concentrations of biacetyl the apparent values of ϕ_{isc} exceeded unity and increased as the concentration of biacetyl decreased. Under these conditions the inequality $k_4^1[B] \gg k_3^1$ is no longer valid, Eq. (26) cannot be simplified to Eq. (27) and there are three parameters which depend on the identity of the sensitizer: ϕ_{isc}, k_3 and k_4. If we assume that the rate constants in Eq. (26) for sensitization of biacetyl by 1 and benzophenone are of the same order of magnitude, the quantum yield of phosphorescence becomes inversely proportional to k_3 ($= 1/\tau^3$) and ϕ_p is directly pro-portional to the triplet lifetime of the sensitizer. Hence a greater intensity of sensitized phosphorescence by 1 indicates that the triplet lifetime of OCDD in solution is significantly longer than that of benzophenone ($\tau^3 = 10$ ns [27]).

3.5. Photolysis of OCDD and OCDF in the presence of triethylamine

Photodechlorinations of chloroaromatic compounds in the presence of electron donors [5,30] show a characteristic

dependence of ϕ_r upon donor concentration: ϕ^{-1} vs. [Don-H]$^{-1}$. Often an electron transfer mechanism leads to a change in the regioselectivity of the dechlorination products compared with homolysis, as seen for pentachlorobenzene [3], 1,2,3,5-tetrachlorobenzene [11] and several tetrachloro-substituted naphthalenes [4] upon photolysis in the presence of triethylamine, and for polychlorobiphenyls, which lose ortho chlorine atoms upon homolysis but exhibit preferential loss of the para substituents in the presence of sodium methyl siliconate [31].

Triethylamine significantly enhances the photodecomposition of OCDD and OCDF (Tables 4 and 5). At a given [Et$_3$N] (Tables 6 and 7) the disappearance of 1 and 2 followed pseudo-first-order kinetics because of incomplete light absorption by the substrate (Fig. 4); ϕ_r increased from 0.0093 in the absence of amine (degassed by nitrogen bubbling) to 0.298 at [Et$_3$N] = 0.233 M for 1 and from 0.0098 ([Et$_3$N] = 0) to 0.687 ([Et$_3$N] = 0.192 M) for 2. Higher material balances were observed in the amine-assisted photolyses compared with the direct photolyses (Tables 4 and 5), reaching 90% for 2 in the presence of 0.19 M Et$_3$N.

Although the Et$_3$N-assisted photodechlorination of 1 was strongly quenched by molecular oxygen, suggesting the involvement of a triplet exciplex, the curvature of the double reciprocal plots ϕ_r^{-1} vs. [Et$_3$N] (for both 1 and 2) is not consistent with reaction from only one excited state. This is consistent with Scheme 7: direct homolysis is not included in this scheme, because the quantum yields of unassisted

Table 4
Yields of lower chlorinated PCDDs in Et$_3$N-assisted photolysis of OCDD

	[Et$_3$N] = 0.0023 M				[Et$_3$N] = 0.23 M		
	Time (min)				Time (min)		
	2	5	15	25	1	3	5
Conversion of 1 (%)	16	53	73	89	66	92	99
Yield of less chlorinated PCDDs (%)	19	27	16	21	62	67	59

Table 5
Yields of lower chlorinated PCDFs in Et$_3$N-assisted photolysis of OCDF

	[Et$_3$N] = 0.0019 M				[Et$_3$N] = 0.192 M		
	Time (s)				Time (s)		
	20	60	120	300	10	20	35	55
Conversion of 2 (%)	23	34	80	96	42	59	88	97
Yield of less chlorinated PCDFs (%)	70	57	24	8	77	94	89	63

Table 6
Quantum yields of disappearance of 1 at various concentrations of Et$_3$N

[Et$_3$N] (10^{-2} M)	0.065	0.11	0.12	0.22	0.43	1.08	2.16	5.39
$\phi \times 10^2$	0.85 ± 0.12	1.08 ± 0.28	1.29 ± 0.03	2.54 ± 0.14	3.18 ± 0.70	7.97 ± 3.65	10.92 ± 1.11	20.33 ± 0.1

Table 7
Quantum yields of disappearance of 2 at various concentrations of Et$_3$N

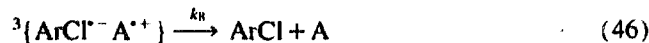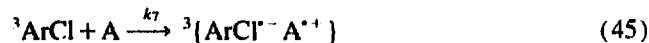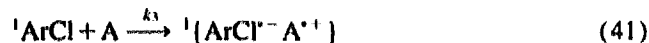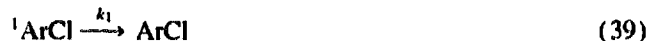| [Et$_3$N] (10^{-2} M)	0.061	0.15	0.31	0.76	1.53	3.82	7.65
$\phi \times 10^2$	2.02	3.65	4.98	9.26	20.18	28.65	33.08
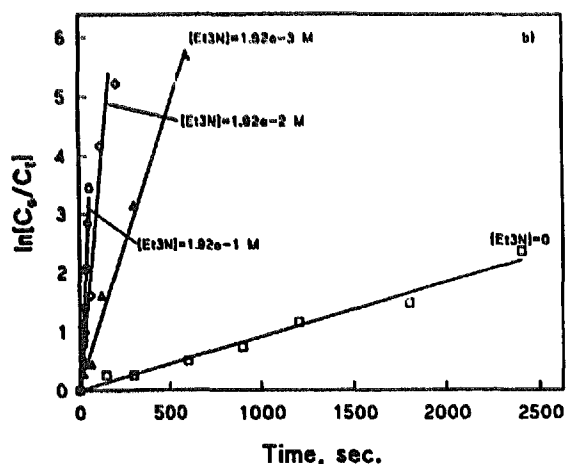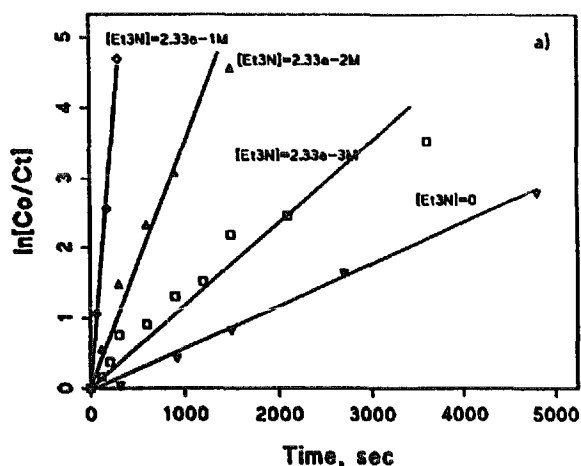
Fig. 4. Pseudo first-order plots of disappearance of (a) OCDD and (b) OCDF at different concentrations of triethylamine.

reactions were negligible compared with those of the assisted reaction.

$$ArCl + h\nu \xrightarrow{I_{abs}} {}^1ArCl \tag{38}$$

$${}^1ArCl \xrightarrow{k_1} ArCl \tag{39}$$

$${}^1ArCl \xrightarrow{k_2} {}^3ArCl \tag{40}$$

$${}^1ArCl + A \xrightarrow{k_3} {}^1\{ArCl^{-} A^{+}\} \tag{41}$$

$${}^1\{ArCl^{-} A^{+}\} \xrightarrow{k_4} ArCl + A \tag{42}$$

$${}^1\{ArCl^{-} A^{+}\} \xrightarrow{k_5} products \tag{43}$$

$${}^3ArCl \xrightarrow{k_6} ArCl \tag{44}$$

$${}^3ArCl + A \xrightarrow{k_7} {}^3\{ArCl^{-} A^{+}\} \tag{45}$$

$${}^3\{ArCl^{-} A^{+}\} \xrightarrow{k_8} ArCl + A \tag{46}$$

$${}^3\{ArCl^{-} A^{+}\} \xrightarrow{k_9} products \tag{47}$$

Scheme 7.

A predominantly singlet ($k_7 = 0$) or predominantly triplet ($k_3 = 0$) reaction would lead to a linear relationship between ϕ^{-1} and $[A]^{-1}$ (Eqs. (48) and (49)).
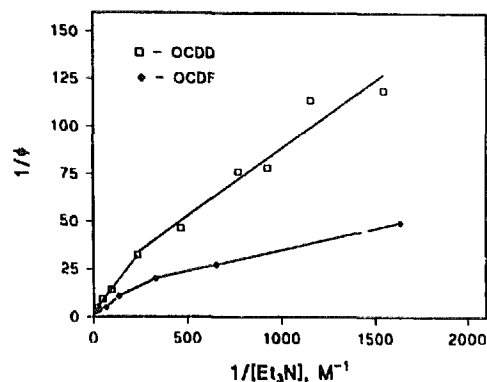

Fig. 5. Double reciprocal plot of ϕ and $[Et_3N]$ in photolysis of 1 and 2 in iso-octane.

$$\frac{1}{\phi} = \left(1 + \frac{k_4}{k_5}\right)\left(1 + \frac{1}{k_3\tau^1[A]}\right), \quad \tau^1 = (k_1 + k_2)^{-1} \tag{48}$$

$$\frac{1}{\phi} = \left(1 + \frac{1}{k_2\tau^1}\right)\left(1 + \frac{k_8}{k_9}\right)\left(1 + \frac{1}{k_7\tau^3[A]}\right), \quad \tau^3 = k_6^{-1} \tag{49}$$

When both singlet and triplet exciplexes are involved, the relationship is non-linear (Eq. (50)), consistent with the present work (Fig. 5).

$$\frac{1}{\phi} = \frac{(k_1 + k_2 + k_3[A])(k_6 + k_7[A])}{k_2\alpha k_7[A] + k_3\beta[A](k_6 + k_7[A])}$$

$$\alpha = \frac{k_9}{k_8 + k_9}, \quad \beta = \frac{k_5}{k_4 + k_5} \tag{50}$$

A slight change in regiochemistry was observed when 1 was photolysed in the presence of triethylamine. The ratio 3:4 changed gradually from about 3:1 ($[Et_3N] = 0$) to about 6:1 at $[Et_3N] = 0.023$ M (however, ratios as high as 9:1 have been observed previously [32]). In the photolysis of 2 under degassed conditions 1,2,3,4,6,7,8-HpCDF was the only primary product regardless of the presence of amine, but in aerated solutions of 2 all four heptachlorodibenzofurans were formed in comparable amounts. A somewhat parallel observation was made by Hileman et al. [33], who found that four HpCDFs were formed upon photolysis of 2 at 254 nm but only one when the irradiation wavelength was changed to 375 nm.

Three distinct reaction pathways may follow complete or partial transfer of an electron from Et_3N to the photoexcited substrate. The radical-anion-like species may lose Cl^- (Scheme 2, Eq. (5)), affording an aryl radical which can abstract a hydrogen atom from the solvent. Alternatively, it may be protonated, either by the amine partner ($Don-H^{+}$) or by an external proton source, followed by loss of a chlorine atom from the resulting cyclohexadienyl radical (Eq. (7)). These mechanisms are distinguishable by deuterium incorporation experiments. Irradiation of OCDD in cyclohexane-d_{12} resulted in greater than 99.9% incorporation of deuterium into the primary photoproducts 3 and 4 when the amine was absent, consistent with homolytic dechlorination. In the pres-
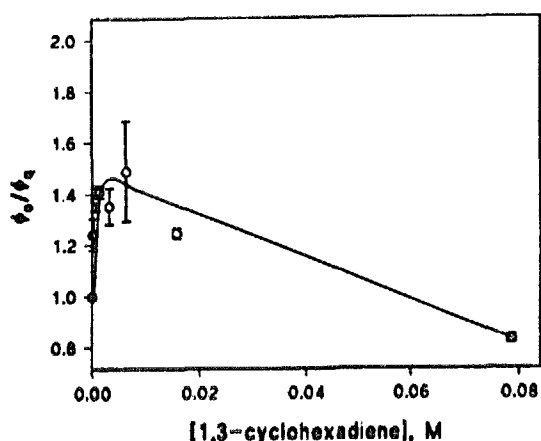
Fig. 6. Dependence of the relative quantum yield of disappearance of 1 (ϕ_o/ϕ_q) on the concentration of 1,3-cyclohexadiene.

ence of Et_3N less than 4% deuterium was incorporated into 3 (and about 14% into 4), indicating that electron transfer from Et_3N followed by proton transfer within the exciplex is the predominant reaction pathway. Analogous results were obtained for 2, with 97% incorporation of deuterium into 1,2,3,4,6,7,8-HpCDF in the absence of Et_3N and less than 2% when [Et_3N] = 0.05 M.

The change in regioselectivity led us to examine other routes for electron-transfer-assisted dechlorination of 1. Photolysis in the presence of N,N-dimethylaniline (DMA; which absorbed all the light) in iso-octane gave 3:4 in the ratio 2:1 and chemical yield 20%–30% over the conversion range 20%–90%. In cyclohexane-d_{12} there was 8% incorporation of deuterium into 3 and 17% into 4. Again the low incorporation of deuterium implies proton transfer from DMA within the solvent cage, comparable with the results of Döpp and Heuber [34], who found that photolysis of halobenzenes with $PhN(CD_3)_2$ afforded benzene-d_1.

Dechlorination via the radical anion of 1 was also observed thermally by reacting 1 with the radical anion formed from lithium and 4,4'-di-$tert$-butyl-biphenyl [3]. The ratio of primary products (3:4) was 1.25:1. In this aprotic system, dechlorination cannot be completed by proton transfer to the radical anion and so the chemical yield was low (8%).

3.6. Photolysis of 1 with 1,3-cyclohexadiene

1,3-Cyclohexadiene (CHD) can function as either a triplet quencher (E_T = 51.4 kcal mol^{-1} [27]; e.g. in the photolysis of pentachlorobenzene [2]) or as a singlet state electron transfer sensitizer (e.g. in the photodehalogenation of 9,10-dibromoanthracene [6]). Both functions were seen when 1 was photolysed in hexane in the presence of CHD: ϕ_r fell at low concentrations of CHD, consistent with triplet quenching, but rose again at [CHD] > 0.003 M (Fig. 6). The regioselectivity also changed, with 4 becoming the predominant photoproduct (Fig. 7) at higher [CHD], as observed previously for other dienes [13]. This change in regioselectivity
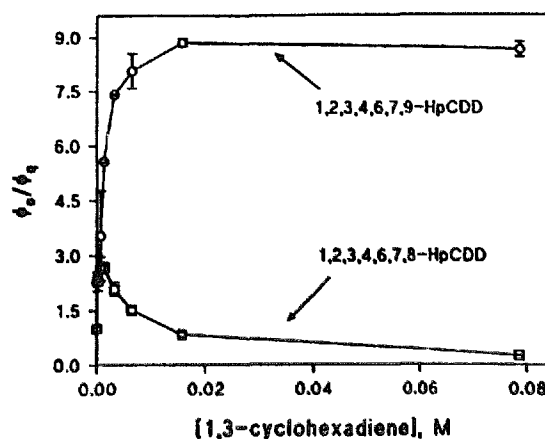

Fig. 7. Dependence of the relative quantum yields of primary products of photolysis of 1 (ϕ_o/ϕ_q) on the concentration of 1,3-cyclohexadiene.

differs from that observed with Et_3N, which enhances the production of 3.

When 1 was irradiated in cyclohexane-d_{12} in the presence of 0.01 M CHD, approximately 30% of primary photodechlorination products contained deuterium. The major portion of the product therefore arises by an electron transfer reaction in which the radical-anion-like moiety from 1 accepts a proton from diene in a solvent cage.

Acknowledgements

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