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THE SENSITIZED PHOTODEHYDROCHLORINATION OF POLY(VINYL CHLORIDE)—II

MODEL COMPOUND STUDIES

S. Hirayama, R. J. Foster, J. M. Mellor, P. H. Whitling, K. R. Grant and D. Phillips
Department of Chemistry, The University, Southampton, S09 5NH England

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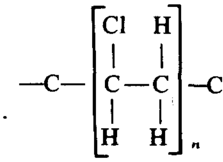
Abstract—p-Cresol, a model compound for an additive shown previously to be a potent photosensitizer of dehydrochlorination in poly(vinyl chloride) PVC, has been shown to sensitize dehydrochlorination in t-butyl chloride, a model for PVC. A quantitative study of the effect of chlorinated alkanes upon the fluorescence of p-cresol in solution reveals that quenching is due to charge transfer interactions, the halogenated compound acting as electron acceptor. Since the mono-halo compound t-butyl chloride does not quench p-cresol fluorescence, it was concluded that the photosensitization occurs via the triplet state of the p-cresol, and this view was confirmed by addition of triplet quenchers. A mechanism for the reaction is proposed, initial exciplex formation being followed by electron transfer.

INTRODUCTION

It has been shown[1] that a component of a commercial thermal anti-oxidant formulation for poly(vinyl chloride) (PVC) acts as a potent photosensitizer of dehydrochlorination accompanied by discoloration. The active species was identified as a p-alkyl substituted phenol, and we report here studies on the use of a model compound, p-cresol, to simulate the action of the commercial additive.

The threshold wavelength for the direct photodehydrochlorination of PVC has been put at 300 nm[2] and 340 nm[3, 4], indicating the dependences of photodecomposition upon method of preparation and pretreatment. Features of this photosensitization have been reviewed[5]. Since alkyl chlorides do not absorb radiation above 200 nm, the photodehydrochlorination results from sensitization by some other species. Polyene unsaturates produced on thermal processing have been implicated[4, 6] in the 'pure' polymer, but added benzophenone and carbonyls in the form of co-polymer have been shown[7] to act as efficient photosensitizers. Because of the complexity of the polymer, attempts have been made to gain an insight into the photodehydrochlorination by use of models for PVC. The basic unit of PVC is shown below, leading to the use of 2,4-dichloropentane as a model for



$$-C-\left[\begin{array}{ccc} Cl & & H \\ | & & | \\ C & - & C \\ | & & | \\ H & & H \end{array}\right]_n-C- \quad \text{where } n = 1 \text{ to } 10[7]$$

the repeat unit[8], and 4-chloro-2-butanone as a model sensitizer for oxidized PVC[8].

Sec-butylchloride is also a reasonable model for the basic PVC unit[3, 9], and t-butyl chloride provides a model for sites in the polymer which arise from branching and crosslinking[9]. 2-Methyl-2-chlorobutane has also been used in this regard[10], and unsaturated chlorinated hydrocarbons have also been used to mimic partially dehydrochlorinated PVC[10]. In the present work *sec*-butylchloride and t-butyl chloride have been used as model compounds.

For sensitization of the reaction, acetone[2] and alkyl aryl ketones[9] have been used previously. In the present case benzophenone and p-cresol were employed.

EXPERIMENTAL

Cast films of PVC were made by making a solution of PVC with or without additives in tetrahydrofuran (THF) by shaking for 24 hr. The solution was left to stand for a further 24 hr to remove air bubbles, and films were cast by pouring into the cavity of a brass mould, the THF being left to evaporate slowly. The films were of good optical quality. Irradiations of the films were carried out using a Hanovia SH100 mercury lamp with a collimated beam passing through a Corning CS 7–54 filter.

Degassed solutions of model compounds *sec*-butyl chloride or t-butyl chloride plus sensitizer were photolysed in a quartz cell using a medium pressure mercury lamp. Volatile products were analysed by GLC using a 10 m silver nitrate/ethylene glycol column with a 2 m precolumn of 20% TCEP on chromosorb W using a Becker 400 instrument with flame-ionization detection. Other products were separated on a 5 m FFAP 5% column on a Pye-Unicam 104 instrument with flame-ionization detection.

The studies on the effect of triplet quenchers were carried out on a merry-go-round photochemical reactor, using n-pentane as an internal standard for GLC estimation.

u.v. Absorption measurements were made on Hilger SP700 or Perkin–Elmer 402 spectrophotometers. Fluorescence spectral quantum yield measurements were made on a Farrand Mk. 1 spectrofluorimeter. Fluorescence decay times were measured using the time-correlated single-photon counting method on an apparatus described adequately elsewhere[11].

Materials

p-Cresol (B.D.H. Ltd) was purified by twice distilling under reduced pressure and collecting the middle fraction (98°, 20 torr). Benzophenone obtained ultrapure from B.D.H. Ltd was used without purification. *sec*-Butyl chloride (Koch-Light Laboratories Ltd) was purified by distillation at 68° and washing with alkaline $KMnO_4$[2]. *t*-Butyl chloride (Koch-Light Laboratories Ltd) was treated as for *sec*-butyl chloride except distillation was at 52°. But-2-enes (Air Products Ltd) *cis* and *trans* isomers were obtained in lecture bottles. Each isomer contained only the other as impurity to a small (0.07%) extent and were used from the cylinder. But-1-ene contaminated by but-2-enes, was prepared for use as a GLC standard by addition of sulphuric acid (100 ml, 4 M) to 1-butanol (25 ml) and refluxing for 3 hr before collection of volatile products over salted ice/water.

Other materials were stock laboratory chemicals.

RESULTS AND DISCUSSION

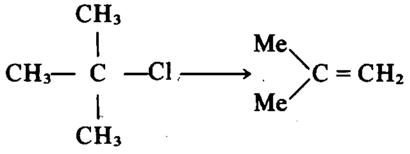
Sensitized dehydrochlorination of PVC

An earlier report[1] described the isolation of a phenol component of a commercial stabilizer formulation capable of acting as a photosensitizer of dehydrochlorination of PVC. It was identified as a *p*-substituted nonyl phenol from its u.v.-spectrum (λ_{max} 279 nm, $E = 305\ l\ \text{mole}^{-1}\ \text{cm}^{-1}$) proton NMR ($\tau$ 3.2–6.4/4H, τ 3.4/1H, τ 7.9–9.2/19H), and the mass-spectral data given in Table 1. The effect of this phenol in producing discoloration through photosensitized dehydrochlorination is shown in Fig. 1 compared with that of *p*-cresol, showing that *p*-cresol reproduces well the action of phenolic additives in the polymer.

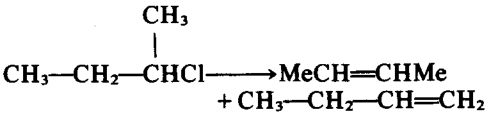
The results discussed below arise from attempts using model compounds to establish a mechanism for the photosensitizing action of *p*-cresol. Earlier work using aliphatic and aromatic ketones as sensitizers is explicable in terms of the triplet state of the carbonyl compound being the active state[3, 9]. In the case of *p*-cresol, either singlet or triplet states could be responsible. We thus studied briefly the triplet benzophenone sensitized decomposition of *sec*-butyl chloride for reference.

Benzophenone sensitization

Neat solutions of 0.5% benzophenone in *sec*-butyl chloride were irradiated in the merry-go-round in sealed ampoules. GLC analysis revealed the presence of *cis* and *trans* but-2-ene and but-1-ene volatile products in the ratio 2:1:0.9 Calibration of the merry-go-round using ferrioxalate actinometry[12] gave the approximate quantum yield for the formation of total olefins as 0.01, which compares favorably with the quantum yield of HCl production in the benzophenone-*t*-butyl chloride system of 0.02[9]. In the latter case, the major product is 2-methyl propene, the overall reaction being represented by (1). Similarly, the overall reaction in the case of


(1)

sec-butyl chloride is represented by (2)


$$CH_3-CH_2-CH(CH_3)Cl \longrightarrow MeCH{=}CHMe + CH_3-CH_2-CH{=}CH_2 \qquad (2)$$

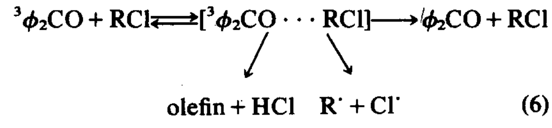
Early attempts to describe the mechanism of (1) and (2) assumed the initial steps (3)–(5)[5], with the hydrogen abstraction reaction (5) initiating the

$$\phi_2CO + h\nu \longrightarrow {}^1\phi_2CO \qquad (3)$$

$${}^1\phi_2CO \longrightarrow {}^3\phi_2CO \qquad (4)$$

$${}^3\phi_2CO + RCl \longrightarrow \phi_2\dot{C}OH + R'Cl\cdot \qquad (5)$$

dehydrochlorination sequence. The experiments of Harriman *et al.*[9] argue powerfully against such an initiation however, and there is good evidence for the formation of a charge-transfer complex between the triplet aromatic ketone formed through (3) and (4) and the chloro compound, resulting ultimately in loss of HCl or $Cl^{\cdot}$ from the substrate (6).


$$ {}^3\phi_2CO + RCl \rightleftharpoons [{}^3\phi_2CO \cdots RCl] \longrightarrow {}^1\phi_2CO + RCl;\quad [{}^3\phi_2CO \cdots RCl] \longrightarrow \text{olefin} + HCl;\quad [{}^3\phi_2CO \cdots RCl] \longrightarrow R^{\cdot} + Cl^{\cdot} \qquad (6)$$

It should be noted that in proposing charge transfer, Harriman *et al.*[9] base their argument on a linear relationship between $\log_{10} k_Q$ and $(-E_T - E_{A-/A})$ implying the alkyl chloride acts as electron donor. For many other sensitizers and chlorinated substrates[13, 14], including the case of the

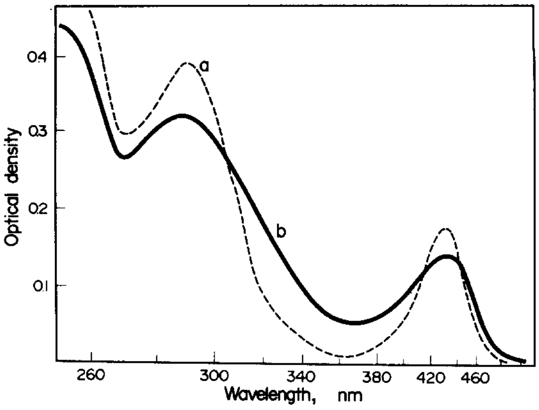


Fig. 1. Effect on u.v. absorption spectrum of PVC film of (a) *p*-cresol 1% (b) Commercial additive, 1% concentration containing unspecified amount of nonyl-phenyl, upon irradiation. Irradiation times (a) 20 min, (b) 120 min.

Table 1. Mass spectrum of phenolic photosensitizer

m/e	Ion	
220	$C_{15}H_{24}O^+$	(parent)
205	$C_{14}H_{21}O^+$	$(-CH_3)$
191	$C_{13}H_{19}O^+$	$(-C_2H_5)$
177	$C_{12}H_{17}O^+$	$(-C_3H_7)$
163	$C_{11}H_{15}O^+$	$(-C_4H_9)$
149	$C_{10}H_{13}O^+$	$(-C_5H_{11})$
135	$C_9H_{11}O^+$	$(-C_6H_{13})$
121	$C_8H_9O^+$	$(-C_7H_{15})$
107	$C_7H_7O^+$	$(-C_8H_{17})$

quenching of the first excited singlet state of dialkyl ketones by alkyl chlorides, charge transfer occurs in the opposite sense. The direction of transfer of charge is dictated by the relative magnitudes of ionization potentials and electrode reduction potentials of the partners. From our later analysis (see below), we prefer a transfer involving the alkyl halide as acceptor noting the difficulty highlighted by Harriman *et al.* of interpreting the earlier data because of the small range of $(-E_T - E_{A/A^-})$ values used. Since there is a little doubt that the benzophenone sensitization is a triplet state reaction, this can now be compared with results obtained using *p*-cresol as a sensitizer.

p-*Cresol sensitization*

Degassed solutions of *p*-cresol in *sec*-butyl chloride and *t*-butyl chloride irradiated in the merry-go-round produced *cis*-but-2-ene, *trans*-but-2-ene and but-1-ene in the ratio 1.5:0.75 in the former case, and a unique product tentatively identified as 2-methylpropene in the latter. It is evident that these products are identical to those produced by triplet benzophenone sensitization. However, in neat *sec*-butyl chloride or *t*-butyl chloride solution, as in PVC itself, the possibility of singlet state quenching of the aromatic molecule by the halogenated compound exists, due to the relatively long lifetime of the singlet state of *p*-cresol compared with that of benzophenone. Accordingly fluorescence measurements were made to investigate this possibility using a varied of chlorinated substrates to study fluorescence quenching from the first excited singlet state.

Fluorescence of p-*cresol*

The absorption spectra of *p*-cresol in cyclohexane, methylene chloride and *t*-butyl chloride, and fluorescence spectra in cyclohexane and methylene chloride solvents are shown in Fig. 2. It is evident that *p*-cresol fluorescence is quenched by methylene chloride. This is also revealed by fluorescence decay time measurements of degassed *p*-cresol (0.008 M) in cyclohexane and CH_2Cl_2, shown in Figs 3(a) and 3(b). Computed lifetime values are 3.4 and 1.5 ns respectively. These results have been confirmed by a study of the quenching of *p*-cresol fluorescence intensity in aerated solution measured on a spectrofluorimeter by the halogenated compounds shown in Table 2. Good linear Stern–Volmer plots were obtained (7)

$$(\phi_F)_0/\phi_F = 1 + k_Q\tau[Q] \qquad (7)$$

with slopes shown in Table 2, and when combined with the fluroescence decay times of *p*-cresol in aerated cyclohexane of 3.0 ns, yield values for the second-order quenching rate constant k_Q also given in Table 2. Values obtained are of the same order of magnitude as that for the quenching of *o*-xylene by CH_2Cl_2[14] $(2 \pm 1 \times 10^7\ l\ \text{mole}^{-1}\ \text{s}^{-1})$[15].

In contrast to the results in polychlorinated alkanes, addition of *t*-butyl chloride in concentrations up to 10 M did not quench the fluorescence of *p*-cresol significantly, as measured on the spectrofluorimeter. These results were confirmed using decay time measurements, where again the decay time of *p*-cresol fluorescence in degassed neat *t*-butyl chloride was measured as 3.3 ns, very close to that in cyclohexane.

The difference in behaviour of the alkyl halides can be understood in terms of charge transfer complex formation with the halogenated compound acting as electron acceptor (8). The measured quenching rate constant k_Q is given in terms of the rate constants show in (8) as

$$^1\text{A} + \text{RCl} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} [^1\text{A}^{\delta+} \ldots \text{RCl}^{\delta+}] \xrightarrow{k_q} \text{products} \qquad (8)$$

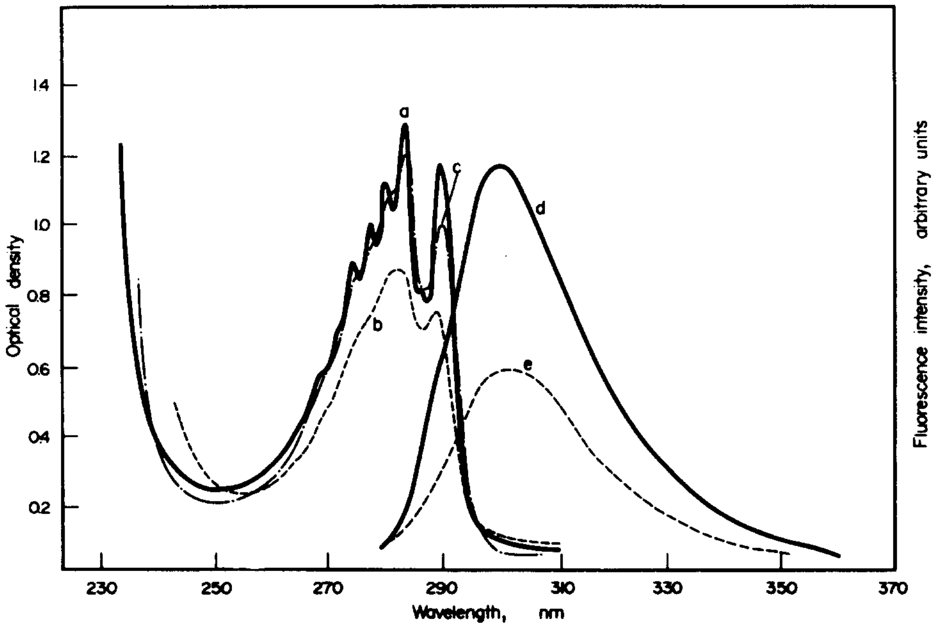


Fig. 2. Absorption spectrum of *p*-cresol in (a) cyclohexane (b) CH_2Cl_2 and (c) *t*-butyl chloride, and corresponding uncorrected fluorescence spectra in (d) cyclohexane, (e) CH_2Cl_2. Concentration for absorption, 6.4×10^{-4} M, for fluorescence 0.01 M. 1 cm path length in each case.

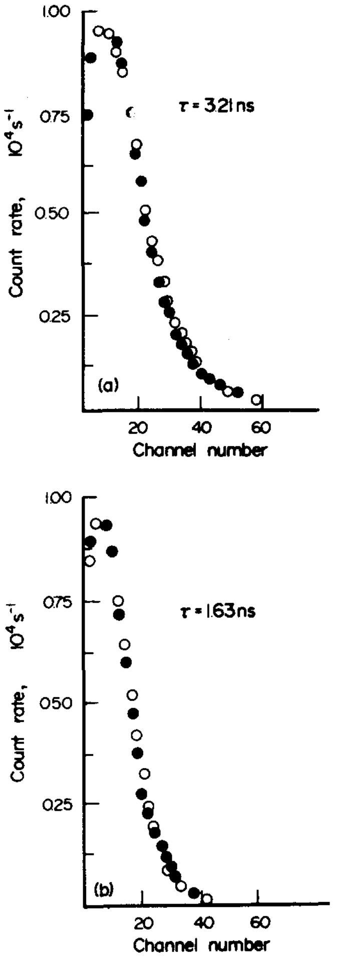


Fig. 3. Fluorescence decay curves of *p*-cresol (0.008 M) in (a) cyclohexane (b) CH_2Cl_2. Experimental data are shown as ○, computed curves from best fit procedure shown as ●, yielding decay times shown. 1 Channel ≡ 0.612 ns.

Table 2. Bimolecular rate constants for quenching of *p*-cresol fluorescence in aerated cyclohexane solution at 25° by chlorinated alkanes

Substrate	Stern–Volmer slope, $k_Q\tau$	k_Q (l mole^{-1} s^{-1}*)
CCl_4	31.75	1.1×10^{10}
$CHCl_3$	13.51	4.5×10^{9}
CH_2Cl_2	0.41	1.3×10^{8}
$ClCH_2CH_2Cl$	0.07	2.4×10^{7}
t-Butylchloride	0	0

*Taking τ as 3.0 ns.

$$k_Q = \frac{k_+ k_q}{(k_q + k_-)} \tag{9}$$

Provided $k_q < k_-$ and k_q does not vary greatly from substrate to substrate, it is easily shown[14, 15, 16] that

$$1_n k_Q \alpha | -(I_D - E_A - C - P - E_s)| \tag{10}$$

where I_d is the ionization potential of the electron donor, E_A the electron affinity (or electrode reduction potential) of the electron acceptor, C the coulombic attraction energy of the ion pair, P the polarization energy of the separate charges and E_s the excitation energy of the excited electronic state. For the present case with a series of alkyl halides interacting with the excited singlet state of *p*-cresol, the only term in (10) which varies is the electron affinity of the halogenated compound, which have the values shown in Table 3. Table 3 shows that the polychloromethanes have very similar ionization potentials to methyl chloride. In a complex with the alkyl chloride acting as an electron donor, as suggested by Harriman *et al.*[9] comparable quenching rate constants k_Q would be expected for all the chloromethanes. This is not observed. The alternative view, which we favour, of complex formation with the alkyl chloride acting as electron acceptor accords with the known electron affinities shown in Table 3. Further chlorine substitution increases the electron affinity and (10) accounts for the more efficient quenching of *p*-cresol fluorescence by CCl_4 in comparison with the less substituted alkyl halides. Indeed with CCl_4 the observed quenching is near diffusion controlled.

Our conclusion of charge transfer within the complex from *p*-cresol acting as donor to alkyl halide acting as acceptor contrasts with the results of Harriman *et al.*[9] where the triplet state of an aromatic carbonyl compound was considered as acceptor and the alkyl halide as donor. It should be noted that in the ground state the ionization potential of typical aromatic ketones (benzophenone 9.35 eV) is not substantially greater than *p*-cresol (8.95 eV). Further the ionization potential of the triplet state will be lowered with respect to the ground state. Hence it is likely that, in complex formation between ketone triplet and alkyl halide, the alkyl halide again acts as electron acceptor. The apparently successful correlation of plots of $\log_{10} k_Q$ against the term $-(E_A + E_T)$ where E_T is the triplet energy of the aromatic ketone was based on five compounds (PhCHO, PhCOEt, PhCOMe, $PhCOBu^n$ and Ph_2CO). It is possible that the observed k_Q values reflect not only a charge transfer phenomenon but also a steric factor in which k_Q is reduced by excessive steric hinderance within the complex.

The importance of the discussion above is that,

Table 3. Ionization potentials and electron affinities of alkyl halides

Compound	Ionization potential (eV)	Electron affinity (eV)
CCl_4	11.28*	2.06‡
$CHCl_3$	11.37*	1.70‡
CH_2Cl_2	11.32*	1.31‡
n-BuCl	10.67†	—
sec-BuCl	10.65†	—
t-BuCl	10.61†	—
MeCl	11.28	—

* Measured by photoionization, A.S. Werner, B.P. Tsai and T. Baer, *J. chem. Phys.* **60**, 3650 (1974).

† Measured by photoionization, K. Watanabe, T. Nakayama and J. Mottl, *J. Quant. Spectros. Radiat. Trans.* **2**, 369 (1962).

‡ Measured by the magnetron method, A. F. Gaines, J. Kay and F. M. Page, *Trans. Faraday Soc.* **62**, 874 (1966).

in the present case, singlet state interactions between *p*-cresol and *sec*-butyl chloride or *t*-butyl chloride are absent, pointing to triplet state sensitization.

Triplet state quenching

The results of experiments carried out on the effect of addition of the triplet quencher *trans*-1,3-pentadiene to the *p*-cresol-*sec*-butyl chloride system in which the but-1-ene product was monitored are shown in Fig. 4 in the form of a Stern–Volmer plot. Since concentrations of up to 0.1 M *trans*-1,3-pentadiene did not appreciably quench the fluorescence of *p*-cresol, the results may be taken as good evidence of triplet state participation in the decomposition mechanism. Given the simple mechanism below, the relative yield of 1-butene product at any concentration of *trans* 1,3-pentadiene P

$$S + h\nu \rightarrow {}^1S^* \qquad I_a \qquad (11)$$

$${}^1S^* \rightarrow S + h\upsilon_F \qquad k_F \qquad (12)$$

$${}^1S^* \rightarrow {}^3S^* \qquad k_{ISC} \qquad (13)$$

$${}^1S^* \rightarrow S \qquad k_{IC} \qquad (14)$$

$${}^3S^* \rightarrow S \qquad k_{NR} \qquad (15)$$

$${}^3S^* + \mathrm{RCl} \rightarrow \text{products} \qquad k_T \qquad (16)$$

$${}^3S^* + \mathrm{P} \rightarrow \text{quenching} \qquad k_Q \qquad (17)$$

to that in the absence of the olefin is given by (18)

$$\frac{(X_0)}{X} = 1 + \frac{k_Q[P]}{k_T[\mathrm{RCl}] + k_{NR}} \qquad (18)$$

Making the reasonable assumption that $k_T[\mathrm{RCl}] \gg k_{NR}$, since neat *sec*-butyl chloride is used, the slope of the line in Fig. 4 corresponds to k_Q/k_T. If k_Q can be taken as diffusion controlled, which for *sec*-butyl chloride would be 9.9×10^{10} l mole^{-1} s^{-1}, k_T has the value 2.6×10^8 l mole^{-1} s^{-1}. This is compared with similar values of Harriman *et al.* for triplet aromatic ketone sensitization shown in Table 4.

Effect of commercial additive

The commercial stabilizer, found earlier[1] to sensitize photodehydrochlorination in PVC, was also used in *sec*-butyl chloride photolysis. The same volatile products, but-1-ene, *cis* and *trans* but-2-ene were obtained, with a quantum yield of formation relative to that from benzophenone sensitization of approximately 0.9.

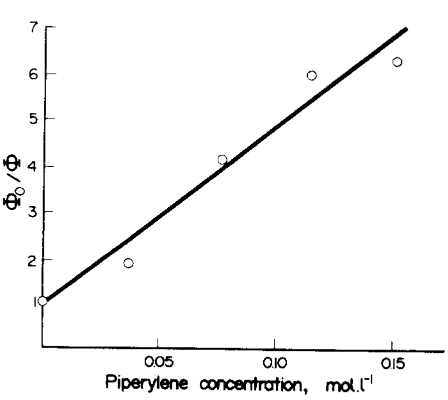


Fig. 4. Plot of relative yield of but-l-ene as function of *trans* 1,3-pentadiene concentration in *p*-cresol sensitized photolysis of *sec*-butyl chloride.

Table 4. Rate constants for quenching of triplet sensitizer by alkyl halides

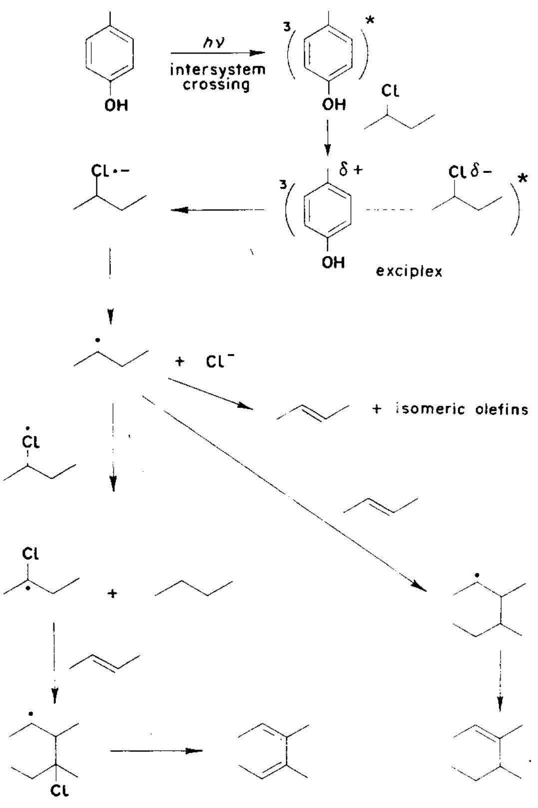
Sensitizer	k_T l mole^{-1} s^{-1}	Ref.
PhCOEt	1.4×10^9	*
p-Cresol	2.6×10^8	†
PhCOMe	1.2×10^8	*
PhCOPh	6.9×10^7	*

* A. Harriman, B. W. Rockett and W. R. Poyner, *J. Chem. Soc.* (*Perkin II*) 485 (1974), *t*-Butyl chloride substrate.

† This work *sec*-butyl chloride substrate.

Mechanism of photodehydrochlorination

GLC/mass spectrometric analysis showed that one of the main non-volatile products in the *p*-cresol/*sec*-butyl chloride system had strong mass peaks at $m/e = 55$, 95, 97, 110 and 112, and Kenyon[3] produced similar products in the acetone sensitized photolysis of *sec*-butyl chloride. These products are most likely to be 3,4-dimethylhex-2-ene and 3,4-dimethyl-2,4-hexadiene. A plausible mechanism, based on recent observations in alkyl halide systems[17] and incorporating the charge transfer interactions discussed above, is given below in Scheme 1. The details of this mechanism are still obscure but the crucial features are (i) the quenching of the triplet state of *p*-cresol by an alkyl halide with charge



Scheme 1.

transfer (ii) subsequent collapse of an exciplex to give alkyl radicals (iii) hydrogen atom transfers leading to olefin formation (iv) addition of radicals to olefins to give compounds of higher molecular weight.

In view of the charge transfer characteristics of the quenching processes, it is not surprising that phenols having low ionisation potential accelerate the photodecomposition of alkyl chlorides, and of poly(vinylchloride).

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