The Mechanism of Photodegradation of Alkyl Halides and Poly(vinyl chloride). Part I. Alkyl Aryl Ketone-sensitized Photolysis of t-Butyl Chloride

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Alkyl aryl ketones were found to sensitize the decomposition of t-butyl chloride in cyclohexane solution. The mechanism for the decomposition involved some degree of charge-transfer complex formation and the lowest excited triplet state of the alkyl aryl ketone was clearly implicated as the sensitizing species.

AROMATIC hydrocarbons sensitize the dissociation of aliphatic halides both in solution [1] and in the vapour phase.[2] The mechanism for the dissociation involves some degree of charge-transfer complex formation.[3] The ionization energies of the aliphatic chloro-compounds used in this study are high, *ca.* 12 eV, which suggests that the aromatic hydrocarbon acts as the donor. This is contrary to the mechanism found for the reaction between aromatic hydrocarbons and amines where the amine acts as the donor.[4] These observations have led to the use of amines as photosensitizers for the degradation of halogenated compounds such as polychlorohydrocarbon pesticides.[5] Aliphatic [6] and aromatic [7] ketones have also been shown to induce decomposition of aliphatic halides. The singlet excited state of the ketone has been proposed as the sensitizing species [6,7] although a charge-transfer mechanism has not been implicated. We have investigated the reaction between alkyl aryl ketones and t-butyl chloride, which is a model compound for the tertiary chloride sites present in commercial poly(vinyl chloride), and present results which show that the sensitizing state of the ketone is the lowest excited triplet state.

EXPERIMENTAL

Materials.—t-Butyl chloride (B.D.H.) was fractionally distilled and the middle fraction collected and redistilled. No impurity was detected upon g.l.c. Benzophenone (B.D.H.) was recrystallized twice from spectroscopic grade ethanol. Benzaldehyde, acetophenone, ethyl phenyl ketone (Hopkin and Williams), and n-butyl phenyl ketone (Koch–Light) were distilled under reduced pressure. G.l.c. indicated the absence of impurities. Cyclohexane (Hopkin and Williams) was spectroscopic grade and was used without further purification.

Procedure.—Quantum yields for the elimination of hydrogen chloride from t-butyl chloride were determined using potassium ferrioxalate actinometry.[8] Cyclohexane solutions of t-butyl chloride (0·1M) and the ketone (0·01M) were irradiated in a Pyrex reactor equipped with a 450 W medium-pressure mercury arc. Isolation of the 313 nm mercury line was achieved using two consecutive filter solutions, potassium hydrogen phthalate and a cobalt sulphate–nickel sulphate solution. The reactant solution was deoxygenated by purging with oxygen-free nitrogen before irradiation. Nitrogen, at a fixed flow rate, was passed continuously through the reactant solution during irradiation and any hydrogen chloride carried by the nitrogen stream was detected and estimated by conductance. After the irradiation, aliquot portions of the reactant solution were extracted with ice-cold, distilled water and the aqueous solution was titrated with standard sodium carbonate solution. The total amount of hydrogen chloride eliminated during the irradiation was calculated from the combined results of the conductance and titration measurements. The reaction was taken to <5% conversion.

Diene quenching experiments were conducted with cyclohexane solutions of t-butyl chloride (0·1M), ketone (0·01M),

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[1] E. J. Bowen and K. K. Rohatgi, *Discuss. Faraday Soc.*, 1953, **14**, 146; G. Kallmann-Oster, *Acta Phys. Chem.*, 1964, **26**, 435.

[2] S. H. Ng, G. P. Semeluk, and I. Unger, *Canad. J. Chem.*, 1968, **46**, 2459.

[3] G. Das Gupta and D. Phillips, *J.C.S. Faraday II*, 1972, 2003.

[4] C. Pac and H. Sakurai, *Tetrahedron Letters*, 1969, 3829; R. S. Davidson, *Chem. Comm.*, 1969, 1450; R. Rao and V. Ramakrishnan, *ibid.*, 1971, 971.

[5] R. S. Narang, *Diss. Abs. Int. B*, 1972, **33**, 603.

[6] M. A. Golub, *J. Amer. Chem. Soc.*, 1969, **91**, 4925; 1970, **92**, 2615; A. S. Kenyon, National Bureau of Standards Circular **53**, Washington, 1953, p. 81.

[7] M. A. Golub, *J. Phys. Chem.*, 1971, **75**, 1168.

[8] J. Calvert and J. N. Pitts, 'Photochemistry,' Wiley-Interscience, New York, p. 783.

and various concentrations of 2,5-dimethylhexa-2,4-diene. The irradiation was carried out using a purpose built ' merry-go-round ' reactor equipped with a 125 W medium-pressure mercury arc. The 313 nm mercury line was isolated using a Pyrex cut-off and a potassium chromate–carbonate filter solution. The reactant solutions were irradiated in sealed Pyrex tubes after purging with oxygen-free nitrogen. The amount of hydrogen chloride eliminated was measured by titration and the quantum yield determined by reference to parallel irradiations of n-butyl phenyl ketone in cyclohexane solution.[9]

The quenching of photoreduction of the alkyl aryl ketones by t-butyl chloride was evaluated with the ' merry-go-round ' reactor. Solutions of the ketone (0·02M) in spectroscopic grade propan-2-ol containing various concentrations of t-butyl chloride were irradiated at 313 nm. Analysis was conducted by absorption spectroscopy at the appropriate wavelength, after exposure to oxygen, and actinometry was by n-butyl phenyl ketone.

The quenching of photoelimination for n-butyl phenyl ketone by t-butyl chloride was also evaluated using the ' merry-go-round ' reactor. Cyclohexane solutions of n-butyl phenyl ketone (0·02M), n-decane as internal standard, and various concentrations of t-butyl chloride were irradiated at 313 nm. The concentration of acetophenone eliminated was determined by g.l.c. using an authentic sample of acetophenone to relate peak area to concentration. Quantum yields were determined by reference to a separate n-butyl phenyl ketone actinometer.

Analysis for products formed during the ketone-induced photolysis of t-butyl chloride was conducted using g.l.c., both by comparison of retention times with authentic samples and by operating in tandem with a mass spectrometer. G.l.c. was carried out with a Pye–Unicam model 104 instrument equipped with a flame-ionization detector and silicone oil and fluorosilicone oil columns temperature programmed between 25 and 200°. The mass spectrometer was a Hitachi–Perkin-Elmer model RMS-4.

RESULTS

The ketone-sensitized photolysis of t-butyl chloride produced at least four hydrocarbon products as well as hydrogen chloride. G.l.c. coupled with mass spectrometry allowed the identification of 2-methylpropene, 2-methylpropane, and bicyclohexyl together with a small amount of chlorocyclohexane; the major product was 2-methylpropene.

$$^{3}\mathrm{PhCOR}^{*} + \mathrm{C_4H_9Cl} \longrightarrow \mathrm{PhCOR} + \mathrm{C_4H_9Cl_{VIB}}^{*} \qquad (1)$$

$$\mathrm{C_4H_9Cl_{VIB}}^{*} \longrightarrow \mathrm{C_4H_9\cdot} + \mathrm{Cl\cdot} \qquad (2a)$$

$$\mathrm{C_4H_9Cl_{VIB}}^{*} \longrightarrow \mathrm{C_4H_8} + \mathrm{HCl} \qquad (2b)$$

$$\mathrm{Cl\cdot} + \mathrm{C_6H_{12}} \longrightarrow \mathrm{HCl} + \mathrm{C_6H_{11}\cdot} \qquad (3)$$

$$\mathrm{C_4H_9\cdot} + \mathrm{C_6H_{12}} \longrightarrow \mathrm{C_4H_{10}} + \mathrm{C_6H_{11}\cdot} \qquad (4a)$$

$$2\mathrm{C_4H_9\cdot} \longrightarrow \mathrm{C_4H_{10}} + \mathrm{C_4H_8} \qquad (4b)$$

$$\mathrm{C_4H_9\cdot} + \mathrm{Cl\cdot} \longrightarrow \mathrm{C_4H_9Cl} \qquad (4c)$$

$$\mathrm{C_4H_9\cdot} + \mathrm{HCl} \longrightarrow \mathrm{C_4H_{10}} + \mathrm{Cl\cdot} \qquad (4d)$$

$$2\mathrm{C_6H_{11}\cdot} \longrightarrow \mathrm{C_{12}H_{22}} \qquad (5a)$$

$$\mathrm{C_6H_{11}\cdot} + \mathrm{Cl\cdot} \longrightarrow \mathrm{C_6H_{11}Cl} \qquad (5b)$$

Every chlorine atom formed by step (2a) may be expected to abstract a hydrogen atom from the solvent cage. The activation energy for the process is probably $\leqslant 4$ kJ mol^{-1} and most of the chlorine atoms would be formed as hot radicals with sufficient energy to escape the recombination step (4c) and abstract a proton from the adjacent cage wall [step (3)]. The reaction was taken to low conversion to minimize step (4d) so that hydrogen chloride formed by step (3) and/or step (2b) was not consumed during the reaction.

The ketone-induced decomposition of t-butyl chloride was followed by measurement of the amount of hydrogen chloride eliminated during photolysis. Table 1 lists values for the quantum yield of hydrogen chloride (ϕ_{HCl}) eliminated during photolysis at 313 nm for a range of alkyl aryl ketone sensitizers. The ϕ_{HCl} values were determined for cyclohexane solutions of t-butyl chloride (0·1M) containing the ketone sensitizer (0·01M). No hydrogen chloride was eliminated during photolysis of t-butyl chloride at 313 nm in the absence of the ketone.

TABLE 1

Values for the photosensitized decomposition of t-butyl chloride

Sensitizer	ϕ_{HCl}	E_S/kJ mol^{-1} [a]	E_T/kJ mol^{-1} [a]
PhCOEt	0·313	336	313
PhCOBu^n	0·106	327	305 [b]
PhCOMe	0·096	330	308
PhCHO	0·037	321	299
Ph$_2$CO	0·019	312	287

[a] Energy of the lowest excited singlet state (E_S) and the lowest excited triplet state (E_T) of the ketone (ref. 8, p. 297). [b] J. A. Barltrop and J. D. Coyle, *J. Amer. Chem. Soc.*, 1968, **90**, 6584.

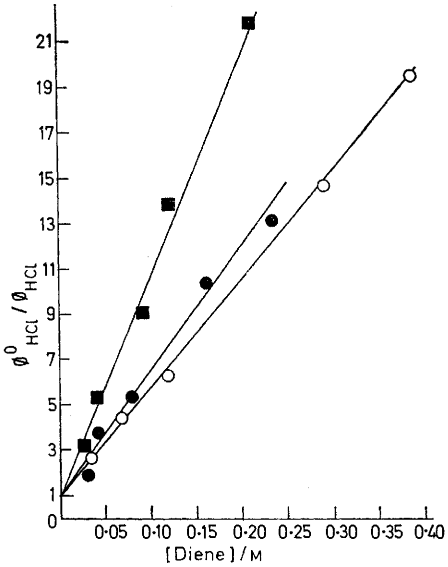

FIGURE 1 Diene quenching of ϕ_{HCl} in cyclohexane solution. The $\phi^0_{\mathrm{HCl}}/\phi_{\mathrm{HCl}}$ values for acetophenone and benzophenone were shown at 10^{-1} times the observed values for clarity: ■, Ph$_2$CO; ●, PhCOMe; ○, PhCOEt

When the photosensitized decomposition of t-butyl chloride was carried out in the presence of 2,5-dimethylhexa-2,4-diene, the extent of quenching observed was dependent on the diene concentration. Linear Stern–Volmer [10] plots were obtained for the diene quenching of hydrogen chloride formation (Figure 1) showing that re-

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[9] J. A. Barltrop and J. D. Coyle, *J. Amer. Chem. Soc.*, 1968, **90**, 6584.

[10] O. Stern and M. Volmer, *Phys. Z.*, 1919, **20**, 183.

action proceeded *via* a single reactive state of the ketone.[11] The slopes determined from the Stern–Volmer plots are given in Table 2. The formation of diene dimers was confirmed by g.l.c. but no product arising from addition of hydrogen chloride to the conjugated diene was observed.

TABLE 2

Values for the diene-quenched, photosensitized decomposition of t-butyl chloride

Sensitizer	Stern-Volmer slope/l mol^{-1}	k_t/l mol^{-1} s^{-1}
PhCOEt	47·5	1·4 × 10^{9}
PhCOMe	550	1·2 × 10^{8}
Ph$_2$CO	970	6·9 × 10^{7}

Alkyl aryl ketones with predominantly n–π^* lowest excited triplet states have been shown to undergo ready photoreduction with suitable hydrogen donors.[12] The quenching of photoreduction by the addition of t-butyl chloride provided a measure of the interaction between a ketone lowest excited triplet and the ground state t-butyl chloride. Linear Stern–Volmer plots were obtained for the t-butyl chloride quenched photoreduction of the alkyl aryl ketones with propan-2-ol. The slopes determined from these Stern–Volmer plots are given in Table 3.

TABLE 3

Values for the quenching of photoreduction with propan-2-ol by the addition of t-butyl chloride

Ketone	Stern–Volmer slope/ l mol^{-1}	k_C/ l mol^{-1} s^{-1}	k_H/ s^{-1}
PhCOEt	27·7	2·5 × 10^{9}	5·4 × 10^{6}
PhCOMe	8·5	1·3 × 10^{8}	9·1 × 10^{5}
PhCHO [a]	26·9	4·5 × 10^{9}	1·3 × 10^{6}
Ph$_2$CO	4·3	4·1 × 10^{7}	5·7 × 10^{5}

[a] k_c For benzaldehyde was calculated for $k_{-t} = 3 \times 10^{8}$ s^{-1} (ref. 11).

n-Butyl phenyl ketone undergoes efficient Norrish Type II photoelimination,[13] a reaction which has been widely used as an actinometer.[14] t-Butyl chloride quenched the formation of acetophenone, the quenching efficiency being dependent upon the chloride concentration. A linear Stern–Volmer plot was obtained with a slope equal to 0·66 l mol^{-1}.

Irradiation of a solution of t-butyl chloride (0·1M) and ethyl phenyl ketone (0·01M) in propan-2-ol gave a ϕ_{HCl} value comparable with those obtained by parallel irradiations in cyclohexane and benzene. Since the polar solvent was capable of complexing with ketone molecules by hydrogen-bonding it follows that complexing between the ketone and chloride reactants was at a minimum. This assumption was borne out by a study of the absorption spectrum of ethyl phenyl ketone. In cyclohexane solution the absorption maximum occurred at 323 nm; in propan-2-ol it was shifted to 311 nm. This blue shift was characteristic of n–π^* transitions. No further change in the spectrum occurred upon addition of t-butyl chloride (0·1M). These observations ruled out the possibility that reaction only occurred if the absorbing ketone molecule was bound to the t-butyl chloride in a ground state complex.

DISCUSSION

There is no trace of structure in the near-u.v. absorption profile of t-butyl chloride. The n–σ^* transition promotes an electron into an orbital which is strongly C–Cl antibonding[15] and the excited molecule is known to dissociate at the C–Cl bond [reaction (6)]. The

$$\mathrm{Bu^tCl} \xrightarrow{h\nu} \mathrm{Bu^{t}\cdot} + \mathrm{Cl\cdot} \qquad (6)$$

absence of even vibrational structure indicates a lifetime of *ca.* 10^{-13} s and it probably dissociates on a repulsive potential energy surface within a single vibrational period. The absorption profile is bell-shaped with a maximum at 198 nm and the extinction coefficient is a Gaussian function of the absorption frequency. The bond dissociation energy of the C–Cl bond[16] is 327 kJ mol^{-1} although the energy associated with the absorption transition is much higher (>500 kJ mol^{-1}) making classical energy transfer using common photosensitizers (energy *ca.* 280—330 kJ mol^{-1}) most improbable.

The ϕ_{HCl} values obtained for a range of alkyl aryl ketones (Table 1) indicated that the efficiency of the sensitizer in causing decomposition of the chloride depended upon the electronic energy of the ketone. The change in ϕ_{HCl} correlated with the change in both singlet and triplet electronic energy values of the sensitizer. At 313 nm excitation, the alkyl aryl ketones underwent an n–π^* absorption transition to the lowest excited singlet state but intersystem crossing to the triplet manifold then occurred exclusively[17] so that the photochemistry of alkyl aryl ketones is dominated by reactions of the longer-lived triplet state.[18] However, Golub[7] has proposed that the decomposition of 1,4-dichlorobutane induced by benzophenone or acetophenone involved sensitization by the ketone lowest excited singlet state. The fact that the electronic energy associated with the triplet states of alkyl aryl ketones (Table 1) is thermodynamically insufficient to rupture the C–Cl bond may offer some support for Golub's proposal. The linear Stern–Volmer plots for the quenching of ϕ_{HCl} by addition of 2,5-dimethylhexa-2,4-diene (Figure 1) indicated that only one excited state of the ketone was involved in the decomposition reaction. Since the triplet energy of the diene (243 kJ mol^{-1}) * was below that of the lowest excited triplet state of each ketone whilst the singlet energy of the diene (>500 kJ mol^{-1}) was much higher than that of the lowest excited singlet state of each ketone (Table 1), it was assumed that the conjugated diene had quenched only the triplet state reaction. This conclusion was supported by the observation that diene dimers had been formed during the irradiations and these are known to arise solely *via*

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* From oxygen perturbation enhanced absorption spectroscopy.

[11] N. C. Yang, R. Loeschen, and D. Mitchell, *J. Amer. Chem. Soc.*, 1967, **89**, 5465.

[12] Ref. 8, p. 532.

[13] F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, **1970**, **92**, 6672.

[14] J. A. Barltrop and J. D. Coyle, *J. Chem. Soc.* (*B*), 1971, 251.

[15] J. P. Simons, ' Photochemistry and Spectroscopy,' Wiley-Interscience, New York, 1971, p. 157.

[16] Ref. 8, p. 824.

[17] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 1965, **43**, 2129.

[18] P. J. Wagner and G. S. Hammond, *Adv. Photochem.*, 1968, **5**, 21.

triplet energy transfer.[19] Although singlet energy quenching of alkyl ketones by conjugated dienes has been observed [20] it is much less efficient than triplet quenching and has not been reported for alkyl aryl ketone singlets. The significance of the slopes of the Stern–Volmer plots is best appreciated when a full kinetic scheme is considered (Scheme 1). S_0, S_1, and T_1

$$\begin{array}{llll}
S_0 + h\nu & \longrightarrow & S_1 & \\
S_1 & \longrightarrow & S_0 & k_{-s} \\
S_1 + C & \longrightarrow & \text{Product} & k_s \\
S_1 & \longrightarrow & T_1 & k_{i.s.c.} \\
S_1 + Q & \longrightarrow & S_0 + Q^* & k_q{}^s \\
T_1 & \longrightarrow & S_0 & k_{-t} \\
T_1 + C & \longrightarrow & \text{Product} & k_t \\
T_1 + Q & \longrightarrow & S_0 + Q^* & k_q{}^t
\end{array}$$

SCHEME 1

represent the ground state, the first excited singlet state, and the lowest excited triplet state of the ketone, k_{-s} and k_{-t} are the decay rate constants which cover all radiative and non-radiative decay modes, k_s and k_t are rate constants for the initial step in product formation arising from interaction with t-butyl chloride (C). The term $k_{i.s.c.}$ is the rate constant for intersystem crossing from S_1 to T_1, and $k_q{}^s$ and $k_q{}^t$ are the bimolecular rate constants for quenching of the excited states by the quencher Q. For quenching of ketone excited states by conjugated dienes it is usually assumed [14] that $k_q{}^s[Q] \ll (k_{-s} + k_{i.s.c.} + k_s[C])$ and this allows the expression for the slope of the Stern–Volmer plot for triplet state quenching to be simplified to equation (7).

$$\text{Slope} = k_q{}^t/(k_t[C] + k_{-t}) \qquad (7)$$

It has been reported by several investigators [21] that triplet quenching by conjugated dienes is diffusion-controlled and therefore a value of $6 \cdot 7 \times 10^9$ l mol^{-1} s^{-1} was assigned to $k_q{}^t$ in cyclohexane solution. An estimate for k_t was made based upon an assumed value of 10^6 s^{-1} for k_{-t}.[22] The estimated k_t values are listed in Table 2. Even for benzophenone the k_t value obtained is much higher than that observed for the triplet state hydrogen abstraction from alkane hydrogen donors.[23] This observation, together with the specificity shown by carbonyl n–π^* triplets in abstracting secondary hydrogens in preference to primary hydrogens, suggested that the decomposition of t-butyl chloride in cyclohexane solution was not a consequence of hydrogen abstraction from the t-butyl group. Quenching of photoreduction of the alkyl aryl ketone with propan-2-ol by the addition of t-butyl chloride was used as a further means to obtain estimates for the rate constant for interaction between the ketone excited state and t-butyl chloride. Rate constants for the hydrogen abstraction process (k_H) in the absence of quencher were determined (Table 3).

Linear Stern–Volmer plots were obtained for quenching of photoreduction by t-butyl chloride and the slopes evaluated using the treatment due to Hammond.[24] The rate constants for interaction between the ketone excited state and t-butyl chloride (k_c) were determined (Table 3) by this treatment [24] and were found to be of a similar magnitude to k_t. A value for k_c for n-butyl phenyl ketone was obtained from a Stern–Volmer plot for the quenching of acetophenone formation by t-butyl chloride. The slope of the Stern–Volmer plot was equal to $0 \cdot 66$ l mol^{-1} which, together with a value [25] for the rate constant for acetophenone formation of $1 \cdot 4 \times 10^8$ l mol^{-1} s^{-1}, gave an estimate of 1×10^8 l mol^{-1} s^{-1} for k_c.

The magnitude of the k_c values obtained was compared with that estimated from the calculated singlet state lifetime of the ketones. The integrated (0,0) band for the alkyl aryl ketone absorption spectra gave values for the ketone singlet excited state lifetimes of *ca.* 10^{-7} s. Since no fluorescence has been observed the quantum yield for fluorescence must be $<10^{-2}$ so that the mean singlet state lifetime was $<10^{-9}$ s. Kasha [26] has predicted that $99 \cdot 9\%$ of the excited singlets produced by n–π^* transitions are converted into triplets in rigid media. This allowed a value of 10^{-10} s as the minimum lifetime of the alkyl aryl ketone singlets and predicted a value for the rate constant for deactivation of the lowest excited singlet state of 10^{10} s^{-1} or greater. The values obtained for k_c varied over a range (Table 3) which showed that the reaction could not compete efficiently with deactivation of ketone singlet states. The overall conclusion drawn from the quenching studies was that the photoinduced dissociation of t-butyl chloride arose from interaction with the lowest excited triplet state of the ketone.

The dependence of ϕ_{HCl} upon the electronic energy of the ketone lowest excited triplet state suggested a triplet energy transfer mechanism. However, there is no available spectroscopic data to indicate that alkyl halides have a low-lying (*i.e.* <320 kJ mol^{-1}) electronic energy level and studies with aromatic triplet state sensitizers [3] have not suggested the occurrence of such an energy level. Efficient quenching of electronic excited states may occur even when the quencher does not have an excited state with a lower energy than that of the donor.[27] Such reactions usually involve either chemical quenching, *i.e.* photoreduction, or charge-transfer complex formation. The high k_t and k_c values obtained and the observation that the decomposition occurred in propan-2-ol, a source of readily abstractable hydrogen atoms, indicated that hydrogen atom abstraction was not an important feature of the decomposition mechanism. The ϕ_{HCl} value for ethyl phenyl ketone sensitiza-

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[19] J. D. Coyle, *J.C.S. Perkin II*, 1973, 233.

[20] J. A. Barltrop and H. A. J. Carless, *J. Amer. Chem. Soc.*, 1972, **94**, 1951.

[21] P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, 1966, **88**, 1245; P. J. Wagner and I. Kochevar, *ibid.*, 1968, **90**, 2232; J. N. Pitts, D. R. Burley, J. C. Manai, and A. D. Broadbent, *ibid.*, p. 5900.

[22] N. C. Yang and R. L. Dusenberg, *J. Amer. Chem. Soc.*, 1968, **90**, 5900; F. D. Lewis, *J. Phys. Chem.*, 1970, **74**, 3332.

[23] C. M. Previtali and J. C. Scaiano, *J.C.S. Perkin II*, 1972, 1672.

[24] W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, 1961, **83**, 2789.

[25] P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, 1968, **90**, 5896.

[26] M. Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14.

[27] F. A. Carroll, M. T. McCall, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1973, **95**, 315.

tion was identical in both cyclohexane and benzene solution which suggested that the ketyl radical was not involved in the mechanism. The low value assigned to the spin–orbit coupling factor for the chlorine atom (587 cm^{-1}) [28] together with the low susceptibility towards spin–orbit coupling shown by excited states which are predominantly n–π^* in character [29] indicated that the chloride was not involved in spin–orbital coupling enhanced, radiationless transitions. These observations appeared to exclude chemical quenching from occupying an important role in the mechanism of decomposition.

Charge-transfer complex formation between aromatic ketone triplets and both amine [30] and sulphide [31] donors has been reported. For these complexes the free energy of formation (ΔG) has been related to fundamental properties of the reactants (8), where IE_D is the ionization

$$\Delta G \approx IE_D - E_{A-/A} - E_T - C \qquad (8)$$

energy of the donor, $E_{A-/A}$ is the reduction potential of ketone, E_T is the energy of the lowest excited triplet state of the ketone, and C is a constant and includes a term for the coulombic interaction. For a series of acceptors and a constant donor, the kinetics predict a linear relationship between $\log_{10} k_{ir}$ and $(-E_T - E_{A-/A})$ where k_{ir} is the rate constant for interaction between the ketone triplets and the donor. The reduction potentials of the ketones were obtained from literature polarographic determinations [32] (Table 4) and k_{ir} was identified as k_c.

TABLE 4

Reduction potentials for alkyl aryl ketones determined by polarography

Ketone	$\log_{10} k_c$	$-E_{A-/A}$/ kJ mol^{-1} [a]	$(-E_T - E_{A-/A})$/ kJ mol^{-1}
PhCOEt	9·40	193	−120
PhCOBu^n	8·00	188	−117
PhCOMe	8·11	192	−116
PhCHO	9·65	173	−126
Ph$_2$CO	7·61	171	−116

[a] Ref. 32.

A linear relationship between $\log_{10} k_c$ and $(-E_T - E_{A-/A})$ was obtained for the reaction between alkyl aryl ketone triplets and t-butyl chloride (Figure 2). This observation suggested that the reaction mechanism involved some degree of charge-transfer complex formation. Since the slope of this plot (Figure 2) was restricted to a small range of $(-E_T - E_{A-/A})$ values no mechanistic conclusion was drawn regarding the actual degree of electron transfer involved in the reaction. The curve levelled off at the diffusion-controlled limit, a characteristic of triplet state reactions in solution,[27] and the $\log k_c$ value for benzaldehyde was restricted to this limit.

The involvement of charge-transfer complex formation in the decomposition mechanism suggested that the ϕ_{HCl} value was a product of two probabilities, (i) that interaction between the reactants occurred and (ii) that interaction led to hydrogen chloride formation. The probability that reaction occurred was measured by k_c since this reflected the free energy of charge-transfer complex formation. The values for ϕ_{HCl} listed in Table 1 indicated that the probability of interaction leading to hydrogen chloride formation was related to the ketone triplet energy. This suggested that the energy of the charge-transfer complex was close to that of the ketone triplet state and that the complex decayed *via* a radiationless transition. Such a decay process [33] would result in the chloride gaining a great excess of vibrational energy (Scheme 2). If this excess of vibrational energy was close to the C–Cl bond dissociation energy then decomposition of the chloride was possible. In the absence of decomposition, radiationless decay to ground-state reactants was the dominant decay mode and a low ϕ_{HCl} was observed.

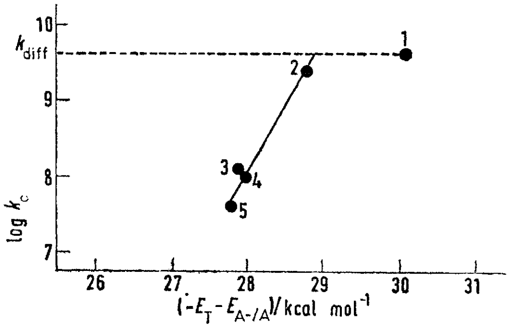
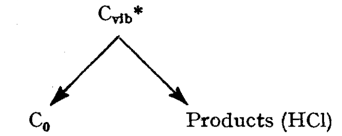


FIGURE 2 log k_c as a function of the ketone reduction potential: 1, PhCHO; 2, PhCOEt; 3, PhCOMe, 4, PhCOBu^n; 5, Ph$_2$CO. k_{diff} Is the diffusion-controlled rate limit.



SCHEME 2

We thank the S.R.C. for a CAPS studentship to A. H. and Dr. J. D. Coyle for helpful discussions.

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