# Quenching of Alkanone Fluorescence by Alkyl Halides in Cyclohexane Solution

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Alkyl halides were found to quench the fluorescence of both acetone and butan-2-one in cyclohexane solution. The fluorescence quenching rate constant ($k_Q$) did not correlate with either the spin–orbital coupling constant of the halogen atom or the ionization potential of the alkyl halide quencher. Substituted benzyl halides were also effective quenchers for butan-2-one fluorescence and the results obtained indicated that iodo-compounds acted as electron donors and chloro-compounds as electron acceptors in the fluorescence quenching mechanism. The results implied an excited state complex formed between alkanone singlets and the alkyl halide quencher which was stabilized by charge transfer interactions. The carbon–halogen bond provided a convenient vibrational energy sink which enabled the complex to decay *via* radiationless decay processes.

THE fluorescence of electronically excited alkyl ketones is often quenched by compounds having no excited singlet state lying at sufficiently low energy to allow transfer of electronic energy available in the quenchee. In particular, the quenching of alkanone fluorescence by unsaturated nitriles,[1] conjugated dienes,[2,3] and inorganic anions [4] has been reported recently, and in most cases, charge-transfer interactions have been postulated to explain the observed effects. Alkyl halides are known to quench benzene [5] and alkanone fluorescence [6,7] and again charge-transfer interactions have been implicated in the quenching mechanism.[5,7] Thus the quenching of an electronically excited singlet state may often be explained by the reversible formation of an encounter complex or charge-transfer complex which may also undergo quenching [reaction (1)]. The overall quenching efficiency of an excited state ($k_Q$) is given by equation (2) and may be influenced by $k_{-a}$, which depends upon the binding energy of the complex, or by $k_q$, which for an alkyl halide quencher may contain a spin–orbital coupling contribution. We have investigated the quenching of alkanone fluorescence by alkyl halides and report results which yield additional insight into the quenching mechanism.

$$A^* + Q \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} [A^* \cdots Q] \xrightarrow{k_q} \text{quenching} \quad (1)$$

$$k_Q = k_a k_q/(k_q + k_{-a}) \quad (2)$$

EXPERIMENTAL

*Materials.*—Cyclohexane (Hopkin and Williams) was spectroscopic grade and was used without further purification. No impurities were detected by absorption or fluorescence spectroscopy. The alkyl ketones, acetone, and butan-2-one (B.D.H.), were distilled twice and a centre cut taken each time. No impurities were detected by g.l.c. A single, structureless fluorescence band, centred at 405 nm, was observed for each of the alkyl ketones in cyclohexane solution (0·1M).

1-Chlorobutane, 2-chlorobutane, 2-chloro-2-methylpropane, 1-bromobutane, 2-bromobutane, and 2-bromo-2-methylpropane (Hopkin and Williams) were fractionally distilled and the centre fraction collected. Iodomethane, iodoethane, and iodopropane (Hopkin and Williams) were fractionally distilled and a centre fraction collected and stored in the dark. A sample was freshly distilled prior to use. G.l.c. indicated the absence of impurities and no absorption at wavelengths above 280 nm was observed for these alkyl halides. No fluorescence was detected for cyclohexane solutions (0·01—1M) of the alkyl halide.

Fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene (B.D.H.) were distilled under reduced pressure and a centre cut taken. No impurities were detected by g.l.c.

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

[2] R. R. Hautala and N. J. Turro, *J. Amer. Chem. Soc.*, 1971, **93**, 5595.

[3] N. C. Yang, M. H. Hui, and S. A. Bellard, *J. Amer. Chem. Soc.*, 1971, **93**, 4056.

[4] A. Harriman and B. W. Rockett, *J.C.S. Perkin II*, 1973, 1624.

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

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

[7] J. O. Pavlik, P. I. Plooard, A. C. Somersall, and J. E. Guilett, *Canad. J. Chem.*, 1973, **51**, 1435.

and no fluorescence was observed for cyclohexane solutions ($10^{-3}$M) of these aryl halides using excitation wavelengths above 290 nm.

Benzyl chloride (B.D.H.) and the *para*-substituted benzyl chlorides (Aldrich) were distilled under reduced pressure and a centre fraction was collected. Similar purification procedures were used for benzyl bromide (B.D.H.) and the *para*-substituted benzyl bromides (Eastman Organic Chemicals). Benzyl iodide and the *para*-substituted benzyl iodides were prepared from the corresponding benzyl tosylates with sodium iodide in acetone; the products were distilled under reduced pressure, stored in the dark and redistilled prior to use.

*Procedure*.—Fluorescence spectra were recorded with a Perkin-Elmer fluorescence spectrophotometer model MPF 2A, using right angle excitation geometry. Samples were prepared in duplicate in quartz cells and were deoxygenated by purging with oxygen-free nitrogen. The solutions contained the ketone (0·1M) in cyclohexane and various concentrations of the halide quencher. The concentration of quencher was always at least five times that of the ketone.

## RESULTS

Alkyl halides were found to quench the fluorescence of both acetone and butan-2-one in cyclohexane solution. The Stern–Volmer relationship (3) was used to determine

$$I_0/I = 1 + k_Q\tau[Q] \qquad (3)$$

the quenching rate constant ($k_Q$) for the quenching of alkanone fluorescence, at 313 nm excitation, by a series of alkyl halides. $I_0$ and $I$ are the uncorrected fluorescence intensities in the absence and presence, respectively, of a concentration [Q] of the alkyl halide and $\tau$ is the singlet state lifetime of the alkanone ($\tau$ = 2·1 and 2·8 ns for acetone [8] and butan-2-one [9] respectively). Linear Stern–Volmer plots were obtained for each of the alkyl halides used in the study and the values obtained for $k_Q$ are listed in Table 1. As evidenced by their absorption spectra all the alkyl halides had lowest excited singlet states higher in energy than the alkyl ketones so that the observed fluorescence quenching was not a consequence of electronic energy transfer. In all cases, the unquenched portion of fluorescence had the same spectral distribution as that observed in the absence of quencher. No new emission was detected in cyclohexane or acetonitrile solution.

Substituted benzyl halides were also found to quench butan-2-one fluorescence in cyclohexane solution. Linear Stern–Volmer plots were obtained for each of the substituted benzyl halides used in the study and the $k_Q$ values calculated from these plots are listed in Table 2. The nature of the substituent was shown to have an important effect upon the magnitude of the fluorescence quenching rate constant (Table 2). Again, no new emission was detected, in cyclohexane or acetonitrile solution, upon addition of the substituted benzyl halide.

A similar quenching effect was exhibited by monohalogenated benzenes except fluorobenzene which did not quench acetone or butan-2-one fluorescence in cyclohexane solution. This allowed a maximum value for the fluorescence quenching rate constant for this aryl halide to be put at $10^6$ l mol$^{-1}$ s$^{-1}$ since this represents the minimum value detectable by fluorescence spectroscopy. The other aryl halides produced linear Stern–Volmer plots for the quenching of alkanone fluorescence and the calculated $k_Q$ values are given in Table 3. No new emission was observed, in cyclohexane or acetonitrile solution, upon the addition of aryl halide and at the excitation wavelength used in the study, 313 nm, the aryl halide did not fluoresce.

TABLE 1

The quenching of alkanone fluorescence of alkyl halides in cyclohexane solution

| | $10^{-7}k_Q$/l mol$^{-1}$ s$^{-1}$ [a] | | | |
|---|---|---|---|---|
| Quencher | Acetone | Butan-2-one | $IP_D$/eV [b] | $\xi$/cm$^{-1}$ [c] |
| MeI | 2·7 | 2·6 | 9·54 | 5060 |
| EtI | 100·0 | 92·0 | 9·33 | 5060 |
| $Pr^nI$ | 21·0 | 21·0 | 9·41 | 5060 |
| $Bu^tBr$ | 1·5 | 1·9 | 9·59 [d] | 2460 |
| $Bu^sBr$ | 1·5 | 0·6 | 9·79 | 2460 |
| $Bu^nBr$ | 7·0 | 5·0 | 10·12 | 2460 |
| $Bu^tCl$ | 12·0 | 18·0 | 10·20 | 587 |
| $Bu^sCl$ | 3·6 | 3·0 | 10·49 [d] | 587 |
| $Bu^nCl$ | 1·8 | 2·1 | 10·96 | 587 |
| $Ph_3CCl$ | 53·0 | | | 587 |
| $Bu_3SnCl$ | 37·0 | | | 2682 |

[a] Error limits ±10%. [b] V. Vedeneyev, L. Gurvich, V. Kondrat'yev, V. Medvedev, and Ye. Frankevich, 'Bond Energies, Ionization Potentials and Electron Affinities,' Edward Arnold, London, 1966. [c] S. P. McGlynn, T. Azumi, and M. Kinoshita, 'Molecular Spectroscopy of the Triplet State,' Prentice-Hall, New York, 1969, p. 264. [d] Calculated from the electronic absorption spectrum.

TABLE 2

Quenching rate constants for the quenching of butan-2-one fluorescence by substituted benzyl halides in cyclohexane solution

| Quencher | $10^{-7}k_Q$/l mol$^{-1}$ s$^{-1}$ |
|---|---|
| $PhCH_2Cl$ | 1·70 |
| $p$-$MeC_6H_4CH_2Cl$ | 0·98 |
| $p$-$FC_6H_4CH_2Cl$ | 2·04 |
| $p$-$ClC_6H_4CH_2Cl$ | 3·43 |
| $PhCH_2Br$ | 12·7 |
| $p$-$MeC_6H_4CH_2Br$ | 14·9 |
| $p$-$MeOC_6H_4CH_2Br$ | 15·2 |
| $p$-$ClC_6H_4CH_2Br$ | 10·3 |
| $PhCH_2I$ | 83·2 |
| $p$-$MeC_6H_4CH_2I$ | 174·0 |
| $p$-$ClC_6H_4CH_2I$ | 34·7 |

TABLE 3

Quenching rate constants for the quenching of alkanone fluorescence by aryl halides in cyclohexane solution

| | $10^{-7}k_Q$/l mol$^{-1}$ s$^{-1}$ | | |
|---|---|---|---|
| Quencher | Acetone | Butan-2-one | $IP_D$/eV [a] |
| PhF | <0·1 | <0·1 | 17 |
| PhCl | 2·1 | 1·2 | 12·8 |
| PhBr | 4·3 | 3·4 | 12·0 |
| PhI | 20·0 | 25·0 | 10·3 |

[a] J. Petruska, *J. Chem. Phys.*, 1961, **34**, 1120.

## DISCUSSION

The fluorescence of simple alkanones was quenched by alkyl halides in cyclohexane solution (Table 1). The structure of the alkyl group was shown to be important in the quenching mechanism but the fluorescence quenching rate constant ($k_Q$) did not correlate with the spin–orbital coupling constant ($\xi$) of the halogen atom (Table 1). This was contrary to the quenching of benzene fluorescence by alkyl halides,[5] in the vapour phase, where a good correlation between $k_Q$ and $\xi$ was

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[8] J. C. Dalton and N. J. Turro, *Ann. Rev. Phys. Chem.*, 1970, **21**, 499.

[9] F. Wilkinson, *Adv. Photochem.*, 1964, **3**, 255.

obtained. However, ketones with lowest ($n,\pi^*$) excited states are not susceptible to heavy-atom effects [10] so that fluorescence quenching *via* enhanced intersystem crossing to the triplet manifold due to spin–orbital coupling with the halogen atom was expected to occupy only a minor role in the quenching mechanism. Since the enhancement of intersystem crossing caused by the external heavy atom effect probably involves the formation of an initial complex between the halogen compound and the excited state quenchee then the absence of a correlation with $\xi$ indicates that spin–orbital coupling does not provide the major pathway for decay of such an excited complex.

Fluorescence quenching by non-heavy atom quenchers in solvents of low polarity is frequently accompanied by the appearance of a new fluorescence emission at longer wavelength, which is attributed to an excited state, charge-transfer, complex (exciplex).[11] The kinetics of charge transfer interactions have been used [12] to predict a relationship between the ionization potential of the donor and $k_Q$. For exciplex formation in solution using the same solvent and acceptor and assuming constancy for the coulombic energy change on forming the complex, in its equilibrium configuration, from the components, there should be a linear relationship between the log of the quenching rate constant and the ionization potential of the donor ($IP_D$) [relationship (4)]. This relationship

$$\log_{10} k_Q \sim \text{constant} + IP_D \qquad (4)$$

was not observed for the quenching of alkanone fluorescence by alkyl halides (Figure 1) and, in fact, the shape of the curve suggested that two distinct mechanisms were in operation. Compounds with relatively low ionization potentials (*i.e.* iodo-compounds) appeared to quench by one mechanism whilst compounds with high ionization potentials (*i.e.* chloro-compounds) appeared to react *via* a different mechanism. This distinction in ionization potentials suggested the possibility that iodo-compounds acted as electron donors whilst chloro-compounds acted as electron acceptors, a trend which reflected the electronegativities of the halogen atoms involved in the quenching mechanism.

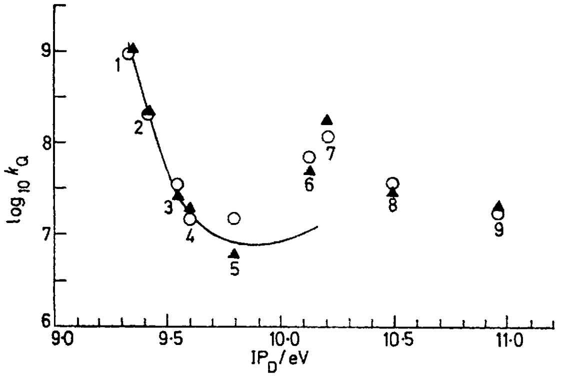

FIGURE 1 Quenching of alkanone fluorescence by alkyl halides: 1, EtI; 2, Pr$^n$I; 3, MeI; 4, Bu$^t$Br; 5, Bu$^s$Br; 6, Bu$^n$Br; 7, Bu$^t$Cl; 8, Bu$^s$Cl; 9, Bu$^n$Cl. ○ Acetone; ▲ butan-2-one

It should perhaps be noted that $k_a$ would be a better reaction parameter than $k_Q$ since the former is a measure of the actual interaction between reactants whilst $k_Q$ is the overall quenching rate constant. Since $k_Q$ has the significance (2) then if $k_q$ is much larger than $k_{-a}$ the relationship reduces to the form of equation (5). In

$$k_Q \sim k_a \qquad (5)$$

other words, $k_Q$ will be governed by factors which control $k_a$ regardless of the subsequent decay of the complex. Charge transfer interactions which affect $k_Q$ can, in this case, be attributed to variations of $k_a$ and $\log_{10} k_Q$ should correlate with $IP_D$. If, however, $k_q$ is slow relative to $k_a$ and $k_{-a}$ the expression for $k_Q$ becomes (6) so that the

$$k_Q = k_a k_q / k_{-a} = K k_q \qquad (6)$$

non-radiative decay of the complex will be concerned with the equilibrium constant $K$. If this relationship holds, charge-transfer effects can be involved in either or both $K$ and $k_q$. The equilibrium constant $K$ is expected to be a function of the free energy of formation of the complex so that (7) and hence equation (8) becomes important.

$$\log_{10} K \sim IP_D + \text{constant} \qquad (7)$$

$$\log_{10} k_Q \sim IP_D + \log_{10} k_q + \text{constant} \qquad (8)$$

Although both the derived expressions [equations (5) and (8)] predict a linear relationship between $\log_{10} k_Q$ and $IP_D$ it may be wrong to expect all alkyl halides to exhibit $k_Q$ values which fall on a single straight line since the relative magnitudes of $k_a$, $k_{-a}$, and $k_q$ may differ for different halides. The mechanism of the reaction needs to be elucidated so that the actual role played by charge-transfer interactions is known before further comment on this aspect can be made. Furthermore, since the formation of the initial complex is a reversible process the observed scatter in $k_Q$ values may possibly be attributable to the varying efficiency of the back-transfer reaction, especially since alkyl chlorides with different alkyl groups have been used as quenchers.

The ability of the halide to act as donor or acceptor in the fluorescence quenching mechanism, depending upon the electronegativity of the halogen atom concerned, was investigated with substituted benzyl halide quenchers. A linear correlation between a $k_Q$ function and the Hammett constant ($\sigma_p$) for the substituent was obtained (Figure 2) for each of the substituted benzyl halide systems studied. The gradients calculated from plots for $\log_{10} [k_Q(X)/k_Q(H)]$ against $\sigma_p$ (Hammett plots) provided information regarding the direction of transfer of electronic charge in the quenching mechanism. A positive value for the gradient $\rho$ of a Hammett plot is usually considered evidence for some degree of charge accession to the benzyl system at the transition state of

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[10] P. J. Wagner, *J. Amer. Chem. Soc.*, 1967, **89**, 2505.

[11] H. Leonhardt and A. Weller, *Ber. Bunsengesellschaft Phys. Chem.*, 1963, **67**, 791; J. B. Birks, ' Photophysics of Aromatic Molecules,' Wiley-Interscience, New York, 1971, p. 425.

[12] K. Kaneta and M. Koizumi, *Bull. Chem. Soc., Japan*, 1967, **40**, 2254; D. Rehn and A. Weller, *Ber. Bungsengesellschaft Phys. Chem.*, 1969, **73**, 834.

the rate-determining step of the quenching reaction.[13] Whilst ρ was positive for substituted benzyl chlorides, a negative ρ value was obtained for substituted benzyl iodides and that for substituted benzyl bromides was intermediate between these two values (Table 4). This clearly demonstrated that the benzyl iodides acted as donors and the benzyl chlorides as acceptors in their respective quenching mechanisms with alkanone singlets. Benzyl bromides appeared to exhibit a reactivity somewhere between these two extremes, a feature which was also shown by Figure 1, and the preference for alkyl bromides to act as donor or acceptor could not be confirmed.

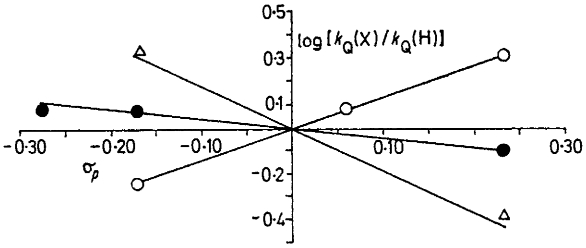


FIGURE 2 Hammett plots for the quenching of butan-2-one fluorescence by substituted benzyl halides: △ X = I, ● X = Br; ○ X = Cl

TABLE 4

Gradients calculated from Hammett plots for the quenching of butan-2-one fluorescence by substituted benzyl halides ($p$-$RC_6H_4CH_2X$; R = H, Me, F, Cl, or OMe) in cyclohexane solution

| X | ρ |
|---|---|
| Cl | +1·35 |
| Br | −0·41 |
| I | −1·85 |

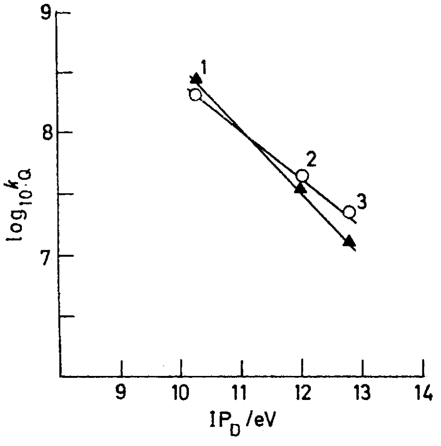
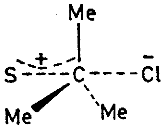


FIGURE 3 Quenching of alkanone fluorescence by monohalogenated benzenes: ○ acetone; ▲ butan-2-one. 1, PhI; 2, PhBr; 3, PhCl; PhF not shown since the maximum and not the absolute value of $k_Q$ is observed

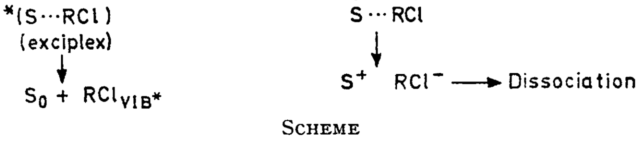
In contrast to the alkyl halides, a linear relationship between $\log_{10} k_Q$ and $IP_D$ was obtained for aryl halide quenchers (Figure 3). This suggested a charge-transfer mechanism with the aryl halide acting as the donor. The difference in behaviour between alkyl and aryl chlorides was attributed to the fact that in the latter the chlorine atom was attached to an $sp^2$ hybridized carbon atom and was not easily ionized. The importance of a labile halogen atom was demonstrated by the high $k_Q$ value obtained for 2-chloro-2-methylpropane compared to 1-chloro- and 2-chloro-butane. High $k_Q$ values were also obtained for other tertiary chlorides, triphenylmethyl chloride, and tributyltin chloride with $k_Q$ values of $5{\cdot}3 \times 10^8$ and $3{\cdot}7 \times 10^8$ l mol $s^{-1}$ respectively (Table 1). The involvement of an easily ionizable halogen atom in the fluorescence quenching mechanism was interpreted in terms of charge donation to the alkyl chloride so that the charge actually resided on the chlorine atom, with cationic character delocalized over the alkanone S and the alkyl group of alkyl halide (A).



(A)

The lowest unoccupied orbital situated on the alkyl halide is σ* in nature[14] and is strongly repulsive so that the $n \longrightarrow \sigma^*$ absorption transition associated with alkyl halides results in dissociation of the molecule. Partial electron charge donation from the excited state ketone must also increase the electron density of the σ* orbital, thus resulting in partial dissociation of the halide. This is in agreement with the model outlined above since the greater the dissociation of the halide the greater the binding energy of an exciplex formed between the excited state alkanone and an alkyl chloride. The binding energy of an exciplex is reflected by the overall fluorescence quenching rate constant $k_Q$ so that an easily ionizable chloride should exhibit a correspondingly high $k_Q$ value.

Although charge-transfer interactions were clearly implicated in the mechanism for the quenching of alkanone fluorescence by alkyl halides it was not clear what role the interaction occupied. It was considered that there were two possible modes for charge transfer influence in the quenching process: (1) an effect upon the binding energy of an exciplex or (2) the formation of a cation–anion radical pair. As demonstrated by the case for an alkyl chloride quencher, the quenching reaction could have been explained by either of these two possible charge-transfer interactions (Scheme). The binding



SCHEME

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

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

energy of an exciplex involves contributions from charge-transfer interactions (9) and the exciplex usually decays *via* radiationless transitions.[13] In this context,

$$*(S \cdots RCl) \equiv (S^{*} \cdots RCl) \leftrightarrow (S \cdots RCl^{*}) \leftrightarrow (S^{+} \cdots RCl^{-})) \leftrightarrow (S^{-} \cdots RCl^{+}) \quad (9)$$

the C–Cl bond of the halide could act as a vibrational energy sink [15,16] and enhance the non-radiative decay process of the exciplex. In a non-polar solvent, it was assumed that the formation of a cation–anion radical pair was inefficient [17] so that the formation of an exciplex occupied the dominant role in the quenching process. This is analogous to the report that the fluorescence observed for exciplexes formed between electron-rich and electron-poor aromatic hydrocarbons was quenched by solvent of high dielectric constant and this phenomenon was explained on the basis of polar solvent enhanced formation of cation–anion radical pairs in competition with formation of the fluorescent exciplex.[18]

Thus, the quenching of alkanone fluorescence in non-polar solvent by alkyl halides was believed to involve the formation of an exciplex and not a cation–anion radical pair. Electronic interactions are necessary not only to stabilize the exciplex but to establish communication between the excited electrons in the alkanone molecule and the vibrating nuclei in the quencher. The coupling of the excited molecule with the vibrational modes of the carbon–halogen bond provides a convenient pathway for radiationless decay of the exciplex. The overall result of the fluorescence quenching reaction was to provide a source of vibrationally excited alkyl halide molecules (Scheme). If this excess of vibrational energy was close to the carbon–halogen bond dissociation energy then decomposition of the chloride was possible. This mechanism may account for the observed alkanone induced decomposition of carbon tetrachloride [7] and dichlorobutanes [19] in solution.

Although this study has been concerned only with fluorescence quenching it is considered that halogeno-compounds will also quench ketone triplets. Thus, aryl halides exhibit weak quenching of acetone and benzophenone triplet states,[20] phenyl ketones sensitize the dissociation of alkyl chlorides,[21] and the excited state lifetime of triplet benzophenone has been reported to be substantially reduced in carbon tetrachloride relative to perfluoromethylcyclohexane.[22]

[4/302 *Received, 15th February, 1974*]

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[15] D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1972, **94**, 3679.

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[17] J. B. Birks, ' Photophysics of Aromatic Molecules,' Wiley-Interscience, New York, 1971, p. 429.

[18] H. Knibbe, K. Rollig, F. P. Schafer, and A. Weller, *J. Chem. Phys.*, 1967, **47**, 1184.

[19] M. A. Golub, *J. Amer. Chem. Soc.*, 1970, **92**, 2615.

[20] R. O. Loutfy and R. W. Yip, *Canad. J. Chem.*, 1973, **51**, 1881.

[21] A. Harriman, B. W. Rockett, and W. R. Poyner, *J.C.S. Perkin II*, 1974, 485.

[22] P. B. Merkel and D. R. Kearns, *J. Chem. Phys.*, 1973, **58**, 398.