# Quenching of Acetone Fluorescence by Inorganic Anions

By **Anthony Harriman** and **Bernard W. Rockett**,* Department of Physical Sciences, The Polytechnic, Wolverhampton WV1 1LY

Simple inorganic anions were found to be effective quenchers of acetone fluorescence in aqueous solution. A linear correlation for the quenching rate constant with the ionization potential of the anion, measured by the energy of the charge-transfer-to-solvent (C.T.T.S.) absorption band maximum, has been observed. Although no fluorescence from an excited-state charge-transfer complex was detected, an electron-transfer quenching mechanism was clearly implicated. Energy transfer complications were suggested for the nitrite and nitrate ions.

INORGANIC anions have been shown to be effective quenchers of the fluorescence of dyes,[1] electron acceptors,[2-4] and aromatic hydrocarbons.[5] Several mechanisms have been proposed to explain the observed fluorescence quenching by inorganic anions. Two important processes have been postulated. (1) Electron transfer occurs from the inorganic anion to the fluorescent species with the consequent formation of a radical anion.[6,7] The formation of the radical anion is usually

$$^1M^* + A^- \rightleftharpoons {}^1M^* \cdots A^- \longrightarrow M^- + A\cdot \qquad (1)$$

preceded by an initial collision complex (encounter complex).[6] (2) There is an external heavy-atom effect in which the inorganic anion increases the triplet-state population of the fluorescent species by a spin–orbit coupling method, involving an intermediate exciplex.[7]

$$^1M^* + A^- \longrightarrow {}^3M^* + A^- \qquad (2)$$

A linear correlation has been obtained [5] between the rate constant for quenching of anthracene fluorescence and the redox potential of the anion which was interpreted in terms of an electron-transfer mechanism. However, in the absence of flash photolysis evidence for the formation of the radical anion, the electron-transfer mechanism cannot be conclusively proved for a fluorescent species known to be susceptible to external heavy-atom effects. In this study, we present the results of an investigation into the efficiency of inorganic anions as quenchers for the fluorescence of acetone in aqueous solution.

Acetone exhibits typical alkanone absorption and emission properties; it is characterised as an $n$–$\pi^*$ absorption transition to the lowest excited singlet state followed by efficient intersystem crossing to the lowest triplet state.[8] The quantum efficiency of fluorescence is subsequently very low and, at 313 nm excitation, is *ca.* 0·001 in cyclohexane solution.[9] External heavy-atom spin–orbit perturbers are much less efficient [10] in promoting intersystem crossing from the singlet to triplet states for $n$–$\pi^*$ species than for $\pi$–$\pi^*$ species. Therefore, the external heavy-atom effect was expected to occupy only a minor role in the mechanism for the quenching of acetone fluorescence by inorganic anions if the quenching rate constant was fairly close to that of the diffusion-controlled process.

## EXPERIMENTAL

*Materials.*—AnalaR grade sodium salts were used throughout the study and were recrystallised twice before use. De-ionised water was distilled from alkaline permanganate.

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*Spectroscopy*.—Fluorescence spectra were recorded with a Perkin-Elmer fluorescence spectrophotometer MPF-2A. Concentrations of acetone used were in the region of $5 \times 10^{-2}$M and the quencher concentration was at least a factor of 2 higher than this concentration. The acetone absorption spectra were unaltered on addition of the anion.

## RESULTS AND DISCUSSION

The Stern–Volmer[11] relationship (3) was used to obtain the quenching rate constant ($k_q$) for the quenching of acetone fluorescence, at 313 nm excitation, by a series of inorganic anions. $I_0$ and $I$ are the uncorrected

$$I_0/I = 1 + k_q\tau[A] \qquad (3)$$

intensities of fluorescence in the absence and presence, respectively, of a concentration [A] of the anion. A value of 2·1 ns was used for the singlet-state lifetime ($\tau$) of acetone under the experimental conditions.[*,9] The Table shows the values obtained for the quenching rate constant and the slope ($k_q\ \tau$) of the Stern–Volmer plot for the quenching of acetone fluorescence by a series of inorganic anions in aqueous solution.

Values for the quenching of acetone fluorescence by the sodium salts of inorganic anions in aqueous solution

| Anion | $k_q$/l mol$^{-1}$ s$^{-1}$ | $10^{-9}\ k_q\tau$/l mol$^{-1}$ | $10^{-3}\nu_{\text{C.T.T.S.}}$/cm$^{-1}$ |
|---|---|---|---|
| $I^-$ | 12·73 | 6·06 | 44·2 |
| $SO_3^{2-}$ | 11·44 | 5·45 | 44·0 |
| $SCN^-$ | 10·76 | 5·12 | 45·0 |
| $NO_2^-$ | 9·32 | 4·44 | 52·0 |
| $NO_3^-$ | 8·96 | 4·23 | |
| $S_2O_3^{2-}$ | 6·14 | 2·92 | 46·5 |
| $S_2O_8^{2-}$ | 5·79 | 2·76 | |
| $Br^-$ | 3·16 | 1·50 | 50·3 |
| $F^-$ | 0·32 | 0·15 | |
| $Cl^-$ | 0·097 | 0·046 | 54·5 |
| $OH^-$ | 0·074 | 0·035 | 52·3 |
| $SO_4^{2-}$ | 0·050 | 0·024 | 57·1 |
| $CO_3^{2-}$ | <0·01 | <0·01 | |

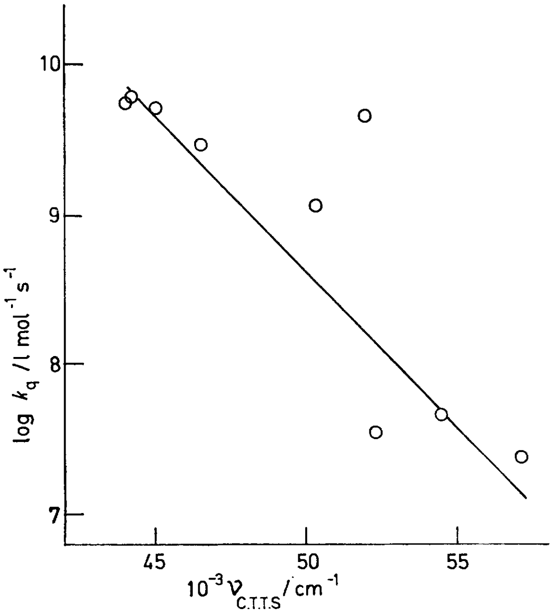
Fluorescence quenching by non-heavy atom quenchers in solvents of low polarity is frequently accompanied by the appearance of a new fluorescence emission at longer wavelength, which is attributed to an excited-state charge-transfer complex (exciplex).[12] As the solvent polarity increases, the fluorescence intensity and the lifetime of the exciplex decrease[13] and in polar solvents the new fluorescence emission can no longer be observed. However the quenching efficiency is still dependent upon the oxidation and reduction potentials of the donor and acceptor[14] and flash photolysis[6] studies have shown the presence of solvated ions. 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 ($IP_D$) [equation (4)].

$$\log_{10} k_q \approx \text{constant} + IP_D \qquad (4)$$

Accurate ionization potentials are not readily available for fluorescence quenchers; however they are related to polarographic redox potentials[15] and to the energy of the charge-transfer-to-solvent (C.T.T.S.) absorption maximum ($\nu_{\text{C.T.T.S.}}$).[5] The energy of the C.T.T.S. band maximum ($E_{\text{max.}}$) varies with ionization potential[16] but also depends on the radius of the potential energy well defining the excited state [equation (5)],[†] and

$$E_{\text{max.}} = IP + h^2/8mR_c^2 \qquad (5)$$

according to the Franck–Condon principle the dimensions of the cavity are defined by ground-state ion–solvent interactions. Therefore, the $E_{\text{max.}}$ is not as accurate a measure of $IP_D$ as is the redox potential, but for aqueous solution provides a sufficiently quantitative value to investigate the relationship between $k_q$ and $IP_D$ for inorganic anions.



Plot of quenching rate constant against the energy of the C.T.T.S. absorption maximum

The Figure shows a plot of log $k_q$ against $\nu_{\text{C.T.T.S.}}$ for the values listed in the Table. A linear correlation between the log of the quenching rate constant and the ionization potential of the anion was observed. The values obtained for the quenching rate constant approach the diffusion-controlled rate[‡] and are of a comparable

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[*] The radiative lifetime calculated from the integrated absorption spectrum.

[†] $m$ is the mass of the electron and $R_c$ is the distance between the ion centre and the inner surface of the potential energy well.

[‡] The diffusion controlled rate constant has a value of $6{\cdot}4 \times 10^9$ l mol$^{-1}$ s$^{-1}$ under the experimental conditions used for this study.

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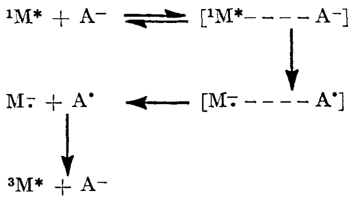
magnitude to those obtained for quenching of aromatic hydrocarbon fluorescence by inorganic anions.[5,7] Although some of the anions used in this study do have considerable spin–orbit coupling parameters, the high values obtained for the quenching rate constants, together with the linear plot of the Figure, point clearly to an electron-transfer mechanism rather than a heavy-atom effect which is inefficient for $n$–$\pi^*$ excited states.[10,17,18] The nitrate and nitrite ions both exhibit an $n$–$\pi^*$ absorption transition[16] at 303 and 355 nm respectively and may be involved in an energy-transfer reaction with the excited state of the acetone. Such a reaction would invalidate the quenching rate constants for these anions since the two different mechanisms cannot be directly compared.

Exciplex fluorescence was not expected due to the high polarity of the solvent and none was observed for any of the systems investigated in this study. With the exception of nitrate and nitrite mentioned previously, an excellent correlation between the quenching rate constant and the ionization potential of the anion was obtained. This provides clear evidence for an electron-transfer mechanism despite the absence of exciplex fluorescence and flash photolysis data for the radical anion. In this mechanism (Scheme) the electronic energy may be dissipated, during the electron-transfer process, as vibrational energy to the solvent sink. Chemiluminescence experiments[19] have shown that ion recombination can lead to triplet-state formation and the overall consequence of the electron-transfer mechanism could be an increase in the population of the acetone triplet state.



Scheme

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