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The fluorescence quenching of 5,6-benzoquinoline and its conjugate acid by Cl^-, Br^-, SCN^- and I^- ions

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Abstract

The fluorescence quenching of the free base and conjugated acid forms of 5,6-benzoquinoline (5,6-BQ) by Cl^-, Br^-, SCN^- and I^- in aqueous solution over the temperature range 25–50 °C has been investigated. Stern–Volmer plots were found to be linear for the quenching of free base 5,6-BQ by Cl^- and Br^- but showed upward curvature for the other quenching systems. The active sphere model was used to analyze the latter systems. As is the case in previous fluorescence quenching studies involving these ions, the rate constants were found to increase with increasing oxidation potential of the quencher. The rate constants for quenching of free base 5,6-BQ by Cl^- and Br^- showed little variation with temperature, while the other systems showed temperature dependences typical of diffusion-limited processes. The activation energies and frequency factors were found to increase with increasing effectiveness of the quencher. Some preliminary low temperature spectra data indicate that the quenching of these systems results in enhanced triplet-state formation.

Keywords: Fluorescence quenching; Thiocyanate ions; Halide ions; 5,6-Benzoquinoline

1. Introduction

It is well known that thiocyanate and halide ions are effective fluorescence quenchers of aromatic molecules, and that the quenching is usually found to increase with increasing oxidation potential of the anion [1–11]. Although this observation suggests that an anion-to-fluorophore electron transfer mechanism is responsible for the quenching, the expected formation of aromatic radical anions is usually not observed [2,3,6]. However, the presence of anion quenchers has been found to cause an increase in triplet-state formation [2,3,6,12]. Such observations led Watkins [2–4] to propose that the anion enhances the intersystem crossing rate of the fluorophore owing to a perturbation of its lowest energy excited singlet state by nearby excited anion-to-fluorophore charge transfer states. Shizuka et al. [6] have examined the effect of quenchers on the light-induced triplet–triplet absorption spectrum of some aromatic molecules and have determined the rate constants for anion-induced intersystem crossing. They have shown that, although the fluorescence quenching increases with increasing oxidation potential of the anion, the anion-induced intersystem crossing rate constant obeys the heavy-atom effect. For example, even though N_3^- is more effective than Br^- in quenching the fluorescence of phenanthrene, Br^- is more effective in enhancing the intersystem crossing rate. On the basis of this observation, these workers conclude that electron transfer is responsible for the fluorescence quenching and that the resulting charge transfer complex is effective in triplet formation. Further evidence for this mechanism has been the recent observation of transient radicals formed by the electron transfer from the anion to the excited aromatic molecule in acetonitrile [12].

Although fluorescence quenching is a topic of extensive investigation, there have been no reports of the fluorescence quenching of azines by these anions. In addition very little work has been done on the temperature dependence of the fluorescence quenching by anions [7,10,11]. In this study, we present the results of fluorescence quenching studies of the free-base of 5,6-benzoquinoline (5,6-BQ) and the conjugate acid form (5,6-BQH$^+$) by Cl^-, Br^-, I^- and SCN^- in aqueous solutions over the temperature range 25–50 °C. We have undertaken these investigations because studies of the temperature dependence of such reactions yield activation energies, frequency factors and entropies of activation, which are essential to a good understanding of any reacting system.

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These studies are also significant because the azine nitrogen can be protonated, and thus the effect of the charge of the fluorophore on the quenching can be examined.

2. Experimental details

5,6-BQ was obtained from Aldrich Chemical Company and was recrystallized from a 90:10 ethanol:water mixture and vacuum sublimed prior to use. Perchloric acid, sodium hydroxide, sodium perchlorate and sodium chloride were all Fisher Scientific reagent grade and were used without further purification. ACS reagent grade sodium bromide, sodium thiocyanate and sodium iodide were obtained from Aldrich Chemical Company and were used without further purification.

Emission spectra and intensities were all obtained on a Perkin–Elmer LS-5B fluorescence spectrophotometer. Decay curves were obtained by the time-correlated single-photon method. The technique and the apparatus employed have been discussed elsewhere [13,14]. Since quenching by oxygen was found to be insignificant in these compounds, the samples were not purged with nitrogen.

3. Results and discussion

The fluorescence spectra of 5,6-BQ in basic and in acidic aqueous solutions are shown in Fig. 1 and are attributed to emissions from the free-base and the conjugate acid forms respectively of the molecule. In order to determine the rate constants for fluorescence quenching of these two species, the fluorescence lifetimes in the absence of quenching were needed. Fluorescence decay measurements of 5,6-BQ in basic and acid solutions were made and were found to show good single-exponential behavior. The resulting fluorescence lifetimes for the two species have been determined over a temperature range from 20 to 50 °C, and the results are shown in Table 1.

We find that the fluorescence of 5,6-BQ and 5,6-BQH$^+$ are quenched by the Cl$^-$, Br$^-$, SCN$^-$ and I$^-$ ions. The effect of SCN$^-$ on the fluorescence spectrum of 5,6-BQH$^+$ is shown in Fig. 2. The solutions used to obtain these spectra all contained 0.10 M HClO$_4$ and were kept at a constant ionic strength of 0.60 M with the addition of the appropriate amount of NaClO$_4$. The effect of increasing concentrations of SCN$^-$ is to diminish the fluorescence intensity of 5,6-BQH$^+$ over the entire spectrum. No evidence of an exciplex emission can be seen. The fluorescence quenching of 5,6-BQH$^+$ by the other ions shows similar behavior. The quenching of the fluorescence of free base 5,6-BQ by the various ions is similar to but less effective than that of 5,6BQH$^+$.

In interpreting the fluorescence quenching results, the Stern–Volmer kinetic model was first used. This model predicts that a plot of I_0/I vs. quencher concentration will be linear with a slope equal to $k_q\tau$, where k_q is the rate constant for fluorescence quenching and τ is the fluorescence lifetime in the absence of quenching. Although such plots are found to exhibit good linearity in the case of the quenching of free base 5,6-BQ by Cl$^-$ and Br$^-$, the quenching of the free base by SCN$^-$ and by I$^-$ show slight upward curvature, and those of the conjugate acid, 5,6-BQH$^+$, all show upward curvatures. The curvature is particularly significant for the case of quenching by SCN$^-$ and I$^-$.

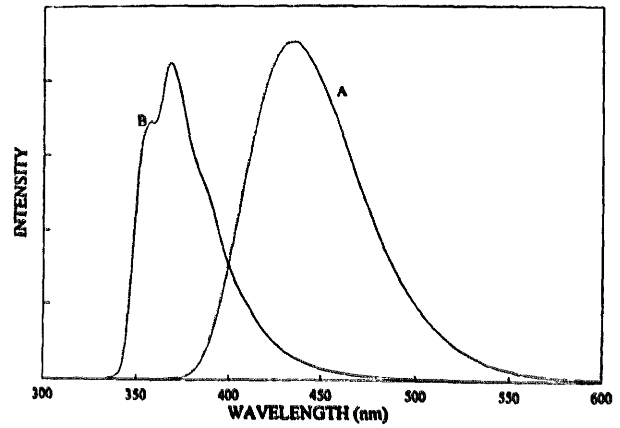

Fig. 1. Fluorescence spectra of 5,6-BQ (6.0 × 10^{-5} M) in aqueous solutions at 25 °C: (A) 0.10 M HClO$_4$; (B) 0.20 M NaOH. An excitation wavelength of 320 nm was used.

Table 1
Fluorescence lifetimes of 5,6-BQ and 5,6-BQH$^+$ in aqueous solutions at various temperatures, where the 5,6-BQ lifetimes were obtained from solutions containing 0.20 M NaOH and the 5,6-BQH$^+$ were obtained from solutions containing 0.10 M HClO$_4$

T (°C)	τ (ns)	
	5,6-BQ	5,6-BQH$^+$
20	8.26	9.25
30	8.11	9.23
40	7.90	9.19
50	7.66	9.16

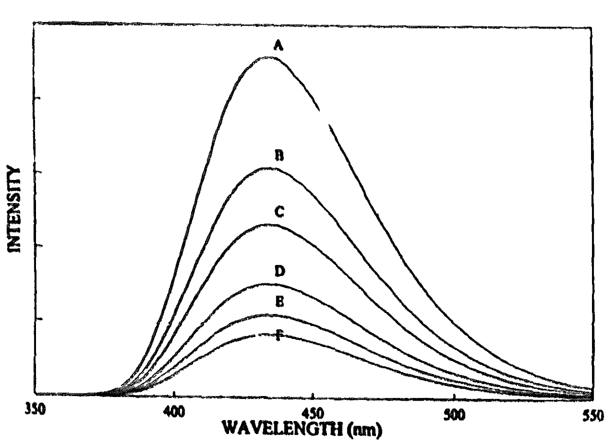

Fig. 2. The fluorescence spectra of the 5,6-BQH$^+$ ion (8.4 × 10^{-5} M) in 0.10 M HClO$_4$ with various concentrations of NaSCN: (A) 0.0 M; (B) 0.0050 M; (C) 0.010 M; (D) 0.020 M; (E) 0.030 M; (F) 0.040. The ionic strength of all solutions were kept constant at 0.60 M with NaClO$_4$.

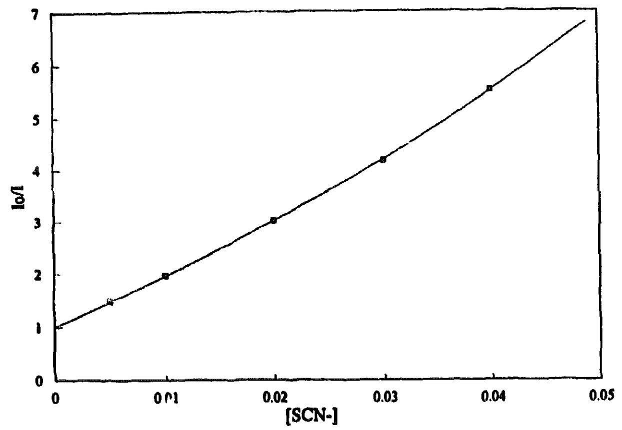

Fig. 3. Stern–Volmer plot for the fluorescence quenching of 5,6-BQH$^+$ ion by SCN$^-$: —, non-linear least-squares fit of the equation $I_0/I = (1 + K_{SV}[SCN^-])\exp(V_0[SCN^-])$ to the data. K_{SV} is the Stern–Volmer constant and V_0 is the molar active sphere volume.

In order to extract rate constants for the various fluorescence quenching systems, we have applied the active sphere model [15] to the quenching data for those systems which showed upward curvature. In this model, it is assumed that, if a quencher is within a certain radius of the fluorophor at the time of excitation, the excited molecule will be quenched immediately. The volume associated with this distance is called the active sphere volume. If V_0 is the active sphere volume per mole and [Q] is the quencher concentration, then $\exp(-V_0[Q])$ is the probability that a quencher is not in the active sphere region. It therefore represents the fraction of the excited molecules which can be quenched by the collisional mechanism. Incorporating this factor into the Stern–Volmer model leads to the following expression:

$$\frac{I_0 \exp(-V_0[Q]}{I} = (1 + k_q\tau[Q]) \qquad (1)$$

Rearrangement of Eq. (1) results in the more usual expression

$$\frac{I_0}{I} = (1 + k_q\tau[Q])\exp(V_0[Q]) \qquad (2)$$

In order to obtain values of k_q and V_0 from the quenching data, a non-linear least-squares analysis was performed to fit the data to Eq. (2). The results of such an analysis of the fluorescence quenching of 5,6-BQH$^+$ by SCN$^-$ is shown in Fig. 3.

The resulting rate constants, active sphere molar volumes and associated active sphere radii are presented in Table 2, together with the associated oxidation potential of the anion quenchers. The rate constants for both systems are found to increase with increasing oxidation potential of the quencher, as is expected for an electron transfer mechanism. The rate constants for quenching of 5,6-BQH$^+$ are larger than those of 5,6-BQ for each of the four quenchers. However, the ratio of k_q(BQH$^+$) to k_q (5,6-BQ) decreases from 19 to 1.3 upon going from Cl$^-$ to I$^-$. This is probably due to the quenching approaching the diffusion-controlled limit with the stronger quenchers.

Table 2 also shows that the active sphere volume increases with increasing effectiveness of the quencher and that the volumes for the 5,6-BQH$^+$ systems are larger than those for the 5,6-BQ systems. An interesting comparison can be made between the 5,6-BQ–I$^-$ and the 5,6-BQH$^+$–Br$^-$ quenching systems. Although the two systems have similar quenching rate constants, the latter system has an active sphere volume that is 50% larger. This indicates that the 5,6-BQH$^+$–quencher systems interact over larger distances than the free-base–quencher systems, a result that is probably due to the coulombic interaction in the former.

The measured active sphere molar volumes are comparable with other quenching systems involving these anions. Moriya [7] has measured the fluorescence quenching of 7-ethoxycoumarin by Br$^-$ and I$^-$ in aqueous solutions and has obtained V_0 values of 0.08 mol^{-1} and 1.6 l mol^{-1} respectively. The observed rate constants for these systems are 4.3×10^9 and 1.0×10^{10} l mol^{-1} s^{-1} respectively. Moriya [8] also measured the fluorescence quenching of protonated 7-ethoxycoumarin by Cl$^-$. The V_0 value obtained for this system was 1.2 l mol^{-1}. Although this value is considerably larger than that found for the 5,6-BQH$^+$–Cl$^-$ quenching system, the measured rate constant for quenching is 5.8 × 10^9

Table 2
Fluorescence quenching rate constants at 25 °C and active sphere volumes for 5,6-BQ and 5,6-BQH$^+$

Quencher	Oxidation potential (V)	5,6-BQ			5,6-BQH$^+$		
		k_q [a] (l mol^{-1} s^{-1})	V (active sphere) [b] (l mol^{-1})	Radius (m)	k_q [c] (l mol^{-1} s^{-1})	V (active sphere) [d] (l mol^{-1})	Radius (m)
Cl$^-$	−1.36	1.2×10^7	0	0	2.3×10^8	0.5	6×10^{-10}
Br$^-$	−1.09	8.9×10^8	0	0	7.9×10^9	3.5	1.1×10^{-9}
SCN$^-$	−0.77	5.7×10^9	1.7	8.8×10^{-10}	9.2×10^9	5.2	1.3×10^{-9}
I$^-$	−0.54	7.6×10^9	2.3	9.7×10^{-10}	9.8×10^9	6.6	1.4×10^{-9}

[a] Experimental errors within ±2%.
[b] Experimental errors within ±10%.
[c] Experimental errors within ±5%.
[d] Experimental errors less than ±10%, except for I− (±20%).

$l\ mol^{-1}\ s^{-1}$ and is also much larger. As is the case in our systems, the active sphere volume for the protonated coumarin quenching system is larger than that of an unprotonated coumarin quenching system of similar quenching efficiency.

If a charge transfer quenching mechanism is operative in these systems, the magnitude of the rate constant should correlate with ΔG_{et}, the free-energy change associated with electron transfer from the anion to the excited benzoquinoline [16]. For the free-base quenching systems, the free-energy change is given by the following expression:

$$\Delta G_{et} = E_{1/2}(A^-/A) - E_{1/2}(B^-/B) - \Delta E \quad (3)$$

where $E_{1/2}(A^-/A)$ and $E_{1/2}(B^-/B)$ are the half-wave potentials corresponding to the following reductions processes:

$$A(aq) + e \longrightarrow A^-(aq) \quad (4)$$

and

$$B(aq) + e \longrightarrow B^-(aq) \quad (5)$$

where A^- and B represent the anion quencher and the free base 5,6-BQ respectively, and ΔE is the energy change associated with the transition from the ground- to the lowest excited singlet-state in 5,6-BQ. The half-wave reduction potentials for Cl^-, Br^- and I^- are 2.55 eV, 2.0 eV and 1.40 eV respectively [17] and that of SCN^- has been estimated to be 1.50 eV from its charge transfer to solvent energy [6,18]. Although the reduction potential of 5,6-BQ has not been measured in water, it has a value of −2.20 V vs. KCl saturated Ag/AgCl (−2.00 V corrected to the standard hydrogen electrode) in dimethylformamide [19]. If this value is combined with the other values in Eq. (2), we calculate ΔG_{et} values of +96 kJ mol^{-1}, +42 kJ mol^{-1}, −6 kJ mol^{-1} and −15 kJ mol^{-1} for Cl^-, Br^-, SCN^- and I^- quenching systems respectively. It is likely that the actual ΔG_{et} values are somewhat lower than these estimates because the reduction potential of 5,6-BQ in water is likely to be higher than that measured in dimethylformamide.

Unfortunately, a good estimate for ΔG_{et} for the 5,6-BQH^+–quencher systems cannot be obtained because the half-wave reduction potential of 5,6-BQH^+ has not been measured. However, it is likely that the reduction potential of 5,6-BQH^+ is higher (less negative) than that of free base 5,6-BQ. Although this change will tend to make the ΔG_{et} values of 5,6-BQH^+–quencher systems more negative than those of the free-base systems, the change in the transition energy has the opposite effect. The energy required to excite 5,6-BQH^+ is lower than that of free base 5,6-BQ by 47 kJ mol^{-1}. Thus it is not possible to compare the electron transfer free energies of the two types of systems.

Since it is difficult to obtain good estimates for ΔG_{et} for these systems, the relationship between the magnitude of the rate constant with the half-wave reduction potential of the anion quenchers will be compared. Figure 4 shows a plot of the logarithm of the quenching rate constant vs. the half-wave reduction potential of the quencher for the two quenching systems. Both systems show that the rate constants increase as the reduction potential of the quencher decreases, and both tend to level off at low values of the reduction potential. However, the plot for the 5,6-BQH^+ systems levels off before that of the 5,6-BQ systems. The rate constants for the quenching of 5,6-BQH^+ by Br^-, SCN^- and I^- are of the order of 10^{10}, and they show only a small increase with decreasing reduction potential of the quencher. This probably arises because the reaction approaches the diffusion-controlled limit; however, it should be noted that there is no correlation between the quenching rate constant and the mobility of the quencher. For example, Br^- is more mobile than SCN^- and yet SCN^- is a better quencher than Br^-.

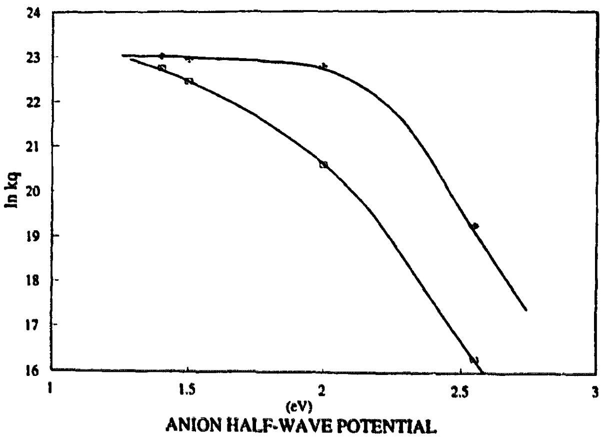

Fig. 4. Plot of the logarithm of the rate constant for fluorescence quenching vs. the half-wave potential of the anion quencher for 5,6-BQ (lower curve) and 5,6-BQH^+ (upper curve).

The magnitude of the rate constants in Table 2 can be compared with what is expected for a diffusion limited reaction. According to Smoluchowski theory [20] the rate constant for a diffusion-controlled reaction between two neutral molecules or between a neutral molecule and an ion is given by the following expression:

$$k_d = 4\pi R_{AB}(D_A + D_B)N1000 \quad (6)$$

D_A and D_B are the diffusion coefficients of the anion and the benzoquinoline respectively, R_{AB} is the contact radius and N is Avogadro's number. It should be noted that Eq. (6) will yield k_d in liters per mole per second if R_{AB} is in meters and D_A and D_B are in square meters per second. The radius of 5,6-BQ was approximated to be 3.7 Å from an estimate of its van der Waals volume. The diffusion coefficient of 5,6-BQ was estimated from the Stokes–Einstein equation using this radius. A value of $6.6 \times 10^{-10}\ m^2\ s^{-1}$ was obtained. The diffusion coefficients of the anion quenchers were determined from their related molar conductivities. Values of $2.03 \times 10^{-9}\ m^2 s^{-1}$, $2.08 \times 10^{-9}\ m^2 s^{-1}$, $1.76 \times 10^{-9}\ m^2 s^{-1}$ and $2.05 \times 10^{-9}\ m^2\ s^{-1}$ were obtained for Cl^-, Br^-, SCN^- and I^- respectively. The radii of these ions were assumed to be the hydrodynamic radii which were obtained from the Stokes-Einstein relationship. Values of 1.21 Å, 1.18 Å, 1.39 Å and 1.20 Å were obtained for Cl^-, Br^-, SCN^- and I^-

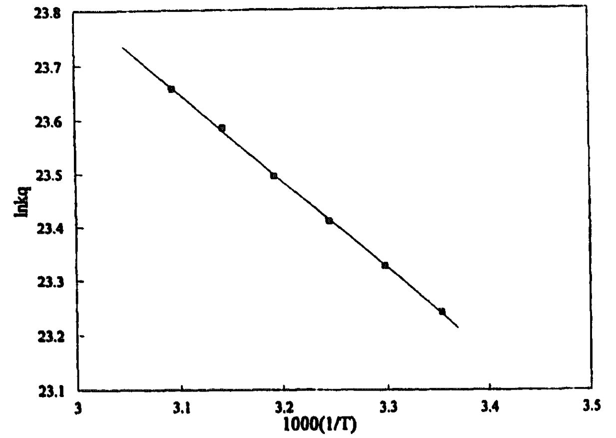

Fig. 5. Arrhenius plot for the fluorescence quenching of the 5,6-BQH$^+$ by SCN$^-$.

respectively. When these values are substituted into Eq. (6) above, a value of 1.0×10^{10} l mol^{-1} s^{-1} is obtained for the diffusion-limited rate constants for the quenching of 5,6-BQ by Cl$^-$, Br$^-$ and I$^-$ at 25 °C. The calculated result for the quenching by the SCN$^-$ ion is 9.3×10^9 l mol^{-1} s^{-1}. The smaller value obtained for SCN$^-$ is because it has a smaller diffusion coefficient. A comparison of these values with the results in Table 2 suggest that the quenching of the free-base benzoquinoline by SCN$^-$ and I$^-$ is near the diffusion limit while the quenching by Br$^-$ and Cl$^-$ is below this limit by one and three orders of magnitude respectively.

In order to estimate the diffusion-limiting rate constant for the quenching of 5,6-BQH$^+$ by the anions, the following expression which was derived by Debye [21] will be used:

$$k_d=\frac{4\pi N z_A z_B e^2 (D_A+D_B) N 1000}{4\pi\epsilon_0 \epsilon RT[\exp(z_A z_B e^2/4\pi\epsilon_0\epsilon RTR_{AB})-1]} \qquad (7)$$

In this expression, z_A and z_B are the charges of the anion and the benzoquinolinium ion respectively, ϵ is the dielectric constant of the solvent and ϵ_0 is the permittivity of free space. In applying this equation, the values for the diffusion coefficient and radius of 5,6-BQH$^+$ were assumed to be the same as those for the free base. Substitution of the appropriate values (MKS units) into Eq. (7) yields a value of 1.7×10^{10} l mol^{-1} s^{-1} for the diffusion-limited rate constant for quenching by SCN$^-$ and 1.9×10^{10} l mol^{-1} s^{-1} for the quenching by each of the other three ions. An examination of Table 2 indicates that the quenching rate constants of Br$^-$, SCN$^-$ and I$^-$ are roughly half these calculated limits while that of Cl$^-$ is almost two orders of magnitude lower.

In addition to performing the fluorescence quenching measurements at 25 °C, we have extended the quenching measurements of all systems except 5,6-BQH$^+$–I$^-$ up to 50 °C. The 5,6-BQH$^+$–I$^-$ system was not included in this study because of the instability of the I$^-$ ion in acid solution during the long time required to perform these experiments. From an analysis of the quenching, we have obtained the rate constants for quenching over this temperature range. We have made and analyzed Arrhenius plots of these results in order to obtain activation energies and frequency factors. Fig. 5 shows such a plot for the fluorescence quenching of 5,6-BQH$^+$ by SCN$^-$.

The activation energies and frequency factors obtained for these systems are shown in Table 3, together with the entropies of activation. The results for the quenching of the free base show considerable variation. The rate constants for quenching of 5,6-BQ by Cl$^-$ and Br$^-$ which are considerably lower than the diffusion-controlled limit show little variation with temperature. The activation energies for these systems are estimated to be less than 3 kJ mol^{-1}. The rate constants for the quenching of 5,6-BQ by SCN$^-$ and I$^-$ are near the diffusion-controlled limit and show a much greater variation with temperature. The activation energies for these systems are 12 kJ mol^{-1} and 13 kJ mol^{-1} respectively. It is interesting to note that I$^-$ is a better quencher than SCN$^-$ in spite of the fact that it has a slightly higher activation energy and because it has a greater frequency factor.

The results for 5,6-BQH$^+$ quenching systems show trends similar to those of 5,6-BQ. The activation energy increases with increasing effectiveness of the quencher, rising from 12.7 kJ mol^{-1} to 15.1 kJ mol^{-1} upon going from Cl$^-$ to

Table 3
Rate constants, activation energies, frequency factors and activation entropies for the fluorescence quenching of 5,6-BQ and 5,6-BQH$^+$

Quenching system	Ion	k_q (l mol^{-1} s^{-1})	E_a (kJ mol^{-1})	A (l mol^{-1} s^{-1})	$\Delta S\ddagger$ (J K^{-1} s^{-1})
5,6-BQ	Cl$^-$	1.2×10^7	<3	4.4×10^{7} [a]	−110
	Br$^-$	8.9×10^8	<3	1.9×10^{9} [a]	−75
	SCN$^-$	5.7×10^9	12.0 [b]	7.3×10^{11} [c]	−26
	I$^-$	7.6×10^9	13.0 [b]	1.4×10^{12} [a]	−21
5,6-BQH$^+$	Cl$^-$	2.3×10^8	12.7 [c]	3.7×10^{10} [d]	−51
	Br$^-$	7.9×10^9	13.3 [c]	1.7×10^{12} [d]	−19
	SCN$^-$	9.2×10^9	15.1 [c]	4.0×10^{12} [d]	−12

[a] Experimental errors within ±2% (except for Cl$^-$ which is ±8%).
[b] Experimental errors within ±4%.
[c] Experimental errors within ±4%.
[d] Experimental errors within ±1%.

SCN^-. The increase in the rate constant in this series is accounted for because the corresponding increase in the frequency factor more than compensates for the increase in the activation energy. We have seen this trend before in the case of proton-transfer quenching of 2-naphthol by anions [22]. In this case, we interpreted the increase in the frequency factor and the activation energy with the effectiveness of the quencher as due to the quenching occurring over a longer range for the more effective quenchers.

The activation energies for these systems can be compared with those of other quenching systems involving these anions. In his study of the fluorescence quenching of 7-ethoxycoumarin by Br^- and I^-, Moriya [7] measured activation energies of 11.7 kJ mol^{-1} and 16.3 kJ mol^{-1} respectively. As in our systems, the more effective quencher has a higher activation energy. Najbar and Mac [11] have measured the fluorescence quenching of some substituted naphthalene and fluoranthene by Br^- and I^- in a methanol–ethanol mixture. They find that the effective quenching systems ($\Delta G_{et} < 0$ and $k_q > 10^9$ l mol^{-1} s^{-1}) have activation energies in the 6–14 kJ mol^{-1} range while the less effective quenching systems ($\Delta G_{et} > 0$ and $k_q < 10^9$ l mol^{-1} s^{-1}) are essentially activationless. These results are quite similar to ours. We observe that the weakly quenching systems 5,6-BQ/Cl^- and 5,6-BQ/Br^-, which have estimated ΔG_{et} values which are positive, are also activationless. Najbar and Mac interpret the low activation energy of the less effective quenching systems as arising because a heavy-atom effect mechanism is the dominant mechanism in these systems.

The measured activation energies for these reactions can be compared with what is expected for a diffusion-controlled reaction. The rate constant for a diffusion-controlled reaction should depend on the diffusion coefficients of the reactants. According to the Stokes–Einstein relationship, the diffusion coefficient is directly proportional to the temperature and inversely proportional to the viscosity of the solvent. For aqueous solutions, a plot of the logarithm of the temperature to viscosity ratio vs. $1/T$ results in a value of 18.5 kJ mol^{-1} for the estimated activation energy for a diffusion-controlled reaction. It should be noted that ln k_d vs. $1/T$ plots using estimates for k_d from Eqs. (6) and (7) result in similar activation energies. A comparison with the activation energies of Table 3 suggests that these values are largely determined by the energetics of diffusion through the solution.

Although most of these quenching reactions are diffusion limited, it is possible to get an estimate for the rate constants k_{et} for electron transfer. In order to do this, the excited state electron-transfer quenching reaction for free base 5,6-BQ was assumed to involve the following mechanism:

$$BQ^* + X^- \underset{k_{-d}}{\overset{k_d}{\longleftrightarrow}} (BQX^-)^* \xrightarrow{k_{et}} BQ^-X \xrightarrow{k_{et'}} (BQX^-) \xrightarrow{k_s} BQ + X^- \quad (8)$$

A similar mechanism can be assumed for the quenching of 5,6-BQH^+.

The first step involves the diffusion of the reactants together to form an encounter complex. The rate constant for this process is k_d, and the rate constant for the diffusion of the reactants out of the solvent cage is k_{-d}. The second step involves the transfer of an electron from the quencher to the excited benzoquinoline molecule. This step has a rate constant k_{et}, and it is assumed to be irreversible. This is followed by a reverse electron transfer to produce the ground-state complex which then rapidly separates. The rate constants for these two processes are $k_{et'}$ and k_s respectively. A similar mechanism was assumed for the quenching of 5,6-BQH^+.

Assuming steady-state kinetics, the following expression for the quenching rate constant k_q is obtained:

$$k_q = \frac{k_{et} k_d}{k_{et} + k_{-d}} \quad (9)$$

Following a method used by Durocher and coworkers [23], the following equation is obtained upon rearrangement of Eq. (9):

$$\frac{1}{k_q} = \frac{1}{k_d} + \frac{1}{K(R_{AB}) k_{et}} \quad (10)$$

where $K(R_{AB}) = k_d / k_{-d}$ is the equilibrium constant for the formation of the encounter complex. According to the Fuoss–Eigen [24] model

$$K(R_{AB}) = \frac{4}{3} \pi N R_{AB}^3 1000 \quad (11)$$

for the free-base system and

$$K(R_{AB}) = \frac{4}{3} \pi N R_{AB}^3 1000 \exp\left(\frac{e^2 N}{4 \pi \epsilon_0 R_{AB} \epsilon R T}\right) \quad (12)$$

for the protonated-base system. The various constants in these equations have been previously defined and MKS units are used.

The estimates for the rate constants for diffusion in the free-base and the protonated-base quenching systems have been previously discussed. See Eqs. (6) and (7).

When the estimated values of $K(R_{AB})$ and k_d are substituted into Eq. (10), values for k_{et} can be calculated. These values are shown in Table 4. As expected, the k_{et} values for both the free-base and the conjugate acid quenching systems

Table 4
Estimates of the rate constants k_{et} for electron transfer

Quenching system	Ion	$K(R)$	k_{et} (s^{-1})
5,6-BQ	Cl^-	0.30	4.0×10^7
	Br^-	0.29	3.4×10^9
	SCN^-	0.33	4.5×10^{10}
	I^-	0.29	1.1×10^{11}
5,6-BQH^+	Cl^-	1.28	1.8×10^8
	Br^-	1 27	1.1×10^{10}
	SCN^-	1.35	1.5×10^{10}

increase with the increasing oxidation potential of the quencher. However, the k_{et} values for the quenching by SCN^- and I^- are larger for the free-base system than for the conjugate acid systems. This is surprising, given the coulombic interaction in the latter system. It may be because this model is inappropriate for the highly quenched BQH^+ systems.

As mentioned in the introduction, a number of flash photolysis studies have shown that the fluorescence quenching by anions results in enhanced triplet-state formation. We have made some preliminary studies that indicate that this is also the case for the 5,6-BQ and 5,6-BQH^+. We have performed some spectral studies of these systems in ethanol glasses at 77 K. We find that the presence of Br^- results in a quenching of the fluorescence and an enhancement in the phosphorescence. The effect is rather small in the case of 5,6-BQ and much more significant in the case of 5,6-BQH^+ systems. Since collisional quenching is not significant at 77 K, the fluorescence quenching and phosphorescence enhancement must be due to active-sphere-type quenching. It is quite likely, however, that the collisional quenching at room temperature also results in enhanced triplet formation.

In summary, it can be concluded that the azine 5,6-BQ and its conjugate acid show anion fluorescence quenching behavior which is similar to that of other systems that have been studied. The quenching increases with increasing oxidation potential of the anion and the conjugate acid is more highly quenched than the free base. The highly quenching systems show both collisional and active sphere quenching, and the active sphere volume increases with increasing effectiveness of the quenching. The activation energies for these systems are especially low for the poorly quenching systems, and the frequency factors and the activation energies increase with increasing effectiveness of the quenching. Indirect and preliminary evidence from low temperature spectra suggests that the fluorescence quenching is accompanied by an increase in triplet formation.

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