

atom results in the more stable ion. The relative stabilities of pairs of isomers are similar at Hartree-Fock and fourth-order Møller-Plesset theory, except for the C- and O-protonated forms of  $C\equiv O$ . However, the Hartree-Fock barrier to proton transfer which separates the isomers is lowered by 11-18 kcal/mol by electron correlation. The Hartree-Fock barriers to proton transfer between lone-pair protonation sites in ions  $H_nAAH_{n+1}^+$  are also significantly lowered by correlation except for  $N_2H^+$ .

(3) Zero-point vibrational energy corrections are sig-

nificant, leading to decreases of 5-10 kcal/mol in protonation energies.

(4) Protonation may lead to an increase or decrease of the A-B bond distance depending on the nature of the A-B bond and the nature of the protonation site. A-B single bonds lengthen upon protonation in homonuclear molecules and in heteronuclear molecules when protonation occurs at the more electronegative atom. The A-B single bond distance decreases when protonation occurs at the preferred more electropositive atom.

## Polyelectrolyte Effect on Fast Interionic Reactions. Quenching of Cationic Phosphorescence Probes with $Co(NH_3)_6^{3+}$ in the Presence of Anionic Polyelectrolytes

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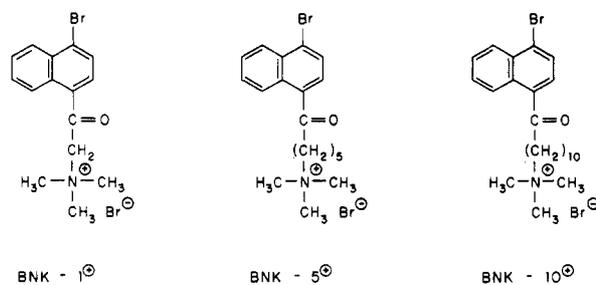
The bimolecular rate constants of quenching of cationic phosphorescence probes with  $Co(NH_3)_6^{3+}$  ( $10^7$ - $10^{10} M^{-1} s^{-1}$ ) were determined from phosphorescence decay measurements in the presence and in the absence of simple polyelectrolytes. The probes used were *n*-(4-bromo-1-naphthyl)alkyltrimethylammonium bromide, alkyl = methyl ( $n = 1$ , BNK-1<sup>+</sup>), pentyl ( $n = 5$ , BNK-5<sup>+</sup>), and decyl ( $n = 10$ , BNK-10<sup>+</sup>). Simple electrolytes (NaCl,  $CaCl_2$ , and  $LaCl_3$ ) enhanced the quenching rates. These results may be explained quantitatively in terms of the Brønsted-Bjerrum-Debye-Hückel theory. Polyelectrolytes such as sodium polystyrenesulfonate, sodium polyethylenesulfonate, and sodium polyacrylate greatly accelerated the quenching. For the slower quenching processes the polyelectrolyte effect suggests that the electrostatic and hydrophobic interactions between reactants (probes) and macroions, and further dehydration of the activated complex with macroions, are very important. However, the specific polymer concentration dependence of the quenching rates suggests that the faster quenching processes are mainly influenced by the diffusional motion of macroions.

### Introduction

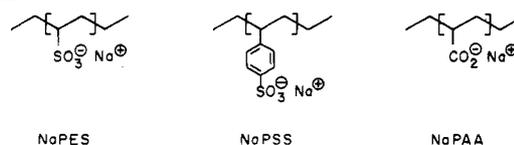
Very fast bimolecular chemical reactions, particularly reactions in aqueous media, are crucial in determining kinetic aspects of biological reactions and of biomolecules and other molecular assemblies.

Recent studies of polyelectrolyte catalyses of interionic reactions have revealed some important general features of this important class of reactions.<sup>1</sup> First, as a result of electrostatic interactions, cationic (or anionic) macroions greatly accelerate the reactions between anionic (or cationic) species, whereas macroions decelerate the interionic reactions between oppositely charged species. These effects of polyelectrolyte are qualitatively interpreted in terms of a local distribution of reactant ions around macroions and more quantitatively interpreted in terms of the change in the thermodynamical activities of reactants and the activated complex via activated-complex theory. Second, in addition to electrostatic interactions, hydrophobic interactions between reactants and macroions are often very important in determining the magnitude of bimolecular reaction rates between charged species. In some cases, even reactions between oppositely charged species are accelerated in the presence of hydrophobic polyelectrolytes. Third, a significant contribution of en-

### Scheme I



### Scheme II



tropic gain associated with the dehydration of reactants and macroions appears to be important in the course of activation.<sup>2</sup> In general it appears that the overall steps of a reaction mechanism are not altered by the polyelectrolyte catalysis in most cases. Interestingly, micellar aggregates of ionic surfactants show similar rate enhancement effects on interionic reactions.<sup>3</sup>

(1) For reviews, see (a) Sakurada, I. *J. Pure Appl. Chem.* 1968, 16, 236; (b) Overberger, C. G. *Acc. Chem. Res.* 1969, 2, 217; (c) Morawetz, H. *Adv. Catal.* 1969, 20, 341; (d) Ise, N. "Polyelectrolytes and the Applications", Rembaum, A.; Selegny, E. Ed.; D. Reidel: Dordrecht, Holland, 1975; p 71; (e) Ise, N.; Okubo, T. *Macromolecules*, 1978, 11, 439.

(2) (a) Ise, N.; Maruno, T.; Okubo, T. *Proc. R. Soc. London, Ser. A*, 1980, 370, 485; (b) Okubo, T.; Maruno, T.; Ise, N. *Ibid.* 1980, 370, 501.

The above general features of the polyelectrolyte effect on bimolecular reaction rates were obtained mainly from experimental evidence derived from relatively slow chemical reactions ( $<10^4 \text{ M}^{-1} \text{ s}^{-1}$ ). In this report we are concerned with the polyelectrolyte enhancement of very fast, even diffusion-controlled, bimolecular reactions.

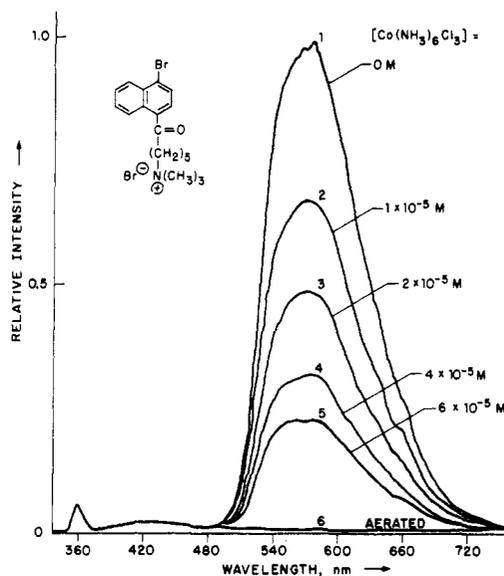
Quenching of fluorescence involving ionic species has been studied in the presence of polyelectrolytes.<sup>4</sup> Meisel et al.<sup>4c</sup> have investigated the rate constant for quenching of  $\text{Ru}(\text{bpy})_3^{2+}$  luminescence in the presence of sodium polyvinylsulfate (quencher =  $\text{Cu}^{2+}$ ). Further determinations of the quenching rates with polyelectrolytes were carried out by Meisel et al.<sup>4f</sup> However, the effect of polyelectrolyte concentration on quenching was not investigated. We further note that LaMer et al. and others have discussed the kinetics of fast ionic reactions of quenching in the presence of simple electrolytes.<sup>5</sup>

We report the quenching of a series of cationic phosphorescence probes, i.e.,  $\text{BNK-1}^+$ ,  $\text{BNK-5}^+$ , and  $\text{BNK-10}^+$  by  $\text{Co}(\text{NH}_3)_6^{3+}$  in the presence of various kinds of polyelectrolytes and simple electrolytes (Schemes I and II). The quenching rate constants were determined directly from the plots of reciprocal lifetime against quencher concentration. The bimolecular quenching rate constants,  $k_{q,0}$  of our probes were found to be between  $2 \times 10^7$  and  $7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  in aqueous solution. We therefore anticipated diffusion-controlled rate ( $\sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) upon the addition of polyelectrolytes, since acceleration factors of  $10^2$ – $10^3$  have been commonly observed.

## Experimental Section

**Chemicals.** 1-(4-Bromo-1-naphthoyl)methyltrimethylammonium bromide ( $\text{BNK-1}^+$ ) and 5-(4-bromo-1-naphthoyl)pentyltrimethylammonium bromide ( $\text{BNK-5}^+$ ) were synthesized and purified by a method described in a separate paper.<sup>6</sup> 10-(4-Bromo-1-naphthoyl)decyltrimethylammonium bromide ( $\text{BNK-10}^+$ ) was kindly donated by Dr. J. D. Bolt. Hexaamminecobalt(III) chloride (Alfa Products),  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ , was recrystallized from water. Sodium chloride (ultrapure grade, Alfa Products), calcium chloride (Gold Label, Aldrich) and lanthanum chloride (Gold Label, Aldrich) are highest grade reagents commercially available and used without further purification.

Sodium polystyrenesulfonate (NaPSS) was generously donated as a gift of Dr. H. Gregor. The sample was purified by dialysis against deionized water, for two weeks, and further by ion exchange by using columns of ion-exchange resins (Amberlite IR-120 and Bio-Rad AG1x8). Finally, the acid solution was neutralized with sodium hydroxide solution after determination of the acid concentration. Sodium polyethylenesulfonate (NaPES) was purchased from Polysciences, Warrington, PA, and was purified by repeated precipitation with acetone. Sodium polyacrylate (NaPAA) of molecular weight 250 000 was obtained from Aldrich. An aqueous solution of the sample in the acid form was dialyzed against water for two weeks and then passed through a column of cation-exchange



**Figure 1.** Emission spectra of  $\text{BNK-5}^+$  in aqueous solution (curve 1) and in the presence of quencher at 25 °C. Excitation at 320 nm. Curve 2:  $[\text{Co}(\text{NH}_3)_6\text{Cl}_3] = 1 \times 10^{-5} \text{ M}$ ; curve 3:  $2 \times 10^{-5}$ ; curve 4:  $4 \times 10^{-5}$ ; curve 5:  $6 \times 10^{-5}$ ; curve 6: aerated,  $[\text{Co}(\text{NH}_3)_6\text{Cl}_3] = 0 \text{ M}$ .

resins (Amberlite IR-120). Water was deionized and distilled.

**Phosphorescence Lifetime Measurements.** The quenching rate constants of phosphorescence of the cationic probes ( $\text{BNK-1}^+$ ,  $\text{BNK-5}^+$ , and  $\text{BNK-10}^+$ ) with  $\text{Co}(\text{NH}_3)_6^{3+}$  were obtained from the slope of the reciprocal lifetime ( $\tau^{-1}$ ) vs.  $\text{Co}(\text{NH}_3)_6^{3+}$  plots. All solutions were nitrogen purged 5–10 min. The methods of the phosphorescence lifetime measurements have been described.<sup>7</sup>

## Results and Discussion

**Phosphorescence Spectra and Lifetimes of  $\text{BNK-1}^+$ ,  $\text{BNK-5}^+$ , and  $\text{BNK-10}^+$ .** Figure 1 shows the emission spectra of  $\text{BNK-5}^+$  in the aqueous solution (curve 1). Addition of  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$  results in quenching of this emission (curves 2–6). The emission (maximum  $\sim 570 \text{ nm}$ ) observed in nitrogen-purged aqueous solution corresponds to phosphorescence of the 1-bromonaphthalene lumophore. The corresponding emission of  $\text{BNK-1}^+$  and  $\text{BNK-10}^+$  was also readily observed in  $\text{N}_2$ -purged solution and was similar to that of  $\text{BNK-5}^+$ . Addition of air to the sample resulted in complete quenching of phosphorescence.

In order to obtain quenching rate constants in the presence of polyelectrolytes, lifetime measurements were carried out under constant probe and polymer concentrations, and quencher concentration was varied. Typical examples of the relaxation curves of the phosphorescence decay are shown in Figure 2. In most cases, single exponential curves were obtained. In the presence of polyelectrolytes such as NaPSS, however, deviations from the linearity are apparent. This effect for interionic reactions between similarly charged species may be due to the binding of the reaction products. The lifetime values were determined from the initial slopes in this case.

Typical examples of the  $\tau^{-1}$  vs. quencher plots, from which the quenching rates in the presence of NaCl and NaPSS were determined, are demonstrated in Figures 3 and 4, respectively. Generally, an excellent linearity was obtained. However,  $\tau^{-1}$  values at zero quencher concen-

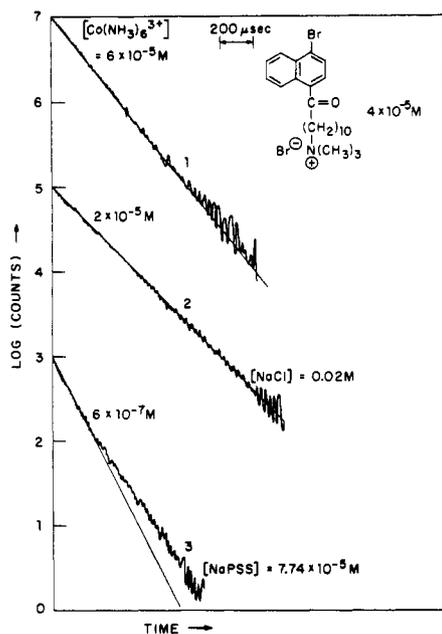
(3) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems", Academic Press: New York, 1975.

(4) (a) Taha, I. A.; Morawetz, H. *J. Am. Chem. Soc.* 1971, 93, 829; (b) Taha, I. A.; Morawetz, H. *J. Polym. Sci.* 1971, 9, 1669; (c) Meisel, D.; Matheson, M. S. *J. Am. Chem. Soc.* 1977, 99, 6577; (d) Meisel, D.; Rabani, J.; Meyerstein, D.; Matheson, M. S. *J. Phys. Chem.* 1978, 82, 985; (e) Meyerstein, D.; Rabani, J.; Matheson, M. S.; Meisel, D. *Ibid.* 1978, 82, 1879; (f) Jonah, C. D.; Matheson, M. S.; Meisel, D. *Ibid.* 1979, 83, 257; (g) Sassoon, R. E.; Rabani, J. *Ibid.* 1980, 84, 1319.

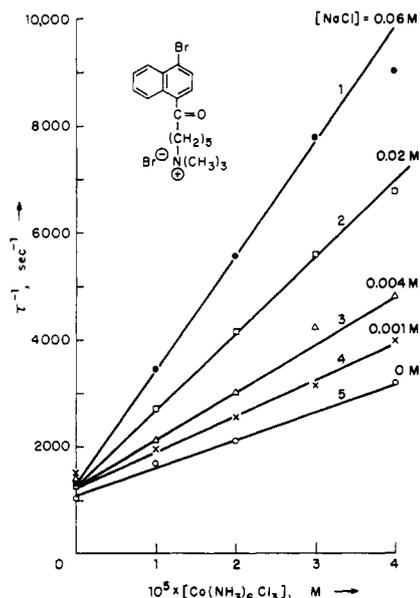
(5) (a) Umberger, J. Q.; LaMer, V. K. *J. Am. Chem. Soc.* 1945, 67, 1099; (b) Stoughton, R. W.; Rollefson, G. K. *Ibid.* 1939, 61, 2634; (c) Harty, W. E.; Rollefson, G. K. *Ibid.* 1954, 76, 4811.

(6) Turro, N. J.; Bolt, J. D. *Photochem. Photobiol.*, submitted.

(7) (a) Turro, N. J.; Liu, K. C.; Chow, M.-F.; Lee, P. C. *Photochem. Photobiol.* 1978, 27, 523; (b) Turro, N. J.; Aikawa, M. *J. Am. Chem. Soc.* 1980, 102, 4866.



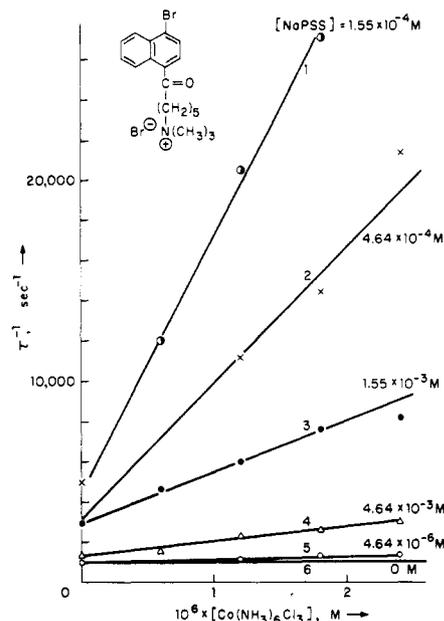
**Figure 2.** Typical traces of phosphorescence decay curves of BNK-10<sup>+</sup> in the presence of quencher at 25 °C. The initial values of the log (counts) were arbitrary taken to be 7, 5, and 3 for curves 1, 2, and 3, respectively. [BNK-10<sup>+</sup>] =  $4 \times 10^{-5} M$ , curve 1:  $[Co(NH_3)_6Cl_3] = 6 \times 10^{-5} M$ ; curve 2:  $2 \times 10^{-5}$ , [NaCl] = 0.02 M; curve 3:  $6 \times 10^{-7}$ , [NaPSS] =  $7.74 \times 10^{-5} M$ .



**Figure 3.** Plots of  $\tau^{-1}$  vs.  $[Co(NH_3)_6Cl_3]$  for the BNK-5<sup>+</sup> + NaCl + H<sub>2</sub>O systems at 25 °C. Curve 1: [NaCl] = 0.06 M; curve 2: 0.02; curve 3: 0.004; curve 4: 0.001; curve 5: 0.

tration were sometimes slightly higher than those extrapolated from the linear lines in the presence of polyelectrolytes.<sup>8</sup>

The quenching rate constants,  $k_{q,0}$  obtained from the  $\tau^{-1}$  vs. quencher plots are  $2.6 \times 10^7$ ,  $5.3 \times 10^7$ , and  $7.2 \times 10^7 M^{-1} s^{-1}$  for BNK-1<sup>+</sup>, BNK-5<sup>+</sup>, and BNK-10<sup>+</sup>, respectively at 25 °C. The rate constants are seen to increase with increasing size of the probe. This probably is due to the fact that the effective charge of the probe decreases with



**Figure 4.** Plots of  $\tau^{-1}$  vs.  $[Co(NH_3)_6Cl_3]$  for the BNK-5<sup>+</sup> + NaPSS + H<sub>2</sub>O systems at 25 °C. Curve 1: [NaPSS] =  $1.55 \times 10^{-4} M$ ; curve 2:  $4.64 \times 10^{-4}$ ; curve 3:  $1.55 \times 10^{-3}$ ; curve 4:  $4.64 \times 10^{-3}$ ; curve 5:  $4.64 \times 10^{-6}$ ; curve 6: 0.

**TABLE I:** Kinetic Parameters of the Quenching of BNK-5<sup>+</sup> with  $Co(NH_3)_6Cl_3$  at 25 °C

salt	salt, M	$k_{q,obs}, M^{-1} s^{-1}$	$E_{act}^{act}, kcal mol^{-1}$	$\log A$	$\Delta S^\ddagger, eu$
none	0	$5.33 \times 10^7$	1.0	8.4	-22
NaCl	0.02	$1.46 \times 10^8$	0.4	8.4	-22
NaPES	0.02	$1.53 \times 10^{10}$	2.1	11.7	-7
NaPSS	$1.55 \times 10^{-3}$	$2.53 \times 10^9$	3.1	11.7	-7

increasing size and the electrostatic repulsive forces between the probes and the quencher becomes less significant. Another possible reason is a steric effect, as recently discussed by Thomas.<sup>9</sup>

We now consider theoretically the absolute value of the quenching rate which is of the order of  $10^7$ – $10^8 M^{-1} s^{-1}$ . For interionic reactions, transition-state theory<sup>10,11</sup> allows the calculation of an electrostatic contribution to the free energy of activation ( $\Delta G_{el}^\ddagger$ ) and the entropy of activation ( $\Delta S_{el}^\ddagger$ ), respectively via eq 1 and 2

$$\Delta G_{el}^\ddagger = \frac{NZ_a Z_b e^2}{\epsilon d_{ab}} \quad (1)$$

$$\Delta S_{el}^\ddagger = \frac{NZ_a Z_b e^2}{\epsilon d_{ab}} \left( \frac{\alpha \ln}{\alpha T} \right)_p \quad (2)$$

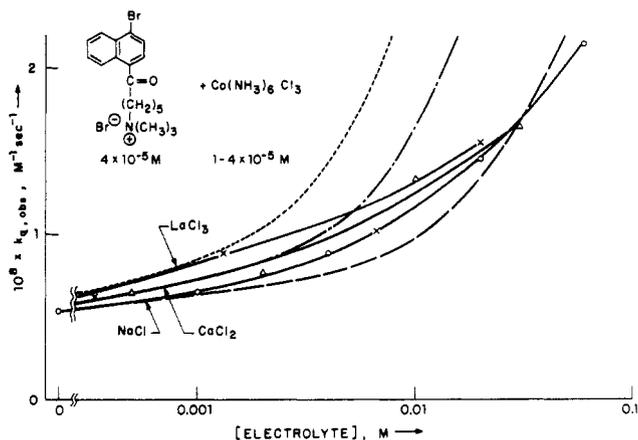
where  $Z_a$  and  $Z_b$  are the charge valencies of reactants A and B,  $N$  is Avogadro's number, and  $\epsilon$  denotes the dielectric constant of water ( $\sim 80$ ). When an equilibrium distance  $d_{ab}$  between ions at the activated complex state equals 3 Å,  $\Delta G_{el}^\ddagger$  and  $\Delta S_{el}^\ddagger$  become  $1.5Z_a Z_b kcal/mol$  and  $-6.7Z_a Z_b eu$ , respectively. If we apply these relations to the present quenching,  $\Delta G_{el}^\ddagger$  and  $\Delta S_{el}^\ddagger$  become 4.5 kcal/mol and -20 eu, respectively. This calculated value of activation entropy is in excellent agreement with the magnitude of the observed one, -22 eu, as seen in Table I. This large negative value of  $\Delta S^\ddagger$  suggests that the

(8) This deviation means that the quenching rates from lifetime measurements do not coincide with those from the Stern-Volmer plot, i.e.,  $I^0/I_q = 1 + \tau^0 k_{q,obs} [Q]$ , where  $I^0$  and  $I_q$  are the phosphorescence intensities in the absence and presence of quencher.  $\tau^0$  is the lifetime in the absence of foreign salt.

(9) Thomas, J. K. *Chem. Rev.* 1980, 80, 283.

(10) Scatchard, G. *Chem. Rev.* 1932, 10, 229.

(11) Wynne-Jones, W. F. K.; Eyring, H. *J. Chem. Phys.* 1935, 3, 492.

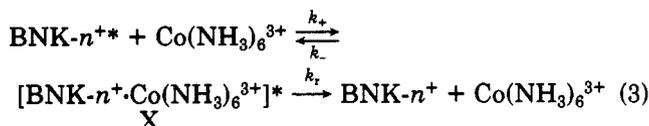


**Figure 5.** Influence of NaCl (O), CaCl<sub>2</sub> (Δ), and LaCl<sub>3</sub> (X) on the  $k_{q,obs}$  values of BNK-5<sup>+</sup> with Co(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> at 25 °C. [BNK-5<sup>+</sup>] =  $4 \times 10^{-5}$  M, [Co(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub>] =  $1-4 \times 10^{-5}$  M; ---, calculated for NaCl; --, for CaCl<sub>2</sub>; ···, for LaCl<sub>3</sub>.

entropy loss due to the enhanced hydration in the course of activation is of major importance in determining the rate of the quenching reaction.

Furthermore, the deceleration factor due to the electrostatic repulsion between probe and quencher is estimated to be  $4.2 \times 10^{-5}$  from the  $\Delta G_{el}^*$  value. This means that if there exists no electrostatic repulsion, the quenching rate would increase up to  $5.33 \times 10^7 / 4.2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ , i.e.,  $\sim 1.3 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$  for BNK-5<sup>+</sup>, for example. This value is clearly larger than the diffusion-controlled rate constant in aqueous solution. From this qualitative calculation, we can conclude that the rate constant for the quenching reaction would be very fast and certainly in the range of the diffusion-controlled quenching by small, noncomplexed molecules in water, if electrostatic repulsive effects were absent. Thus, we conclude that electrostatic interactions between reactants are striking and of dominant importance in the determination of the quenching rate constant for the systems studied here. The rate enhancement with simple and polyelectrolytes is also quite understandable, since the electrolytes can shield the electrostatic repulsion between ionic reactants.

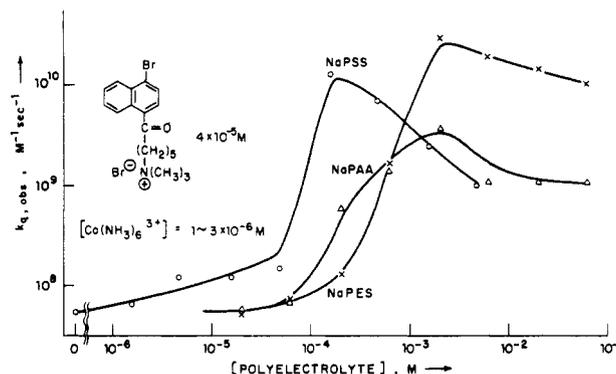
**Rate Enhancement with Simple Electrolytes.** The quenching rate constant,  $k_{q,obs}$  increases with simple electrolytes added (Figure 5). The reaction is believed to proceed as shown in eq 3. The formation of an acti-



vated complex (X) (via molecular diffusion of BNK- $n^+$  and Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> to within collision separations) is assumed to be a rate-determining step.<sup>12</sup> If the activated complex theory is applicable to the present reaction, the quenching rate constant,  $k_{q,obs}$ , in the presence of foreign salt is given as eq 4 from the Brönsted-Bjerrum theory.<sup>13</sup>

$$k_{q,obs} = k_{q,0}^* \frac{f_{\text{BNK-}n^+} f_{\text{Co}(\text{NH}_3)_6^{3+}}}{f_X} \quad (4)$$

In eq 4,  $f$  are the (single ion) activity coefficients of the



**Figure 6.** Influences of NaPSS (O), NaPES (X), and NaPAA (Δ) on the  $k_{q,obs}$  values of BNK-5<sup>+</sup> with Co(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> at 25 °C. [BNK-5<sup>+</sup>] =  $4 \times 10^{-5}$  M; [Co(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub>] =  $1-3 \times 10^{-5}$  M.

reactants and the activated complex (X),  $k_{q,0}^*$  is the rate constant at zero ionic strength.

When the activity coefficient terms are evaluated by the Debye-Hückel theory, the  $k_{q,obs}$  value is given by eq 5.<sup>1e,14</sup>

$$\log k_{q,obs} = \log (kTK^*/h) + 1.018Z_{\text{BNK-}n^+}Z_{\text{Co}(\text{NH}_3)_6^{3+}}I^{1/2} \quad (5)$$

In eq 5,  $K^*$  denotes the equilibrium constant (in activity units) between X and the reactants,  $I$  is the ionic strength of the reaction system, and  $k$ ,  $T$ , and  $h$  have the usual meanings. The rate-enhancing effect with simple electrolyte is given by eq 6.

$$\log k_{q,obs} = \log k_{q,0} + 3.054 (I^{1/2} - I_0^{1/2}) \text{ at } 25 \text{ °C in water} \quad (6)$$

In eq 6,  $k_{q,0}$  is the quenching rate constant in the absence of foreign salt, and  $I_0$  is the ionic strength of the reactant ions only, i.e., BNK- $n^+$ , Br<sup>-</sup>, Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, and Cl<sup>-</sup>. In Figure 5, the calculated values using eq 6 are given. The agreement between the theory and the experiment is excellent in the lower concentration region ( $<10^{-3}$  M). This is reasonable because the Debye-Hückel theory is a limiting law and valid below  $10^{-3}$  M.

From the above results, it is clear that the quenching rate constants in the presence of simple electrolytes ( $k_{q,obs} = 10^7-10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) are nicely explained quantitatively with the Brönsted-Bjerrum-Debye-Hückel theory. This confirms the earlier conclusion that below the diffusion-controlled rate, the electrostatic interactions between reactant ions and simple electrolyte is of dominant importance once in determining the quenching rate.

In Table I the Arrhenius activation energy ( $E_{act}$ ), frequency factor ( $\log A$ ), and entropy of activation ( $\Delta S^\ddagger$ ) for the quenching reaction are listed. As we discussed earlier, the observed  $\Delta S^\ddagger$  values are very close to the calculated values from eq 2. The negative value of  $\Delta S^\ddagger$  is associated with the occurrence of enhanced hydration during the course of activation. This would be expected if the valency of the activated complex (i.e., +4) is higher than those of reactants (+1 and +3). The important role of hydration in the determination of interionic reaction rates was discussed earlier by Laidler et al.<sup>15</sup>

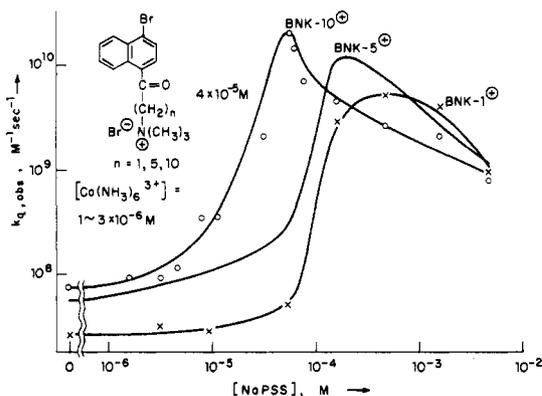
**Rate Enhancement with Polyelectrolytes.** Figure 6 demonstrates the acceleration effects of three kinds of macroions on the quenching of BNK-5<sup>+</sup>. The rather large acceleration observed is undoubtedly due to the large

(12) The observed quenching rate,  $k_{q,obs}$  is given by  $k_{q,obs} = k_t k_+ / (k_- + k_t)$  (a). When  $k_t \ll k_-$ , eq 4 becomes  $k_{q,obs} = k_+$ . Therefore, when  $k_+$  is enhanced to diffusion-controlled,  $k_{q,obs}$  is also diffusion-controlled.

(13) (a) Brönsted, J. N. *Z. Phys. Chem. (Leipzig)* **1922**, *102*, 169; (b) Brönsted, J. N. *Ibid.* **1925**, *115*, 337; (c) Bjerrum, N. *Ibid.* **1924**, *108*, 82; (d) Bjerrum, N. *Ibid.* **1925**, *118*, 251.

(14) See, for example, Moore, W. J. "Physical Chemistry", 3rd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1962; p 368.

(15) (a) Laidler, K. J. "Reaction Kinetics"; Pergamon Press: London, 1963; (b) Laidler, K. J.; Bunting, P. S. "The Chemical Kinetics of Enzyme Action", 2nd ed.; Clarendon Press: Oxford, 1973.



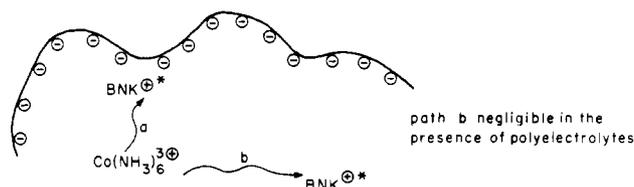
**Figure 7.** Influences of NaPSS on the  $k_{q,obs}$  values of BNK-1<sup>+</sup> (X), BNK-5<sup>+</sup> and BNK-10<sup>+</sup> (O) with  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$  at 25 °C.  $[\text{BNK}-n^+] = 4 \times 10^{-5} \text{ M}$ ;  $[\text{Co}(\text{NH}_3)_6\text{Cl}_3] = 1-3 \times 10^{-6} \text{ M}$ .

electrostatic potential of macroions. If the electrostatic forces between reactants and macroions is the dominant factor that is responsible for the acceleration,  $k_{q,obs}$  should increase in proportion to the polymer concentration, and, furthermore, the acceleration factor should be independent to the charge density of macroions. These expectations have been confirmed experimentally for slow interionic reactions.<sup>16</sup> However, these predictions are not supported by the experimental findings appearing in Figure 6; i.e. (1) in a diluted polymer concentration region the acceleration factor increased in the order, NaPES  $\approx$  NaPAA < NaPSS; (2) the maximum acceleration factor ( $\alpha$ ) is between 50 and 500; (3) maximum rates of quenching are between  $5 \times 10^9$ – $3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  and increase with the order of NaPAA < NaPSS < NaPES.

Result (1) demonstrates the importance of the hydrophobic interactions, rather than electrostatic forces, for the acceleration, because the polystyrenesulfonate anions are strongly hydrophobic compared with PAA and PES macroions.<sup>1d</sup> It appears that the contributions of these electrostatic and hydrophobic forces on the acceleration are very important only when the quenching rate constants are below the diffusion-controlled ( $k_{q,obs} = 10^7$ – $10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) ones. Results (2) and (3) suggest that the maximum rates of quenching obtained ( $\sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) are quite near or in the diffusion-controlled limit for bimolecular reactions. The maximum acceleration factors [ $(k_{q,obs}/k_{q,0})_{max} = \alpha$ ] are small compared with those observed for slower interionic reactions, i.e.,  $\alpha \sim 10^7$  for  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+} + \text{Hg}^{2+}$ ,<sup>17</sup>  $\sim 10^6$  for  $\text{Fe}(\text{CN})_6^{4-} + \text{S}_2\text{O}_8^{2-}$ ,<sup>18</sup> and  $\text{Fe}^{2+} + \text{trans-Co}(\text{NH}_3)_5\text{Cl}^{2+}$ ,<sup>17b</sup>  $10^4$  for  $\text{U}^{4+} + \text{Tl}^{3+}$ ,<sup>18</sup> and  $\text{Co}(\text{NH}_3)_5\text{Br}^{2+} + \text{Hg}^{2+}$ ,<sup>19</sup> and  $\sim 10^3$  for  $\text{Co}(\text{NH}_3)_5\text{Br}^{2+} + \text{Ag}^{+}$  and  $\text{Fe}^{2+} + \text{cis-Co}(\text{NH}_3)_4(\text{N}_3)_2^+$ , for example.<sup>17b</sup> This small  $\alpha$  means that the macroions cannot accelerate the already fast quenching beyond diffusion-controlled limits.

Figure 7 shows how  $k_{q,obs}$  varies with the concentration of NaPSS for three probes and allows the following conclusions: (4) stronger hydrophobic probes are more rapidly quenched, i.e., the magnitude of the acceleration factors is in the order BNK-1<sup>+</sup> < BNK-5<sup>+</sup> < BNK-10<sup>+</sup> for low NaPSS concentrations. This result provides further support for the important contribution of hydrophobic forces to acceleration of reaction rates below diffusion-controlled region; (5)  $\alpha$ 's are ca. 200 for these probes; and (6) maximum rates of quenching are between  $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and

## Scheme III



$2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . Conclusions (5) and (6) are quite similar to (2) and (3), respectively.

Figure 7 further shows that (7)  $k_{q,obs}$  decreases with polymer concentration in the high concentration region, and (8) the maximum of  $k_{q,obs}$  shifts to lower concentration when the probes and/or polymer are strongly hydrophobic. These observations suggest that both the probes and the quenchers occupy positions very near the macroions, and diffusional motions are strongly restricted and influenced by the local movement of the ionized groups of the polymer. The translational relaxation time of the strongly hydrophobic ions of the polymer be large because of their bulkiness in size.<sup>20</sup> Then the retardation of the quenching reaction should occur easier when the probes and/or polymer are stronger in hydrophobicity. Finding (7), therefore, is explained by an increase in microviscosity around macroions with increasing polymer concentration.<sup>21</sup> Quite recently, the microviscosity ( $\eta$ ) around macroions was evaluated from the fluorescence depolarization measurements, and an extremely high value of microviscosity ( $\sim 150 \text{ cP}$ ) was obtained.<sup>22</sup>

The influence of polyelectrolytes on the activation parameters is given in Table I. The activation energy ( $E_{act}$ ), frequency factor ( $\log A$ ), and the entropy of activation increased significantly upon addition of macroions. The increase in  $E_{act}$  may be interpreted as resulting from the retarded diffusional motion of both phosphorescence probes and quenchers which are localized around the macroions. The increase in  $\log A$  or  $\Delta S^\ddagger$  indicates that the role of the dehydration effect of the reactant ions is still important even for very fast quenching reactions.

In conclusion, polyelectrolytes do not enhance the rates of bimolecular quenching reactions between ionic species beyond the so-called diffusion-controlled rate. Diffusional motion and microviscosity of the macroions are deduced to be very important for very fast quenching reactions whose rates approach the diffusion-controlled limit. However, when the reaction rates are below diffusion-controlled, the rate enhancing action of simple and polyelectrolytes was quite similar to those found for slow chemical reactions (Scheme III).

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(20) Our knowledge on the diffusional motion of the macroion segments in aqueous media is very scanty. The measurements on the lifetime of the conformational fluctuation of macroions were recently carried out by using the conductance stopped-flow technique. However, the local motions of the macroions were not discussed: Okubo, T. *Biophys. Chem.* 1980, 11, 425.

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