Since starting to write this paper, we have discovered that a relationship very similar to eq 6, but involving free energy changes (logarithms of acidity constants), was proposed much earlier by Gordon[22] in a paper dealing with stabilities of B^-–HR compounds in liquid solutions.

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Quenching of the Uranyl Fluorescence by Aromatic Molecules

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Abstract: Quenching constants, K_q's, for the uranyl fluorescence quenching by aromatic molecules having widely different substituents were measured in aqueous acetone solutions at room temperature. The Stern–Volmer relationship was obtained between relative fluorescence intensity and the concentration of most of the aromatic quenchers. The rates decreased with the viscosity of the medium. A linear relationship was found between log K_q and $\sigma + 0.25(\sigma^+ - \sigma)$ of the substituents, with ρ values of -1.10 in aqueous 80% acetone and -0.83 in aqueous 10% acetone. A correlation was found between the rates of fluorescence quenching and the respective rates of nitration. The results suggest that the rate-determining step of the quenching process involves a π-complex formation between the excited uranyl ions and the quenchers.

One of the most important processes for fluorescence quenching reactions is the mechanism in which a complex (exciplex) formation between the fluorescer, F*, and the quencher, Q, by encounter collision is involved:[1] $F^* + Q \rightleftharpoons \text{complex} \rightarrow \text{quenching}$.

On the other hand, the formation of σ[2] and π[3] complexes between the aromatic system and inorganic cations has been proposed as the reaction intermediates. It was expected that the uranyl fluorescence quenching by the aromatic molecule might relate to the above interesting problems, since it is possible that donor–acceptor interaction arises in the excited state even though there is no affinity in the ground state between the uranyl ion and aromatic molecule.

The present work was undertaken to investigate the mechanism of the uranyl fluorescence quenching by the aromatic system in solution on the basis of kinetic data, especially the substituent effects on the rates, in comparison with the similar and well-established mechanisms.

Experimental Section

Guaranteed reagents and doubly distilled water were used for all preparations. The uranyl concentration (as nitrate) was usually 0.02 *M*. The temperature was kept constant within the error ±1° by means of a simple attachment of water circulation through a thermostat. The measurements of fluorescence intensities were carried out by means of a Hitachi 204 fluorescence spectrophotometer.

Results and Discussion

Evidence for Encounter Collision Mechanism. Figure 1 illustrates the Stern–Volmer plots for the quenching of the uranyl fluorescence by aromatic molecules, where I_f^0 and I_f are the relative intensities of fluorescence in the absence and in the presence of quencher (Q), and the slope, or the quenching constant, K_q, is a measure of the relative quenching rate. The linear relationship is evidence for the mechanism of bimolecular (collisional) deactivation by the quencher, assuming that the efficiency of unimolecular quenching *via* initial complex formation is not equal to that of bimolecular (collisional) quenching. The long lifetime of the excited state of the uranyl ion, 10^{-4}–10^{-3} sec,[4] is favorable for the collisional mechanism.

Another way to determine whether the quenching reaction is unimolecular (initial complex formation between the quencher and the ground state uranyl ions) or bimolecular collision between the quencher and the excited uranyl ions is to see the effect of viscosity of the medium on the rate.[5] The effect of viscosity using liquid paraffin (Table I) supports the excited state collision mechanism. This is also supported by other facts: (1) very low solubility of the uranyl ions in benzene and (2) no change in the absorption spectra of the mixture solution of benzene and the uranyl ions, sug-

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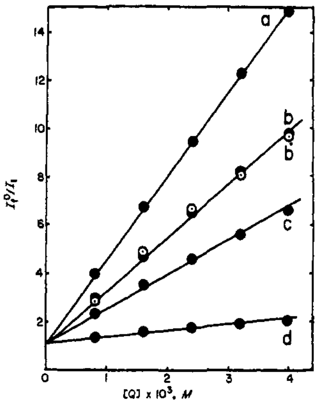

Figure 1. Stern–Volmer plots for the quenching of the uranyl fluorescence by aromatic molecules: (a) toluene, (b) benzene, (b') deuterated benzene (C_6D_6), (c) acetophenone, (d) nitrobenzene; λ(excitation) 405 nm; λ(emission) 510 nm; temperature 10°; $[UO_2(NO_3)_2]$, 0.02 *M* in aqueous 10% acetone.

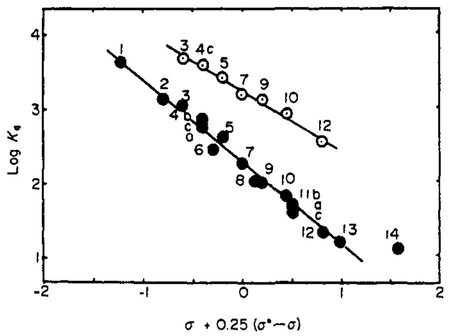

Figure 2. Plot of log K_q *vs.* $\sigma + 0.25(\sigma^+ - \sigma)$: (1) hexamethylbenzene, (2) durene, (3) pseudocumene, (4a) *o*-xylene, (4b) *m*-xylene, (4c) *p*-xylene, (5) toluene, (6) *tert*-butylbenzene, (7) benzene, (8) benzyl chloride, (9) chlorobenzene, (10) methyl benzoate, (11a) *o*-dichlorobenzene, (11b) *m*-dichlorobenzene, (11c) *p*-dichlorobenzene, (12) nitrobenzene, (13) *p*-chloronitrobenzene, (14) *m*-dinitrobenzene; ●, in aqueous 80% acetone; ⊙, in aqueous 10% acetone; temperature 15 ± 1°; σ^+ and σ were taken from H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

gesting that initial complex formation between benzene and the ground state uranyl ions is unlikely.

However, it is possible that the quenching reaction occurs *via* the formation of an intermediate complex between the *excited* uranyl ions and the quencher by encounter collision, since donor–acceptor interaction can arise in the excited state even though there is no affinity in the ground state. By substituting $\tau_0 = 10^{-4}$ sec into $k = K_q/\tau_0$, the quenching rate constants for aromatic molecules have values ranging from 1.2×10^5 to 4.2×10^7 l. mol⁻¹ sec⁻¹, much smaller than the diffusion-controlled rate constants.

Table I. Effect of the Viscosity of the Medium on the Quenching Constant

Liquid paraffin in MEK,[a] v/v %	K_q,[b] l./mol	Liquid paraffin in MIBK,[c] v/v %	K_q,[d] l./mol
0.0	73	0.0	24.5
2.0	49	2.5	13.7
3.3	34	5.0	5.8
5.0	28	7.5	5.5
10.0	13	10.0	4.5

[a] MEK, mixture of methyl ethyl ketone (80%) and acetone (20%). [b] MIBK, mixture of methyl isobutyl ketone (80%) and acetone (20%). [c] Quencher, benzene. [d] Quencher, hexamethylbenzene.

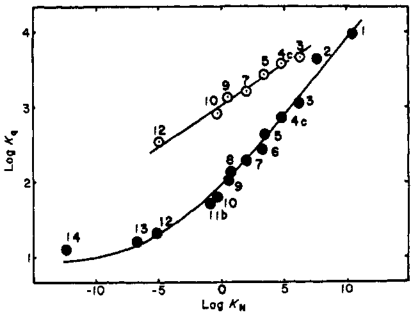

Figure 3. Correlation of the quenching constant with the rate of nitration. The total nitration rates, k_N's, were taken from ref 9c, p 290. Other descriptions are the same as those in Figure 2.

Substituent Effects. Figure 1 shows that the rate of the quenching is changed by substitution on benzene with either electron-attracting or -donating groups. In order to see quantitatively the substituent effects on the rate, quenching constants of several aromatic compounds with widely different and chemically inert substituents were measured. Figure 2 shows the plot of log K_q as a function of σ applying the Yukawa–Tsuno's equation,[6] $\sigma + 0.25(\sigma^+ - \sigma)$, for aromatic substituents. It is notable that a linear free energy relationship exists between the reactivity of the uranyl fluorescence quenching and the polarity of the aromatic quencher. The deviation of point 14 from the straight line would be partly due to its inner filter effect. The decrease in the quenching constants with the increase in the substituent constant or negative ρ value indicates that aromatic molecules act as electrophilic quenchers. The fact that K_q for cyclohexane was two orders of magnitude smaller than that for benzene also suggests the important role of aromaticity (π electron) in the quenching process.

From Figure 2 the ρ values (the slope) for the reaction in aqueous 80 and 10% acetone solutions were obtained to be −1.10 and −0.83, respectively. Since these ρ values are much less negative than those for many other electrophilic processes in which charge-transfer intermediates are involved, it seems unlikely that the deactivation of the uranyl fluorescence by aromatic molecules proceeds through an electron or charge-transfer intermediate.[7]

$$F^* + Q \rightleftharpoons F^-\text{---}Q^+ \longrightarrow \text{deactivation}$$

It is notable that the rates tend to be larger in the more polar solvent, K_q(in 10% aqueous acetone)/ K_q(in 80% aqueous acetone), suggesting that the stability of the intermediate species (collision complex, etc.) is increased in the more polar solvent. The solvent effect on the ρ value, ρ(in 80% aqueous acetone)/ρ(in 10% aqueous acetone) = 1.3, may be interpreted as due to the change

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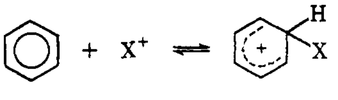
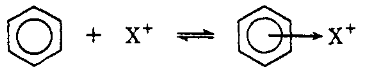
in the dielectric constant of the medium, according to Hammett's theory.[8]

Comparison with Electrophilic Aromatic Substitution. It seemed interesting to compare the results of the uranyl fluorescence quenching by aromatic molecules with those of aromatic nitration whose mechanism is well established, since both reactions involve electrophilic attack by inorganic cations on the aromatic system in the rate-determining steps. Figure 3 shows a close correlation between relative rates of the quenching and those of nitration. No isotope effect has been found and the C–H bond is not broken in the rate-determining step of nitrations.[9] These points are also analogous to those in the case of the uranyl fluorescence quenching by aromatic molecules, where neither isotope effect is found (Figure 1) nor the C–H bond is broken. It has been suggested that the aromatic nitration involves a π-complex formation in the rate-determining step between the cation and the aromatic ring,[2a,10] while many aromatic electrophilic substitutions involve σ-complex formation. The close correlation of the quenching rates with the nitration rates suggests that a π-complex intermediate is involved in the uranyl fluorescence quenching process. This suggestion is supported by the fact that the relative rates for the quenching process seem to be more closely related to the π-complex stabilities[11] than to the σ-complex stabilities[12] (Table II). Also, the ρ value would support this. Since the σ complex in electrophilic substitutions is a charge-transfer complex[2e]



(1)

its ρ value should be highly negative ($\rho \leq -4.5$),[13] while a π-complex mechanism (eq 2) should give a less



(2)

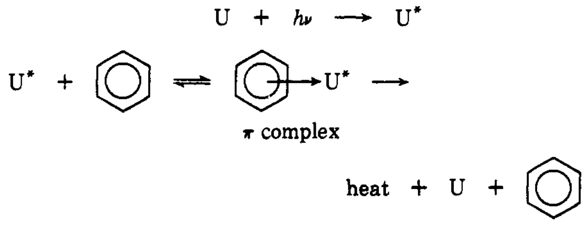
negative ρ value. The ρ values (-0.83, -1.10) for the uranyl fluorescence quenching seem to prefer a π-complex mechanism to a σ-complex mechanism.

Table II. Relative Rates of the Uranyl Fluorescence Quenching and Relative Stabilities of π and σ Complexes

Substituent	Rel rate of quenching[a]	π-Complex stabilities		σ-Complex stabilities	
		I_2[b]	PA[c]	Cl_2[d]	HF[e]
H	0.28	0.48	0.70	0.0005	0.09
Me	0.62	0.51	0.84	0.17	0.63
p-Me_2	1.00	1.00	1.00	1.00	1.00
o-Me_2	0.93	0.87	1.03	1.03	1.1
m-Me_2	1.06	0.99	0.98	90	26
1,3,5-Me_3	1.67	1.85	1.12	15,000	13,000
1,2,4,5-Me_4	1.91	2.10	1.65	790	140
Me_6	6.14	4.81	2.83		97,000
tert-Butyl	0.40		0.51		

[a] K_q/K_q (*p*-xylene). [b] Alkylbenzene–iodine complexes in CCl_4.[11a,b] [c] Alkylbenzene–picric acid complexes in $CHCl_3$.[11c] [d] Relative rate of aromatic chlorination in acetic acid.[12a] [e] Relative basicity of alkylbenzenes to hydrofluoric acid in anhydrous hydrofluoric acid.[12b]

Consequently, the mechanism for the uranyl fluorescence quenching by aromatic molecules may be summarized as (1) excitation of the uranyl ion, (2) bimolecular collision between the excited uranyl ion and the aromatic quencher, and (3) deactivation whose transition state intermediate is closely related to a π complex, without chemical changes



(3)

where U and U* are the uranyl ion in the ground and the excited states, respectively.

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