Competition Experiments. The general conditions, procedures, and results are described above. Several additional points will be described in a general procedure.

Carbene precursor (50–100 mg) and a stirring bar were contained in a 10-ml flask, which was fitted with a reflux condenser capped with a gas inlet tube. The latter was connected to a nitrogen-vacuum manifold. A carefully weighed mixture of olefins A and B (200–700 mg of each) was diluted with 4 ml of benzene, and the benzene solution was injected onto the solid precursor. The stirrer was started, and the flask was immediately lowered into an oil bath preheated to ~83°. Slow reflux and stirring was maintained for 3.5–7 hr. Then, the product mixture was cooled (0°) and filtered through a medium sintered glass funnel. Gc analysis was immediately performed on the filtrate. Competition **5**/**6** was performed in the same general manner, except that the CCl_2 precursor was sodium trichloroacetate (dried at <1 mm, 90°, 18 hr) and the solvent was dimethoxyethane distilled first from $LiAlH_4$ and then from sodium.

In runs involving **4**, **6**, and **7**, only unreacted olefin and the expected cyclopropanes were observed in the product mixtures. Runs involving **5**, **8**, and **9** gave more complicated product mixtures. However, prepared, determined, dimethoxyethane or benzene solutions of product mixtures **13** and **14** and **16**, **17**, and **18** could be refluxed with PhHgBr without alteration of the product ratios. Additionally, all competition experiments were run as duplicates; the second reaction mixture was subjected to twice the reflux time of the first. Reproducibility (Table I) was good.

The analytical gc conditions included injector and detector temperatures of 245–255° and 225–230°, respectively; details follow for the competition experiments of Table I.

Competition **6**/**4** was analyzed on an SE-30 column. The initial temperature was 117°. After **4**, **6**, and **13** had eluted, the column temperature was rapidly raised to 142° to elute **15**.

Competition **7**/**4** was analyzed on a Carbowax column. The initial temperature was 112°. After **4** and **13** had eluted, the temperature was rapidly raised to 151° to elute **7** and **16**.

Competition (**8** and **9**)/**7** was analyzed on a Carbowax column. The initial temperature was 151°. After **7** and **16** had eluted, the temperature was rapidly raised to 202° to elute **8** and **9**, **17**, and **18**.

Competition **5**/**6** was analyzed at Rutgers University, by Mr. Ulf Dolling on a Barber-Colman, Series 5000 gc equipped with a flame ionization detector and fitted with a 100 ft Apeizon-L Golay column. Typical operating conditions included injector 250°, column 160°, and detector 240°.

Detectors were calibrated with pure products.[58] Peak integrals were determined by cut-and-weigh of Xerox copies of the gc traces. Two traces were run for each experiment, and two copies were analyzed for each trace. Mean values were recorded.

Acknowledgments. I am very grateful to Professor D. S. Kemp and to the Massachusetts Institute of Technology for their hospitality and provision of laboratory space. Financial support by NIH and NSF is acknowledged with gratitude. Helpful discussions were held with Professors W. R. Moore, G. M. Whitesides, and Mr. D. C. Roberts.

---

(58) See, however, footnote *d* in Table I.

Mechanism of Quenching of the Uranyl Fluorescence by Organic Compounds

Ryoka Matsushima

Contribution from the Department of Industrial Chemistry,
Faculty of Engineering, Shizuoka University, Hamamatsu, Japan.

Received December 16, 1971

Abstract: Quenching constants of the uranyl fluorescence by aromatic molecules and aliphatic alcohols were obtained from the Stern–Volmer plots in solutions at room temperature. Quenching by the aromatic quenchers, which have no excited states lying below that of the uranyl ions, occurred very efficiently without chemical changes. There was no kinetic isotope effect, *i.e.*, $K_q(C_6H_6)/K_q(C_6D_6) = 1.0$, which would indicate no contribution of vibrational factors of aromatic quenchers in the rate-determining step. Relative quenching rates of aromatic quenchers showed close correlations with Yukawa–Tsuno's σ values, with ionization potentials, and with rates of thermal aromatic nitrations, suggesting an important role of electron donor–acceptor interactions. Further, close correlation of relative quenching rates with relative π complex stabilities of alkylbenzenes suggested the formation of a π complex between the quenchers and the excited uranyl ions, though there would be no affinities in the ground state. On the other hand, quenching by aliphatic alcohols appeared to involve a chemical process (α-hydrogen abstraction), on the basis of kinetic isotope effects, positive activation energies for the photoredox rates, and correlation of the photoredox quantum yield with the sum of Taft's σ values, $\Sigma\sigma^*$. From these facts it was suggested that quenching of the uranyl fluorescence by aromatic quenchers and aliphatic alcohols took place *via* nonelectronic–electronic energy transfer; quenching by aromatic quenchers appeared to proceed through physical radiationless decay of an exciplex intermediate, while quenching by aliphatic alcohols seemed to proceed through a chemical decay of a similar intermediate.

The role of exciplex formation in fluorescence quenching has been widely investigated.[1] Recently, fluorescence quenching of aromatic hydrocarbons by olefins which have no excited states lying below the excited levels of the fluorescers has been observed

---

(1) (a) H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1963); (b) N. Mataga, K. Ezumi, and T. Okada, *Mol. Phys.*, **10**, 201, 203 (1966); (c) N. Mataga, T. Okada, and N. Yamamoto, *Bull. Chem. Soc. Jap.*, **39**, 2562 (1966); (d) N. Mataga, T. Okada, and N. Yamamoto, *Chem. Phys. Lett.*, **1**, 119 (1967); (e) K. Knibbe and A. Weller, *Z. Phys. Chem.*, **56**, 95, 99 (1967); (f) H. Beens, H. Knibbe, and A. Weller, *J. Chem. Phys.*, **47**, 1183 (1967); (g) H. Knibbe, D. Rehm, and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **72**, 257 (1968); (h) T. Okada, H. Matsui, H. Oohari, H. Matsumoto, and N. Mataga, *J. Chem. Phys.*, **49**, 4717 (1968); (i) M. Kuzmin and L. N. Guseva, *Chem. Phys. Lett.*, **3**, 71 (1969); (j) T. Okada, H. Oohari, and N. Mataga, *Bull. Chem. Soc. Jap.*, **43**, 2750 (1970); (k) N. Mataga, *ibid.*, **43**, 3623 (1970); (l) A. E. W. Knight and B. K. Selinger, *Chem. Phys. Lett.*, **10**, 43 (1971); (m) C. R. Goldschmidt, R. Pottashnik, and M. Ottolenghi, *J. Phys. Chem.*, **75**, 1025 (1971).

and assumed to proceed through formation of some type of complex.[2]

Similar to these are quenching of the uranyl fluorescence by various organic compounds such as aromatic hydrocarbons and aliphatic alcohols in solutions. The uranyl fluorescence, ranging from 470 to 580 nm, is efficiently quenched by such organic quenchers whose lowest excited states lie much higher than that of the uranyl ion. Electronic–electronic energy transfer from the fluorescer to these quenchers is quite improbable.

Quenching of the uranyl fluorescence by aromatic quenchers,[3] which is not accompanied by formation of photochemical products, features a physical process, while quenching by aliphatic alcohols[4] is accompanied by formation of the photoredox intermediates and products. In the present work mechanistic interpretations of quenching of the uranyl fluorescence by physical (aromatic) and chemical (alcohol) quenchers were made in terms of radiationless physical and chemical decays of exciplex intermediates. Efficient interactions *via* donor–acceptor interactions in the excited states or exciplex formation in organic–inorganic systems seemed to be interesting and important, since most studies on exciplex have been made in organic–organic systems.[1]

Experimental Section

Quenching Constants. Relative intensities of the uranyl fluorescence near 510 nm were measured for solutions containing 0.01–0.02 *M* uranyl nitrate and various quencher concentrations without deaeration.

There were no changes in light absorptivity by the addition of quenchers used here. Solvent effects on the absorption and the emission spectra of the uranyl ions are shown in Figure 1, whose correlations with relative quenching efficiencies were not straightforward. The Stern–Volmer relationship (1) between I_f^0/I_f and [Q] was obtained in each solvent used here.

$$I_f^0/I_f = 1 + K_q[\mathrm{Q}] \qquad (1)$$

Here, [Q] is the concentration of aliphatic alcohol or aromatic quencher; I_f^0 and I_f are relative fluorescence intensities in the absence and presence of a quencher, respectively. Though no changes in the quenching constants were observed with changes in the excitation wavelengths, the 436-nm excitation wavelength was mostly used in order to avoid the absorption by the quenchers and to minimize the solvent (blank) emission. Fluorescence measurements were carried out using a Hitachi 204-type fluorescence spectrophotometer, where the fluorescence leaves the sample at right angles to the excitation path. A homemade attachment, which involves circulation of water through a thermostat, was employed for temperature regulation of the sample chamber. The temperature of the sample chamber was monitored with a microthermistor–thermometer. Guaranteed reagents and doubly distilled water were used for the fluorescence measurements and photolysis. Viscosity was measured with an Ostwald viscosimeter.

Photolysis. The pH values of the solutions to be photolyzed were adjusted to desired values (usually 1.0) with 1 *N* NaOH and 1 *N* $HClO_4$ solutions using a pH meter. The light absorptivity of the uranyl–alcohol solutions was constant against the change in the acidity of the medium from pH 1.2 to 1 *M* perchloric acid. These solutions were deaerated by the passage of oxygen-free nitrogen for 20–30 min per 10 ml, were kept air tight with liquid paraffin, and were then exposed to the desired radiations (mostly 405 and 436 nm) using either an interference filter or a suitable combination of glass filters. The light source was a 100- or 500-W high pressure mercury lamp with a suitable arrangement for obtaining a parallel light beam. The temperature was controlled by using a thermostat. The time of exposure was controlled so that the reaction was not more than 5% complete when measurements were taken of the quantum yield of uranium(IV) formation in order to avoid its inner filter effect. The concentration of the uranium(IV) formed was determined by a colorimetric method using arsenazo(III).[5] Aldehydes or ketones formed were separated as the precipitates of the corresponding 2,4-dinitrophenylhydrazones and washed with water. The precipitates were dissolved in ethyl alcohol; then the absorbances at the peaks around 360 nm were measured. The molar ratio of the products, [aldehyde or ketone]/[uranium(IV)], was 1.0, whatever the extent of the reaction (up to 20%) and whatever the pH (1.0–3.8).[4c] Measurements of the quantum yields of the products were made using a ferric oxalate actinometer.[6] Absorption was measured with a Hitachi 124 type spectrophotometer.

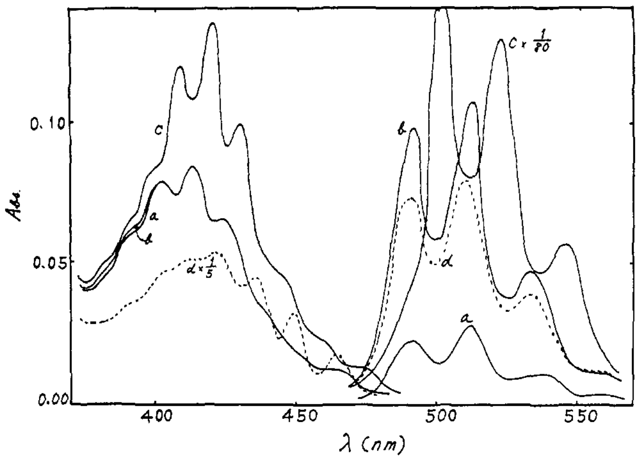


Figure 1. Absorption (left) and fluorescence (right, uncorrected) spectra of 0.01 *M* uranyl nitrate in aqueous 0.1 *M* perchloric acid (a), 1 *M* perchloric acid (b), 1 *M* phosphoric acid (c), and acetone (d).

Results and Discussion

Exclusion of Electronic–Electronic Energy Transfer. The uranyl fluorescence was efficiently quenched by various organic compounds, such as aliphatic alcohols and aromatic compounds, without changes in the shape of the fluorescence spectra. Typical absorption and fluorescence spectra in several solvents are illustrated in Figure 1. For most of the quenchers used in this work, there was neither absorption in the region of the excitation wavelengths (366, 405, and 436 nm) nor emission in the wavelength region of the uranyl fluorescence.

The wavelength region of the uranyl fluorescence, 470–580 nm, indicates that the level of the excited state of the uranyl ion to be quenched is in the range of 59–51 kcal/mol, much lower than the lowest excited states of the quenchers (about 80 kcal/mol for the substituted benzenes and even much higher for aliphatic alcohols). That is, electronic energy transfer from the excited uranyl ions (U*) to these quenchers (Q), $U^* + Q \rightarrow U + Q^*$, is a highly endothermic process. Efficient transfer in such a highly endothermic process would not occur.[7] Also, the temperature effect on the quench-

---

[2] (a) S. L. Murov, R. S. Cole, and G. S. Hammond, *J. Amer. Chem. Soc.*, **90**, 2957 (1968); (b) S. L. Murov and G. S. Hammond, *J. Phys. Chem.*, **72**, 3797 (1968); (c) A. Marikawa and R. J. Cvetanovic, *J. Chem. Phys.*, **49**, 1214 (1968); (d) E. M. Anderson and G. B. Kistiakowsky, *ibid.*, **48**, 4787 (1968).

[3] R. Matsushima and S. Sakuraba, *J. Amer. Chem. Soc.*, **93**, 7143 (1971).

[4] (a) K. Venkatarao and M. Santappa, *Z. Phys. Chem. (Frankfurt am Main)*, **66**, 308 (1969); (b) S. Sakuraba and R. Matsushima, *Bull. Chem. Soc. Jap.*, **43**, 2359 (1970); (c) S. Sakuraba and R. Matsushima, *ibid.*, **44**, 2915 (1971); (d) R. Matsushima and S. Sakuraba, *J. Amer. Chem. Soc.*, **94**, 2622 (1972).

[5] H. Onishi and Y. Toita, *Bunseki Kagaku*, **14**, 1141 (1965).

[6] (a) C. A. Parker, *Proc. Roy. Soc., Ser. A*, **220**, 104 (1953); (b) J. C. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, pp 783–786.

[7] (a) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, pp 92–136; (b) D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 834 (1969); (c) A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry," International Publishers, New York, N. Y., 1969, pp 46–54.

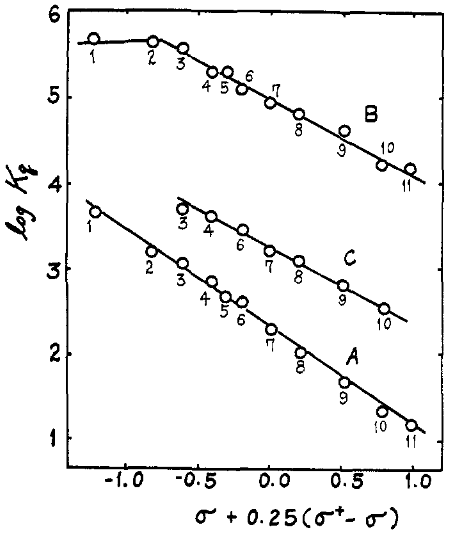


Figure 2. Linear free-energy relationship of quenching constants of substituted benzenes with Yukawa–Tsuno's σ in 80% aqueous acetone (A), 1 *M* aqueous phosphoric acid (B), and 10% aqueous acetone (C): (1) hexamethylbenzene, (2) durene, (3) pseudocumene, (4) *p*-xylene, (5) *tert*-butylbenzene, (6) toluene, (7) benzene, (8) chlorobenzene, (9) *p*-dichlorobenzene, (10) nitrobenzene, and (11) *p*-chloronitrobenzene.

ing constant seems to argue against the electronic energy transfer process. If such endothermic transfer should be operating, it would require vibrational activation or else it should proceed as an activated process (involving Boltzmann distribution of initial states) with an activation energy equal to the difference in the lowest excited state energies of the donor and acceptor.[8] However, the temperature effect showed negligible apparent activation energies for quenching by a series of substituted benzenes. These facts cannot be explained in terms of the electronic–electronic energy transfer mechanism and indicate a nonelectronic energy transfer mechanism such as physical and chemical quenching ones *via* some donor–acceptor interactions.

Indeed, both physical and chemical quenching processes seem to operate in the uranyl fluorescence quenching by these quenchers; aromatic molecules feature physical quenchers, while aliphatic alcohols act as chemical quenchers, as will be shown below.

Physical Quenching by Aromatic Compounds. A chemical quenching process such as photosubstitution or redox reaction would be excluded on the basis of the facts that: (1) no final redox products were found after an irradiation of the uranyl–benzene system, while efficient photoredox reactions were found for the uranyl–alcohol system; (2) no kinetic isotope effect was found, *i.e.*, $K_q(C_6H_6)/K_q(C_6D_6) = 1.0$, as is shown in Table I, while $K_q{}^H/K_q{}^D = 2\text{–}3$ for aliphatic alcohols (Table IV); and (3) the quenching constant of hexamethylbenzene, which has no aromatic protons to be substituted, is very large. Thus the process should essentially be a physical quenching one. The fact that the quenching constant of cyclohexane is much smaller than that of benzene (Table I) suggests an important role of π electrons in the quenching reactions. Also, the quenching constant of triethylbenzene is smaller than that of trimethylbenzene (Table I) in spite of the more negative σ value of the former than the latter, showing the steric effect.

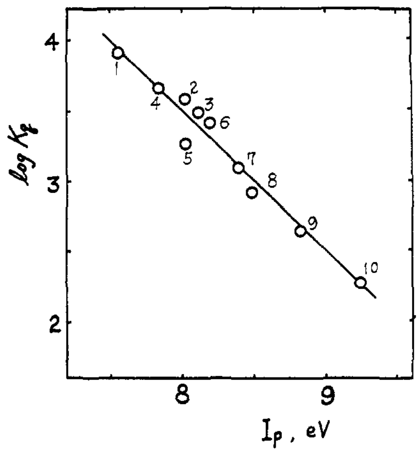


Figure 3. Correlation of quenching constants with ionization potentials:[9] (1) anthracene, (2) phenanthrene, (3) naphthalene, (4) hexamethylbenzene, (5) durene, (6) methoxybenzene, (7) pseudocumene, (8) *p*-xylene, (9) toluene, and (10) benzene.

Table I. Substituent Effects on the Quenching Constant[a]

Quencher	Quenching constant, M^{-1}
1,3,5-Triethylbenzene	435
1,3,5-Trimethylbenzene	470
Benzene	186
Benzene C_6D_6	186
Cyclohexane[b]	<8

[a] In aqueous 80% acetone. [b] For comparison with benzene.

The effect of the steric hindrance would suggest some short-range interactions and not the long-range ones.[7a] Further, plots of log K_q as a function of Yukawa–Tsuno's σ (Figure 2) or ionization potential[9] of the quenchers (Figure 3) show a linear free-energy relationship, suggesting an important role of electron donor–acceptor interactions in the quenching process. Then, it is interesting to compare this with a reaction in which the electron donor–acceptor interactions play an important role. It seemed reasonable to compare the quenching reaction with aromatic nitrations which are known to involve a typical charge transfer intermediate,[10] since both reactions involve electrophilic attack by structurally similar (dioxo) cations on the aromatic system.

A close correlation is seen between them (Figure 4). Since neither is the kinetic isotope effect found (Table I) nor is the C–H bond broken in the quenching reactions, these points are also analogous to aromatic nitrations where no kinetic isotope effect has been found, and the C–H bond is not broken in the rate-determining step.[11] The close correlation between the quenching

---

(8) (a) K. Sandros, *Acta Chem. Scand.*, **18**, 2355 (1964); (b) W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

(9) Ionization potentials of anthracene and phenanthrene were taken from M. E. Wacks and V. H. Dibeler, *J. Chem. Phys.*, **31**, 1557 (1959), that of hexamethylbenzene was from ref 10d, p 307, while those of others were from K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

(10) (a) G. A. Olah, S. T. Kuhn, and S. H. Flood, *J. Amer. Chem. Soc.*, **83**, 4571, 4581 (1961); (b) C. D. Ritchie and H. Win, *J. Org. Chem.*, **29**, 3093 (1964); (c) C. K. Ingold, "Structure and Mechanisms in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1969, pp 320–340; (d) R. S. Mullken and W. B. Person, "Molecular Complexes," Wiley-Interscience, New York, N. Y., 1969, pp 247–249.

(11) (a) L. Melander, *Nature (London)*, **163**, 599 (1949); (b) T. G. Bowyer and G. Williams, *J. Chem. Soc.*, 2650 (1953); (c) ref 10c, pp 331–334.

reactions and aromatic nitrations suggests a similar mechanism or similar intermediates, *e.g.*, a charge-transfer intermediate such as $U^{*\delta-}$–$Q^{\delta+}$.

Suggestion for Exciplex Formation Mechanism. It is noticed that the quenching constants of polyalkylbenzenes are more closely related to the π complex stabilities[12] than to the σ complex stabilities[13] (Table II).

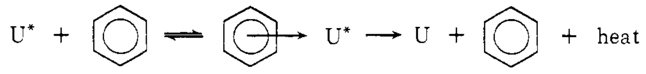
Table II. Relative Rates of the Uranyl Fluorescence Quenching and Relative Stabilities of π and σ Complexes of Alkylbenzenes (*p*-Xylene = 1.00 in Each Case)

Substituent	Relative rate of quenching K_q/K_q^0 A[a]	P[b]	π complex stabilities I_2[c]	PA[d]	σ complex stabilities Cl_2[e]	HF[f]
H	0.28	0.42	0.48	0.70	0.0005	0.09
Me	0.62	0.63	0.51	0.84	0.17	0.63
p-Me$_2$	1.00	1.00	1.00	1.00	1.00	1.00
o-Me$_2$	0.93	0.89	0.87	1.03	1.03	1.1
m-Me$_2$	1.06	0.50	0.99	0.98	90	26
1,2,4-Me$_3$	1.67	1.85	1.85	1.12	15000	13000
1,2,4,5-Me$_4$	1.91	2.11	2.10	1.65	790	140
Me$_6$	6.14	2.41	4.81	2.83		97000
tert-Butyl	0.40	0.81		0.51		

[a] In acetone. [b] In 1 *M* aqueous phosphoric acid. [c] Alkylbenzene–iodine complexes in CCl_4.[12a,b] [d] Alkylbenzene–picric acid complexes in $CHCl_3$.[12c] [e] Relative rate of aromatic chlorination in acetic acid.[13a] [f] Relative basicity of alkylbenzenes to hydrofluoric acid in anhydrous hydrofluoric acid.[13b]

The π complex is considered to involve a perturbation only of the aromatic π electrons, whose perturbation would be much more effective than *n* electron systems such as alcohols (as is shown in the subsequent section).

On the other hand, it is unlikely that the formation of donor–acceptor pairs in the ground state plays a predominant role, since: (1) the uranyl ions are insoluble in benzene and more so in polymethylbenzenes, indicating very low affinities in the ground state; (2) no change in the absorption and emission spectra due to such a complex has been found; (3) the quenching constant of hexamethylbenzene, $4.5 \times 10^3\ M^{-1}$ in 80% aqueous acetone or $4.8 \times 10^5\ M^{-1}$ in 1 *M* phosphoric acid, means that the mean number of the uranyl ions to be effectively quenched by one quencher is about 20 (in 80% acetone) or 200 (in 1 *M* phosphoric acid) (such high efficiencies would prefer a bimolecular collision mechanism between quenchers and the excited uranyl ions to a mechanism of ground-state complex formation); and (4) there is the upper limit of the quenching rate constant (the B plot in Figure 2 or 4), which is very close to the diffusion-controlled rate constant (assuming that the fluorescence lifetime of the uranyl ions is in the range of $\sim 10^{-4}$ sec). These facts suggest the formation of a π complex intermediate in the excited state (or an exciplex mechanism).



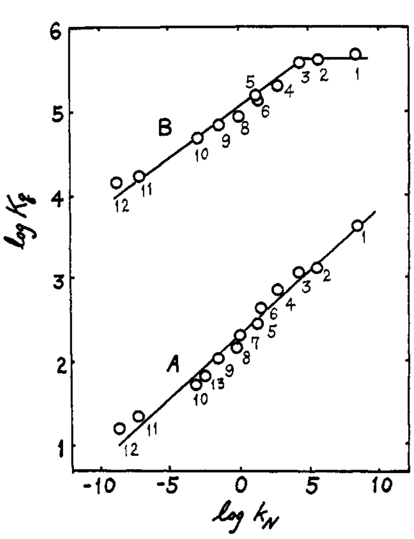


Figure 4. Correlation of quenching constants with rate of aromatic nitrations. The total nitration rates (k_N's) were taken from ref 10c, p 290. Other descriptions are the same as those in Figure 2.

Formation of such an excited state complex is possible since donor–acceptor interaction can arise in the excited state even though there is no affinity in the ground state,[14] and since the long fluorescence lifetime of the uranyl ions[15] allows such interaction in the excited state. In order to explain the results, the following mechanism is assumed

$$U + h\nu \xrightarrow{I_a} U^* \tag{2}$$

$$U^* \xrightarrow{k_f} U + h\nu' \tag{3}$$

$$U^* \xrightarrow{k_d} U + \text{heat} \tag{4}$$

$$U^* + U \xrightarrow{k_s} 2U + \text{heat} \tag{5}$$

$$U^* + Q \underset{k_2}{\overset{k_1}{\rightleftharpoons}} U^{*\delta-}Q^{\delta+} \xrightarrow{k_3} U + Q + \text{heat} \tag{6}$$

where Q, U, and U* are the quencher, the ground-state, and the excited uranyl ions, respectively; I_a is the rate of light absorption in einsteins/(l. sec); and *k*'s are specific rate constants. The steady-state approximation for U* and $U^{*\delta-}$–$Q^{\delta+}$ yields

$$I_f^0/I_f = 1 + k_1\tau_0 k_3[Q]/(k_2 + k_3) \tag{7}$$

$$\tau_0 = (k_f + k_d + k_s[U])^{-1} \tag{8}$$

Figure 2 agrees well with eq 7. Comparison of eq 7 with eq 1 leads to

$$K_q = k_1 k_3 \tau_0/(k_2 + k_3) \tag{9}$$

k_1 may be given using the diffusion-controlled rate constant (k_D) and the probability of the exciplex formation on encounter collision

$$k_1 = \alpha k_D \tag{10}$$

Then eq 9 may be rewritten as eq 11 or 12.

$$K_q = \alpha\tau_0 k_D k_3/(k_2 + k_3) \tag{11}$$

$$K_q = \alpha\tau_0 k_D/(1 + k_2/k_3) \tag{12}$$

---

[12] (a) L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, **74**, 4500 (1952); (b) R. M. Keefer and L. J. Andrews, *ibid.*, **77**, 2164 (1955); (c) H. D. Anderson and D. L. Hammick, *J. Chem. Soc., London*, 1089 (1950); (d) N. B. Jurinsky and P. A. D. de Maine, *J. Amer. Chem. Soc.*, **86**, 3217 (1964); (e) M. Charton, *J. Org. Chem.*, **31**, 2996 (1966).

[13] (a) E. Baciocchi and G. Illuminati, *Gazz. Chim. Ital.*, **92**, 89 (1962); (b) M. Kilpatrick and F. E. Luborsky, *J. Amer. Chem. Soc.*, **75**, 577 (1953).

[14] D. M. Hercules, "Fluorescence and Phosphorescence Analysis," Wiley, New York, N. Y., 1966, pp 15–16, 125–135.

[15] E. Rabinowitch and R. L. Belford, "Spectroscopy and Photochemistry of Uranyl Compounds," Pergamon Press, London, 1964, pp 103, 214.

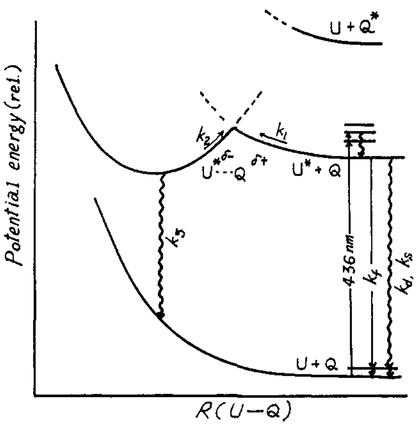


Figure 5. A schematic energy profile for quenching of the uranyl fluorescence by aromatic quenchers.

The process of the unimolecular radiationless decay of the exciplex to ground-state species should be highly exothermic and hence should not be rate determining.[7b] The physical exothermic decay process should involve (1) conversion of the exciplex energy to vibrational (excess) energy followed by (2) relaxation and/or dispersion of the excess vibrational energy to the environments (solvent); both points 1 and 2 involve vibrational energy factors. Then if the decay process (k_3) is the rate-determining step, it should show significant effects due to the changes in the vibrational factors. The lack of a kinetic isotope effect for benzene and the lack of possible correlation of the relative quenching rates with vibrational factors of the quenchers indicate that the decay process (k_3) is unlikely to be the rate-determining step, or k_3 is assumed to be constant for a series of the aromatic quenchers. Then the variation in K_q is mainly attributable to those in the rate of the reverse process (k_2), *i.e.*, the stability or lifetime of the exciplex, $\tau^* = (k_2 + k_3)^{-1}$, on the assumption that α is not greatly different for the substituted benzenes. A schematic energy profile is illustrated in Figure 5. An increase in the exciplex stability would lower its energy level and hence reduce the rate of the reverse process, k_2 (Figure 5), resulting in an increase in the relative quenching rate.

The B plot (Figure 2 or 4), where the quenching constants are very large (close to the diffusion-controlled rate constant), deviated from the linearity, while the A plot, where the quenching constants are much smaller, shows no such a deviation as the B plot. The deviation is not due to the experimental errors, since there was experimental reproducibility of the K_q measurements of the system. Thus the deviation of the B plot from the linearity is interpreted as being due to the upper limit of the quenching rate constant, which is equal to the diffusion-controlled rate constant. For the upper limit of the quenching constant, $k_2/k_3 \ll 1$ and $\alpha \simeq 1$ may be assumed; hence eq 13 is derived from eq 12

$$k_q(\text{upper limit}) = \tau_0 k_D \qquad (13)$$

where k_D, the diffusion-controlled rate constant, may be given by

$$k_D = 8RT/3000\eta \qquad (14)$$

From eq 13 and 14 fluorescence lifetime of the uranyl ion in the absence of quenchers, τ_0, is given by eq 15.

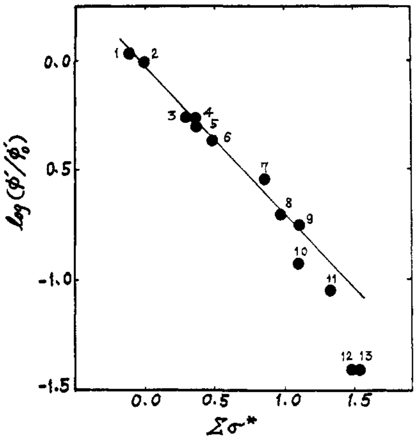


Figure 6. Plot of log (ϕ'/ϕ_0') *vs.* $\Sigma\sigma^*$. ϕ_0' is the quantum yield with isopropyl alcohol whose $\Sigma\sigma^* = 0$; ϕ' is the formation quantum yield divided by the number of the α-hydrogen atoms of each alcohol. Deviation of the plots 10–13 is due to high efficiencies of the physical quenching: (1) *sec*-butyl alcohol, (2) isopropyl alcohol, (3) isobutyl alcohol, (4) *n*-butyl alcohol, (5) *n*-propyl alcohol, (6) ethanol, (7) 3-chloro-1-propanol, (8) methanol, (9) ethylene glycol, (10) benzyl alcohol, (11) 2-phenoxyethanol, (12) 2-bromoethanol, and (13) 2-chloroethanol.

$$\tau_0 = 3000\eta K_q/8RT \qquad (15)$$

Substituting $K_q = 4.83 \times 10^3\ M^{-1}$, $\eta = 1.9 \times 10^{-2}$ P (for 1 *M* aqueous phosphoric acid), $R = 8.31 \times 10^7$ ergs/(°K mol), and $T = 293$ °K in eq 15 yields $\tau_0 = 1.4 \times 10^{-4}$ sec. This agrees with natural fluorescence lifetime of the uranyl ions in solutions $(1\text{–}1.6) \times 10^{-4}$ sec.[15] The agreement verifies the above interpretation for the deviation (B plot).

Figures 2–4 show relatively small slopes, $-\rho = 0.83\text{–}1.1$, $-\Delta \log K_q/\Delta I_p = 0.05$ kcal^{-1}, and $\Delta \log K_q/\Delta \log k_N = 0.14$, respectively; these values are smaller than those deduced by assuming a complete charge transfer intermediate with $\delta = 1$,[16] or $-\rho = 4\text{–}8$, $-\Delta \log K_q/\Delta I_p = 0.73$ kcal^{-1}, and $\Delta \log K_q/\Delta \log k_N \simeq 1$. The comparison suggests that the degree of charge transfer in the transition state is small, namely $\delta \sim 0.2$.

Chemical Quenching by Aliphatic Alcohols. Quenching of the uranyl fluorescence by aliphatic alcohols is accompanied by formation of the redox intermediates, U(V) species,[4,17] and $R_1R_2\dot{C}OH$,[4] or final redox products, U(IV) species, H^+, and R_1R_2CO.[4] It may be noticed that the quenching constants of aliphatic alcohols (as electron n donors) are relatively small compared to those of aromatic π donors, though there is a correlation between the photoredox quantum yields and the donor strength of the quencher, $\Sigma\sigma^*$. A linear free-energy relationship is found between $\Sigma\sigma^*$ and ϕ' (the photoredox quantum yield divided by the number of the α-hydrogen atoms in each alcohol), as shown in Figure 6, where $\Sigma\sigma^*$ is the sum of Taft's σ values[18] of the substituents R_1 and R_2 in R_1R_2CHOH. These indicate a predominant role of the chemical process in the quenching of the uranyl fluorescence by aliphatic

---

(16) (a) P. J. Amdrulis, M. J. Dewar, R. Dietz, and R. L. Hunt, *J. Amer. Chem. Soc.*, 88, 5473 (1966); (b) T. Aratani and M. J. S. Dewar, *ibid.*, 88, 5479 (1966); (c) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppeler, *ibid.*, 89, 370 (1967); (d) D. S. Noyce and G. V. Kaiser, *J. Org. Chem.*, 34, 1008 (1969).

(17) (a) L. J. Heidt and K. A. Moon, *J. Amer. Chem. Soc.*, 75, 5803 (1953); (b) L. J. Heidt, *ibid.*, 76, 5962 (1954).

(18) M. S. Newman, "Steric Effects in Organic Chemistry," Wiley, New York, N. Y., 1956, p 619.

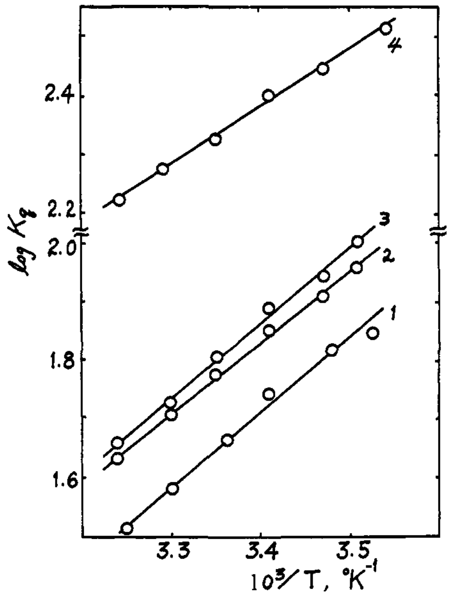


Figure 7. Temperature dependency of quenching constants in aqueous acidic solution (pH 1); $[UO_2^{2+}]$, 0.02 *M*, λ(excitation) 436 nm, λ(analysis) 510 nm: (1) *n*-propyl alcohol; (2) isobutyl alcohol; (3) *sec*-butyl alcohol; and (4) benzene.

alcohols, though the physical quenching process becomes important for alcohols having halogen atoms or a phenyl group.

Quenching of the uranyl fluorescence by aliphatic alcohols may be explained in terms of the mechanism similar to that for quenching by aromatic compounds, with minor modifications involving the chemical quenching process (k_4) and successive (secondary) chemical processes (k_5, k_6)

$$\begin{tikzcd}
U^* + Q \arrow[r, shift left, "k_1"] & U^{*\delta-}\text{–}Q^{\delta+} \arrow[l, shift left, "k_2"] \arrow[r, "k_3"] \arrow[dr, "k_4"] & U + Q + \text{heat} & \\
 & & U' + Q' \arrow[u, "k_5"] \arrow[r, "k_6"] & U'' + Q''
\end{tikzcd}$$

with the resulting expression 16 for K_q, where U′, Q′,

$$K_q = \alpha\tau_0 k_D/(1 + k_2/(k_3 + k_4)) \qquad (16)$$

U′′, and Q′′ are UO_2H^{2+}, $R_1R_2\dot{C}OH$, U(IV) species, and R_1R_2CO, respectively.

Since quenching rate constants of alcohols are much smaller than the diffusion-controlled rate constant, *i.e.*, $K_q/\tau_0 \ll k_D$, the approximation $k_2/(k_3 + k_4) \gg 1$ may be permissible. Equation 16 is, therefore, rewritten as

$$K_q = \alpha\tau_0 k_D(k_3 + k_4)/k_2 \qquad (17)$$

For alcohols having neither halogen atoms nor a phenyl group the physical quenching (k_3) would be negligibly small[4b] compared to the chemical quenching (k_4), and hence $K_q \simeq \alpha\tau_0 k_D k_4/k_2$. This explains the correlation between K_q and ϕ or β^{-1} in Table III. Further, formation of the photoredox products includes secondary chemical processes, *i.e.*, disproportionation reactions of the U(V) species[17] and radicals $R_1R_2\dot{C}OH$,[4] which may involve activation processes, and hence the formation quantum yields may be temperature dependent. In fact, there exists a distinct difference in the temperature effects on the rates of the two processes: negative apparent activation energies for the quenching process (Figure 7), positive apparent activation energies for the formation of the photoredox products (Figure 8) under similar conditions.

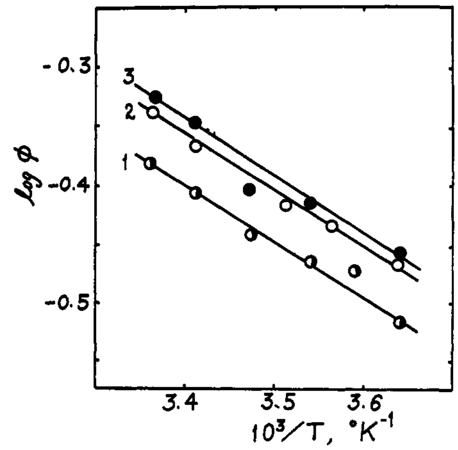


Figure 8. Temperature dependency of the photoredox quantum yields in aqueous acidic solution (pH 1) with 405- and 436-nm irradiation; $[UO_2^{2+}]$, 0.02 *M*, [alcohol], 0.1 *M*: (1) *n*-propyl alcohol, (2) isopropyl alcohol, and (3) *sec*-butyl alcohol.

Table III. Correlation among the Rate Parameters and Polar Substituent Constants in Aqueous Solution (pH 1)

Alcohol	$\Sigma\sigma^*$ [a]	ϕ [b]	β^{-1} [c]	K_q [d]
sec-Butyl	−0.10	0.36	46	174
Isopropyl	0.00	0.34	35	113
Isobutyl	0.30	0.36	47	138
n-Butyl	0.36	0.36	46	130
n-Propyl	0.39	0.34	35	105
Ethyl	0.49	0.31	27	62.5
Trimethylenechlorohydrin	0.88	0.20		375
Methyl	0.98	0.15	7.2	12
Ethylene glycol	1.05	0.087	4.7	40
Benzyl alcohol	1.09	0.071		3200
2-Phenoxyethanol	1.34	0.031		3900
Ethylenebromohydrin	1.49	0.026		2550
Ethylenechlorohydrin	1.54	0.026		75

[a] $\Sigma\sigma^* = \sigma^*(R_1) + \sigma^*(R_2)$; $\sigma^*(R_1)$ and $\sigma^*(R_2)$ are Taft σ^* values[18] of the substituents R_1 and R_2 when alcohols are represented by the formula R_1R_2CHOH. [b] Quantum yield of the photolysis of aqueous solutions containing 0.02 *M* uranyl nitrate and 0.06 *M* alcohols by 405-nm irradiation. [c] The reciprocal of the slope of the ϕ^{-1} *vs.* $[\text{alcohol}]^{-1}$. [d] Quenching constant measured under similar conditions to those of the photolysis, with λ(excitation) = 405 nm and λ(analysis) = 510 nm.

It might be considered that the primary chemical process (k_4) would proceed either through α-hydrogen abstraction or through electron transfer, since the polar substituent effect, $\Sigma\sigma^*$, would affect in the same direction on both hydrogen abstraction and electron transfer processes.

However, very small rate parameters of *tert*-butyl alcohol compared to three other isomeric butyl alcohols, and kinetic isotope effects on the rate parameters (Table IV), prefer the α-hydrogen abstraction mechanism to the electron transfer one. Efficient abstraction of α hydrogen by one of the oxygen atoms of the (excited) uranyl ion would occur in a similar manner to those assumed in the thermal oxidations of alcohols by oxygen-containing metal ions.[19]

---

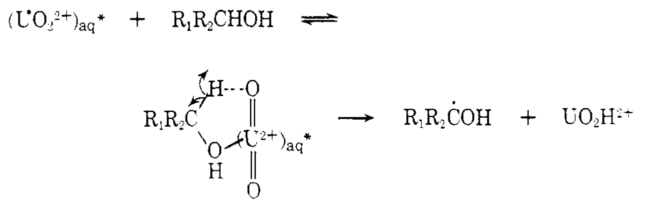
(19) (a) K. B. Wiberg, "Oxidation in Organic Chemistry," Academic Press, New York, N. Y., 1965, pp 159–172; (b) W. A. Waters, "Mechanisms of Oxidation of Organic Compounds," Methuen, London, 1964, Chapter 4.

Table IV. Comparison of the Rate Parameters of Deuterated Alcohols and *tert*-Butyl Alcohol with Those of the Corresponding Nondeuterated and Isomeric Alcohols[a]

Alcohol	ϕ	K_q, M^{-1}
C_2H_5OH	0.31	62.5
C_2H_5OD	0.30	
C_2D_5OD	0.14	29
$(CH_3)_2CHOH$	0.34	113
$(CD_3)_2CDOD$	0.18	41
n-Butyl alcohol Isobutyl alcohol *sec*-Butyl alcohol	0.36	130–174
tert-Butyl alcohol	0.02	5

[a] Same conditions as in Table III.

Such special geometrical configuration, needed for the chemical quenching, may be partly responsible for the relatively small quenching constants of aliphatic



alcohols (having neither halogen atoms nor a phenyl group). However, this point needs further clarification.

As a summary, quenching of the uranyl fluorescence by aromatic quenchers and aliphatic alcohols involves nonelectronic–electronic energy transfer; quenching by aromatic molecules proceeds through physical radiationless decay of an excited state π complex, while quenching by aliphatic alcohols proceeds through chemical decay (*via* hydrogen abstraction) of an exciplex or collision complex.

Polar Electrophilic Additions to Styrene. Secondary Deuterium Isotope Effects[1a–c]

Charles L. Wilkins* and Thomas W. Regulski[1d]

Contribution from the Department of Chemistry, University of Nebraska at Lincoln, Lincoln, Nebraska 68508. *Received April 4, 1972*

Abstract: α-Secondary deuterium isotope effects for polar additions of electrophiles to styrene, *trans*-1-phenylpropene, *p*-bromo-, *p*-chloro-, and *p*-nitrostyrene have been measured. The reactions were carried out at 40° in dry acetic acid using bromine, chlorine, and 2,4-dinitrobenzenesulfenyl halides as the electrophiles. Very small isotope effects (k_H/k_D = 0.97–1.00) were found for bromine and chlorine additions to all but *p*-nitrostyrene. In that case, k_H/k_D values of 0.95 and 0.96, respectively, were found. For the additions of 2,4-dinitrobenzenesulfenyl halides, k_H/k_D values in the range of 0.94–0.97 were found for all the styrenes examined. These results are interpreted with the help of stereochemical and kinetic data.

Since Lewis'[2] and Shiner's[3] pioneering work in the 1950's, secondary deuterium isotope effects have proven to be an invaluable aid in the elucidation of reaction mechanisms. To date, investigations of a wide range of reactions have employed this tool in probing transition state chemistry.[4]

Surprisingly, secondary deuterium isotope effects have been little used to study polar electrophilic additions to olefins. In an early qualitative study, Denney and Tunkel,[5] testing the suggestions of Streitwieser,[6] found inverse isotope effects for the reactions of *trans*-stilbene-d_2 with a variety of reagents. The isotope effects for two known polar electrophilic reagents, bromine (k_H/k_D = 0.91) and 2,4-dinitrobenzenesulfenyl chloride (k_H/k_D = 0.87), were measured, but these data were said to be qualitative. The conclusion of that study was that inverse isotope effects predominate in addition reactions of olefins. More recently, Schubert and Lamm[7] have reported a k_H/k_D of 0.97 ± 0.03 for the acid-catalyzed hydrolysis of styrene-α-d_1. This value is consistent with a mechanism involving carbonium ion formation by solvolytic proton transfer to styrene during the rate-determining step. Since much of the previous work has been qualitative, it was our hope in the present investigation to make quantitative measurements of these effects.

Most previous evidence for the reaction mechanisms of polar electrophilic additions to olefins is based largely on data such as reaction stereochemistry.[8–10] More evidence, such as the direction and magnitude of secondary deuterium isotope effects, is highly desirable. It has been pointed out by Wolfsberg[11] that determination of transition state geometry cannot be

---

[1] (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. (b) Partial support was also received from the University of Nebraska Research Council. (c) Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract ORGN-094. (d) Abstracted from the Ph.D. Dissertation of T. W. Regulski, The University of Nebraska at Lincoln, 1971.

[2] E. S. Lewis and C. E. Boozer, *J. Amer. Chem. Soc.*, **74**, 6306 (1952).

[3] V. J. Shiner, *ibid.*, **75**, 2925 (1953).

[4] E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

[5] D. B. Denney and N. Tunkel, *Chem. Ind.*, (*London*), 1383 (1959).

[6] A. Streitwieser, R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, **80**, 2326 (1958).

[7] W. M. Schubert and B. Lamm, *ibid.*, **88**, 120 (1966).

[8] R. P. Bell and M. Pring, *J. Chem. Soc. B*, 1119 (1966).

[9] R. C. Fahey, *J. Amer. Chem. Soc.*, **88**, 4681 (1966).

[10] N. R. Slobodkin and N. Kharasch, *ibid.*, **82**, 5837 (1960).

[11] M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 325 (1964).