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Photochemical Reactions of Uranyl Ions with Organic Compounds. IV. The Uranyl Fluorescence Quenching by Aliphatic Alcohols

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The relative rates for uranyl fluorescence quenching by aliphatic alcohols (methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, and *s*-butyl alcohols) were measured under various conditions. The rates were increased in proportion to the perchloric acid concentration at pH <1, whereas the rates were smaller and nearly constant at the pH's between 1—4; thus showing the involvement of both acid-dependent and acid-independent processes. Though the rates for both processes changed with the change in the alcohol structure (the polar substituent effect), the ratio of the two rate constants was nearly constant. The inhibitory effects of cupric ions (as a scavenger for the one-equivalent redox intermediates) suggested that the acid-dependent quenching process involves a two-equivalent redox or two consecutive one-equivalent redox steps between the same partners. The mechanisms of these quenching processes are discussed.

A kinetic study has been made of the photo-redox reaction of the uranyl ions with alcohols in solution with pH's ranging from 1 to 3, where the rates seemed to be insensitive to the acidity of the medium.[1] However, in the course of the investigation of the effects of the acid concentration (up to 2M in perchloric acid) on the rates, it appeared that the rates of both the quenching and the photo-redox reactions were increased with the acid concentration in the pH region below 1, suggesting the involvement of an acid-catalyzed process as well as an acid-independent process. Further, the former process seemed to involve a two-equivalent redox or two consecutive one-equivalent redox steps between the same partners, while the latter process features *via* α-hydrogen abstraction (followed by proton liberation) *i.e.*, a one-equivalent redox process, followed by the disproportionation reactions to produce the photo-redox products. The quenching mechanisms are discussed in connection with photo-redox reaction mechanisms.

Experimental

Guaranteed reagents and doubly-distilled water were used. Preliminary experiments showed that traces of such impurities as halogen ions and aldehydes or ketones which might be present in the reagents were negligible under the present conditions.

Aqueous solutions of the 0.02M uranyl nitrate containing various concentrations of the substrates and perchloric acid

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[1] S. Sakuraba and R. Matsushima, This Bulletin, **43**, 2359 (1970).

were prepared. After the desired temperature (usually 20°C) was attained, the relative fluorescence intensities were rapidly measured. The fluorescence measurements were carried out using a fluorescence spectrophotometer (Hitachi 204 Type) without an attachment for temperature control. The errors in the determination of the temperature inherent in the procedure were estimated to be within $\pm 1°$C. De-oxygenation with oxygen-free nitrogen (keeping air-tight) produced no change in the fluorescence intensities. The relative intensities at the 510 nm peak of the uranyl fluorescence were measured with 405 nm excitation, though no significant changes in the quenching constants were observed with the changes in the analyzing (490, 510, 533 nm) and the excitation (313, 366, 405 nm) wavelengths with the exception of a slight lowering in the quenching constants with the 436 nm excitation. The methods for the analysis of the photo-redox products and the measurements of their quantum yields were previously described.1)

Results and Discussion

Effects of pH and Ionic Strength on the Rate. The quenching constants of the uranyl fluorescence by some alcohols at various pH's are shown in Fig. 1. In the pH region below 1 the quenching constant was markedly increased with the increase in acidity, while it was nearly constant in the pH region from 1 to 4. Perchloric acid did not quench the fluorescence of a 0.02M uranyl solution in the absence of alcohols. Thus, the quenching reaction involves both acid-dependent and acid-independent processes. The rates of these processes, then, can be expected to result in a difference in their sensitivities to ionic strength. The effects of the ionic strength on the rates at different acid concentrations are shown in Fig. 2. The slope of the plot for the 0.5M $HClO_4$ solution was 0.28, larger than that for the solutions of pH 1 and 2, 0.07. Since the quenchers (alcohols) have no net charge, the rate for a simple bimolecular quenching process between the excited uranyl ion and the quencher should not be affected largely by the ionic strength, while the rate of the quenching process in which the hydrogen ions participate should show a greater sensitivity to the ionic strength.2)

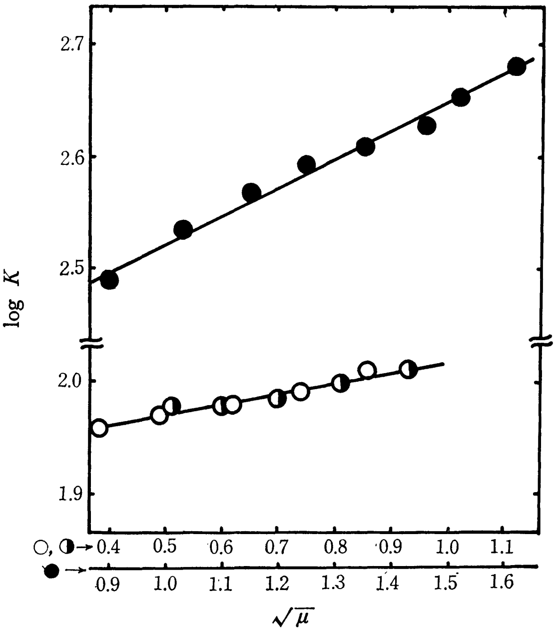

Fig. 2. Effects of ionic strength on the quenching constant (*n*-Propyl alcohol).
$[UO_2(NO_3)_2]=0.02$M, [*n*-Propyl alcohol]$=0.005-0.05$M, λ(excitation)$=405$ nm, λ(emission)$=510$ nm,
●: $[HClO_4]=0.5$M ($\mathrm{pH}\doteqdot 0$), ○: pH=2.0,
◑: pH=1.0.

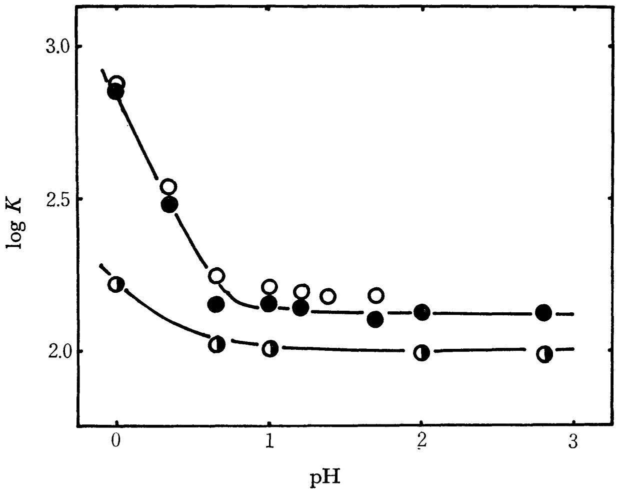

Fig. 1. Variation in the quenching constant with pH.
$[UO_2(NO_3)_2]=0.02$M, [substrate]$=0.005-0.05$M, λ(excitation)$=405$ nm, λ(emission)$=510$ nm.
◑: *n*-Propyl alcohol, ●: *s*-Butyl alcohol,
○: Glucose.

Inhibitory Effects by Cupric Ions. Table 1 shows the inhibitory effects of cupric ions (as scavengers for one-equivalent redox intermediates[1,3]) on the formation of the photo-redox products. The direct quenching of the uranyl fluorescence by cupric ions was negligible. Cupric ions can only scavenge the one-equivalent redox intermediates, U(V) and/or R· species; the effect should be less sensitive to the two-equivalent redox process. Therefore the change in the effects on the ratio of the products, [U(IV)]/[Ox], with the acid concentration suggests that the acid-dependent chemi-

TABLE 1. INHIBITORY EFFECTS OF CUPRIC IONS ON THE PRODUCT RATIO [U(IV)]/[Ox] AT DIFFERENT ACID CONCENTRATION[a)]

$[HClO_4]$, M	$[U(IV)]\times 10^3$M	$[Ox]\times 10^3$M	[U(IV)]/[Ox]
0.02	0.47	3.00	0.16
0.04	1.34	2.98	0.45
0.16	1.72	3.17	0.54
0.30	3.10	3.20	0.97
0.08	3.39	3.23	1.05[b)]

Initial concentrations of $UO_2(NO_3)_2$, *n*-propyl alcohol, and $CuSO_4$ were 0.02, 0.20, and 0.005M, respectively.
a) Solutions to be photolyzed were de-oxygenated with oxygen-free nitrogen and kept air-tight.
b) In the absence of cupric ions.

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2) K. J. Laidler, "Chemical Kinetics," McGraw Hill, New York (1965), pp. 219—222.

3) a) A. C. Harkness and J. Halpern, *J. Amer. Chem. Soc.*, **81**, 3526 (1959); b) F. A. Jones and E. S. Amis, *J. Inorg. Nucl. Chem.*, **26**, 1045 (1964).

cal quenching process involves a two-equivalent redox or two consecutive one-equivalent redox steps between the same partners within a solvent cage. Table 1 also shows that cupric ions mainly scavenge the U(V) species, since the amount of the oxidation product, [Ox], is only slightly decreased in the presence of cupric ions.

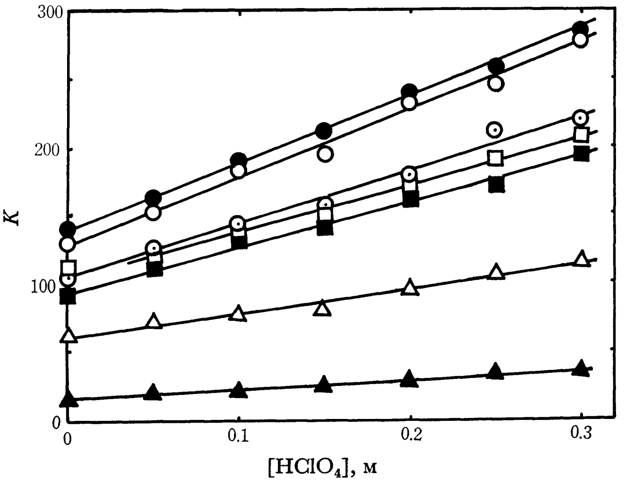

Fig. 3. Linear relationship between the quenching constant and the acid concentration.
[UO$_2$(NO$_3$)$_2$] = 0.02 M, [Alcohol] = 0.005 – 0.5 M, λ(excitation) = 405 nm, λ(emission) = 510 nm, Temperature = 20 ± 1°C. ●: *s*-Butyl alcohol, ○: Isobutyl alcohol, ⊙: *n*-Butyl alcohol, □: Isopropyl alcohol, ■: *n*-Propyl alcohol, △: Ethyl alcohol, ▲: Methyl alcohol.

Separation of the Quenching Constants. The quenching constants, K's, in the Stern-Volmer equation[4] (1), were measured as a function of the perchloric acid concentration (Fig. 3):

$$I_f{}^0/I_f = 1 + K[\mathrm{R}] \tag{1}$$

Figure 3 shows that the quenching constants, K, can be represented by the following equation:

$$K = K_1 + K_2[\mathrm{H}^+] \tag{2}$$

where K_1 and K_2 refer to the quenching constants for the acid-independent and the acid-dependent processes respectively. In Table 2, K_1 (the intercept) and K_2 (the slope) obtained from the plot of K *vs.* [H$^+$] are listed. It may be noticed that the ratio of the quenching constant for the acid-dependent process to that for the acid-independent process, K_2/K_1, is nearly constant, whereas both K_1 and K_2 vary considerably, with the variation in the alcohol structure.

Table 2. The quenching constants, K_1 and K_2 in Eq.(2), for aliphatic alcohols (from Fig. 3).

Alcohols	K_1, M^{-1}	K_2, M^{-2}	K_2/K_1, M^{-1}
Methyl	16	60	3.8
Ethyl	60	180	3.0
n-Propyl	90	340	3.8
Isopropyl	107	340	3.2
n-Butyl	105	400	3.8
Isobutyl	130	480	3.7
s-Butyl	140	490	3.5

The Mechanism. The following mechanism may be assumed for the quenching reaction of the uranyl fluorescence by aliphatic alcohols in an acidic aqueous solution:

$$\mathrm{U} + h\nu \xrightarrow{I_a} \mathrm{U} \tag{3}$$

$$\mathrm{U}^* \xrightarrow{k_f} \mathrm{U} + h\nu' \tag{4}$$

$$\mathrm{U}^* \xrightarrow{k_d} \mathrm{U} + \text{heat} \tag{5}$$

$$\mathrm{U}^* + \mathrm{U} \xrightarrow{k_s} 2\mathrm{U} + \text{heat} \tag{6}$$

$$\mathrm{U}^* + \mathrm{R} \xrightarrow{k_1} \mathrm{U(V)} + \mathrm{R}\cdot + \mathrm{H}^+ \tag{7}$$

$$\mathrm{U}^* + \mathrm{R} \xrightarrow{k_1'} \mathrm{U} + \mathrm{R} + \text{heat} \tag{8}$$

$$\begin{aligned}&\mathrm{U}^* + \mathrm{R} + \mathrm{H}^+ \xrightarrow{k_2}\\ &\quad \mathrm{U(IV)} + \mathrm{Ox} + 3\mathrm{H}^+ (\text{or } \mathrm{U(V)} + \mathrm{R}\cdot + 2\mathrm{H}^+)\end{aligned} \tag{9}$$

$$\mathrm{U}^* + \mathrm{R} + \mathrm{H}^+ \xrightarrow{k_2'} \mathrm{U} + \mathrm{R} + \mathrm{H}^+ + \text{heat} \tag{10}$$

Here, U, R, U(V), R·, U(IV), and Ox refer to $(\mathrm{UO}_2^{2+})_{aq}$, R$_1R_2$CHOH, $(\mathrm{UO}_2{}^+)_{aq}$ R$_1$R$_2\dot{\mathrm{C}}$OH, U(IV) species, and R$_1$R$_2$CO respectively; I_a is the rate of the light absorption in einsteins·l^{-1}sec^{-1}; k_1 and k_2 refer to the rate constants for the acid-independent and the acid-dependent quenching processes respectively. Process (7) has been shown to involve a one-equivalent redox (α-hydrogen abstraction[1,5]), followed by fast disproportionation reactions:

$$2\mathrm{U(V)} \xrightarrow{\mathrm{H}^+} \mathrm{U(IV)} + \mathrm{U}, \text{ and } 2\mathrm{R}\cdot \longrightarrow \mathrm{R} + \mathrm{Ox}.$$

The acid-dependent chemical quenching process (9) may involve a two-equivalent redox or two consecutive one-equivalent redox steps between the same partners. This is suggested by the facts that (i) the product quantum yield is higher than 0.5 in the 1 N HClO$_4$ solution (the maximun quantum yield for the photoredox products expected from the one-equivalent transfer is 0.5), and (ii) the cupric ions have minor inhibitory effects. However, the initial reacting species in the process has not yet been clarified, and the description drawn here may not be valid; alternative mechanisms, such as those involving a fast pre-equilibrium of proton-addition on the uranyl ion or of the formation of a complex or an ester-intermediate, may explain the results equally well.

Since neither the change in the concentration of alcohol nor that of perchloric acid resulted in a change in the absorption of the system (pH<2), the steady state assumption for U* leads to the following expression:

$$\begin{aligned} I_f{}^0/I_f &= 1 + \tau_0\{k_1 + k_1' + (k_2 + k_2')[\mathrm{H}^+]\}[\mathrm{R}] & (11)\\ &= 1 + \tau_0(k_1 + k_1')[\mathrm{R}] + \tau_0(k_2 + k_2')[\mathrm{R}][\mathrm{H}^+] & (12)\\ \tau_0 &= \{k_f + k_d + k_s[\mathrm{U}]\}^{-1} & (13)\end{aligned}$$

From Eqs. (1), (2), (11), and (12), the following equations result:

$$K_1 = \tau_0(k_1 + k_1') \tag{14}$$

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[4] O. Stern and M. Volmer, *Physik. Z.*, **20**, 183 (1919).

[5] To be published.

$$K_2 = \tau_0(k_2+k_2') \tag{15}$$

$$K_2/K_1 = (k_2+k_2')/(k_1+k_1') \tag{16}$$

While both K_1 and K_2 in Table 2 decrease with the increase in the polar substituent effect, $\sum\sigma^*$[6] of the substrate (alcohol), the K_2/K_1 ratio is nearly constant; *i.e.*, the sensitivities of the rates of the two processes (acid-dependent and independent processes) are similar. This suggests that the rate-determining steps of the two processes involve the same primary act, *i.e.*, α-hydrogen abstraction. The two processes, however, differ in their secondary steps: the secondary step of the acid-dependent process involves a second one-equivalent redox reaction between the same partners, whereas that of the acid-independent process involves the disproportionation reaction of the UO_2^+ species, each of which is formed in a separate solvent cage.[1] The change in the rate with the acid concentration may be attributable to the change in the species of the uranyl ions excited or to be excited. One can assume, for example, that the protonated uranyl ions are formed through a fast equilibrium[7]: $UO^{2+} + H^+ \rightleftharpoons UO_2H^{3+}$, and have stronger oxidation power in their excited states (and/or intermediate states) than the unprotonated uranyl ions. The formation of a complex[8] or an ester-like intermediate[9] (as has been proposed for the thermal oxidations by many transition metal ions) prior to the photolysis is also conceivable. However, no evidence for such pre-equilibria was found from absorption, emission, and excitation spectra. At this stage we cannot decide the initial species in the acid-dependent process; hence, only a tentative stoichiometry has been outlined here. These problems will be discussed later in detail, with more experimental date.

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[6] M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, New York (1956), p. 619.

[7] Analogous to that of the thermal oxidations with the vanadyl ions: J. S. Littler and W. A. Waters, *J. Chem. Soc.*, **1959**, 4046.

[8] a) G. E. Heckler, A. E. Taylor, C. Jensen, D. Percival, R. Jensen, and P. Fung, *J. Phys. Chem.*, **67**, 1, (1962); b) K. Venkatarao and M. Santappa, *Indian J. Chem.*, **5**, 304 (1967); c) *Chem. Abstr.*, **66**, 9476 (1967); d) S. Sakuraba and R. Matsushima, This Bulletin, **43**, 1950 (1970);

[9] a) F. H. Westheimer and N. Nicolaides, *J. Amer. Chem. Soc.*, **71**, 25 (1949); b) W. A. Waters, "Mechanisms of Oxidation of Organic Compounds," Methuen and company, London (1964); c) K. B. Wiberg and H. Schöfer, *J. Amer. Chem. Soc.*, **91**, 933 (1969).