Substituent Effects on the Photochemical Reaction Rates of the Uranyl–Alcohol System

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Abstract: The substituent effects of the substrate (alcohol) on the photochemical reaction rates of the uranyl–alcohol system were investigated on the basis of both the fluorescence quenching and the photoredox data. There was a parallel relation between the quenching and the photoredox reaction rates. Plots of the logarithm of the photoredox quantum yield as a function of the polarity of the substrate, $\Sigma\sigma^*$ (sum of the Taft σ^* values), showed a linear relationship, with $\rho^* = -1.1$. The steric effect on the rates appeared to be less important. A mechanism involving α-hydrogen abstraction in the rate-determining step was suggested from the kinetic isotope effects and the markedly small rate with *tert*-butyl alcohol, as well as from the ρ^* value of -1.1.

Irradiation with visible light of aqueous solutions containing a series of alcohols and uranyl ions led to a photoredox reaction giving uranium(IV) species and equimolar amounts of aldehydes or ketones, accompanied by an increase in the hydrogen ion concentration.[1] Plots of the reciprocal of the quantum yield for the formation of the U(IV) species or carbonyl compounds against the reciprocal of the initial alcohol concentration gave straight lines with intercepts α, being 2 for most aliphatic alcohols, and the slopes, β, the reciprocals of which are a measure of photoreactivity; $\phi^{-1} = \alpha + \beta[\text{alcohol}]^{-1}$ (Figure 1). On the other hand, plots of the relative intensity of uranyl fluorescence against alcohol concentration obeyed the Stern–Volmer equation; $I_f^0/I_f = 1 + K_q \cdot [\text{alcohol}]$ (Figure 2), where the quenching constant K_q is a measure of the rate for a bimolecular radiationless deactivation of the excited uranyl ions by the quencher.

The present work was undertaken to investigate the substituent effects on the rates of photochemical reactions of the uranyl–alcohol system on the basis of the kinetic data of both quenching and photoredox reactions.

Table I. Substituent Effects of Aliphatic Alcohols on the Rate Parameters

Alcohol	ϕ^a	$\beta^{-1\,b}$	$K_q{}^c$	$\Sigma_i\sigma_i{}^{*\,d}$
sec-Butyl	0.36	46	174	−0.10
Isopropyl	0.35	35	113	0.00
Isobutyl	0.36	47	138	+0.30
n-Butyl	0.36	46	130	+0.36
n-Propyl	0.34	35	105	−0.39
Ethyl	0.31	27	60	+0.49
Methyl	0.15	7.2	12	+0.98
Ethylene glycol	0.11	4.7	40	+0.01

[a] Quantum yield of the photolysis under the conditions $[UO_2{}^{2+}]_i = 0.02\ M$, [alcohol] = 0.06 *M*, pH 1, 20°, λ 405 nm. [b] The reciprocal of the slope of the ϕ^{-1} *vs.* $[\text{alcohol}]^{-1}$ plot, at pH 1, 20°, $[UO_2{}^{2+}]_i = 0.02\ M$, $[\text{alcohol}]_i = 0.005–0.2\ M$. [c] The quenching constants measured under the conditions $[UO_2{}^{2+}] = 0.02\ M$, [alcohol] = 0.002–0.2 *M*, pH 1, 20 ± 2°, λ(excitation) 405 nm. λ(emission) 510 nm. [d] $\Sigma_i\sigma_i{}^* = \sigma^*(R_1) + \sigma^*(R_2)$; $\sigma^*(R_1)$ and $\sigma^*(R_2)$ are Taft σ^* values[4] of the substituents R_1 and R_2 when alcohols are represented by the formula R_1R_2CHOH.

Results and Discussion

The Quenching Constants. The quenching constants, K_q, for aliphatic alcohols are listed in Table I. Two points may be noticed, relatively small quenching constants and the tendency of the quenching constant to decrease with an increase in the polarity, $\Sigma\sigma^*$, of the substrate. Since the natural lifetime, τ_0, of the excited uranyl ions in solution ranges from 5×10^{-5} to 5×10^{-4} sec,[2] the quenching rate constants, $k_q = K_q/\tau_0$, should range from 2×10^4 to 4×10^6 sec^{-1} M^{-1}, being much smaller than the normal diffusion-controlled rate constant, k_d ($k_q/k_d \simeq 10^{-4}$–10^{-6}). The interpretation of this is that the quenching process is endothermic by several kilocalories per mole[3] (in fact, the region of the uranyl emission band corresponds to only 54–58 kcal/mol). The apparent activation energy for the photoredox reaction, $\Delta E_a = 8.5$ kcal/mol[1] (both with ethyl alcohol and with *n*-propyl alcohol), is nearly comparable to that for the quenching reaction, suggesting that the rate-determining step of the photoredox reaction is the same as that of the quenching reaction.

Substituent Effects on the Rate Parameters. The rate parameters ϕ and β^{-1} for the photoredox reaction of the uranyl–alcohol system are listed in Table I. The term $\Sigma\sigma^*$ in Table 1 represents the sum of the polar substituent constants, *i.e.*, $\Sigma\sigma^* = \sigma^*(R_1) + \sigma^*(R_2)$, where $\sigma^*(R_1)$ and $\sigma^*(R_2)$ are the Taft σ^* values[4] when alcohols are represented by the formula R_1R_2CHOH. Figure 3 shows the relation between the photoredox quantum yield and the $\Sigma\sigma^*$ value, with substrates having rather widely different polarity. It is noticed that the rate parameters decrease with the increase in the $\Sigma\sigma^*$ value, while the effects of steric hindrance on the rate are of no importance. The photoredox rates with benzyl alcohol derivatives increased in the order $C_6H_5CH_2OH < C_6H_5CH(CH_3)OH < C_6H_5CH(C_2H_5)OH$, showing results similar to those of previous work.[5]

Rate Parameters with Deuterated Alcohols and with *tert*-Butyl Alcohol. The rate parameters for reactions

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[1] S. Sakuraba and R. Matsushima, *Bull. Chem. Soc. Jap.*, 43, 2359 (1970).

[2] E. Rabinowitch and R. L. Belford, "Spectroscopy and Photochemistry of Uranyl Compounds," Pergamon Press, London, 1964, pp 209–228, 335–349.

[3] P. A. Leermakers and A. Weissberger, *Tech. Org. Chem.* **14**, 48 (1969).

[4] M. S. Newman, "Steric Effects in Organic Chemistry," Wiley, New York, N. Y., 1956, p 619.

[5] Our unpublished data.

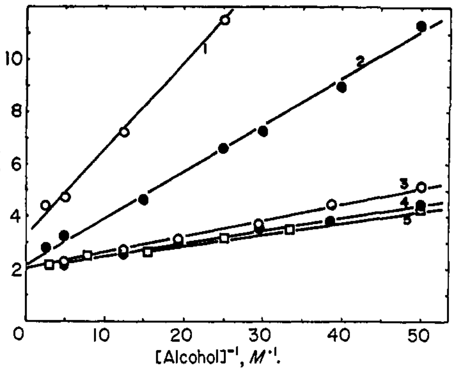

Figure 1. Plot of ϕ^{-1} as a function of [alcohol]$^{-1}$; $[UO_2^{2+}]_i$ = 0.02 *M*, pH 1.0, 20°: (1) ethylene glycol, (2) methyl alcohol, (3) ethyl alcohol, (4) *n*-propyl alcohol, (5) *n*-butyl, *sec*-butyl, and isobutyl alcohols.

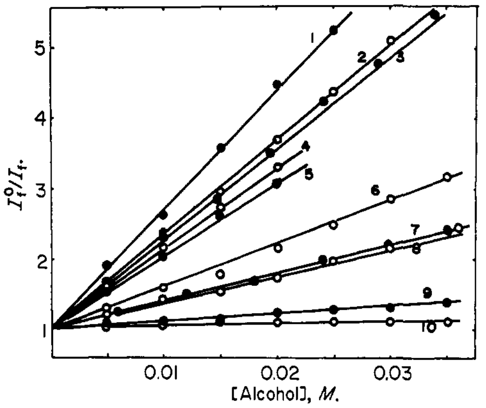

Figure 2. The Stern-Volmer plot; $[UO_2^{2+}]_i$ = 0.02 *M*, pH 1.0, 20 ± 2°: (1) *sec*-butyl alcohol, (2) isobutyl alcohol, (3) *n*-butyl alcohol, (4) isopropyl alcohol, (5) *n*-propyl alcohol, (6) ethyl alcohol, (7) deuterated isopropyl alcohol (C_3D_8O), (8) ethylene glycol, (9) methyl alcohol, (10) *tert*-butyl alcohol. The number of quanta of light absorbed by the system was constant against the alcohol concentration.

with deuterated alcohols and *tert*-butyl alcohol are shown in Table II for comparison. Table II shows that the rate parameters both with deuterated alcohols and with *tert*-butyl alcohol are small compared to those with corresponding normal (undeuterated) alcohols and three butyl alcohol isomers, respectively. The comparison suggests a participation of α hydrogen in the rate-determining step. Further, it should be noticed in Tables I and II that the quenching constants parallel the photoredox rates, particularly that the deuterium isotope effect on the quenching constant, $(K_q)_H/(K_q)_D$, is nearly equal to that on the photoredox quantum yield, ϕ_H/ϕ_D. These parallel relations suggest that the rate-determining step in the quenching reaction is the same as that in the photoredox reaction, *e.g.*, the step involving α-hydrogen abstraction or the charge-transfer process.

Table II. Rate Parameters with Deuterated Alcohols and *tert*-Butyl Alcohol[a]

Alcohol	ϕ	K_q
C_2D_5OD	0.14	29
$(CD_3)_2CDOD$	0.18	41
$(CH_3)_3COH$	0.02	5

[a] Same conditions as in Table I.

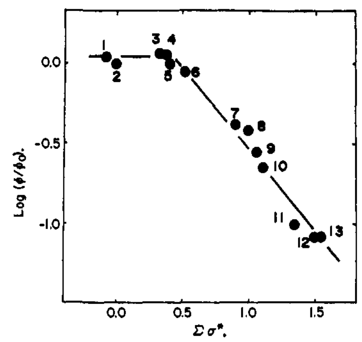

Figure 3. Plot of log (ϕ/ϕ_0) as a function of $\Sigma\sigma^*$; ϕ_0 is the quantum yield, with $\Sigma\sigma^*$ = 0 (isopropyl alcohol): (1) *sec*-butyl alcohol, (2) isopropyl alcohol, (3) isobutyl alcohol, (4) *n*-butyl alcohol, (5) *n*-propyl alcohol, (6) ethyl alcohol, (7) 3-chloro-1-propanol, (8) methyl alcohol, (9) ethylene glycol, (10) benzyl alcohol, (11) 2-phenoxyethanol, (12) 2-bromoethanol, (13) 2-chloroethanol, $[UO_2^{2+}]_i$ = 0.02 *M*, $[\text{alcohol}]_i$ = 0.04 *M*, pH 1, 20°.

Mechanisms. Intermolecular electron-transfer or charge-transfer mechanisms have been widely proposed for fluorescence-quenching reactions of various systems.[6] In fact, the negative ρ^* value of −1.1 (*i.e.*, the slope of the plot in Figure 3) might be explained at least qualitatively by the assumption that the substrate part of the transient intermediate has some cation character, suggesting an electron-transfer or hydride-ion-transfer mechanism. The evidence for the existence of 1-equiv charge-transfer intermediates, UO_2^{+}[1,7] and $R_1R_2\dot{C}OH$[1,8] species, would exclude a two-electron- or hydride-ion-transfer mechanism (the latter may be thought to be identical with the former) such as those proposed for the thermal oxidations of alcohols by chromic acid.[9]

A one-electron-transfer mechanism, $(UO_2^{2+})_{aq}^* + R_1R_2CHOH \rightleftharpoons UO_2^{+}\cdots R_1R_2C^{+}HOH \rightarrow UO_2^{+} + R_1R_2\dot{C}OH + H^{+}$, may seem to explain the above results to some extent. The electron-donating substituents (small $\Sigma\sigma^*$ value) would increase the stability of the carbonium ion or raise the rate of the forward direction of the reversible processes, resulting in larger rate parameters K_q, ϕ, and β^{-1}. In addition, the relatively small isotope effects, k_H/k_D, ranging from 1.7 to 2.5, may suggest a charge- (or electron) transfer rather than an α-hydrogen abstraction in the rate-determining step. Nevertheless, the alternative mechanism involving α-hydrogen abstraction in the rate-determining step seems more reasonable for the following reasons. (i) The rate parameters with *tert*-butyl alcohol (having no α hydrogen) are markedly small compared to those

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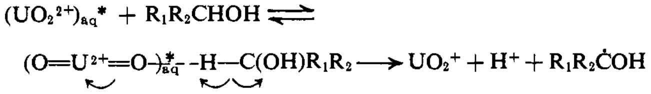
with the three butyl alcohol isomers. (ii) The ρ^* value of -1.1 is closer to the range of ρ^*'s reported for radical reactions,[10] -0.66 to -1.4, than the more negative values for cation processes, -4.5 to -7.5.[11] (iii) Though the kinetic isotope effect, k_H/k_D, ranging from 1.7 to 2.5, seems too small to regard as a primary isotope effect, compared to those for thermal oxidation of alcohols by metal ions,[8a,e,12] hydrogen-abstraction reactions, having relatively small activation energies, can have such low values.[13]

The α-hydrogen abstraction process appeared to take place *via* an intermolecular collision[1] (without the formation of a complex or an ester intermediate prior to the photolysis), presumably followed by the abstraction of α hydrogen by one of the oxygen atoms of the excited uranyl ion, *i.e.*



$$(UO_2{}^{2+})_{aq}{}^* + R_1R_2CHOH \rightleftharpoons$$
$$(O{=}U^{2+}{=}O)^*_{aq}\text{- -}H{-}C(OH)R_1R_2 \longrightarrow UO_2{}^+ + H^+ + R_1R_2\dot{C}OH$$

The long lifetime of the excited uranyl ion in solution, $\tau_0 = (0.5\text{–}5) \times 10^{-4}$, would enable the intermolecular process to be efficient. The reversibility of the first step seems reasonable because of the endothermicity of the forward process and the very low efficiency of the physical quenching[1] (the radiationless deactivation process without the chemical change).

Further experiments designed to establish our postulates and to investigate other aspects for the reaction are in progress.

Experimental Section

Reagents. Doubly distilled water was used, and all chemicals used were guaranteed reagent grade. Preliminary experiments showed that though the efficiency of uranyl fluorescence quenching by impurities such as aldehydes or halogen ions was about one order of magnitude larger than that by the substrate alcohols, traces of such impurities which might be contained in the reagents could be neglected.

Photolysis. The pH's of the solutions to be photolyzed were adjusted to desired values (usually 1.0) with 1 *N* NaOH and 1 *N* $HClO_4$ solutions by using a pH meter. These solutions were deaerated by passage through oxygen-free nitrogen for 20–30 min per 10 ml, were kept air tight with liquid paraffin, and were then exposed to the desired radiation using either an interference filter or a suitable combination of glass filters.

The temperature was regulated to 20 ± 1° during the photolysis 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.[14] The aldehydes or ketones formed were separated as precipitates of the corresponding 2,4-dinitrophenylhydrazones and washed with water. The precipitates were dissolved with ethyl alcohol; then the absorbancies at the peaks around 360 nm were measured. The molar ratio of the products, [aldehyde or ketone]/[uranium(IV)], was always 1.0[1] whatever the extent of the reaction (up to 20%) and whatever the pH (1.0–3.8). Measurements of the quantum yields of the products were made using a ferric oxalate actinometer.[15] The light source was a 100- or 500-W high-pressure mercury lamp with suitable arrangement for obtaining a parallel light beam.

Quenching Constants. Relative intensities of the uranyl fluorescence at the 510-nm peak, I^0/I, were measured for solutions containing 0.02 *M* uranyl nitrate and various concentrations of alcohol, with a 405-nm excitation beam. Though no significant changes in the quenching constants were observed with changes in pH (1.0–4.0), ionic strength (0.1 to about 1), or the analyzing or excitation wavelengths, the experimental conditions of the fluorescence measurements were chosen as close as possible to those of the photolysis.

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