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Photochemical Reactions of Uranyl Ions with Organic Compounds. II. The Mechanism of the Photo-Oxidation of Alcohols by Uranyl Ions

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Quantum yields were measured under various conditions for the photo-oxidation of aliphatic alcohols by uranyl ions in aqueous solutions and kinetic treatments were made. The measurements of uranyl fluorescence quenching by the alcohols showed that a complex formation between uranyl ions and alcohol molecules prior to the photolysis is not likely to be involved. The temperature effect on the quantum yield is strong evidence for a collisional energy transfer from the excited uranyl ions to the alcohol molecules. The relative rates of the photolysis of four isomeric butyl alcohols, and the isotope effect on the photo-reactivity by using alcohols labeled with deuterium, showed that the alcohol molecules are attacked on the α-hydrogen atom as a primary photochemical act.

There have been few studies of the mechanisms of the photo-reactions of uranyl ions with alcohols in aqueous solutions, and many basic problems remain unsolved. Kinetic studies have been made of the reaction mechanisms of uranyl ions with carbohydrates[1] and with alcohols,[2-4] but these experimental data are not enough to discuss the mechanism, as has been pointed out by Rabinowitch and Belford.[5] For example, a complex of an uranyl-organic substrate has been assumed to be a photosensitive cluster:

$$UO_2^{2+} + S(\text{substrate}) \rightleftharpoons UO_2S^{2+},$$

and it has been assumed to undergo an intramolecular photo-redox reaction:

$$UO_2S^{2+} + h\nu \rightarrow (UO_2S^{2+})^* \rightarrow\rightarrow U(IV) + \text{Products}.$$

However, the linear relation between the reciprocal quantum yield of the U(IV) formation, ϕ^{-1}, and the reciprocal concentration of the substrate, $[S]^{-1}$, which is inferred from the above assumed mechanism dose not support the above assumption, since the linearity can be inferred both from the mechanism assuming such a complex formation and from the alternative mechanism, in which a collisional energy transfer from the excited uranyl ions to the substrate molecules is involved.

Recently several piecies of evidence for collisional-excitation energy transfer between rare earth metal ions and α-diketones in solution have been reported.[6-8] The present investigation was undertaken

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[1] L. J. Heidt and K. A. Moon, *J. Amer. Chem. Soc.*, **75**, 5803 (1953).

[2] L. J. Heidt, *ibid.*, **76**, 5962 (1954).

[3] S. K. Bhattacharyya and S. Gulvedy, *J. Indian Chem. Soc.*, **29**, 649 (1952).

[4] S. K. Bhattacharyya and S. Gulvedy, *ibid.*, **29**, 659 (1952).

[5] Rabinowitch and Belford, "Spectroscopy and Photochemistry of Uranyl Compound," Pregamon Press, London (1964), p. 324.

[6] A. Heller and E. Wasserman, *J. Chem. Phys.*, **42**, 949 (1965).

[7] N. Filipescu and G. W. Mushrush, *J. Phys. Chem.*, **72**, 3516 (1968).

[8] N. Filipescu and G. W. Mushrush, *ibid.*, **72**, 3512 (1968).

in order to elucidate in some detail the mechanism of the photo-oxidation of alcohols with uranyl ions.

Experimental

Doubly-distilled water and guaranteed reagents (Koso Chemical) were used. The solutions to be tested were de-aerated by the passage through of oxygen-free nitrogen, placed into a cylindrically-shaped, sealed pyrex cell with flat windows (5 m*l* volume), and then exposed to light of the desired wavelength by using an interference filter or by a combination of glass filters. The absorbance at every wavelength, or the rate of light absorption, I_a, of the uranyl - alcohol system was independent of the alcohol concentration. The quantum yields were measured by the usual method[9,10] by using a ferric oxalate solution. The time of exposure was so regulated that the reaction was not more than 5% completed, in order to avoid the complications which might arise from the subsequent reactions of the products or from the inner filter effect of the uranium(IV) ions. The temperature was usually 20±0.1°C. The light sources were a 500-W or 100-W high-pressure Hg lamp. The amounts of uranium(IV) formed were measured colorimetrically by the use of arsenazo III.[11] The aldehydes or ketones formed were determined by means of 2,4-dinitrophenylhydrazine. The spectrophotometric measurements and fluorescence measurements were carried out with a Hitachi 124 spectrophotometer and with a Hitachi fluorescence spectrophotometer respectively. The acidities of the solutions were regulated by using a Toa Denpa pH-meter.

Results and Discussion

Effect of Light Intensity on the Rate. Figure 1 shows that the rate of uranium(IV) formation is directly proportional to the absorbed light intensity (I_a), *i.e.*, the quantum yield is independent of I_a.

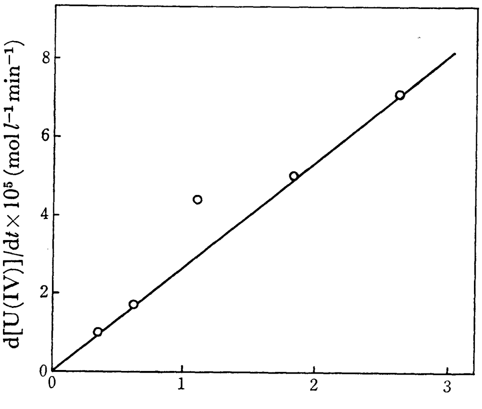

Fig. 1. Effect of light intensity on the rate. $[UO_2^{2+}]=0.02\text{M}$, $[CH_3CH_2OH]=0.21\text{M}$ pH=1.0, λ=4047,4358 Å

Table 1. Molar ratio of the products at various of reaction
$[UO_2^{2+}(NO_3)_2]=0.02\text{M}$, $[CH_3CH_2OH]=0.2\text{M}$, pH=1.0

Reaction extent (%)	[U(IV)] ×10³M	[CH₃CHO] ×10³M	molar ratio [CH₃CHO]/[U(IV)]
2	0.4	0.5	1.2
5	1.0	1.1	1.1
10	2.0	2.0	1.0
16	3.1	3.0	1.0

Table 2. Molar ratio of the products at various pH
$[UO_2^{2+}(NO_3)_2]=0.02\text{M}$, $[CH_3CH_2OH]=0.2\text{M}$.

pH	[U(IV)] ×10³M	[CH₃CHO] ×10³M	molar ratio [CH₃CHO]/[U(IV)]
1.0	3.1	3.0	1.0
1.7	3.2	3.1	1.0
2.3	2.3	2.2	1.0
3.3	1.5	1.5	1.0
3.8	1.5	1.5	1.0
3.8	2.1	2.1	1.0

Molar Ratio of the Products at Various Extents of the Reaction and at Various pH's. Tables 1 and 2 show that the molar ratio of the products is always unity whatever the extent of the reaction and whatever the pH.

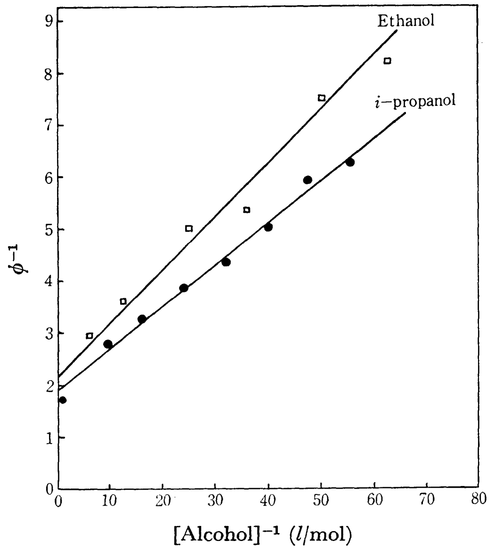

Fig. 2. Reciprocal quantum yield of formation of U(IV) as a function of reciprocal concentration of alcohol.
$[UO_2^{2+}]=0.02\text{M}$, pH=1, λ=4047, 4358 Å

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[9] C. A. Parker, *Proc. Roy. Soc.* (London), **A220**, 104 (1953).

[10] M. Koizumi, S. Shida, S. Kato, N. Mataga and M. Imamura, "Jikken Kagaku Koza," Vol. 6, Maruzen, Tokyo (1956), pp. 282—286.

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

Effect of Alcohol Concentration on the Rate. The quantum yields of uranium(IV) formation were measured at various initial concentrations. The plot of $1/\phi$ *vs.* $1/C$ gave a straight line with an intercept $\fallingdotseq 2$, as is shown in Fig. 2. This result is similar to that obtained with the uranyl-carbohydrates system by Heidt and Moon.1) The question as to whether a photo-activated uranyl ion reacts with a substrate molecule by encounter collisions or whether a certain complex between UO_2^{2+} and substrate is activated to produce the reaction cannot be decided on the basis of this result, since the linear relation, $1/\phi$ *vs.* $1/C$, is inferred both from the mechanism proposed by Heidt1) assuming a complex as to be a photosensitive cluster and from the alternative mechanism assuming a collisional energy transfer.

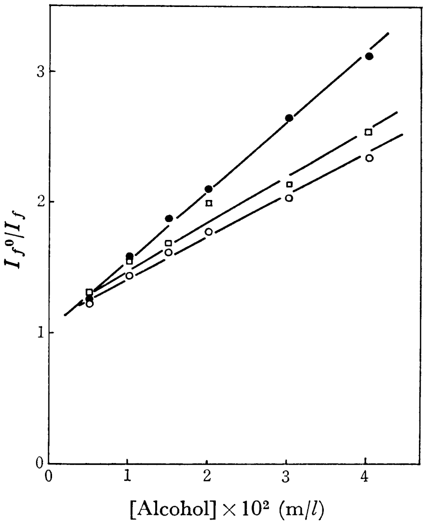

Fig. 3. Reciprocal relative fluorescence intensity of uranyl ions as a function of alcohol concentration. Excited at 4358 Å. Measured at 5090 Å. $UO_2(NO_3)_2=0.02$M.

○: Ethyl alcohol, pH=1.5, □: Ethyl alcohol, pH=3.5, ●: Isopropyl alcohol, pH=1.5, I_f^0 and I_f are the fluorescence intensities in the absence and in the presence of alcohol, respectively.

Fluorescence Intensities at Various Concentrations of Alcohol. The results shown in Fig. 3 can be expressed by the Stern-Volmer equation:

$$\frac{I_f^0}{I_f} = 1 + K_q[Q],$$

where I_f^0 and I_f are the fluoresence intensities in the absence and in the presence of a quencher respectively. K_q is the quenching constant, and [Q] is the concentration of a quencher. It can be seen that the slope, K_q, varied with the nature of the alcohol and not with the acidity of the solution.

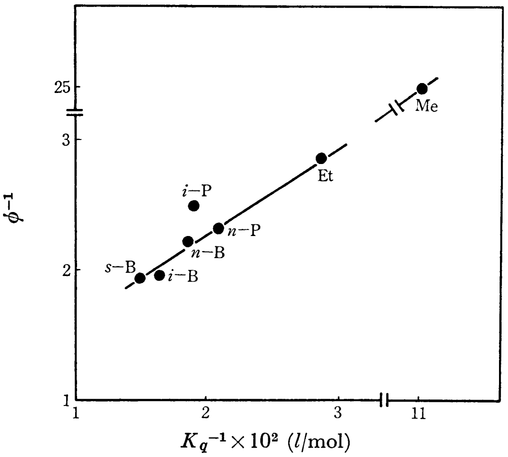

Fig. 4. Photoreactivity and fluorescence quenching constants in the system of aqueous uranyl-alcohols. ϕ_r: quantum yield of uranium(IV) formation at 3650—3606 Å, $[UO_2^{2+}]=0.02$M, [alcohol]=0.02M. pH=1.5 λ(emission)=5090 Å, λ(excitation)=4360 Å.

Correlation between the Photo-Reactivity and Fluorescence Quenching. The K_q's for aliphatic alcohols were measured. Figure 4 shows the correlation between the photo-reactivity, ϕ_r, and the fluorescence quenching constant, K_q. Neither the quenching efficiency nor the photochemical reactivity of alcohols seems to be related to the stability of the uranyl-alcohol complexes assumed, on the supposition that the steric factor

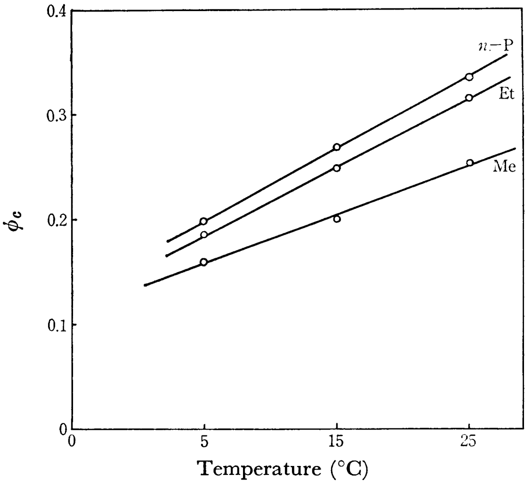

Fig. 5. Temperature effect on the rate of uranium(IV) formation. $[UO_2^{2+}]=0.02$M. [alcohol]=0.2M. pH=1.5 λ=3650—3660 Å. The quantum yields were corrected for the self-quenching; $(UO_2^{2+})^*+UO_2^{2+}\rightarrow 2UO_2^{2+}$, on the assumption that the temperature dependence of the self-quenching is mainly due to that of the viscosity of the medium.12)

Apparent activation energy, $\Delta E^{\ddagger}$, obtained was 8.5 kcal/mol for both ethyl alcohol and *n*-propyl alcohol.

dominates the stability of the complex; rather, it seems likely that the photo-sensitivity is related to the bond strength between the α-hydrogen atom and the carbon atom adjacent to the hydroxy group, on the assumption that the increasing order of the bond-dissociation energies in solution is approximately the same as that in the gaseous phase.

The close correlation between the quenching efficiency, K_q, and the chemical reactivity, ϕ_r, suggests that chemical quenching is predominant in the radiationless deactivation of the excited uranyl ions by alcohol molecules, while physical quenching is less important.

Temperature Effect on the Reaction Rate. The quantum yield increases with an increase in the temperature, as is shown in Fig. 5; this suggests that the reaction mechanism involves a collisional transfer from the excited uranyl ions to alcohol molecules. The values of the quantum yield in Fig. 5 were corrected for the self-quenching of uranyl ions.[12]

Relative Rates of Butyl Alcohols and the Isotope Effect on the Rate. The relative rates of *n*-butyl, isobutyl, *s*-butyl, and *t*-butyl alcohol (the last one has no α-hydrogen) were measured in order to decide which of two alternatives is the primary process. The results are listed in Table 3.

TABLE 3. RELATIVE REACTIVITY OF BUTYL ALCOHOLS

k and k_n are relative rate constants for uranium (IV) formation with butyl alcohol isomer and with *n*-butyl alcohol, respectively.

Butyl alcohol	k/k_n
n-Butyl	1.00
Isobutyl	1.14
s-Butyl	1.05
t-Butyl	0.11

Further, the rate constants of the uranium(IV)-formation with deuteriated alcohols were compared to those with non-deuteriated alcohols in an ordinary water solution. The ratios obtained were $k_{(CH_3CH_2OH)}/k_{(CD_3CD_2OD)}=2.33$ and $k_{(CH_3CH_2OH)}/k_{(CH_3CH_2OD)}=1.02$. These results indicate that the path:

$$R_1R_2CHOH + U(VI)^* \rightarrow R_1R_2\dot{C}OH + U(V) + H^+,$$

is predominant in the primary act, while the alternative path:

$$R_1R_2CHOH + U(VI)^* \rightarrow R_1R_2CHO\cdot + U(V) + H^+,$$

is less important.

TABLE 4. INTERFERING EFFECT OF CUPRIC IONS

$[CH_3CH_2OH]=0.2$M, $[UO_2(NO_3)_2]=0.02$M, $\lambda=4047$, 4358 Å

The fraction of light absorbed by cupric ions was negligible under the experimental conditions.

$[CuSO_4]$ added $\times 10^3$M	[U(IV)] formed $\times 10^3$M	$[CH_3CHO]$ formed $\times 10^3$M
0.0	6.7	6.6
5.0	0.1	6.4

Effect of Cupric Ions. As is shown in Table 4, the formation of uranium(IV) is nearly completely interfered with by the addition of a small quantity of cupric ions, while acetaldehyde-formation is not affected.

Since cupric ions do not quench the excited uranyl ions,[13] the interfering effect must be due to the reaction between cupric ions and the intermediates, U(V); *i.e.*;

$$U(VI)^* + R_1R_2CHOH \rightarrow U(V) + R_1R_2\dot{C}OH + H^+,$$

$$U(V) + Cu(II) \rightarrow U(VI) + Cu(I),$$

$$2Cu(I) \rightarrow Cu^0 + Cu(II).$$

The selective interfering effect by cupric ions indicates that the secondary process of uranium(IV)-formation is:

$$U(V) + U(V) \rightarrow U(VI) + U(IV)$$

and not the alternative process:

$$U(V) + R_1R_2\dot{C}OH \rightarrow U(IV) + R_1R_2CO.$$

The radical intermediate, $R_1R_2\dot{C}OH$, would seem to be rapidly oxidized by the ground-state uranyl ions; *i.e.*:

$$R_1R_2\dot{C}OH + U(VI) \rightarrow R_1R_2CO + U(V) + H^+,$$

before the disproportionation reaction of the radical:

$$2R_1R_2\dot{C}OH \rightarrow R_1R_2CO + R_1R_2CHOH,$$

since the concentration of uranyl ions is much higher than that of the radical, $R_1R_2\dot{C}OH$. However, the selective inhibitory effect by maleic acid, as is shown in Table 5, indicates that the latter path (the disproportionation of the radical) is predominant.

TABLE 5. EFFECT OF MALEIC ACID

$[UO_2(NO_3)_2]=0.02$M, $[CH_3CH_2CH_2OH]=0.2$M

$\lambda=4047$, 4358 Å, Irradiation time=30 min

$[(CHCOOH)_2]$ added $\times 10^2$M	[U(IV)] formed $\times 10^3$M	$[CH_3CH_2CHO]$ formed $\times 10^3$M
0.0	4.1	4.0
2.0	3.2	0.4

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[12] E. Rabinowitch and R. L. Belford, "Spectroscopy and Photochemistry of Uranyl Compounds," Pergamon Press, London (1964), p. 220.

[13] Y. Volmar and Mathis, *Bull. Soc. Chim. Fr.*, **53**, 385 (1933).

A slight decrease in the amount of U(IV) upon the addition of maleic acid in Table 5 may be attributed to a weak masking effect of maleic acid or to a reaction between U(V) and maleic acid.

On the basis of the above data, the following mechanism may be proposed:

$$\mathrm{U(VI)} + h\nu \xrightarrow{I_a} \mathrm{U(VI)}^*,\ \text{(absorption)} \quad (1)$$

$$\mathrm{U(VI)}^* \xrightarrow{k_1} \mathrm{U(VI)} + h\nu',\ \text{(fluorescence emission)} \quad (2)$$

$$\mathrm{U(VI)}^* \xrightarrow{k_2} \mathrm{U(VI)} + \text{heat},\ \text{(radiationless deactivation)} \quad (3)$$

$$\mathrm{U(VI)}^* + \mathrm{U(VI)} \xrightarrow{k_3} 2\mathrm{U(VI)},\ \text{(self-quenching)} \quad (4)$$

$$\mathrm{U(VI)} + \mathrm{R_1R_2CHOH} \xrightarrow{k_4} \mathrm{U(VI)} + \mathrm{R_1R_2CHOH},\ \text{(physical quenching)} \quad (5)$$

$$\mathrm{U(VI)}^* + \mathrm{R_1R_2CHOH} \xrightarrow{k_5} \mathrm{U(V)} + \mathrm{R_1R_2\dot{C}OH} + \mathrm{H^+},\ \text{(chemical quenching)} \quad (6)$$

$$2\mathrm{R_1R_2\dot{C}OH} \xrightarrow{k_6} \mathrm{R_1R_2CO} + \mathrm{R_1R_2CHOH},\ \text{(disproportionation)} \quad (7)$$

$$2\mathrm{U(V)} \xrightarrow{k_7,\ \mathrm{H^+}} \mathrm{U(VI)} + \mathrm{U(IV)}.\ \text{(disproportionation)} \quad (8)$$

Here I_a is the rate of light absorption in einsteins$\cdot$mol$^{-1}\cdot$min^{-1}.

The steady-state assumption for U(VI),* U(V), and $\mathrm{R_1R_2\dot{C}OH}$ leads to:

$$\phi_U = \phi_C = k_5[\mathrm{R_1R_2CHOH}]/2\{k_1+k_2+k_3[\mathrm{U(VI)}] + (k_4+k_5)[\mathrm{R_1R_2CHOH}]\}, \quad (9)$$

where ϕ_U and ϕ_C are the quantum yields for the formations of U(IV) and $\mathrm{R_1R_2CO}$ respectively. The reciprocal expression is:

$$1/\phi_U = 1/\phi_C = 2 + 2k_4/k_5 + 2(k_1+k_2+k_3[\mathrm{U(VI)}])/k_5[\mathrm{R_1R_2CHOH}]. \quad (10)$$

The relative intensity of uranyl fluorescence becomes:

$$I_f{}^0/I_f = 1 + K_q[\mathrm{R_1R_2CHOH}], \quad (11)$$

where:

$$K_q = (k_4+k_5)/(k_1+k_2+k_3)[\mathrm{U(VI)}]. \quad (12)$$

The comparison of Eq. (10) with the experimental results in Fig. 2 leads to:

$$k_4/k_5 = 0 \quad (13)$$

i.e., the physical quenching is much less important than the chemical quenching. This is in agreement with the conclusion from the results shown in Fig. 4. The low probability of electronic-vibration energy transfer without a chemical reaction seems plausible.[14]

From Eqs. (10),(12) and (13), we obtain:

$$1/\phi = 2 + 2/K_q[\mathrm{R_1R_2CHOH}]. \quad (14)$$

The plot of $1/\phi$ *vs.* $1/K_q$ should be a straight line with an intercept of 2 and a slope of $2/[\mathrm{R_1R_2CHOH}]$. The slope in Fig. 4 is 70, roughly in agreement with the theoretical value from Eq. (14), $2/[\mathrm{R_1R_2CHOH}]=100$. The discrepancy between Eq. (14) and the experimental results in Fig. 4 may be partly due to the inaccuracy in the value of K_q.

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14) P. G. Ashmore, F. S. Dainton and T. M. Sugden, "Photochemistry and Reaction Kinetics," Cambridge University Press, London (1967), p. 133.