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Photochemical Reactions of Uranyl Ions with Organic Compounds III. The Correlation between the Reaction Mode and the Pre-Equilibrium in the Photolysis of the Uranyl-lactate System

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On the basis of the assumed mechanism for the photolysis of the uranyl-lactate system, the equilibrium constant for the complex formation, K, was evaluated from the photo-kinetic data by using a monochromatic 4047 Å light; it was then compared with those obtained from the usual spectrophotomeric measurements. A comparison of the K values obtained by means of the photo-kinetic data ($1.0-1.1\times10^{-1}$) and by means of the analytical data ($1.1-1.2\times10^{-1}$) gave an excellent agreement; there was also a good agreement between the slope of the plot of the photo-kinetic data and that predicted from the assumed mechanism. The results supported the crude mechanism assumed earlier.

In a previous paper[1] it was reported that the photo-oxidation of lactic acid by uranyl ions gave acetaldehyde (with an evolution of carbon dioxide) and pyruvic acid as the oxidation products besides, the equimolar uranium-(IV) species as the reduction product. The dependence of the relative ratio of the organic products upon the various experimental conditions was attributed to the difference in the initial species of the system to be photolized; the formation of acetaldehyde involves an intra-molecular decomposition of the uranyl-lactate complex initially formed, while the formation of pyruvic acid involves encounter collisions between lactic acid and the excited uranyl ions (initially uncomplexed):

$$\mathrm{U} + \mathrm{HL} \rightleftharpoons \mathrm{UL} + \mathrm{H}^+$$

$$\mathrm{U} + h\nu \longrightarrow \mathrm{U}^*$$

$$\mathrm{UL} + h\nu \longrightarrow \mathrm{UL}^*$$

$$\mathrm{U}^* \xrightarrow{k_1} \mathrm{U} + h\nu' \text{ or heat}$$

$$\mathrm{UL}^* \xrightarrow{k_2} \mathrm{UL} + h\nu'' \text{ or heat}$$

$$\mathrm{U}^* + \mathrm{HL} \xrightarrow{k_3} \mathrm{U(V)} + \mathrm{HL}^+$$

$$\mathrm{UL}^* \xrightarrow{k_4} \mathrm{UL}' + \mathrm{CO}_2$$

$$\mathrm{HL}^+ + \mathrm{U} \xrightarrow{\text{fast}} \text{pyruvic acid} + \mathrm{U(V)} + 2\mathrm{H}^+$$

$$2\mathrm{U(V)} \xrightarrow[\mathrm{H}^+]{\text{fast}} \mathrm{U(IV)} + \mathrm{U}$$

$$\mathrm{UL}' \xrightarrow{\text{fast}} \text{acetaldehyde} + \mathrm{U(IV)} + \mathrm{H}^+$$

where U: uranyl ion; HL: lactic acid; HL^+: intermediate radical cation $\mathrm{CH_3C^+H(OH)CO_2H}$, and UL′: intermediate species, such as  $\mathrm{CH_3C^+H}\diagdown\underset{\mathrm{H}}{\mathrm{O}}\diagup\mathrm{UO^+_2}$ (the last

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[1] S. Sakuraba and R. Matsushima, This Bulletin, **43**, 1950 (1970).

two intermediates would lose protons to form radicals, but the true intermediate species are still uncertain).

The present investigation was undertaken to see whether or not the equilibrium constant (for the uranyl lactate complex) which can be evaluated from the kinetic data by using the assumed equations is consistent with that determined by means of the usual analytical method.

Experimental

De-oxygenated solutions containing 0.2M lactic acid and 0.02M uranyl nitrate, of the pH-range of 0.1—2.5 and the ionic strength of 0.3—0.5, were irradiated with the light of the 4047—4078 Å region at 20°C by means of an interference filter and a 500-W high-pressure mercury arc. The concentrations of the acetaldehyde (A) and pyruvic acid (P) formed were determined spectrophotometrically as their 2,4-dinitrophenylhydrazones. The separation of the hydrazone derivative from each other was carried out with ethyl acetate[2] and an aqueous Na_2CO_3 (0.5N) solution.[1]

The quantum yield of the formation of pyruvic acid, ϕ_P, and that of acetaldehyde, ϕ_A, under various pH's were obtained from the molar ratios [A]/[P] by using a calibrated graph of the total quantum yield[3] as a function of the pH preliminarily measured repeatedly with a much more stable Hg-lamp source(100W). This method seems to make possible simplified procedures and a much higher accuracy than the direct measurements of the quantum yields, since the [A]/[P] ratio is independent of the total number of the light quanta absorbed by the system.[1] The adjustments of the pH(or [H]) of the solutions, both that to be photolyzed and that for analytical use (for the measurement of the *k* value), were carried out with solutions of perchloric acid and sodium hydroxide, using a pH-meter (Toa Denpa Co., Ltd.).

Results and Discussion

The Photo-Kinetic Results. For simplification, the experimental conditions were so chosen that only the 1:1 complex of the uranyl-lactate was formed;

$$U + HL \overset{K}{\rightleftharpoons} UL + H^+$$

It is evident both from Fig. 1 and from the linearity of the plots in Figs. 5 and 6 that only the 1:1 complex[4] is formed when the initial concentrations, at pH≤3, of the uranyl ions and lactic acid are 0.02M and 0.2M respectively. The hydrolysis and polymerizations of uranyl ions are negligible at pH values below 2.5.[5]

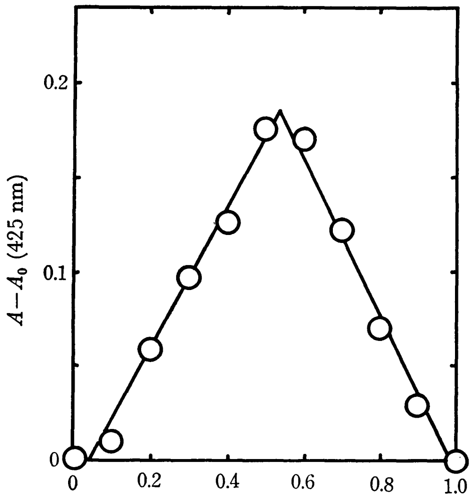

Fig. 1. Application of the continuous variation method to the uranyl-lactate system, as measured at 425 nm peak. [U]+[HL]= 0.04M, pH=3.0.

The formation quantum yields, ϕ_P and ϕ_A, for the photolysis of the uranyl-lactate system in which initial formation of the 1:1 complex is involved will be given by the following equations, (1) and (2) respectively, which are based on the assumed mecahnism.

$$\phi_P = \frac{k_3[HL]}{k_1 + k_3[HL]} \cdot \frac{\varepsilon_1[U]}{\varepsilon_1[U] + \varepsilon_2[UL]} \tag{1}$$

$$\phi_A = \frac{k_4}{k_2 + k_4} \cdot \frac{\varepsilon_2[UL]}{\varepsilon_1[U] + \varepsilon_2[UL]} \tag{2}$$

Equations (1) and (2) can be rewritten as Eqs. (1′) and (2′):

$$\log\left(\frac{\phi_P{}^0}{\phi_P} - 1\right) = \log C + \text{pH} \tag{1′}$$

$$\log\left(\frac{\phi_A{}^0}{\phi_A} - 1\right) = -\log C - \text{pH} \tag{2′}$$

where:

$$\phi_P{}^0 = k_3[HL]/(k_1+k_3[HL]) \tag{3}$$

$$\phi_A{}^0 = k_4/(k_2+k_4) \tag{4}$$

$$C = \varepsilon_2 K[HL]/\varepsilon_1 \tag{5}$$

$$K = [UL][H]/[U][HL] \tag{6}$$

ε_2 and ε_1 are the absorption coefficients of the complex and the uncomplexed uranyl ions respectively at the

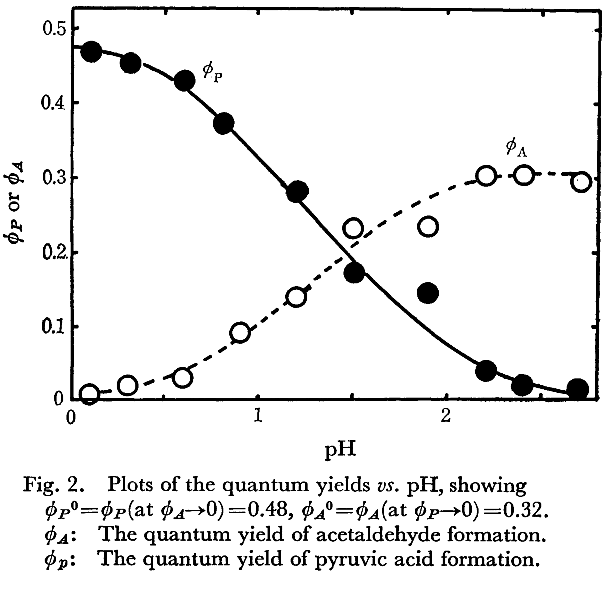

Fig. 2. Plots of the quantum yields *vs.* pH, showing $\phi_P{}^0=\phi_P(\text{at } \phi_A \to 0)=0.48$, $\phi_A{}^0=\phi_A(\text{at } \phi_P \to 0)=0.32$.
ϕ_A: The quantum yield of acetaldehyde formation.
ϕ_P: The quantum yield of pyruvic acid formation.

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[2] The extraction by ethyl acetate was superior to the extraction by chloroform or carbon tetrachloride because of its higher solubility and more complete separation.

[3] The total quantum yield was equal to the quantum yield of the U(IV) formation.[1]

[4] See also I. Feldman and J. R. Harvill, *J. Amer. Chem. Soc.*, **76**, 2114, 4726 (1954).

[5] E. Rabinowitch and R. L. Belford, "Spectroscopy and Photochemistry of Uranyl Compounds," Pergamon Press, London (1964) pp. 91—110.

[6] Y. Oka, "Zikken Kagaku Koza," 2nd Series, Vol. 7, Maruzen, Tokyo (1966), p. 210.

irradiated wavelength (4047 Å). $\phi_P{}^0$ can be regarded as a limited value of ϕ_P when ϕ_A reaches zero (Eqs. (1) and (3)), and $\phi_A{}^0$ as a limited value of ϕ_A when ϕ_P reaches zero (Eqs. (2) and (4)) (*cf.* Fig. 2). When the initial concentration of lactic acid is much higher than that of the uranyl ion, the change in the lactic acid concentration due to the complex formation may be neglected: $[\mathrm{HL}]_t \gg [\mathrm{U}]$, $[\mathrm{HL}]_t \gg [\mathrm{UL}]$. Thus, Eqs. (5) and (6) may be rewritten as Eqs. (5′) and (6′):

$$C = \varepsilon_2 K[\mathrm{HL}]_t/\varepsilon_1 \ (=\text{constant}) \qquad (5')$$

$$K = [\mathrm{UL}][\mathrm{H}]/[\mathrm{U}][\mathrm{HL}]_t \qquad (6')$$

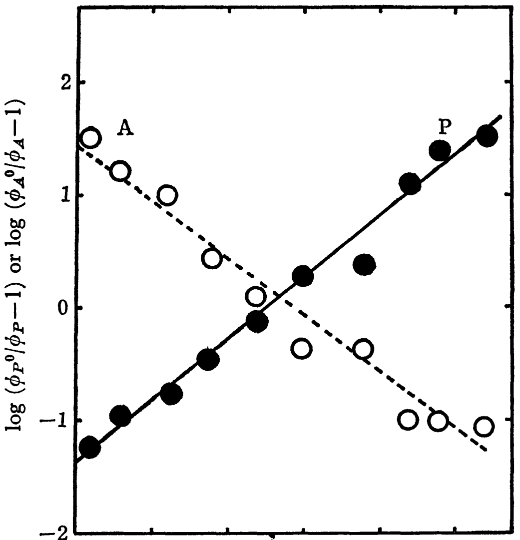

Fig. 3. Plots of log ($\phi_P{}^0/\phi_P-1$) and log ($\phi_A{}^0/\phi_A-1$) *vs.* pH.
P: Plot of log ($\phi_P{}^0/\phi_A-1$) *vs.* pH
A: Plot of log ($\phi_A{}^0/\phi_A-1$) *vs.* pH
$[\mathrm{U}]_t=0.02$ M, $[\mathrm{HL}]_t=0.2$ M, $\lambda=4047$ Å, Temperature=20°C.

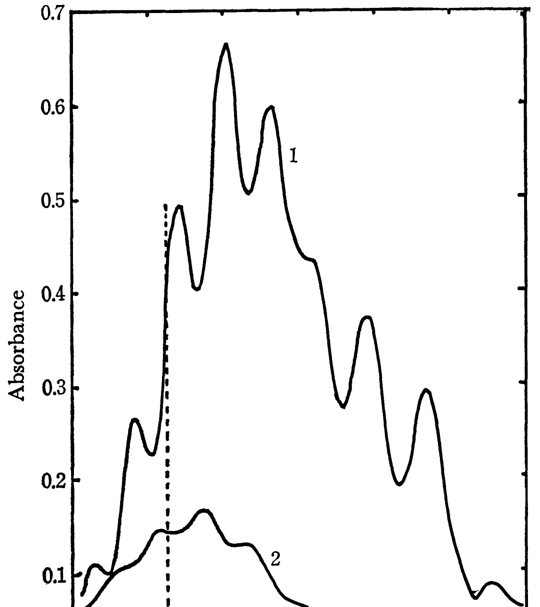

Fig. 4. Absorption spectra of the uranyl-lactate complex and the uncomplexed uranyl ions.
1: The increment in absorption due to the complex formation, $(A-A_0)\times 10$, at pH=1.7 and $[\mathrm{UO_2}^{2+}]_t=0.02$M.
2: Absorption spectrum of the uncomplexed uranyl ion at pH values 0.1 to 2.4. The dotted vertical line indicates the wavelength of the 4047 Å radiation used for the photolysis.

Then, if the quantum yields, ϕ_P and ϕ_A, are measured under various pH's, with the initial concentration of lactic acid kept constant and much higher than that of the uranyl ion, the plot of log ($\phi_P{}^0/\phi_P-1$) *vs.* pH and log ($\phi_A{}^0/\phi_A-1$) *vs.* pH should be straight lines with slopes of 1 and −1 respectively. A good agreement with these predictions is shown in Fig. 3, though the A plot is somewhat scattered. Either from the intercept of the P plot or from that of the A plot, the equilibrium constant, K, can be evaluated by using Eq. (5′) if ε_1 and ε_2 are determined by an appropriate method. The absorption coefficient of the uranyl ions, ε_1, at 4047 Å was 7.0 and was constant over the pH range from 0.1 to 2.4 (Fig. 4). The absorption coefficient of the complex, ε_2, at 4047 Å can be obtained from the intercept of the corresponding plot in Figs. 5 or 6 by using Eq. (7). The 3 plot in Fig. 5 gives $\varepsilon_2-\varepsilon_1$ (at 405 nm)=7.0, and the 1 plot in Fig. 6 gives $\varepsilon_2-\varepsilon_1$(at 405 nm)=7.1. When [HL]=0.20 M, $\varepsilon_1=7.0$, $\varepsilon_2=14.0$, and log $C=-1.35$ (the intercept of plot P in Fig. 3), are substituted in Eq. (5′), K becomes 1.1×10^{-1}; while the substitution of −log $C=1.4$ (the intercept of plot A) gives $K=1.0\times 10^{-1}$.

Determination of the Equilibrium Constant by the Spectrophotometric Method[6,7] In order to compare the K-value evaluated on the basis of the photo-kinetic data with those evaluated by means of the usual analytical

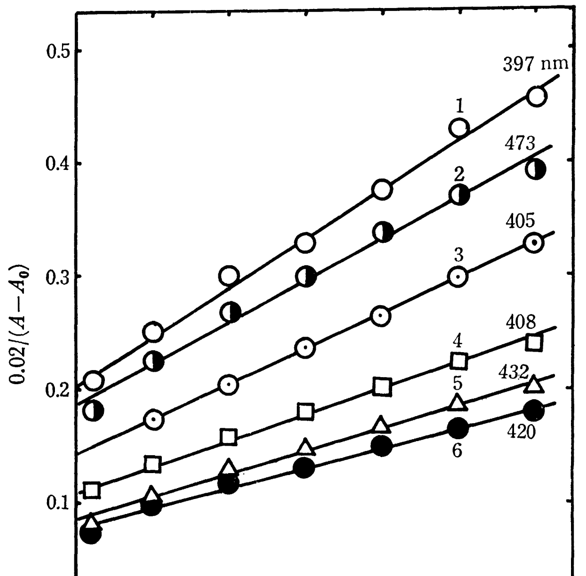

Fig. 5. Plots of $[\mathrm{U}]_t/(A-A_0)$ *vs.* [H].
$[\mathrm{U}]_t=0.02$M, $[\mathrm{HL}]_t=0.2$M, Temperature=20°C.
Plot 3 gives $\varepsilon_2-\varepsilon_1$ (at 405 nm)=7.0

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[7] Y. Oka, "Zikken Kagaku Koza," 2nd Series, Vol. 7, Maruzen, Tokyo (1966), p. 202.

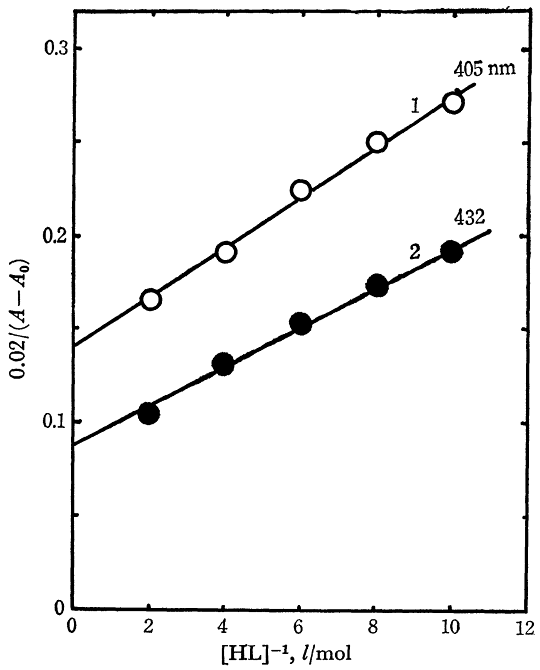

Fig. 6. Plots of $[U]_t/(A-A_0)$ vs. $[HL]_t^{-1}$.
$[U]_t=0.02$ M pH=2.0, Temperature=20°C.
Plot 1 gives $\varepsilon_2-\varepsilon_1$ (at 405 nm) =7.1

method, spectrophotometric measurements were made for the uranyl-lactate system prior to photolysis under the conditions mentioned above. The absorption spectra of the uranyl-lactate complex and the uncomplexed uranyl ions are shown in Fig. 4. The equilibrium constant, K, can be obtained from the plot of $[U]_t/(A-A_0)$ either as a function of [H] by keeping $[HL]_t$ constant, or as a function of $[HL]_t^{-1}$ by keeping [H] constant, using Eq. (7):

$$\frac{[U]_t}{A-A_0}=\frac{1}{\varepsilon_2-\varepsilon_1}+\frac{[H]}{(\varepsilon_2-\varepsilon_1)K[HL]_t} \tag{7}$$

Here, A is the total absorption of the system at a wavelength in the visible region (where absorption by lactic acid is zero), A_0 is equal to $\varepsilon_1[U]_t$ at the same wavelength, and $[U]_t$ is kept constant (0.02M). The results,

Table 1. Equilibrium constant of the complex formation, measured by spectrophotometric method

Wavelength (nm)	$K^{a)}\times 10$	$K^{b)}\times 10$
363	1.19	
397	1.27	
405	1.20	1.13
408	1.20	
432	1.03	1.00
458	1.20	

a) Obtained from the plot of $[U]_t/(A-A_0)$ vs. [H]
b) Obtained from the plot of $[U]_t/(A-A_0)$ vs. $[HL]_t^{-1}$

measured at several wavelengths, are shown in Figs. 5 and 6, while the K values are listed in Table 1. A comparison of these values with those evaluated from the photo-kinetic data (1.0—1.1×10^{-1}) gave excellent agreement.

The close relationship indicates that the variation in the reaction mode (or in the molar ratio of the products) is merely a direct reflection of the initial equilibria of the solutions to be photolyzed. Thus, the assumptions that the formation of acetaldehyde involves an intramolecular decomposition of the uranyl-lactate complex initially formed, and that the formation of pyruvic acid involves collisions between the excited uranyl ions initially uncomplexed, are supported. The results also suggest that the formation of an intermediate donor-acceptor complex during the lifetime of the excited state is not likely to be an important factor in governing the variations in the reaction mode in the photolysis of the uranyl-lactate system, though such an intermediate complex (exciplex) seems to play an important role in the transfer mechanisms of many other systems.[8,9] Of course, our results give no information on the redox-intermediate species (radical or radical ions), on which further clarification is needed.

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8) N. Uri, *Advan. Chem. Ser.*, **36**, 102 (1962).

9) G. W. Robinson and R. P. Forsch, *J. Chem. Phys.*, **38**, 1187 (1963); R. E. Kellogg and N. C. Wyeth, *ibid.*, **45**, 3156 (1966); W. Siebrand, *ibid.*, **47**, 2411 (1967); D. P. Chock, J. Jorther, and S. A. Rice, *ibid.*, **49**, 610 (1968); E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.*, **92**, 3586 (1970).