BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1950—1955 (1970)

Photochemical Reactions of Uranyl Ions with Organic Compounds. I. The Mechanism of the Uranyl Ion-Photosensitized Oxidation of Lactic Acid

Shukichi SAKURABA and Ryoka MATSUSHIMA

Faculty of Engineering, Shizuoka University, Hamamatsu

(Received November, 12, 1969)

The photochemical reaction of lactic acid with uranyl ions in an aqueous solution was studied with radiations of 4050 and 4360 Å. The quantum yields and molar ratios of the reaction products were measured under various conditions. Two competing photo-reactions appeared to take place; through them lactic acid was oxidized to form pyruvic acid at a lower pH and to form acetaldehyde, with an evolution of carbon dioxide, at a higher pH. The results obtained can be well explained by assuming that the excitation of the uranyl lactate complex is involved in the formation of acetaldehyde and that a collision between lactic acid and the excited uranyl ion, without any complex formation, is involved in the formation of pyruvic acid.

Both the intermolecular (collisional) mechanism[1,2] of the energy transfer from the excited uranyl ions to organic substrates and the intramolecular mechanism,[3-6] in which the formation of complexes between uranyl ions and substrates prior to the photolysis is involved, have been proposed for the photo-reactions of organic acids, alcohols, and aldehydes by uranyl ions in an aqueous solution. Evidence for both the mechanisms

---

1) R. H. Muller, *Proc. Roy. Soc.*, *A*, **121**, 314 (1928).

2) W. C. Pierce, *J. Amer. Chem. Soc.*, **51**, 2732 (1929).

3) P. F. Büchi, *Z. Phys. Chem.*, **111**, 275 (1924).

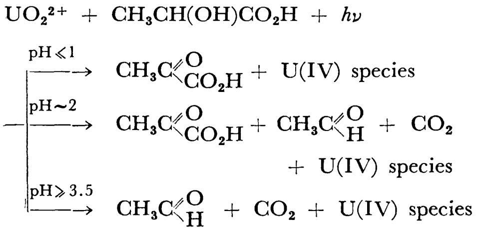
4) W. G. Leighton and G. S. Forbes, *J. Amer. Chem. Soc.*, **52**, 3139 (1930).

5) L. J. Heidt, *J. Phys. Chem.*, **46**, 624 (1942).

6) G. E. Heckler, A. E. Taylar, C. Jenson, D. Percival, R. Jenson and P. Fung, *J. Phys. Chem.*, **67**, 1 (1963).

has been found in the photolysis of uranyl oxalate.[7,8] However, the collisional mechanism has been assumed to be less important in the photooxidations of alcohols,[9] aldehydes,[10] α-hydroxy acids,[11] and other organic acids[6] with uranyl ions.

We observed that lactic acid in an aqueous solution containing uranyl ions decomposed upon irradiation with visible light to produce acetaldehyde, carbon dioxide, pyruvic acid,[*1] and uranium(IV), and that the molar ratios of the reaction products depended on the acidity of the solution, *i.e.*,



$$\mathrm{UO_2^{2+}} + \mathrm{CH_3CH(OH)CO_2H} + h\nu$$

$$\xrightarrow{\mathrm{pH}\leqslant 1} \mathrm{CH_3C}\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow \mathrm{CO_2H}} + \mathrm{U(IV)\ species}$$

$$\xrightarrow{\mathrm{pH}\sim 2} \mathrm{CH_3C}\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow \mathrm{CO_2H}} + \mathrm{CH_3C}\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow \mathrm{H}} + \mathrm{CO_2} + \mathrm{U(IV)\ species}$$

$$\xrightarrow{\mathrm{pH}\geqslant 3.5} \mathrm{CH_3C}\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow \mathrm{H}} + \mathrm{CO_2} + \mathrm{U(IV)\ species}$$

The present investigation was undertaken in order to elucidate the mechanisms by means of kinetic treatments.

Experimental

Doubly-distilled water and guaranteed reagents (Koso Chemical) were used. The solutions were de-aerated by the passage through of oxygen-free nitrogen for 40 to 60 min per 25 m*l* and then placed into 1-cm spectrophotometer quartz cells with pipets kept air-tight with liquid parafine; they were further de-aerated for several minutes, and then exposed to light (4050 or 4360 Å) using either an interference filter or a suitable combination of glass filters. The intensities of light absorbed by the reactants, needed for the estimation of the quantum yield, were measured by using a ferricoxalate actinometer.[13] In order to minimize the inner filter effect of the uranium(IV) formed and in order to avoid further oxidations of organic products, the measurements were carried out within 5% of the reaction extent. The light source was a 100-W high-pressure mercury lamp (Riko Co., Ltd.) or a 500-W xenon lamp (Ushio Co., Ltd.). The acidities of the solutions were adjusted with 1 N NaOH and 1 N $HClO_4$ by using a pH meter (Toa-Dempa Co., Ltd.). The pH values of the solutions were constant during the irradiation. No direct photodecomposition of lactic acid occurred in the absence of uranyl ions, and no thermal decomposition was detected in the dark in 8 hours at 70—80°C in the presence of uranyl nitrate.

The concentrations of the uranium(IV) formed were measured colorimetrically with arsenazo-III.[14] The acetaldehyde and pyruvic acid formed were identified as 2,4-dinitrophenyl hydrazones by comparing their infrared spectra, melting points, and R_f values (TLC) with those of authentic samples. To aliquots of the irradiated solutions, excess acidic solutions of 2,4-dinitrophenyl hydrazine were added; orange precipitates were then isolated and washed with water. To the precipitates, an aqueous solution of 0.5 N Na_2CO_3 and an equal volume of chloroform were added and shaken well; then the aqueous layer (containing 2,4-DNP of pyruvic acid) and the chloroform layer (containing 2,4-DNP of acetaldehyde) were separated. The absorbances of the aqueous solutions and of the chloroform solutions were measured at 380 nm and 360 nm respectively. The reproducibility of this method was checked. Carbon dioxide was identified with barium hydroxide. Spectrophotometric measurements were carried out by means of a recording spectrophotometer (Hitachi 124-Type). Fluorescence was measured by using a Hitachi fluorescence photometer.

Results

The Equilibria of the Uranyl Lactate System Mononuclear complexes having combining ratios (lactate/uranyl) of one, two, and three to one have been reported in the uranyl lactate system in the pH range from 2 to 3.5,[15-17] while Rajan and

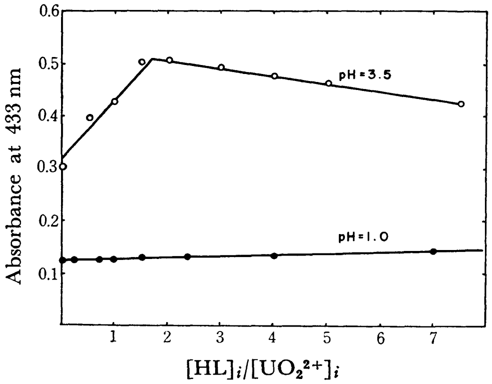


Fig. 1. Application of the molar ratio method to the uranyl-lactate system.
Initial concentration of UO_2^{2+} (as nitrate) is 0.02 M.

---

[7] A. H. Carter and J. Weiss, *Proc. Roy. Soc.*, *A*, **174**, 351 (1950).

[8] D. H. Volman and J. R. Seed, *J. Amer. Chem. Soc.*, **86**, 5095 (1964).

[9] K. Venkatarao and M. Santappa, *Indian J. Chem.*, **5**, 304 (1967).

[10] K. Venkatarao and M. Santappa, *Z. Phys. Chem.*, **54**, 101 (1967).

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

[*1] This product was overlooked by earlier researchers.[11,12]

[12] E. Rabinowitch and R. L. Belford, "Spectroscopy and Photochemistry of Uranyl Compounds," Pergamon Press, London (1964), p. 311.

[13] C. A. Parker, *Proc. Roy. Soc.*, *A*, **220**, 104 (1953).

[14] H. Onishi and Y. Toita, *Bunsekikagaku*, **14**, 1141 (1965).

[15] I. Feldman and J. R. Havill, *J. Amer. Chem. Soc.*, **76**, 2114 (1954).

[16] I. Feldman, J. R. Havill and W. F. Neuman, *ibid.*, **76**, 4726 (1954).

[17] C. Miyake and H. W. Nurnberg, *J. Inorg. Nucl. Chem.*, **29**, 2411 (1967).

Martell[18,19] suggested the existence of polynuclear complexes as well. At the pH range of less than unity, no complexes between the uranyl and the lactate ions were found by spectrophotometric studies to exist. Examples at pH=1 and at pH=3.5 are shown in Fig. 1.

The Effect of Acidity on the Quantum Yield. The quantum yields of uranium(IV) formation at various pH's are shown in Table 1. It may be seen that the quantum yield decreases with the increase in pH, though the apparent rate of photolysis may be increased due to the remarkable increase in the absorption coefficient with the pH (Fig. 2). The acidity-dependency of the quantum yield is contrary to the view[3-6,11] that the reacting species are complexes between the uranyl ions and the substrates.

Table 1. Effect of pH on the quantum yield of uranium(IV) formation

pH	ϕ	pH	ϕ
1.0	0.45	3.5	0.24
1.5	0.42	4.0	0.19
2.0	0.39	4.5	0.15
2.5	0.34	5.0	0.11
3.0	0.29		

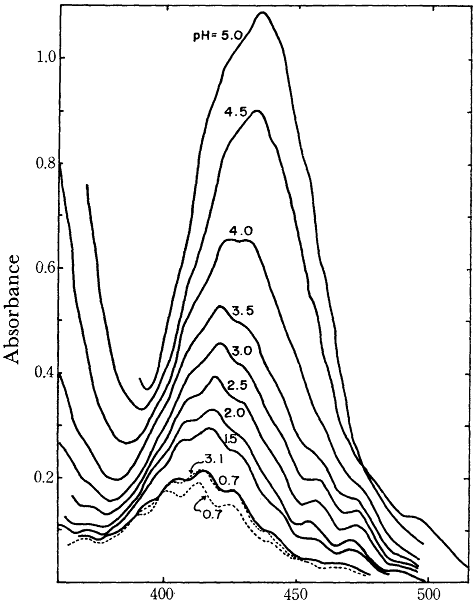


Fig. 2. Variation of the absorption spectrum of uranyl-lactic acid solution (full lines) and of a uranyl solution (dotted line) with pH.
Initial concentration of uranyl nitrate and lactic acid were 0.02 M and 0.2 M, respectively.

The Effect of Acidity on the Molar Ratios of the Products. The molar ratios of the total organic products to the uranium(IV) are about unity, as is shown in Table 2, but the pH-dependency of the molar ratio of pyruvic to the uranium (IV) is in contrast with that of acetaldehyde (Fig. 3). The increase in acetaldehyde formation with the increase of pH is interpreted as indicating that the photoreactive species are the complexes between the uranyl and the lactate ions; this is in accord with the earlier view. However, the pH-dependency of pyruvic acid formation cannot be explained by the same theory. Further, it is noticed that the pyruvic acid formation is interfered with by the addition of a small amount of iodine, the iodide ion, the chloride ion, or oxygen (in this order), while the acetaldehyde formation is not affected. The influence of the iodide ion is shown in Fig. 4. Thus, a mechanism involving encounter collisions between the excited uranyl ion and lactic acid is proposed for the formation of pyruvic acid.

Table 2. The ratio of the sum of acetaldehyde and pyruvic acid to the uranium(IV) at various extents of the photolysis

pH=1		pH=3.5	
Extent (%)	$(A+P)$/U(IV)	Extent (%)	$(A+P)$/U(IV)
5	0.98	6	0.94
16	0.97	16	0.97
20	1.12	26	0.99
		41	0.98
70	0.91	69	0.94

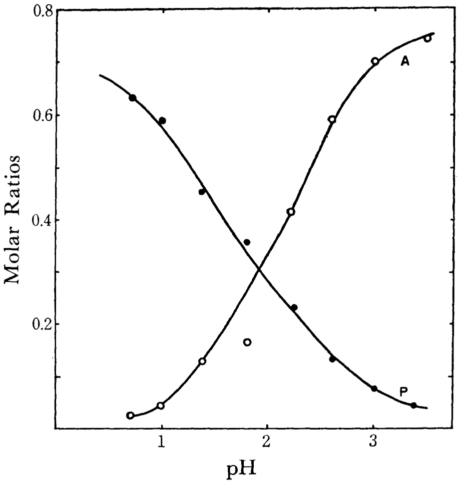


Fig. 3. Effect of pH on the molar ratios of the products. Curve A and curve P represent the molar ratios of acetaldehyde and pyruvic acid to uranium(IV), respectively.
Initial concentration of uranyl nitrate and lactic acid were 0.02 M and 0.2 M, respectively.

---

[18] K. S. Rajan and A. E. Martell, *ibid.*, **26**, 789 (1964).

[19] K. S. Rajan and A. E. Martell, *ibid.*, **26**, 1927 (1964).

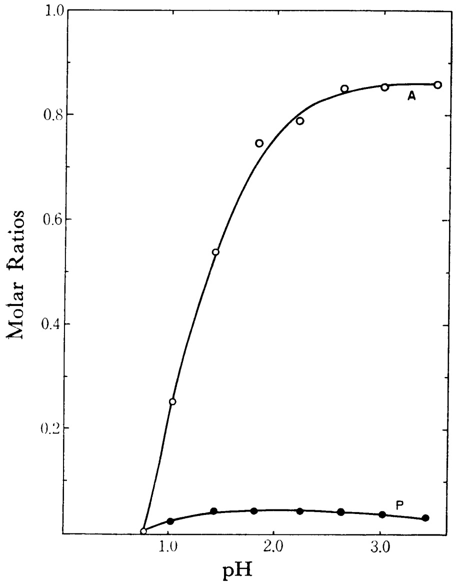


Fig. 4. Effect of iodide ions.
The concentration of potassium iodide was 0.008 M and other experimental conditions were the same as those of Fig. 3.

Table 3. Effect of initial concentration of lactic acid on the quantum yield of uranium(IV) at pH=1.0 (initial concentration of $UO_2^{2+}=2\times10^{-2}$ M)

Initial concentration of lactic acid ($\times10^2$ M)	ϕ	Initial concentration of lactic acid ($\times10^2$ M)	ϕ
1.0	0.03	8.0	0.26
2.0	0.07	10.0	0.31
3.0	0.10	14.0	0.39
5.0	0.18	18.0	0.45

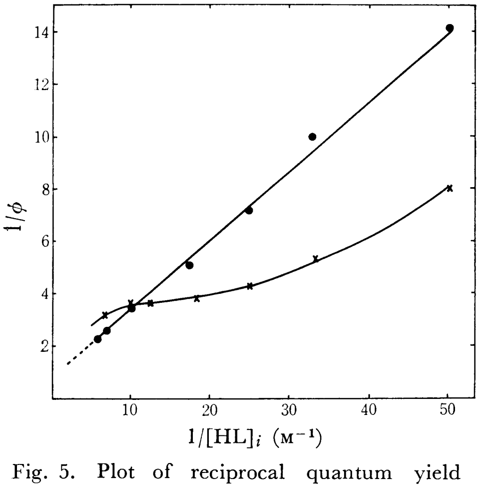


Fig. 5. Plot of reciprocal quantum yield of uranium(IV)-formation *vs.* reciprocal intial concentration of lactic acid at pH=1.0 (●) and at pH=3.5 (×).
Initial concentration of uranyl nitrate was 0.02 M.

The Effect of the Initial Concentration of Lactic Acid on the Quantum Yield. The dependency of the quantum yield on the initial concentration of lactic acid at pH=1 (not complexed) and that at pH=3.5 (complexed) are shown in Table 3 and Fig. 5 and in Fig. 6, respectively. At pH=1, a straight line of reciprocal quantum yields *versus* reciprocal initial concentrations of lactic acid was obtained, while such was not the case at pH=3.5 (Fig. 5). At pH=3.5 the quantum yield reaches a limiting value (Fig. 6).

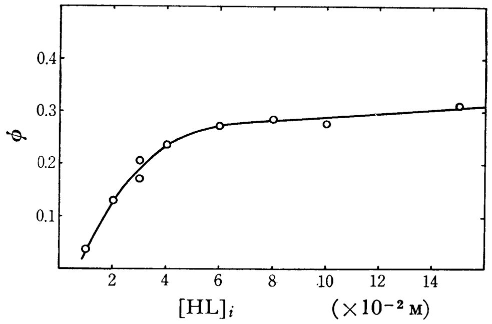


Fig. 6. Plot of the quantum yield of uranium(IV) *vs.* initial concentration of lactic acid at pH=3.5.
Initial concentration of uranyl nitrate was 0.02 M.

Discussion

The acidity-dependency of the formation of acetaldehyde is in contrast to that of pyruvic acid, as is shown in Fig. 3. Figure 1 shows that complex formation between the uranyl and lactate ions takes place in the system at pH=3.5 prior to the photolysis, while such is not the case at pH=1. Therefore, it seems reasonable to assume that the opposite dependency of the product-ratios on the acidity is attributable to the difference in the initial species of the system to be photolyzed. Further, the formation of pyruvic acid is inhibited by the trapping agents, while acetaldehyde formation is not affected (Fig. 4). This difference in the inhibitory effect suggests that the primary intermediates at pH=1 are $CH_3\dot{C}(OH)CO_2H$ and UO_2^+, while intramolecular photoredox reactions of the uranyl-substrate complexes are involved at pH=3.5. The following mechanism is, therefore, proposed for the photolysis at pH=1:

$$UO_2^{2+} + h\nu \xrightarrow{I_a} (UO_2^{2+})^*$$

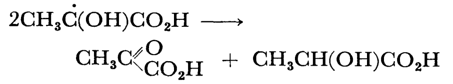
$$(UO_2^{2+})^* \xrightarrow{k_1} UO_2^{2+}$$

$$(UO_2^{2+})^* + CH_3CH(OH)CO_2H \xrightarrow{k_2} CH_3\dot{C}(OH)CO_2H + UO_2^+ + H^+$$

$$CH_3\dot{C}(OH)CO_2H + UO_2^{2+} \xrightarrow{k_3} CH_3C{\overset{\displaystyle\nearrow O}{\underset{\displaystyle\searrow CO_2H}{}}} + UO_2^+ + H^+$$

$$2UO_2^+ + H^+ \xrightarrow{k_4} UO_2^{2+} + U(IV)\ \text{species}^{20)}$$

I_a is the rate of light absorption in einsteins$\cdot l^{-1}\,sec^{-1}$. A similar scheme was proposed for the photolysis of uranyl oxalate by Carter and Weiss[7] and later by Volman and Seed.[8] The radical $CH_3\dot{C}(OH)CO_2H$ would be rapidly oxidized by $UO_2^{2+}(k_3)$ before the disproportionation reaction:



$$2CH_3\dot{C}(OH)CO_2H \longrightarrow CH_3C\begin{smallmatrix}\nearrow O\\ \searrow CO_2H\end{smallmatrix} + CH_3CH(OH)CO_2H$$

since the concentration of $CH_3\dot{C}(OH)CO_2H$ would be small compared to that of UO_2^{2+}. Assuming the steady state with respect to $(UO_2^{2+})^*$, UO_2^+, and $CH_3\dot{C}(OH)CO_2H$, the quantum yield of the uranium(IV) formation is given by:

$$\phi = \frac{1}{I_a} \cdot \frac{d[U(IV)]}{dt} = \frac{k_2[HL]}{k_1 + k_2[HL]},\quad \text{HL: Lactic acid}$$

$$\text{or,}\quad \frac{1}{\phi} = 1 + \frac{k_1}{k_2} \cdot \frac{1}{[HL]}$$

That is, the reciprocal quantum yields *vs.* the reciprocal concentrations of lactic acid should form a straight line. This is consistent with the experimental facts (Fig. 5). In addition, the plot of the relative reciprocal intensity of uranyl fluorescence *vs.* the concentration of lactic acid obeys the Stern-Volmer equation, as in the case of isopropyl alcohol, but such is not the case at pH=3.5 (Fig. 7). It has been reported that the efficiency of intramolecular energy transfer between lanthanide ions and organic ligands is much higher than that of collisional (intermolecular) transfer between lanthanide ions and non-chelating molecules.[21-23] Figure 7 shows that the quenching constant (or the slope) of lactic acid at pH=1 nearly equals that of non-chelating isopropyl alcohol, indicating an intermolecular energy transfer from excited uranyl ions to lactic acid molecules in stronger acidic media.

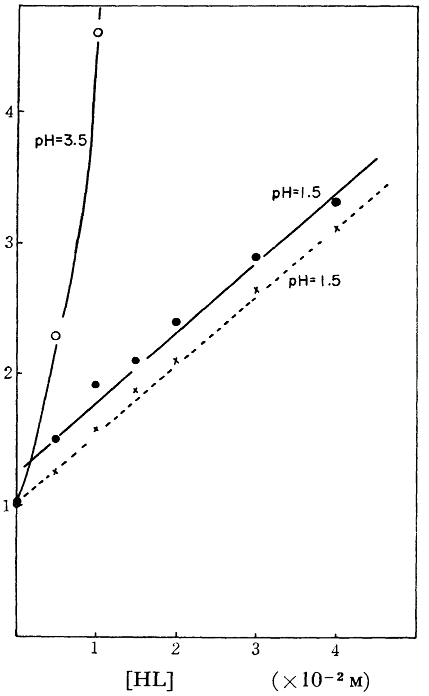
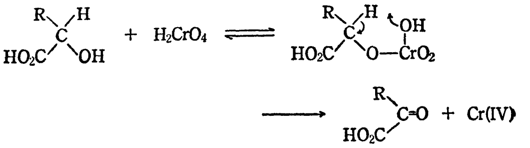


Fig. 7. Plot of $I_f{}^\circ/I_f$ *vs.* concentration of lactic acid. $I_f{}^\circ$ and I_f are the relative intensities of uranyl fluorescence at 509 nm in the absence and in the presence of lactic acid, respectively. Excitation was at 436 nm. $[UO_2(NO_3)_2]=0.02$ M. Isopropyl alcohol was included for comparison (dotted line).

The alternative explanation for the formation of pyruvic acid is a mechanism involving ester-like intermediates, as has been proposed for the thermal oxidation of α-hydroxy acid by chromic acid[24-26]:



This, however, is not the case with the formation of pyruvic acid in the photolysis of lactic acid by uranyl ions, since pyruvic acid was also obtained upon the irradiation of lactic acid with cupric ions in an aqueous acidic solution, where no such ester-like intermediates are conceivable.

In the case of the photolysis at pH=3.5, the quantum yield reaches a limiting value (Fig. 6). Heckler and his co-workers[6] found a phenomenon similar to that shown in Fig. 6 for the uranyl ion-photosensitized decomposition of such organic acid as malonic, succinic and glutaric acids in solution; they concluded that the photosensitive species are complexes formed between uranyl ions and organic acid ions.

Thus, the photosensitive species for the formation of acetaldehyde are the UO_2^+L and UO_2L_2 complexes, both formed prior to the photolysis;

$$UO_2^{2+} + HL \underset{}{\overset{K_1}{\rightleftharpoons}} UO_2^+L + H^+$$

$$UO_2^+L + HL \overset{K_2}{\rightleftharpoons} UO_2L_2 + H^+$$

---

20) J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," Methuen and Co., London (1957), p. 176.

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

22) R. G. Charles and E. P. Riedal, *J. Inorg. Nucl. Chem.*, **28**, 527 (1966).

23) N. Filipescu and G. W. Mashrush, *J. Phys. Chem.*, **72**, 3516 (1968).

24) G. V. Bakore and S. Narain, *J. Chem. Soc.*, **1963**, 3419.

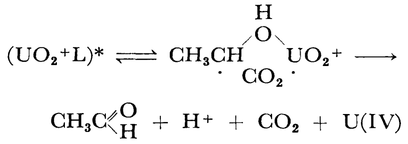
25) T. J. Kempa and W. A. Waters, *ibid.*, **1964**, 1192.

26) G. V. Bakore and R. Shanker, *Can. J. Chem.*, **44**, 1717 (1966).

where HL and L represent $CH_3CH(OH)CO_2H$ and $CH_3CH(OH)CO_2^-$ respectively and where K_1 and K_2 are the equilibrium constants. The following mechanism may be proposed for the formation of acetaldhyde though more experimental data are needed to describe it in detail:

$$UO_2^+L + h\nu \longrightarrow (UO_2^+L)^*$$

$$(UO_2^+L)^* \longrightarrow UO_2^+L$$

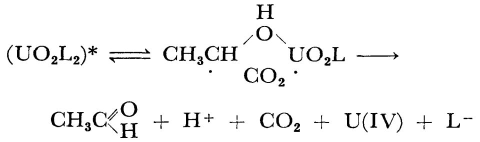


$$(UO_2^+L)^* \rightleftharpoons CH_3\overset{\cdot}{C}H\overset{\overset{H}{|}}{\underset{\underset{CO_2\cdot}{}}{\text{/O\\}}}UO_2^+ \longrightarrow CH_3C{\scriptstyle \begin{matrix}\nearrow O\\ \searrow H\end{matrix}} + H^+ + CO_2 + U(IV)$$

Similarly,

$$UO_2L_2 + hv \longrightarrow (UO_2L_2)^*$$

$$(UO_2L_2)^* \longrightarrow UO_2L_2$$



$$(UO_2L_2)^* \rightleftharpoons CH_3\overset{\cdot}{C}H\overset{\overset{H}{|}}{\underset{\underset{CO_2\cdot}{}}{\text{/O\\}}}UO_2L \longrightarrow CH_3C{\scriptstyle \begin{matrix}\nearrow O\\ \searrow H\end{matrix}} + H^+ + CO_2 + U(IV) + L^-$$

Though the details of the mechanism at high pH are not clear, it may safely be concluded that the variation in the products and mechanisms with pH is to be attributed to the subject whether the formation or dissociation of the uranyl-lactate complex is predominant.

The authors wish to express their thanks to Mr. M. Koshio for a grant given to our research from the "Koshio-Hōonkai".