

The Photolysis of the Uranyl Formic Acid/Formate System in Acidic Aqueous Solution

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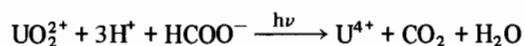
Received November 17, 1977

The photolysis of the uranyl formic acid/formate system has been studied in the acidity range $1 \leq \text{pH} \leq 4$, for [uranyl] to [total formate] ratios from 1 to 0.5 up to 1 to 30 at 25 °C. Qualitative and quantitative information was obtained by using spectrophotometric, polarographic and radiochemical techniques. Evidence is presented for the participation of an uranyl formate complex in the pH range where formate ions are present in appreciable quantities. The photolysis proceeds via uranyl sensitized decomposition of formic acid and formate ion, and via direct decomposition of the mentioned complex. U(IV) and CO₂ are the only detectable photolysis products. The results are discussed in reference to earlier work on the uranyl oxalate system and data reported in the literature.

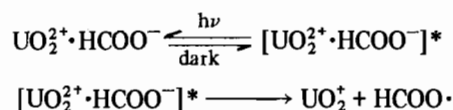
Introduction

In contrast to the photolysis of the uranyl oxalic acid/bioxalate/oxalate system, which has been studied by numerous investigators [1, 2], relatively little is known about the photolysis of the uranyl formic acid/formate system in acidic aqueous solution.

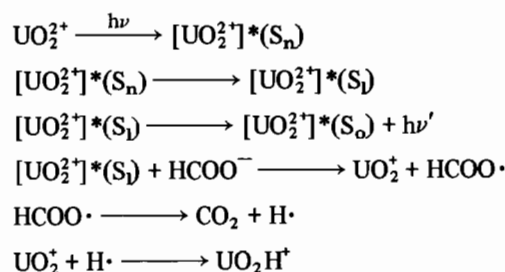
In 1912, Schiller [3] reported the photochemical reaction of the uranyl formate system and presented it as



Courtois [4] isolated an uranyl formate (1:2) complex and identified it as $\text{UO}_2(\text{HCOO})_2 \cdot \text{H}_2\text{O}$. He and others [5–7] provided evidence for the formation of U(IV) and CO₂ during the photolysis, and CO was not reported to be formed. Rabinowitch [2] interpreted Quillet's data [7] as evidence for the participation of an uranyl formate (1:1) complex in the photolysis process and suggested the following mechanism



In a recent study, Claudel and co-workers [8] investigated the solid state photochemistry of uranyl formate monohydrate and proposed the following reaction sequence



The reaction proceeds via the excitation of only the uranyl ion, and the uranyl formate (1:2) complex (starting material) as such, does not participate in this process.

In general two types of mechanisms can be distinguished in the photolysis of uranyl systems [1, 2, 9]: those involving excitation of an uranyl ligand complex, and those involving the excitation of the uranyl ion followed by a reaction with the substrate. In both cases U(V) is produced as an intermediate and the final product is U(IV) [8, 10–12]. In our previous work [13–17] we reported that the photolysis of the uranyl oxalic acid/bioxalate/oxalate system, for the experimental conditions concerned, only proceeds via the excitation of uranyl bioxalate and oxalate complexes and no contribution of excitation via uranyl ion could be detected. The insight gained in the latter system was the result of a thorough investigation during which spectroscopic, polarographic, titrimetric, radiochemical and electrochemical techniques were employed. Following this work, the present investigation was undertaken to determine the role played by uranyl formate complexes in the photolysis of uranyl formic acid/formate aqueous solutions.

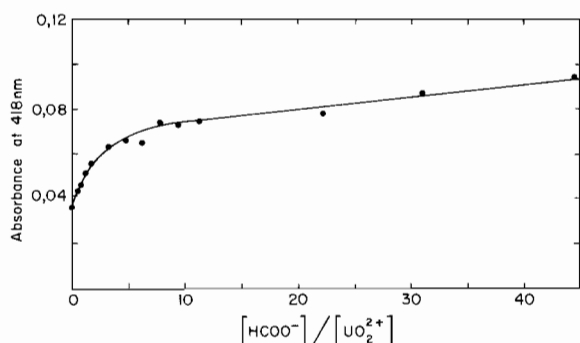


Figure 1. Absorbance as a function of the [formate] to [uranyl] ratio at pH 3.5, optical path length = 1 cm, $[UO_2^{2+}] = 0.004 M$.

Experimental

The experimental procedures and analytical techniques employed, were very similar to those outlined before [13, 14, 16]. In addition, the polarographic analyses were improved by using an a.c. modification. C^{14} -labelled formic acid was used in the radiochemical work. General experimental conditions were: $0.004 M UO_2(NO_3)_2 \cdot 6H_2O$, ionic strength $0.5 M$ by the addition of KNO_3 , temperature $25^\circ C$, 20 ml solutions were irradiated in the photolysis cell [14] using a 10 mm slit width. A wide range of different experiments was performed and some experimental detail, where necessary, is included under Results and Discussion.

Results and Discussion

Equilibrium Studies of the Uranyl Formic Acid/Formate System

The pK value for formic acid was experimentally determined as 3.40 ($25^\circ C$, $0.5 M KNO_3$), which is in good agreement with 3.50 ($25^\circ C$, $1 M KNO_3$) and 3.35 ($25^\circ C$, $1 M NaClO_4$) determined previously in this laboratory [18, 19].

The characteristic fingerprint visible absorption spectrum [13] of UO_2^{2+} shows no change on the addition of an excess of formic acid at pH 1.7. On addition of formic acid at pH 3.5 (where approx. 50% formate ions are present) an increase in absorbance is observed and two new peaks become visible at 470 and 488 nm. These peaks are very weak and the change in absorbance as a function of [formate] was, therefore, measured at 418 nm. The results in Fig. 1 provide evidence for the formation of an uranyl formate complex of which the coordination number and formation constant cannot be determined very accurately. This is mainly due to the absence of a limiting absorbance value at high formate concentrations (see the corresponding oxalate study

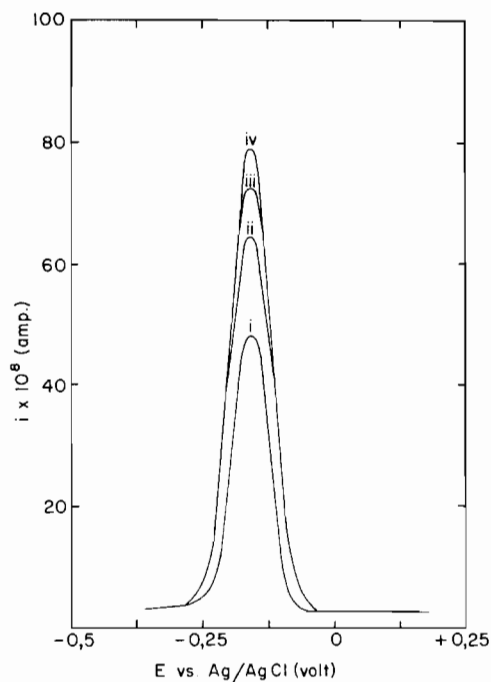


Figure 2. A.C. polarograms of various uranyl formate mixtures at pH 3.5:

- i. $[UO_2^{2+}] = 0.004 M$, [total formate] = $0.0000 M$
- ii. $[UO_2^{2+}] = 0.004 M$, [total formate] = $0.0036 M$
- iii. $[UO_2^{2+}] = 0.004 M$, [total formate] = $0.0054 M$
- iv. $[UO_2^{2+}] = 0.004 M$, [total formate] = $0.0126 M$

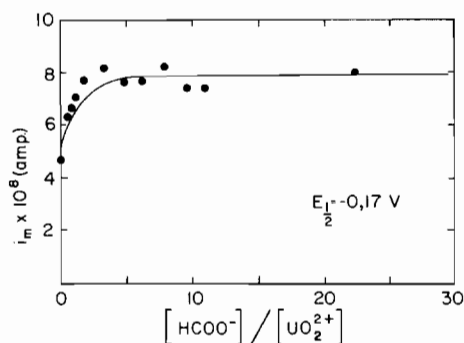


Figure 3. Polarographic peak height as a function of the [formate] to [uranyl] ratio at pH 3.5, $[UO_2^{2+}] = 0.004 M$.

[13]), and points towards weak complex formation. The inflection in Fig. 1 occurs at an uranyl to formate ratio of approx. 1 to 2, and the formation constant is approx. $1.25 \times 10^5 M^{-2}$.

The inverse polarograms recorded on a d.c. polarograph, of uranyl ion in the absence and presence of an excess of formic acid at pH 1.7 and 3.5, show similar tendencies to the above-reported absorption spectra. The half-wave potentials for UO_2^{2+} are -0.204 and $-0.200 V$ (vs. Ag/AgCl) at pH 1.7 and 3.5 respectively. No change is observed on addition of formic acid at pH 1.7, and only a slight shift in

potential to -0.253 V is observed on addition of formic acid at pH 3.5. The latter, once again, confirms complex formation between uranyl and formate ion. The shift in half-wave potential is, however, too small to perform any meaningful calculations with regard to the nature of the produced complex. Further information on the complexation was obtained from polarograms, measured with a.c. polarograph, which are reported in Fig. 2. A plot of the diffusion current i_m versus $[\text{HCOO}^-]/[\text{UO}_2^{2+}]$ is presented in Fig. 3, from which it is seen that an uranyl formate (1:2) complex is formed with a stability constant of $10.5 \times 10^4 M^{-2}$. The latter value is in good agreement with that obtained spectrophotometrically and we conclude that, under the present experimental conditions, evidence for the presence of a $\text{UO}_2(\text{HCOO})_2$ complex does exist. As in the case of oxalic acid [13], no complexation between uranyl ion and formic acid could be detected. These results are in agreement with those reported by Courtois [4].

Photochemical Behaviour of the Uranyl Formic acid/Formate System

At low formate ion concentrations, *i.e.* $[\text{HCOO}^-]:[\text{UO}_2^{2+}] \leq 5:1$, precipitates are formed during irradiation at pH 3.5. The mass of the precipitate decreases with an increase in the ratio of $[\text{HCOO}^-]$ to $[\text{UO}_2^{2+}]$. Spectrophotometric analyses of the precipitates [16] indicate that they mainly consist of U(IV). The U(IV) content of the filtrate becomes observable when less precipitate is formed, *i.e.* at higher $[\text{HCOO}^-]$.

At high formate ion concentrations, *i.e.* $[\text{HCOO}^-]:[\text{UO}_2^{2+}] = 5.6:1$ to $17:1$, no precipitates are formed during irradiations at pH 3.5. Spectra and polarograms provide evidence for the formation of U(IV) formate species. The a.c. $E_{1/2}$ for U(IV) shifts from $+0.076$ to $+0.112$ V, and the absorption spectrum changes from a single peak at 650 nm to two intense peaks at 652 and 662 nm at the increase in the $[\text{HCOO}^-]$ to $[\text{UO}_2^{2+}]$ ratio for a constant irradiation period. Comparison of these results with the polarograms and spectra obtained for synthetic U(IV) formate mixtures, indicates that different U(IV) formate complexes can exist in solution, of which the coordination state is determined by the excess of formate ions present. A similar result was reported for the formation of U(IV) oxalate species [16]. The quantity of U(IV) species formed during irradiation, also increases with an increase in the $[\text{HCOO}^-]$ to $[\text{UO}_2^{2+}]$ ratio. It follows that the formation of U(IV) precipitates (hydrolysed species) or U(IV) formate complexes, is governed by the excess of formate ions present, which again also determines the extent to which UO_2^{2+} is complexed prior to irradiation.

The loss in [U(VI)] and gain in [U(IV)], as a function of the irradiation time, was studied for a solution

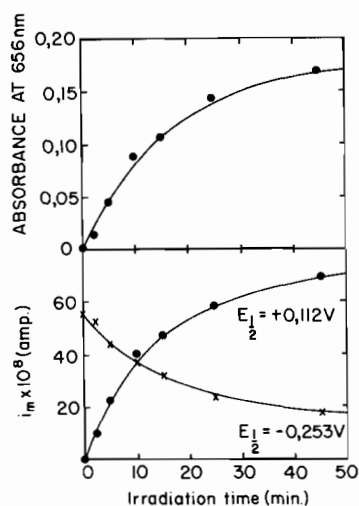


Figure 4. Formation of U(IV) and decomposition of U(VI) as a function of irradiation time, $[\text{UO}_2^{2+}] = 0.004 M$, [total formate] = $0.12 M$, pH = 3.5, optical path length = 1 cm.

at pH 3.5 for which $[\text{HCOO}^-]:[\text{UO}_2^{2+}] = 16.5:1$. The decrease in [U(VI)] was measured polarographically at $E_{1/2} = -0.253$ V whereas the increase in [U(IV)] was measured polarographically at $E_{1/2} = +0.112$ V and spectrophotometrically at 656 nm, the results of which are summarized in Fig. 4. The decrease in [U(VI)] differs considerably from that reported for the oxalate case under similar conditions [14]. Immediate decomposition to U(IV) occurs and it seems as if the reverse reaction of a possible U(V) intermediate species to form U(VI), does not play such an important role as in the oxalate case. A further significant feature of the results in Fig. 4, is the fact that the reaction does not develop to completion at long irradiations. An equilibrium position is reached, due to a reverse reaction during which U(IV) is oxidized by dissolved oxygen to U(VI). The rate constant for this oxidation reaction is $1 \times 10^{-2} \text{ min}^{-1}$ under the present experimental conditions, in comparison with a value of $3.6 \times 10^{-2} \text{ min}^{-1}$ for the initial rate of increase in [U(IV)] or decrease in [U(VI)], calculated from the data in Fig. 4. When nitrogen or argon is bubbled through the test solutions prior to irradiation, the reverse oxidation reaction is greatly eliminated and the photochemical reaction proceeds to completion. The reverse oxidation reaction is independent of pH and its rate constant is approx. $7 \times 10^{-4} \text{ min}^{-1}$ at 25°C in the absence of oxygen.

In our earlier work on the uranyl oxalate system [14], we reported that the gaseous decomposition products consisted of CO_2 and CO (in the ratio 2 to 1) for irradiations at pH 1.7, and only CO_2 for irradiations at pH 4.5. These analyses were performed mass-spectrometrically and involved some error. More consistent results can now be obtained by using a Perkin Elmer through/flow reactor RGC 170 in which

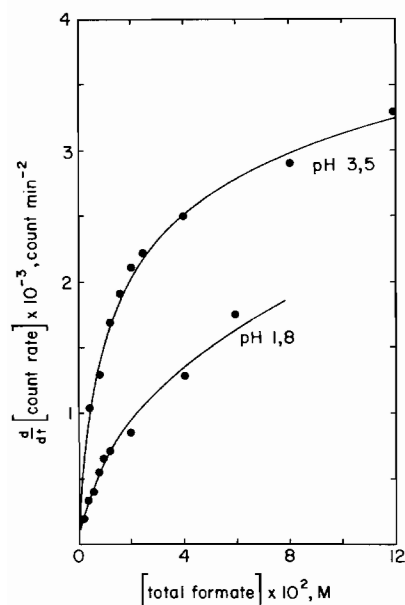


Figure 5. Plots of $d/dt[\text{count rate}]$ versus $[\text{total formate}]$ for irradiations at pH 1.8 and 3.5, $[\text{UO}_2^{2+}] = 0.004 \text{ M}$; see text for further detail.

CO is oxidized at 650°C to CO_2 and then determined in the usual way [14, 20], using a liquid scintillation technique. The CO_2 to CO ratio now obtained in this manner for the photolysis of the uranyl oxalate system at pH 1.7 is 2.2 to 1. For the photolysis of the uranyl formate system at pH 3.5, the above procedure indicated that only CO_2 is formed as a gaseous decomposition product. This created the possibility to follow the photolysis of the uranyl formate system radiochemically. $150 \mu\text{Ci } \text{C}^{14}$ -labelled formic acid was added to one litre 0.4 M formic acid, from which all test solutions were prepared. Count rates were obtained for the irradiation of a series of uranyl formate mixtures at pH 1.8 and 3.5, as a function of irradiation time (2, 4, 6 and 8 minutes). The initial reaction rate was calculated from the initial slope of plots of count rate versus irradiation time and is, therefore, expressed as count min^{-2} . A plot of initial reaction rate versus $[\text{total formate}]$ is given, for both pH values, in Fig. 5, from which some interesting conclusions are drawn.

No limiting rate is reached at high $[\text{total formate}]$, in contrast to that found for the corresponding oxalate system [15], but in agreement with the tendency observed for pH 3.5 in Fig. 1.

The data for pH 3.5, furthermore, does not show a sharp inflection that could possibly point to the participation of a particular uranyl formate complex. Even more significant are the relatively high reaction rates reported for the irradiation at pH 1.8 where it is known that no complex formation occurs. The latter can only be ascribed to the uranyl sensitized

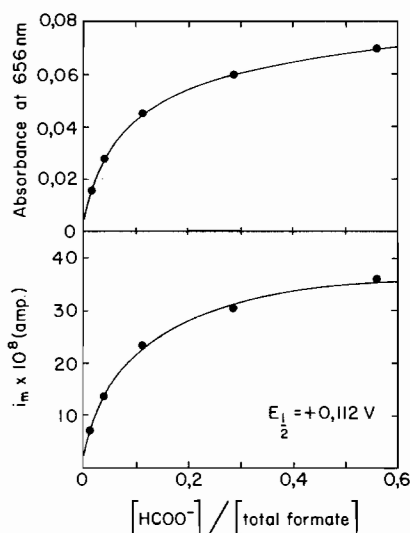


Figure 6. Formation of U(IV) as a function of the pH of the test solutions prior to irradiation, $[\text{UO}_2^{2+}] = 0.004 \text{ M}$, $[\text{total formate}] = 0.12 \text{ M}$, irradiation time = 10 min, optical path length = 1 cm, $1.5 \leq \text{pH} \leq 3.5$. All i_m and absorbance measurements after irradiation were performed at pH 3.5 to eliminate the influence of pH on the latter.

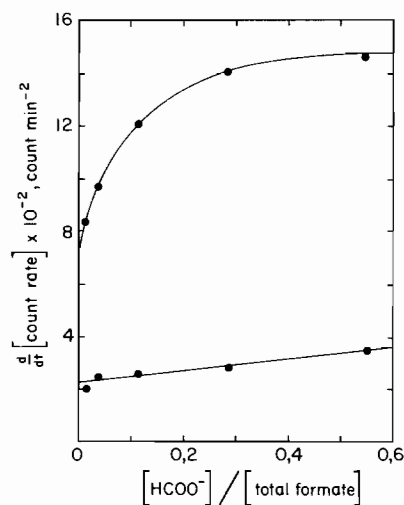


Figure 7. $d/dt[\text{count rate}]$ as a function of the pH of the test solutions prior to irradiation, $[\text{total formate}] = 0.12 \text{ M}$, irradiation time = 10 min, $1.5 \leq \text{pH} \leq 3.5$, $[\text{UO}_2^{2+}] = 0.004 \text{ M}$ – upper curve, $[\text{UO}_2^{2+}] = 0.0 \text{ M}$ – lower curve.

photolysis of formic acid, once again in contrast to that reported for the oxalic acid case [14] (see further discussion). The increase in reaction rate on going from pH 1.8 to 3.5 is ascribed to the participation of an uranyl formate complex, although its exact nature cannot be deduced from the kinetic data in Fig. 5, as mentioned above.

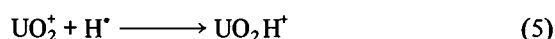
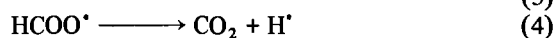
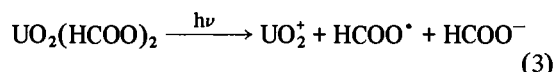
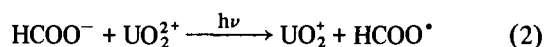
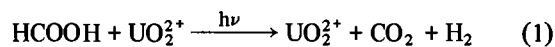
The above results show that the photolysis of the uranyl formate system strongly depends on the pH of the test solutions. A series of experiments was performed to study the influence of pH on the formation of U(IV), measured spectrophotometrically and polarographically, and CO₂, measured radiochemically, during the photolysis. No change in pH was observed during the irradiation of the solutions, and the results for a series of initial pH values are reported in Figs. 6 and 7. The formation of U(IV), expressed as i_m and absorbance in Fig. 6, increases with an increase in pH, the latter being expressed as the fraction of [total formate] present as HCOO⁻, *i.e.* [HCOO⁻]/[total formate]. Both curves show an increase in [U(IV)] with increasing pH and point towards the reaching of a limiting [U(IV)] at high pH.

A similar tendency is observed for the formation of CO₂, expressed in terms of count rate in Fig. 7, where the upper curve represents the data for the photolysis in the presence of, and the lower curve in the absence of uranyl ion. The lower curve corresponds with the photolysis of formic acid/formate ion and is in good agreement with that reported for oxalic acid/bioxalate/oxalate ion [14]. When the data for the photolysis in the presence of uranyl ion (upper curve Fig. 7) are extrapolated to the point where only formic acid is present, *i.e.* [HCOO⁻]/[total formate] = 0, a large intercept is obtained which is ascribed to the uranyl sensitized decomposition of formic acid. The latter is in good agreement with that reported in Fig. 5. In the oxalate case [14] however, this extrapolated intercept coincided with that obtained in the absence of uranyl ions, and led to the conclusion that oxalic acid does not undergo any uranyl sensitized photolysis. The increase in CO₂ production (upper curve Fig. 7) with increase in pH is ascribed to the participation of an uranyl formate complex. The slope observed for the lower curve is ascribed to the increase in photochemical reactivity in going from formic acid to formate ion. According to the upper curve in Fig. 7 the reaction rate approx. doubles on increasing the pH to 3.5. This is in good agreement with the rate plots in Fig. 5, which also show an increase of approx. a factor of 2 in going from pH 1.8 to 3.5.

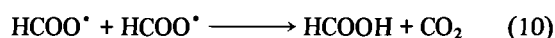
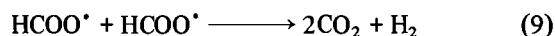
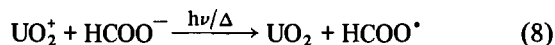
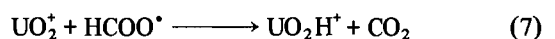
The two curves in Fig. 6 and the upper curve in Fig. 7 are considered as further evidence for the participation of an uranyl formate complex species. Extrapolation of the limiting parts of the curves, at low and high pH respectively, produces inflections at [uranyl] to [formate] ratios of approx. 1 to 2 for all three cases. The stability constants are $9.04 \times 10^4 M^{-2}$ (absorbance curve – Fig. 6), $8.17 \times 10^4 M^{-2}$ (i_m curve – Fig. 6) and $9.12 \times 10^4 M^{-2}$ (upper curve – Fig. 7), with an average value of $(8.8 \pm 0.5) \times 10^4 M^{-2}$. These results are in good agreement with those obtained from the equilibrium study reported in the first section. From a comparison of the two

curves in Fig. 6 with the upper curve in Fig. 7, the conclusion is reached that U(IV) is not produced during the uranyl sensitized photolysis of formic acid (intercepts of curves), but only at pH > 1.5, *i.e.* where formate ions are present and complexation may occur.

The photochemical decomposition of formic acid/formate ion in the presence of uranyl ion may be presented by the following reaction scheme:



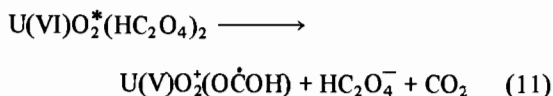
Alternative reactions are



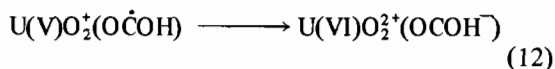
Reactions (1) and (2) present the uranyl sensitized photolysis of formic acid and formate ion respectively, during which the uranyl ions are primarily photoactivated. In reaction (2) the decomposition of formate ion is accompanied by the reduction of uranium from U(VI) to U(V) and finally to U(IV), in agreement with the fact that U(IV) is only produced at pH > 1.5 (Fig. 6). Reactions (3) and (6) present the decomposition of the uranyl formate complex involving a one and two electron transfer, respectively. The U(V) intermediate produced in reactions (2) and (3), may, according to the suggestions of Claudel [8], be further reduced to U(IV) by hydrogen radicals in reaction (5), and alternatively by HCOO[•] in reaction (7) or HCOO⁻ in reaction (8). The HCOO[•] radicals are suggested to decompose to CO₂ and H[•] in reaction (4), and reactions (9) and (10) present alternative possibilities. The U(IV) produced during photolysis, is presented by UO₂H[•] in reactions (5) and (7) and by UO₂ in reactions (6) and (8). The polarographic and spectrophotometric measurements, however, indicated that U(IV) is, in the presence of an excess of formate ions, present as an uranium(IV) formate complex. Since the exact nature of this complex is unknown, it is not stated in the suggested reaction scheme. The suggested reactions are in good

agreement with those suggested for the solid state photolysis of $\text{UO}_2(\text{HCOO})_2 \cdot \text{H}_2\text{O}$; they point out the role played by the uranyl formate complex, and fit all the reported experimental observations.

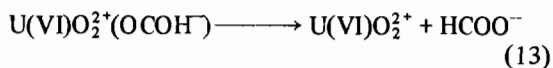
The results of this investigation has led to a better understanding of the photolysis of the uranyl oxalate system studied previously [14–17]. In the proposed mechanism for the latter system, uranyl bioxalate and oxalate complexes decompose photochemically to mainly UO_2^{2+} and very little U(IV) in the presence of an excess of bioxalate/oxalate ion. In the primary reaction the excited complex undergoes, by applying the suggestions made by Heidt [12] to the bioxalate complex, an internal electron transfer can be presented as [17]



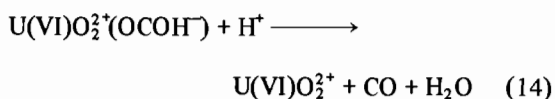
This is followed by oxidation of U(V) to U(VI)



and the latter species then decomposes according to



or



Reaction (14) is in agreement with the fact that CO was only reported to be formed at low pH. No evidence could be found for the presence of HCOO^- , formed in reaction (13), and it was suggested [15] that the formate ions should undergo uranyl sensitized photolysis. With the information now available for the photolysis of the uranyl formate system, further proof for this suggestion exists. In the oxalate case formate ion will only be present in low quantities, such that reactions (1) and (2) will contribute mostly

to its photochemical decomposition. A contribution made by reactions (3) and (6) is not ruled out.

Acknowledgement

The authors gratefully acknowledge financial support from the S.A. Council for Scientific and Industrial Research and the S. A. Atomic Energy Board.

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