

## The Photolysis of the Uranyl Malonic Acid/Bimalonate System in Acidic Aqueous Solution

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*The photolysis of the uranyl malonic acid/bimalonate system has been studied in the acidity range  $0 \leq \text{pH} \leq 3.0$ , for [uranyl] to [total malonate] ratios from 1 to 0.25 up to 1 to 40 at 25 °C. Qualitative and quantitative data were obtained by using spectrophotometric, polarographic and radiochemical techniques. Equilibrium and kinetic evidence are presented for the participation of an uranyl bimalonate (1:1) complex as the primary photosensitive species. Malonic acid does not undergo uranyl sensitized photolysis.  $\text{CO}_2$  is the only detectable gaseous photolysis product. The results are discussed in reference to earlier work on the uranyl oxalate and uranyl formate systems, and data reported in the literature.*

### Introduction

An important aspect of the uranyl sensitized photolysis of carboxylic acids/carboxylate ions, concerns the role played by the uranyl ions in these processes. Two types of mechanisms have been distinguished [1–3]: one involving the excitation of uranyl carboxylate complexes, and another involving the excitation of the uranyl ion followed by a reaction with the carboxylic acid/carboxylate ions. In an earlier study we reported [4, 5] evidence that the photolysis of the uranyl oxalic acid/bioxalate/oxalate system *only* proceeds via the excitation of uranyl bioxalate/oxalate complexes, and that no contribution from excitation via free uranyl ion could be detected. In a later study [6] of the uranyl formic acid/formate system direct evidence was presented for the occurrence of both the above-mentioned reaction modes. These contradicting findings led to the present investigation of the photolysis of the uranyl malonic acid/bimalonate system.

Berthelot and Gaudechon [7] were the first to report the photolysis of uranyl malonic acid mixtures

in 1913. They were later followed by different investigators, whose work is reviewed elsewhere [8]. The reported data are of such nature that it confirms both possible reaction routes, *viz.* photolysis via excitation of uranyl malonate complexes and via excitation of uranyl ion. In a more recent investigation Heckler *et al.* [9] studied the photolysis process micromanometrically and reported data which confirmed that an uranyl malonate (1:1) complex is the photoreactive species. Although we followed the photolysis process in an entirely different way, our findings support the latter viewpoint.

### Experimental

The experimental procedures and analytical techniques employed are similar to those outlined before [4–6].  $\text{C}^{14}$ -labelled malonic acid in the form  $\text{HOOC}^{14}\text{-CH}_2\text{-C}^{14}\text{OOH}$  was used to obtain the reported radiochemical results. In addition, some experiments were performed with  $\text{HOOC-C}^{14}\text{H}_2\text{-COOH}$ . General experimental conditions, unless otherwise indicated, were: 0.004 M  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , ionic strength 0.5 M by the addition of  $\text{KNO}_3$ , temperature 25 °C, 20 ml solutions were irradiated in the photolysis cell [4] using a 10 mm slit width. Some experimental detail, where necessary, will be included in the following section.

### Results and Discussion

#### *Equilibrium Studies of the Uranyl Malonic Acid/Bimalonate system*

The acid dissociation constants for malonic acid were experimentally determined by pH titration at 25 °C in 0.5 M  $\text{KNO}_3$ :  $\text{pK}_1 = 2.65 \pm 0.05$ ,  $\text{pK}_2 = 5.15 \pm 0.05$ . These values are in good agreement with those previously determined in this laboratory [10, 11], and will be used to estimate the composition of the reaction mixtures in terms of the [malonic acid], [bimalonate] and [malonate] in solution.

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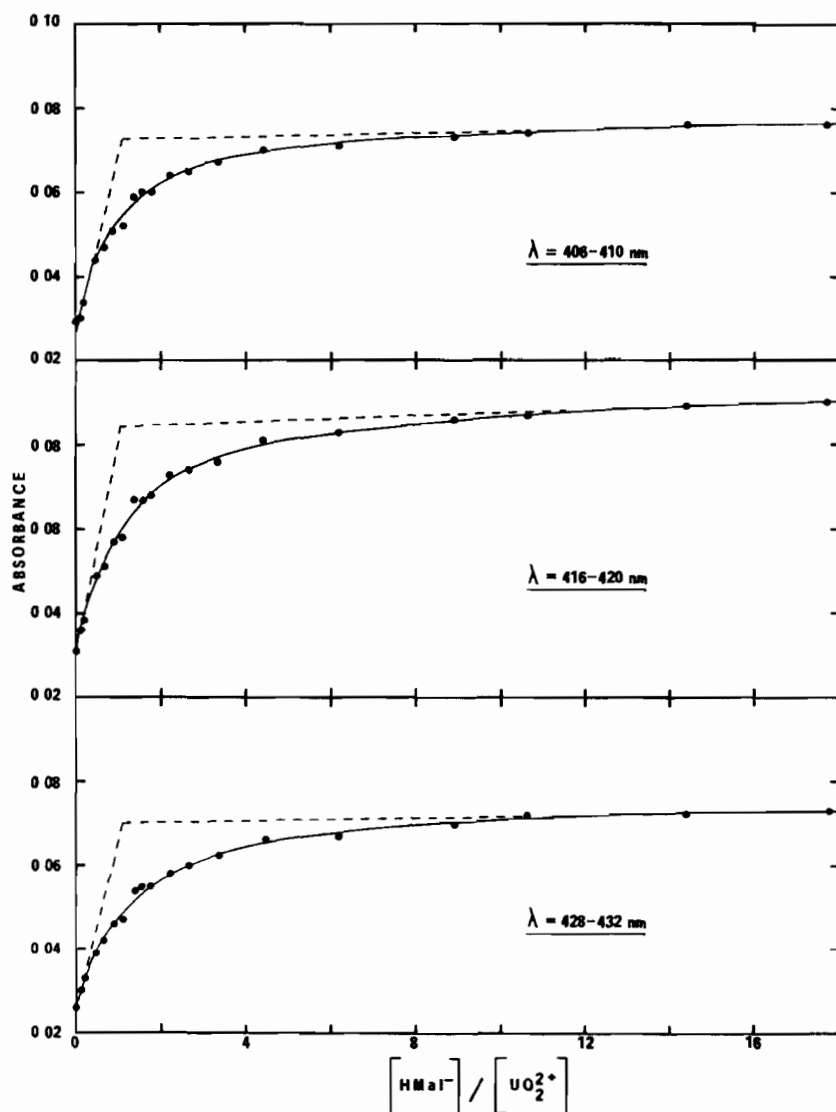


Fig 1 Absorbance as a function of the [bimalonate] to [uranyl] ratio at pH 2.55, optical path length = 1 cm,  $[UO_2^{2+}] = 0.004 M$

The possible formation of uranyl malonic acid/bimalonate/malonate complex species in solution was studied spectrophotometrically in the near UV-visible range. At  $pH \leq 0.5$ , where malonate is mainly present as malonic acid, no change in the characteristic finger-print spectrum [4, 12] of  $UO_2^{2+}$  could be observed during the addition of an excess of malonic acid. This indicates that no complex formation between malonic acid and uranyl ions occurs under such conditions, in agreement with that found for oxalic [4] and formic [6] acid. On the other hand, addition of malonic acid to uranyl solutions at pH 2.55, where approx 50% of the [total malonate] exists as bimalonate ions, causes significant increases in absorbance at 406, 416 and 428 nm and three new low intensity peaks are formed at 460, 474 and 494

nm. The increase in absorbance around 406, 416 and 428 nm was measured as a function of [bimalonate] for which the results are summarized in Fig 1. The latter provides evidence for the formation of an uranyl bimalonate complex with an  $[UO_2^{2+}]$  to  $[HMal^-]$  ratio of 1:1:1 ( $\lambda = 406-410$  nm), 1:1:0.8 ( $\lambda = 416-420$  nm) and 1:1:1 ( $\lambda = 428-432$  nm). The average ratio of 1:1:0.9 points within experimental error limits to the formation of an 1:1 uranyl to bimalonate complex species. The formation constant for this complex was calculated in the usual way to be  $7.5 \times 10^2$ ,  $5.9 \times 10^2$  and  $5.7 \times 10^2 M^{-1}$  for the three sets of measurements, respectively, with an average value of  $(6.4 \pm 1.0) \times 10^2 M^{-1}$ .

To investigate the complex formation between uranyl and malonate ion, the pH of such solutions

must be 5.5 or higher to ensure that mainly malonate ions will be present in solution. Unfortunately, under such conditions  $\text{UO}_2^{2+}$  exists as hydrolysed species which tend to precipitate [4, 12, 13]. One is thus limited by solubility properties to a pH range where both bimalonate and malonate ions will be present in solution, such that the complexation mode of  $\text{UO}_2^{2+}$  cannot be determined unequivocally. In the lower pH range ( $\sim 2.5$ ) no interference of any malonate ions is expected and the complexation of  $\text{UO}_2^{2+}$  with bimalonate ions could be measured accurately.

In addition to the spectrophotometric method, d.c. and a.c. polarography were also employed to study the equilibria involved. The d.c. half-wave potential for  $\text{UO}_2^{2+}$ , which is  $-0.18$  V (vs. Ag/AgCl) under the present experimental conditions at pH < 3.0, does not show any change on the addition of malonic acid at pH < 0.5. A slight shift in potential to  $-0.26$  V is observed on addition of bimalonate ion at pH 2.6. This shift is very similar to that observed on addition of formate ion [6] and confirms complex formation between uranyl and bimalonate ion. It is however, too small to perform any meaningful calculations with regard to the nature of the produced complex. The a.c. polarographs show very similar tendencies and the shift in potential on addition of bimalonate ion at pH 2.6 is accompanied by a marked decrease in the peak intensity.

To summarize, the obtained data suggest the formation of an uranyl bimalonate (1:1) complex with a formation constant of  $(6.4 \pm 1.0) \times 10^2 \text{ M}^{-1}$ . This is in agreement with the kinetic evidence reported by Heckler *et al.* [9] for the occurrence of a 1:1 photosensitive complex species, although they strongly support the idea that complexation occurs between uranyl and the diionized malonate ion. On the other hand, however, they [9] do report evidence for the formation of 1:1 complexes between uranyl ion and the monoionized form of succinic and glutaric acid.

#### Photochemical Behaviour of the Uranyl Malonic Acid/Bimalonate System

Some preliminary experiments were performed to determine the general nature of the photolysis process. During irradiation of uranyl bimalonate mixtures at pH 2.6 of compositions varying from 1:0.1 to 1:14.4 for periods up to 60 minutes, no precipitates were formed, the intensity of the visible absorption peaks decreased and gaseous decomposition products were produced. Some typical absorbance time plots during irradiation are given in Fig. 2. The decrease in absorbance during irradiation is accompanied by a similar decrease in  $[\text{H}^+]$  (increase in pH), which is more pronounced at lower ratios of  $[\text{HMal}^-]$  to  $[\text{UO}_2^{2+}]$ . These tendencies are very similar to those reported previously for the photolysis of

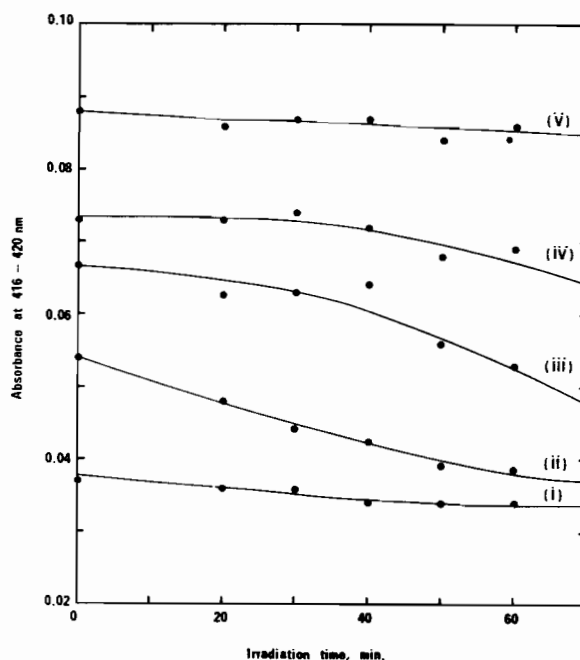


Fig. 2. Absorbance at 416–420 nm as a function of irradiation time, pH = 2.55,  $[\text{UO}_2^{2+}] = 0.004 \text{ M}$ , optical path length = 1 cm,  $[\text{HMal}^-]/[\text{UO}_2^{2+}] = 0.11$ (i), 0.44(ii), 1.11(iii), 2.22(iv), 6.21(v).

uranyl bioxalate mixtures at pH 1.7 [4], and similar explanations will be adopted (see later discussion). No spectrophotometric or polarographic evidence for the formation of U(IV) during photolysis at pH 2.6, could be found following the procedures outlined before [4, 6]. Analyses [6] of the gaseous decomposition products indicated that it consists 99% of  $\text{CO}_2$ , which is in good agreement with the findings of Heckler *et al.* [9].

The formation of  $\text{CO}_2$  created the possibility to follow the photolysis of the uranyl malonate system radiochemically.  $150 \mu\text{Ci } \text{C}^{14}$ -labelled malonic acid, *viz.*  $\text{HOOC}^{14}\text{-CH}_2\text{-C}^{14}\text{OOH}$ , was added to one litre 0.2 M malonic acid, from which all test solutions were prepared. A liquid scintillation technique [4, 14] was adopted to obtain count rate measurements for the irradiation of a series of uranyl malonate mixtures at pH 2.55 as a function of irradiation time (20, 30, 40, 50 and 60 minutes). The initial reaction rate was calculated from the slope of plots of count rate versus irradiation time and is expressed as count  $\text{min}^{-2}$ . The results of such a study are summarized in Fig. 3 in the form of a plot of initial reaction rate versus  $[\text{HMal}^-]/[\text{UO}_2^{2+}]$ . These kinetic data illustrate that a limiting rate is reached at high  $[\text{HMal}^-]$ , in accord with our earlier findings on the uranyl

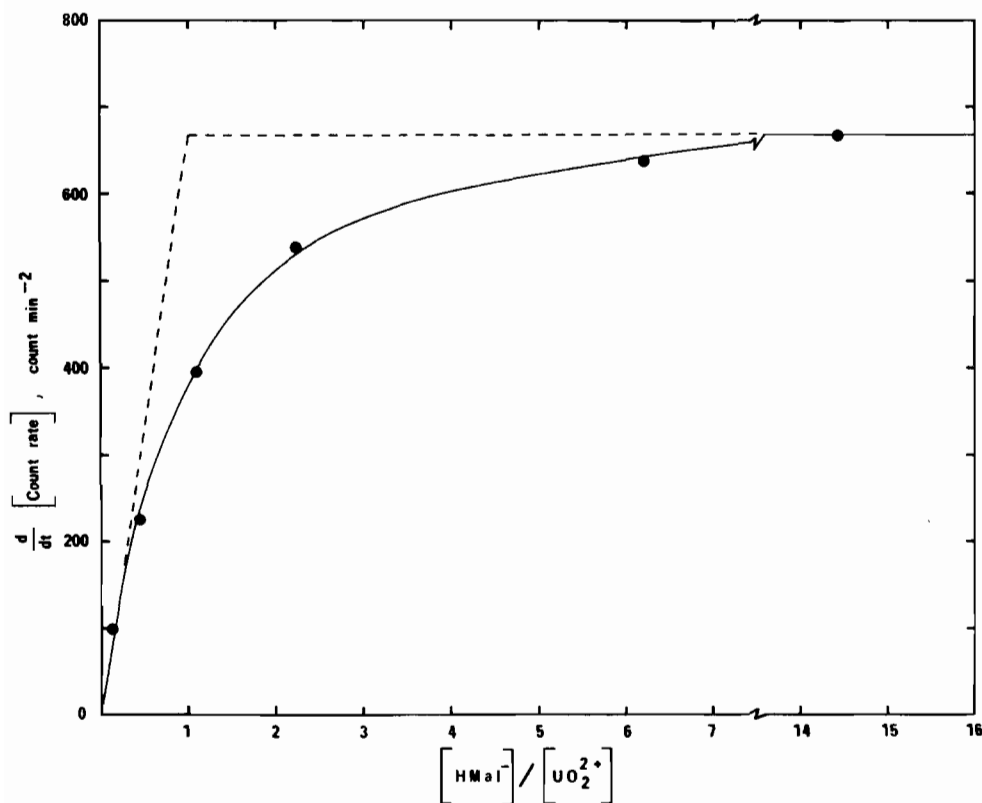


Fig. 3. Plot of  $d[\text{count rate}]/dt$  versus [bimalonate] to [uranyl] ratio at  $\text{pH} = 2.55$ ,  $[\text{UO}_2^{2+}] = 0.004 \text{ M}$ .

bioxalate system [4]. An inflection is observed in the data at an uranyl to bimalonate ratio of 1:1, which suggests that a complex of such composition acts as the primary photosensitive species. The formation constant of this complex, calculated from the kinetic data, is  $7.2 \times 10^2 \text{ M}^{-1}$ , which is in very good agreement with the value reported in the equilibrium study.

A series of experiments was performed to study the influence of pH on the formation of  $\text{CO}_2$  during photolysis. The initial reaction rate was estimated from count rate data as a function of irradiation periods up to 60 minutes, as outlined above, and is plotted as a function of pH, i.e.  $[\text{HMal}^-]/[\text{total malonate}]$ , in Fig. 4. A similar experiment was repeated in the absence of uranyl ion. The results indicate that an increase in  $[\text{H}^+]$  (decrease in pH) drastically decreases the rate of formation of  $\text{CO}_2$  in the presence of uranyl ion (curve A). The intercept at low pH corresponds to that obtained for the irradiation of malonate solutions in the absence of uranyl ion (curve B). These results clearly indicate that malonic acid (the main species at low pH) does not undergo any uranyl sensitized photochemical decomposition. The increase in initial rate with increase in pH (curve A) must be due to the forma-

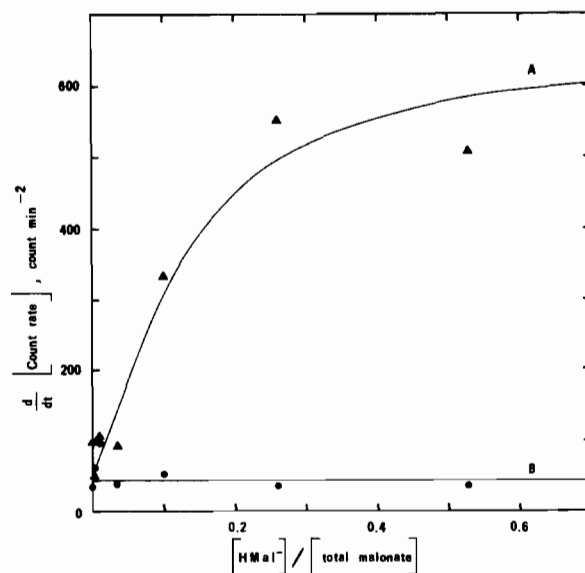
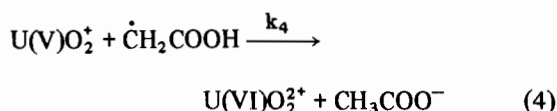
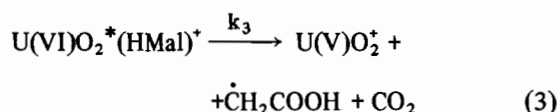
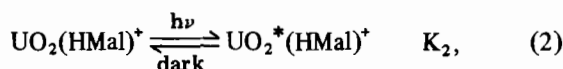
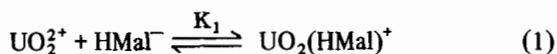


Fig. 4.  $d[\text{count rate}]/dt$  as a function of the [bimalonate] to [total malonate] ratio of the test solutions prior to irradiation, [total malonate] =  $0.056 \text{ M}$ , ionic strength =  $1.0 \text{ M}$ ,  $[\text{UO}_2^{2+}] = 0.004 \text{ M}$  (curve A),  $[\text{UO}_2^{2+}] = 0.0 \text{ M}$  (curve B),  $0 < \text{pH} \leq 3.0$ , irradiation time 20 to 60 min.

tion of the 1:1 uranyl bimalonate complex, since bimalonate ion will be present under such conditions. This result is in agreement with that reported for the uranyl sensitized photolysis of oxalic acid [4], but differs from that reported for the uranyl sensitized photolysis of formic acid [6]. In the latter, the equivalent plot of Fig. 4 revealed a significant difference between the intercepts of curves A and B, which was ascribed to the uranyl sensitized photolysis of formic acid.

A reaction mechanism suggested to fit the experimental results, consists of the following equilibria and reactions:



Equilibrium (1) presents the formation of the uranyl bimalonate (1:1) complex for which  $K_1 = (6.4 \pm 1.0) \times 10^2 \text{ M}^{-1}$  (from Fig. 1) and  $7.2 \times 10^2 \text{ M}^{-1}$  (from Fig. 3). Reaction (2) describes the photo-activation of the uranyl bimalonate complex, which may return to the ground energy state during the reverse process.  $K_2$  will depend on the intensity of the energy source and the quantum efficiency of the process. Reaction (3) is the rate-determining step in which an uranyl(V) species,  $\text{CO}_2$  and the radical  $\dot{\text{C}}\text{H}_2\text{COOH}$  are produced. This reaction is a one-electron transfer process and similar in nature to such reactions proposed for the uranyl sensitized photolysis of other carboxylate ions [6, 15]. Reaction (4) is a non-rate-determining step in which  $\text{U(V)O}_2^+$  is oxidized to  $\text{U(VI)O}_2^{2+}$ , and  $\text{CH}_3\text{COO}^-$  is produced. The  $\dot{\text{C}}\text{H}_2\text{COOH}$  radical presumably rearranges to  $\text{CH}_3\text{COO}\cdot$  before it reacts with the uranyl(V) species in reaction (4).

The rate law for the suggested mechanism is

$$\frac{d}{dt} [\text{CO}_2] = \frac{k_3 K_1 K_2 [\text{HMal}^-]_{\text{F}} [\text{UO}_2^{2+}]_{\text{T}}}{(K_1 [\text{HMal}^-]_{\text{F}} + 1)(1 + K_2)}$$

where  $[\text{HMal}^-]_{\text{F}}$  is the concentration of the free bimalonate ion in solution and  $[\text{UO}_2^{2+}]_{\text{T}}$  the total uranyl content of the solution. This rate law is in agreement with the kinetic data in Fig. 3 since it has the limiting forms:

At low  $[\text{HMal}^-]_{\text{F}}$  and constant  $[\text{UO}_2^{2+}]_{\text{T}}$ ,

$$\begin{aligned} \frac{d}{dt} [\text{CO}_2] &= \frac{k_3 K_1 K_2 [\text{HMal}^-]_{\text{F}} [\text{UO}_2^{2+}]_{\text{T}}}{1 + K_2} \\ &= \frac{k_3 K_1 K_2 [\text{HMal}^-]_{\text{T}} [\text{UO}_2^{2+}]_{\text{T}}}{(1 + K_2)(1 + K_1 [\text{UO}_2^{2+}]_{\text{T}})} \\ &= k' [\text{HMal}^-]_{\text{T}} \end{aligned}$$

At high  $[\text{HMal}^-]_{\text{F}}$  and constant  $[\text{UO}_2^{2+}]_{\text{T}}$

$$\frac{d}{dt} [\text{CO}_2] = \frac{k_3 K_2 [\text{UO}_2^{2+}]_{\text{T}}}{1 + K_2} = k''$$

The ratio  $k'/k'' = K_1/(1 + K_1 [\text{UO}_2^{2+}]_{\text{T}}) = 1.9 \times 10^2 \text{ M}^{-1}$  if  $K_1$  is taken as  $7.2 \times 10^2 \text{ M}^{-1}$  (from Fig. 3). Similarly,  $k'/k''$  can also be estimated from the values of the initial slope and limiting rate in Fig. 3. This turns out to be  $2.4 \times 10^2 \text{ M}^{-1}$ , which is reasonably close to the above value if the experimental error limits are taken into consideration.

The suggested reaction mechanism is, furthermore, in good agreement with the tendencies reported in Fig. 2. The final photolysis product, *viz.*  $\text{UO}_2^{2+}$ , is once again capable of forming a complex with bimalonate ion (equilibrium (1)), such that the complex concentration will only decrease significantly after the excess of bimalonate ion has been decomposed photochemically. At lower  $[\text{HMal}^-]$  to  $[\text{UO}_2^{2+}]$  ratios, (curves (i) and (ii) in Fig. 2) the decrease in the concentration of the uranyl bimalonate complex occurs immediately during irradiation.

No evidence for the formation of any U(IV) species could be found at low pH. The oxidation of U(V), formed in reaction (3), to U(VI) by  $\dot{\text{C}}\text{H}_2\text{COOH}$  (or  $\text{CH}_3\text{COO}\cdot$ ) is very similar to the oxidation process suggested to occur in the photolysis of the uranyl bioxalate system [4, 6]. A high yield of U(IV) was only found during the photolysis of the uranyl formate system, which is understandable since the latter process differs markedly from those for the oxalate [4] and malonate systems. The photolysis of a ring-closed uranyl malonate (1:1) complex may lead to the formation of U(IV), since such a complex is capable of undergoing a two-electron transfer reaction [4]. Some preliminary experiments at pH  $\sim 6$ , where such a complex may exist, indicated the formation of some U(IV) species. However, due to the difficulties encountered under such conditions (see earlier discussion), this aspect was not investigated any further.

The formation of  $\text{CH}_3\text{COO}^-$  or  $\text{CH}_3\text{COOH}$  as a photolysis product, has been confirmed by Heckler *et al.* [9]. Some radiochemical experiments were repeated using  $\text{HOOC}-\text{C}^{14}\text{H}_2-\text{COOH}$  as the labelled malonic acid. No radio-active gaseous photolysis products could be detected in these experiments, in agreement with the formation of acetate/acetic acid.

Finally, it is of interest to mention that in an earlier study [14] of the thermal decomposition of the tris-malonatocobalt(III) ion, the above technique led to the identification of acetaldehyde as a decomposition product.

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