942. *The Formation and Photochemical Oxidation of Uranium*(IV) *Citrate Complexes.*

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The behaviour of uranium(IV) in the presence of citric acid has been studied, and the stability constant of the complex formed measured over a pH range. The stability constants measured illustrate the effect of hydrolysis of the uranium(IV). The photochemical oxidation of uranium(IV) citrate by oxygen has been studied and compared with that of uranium(IV) tartrate obtained in the presence of tartaric acid.

NO quantitative study of the complex of citrate with uranium(IV) has been made, although that of the uranyl ion has been widely investigated. Newman *et al.*[1] postulated the uranyl citrate 1 : 1 complex as a dimer, but Heitner and Bobtelsky [2] state that at pH 7 the uranyl citrate complex is a monomer, and a value of 8·5 for log $K^{\mathrm{M}}_{\mathrm{MHL}}$ of the complex was recently reported by Li *et al.*[3]

It has long been known that the uranyl ion is active in various photochemical reductions. In Heidt and Moon's work [4] on the photochemical reduction of uranyl ion in the presence of sugars, the existence of uranium(V) in solution was discovered. This uranium(V) then disproportionated by a thermal reaction into uranium(VI) and uranium(IV). Evidence has been presented to indicate that uranium(IV) salt solutions are more rapidly oxidised by oxygen when illuminated than when allowed to oxidise by thermal dark reaction,[5] and Heal and Thomas have shown that uranium(V) is formed by a light-accelerated reaction of uranium(VI) and uranium(IV).

EXPERIMENTAL

Spectra were measured with a Unicam S.P. 500 spectrophotometer. Solutions of uranium(IV) were prepared as previously described, and a constant ionic strength of 0·1M-sodium perchlorate was maintained.[7] The stability constant of the uranium(IV) citrate complex was calculated from optical-density measurements at 6700 Å, with a small correction for the uranium(IV) absorption. The pH measurements were made by using a Pye pH meter, the solutions being kept under nitrogen and at 20° ± 0·1°. Reagents were of " AnalaR " quality where available.

For irradiation of the uranium complex solutions a 150 w tungsten lamp was held at ~20 cm. from the solutions, which were kept at room temperature. The solutions were contained in a thin-walled glass vessel and subjected to a stream of oxygen or nitrogen which was dispersed in the solutions by a glass sinter.

[1] Newman, Havill, and Feldman, *J. Amer. Chem. Soc.*, 1951, **73**, 3593.
[2] Heitner and Bobtelsky, *Bull. Soc. chim. France*, 1954, 356.
[3] Li, Lindenbaum, and White, *J. Inorg. Nucl. Chem.*, 1959, **12**, 122.
[4] Heidt and Moon, *J. Amer. Chem. Soc.*, 1953, **75**, 5803.
[5] Ushatskiĭ and Tolmachev, *Trudy Radievogo. Inst. im V.G. Khlopina Kimi Geokim.*, 1956, **7**, 98; *Chem. Abs.*, 1957, **51**, 17,467*a*.
[6] Heal and Thomas, *Trans. Faraday Soc.*, 1949, **45**, 11.
[7] Smith, *J. Inorg. Nucl. Chem.*, 1959, **11**, 314.

Results.—Addition of citric acid to solutions containing uranium(IV) at low pH's results in formation of the uranium(IV) chelate of citric acid. By quantitative observation of changes in the absorption spectra the stability constant of the chelate may be deduced. Evaluation of the stability constant involves a knowledge of the dissociation constants of citric acids, and values appropriate to this determination were those used by Warner and Weber.[8] The appropriate molar extinction coefficients were determined at 670 mμ, where the complex and uranium(IV) obeyed Beer's law. The stability constants of the uranium(IV) citrate complex were measured over a pH range 1·50—4·50. All solutions were prepared from stock solutions and absorptions were recorded immediately after the solutions were mixed. The results obtained, shown in the Table, are calculated on the basis that a 1 : 1 complex is formed and that the three carboxylic groups are ionised.

pH	U(IV) citrate	U(IV)	$[HL^{3-}]$	$\log K^{M}_{MHL}$	pH	U(IV) citrate	U(IV)	$[HL^{3-}]$	$\log K^{M}_{MHL}$
	(mmoles/l.)					(mmoles/l.)			
1·50	2·99	2·01	$2·77 \times 10^{-10}$	9·72	2·90	3·87	1·13	$2·29 \times 10^{-6}$	6·17
1·60	2·97	2·03	$5·46 \times 10^{-10}$	9·43	3·00	3·99	1·01	$4·01 \times 10^{-6}$	5·99
1·70	3·01	1·99	$1·08 \times 10^{-9}$	9·15	3·20	4·24	0·66	$1·22 \times 10^{-5}$	5·72
1·80	3·05	1·95	$2·12 \times 10^{-9}$	8·87	3·40	4·39	0·61	$3·20 \times 10^{-5}$	5·35
1·90	3·10	1·90	$4·16 \times 10^{-9}$	8·59	3·60	4·50	0·50	$8·13 \times 10^{-5}$	5·04
2·00	3·14	1·86	$8·12 \times 10^{-9}$	8·32	3·80	4·57	0·43	$2·65 \times 10^{-4}$	4·60
2·20	3·23	1·77	$2·22 \times 10^{-8}$	7·91	3·90	4·61	0·39	$2·89 \times 10^{-4}$	4·61
2·40	3·34	1·66	$1·38 \times 10^{-7}$	7·16	4·00	4·67	0·33	$7·80 \times 10^{-4}$	4·52
2·60	3·49	1·51	$3·87 \times 10^{-7}$	6·78	4·30	4·76	0·24	$7·80 \times 10^{-4}$	4·40
2·70	3·62	1·38	$7·14 \times 10^{-7}$	6·57	4·40	4·80	0·20	$1·76 \times 10^{-3}$	4·15
2·80	3·72	1·28	$1·31 \times 10^{-6}$	6·34	4·50	4·81	0·19	$2·32 \times 10^{-3}$	3·93

At pH's above 7·5 the uranium(IV) citrate solution darkened, and if stored for a few days in the dark formed a black solution of colloidal uranium(IV) hydroxide stabilised by the presence of the citric acid.

It was established that a uranium(IV) citrate solution at pH 4·5 irradiated by a tungsten lamp and exposed to oxygen became oxidised. These changes were followed spectrophotochemically and are illustrated in Fig. 1. The reduction of the peak at 665 mμ indicates the decrease in the concentration of uranium(IV) citrate. Curve *B* indicates that the most significant changes occur within 24 hr. of the commencement of irradiation. However, in the region 370—400 mμ a high absorption occurs which cannot be explained in terms of an absorption by single uranium(IV) or uranium(VI) species. Irradiation of a uranium(VI) citrate solution in the absence of oxygen resulted in complete reduction to uranium(IV) citrate, but reduction was only partial if a similar solution was irradiated in a stream of oxygen (as shown by Fig. 2) and the resulting yellow solution did not yield simple uranyl ions upon addition of acid.

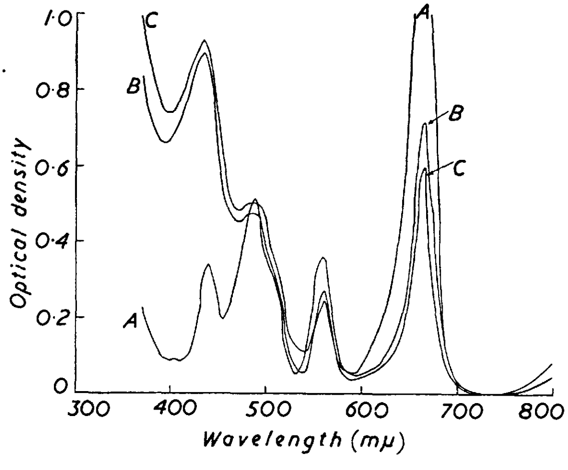

FIG. 1. *Irradiation of a* 5·0 × 10^{-3}M-*solution of uranium*(IV) *citrate at* pH 5·0 *containing* 7·5 × 10^{-2}M-*citrate*; 4 *cm. cell.* (*A*) *Before irradiation*; (*B*) *after* 24 *hr.*; (*C*) *after* 144 *hr.*

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[8] Warner and Weber, *J. Amer. Chem. Soc.*, 1953, **75**, 5086.

A possible explanation is that the uranium(VI) present in these solutions underwent a photochemical hydrolysis to polymeric forms not easily decomposed by acids.

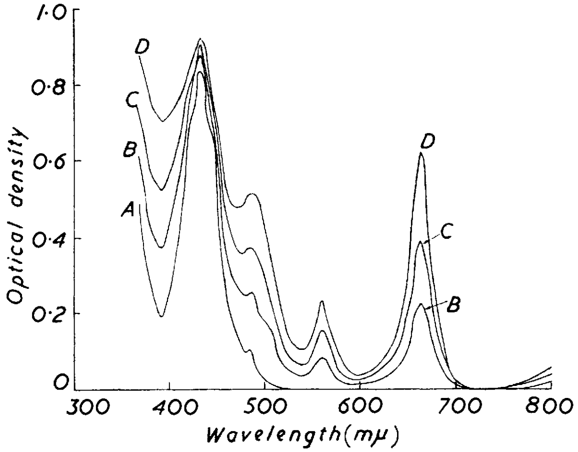

FIG. 2. *Irradiation of a* 5·0 × 10^{-3}M-*solution of uranium*(VI) *citrate at* pH 5·0 *containing* 7·5 × 10^{-2}M-*citrate*; 4 *cm. cell.* (*A*) *Before irradiation*, (*B*) *after* 24 *hr.*; (*C*) *after* 48 *hr.*; (*D*) *after* 120 *hr.*

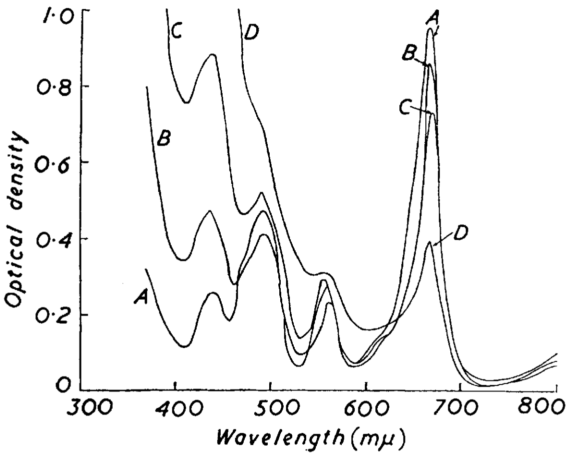

FIG. 3. *Irradiation of a* 5·0 × 10^{-3}M-*solution of uranium*(IV) *tartrate at* pH 5·0 *containing* 7·5 × 10^{-2}M-*tartrate*; 4 *cm. cell.* (*A*) *Before irradiation*, (*B*) *after* 24 *hr.*; (*C*) *after* 48 *hr.*; (*D*) *after* 144 *hr.*

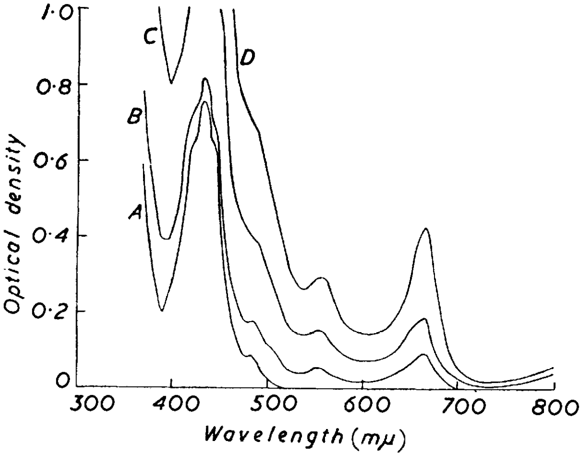

FIG. 4. *Irradiation of a* 5·0 × 10^{-3}M-*solution of uranium*(VI) *tartrate at* pH 5·0 *containing* 7·5 × 10^{-2}M-*tartrate*; 4 *cm. cell.* (*A*) *Before irradiation*, (*B*) *after* 24 *hr.*; (*C*) *after* 48 *hr.*; (*D*) *after* 120 *hr.*

In order to elucidate this aspect of the photochemical changes, similar irradiations were carried out with tartrate as a complexing agent. These changes, shown by Figs. 3 and 4, are similar to those obtained in the case of citric acid, though the absorption due to hydrolytic polymer of uranium(VI) was much greater. Fig. 5 shows the effect of acid added to uranium(IV) tartrate after a prolonged irradiation and the difficulty in regaining a single uranium(VI) solution. The colour of the uranium tartrate solution after prolonged irradiation was dark brown, the pH having changed from the original 4·50 to 7·50. An additional feature of this system, however, is that, when stored in the dark, the brown tartrate solution became yellow though a simple uranyl-ion solution was not obtained and no uranium(IV) was present. The brown colour could be formed again by still further irradiation, though no photoreduction took place.

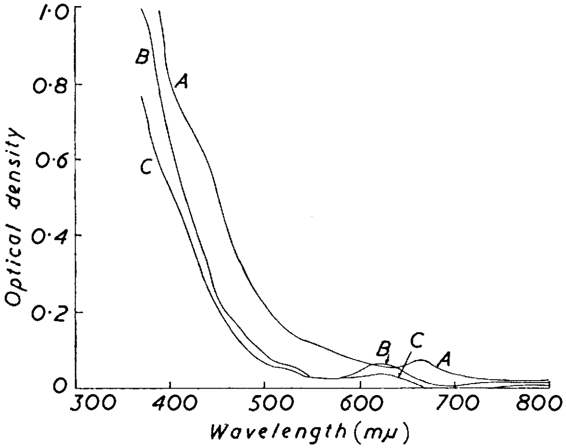

FIG. 5. *Prolonged irradiation of* 5·0 × 10^{-3}M-*solution of uranium*(IV) *tartrate.* (*A*) *6 weeks' irradiation*; *1 cm. cell*; (*B*) *4 cm. cell, acid added to* pH 1·0; (*C*) *acid added to a final concentration of* 1N, *4 cm. cell.*

These changes may be explained by the formation of a simple hydrolytic polymer of uranium which on further irradiation undergoes a greater degree of hydrolytic action which is reversed on standing in the dark.

DISCUSSION

Most determinations of the stability constants of citric acid complexes have involved the representation of the reagent as a tridentate ligand. Warner and Weber[8] have shown that this acid may behave as a tetradentate molecule even when no excess is present. In the case of uranium(IV) an excess of reagent is required to prevent hydrolytic precipitation of the cation, whilst even in these conditions hydrolytic polymerisation takes place above pH's of about 8. It seems likely, therefore, that the reagent behaves as a tridentate ligand.

Amongst the chief difficulties is the complicated behaviour of uranium(IV) ions upon hydrolysis, which makes it extremely difficult to know precisely the hydrolytic state of the uranium(IV) in its complexes with citrate. The equilibrium may be represented as follows, where the uranium is taken as being essentially in the form of a 1 : 1 complex:

$$\mathrm{U(OH)}_n{}^{(4-n)+} + \mathrm{HL}^{3-} \rightleftharpoons [\mathrm{U(OH)}_n\mathrm{HL}]^{(1-n)+}$$

However, evidence has been presented for the formulation of the corresponding thorium citrate complex as $[\mathrm{Th(OH)}]_2\mathrm{Cit}_3$ which involves the bridging of two 1 : 1 complexes by a third citrate anion, and a similar formulation may be used for the uranium(IV) complex.[9]

A plot of log $K^{\mathrm{M}}_{\mathrm{MHL}}$ against pH and extrapolation to 1N-acid, where little hydrolysis of uranium(IV) occurs, gives a value of about 13·5 for log $K^{\mathrm{M}}_{\mathrm{MHL}}$, which compares with that given for iron(III). The fall in the value of log $K^{\mathrm{M}}_{\mathrm{MHL}}$ may be attributed to the increasing hydrolysis of uranium(IV) with pH, such that at pH 4·5 the value is similar to that given for bivalent cations[10] and that the complex would approximate to $\mathrm{U(OH)_2HL^{1-}}$.

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[9] Bobtelsky and Goldschmidt, *Bull. Res. Council Israel*, 1958, **7***A*, 123.
[10] " Stability Constants, Part 2," *Chem. Soc. Special Publ.* No. 7, 1957.

In the absence of air no photochemical oxidation of uranium(IV) complexes takes place, but irradiation with visible light causes almost quantitative reduction of uranium(VI) citrate complex. However, on admission of oxygen to solutions of uranium(IV) citrate a photochemical oxidation begins: the process does not go to completion, the greatest change occurring in the first 24 hr.

The photo-oxidation competes with the photo-reduction and so, in oxygen, a state of equilibrium would exist. However, the hydrolytic polymer of uranium(VI) generated by photochemical action upsets the equilibria by removal of simple uranium(VI) species to forms not easily broken up, even by acid. The development of this hydrolytic polymerised form of the uranium(VI) complex renders the quantitative study of these changes difficult. Nevertheless, a possible mechanism for the photo-oxidation by oxygen is outlined in the following scheme which resembles one suggested by Posner [11] to account for the oxidation of iron(II) by oxygen:

$$\mathrm{HLU(OH)_2{}^{1-}} \xrightarrow{h\nu} \mathrm{HLUO{\cdot}OH^{1-}} + \mathrm{H} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\mathrm{HLUO{\cdot}OH^{1-}} \longrightarrow \mathrm{HLUO_2{}^{2-}} + \mathrm{H^+} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$\mathrm{HLUO_2{}^{2-}} + {\cdot}\mathrm{O_2H} \longrightarrow \mathrm{HLUO_2{}^{1-}} + \mathrm{O_2H^-} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$\mathrm{O_2H^-} + \mathrm{H^+} \longrightarrow \mathrm{H_2O_2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

$$\mathrm{H_2O_2} + \mathrm{HLUO_2{}^{2-}} \longrightarrow {\cdot}\mathrm{OH} + \mathrm{OH^-} + \mathrm{HLUO_2{}^{1-}} \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

$$\mathrm{HLUO_2{}^{2-}} + {\cdot}\mathrm{OH} \longrightarrow \mathrm{OH^-} + \mathrm{HLUO_2{}^{1-}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

Process (1) involves a photochemically produced hydrogen atom, which combines rapidly [12] with oxygen to produce the hydroperoxy-radical $\cdot\mathrm{O_2H}$, and the uranium(V) complex is formed as in (2). Uranium(VI) is then formed by electron transfer from uranium(V) to the radical $\cdot\mathrm{O_2H}$ as in (3). This finally leads to hydrogen peroxide (4) which may give rise to further oxidation. An alternative or concurrent scheme would involve the production of uranium(V), followed by its disproportionation into quadri- and sexi-valent forms. The hydrolytic polymerisation of the uranium(VI) complex then gradually removes uranium(VI) from taking part in the series of reactions concerned with photoreduction.

A similar series of reactions may occur to account for the photochemical oxidation by oxygen of the uranium(IV) tartrate system, though here the photochemical hydrolytic polymeristion of the uranium(VI) tartrate plays a more important rôle, the colour of the final solution being deep brown. Only in the case of an amino-carboxylic acid such as nitrilotriacetic acid, was a photochemical oxidation by oxygen obtained substantially free from the complication of hydrolytic uranium(VI) products, and upon addition of acid a simple uranium(VI) solution was produced. This will be an inevitable consequence of the stronger chelating properties of these reagents which enable the products to resist hydrolysis.

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[11] Posner, *Trans. Faraday Soc.*, 1953, **49**, 382.

[12] Dainton and Hardwick, *Trans. Faraday Soc.*, 1957, **53**, 333.