Some Observations on the 8-Quinolinol and 5,7-Dihalo-8-quinolinol Chelates of Uranium(VI)

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Uranium(VI), like thorium,[1,2] plutonium(VI)[3] and scandium,[4] forms with 8-quinolinol both a normal chelate and a chelate containing an added mole of reagent.[1] The latter, a red compound of composition $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$, is obtained by direct precipitation at controlled *p*H[1,5–9] and is converted into the green normal chelate by heating at 210–215°.[9–11] The red compound is useful for the gravimetric determination of uranium, and colorimetric methods based upon extractions into chloroform and measurement at 400, 420 or 440 mμ[12] or at 425 mμ[13] have been described. No data upon comparable chelates derived from substituted 8-quinolinols appear to have been published.

Inasmuch as investigations upon the 8-quinolinol[2] and 5,7-dihalo-8-quinolinol[14] chelates of thorium have indicated differences between the normal compounds and those containing an extra mole of reagent to be restricted to the solid state and have shown that enhanced resistance to hydrolytic decompositions is effected by inclusion of halogens, it has been of interest to extend these studies to the comparable uranium(VI) systems. A detailed study of absorption spectra of non-aqueous solutions of these compounds has been prompted further by the fragmentary published data of this type[12,13] and by the use of wave lengths not corresponding to absorption bands for colorimetric determinations.[12,13]

Experimental

Materials Used.—All chelates were prepared from a sample of dioxouranium(VI) nitrate 6-hydrate of analytical reagent quality. The 8-quinolinol type reagents were analytical quality materials obtained from the Eastman Kodak Co. and the Matheson Co. and were purified prior to use by recrystallization from acetone and ethanol. Other chemicals were of reagent quality and were used without further treatment. The uranium(VI) stock solution employed contained 30.64 mg. uranium/ml. Substituted 8-quinolinols were used as acetone solutions containing 3 g. of reagent per liter.

Apparatus.—All absorption spectra were measured at *ca.* 25° with a Cary Recording Spectrophotometer, using 5.0 cm. demountable cells with quartz windows. All *p*H measurements were made with a Beckman Model G *p*H meter.

Preparation of Chelates.—The 1 to 3 and 1 to 2 8-quinolinol chelates were prepared as outlined by Moeller and Wilkins.[9] Preliminary experiments showed that although the 5,7-dihalo-8-quinolinols studied give both 1 to 3 and 1 to 2 chelates with dioxouranium(VI), the latter type cannot be obtained pure by thermal decomposition of the former. Instead, as is true with thorium,[11] separate reactions in the 1 to 3 and 1 to 2 stoichiometries under carefully controlled conditions are necessary. For each compound, the conditions employed were those yielding the product of highest purity with quantitative uranium recovery. In no instance did the difficulties of manipulation permit preparation of more than one gram of product in a single batch. All products were analyzed for uranium by igniting with oxalic acid and weighing as the oxide U_3O_8 and for carbon, hydrogen, nitrogen and halogen by the usual microanalytical techniques.

The following general procedure is applicable to all of the dihalo-type chelates: To 5 ml. of the standard dioxouranium(VI) nitrate solution 5 ml. of 2 *M* hydrochloric acid solution and 200 ml. of water are added. To this solution is added the calculated quantity of 0.3% solution of the 8-quinolinol type reagent in acetone. The *p*H is raised to the optimum value (6 for the 1:3 dichloro compound, 9 for the 1:2 chloroiodo compound, and 8 for the others) by slow addition of 2 *M* aqueous ammonia with vigorous mechanical stirring. The acetone concentration is reduced to 30% by dilution with water. Stirring is continued for 10 min., and the suspension is digested 10–15 min. on the steam-bath, evaporation of acetone being minimized by covering the container with a watch glass. The cooled suspension is filtered through a fine porosity sintered glass crucible and washed until chloride-free with 10% acetone in water. The air-dried product is dried in the oven for 2–3 hr. (at 85–90° for the 1:3 chelates; 100–110° for the 1:2 chelates).

Anal. Calcd. for $UO_2(C_9H_6NO)_2$: C, 38.74; H, 2.16; N, 5.02; U, 42.7. Found: C, 39.46; H, 2.26; N, 5.21; U, 42.20. Calcd. for $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$: C, 46.09; H, 2.72; N, 5.97. Found: C, 46.29; H, 2.90; N, 5.99.

Calcd. for $UO_2(C_9H_4Cl_2NO)_2$: C, 31.06; H, 1.16; N, 4.03; Cl, 20.36; U, 34.30. Found: C, 30.71; H, 1.66; N, 3.78; Cl, 20.53; U, 33.00. Calcd. for $UO_2(C_9H_4Cl_2NO)_2 \cdot C_9H_4Cl_2NOH$: C, 35.63; H, 1.44; N, 4.62; Cl, 23.36; U, 26.22. Found: C, 35.42; H, 1.68; N, 4.20; Cl, 23.13; U, 26.10.

Calcd. for $UO_2(C_9H_4Br_2NO)_2$: C, 24.73; H, 0.91; N, 3.21; Br, 36.60, U, 27.20. Found: C, 25.44; H, 1.56; N, 2.91; Br, 35.24; U, 26.53. Calcd. for $UO_2(C_9H_4Br_2NO)_2 \cdot C_9H_4Br_2NOH$: C, 27.55; H, 1.11; N, 3.57; Br, 39.90; U, 20.22. Found: C, 27.63; H, 1.47; N, 3.44; Br, 39.96; U, 21.00.

Calcd. for $UO_2(C_9H_4ClIO)_2$: C, 24.60; H, 0.91, N, 3.19; U, 27.10. Found: C, 23.66; H, 1.69; N, 2.54; U, 25.41.[15]

Absorption Spectra Measurements.—All solutions for these studies were prepared in the dark room under red light from weighed samples of the chelates. These solutions were protected from light until measured in the spectrophotometer. Under these conditions photochemical decompositions were unimportant.

Results and Discussion

Preparation of Chelates.—Although both 1 to 3 and 1 to 2 type chelates are obtained, conversion of the former to the latter by heat is quantitative only when unsubstituted 8-quinolinol is used. As was found with the thorium compounds,[14] the presence of halogen decreases water solubility and increases thermal stability.

Absorption Spectra Studies.—The absorption spectra of solutions of these chelates are generally similar to those reported for the corresponding thorium compounds.[2,14] In every instance, spectra for solutions of the 1 to 3 and 1 to 2 derivatives of a given chelating agent differed only in absorption intensities. These observations indicate that the 1 to 3 and 1 to 2 compounds possess different identities only in the solid state and are not inconsistent with the view already advanced for the

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[13] B. Hök, *Svensk Kem. Tid.*, **65**, 106 (1953).

[14] T. Moeller and M. V. Ramaniah, This Journal, **76**, 2022 (1954).

[15] The 1 to 3 chloroiodo chelate could not be obtained in a state of purity.

comparable thorium materials[2,14] that the distinguishing mole of 8-quinolinol reagent is held in the solid by lattice forces.

Spectra of chloroform solutions of the chelates, as shown in Fig, 1, suggest that hydrolytic decompositions, although measurable, are less pronounced than with the corresponding thorium compounds.[2,14] As with thorium,[2,14] introduction of halogen decreases hydrolysis, but in no instance could rigorous adherence to Beer's law be obtained. Absolute ethanol solutions of the uranium(VI) chelates give spectra more nearly free from hydrolysis effects, as shown in Fig. 2, and are markedly more resistant to the addition of water. That such solutions give only minor deviations from Beer's law is apparent from the following data: $UO_2(C_9H_6NO)_2$: 2.5–12.5 mg. U/l., $k_{\text{av.}}$[16] at 3340 Å. = 17.8, $k_{\text{av.}}$ at 3760 Å. = 20.8; $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$[17]: 2.5–12.5 mg. U/l., $k_{\text{av.}}$ at 3340 Å. = 24.5, $k_{\text{av.}}$ at 3760 Å. = 24.2; $UO_2(C_9H_4Cl_2NO)_2$: 2.5–10.0 mg. U/l., $k_{\text{av.}}$ at 3420 Å. = 24.5, $k_{\text{av.}}$ at 3900 Å. = 30.4; $UO_2(C_9H_4Cl_2NO)_2 \cdot C_9H_4Cl_2NOH$: 2.5–12.5 mg. U/l., $k_{\text{av.}}$ at 3420 Å. = 35.5, $k_{\text{av.}}$ at 3900 Å. = 33.9; $UO_2(C_9H_4Br_2NO)_2$: 2.0–10.0 mg./l., $k_{\text{av.}}$ at 3420 Å. = 24.9, $k_{\text{av.}}$ at 3920 Å. = 31.3; $UO_2(C_9H_4Br_2NO)_2 \cdot C_9H_4Br_2NOH$: 2.0–10.0 mg. U/l., $k_{\text{av.}}$ at 3420 Å. = 37.0, $k_{\text{av.}}$ at 3920 Å. = 35.9; $UO_2(C_9H_4ClINO)_2$: 2.0–10.0 mg. U/l., $k_{\text{av.}}$ at 3460 Å. = 23.6, $k_{\text{av.}}$ at 3950 Å. = 26.6.

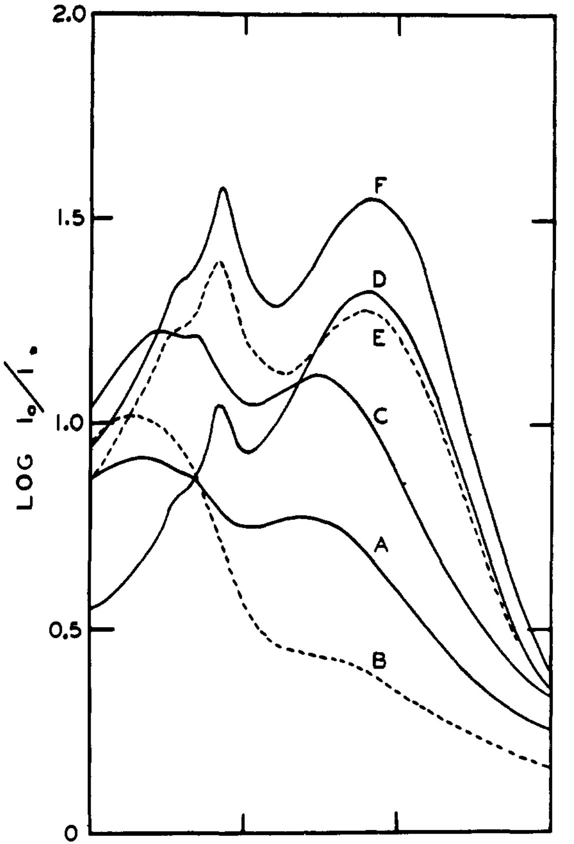

Fig. 1.—Absorption spectra of chloroform solutions of typical chelates: A, $UO_2(C_9H_6NO)_2$, 10 mg. U/l.; B, same as A with 1 drop water; C, $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$, 10 mg. U/l.; D, $UO_2(C_9H_4Cl_2NO)_2$, 10 mg. U/l.; E, $UO_2(C_9H_4Cl_2NO)_2$, 12.5 mg. U/l. with one drop water; F, $UO_2(C_9H_4Cl_2NO)_2.C_9H_4Cl_2NOH$, 10 mg. U/l.

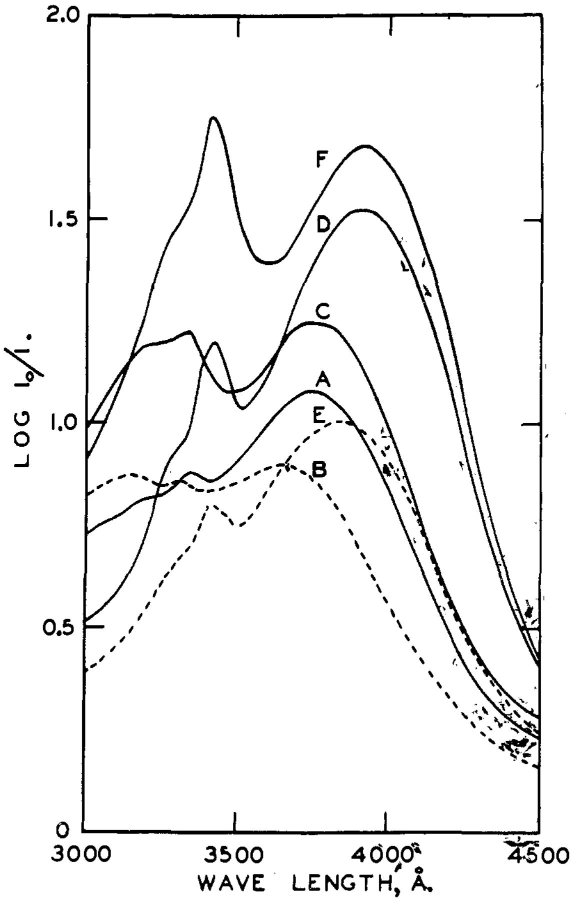

Fig. 2.—Absorption spectra of absolute ethanol solutions of typical chelates: A, $UO_2(C_9H_6NO)_2$, 10 mg. U/l.; B, same as A with 50% water by volume; C, $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$, 10 mg. U/l.; D, $UO_2(C_9H_4Cl_2NO)_2$, 10 mg. U/l.; E, $UO_2(C_9H_4Cl_2NO)_2$, 7.5 mg. U/l. with 50% water by volume; F, $UO_2(C_9H_4Cl_2NO)_2 \cdot C_9H_4Cl_2NOH$, 10 mg. U/l.

It is apparent that solutions of the uranium(VI) chelates do not absorb light as strongly as do solutions of their thorium analogs.[2,14] It follows that any spectrophotometric determinations of uranium by means of these chelates must be correspondingly less sensitive. It is also apparent that the wave lengths suggested for spectrophotometric determination of uranium(VI) with 8-quinolinol[12,13] are on descending branches of the absorption curve (Fig. 1) and are therefore very sensitive to exact wave length adjustment and reading.

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[16] Specific extinction, *k*, is given by the relationship $k = (\log I_0/I)/cl$, *l* being in cm. and *c* being expressed as g. U/liter.

[17] B. Hök, ref. 13, reports major absorption at 370 mμ and minor absorption at *ca.* 335 mμ in chloroform.