and Shomate's[6] heat of formation value for manganomanganic oxide (−331,300 ± 250 cal./mole, after applying a minor correction).

The impurity corrections also were calculated from the above heat of formation values. The compositions assumed for these corrections were: for Mn_5N_2, 0.44% MnO, 0.80% Mn and 98.76% Mn_5N_2; for Mn_4N, 0.40% MnO, 1.30% Mn and 98.30% Mn_4N. These proportions conform with the chemical analyses.

The mean value of the heat of combustion of Mn_5N_2 corresponds to $\Delta E_{303.15} = -502.36$ kcal./mole under bomb conditions. Corrections to unit fugacities of oxygen and nitrogen (−215 cal.), to a constant pressure process (−1406 cal.), and to 298.15°K. (−6 cal.) gives $\Delta H_{298.15} = -503.99 \pm 0.40$ kcal./mole as the standard heat of combustion of Mn_5N_2. Combination with the heat of formation of manganomanganic oxide (−331.3 kcal.) leads to $\Delta H_{298.15} = -48.2 \pm 0.6$ kcal./mole as the standard heat of formation of Mn_5N_2 from the elements.

Similarly, the mean heat of combustion of Mn_4N yields $\Delta E_{303.15} = -409.94$ kcal./mole under bomb conditions. Corrections to unit fugacities (−195 cal.), to constant pressure (−1305 cal.) and to 298.15°K. (−4 cal.) gives $\Delta H_{298.15} = -411.44 \pm 0.20$ kcal./mole as the standard heat of combustion of Mn_4N. Again, combining with the heat of formation of manganomanganic oxide gives $\Delta H_{298.15} = -30.3 \pm 0.4$ kcal./mole as the standard heat of formation of Mn_4N from the elements.

The value of the heat of formation of Mn_4N does not differ greatly from that similarly obtained by Neumann and co-workers[3] for material of composition $Mn_{4.74}N$ (−31.2 kcal.). The present value for Mn_5N_2, however, deviates widely from their result (−57.8 kcal.), which was obtained by the direct nitriding of manganese (containing 0.25% hydrogen) in a bomb calorimeter.

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[6] C. H. Shomate, THIS JOURNAL, **65**, 785 (1943).

[CONTRIBUTION FROM ARTHUR D. LITTLE, INC., WESTERN DIVISION]

The Nature of Uranyl 8-Quinolinolate[1]

BY E. P. BULLWINKEL AND PAUL NOBLE, JR.

RECEIVED FEBRUARY 21, 1957

It is shown that the three moles of 8-quinolinol in the uranyl 8-quinolinolate are coördinated in an equivalent manner and that the acidic nature of this chelate is best represented by the formula $H(UO_2(C_9H_6NO)_3)$, where the anions, $UO_2(C_9H_6NO)_3^{-1}$, are linked together by hydrogen bonding of the uranyl oxygens. The uranyl tri-8-quinolinolate anion is shown to be stable in alkaline solutions and to form stable salts with cations, such as Na^+, R_4N^+ and $(C_6H_5)_4As^+$. The absorption spectra of aqueous alkaline solutions of the uranyl tri-8-quinolinolate anion and chloroform solutions of the tetraphenylarsonium salt of this anion are reported. The chemical behavior of the uranyl di-8-quinolinolate is reported and discussed with respect to its possible structure.

It has long been known that uranium forms two compounds with 8-quinolinol, one of which contains an "added mole of reagent."[2] The red compound of composition $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ is easily obtained by direct precipitation at controlled *p*H and is converted into the green "normal" chelate $UO_2(C_9H_6NO)_2$ by heating at 210–215°.[3] In the course of an investigation in this Laboratory concerning possible uranium chelating agents,[4] it was observed that the addition of 8-quinolinol to sodium carbonate solutions of the very stable uranium complex, $UO_2(CO_3)_3^{-4}$, causes the uranium to precipitate as an orange solid, which contains sodium. This interesting precipitate, later identified as $Na(UO_2(C_9H_6NO)_3)$, and the fact that the precipitation only occurs in carbonate solutions at an elevated *p*H (11–12) led to the studies presented below.

Treatment of solid $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ with dilute sodium hydroxide (∼0.01 *M*) leads to its dissolution and the formation of an intense red solution. Such solutions are decomposed at higher hydroxide ion concentrations to yield the familiar yellow solutions of the 8-quinolinolate ion and a precipitate of orange U(VI) uranates.[5] This behavior of $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ leads to the strong presumption that this chelate is an acid. In support of this presumption, it was found that the soluble red complex could be precipitated from alkaline solution by providing suitable concentrations of various cations, *e.g.*, Na^+, R_4N^+, $(C_6H_5)_4As^+$.[6] These precipitates were shown by analysis to have the general composition $M^IUO_2(C_9H_6NO)_3$ where M^I is a monovalent cation. It was further observed that the soluble red complex could be extracted readily from aqueous alkaline solutions into organic solvents ($CHCl_3$, MIBK) when quaternary ammonium or arsonium cations were present, *but not when these organic cations were absent*. This fact, when considered in conjunction with the analyses mentioned above, certainly implies that the soluble red complex is the anion, $UO_2(C_9H_6NO)_3^{-1}$.

Titration of the red uranyl 8-quinolinolate, $H(UO_2(C_9H_6NO)_3)$, in acetonitrile with potassium methoxide led to the results in Fig. 1. Here the acidity of the chelate is compared under identical conditions with 8-quinolinol and benzoic acid. These results demonstrate conclusively that the ex-

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[1] Work reported here was carried out under Contract AT(49-6)-923, for the Atomic Energy Commission.

[2] F. J. Frere, THIS JOURNAL, **55**, 4362 (1933).

[3] T. Moeller and D. H. Wilkins, *Inorg. Syntheses*, **4**, 101 (1953). See also ref. 10 for earlier references.

[4] W. E. Clifford, P. Noble, Jr., and E. P. Bullwinkel, A. E. C. Report RMO-2623.

[5] J. E. Ricci and F. J. Loprest, THIS JOURNAL, **77**, 2119 (1955).

[6] Salts prepared by this method are not of high purity. Improved methods of synthesis are presented in the Experimental Section.

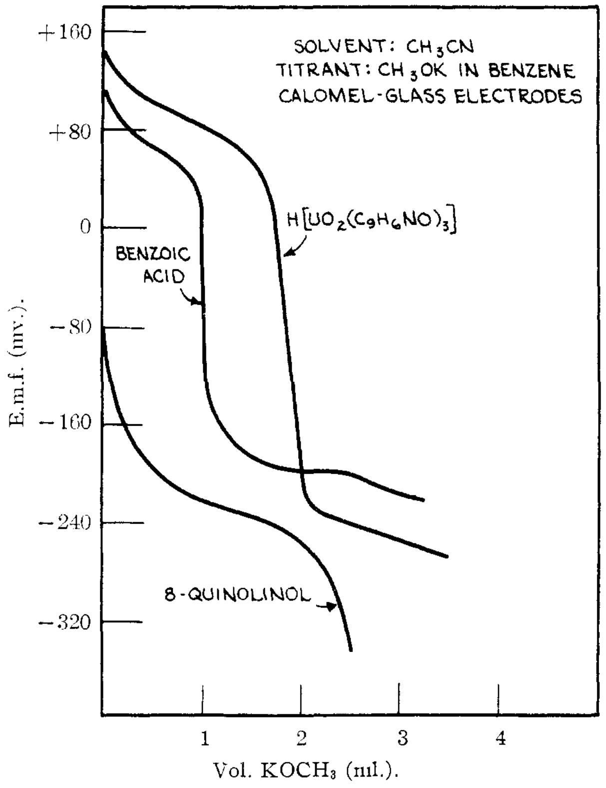

Fig. 1.—Relative acid strength of uranyl 8-quinolinolate. The compounds were dissolved in acetonitrile (0.2 mmole except benzoic acid, 0.1 mmole) and titrated with 0.1 *M* potassium methoxide in benzene.

tra mole of 8-quinolinol of the chelate is not comparable in acid strength to 8-quinolinol itself. In fact, the chelate is considerably more acidic. It is further seen from Fig. 1 that the results are in accord with the stoichiometric equation

$$H(UO_2(C_9H_6NO)_3) + CH_3O^{-1} \longrightarrow UO_2(C_9H_6NO)_3^{-1} + CH_3OH$$

The red acid chelate may also be titrated quantitatively in aqueous solution. However, the insolubility of the acid chelate requires the use of elevated temperatures (70°).

From the foregoing, it would appear that the *three* moles of 8-quinolinol in the red complex are equivalent in coördinating the uranyl ion in the solid as well as in solution. A plausible structure for the anion portion of this complex is shown in Fig. 2, where the complex anion is viewed along the O–U–O axis of the linear uranyl ion. This structure is consistent with the strong tendency for the uranyl ion to exhibit hexa-coördination about the equator of the uranium, providing that the spatial requirements are sufficient.[7,8] In support of the proposed structure, an entirely analogous structure has been found in the case of the uranyl chelate of cupferron,[9] $NH_4(UO_2(Cup)_3)$.

We further propose that in the acid form of the

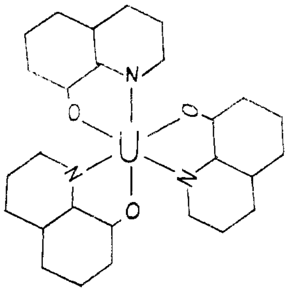

Fig. 2.—Proposed structure of the anion, $UO_2(C_9H_6NO)_3^{-1}$, viewed along the O–U–O axis (the two uranyl oxygens, lying above and below the uranium have been omitted).

chelate, $H(UO_2(C_9H_6NO)_3)$, the acidic hydrogens are attached to the uranyl oxygens to form long chains of the type . . .O–U–O. . .H. . .O–U–O. . .H- . . .O–U–O. Such a hydrogen bonded structure would certainly explain the low solubility of $H(UO_2(C_9H_6NO)_3)$ in various organic solvents as contrasted to that observed for organic salts of this complex.[5]

The absorption spectra of aqueous alkaline solutions of the uranyl tri-8-quinolinolate anion, $UO_2(C_9H_6NO)_3^{-1}$, and chloroform solutions of the tetraphenylarsonium salt of this anion are shown in Fig. 3. As expected, the tetraphenylarsonium salt spectrum is in good agreement with that re-

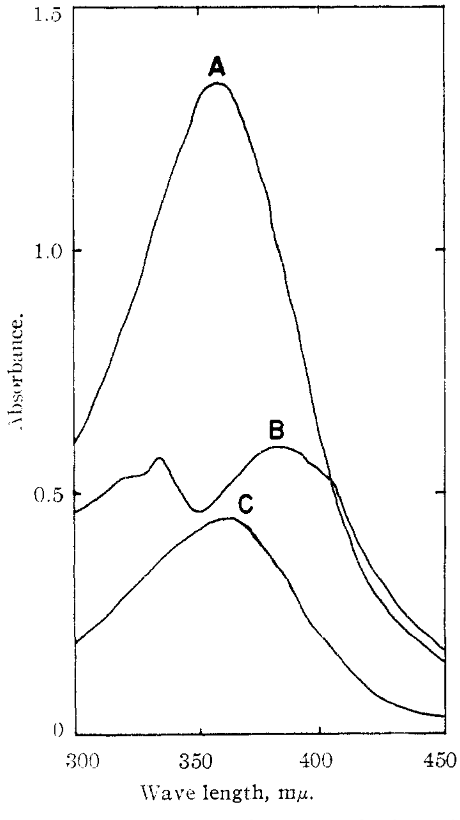

Fig. 3.—Absorption spectra of the uranyl tri-8-quinolinolate anion, $UO_2(C_9H_6NO)_3^{-1}$: A, 2.0 × 10^{-3} *M*, aq. soln. (0.1 cm. cell); B, $(C_6H_5)_4As^+$ salt, 1.82 × 10^{-4} *M*, $CHCl_3$ soln. (1 cm. cell); C, 1.62 × 10^{-2} *M*, aq. soln. (2.5 × 10^{-3} cm. cell).

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[7] A. F. Wells, "Inorganic Chemistry," 2nd Ed., Oxford Univ. Press, London, 1950.

[8] G. T. Seaborg and J. J. Katz, "The Actinide Elements," Chapt. 18 by W. H. Zachariasen, McGraw-Hill Book Co., New York, N. Y., 1954.

[9] W. S. Horton, THIS JOURNAL, **78**, 897 (1956).

ported for chloroform solutions of the parent acid,[10] $H(UO_2(C_9H_6NO)_3)$. However, the spectrum of the complex anion in aqueous solution is more intense and lacks structure compared to that observed for chloroform solutions of the anion. It is suggested that this difference arises from charge transfer effects between the anion and water. At any rate, the difference is much greater than can be accounted for by various hydrolysis reactions.

Recently, the spectra of the di- and tri-8-quinolinolates of U(VI) in chloroform and ethanol were investigated by Moeller and Ramaniah.[10] They conclude that the data are not inconsistent with the view advanced for the structures of the comparable thorium compounds,[11] namely, that the third mole of 8-quinolinol exists only in the solid state and is held by weak lattice forces. The evidence advanced for this structure of the uranyl 8-quinolinolates depends principally upon the absorption spectra obtained. The spectra of the two uranyl 8-quinolinolates reportedly differed only in absorption intensities. It is our hypothesis that the spectra observed are in reality those of the completely coördinated chelate, $UO_2(C_9H_6NO)_3^{-1}$, and that the decrease in intensity of the spectra for a solution of the di-8-quinolinolate, $UO_2(C_9H_6NO)_2$, is due to a lower concentration of the tri-8-quinolinolate in solution formed by *complete* decomposition of the dichelate.[12]

This decomposition would be in accordance with the reaction

$$3UO_2(C_9H_6NO)_2 \xrightarrow{\text{solvent}} UO_2^{++}\text{ (solvated)} + 2UO_2(C_9H_6NO)_3^{-1}$$

The molar extinction coefficient of UO_2^{++} in the region 3000–4000 Å. is very small (~60–10) compared to that of $UO_2(C_9H_6NO)_3^{-1}$ (~5000). Therefore, the observed absorbancies may be attributed entirely to $UO_2(C_9H_6NO)_3^{-1}$. From the stoichiometry of the above reaction, one would expect that the absorbance ratio of $UO_2(C_9H_6NO)_2$ to $H(UO_2(C_9H_6NO)_3)$ in solutions of the *same* uranium concentration should equal $^2/_3$. This expectation is approximately borne out by the data presented in Table I which have been calculated from the spectra given by Moeller and Ramaniah.[10]

TABLE I

Wave length, Å.	$UO_2(C_9H_6NO)_2/H(UO_2(C_9H_6NO)_3)$ Absorbance ratios	
3340	0.7	0.7
3760	0.6	0.8

This explanation is of course an oversimplification since the possibility of various solvolysis reactions has been ignored.

Some observations on the chemical behavior of the "normal" green chelate, $UO_2(C_9H_6NO)_2$, are presented in Table II (Experimental section). The high temperatures used in the preparation of this compound and its unusual color (for a uranyl chelate) led us initially to question whether this compound actually contains +6 uranium.[13] However, a careful investigation of this question showed conclusively that this compound contains only +6 uranium.

All attempts to prepare the green dichelate by precipitation from aqueous solution failed.[14] Indeed, the fact that the reaction

$$3UO_2(C_9H_6NO)_2\text{ (s)} + 2H^+ \longrightarrow 2H(UO_2(C_9H_6NO)_3)\text{ (s)} + UO_2^{++}$$

is essentially quantitative in dilute acid offers little promise that this dichelate can ever be prepared from aqueous solutions. More esoteric attempts at synthesis of this chelate also failed, such as

$$UO_3(s) + 2H(UO_2(C_9H_6NO)_3) \xrightarrow[\text{reflux}]{CHCl_3} 3UO_2(C_9H_6NO)_2 + H_2O$$

The behavior of the "normal" chelate suggests that it is not made up of simple $UO_2(C_9H_6NO)_2$ molecules but rather that it is an "infinite type" complex[7,8] with extensive polymerization of the uranyl groups. Its true nature must await X-ray studies.[15]

Experimental

Materials Used.—The chelates were prepared from reagent grade uranyl nitrate hexahydrate. The 8-quinolinol was analytical quality obtained from the Eastman Kodak Co. The acetonitrile was obtained from Matheson, Coleman & Bell, Inc., and carefully fractionated prior to use. The $KOCH_3$ solution was prepared from analytical reagents without further purification.[16]

Apparatus.—The titrations were carried out in a magnetically stirred, nitrogen flushed vessel. The electrodes were arranged so that the fiber tip of the calomel electrode was almost touching the bulb of the glass electrode. The e.m.f. measurements were made with a Beckman Model H2 *p*H meter. Erratic meter fluctuations were avoided by "grounding" the titration vessel and magnetic stirrer to the *p*H meter chassis.

A Beckman Model DK-2 recording spectrophotometer with linear wave length drive was used for all absorption spectra measurements. In the case of highly absorbing solutions, capillary type absorption cells constructed from optically flat silica discs and metal foil spacers were used.

Absorption Spectra Measurements.—The aqueous uranyl tri-8-quinolinolate anion solutions were prepared by combining stoichiometric quantities of standard uranyl perchlorate and sodium 8-quinolinolate solutions. These solutions contained sufficient hydroxide ion (0.01–0.03 *M*) to prevent hydrolysis of the anion with accompanying precipitation of $H(UO_2(C_9H_6NO)_3)$. The presence of slight excesses of either uranium or 8-quinolinolate has no appreciable effect on the structure of observed spectra. Chloroform solutions of the tetraphenylarsonium salt were prepared from the solid. All solution spectra were recorded within 15 minutes of preparation.

Tetraethylammonium Uranyl 8-Quinolinolate, $(C_2H_5)_4N(UO_2(C_9H_6NO)_3)$.—To a solution of 3.5 g. (0.024 mole) of 8-quinolinol and 1 g. (0.025 mole) of sodium hydroxide in

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(10) T. Moeller and M. V. Ramaniah, THIS JOURNAL, **76**, 5251 (1954).

(11) T. Moeller and M. V. Ramaniah, *ibid.*, **75**, 3946 (1953); **76**, 2022 (1954).

(12) In this connection, it is interesting to note that evaporation of chloroform and acetone extracts of the green dichelate yields only orange-red residues.

(13) Elemental analyses of this compound, such as reported by Moeller and Ramaniah (ref. 10) could hardly be expected to distinguish between $UO_2(C_9H_6NO)_2$, 2.17% H and a plausible +5 uranium compound, $H(UO_2(C_9H_6NO)_2)$, 2.34% H.

(14) The method employed was similar to that described by Moeller and Ramaniah (ref. 10) for the preparation of uranyl di-(5,7-dihalo-8-quinolinolates).

(15) One of the referees of this paper has raised the interesting question of other "abnormal" 8-quinolinolates, *viz.*, $PuO_2(Ox)_2 \cdot HOx$, $Th(Ox)_4 \cdot HOx$, and $Sc(Ox)_3 \cdot HOx$. The first of these chelates is undoubtedly analogous to the uranyl chelate. However, the remaining two chelates, if interpreted on the basis of the present paper, would give rather large coördination numbers (as pointed out by the referee) as well as the perplexing problem of where the hydrogens are located.

(16) J. S. Fritz and R. T. Keen, *Anal. Chem.*, **25**, 179 (1953).

100 ml. of water was added 5 g. (0.02 mole) of tetraethylammonium bromide. The undissolved material was filtered off and 10 ml. of uranyl nitrate solution (0.02 *M*) added to the filtrate. The orange precipitate was collected and extracted with methyl isobutyl ketone. Upon recrystallization from methyl isobutyl ketone a bright red crystalline solid was obtained which, after drying *in vacuo*, gave the following results. *Anal.* Calcd. for $(C_2H_5)_4N(UO_2(C_9H_6NO_3)_3)$: C, 50.5; H, 4.57; U, 28.6. Found: C, 49.9; H, 4.64; U, 28.4.

Sodium Uranyl 8-Quinolinolate, $Na(UO_2(C_9H_6NO)_3)$.—To a solution of 3.5 g. (0.024 mole) of 8-quinolinol in 200 ml. of 10% sodium carbonate (filtered free of undissolved 8-quinolinol) was added 2 ml. of 1.0 *M* uranyl nitrate solution. The orange precipitate was collected and washed repeatedly with 0.5 *M* sodium carbonate and dried at 80–85°. *Anal.* Calcd. for $Na(UO_2(C_9H_6NO)_3)$: U, 32.8; Na, 3.18; C, 44.69; H, 2.50. Found: U, 33.1; Na, 3.61; C, 44.66; H, 2.80.

Uranyl 8-Quinolinolate.—This 3 to 1 chelate was prepared as outlined by Moeller.[3]

Tetraphenylarsonium Uranyl 8-Quinolinolate, $(C_6H_5)_4As(UO_2(C_9H_6NO)_3)$.—A clear, red solution of the uranyl tri-8-quinolinolate anion was prepared by adding 50 ml. (2 mmoles) of 0.040 *M* uranyl nitrate to 100 ml. of solution containing 870 mg. (6 mmoles) of 8-quinolinol and 400 mg. (10 mmoles) of sodium hydroxide. Addition of 837 mg. (2 mmoles) of tetraphenylarsonium chloride (Hach Chemical Co.) dissolved in 15 ml. of water to the above solution precipitated the complex salt as a voluminous, orange-colored solid. Upon warming this mixture to 80–90°, aggregation occurs with the formation of a sticky, dark red mass of the complex salt, which solidifies on cooling.[17] By using this phenomenon, the complex salt was separated easily in a relatively pure, anhydrous form. The salt is infinitely soluble in chloroform but only slightly soluble in ketones. Attempts to recrystallize it from such solvents always lead to glasses. The yield is essentially quantitative; m.p. 145–150° (premelting occurs).

Anal. A weighed portion of the compound was decomposed with 2 *M* perchloric acid to yield the very insoluble perchlorate, $(C_6H_5)_4AsClO_4$, and a solution of the acid 8-quinolinol ion, $C_9H_6NOH_2^+$. Following filtration, washing and drying, the perchlorate was weighed. The 8-quinolinol concentration in the combined filtrate and washings was determined spectrophotometrically at 317 mμ by using a Beer's law plot obtained from known concentrations of 8-quinolinol in 2 *M* perchloric acid. A second weighed portion of the compound was used for the determination of arsenic and uranium following decomposition in a Parr peroxide bomb. Calcd. for $(C_6H_5)_4As(UO_2(C_9H_6NO)_3)$: $(C_6H_5)_4As^+$, 35.3; $C_9H_6NO^-$, 39.8; U, 21.9; As, 6.9. Found: $(C_6H_5)_4As^+$, 36.8; $C_9H_6NO^-$, 42.3; U, 22.0; As, 6.8.

Uranyl Di-8-quinolinolate, $UO_2(C_9H_6NO)_2$.—This compound was prepared by heating $H(UO_2(C_9H_6NO)_3)$ *in vacuo* at 250–270° for 6 hr. This temperature range was selected on the basis of recent thermogravimetric studies by Wendlandt.[18]

Anal. Calcd. for $UO_2(C_9H_6NO)_2$: U, 42.7. Found: U, 42.5.

Detection of Reduced Uranium in Uranyl Di-8-quinolinolate, $UO_2(C_9H_6NO)_2$.—A spectrophotometric method based on the characteristic absorption spectrum (600–700 mμ) exhibited by solutions of +4 uranium in 85% phosphoric acid was used.[19] In this spectral range, any absorption due to +6 uranium or 8-quinolinol is negligible. Another desirable feature of this method is the great stability of +4 uranium in 85% phosphoric acid. This stability is such that any +3 or +5 uranium present in the chelate would be converted to +4 uranium, the former by oxidation and the latter by disproportionation.

Using 1.0 cm. cells, a solution of 558 mg. (1.0 mmole) of uranyl di-8-quinolinolate in 100 ml. of 85% phosphoric acid was examined spectrophotometrically *vs.* 0.020 *M* 8-quinolinol in 85% phosphoric acid in the region 600–700 mμ. No absorbance (±0.001 unit) was noted. From this result and known +4 uranium extinction coefficients, it may be calculated that any reduced uranium in this chelate is less than 0.02% of the total uranium content.

Chemical Behavior of Uranyl Di-8-quinolinolate, $UO_2(C_9H_6NO)_2$.—The qualitative action of various reactants summarized in Table II below was investigated on a "test-tube" scale using ~50 mg. quantities of the chelate. Because of the various colors involved, visual examination sufficed to identify the products.

Table II

	Reactant, conditions	Products identified[a]
1.	H^+, 0.01 *M*	$H(UO_2(Ox)_3)$, UO_2^{++}
2.	H^+, 1.0 *M*	H_2Ox^+, UO_2^{++}
3.	H_2O, 100°	No reaction
4.	H_2O, 80 P.S.I. steam[b]	$H(UO_2(Ox)_3)$, UO_3, HOx
5.	OH^-, 0.01 *M*	$UO_2(Ox)_3^{-1}$, uranate
6.	OH^-, 1.0 *M*	Ox^{-1}, uranate
7.	HOx, molten	$H(UO_2(Ox)_3)$ in HOx melt[c]

[a] HOx = C_9H_6NOH, Ox^- = $C_9H_6NO^{-1}$, etc. [b] Carried out in a small autoclave. [c] F. Feigl and L. Baumfeld, *Anal. Chim. Acta*, **3**, 15 (1949).

The Reaction: $3UO_2(C_9H_6NO)_2 + 2H^+ \rightarrow UO_2^{++} + 2H(UO_2(C_9H_6NO)_3)$.—A suspension of 279 mg. (0.500 mmole) of uranyl di-8-quinolinolate in 50 ml. of a 0.1 *M* sodium acetate–0.01 *M* acetic acid buffer solution (*p*H 4.7) was kept at 70–80° for 5 hr. At the end of this period, the initially green solid phase had assumed a brick-red color, while the aqueous phase had turned yellow. The solid phase was filtered off, washed, dried (110°) and then weighed. The identity of this solid with $H(UO_2(C_9H_6NO)_3)$ was established by various tests ($CHCl_3$ solution absorption spectra, thermal decomposition to uranyl di-8-quinolinolate, etc.). The aqueous phase plus washings was fumed with nitric acid to destroy any organic matter prior to uranium analysis.

Anal. Calcd. for above reaction: $H(UO_2(C_9H_6NO)_3)$, 0.333 mmole; UO_2^{++}, 0.167 mmole. Found: $H(UO_2(C_9H_6NO)_3)$, 0.312 mmole; UO_2^{++}, 0.184 mmole.

These results have not been corrected for the solubility of $H(UO_2(C_9H_6NO)_3)$ in the acetate buffer.

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[17] This so-called "melting under solvent" is the result of a slight mutual solubility between the complex salt and water at elevated temperatures.

[18] W. W. Wendlandt, *Anal. Chem.*, **28**, 499 (1956).

[19] C. J. Rodden, "Analytical Chemistry of the Manhattan Project," National Nuclear Energy Series, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 80.