however, because those species which are free to rotate or coil about in the plane of the copper chelate ring may exhibit a larger diffusion coefficient than those ligands whose rotation is restricted. For example, a phenyl group substituted in the 3-position of 2,4-pentanedione cannot become coplanar with the heterocyclic ring of the chelate molecule and results in a marked decrease in the $D\eta$ value (Table I).

Acknowledgment.—The assistance of H. D. Russell in measuring the viscosities of the solutions is acknowledged.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA]

Kinetics of the Oxidation of Uranium(IV) by Thallium(III)[1]

BY A. C. HARKNESS AND J. HALPERN

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The kinetics of the reaction U(IV) + Tl(III) → U(VI) + Tl(I) were examined in aqueous perchloric acid solution and found to be of the form $-d[U(IV)]/dt = [U^{4+}][Tl^{3+}](k_1[H^+]^{-1} + k_2[H^+]^{-2})$. The two rate constants were identified with reaction paths involving activated complexes of the compositions $(U\cdot OH\cdot Tl)^{6+}$ and $(U\cdot O\cdot Tl)^{5+}$, respectively. The corresponding heats and entropies of activation, evaluated from rate measurements over the temperature range 16 to 25°, are $\Delta H_1^* = 24.6$ kcal./mole, $\Delta H_2^* = 21.7$ kcal./mole, $\Delta S_1^* = 16$ e.u. and $\Delta S_2^* = 7$ e.u. The effect of ionic strength and the specific effects of various anions and cations on the rate were examined. The results suggest, but do not demonstrate conclusively that the reaction occurs through a single two-equivalent step rather than through successive one-electron changes.

Introduction

This work forms part of a program of investigations being conducted in this Laboratory[2] on the kinetics and mechanisms of simple inorganic oxidation–reduction reactions between two-equivalent oxidants and two-equivalent reductants. The present reaction

$$U(IV) + Tl(III) \longrightarrow U(VI) + Tl(I) \quad (1)$$

is of this type. One objective of these studies is to determine whether reactions of this type occur in a single step or through successive one-electron changes.

Of immediate interest in connection with the present study are earlier kinetic investigations of the oxidation of U(IV) to U(VI) by other oxidants including Fe(III),[3] Ce(IV),[4] Pu(VI)[5] and O_2.[6] In each of these systems the evidence suggests that the over-all reaction involves two successive one-equivalent changes, U(V) being formed as an intermediate. It is probable that the mechanisms of the first three of these reactions, involving one-equivalent oxidants, are all of the type

$$U(IV) + Fe(III) \xrightarrow{\text{slow}} U(V) + Fe(II) \quad (2)$$

$$U(V) + Fe(III) \xrightarrow{\text{fast}} U(VI) + Fe(II) \quad (3)$$

On the other hand the reaction of U(IV) with O_2, a multi-equivalent oxidant, proceeds through a chain mechanism of the type

$$\text{Initiation: } U(IV) + O_2 \longrightarrow U(V) + HO_2 \quad (4)$$

$$\text{Propagation: } \begin{cases} U(V) + O_2 \longrightarrow U(VI) + HO_2 & (5) \\ HO_2 + U(IV) \longrightarrow U(V) + H_2O_2 & (6) \end{cases}$$

In the light of this it seemed of interest to examine the oxidation of U(IV) by a two-equivalent metal ion oxidant, and Tl(III) whose reactions with other reducing agents have been extensively investigated from related standpoints was considered a logical choice for this purpose. Some measurements also were attempted on the oxidation of U(IV) by the isoelectronic ion, Hg(II), and it is of interest that this reaction, although also thermodynamically favorable, was found to be too slow for convenient kinetic study.

Experimental

Stock solutions of thallium(III), thallium(I), uranium(IV) and uranium(VI) perchlorates and of sodium perchlorate were prepared as described earlier.[2b,6] Silver perchlorate, obtained from G. F. Smith Co., was purified by recrystallization from perchloric acid. All other chemicals were of reagent grade. Water was purified by redistillation from alkaline permanganate in a Pyrex still.

The kinetic measurements were made by measuring the U(IV) concentration with a Beckman DU spectrophotometer using the 6500 Å. absorption peak; at this wave length interference from U(VI) and other ions was found to be negligible. To minimize zero-time errors, the reaction was started by mixing suitable aliquots of solutions of the separate reactants, which previously had been brought to the reaction temperature. In most of the experiments the readings were made on the same sample of solution which remained in the spectrophotometer cell compartment (thermostated to ±0.1°) throughout the reaction. Identical results were obtained when the reacting solution was kept in a thermostated water-bath and sampled periodically for analysis.

Results and Discussion

It was established that the stoichiometry of the reaction conforms, within experimental error, to equation 1. At constant $HClO_4$ and $NaClO_4$ concentrations, the kinetics were found to be consistently of second order (first order each with respect to U(IV) and to Tl(III)), as shown by the linear second-order kinetic plots in Fig. 1. The apparent second-order rate constants, k', determined from the slopes of these plots were unaffected by variation of the initial U(IV) concentration between 0.0035 and 0.011 M and of the initial Tl(III) concentration between 0.005 and

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(1) Support of this work through a grant from the National Research Council of Canada and through a Fellowship (to A.C.H.) from the Consolidated Mining and Smelting Co. of Canada Ltd. is gratefully acknowledged.

(2) Related studies are described in (a) J. Halpern, *Can. J. Chem.*, **37**, 148 1959; (b) A. M. Armstrong, J. Halpern and W. C. E. Higginson, *J. Phys. Chem.*, **60**, 1661 (1956); A. M. Armstrong and J. Halpern, *Can. J. Chem.*, **35**, 1020 (1957); (c) H. N. Halvorson and J. Halpern, THIS JOURNAL, **78**, 5562 (1956).

(3) R. H. Betts, *Can. J. Chem.*, **33**, 1780 (1955).

(4) F. B. Baker and T. W. Newton, private communication.

(5) T. W. Newton, *J. Phys. Chem.*, **62**, 943 (1958).

(6) J. Halpern and J. G. Smith, *Can. J. Chem.*, **34**, 1419 (1956).

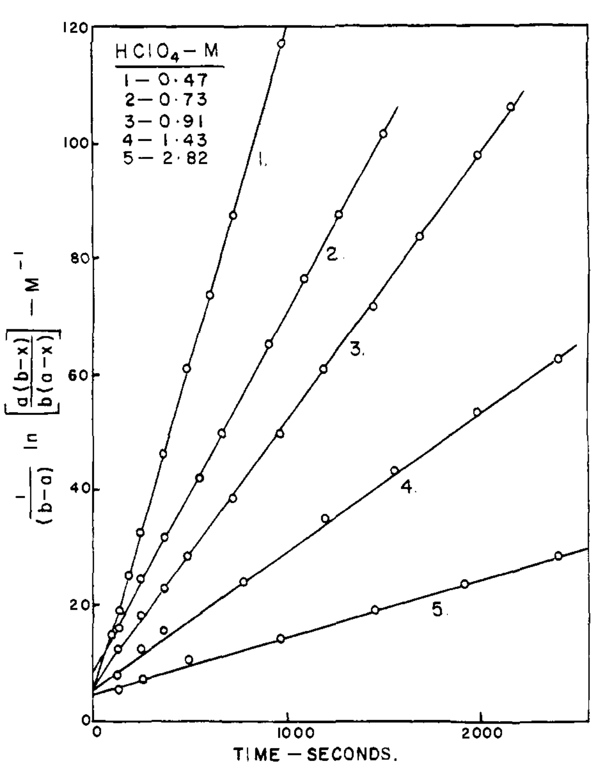

Fig. 1.—Second-order kinetic plots for the reaction between U(IV) and Tl(III) at 25° and various $HClO_4$ concentrations. Ionic strength adjusted to 2.9 with $NaClO_4$: $a = [U(IV)]_0 = 0.0024\ M$; $b = [Tl(III)]_0 = 0.0090\ M$.

0.021 M. Addition of U(VI) and of Tl(I) was also without effect. No conclusive explanation can be given for the slight ordinate intercepts which appear in most of the kinetic plots (Fig. 1). Zero-time errors or rapid initial oxidation of some U(IV) by dissolved oxygen or other impurities may be responsible.

k' was found to depend inversely on the $HClO_4$ concentration when the latter was varied between 0.5 and 2.8 M, the ionic strength being held constant with $NaClO_4$ (Fig. 1). When fitted to an empirical rate law of the form

$$-\mathrm{d}[\mathrm{U(IV)}]/\mathrm{d}t = k[\mathrm{U(IV)}][\mathrm{Tl(III)}][\mathrm{H}^+]^{-n} \quad (7)$$

n was found to range from 1.48 at 16° to 1.39 at 25°.

In line with similar behavior encountered in other oxidation reactions of U(IV), the non-integral inverse order in H^+ can be interpreted in terms of simultaneous contributions from two separate paths inversely first- and second-order, respectively, in H^+. The corresponding rate law is

$$-\mathrm{d}[\mathrm{U(IV)}]/\mathrm{d}t = [\mathrm{U}^{4+}][\mathrm{Tl}^{3+}](k_1[\mathrm{H}^+]^{-1} + k_2[\mathrm{H}^+]^{-2}) \quad (8)$$

$$= [\mathrm{U(IV)}][\mathrm{Tl(III)}](k_1[\mathrm{H}^+] + k_2)/([\mathrm{H}^+] + K_\mathrm{U})([\mathrm{H}^+] + K_\mathrm{Tl}) \quad (9)$$

Hence

$$k' = (k_1[\mathrm{H}^+] + k_2)/([\mathrm{H}^+] + K_\mathrm{U})([\mathrm{H}^+] + K_\mathrm{Tl}) \quad (10)$$

where K_U and K_{Tl} are the hydrolysis constants of U^{4+} and Tl^{3+}, whose values at 25° and $\mu \approx 3$ are 0.021 and 0.073 M, respectively.[7,8] Values of K_U and K_{Tl} for the other reaction temperatures (0.016 and 0.056 at 20°; 0.012 and 0.041 at 16°) were estimated using, in each case, an enthalpy of hydrolysis of 11.0 kcal./mole. This corresponds to the measured value[9] for U^{4+} and is probably also a reasonable estimate for Tl^{3+} as most known heats of hydrolysis of metal ions are of this order. Fortunately the extent of hydrolysis of both ions is small in this case so that the kinetic results are insensitive to errors in the hydrolysis constants.

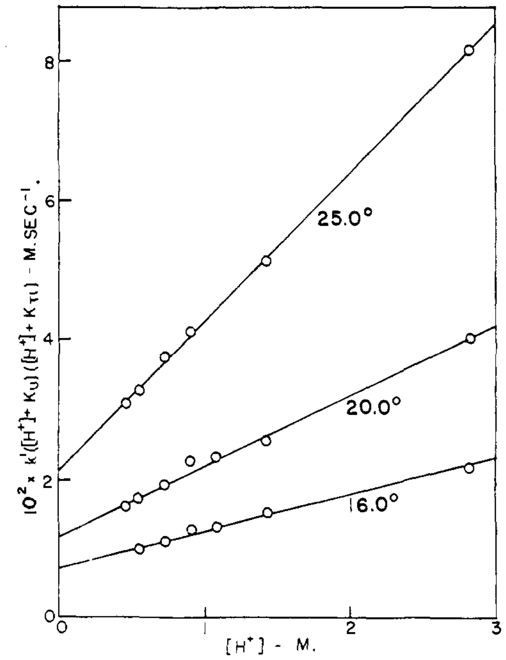

Fig. 2.—Dependence of the rate on the H^+ concentration at various temperatures (μ = 2.9).

This treatment yields the linear plots of $k'([H^+] + K_U)([H^+]+K_{Tl})$ vs. $[H^+]$ in Fig. 2 which are in accord with equation 10 and give the values of k_1 and k_2 listed in Table I. These, as well as the corresponding free energies, enthalpies and entropies of activation, refer to the formation of activated complexes of the composition $(U{\cdot}OH{\cdot}Tl)^{6+}$ and $(U{\cdot}O{\cdot}Tl)^{5+}$, respectively, from the unhydrolyzed metal ions which predominate in the acidity range used, *i.e.*

TABLE I

KINETIC DATA FOR THE OXIDATION OF U(IV) BY Tl(III)
(μ = 2.9)

Path[a]	$k \times 10^2$ 16.0°	20.0°	25.0°	ΔF^*, kcal./mole	ΔH^*, kcal./mole	ΔS^*, e.u.
1	0.57	1.02	2.11	19.7	24.6 ± 2	16 ± 7
2	0.67	1.17	2.13	19.7	21.7 ± 2	7 ± 7

[a] Path 1 refers to k_1 and path 2 to k_2. Units of k_1 are sec.$^{-1}$ and of k_2, M sec.$^{-1}$.

$$\mathrm{U}^{4+} + \mathrm{Tl}^{3+} + \mathrm{H_2O} \underset{}{\overset{k_1}{\rightleftarrows}} (\mathrm{U{\cdot}OH{\cdot}Tl})^{6+} + \mathrm{H}^+ \quad (11)$$

$$\mathrm{U}^{4} + \mathrm{Tl}^{3} + \mathrm{H_2O} \overset{k_2}{\rightleftarrows} (\mathrm{U{\cdot}O{\cdot}Tl})^{5+} + 2\mathrm{H}^+ \quad (12)$$

It is of interest that the order of the enthalpies (as well as of the corresponding entropies) of acti-

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(7) K. A. Kraus and F. Nelson, THIS JOURNAL, **72**, 3901 (1950).

(8) G. Biederman, *Arkiv Kemi*, **5**, 441 (1953).

(9) R. H. Betts, *Can. J. Chem.*, **33**, 1775 (1955); K. A. Kraus and F. Nelson, THIS JOURNAL, **77**, 3721 (1955).

vation for the two paths is the reverse of that for the oxidation of U(IV) by Fe(III) ($\Delta H_1^* = 21.9$, $\Delta H_2^* = 23.9$; $\Delta S_1^* = 17.1$, $\Delta S_2^* = 26.5$).[3] The significance of this is not clear.

Alternatively, it is possible to interpret the kinetics in terms of reactions between hydrolyzed ions (UOH^{3+} and/or $TlOH^{2+}$) with rate constants related to k_1 and k_2 through the corresponding hydrolysis constants. The kinetics, of course, identify only the composition of the activated complex and cannot distinguish between alternative paths in which the same activated complex is formed from different species which are in equilibrium with each other. The representation of the activation process through equations 11 and 12 follows the convention adopted by Newton and Rabideau[10] in discussing reactions of this type. These authors have interpreted the general inverse dependence on H^+, observed in all oxidation reactions of U(IV), as reflecting formation of U–O bonds in the activated complex, the state of uranium in the activated complex being intermediate between U^{4+} and UO_2^+ (or UO_2^{++}).

Addition of $NaClO_4$ was found to increase the reaction rate significantly (Table II). There is no evidence for specific complexing of either U^{4+} or Tl^{3+} with ClO_4^- and a medium (ionic strength) effect is the most probable explanation. While the effect is in the direction predicted by the Debye–Hückel theory for a reaction between two ions of like charge (a similar effect was observed for the U(IV)–Fe(III) reaction)[3] a quantitative interpretation is not possible because of the high ionic strengths involved.

Table II

Effects of Various Salts[a]

$HClO_4$, M	Added salt	$k' \times 10^2$, M^{-1} sec.$^{-1}$
1.76	....	1.08
	0.84 M $NaClO_4$	1.55
	1.29 M $NaClO_4$	2.00
	2.58 M $NaClO_4$	3.24
	2.96 M $NaClO_4$	3.83
2.83	....	0.98
	0.0015 M NaCl	.92
	.0029 M NaCl	.68
	.0059 M NaCl	.50
	.012 M NaCl	.090
	.018 M NaCl	.035
	.021 M NaCl	.078
	.029 M NaCl	.110
	.032 M NaCl	.110
2.83	.0017 M Na_2SO_4	1.83
	.0035 M Na_2SO_4	2.65
	.0052 M Na_2SO_4	3.40
	.0070 M Na_2SO_4	3.83
	.0087 M Na_2SO_4	4.88
	.0113 M Na_2SO_4	5.62
	.0140 M Na_2SO_4	6.02
2.82	.0020 M $Cu(ClO_4)_2$	0.95
	.0012 M $Hg(ClO_4)_2$	1.02
	.0004 M $AgClO_4$	0.90
	.0008 M $AgClO_4$	.83
	.0021 M $AgClO_4$	.70
	.0034 M $AgClO_4$	.70
	.0053 M $AgClO_4$	.70
	.0084 M $AgClO_4$	.68

[a] Based on measurements at 25°, $\mu = 2.9$ and initial U(IV) and Tl(III) concentrations of 0.0035 and 0.009 M, respectively.

The specific effects of various anions and cations on the reaction were examined and are summarized in Table II. In all cases the kinetics remained first-order in U(IV) and in Tl(III) and rates are expressed in terms of the apparent second-order rate constant, k'. Cl^- was found to inhibit the reaction markedly. The rate decreased with increasing NaCl concentration, passing through a minimum (about $^1/_{30}$ of the uninhibited rate) at a concentration ratio $[Cl^-]/[Tl(III)] \sim 2$, and then increasing slightly to a constant value. On the other hand, $SO_4^=$ exerted a marked catalytic effect, k' increasing by a factor of 6 on addition of 0.014 M Na_2SO_4. These effects parallel in some degree those observed in other reactions of Tl(III), (*e.g.*, the Tl(I)–Tl(III) isotopic electron exchange[11] and the oxidation of Fe(II) by Tl(III)[12]) and are attributable to complexing of Tl^{3+}, the chloride complex being less reactive and the sulfate complex more reactive, than the uncomplexed ion.

The cations examined included Cu^{2+}, Hg^{2+} and Ag^+, selected in view of their marked effects on the oxidation of U(IV) by O_2.[6] Additions of 0.001–0.002 M $Cu(ClO_4)_2$ or $Hg(ClO_4)_2$ (both catalysts for the latter reaction) were without effect. Ag^+, a marked inhibitor in the U(IV)–O_2 reaction (10^{-4} M effected complete inhibition for 1 hr.) manifested only a slight effect in the present case, whose cause is not clear; maximum inhibition (corresponding to a reduction of about 30% in the rate) was attained with about 0.002 M $AgClO_4$, further addition being without effect.

A question of basic interest in connection with the multi-equivalent oxidation–reduction reactions in general is whether they are accomplished in a single step or through successive one-electron changes.[2a,13,14] While it does not appear possible to answer this question conclusively in the present instance, it is felt that the above results are more readily reconciled with a mechanism of the former type. The following features seem particularly pertinent in this connection.

1. When compared to other reactions of U(IV) and of Tl(III) (particularly the reaction between Tl(III) and Fe(II) which is known to proceed through one-electron steps),[15] the present reaction seems too fast to be reconciled with a rate-determining step involving the formation of two unstable intermediates, U(V) and Tl(II).

2. It has been noted that other reactions (*e.g.*, that between Fe(II) and Tl(III)), in which Tl(II)

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[10] T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).

[11] G. Harbottle and R. W. Dodson, This Journal, **73**, 2442 (1951); C. H. Brubaker, Jr., and J. P. Mickel, *J. Inorg. Nucl. Chem.*, **4**, 55 (1957).

[12] F. R. Duke and B. Bornong, *J. Phys. Chem.*, **60**, 1015 (1956).

[13] F. H. Westheimer, in "The Mechanism of Enzyme Action," Ed. by W. D. McElroy and B. Glass, Johns Hopkins Press, Baltimore, Md., 1954, p. 321.

[14] W. C. E. Higginson and J. W. Marshall, *J. Chem. Soc.*, 447 (1957).

[15] K. G. Ashurst and W. C. E. Higginson, *ibid.*, 3044 (1953).

is formed in the rate-determining step are characterized by abnormally high activation energies and entropies and an explanation of this effect has been suggested.[2a] There is no indication that the kinetics of the present reaction follow this pattern.

3. If the initial step involved a one-equivalent change, *i.e.*

$$\mathrm{U(IV) + Tl(III) \longrightarrow U(V) + Tl(II)} \quad (13)$$

some contribution to the reaction would be expected from a chain mechanism similar to that observed in the oxidation of U(IV) by O_2, *i.e.*

$$\mathrm{U(IV) + Tl(II) \longrightarrow U(V) + Tl(I)} \quad (14)$$

$$\mathrm{U(V) + Tl(III) \longrightarrow U(VI) + Tl(II)} \quad (15)$$

The kinetics of the reaction and, in particular, the insensitiveness of the rate to ions such as Cu^{2+}, suggest that this is not the case. An alternative interpretation, consistent with this observation, is that reaction 13 occurs initially but that the U(V) and Tl(II) ions formed react with each other (to form the products U(VI) and Tl(I)) in a shorter time than that required for them to diffuse out of their "solvent cage" and react with other species. In view of the practical difficulty of distinguishing this from a single two-equivalent change, Westheimer,[13] in a discussion of one- and two-electron reactions, has included processes of this type in the latter classification.

The conclusion that the oxidation of U(IV) by Tl(III) occurs through a two-equivalent mechanism is in line with Higginson and Marshall's[14] generalizations and appears to be applicable also to reactions of Tl(III) with other two-equivalent reductants.[2] The question of whether this and related reactions proceed through actual electron transfer between reactants or through group transfer mechanisms (*e.g.*, transfer of oxygen atoms) remains open.

VANCOUVER, CANADA

[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY]

The Heat Capacity and Thermodynamic Functions of β-Uranium Hydride from 5 to 350°K.[1,2]

BY HOWARD E. FLOTOW, HAROLD R. LOHR, BERNARD M. ABRAHAM AND DARRELL W. OSBORNE

RECEIVED JANUARY 21, 1959

The heat capacity of β-UH_3 has been measured from 5 to 350°K. in an adiabatic calorimeter. The enthalpy and entropy at 298.15°K. calculated from the data are 2155 cal. mole^{-1} and 15.24 cal. deg.$^{-1}$ mole^{-1}, respectively. The entropy and free energy of formation for UH_3 at 298.15°K. as well as the heat of formation at absolute zero were calculated from these data and the previously determined heat of formation and have the values −43.60 cal. deg.$^{-1}$ mole^{-1}, −17.353 cal. mole^{-1} and −27.945 cal. mole^{-1}. It was found that the calculated and observed dissociation pressures are not in agreement. The discrepancy is believed due to a particle size effect in the dissociation pressure measurements or to the heat of transition from α-UH_3 to β-UH_3. An anomaly is observed in the heat capacity which arises from the transition from the ferromagnetic to the paramagnetic state. The maximum in the heat capacity is 10.72 cal. deg.$^{-1}$ mole^{-1} and occurs at 170.7 ± 0.5°K. It was estimated that 1.01 cal. deg.$^{-1}$ mole^{-1} is the entropy change in the transition which is less than $R \ln 2 = 1.38$ cal. deg.$^{-1}$ mole^{-1} expected from the Heisenberg theory of ferromagnetism.

Introduction

Measurements of the low temperature heat capacity of uranium hydride were undertaken to complement studies of the dissociation pressure[3,4] and the determination of the heat of formation[5] which have been reported previously. Neither heat capacity nor experimental entropy values for this compound have been published heretofore. Our interest in these measurements was increased by the discovery that UH_3 is ferromagnetic below 173°K.[6,7]

Two allotropic forms of uranium hydride are known. The β-phase, which is the one usually formed by the reaction between uranium and hydrogen, is cubic with $a_0 = 6.63$ kX. and with eight atoms of uranium per unit cell arranged as in α-tungsten, *i.e.*, $2U_I$ at (0, 0, 0) and (1/2, 1/2, 1/2) and $6U_{II}$ at ±(1/4. 0, 1/2).[8] Each U_I atom is surrounded by twelve hydrogen atoms at the corners of an icosahedron of symmetry T_h, and each U_{II} atom is surrounded by twelve hydrogens in sets of three, each set forming a face of a different icosahedron. All of the U–H distances are equal to 2.32 Å.[9]

The α-form is also cubic, with $a_0 = 4.153$ kX. and with two molecules per unit cell.[10,11] The two uranium atoms are equivalent and occupy the positions (0, 0, 0) and (1/2, 1/2, 1/2), and there are six hydrogen atoms at ±(1/4, 0, 1/2). Each uranium atom is surrounded by twelve hydrogen atoms at 2.32 Å., the same distance as in the β-form. The X-ray density of α-UH_3 is 11.11 g./cc., whereas that of β-UH_3 is 10.92. Small quantities of α-UH_3 have been formed on a uranium cathode by electrolysis of a perchloric acid solution or of a sodium carbonate solution below 20°. Mixtures of α-UH_3 and β-UH_3 containing up to 52% α have been pre-

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Presented before the Division of Physical and Inorganic Chemistry at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 16 to 21, 1956.

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