reduction of $Na^+(bipy^-)$ to $Na^+_2(bipy^{2-})$ three isosbestic points were observed at 487, 608, and 714.5 $m\mu$. Thus, the reduction of the neutral molecule occurred in a stepwise fashion, and no appreciable amounts of $Na^+_2(bipy^{2-})$ and the neutral molecule coexisted in DME as has been implied[2] by the equation written for the reduction of $FeCl_3$ by $Li^+_2(bipy^{2-})$. The molar extinction coefficients of bipyridine for the 282- and 237-$m\mu$ absorption peaks were 14.7×10^3 and 11.5×10^3 M^{-1} cm^{-1}, respectively; these are somewhat larger than those reported[4] for other organic solvents. The spectrum of $Na^+(bipy^-)$ has absorption peaks at 560, 530, and 386 $m\mu$; the first two have equal intensities and a molar extinction coefficient of 4300 ± 200, and the latter has a molar extinction coefficient of 18,000 ± 2000 M^{-1} cm^{-1}.

The iron(0) compound dissolved sparingly in DME to give a blue-violet solution which had absorption peaks at 525, 502, and 357 $m\mu$; except for the blue shift of approximately 30 $m\mu$, the spectrum of the iron(0) compound in solution closely resembled the $Na^+(bipy^-)$ spectrum. Shifts of the same order of magnitude have been observed[5] in optical spectra of some negative organic radical ions when they have formed an ion pair with alkali metal ions in solvents such as DME, and since $Na^+(bipy^-)$ has a very small sodium coupling constant[6] and can be regarded as an ion pair rather than as a covalent molecule, the optical evidence indicated that the iron(0) complex in solution contained an iron cation and $bipy^-$ anions. If the iron(0) species in solution was ionic, it did not dissociate appreciably into ions. No esr spectrum of $bipy^-$ was found for the solution. Since the presence of iron (if paramagnetic) could have broadened the esr signal beyond detection, a conductance measurement was made. In a conductance cell with platinum electrodes 1 cm apart the iron(0) solution had a resistance greater than 150,000 ohms, showing that ionic dissociation was negligible. The composition of the iron(0) species in solution is not precisely known; some dissociation of neutral bipyridine (detected by its intense 283-$m\mu$ peak) occurred when the $Fe(bipy)_3$ dissolved. Upon long standing (20 hr) the dissociation was virtually complete.

The solid $Fe(bipy)_3$ was paramagnetic, but attempts to determine its magnetic susceptibility by the Gouy method failed because of traces of metallic iron impurity.

An esr spectrum of $Fe(bipy)_3$ at 9.487×10^9 cps gave an average g value of 2.075 ± 0.003 showing more spin-orbit coupling than could be expected for electrons residing entirely in the $bipy^-$ anions in an ionic complex. The value found for iron(0) is in agreement with the reported[7] values of 2.2125 ± 0.0005 for Ni^{2+} and 2.1728 ± 0.0005 for Co^+, both d^8 ions. Despite the evidence of the optical spectrum to the contrary, the measured g value for iron(0) indicated that the iron had a d^8 configuration in a covalent complex of $Fe(bipy)_3$ with neutral ligands.

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The Oxidation of Uranium(IV) Acetate by Silver Acetate in Liquid Ammonia

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Silver acetate is a convenient oxidizing agent for use in liquid ammonia. It is readily prepared and purified and produces a heavy metal as a product of the reaction. This can be easily isolated and weighed to give a measure of the reaction.

A green solution of uranium(IV) acetate in liquid ammonia is converted to the yellow of U(VI) in a few hours at room temperature by silver acetate. This reaction is followed by the slow precipitation of a pale yellow substance as the solution color fades. We have examined this reaction in some detail and now report the results of our experiments.

Experimental Section

Materials.—The anhydrous acetates were prepared from hydrated nitrates or chlorides by treatment with acetic anhydride at reflux temperatures. Usually the anhydrous acetates settled out as formed and were purified by recrystallization from glacial acetic acid.

Dioxouranium(VI) acetate was prepared from Baker Analyzed reagent grade dioxouranium(VI) nitrate hexahydrate. *Anal.* Calcd for $UO_2(C_2H_3O_2)_2$: U, 61.32. Found: U, 61.34.

Uranium(IV) acetate was prepared from "specially purified" UCl_4 obtained from the Los Alamos Scientific Laboratories. *Anal.* Calcd for $U(C_2H_3O_2)_4$: U, 50.20. Found: U, 50.14.

Silver acetate was prepared from Baker Analyzed reagent grade silver nitrate. *Anal.* Calcd for $AgC_2H_3O_2$: Ag, 64.62. Found: Ag, 64.56.

Ammonium diuranate was prepared from Baker Analyzed reagent grade dioxouranium(VI) nitrate hexahydrate by precipitation from aqueous solution with dilute ammonium hydroxide. It was purified by dissolution in aqueous sodium carbonate solution, conversion to the nitrate by boiling with nitric acid, and reprecipitation with dilute ammonium hydroxide, filtered, and dried at 110°. *Anal.* Calcd for $(NH_4)_2U_2O_7$: U, 76.3. Found: U, 76.9.

Ammonium dioxotris(acetato)uranate(VI) was obtained by the slow evaporation of a solution of dioxouranium(VI) acetate in saturated aqueous ammonium acetate. The compound was

TABLE I

THE REACTION OF URANIUM(IV) ACETATE WITH SILVER ACETATE IN LIQUID AMMONIA AT ROOM TEMPERATURE

Time, days	Moles of $AgC_2H_3O_2 \times 10^3$	Moles of $U(C_2H_3O_2)_4 \times 10^3$	Moles of $Ag \times 10^3$	$\overline{OX}$	Moles of U(VI) $\times 10^3$		Moles of acetamide per mole of U(VI)
					Sol	Insol	
0.42	2.11	1.05	2.08	1.98	1.05	0.000	1.96
3	1.30	0.380	0.752	1.98	0.380	0.000	...
3	2.61	1.30	2.58	1.98	1.30	0.000	...
4	2.11	1.05	2.08	1.98	0.858	0.184	3.41
26	2.67	1.33	2.64	1.98	0.444	0.816	...
42	1.27	0.637	1.23	1.93	0.099	0.538	3.81
121	1.63	0.818	1.62	1.98	0.050	0.729	4.43
135	1.43	0.719	1.43	1.99	0.000	0.719	5.12

purified by recrystallization from glacial acetic acid. *Anal.* Calcd for $NH_4UO_2(C_2H_3O_2)_3$: U, 51.17; N, 3.01. Found: U, 51.08; N, 2.95.

The acetic acid used was Du Pont reagent grade material which had been dried by distillation from triacetylborate solution.

The liquid ammonia was of refrigeration grade which was dried by distillation from sodium metal.

Analytical Procedures.—The uranium compounds were assayed by conversion to U_3O_8 in a muffle furnace at 850°.

Silver metal was determined by conversion to the dicyanoargentate(I) ion followed by electrolytic deposition on a silver cathode in an H-type cell.

Acetamide was determined spectrophotometrically by the acethydroxamic acid method.[1]

The Kjeldahl method was used for the determination of nitrogen.

The infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride optics. Samples were prepared as Nujol oil mulls.

The X-ray powder patterns were taken on a North American Phillips diffractometer with a Debye–Scherrer-type camera of 114.6-mm diameter. Copper Kα radiation (Ni filtered) was used. Intensities were estimated visually.

Procedure.—Weighed quantities of the reactants were combined on a vacuum line in heavy-walled Pyrex tubes. These tubes were equipped with fritted-glass filters of medium porosity which allowed the separation of soluble and insoluble substances. Approximately 10 ml of liquid ammonia was condensed, and the tubes were immersed in liquid nitrogen and sealed. The reaction tubes were encased in brass pipes and maintained at reasonably constant room temperature.

The reaction products were separated by repeated extractions through the glass frits. The ammonia was manipulated by cooling one chamber while warming the other.

The tubes were then immersed in liquid nitrogen and opened. Excess ammonia was evaporated to leave solid residues which were handled in a nitrogen-filled drybox. Acetamide was obtained as a sublimate at 100° under vacuum. At temperatures above 150°, ammonium acetate was evolved leaving a residue of $NH_4UO_2(C_2H_3O_2)_3$.

Results and Discussion

In Table I are given the results of the experiments. The column headed $\overline{OX}$ is the number of moles of silver deposited per mole of uranium(IV) used. The constant value of this number indicates that the reactions produced U(VI) in nearly quantitative amount. The uranium(VI) product was obtained in the soluble fraction in experiments of short duration (column 6), but increasingly in the insoluble fraction in the longer experiments (column 7). The sum of columns 6 and 7 gives the total uranium(VI) recovered. The acetamide produced per mole of uranium(VI) increased with time, but even in the shortest experiment, about 2 moles of acetamide per mole of U(VI) was obtained.

The acetamide, isolated by sublimation, melted at 79.5° and gave a mixture melting point with an authentic sample of 80.0°; (lit.[2] mp 81.5°). Strong infrared bands were observed as follows (corresponding bands of the known compound are given in parentheses[3]): 3200 (3240); 1675 (1680); 1500–1640 (1590–1625); 1310 (1325); 1156 (1140); 871 (870) cm^{-1}.

Ammonium dioxotris(acetato)uranate(VI) was obtained as the residue from the sublimation of the soluble fraction. Strong infrared bands were found at (with corresponding bands for a known preparation given in parentheses): 1545 (1554); 1531 (1543); 925 (923); 675 (677) cm^{-1}. The X-ray powder patterns are as follows (the *d* spacings in A and relative intensities of the unknown are followed by the *d* spacings and relative intensities of the known preparation): 6.9, 0.50 (7.0, 1.00); 5.7, 1.00 (5.7, 1.00); 4.95, 0.50 (4.95, 0.30); 3.72, 1.00 (3.75, 0.90); 3.60, 0.20 (3.60, 0.20); 3.49, 0.20 (3.50, 0.20); 3.12, 0.90 (3.14, 0.50); 2.98, 0.40 (2.98, 0.50); 2.84, 0.40 (2.87, 0.50); 2.55, 0.40 (2.58, 0.50); 2.45, 0.40 (2.48, 0.50); 2.32, 0.40 (2.32, 0.50).

Chemical analyses of two samples of the insoluble uranium(VI) compound gave: U, 73.5, 72.4; N, 9.98, 11.2, which agree fairly well with the formula $(NH_4)_2U_2O_7 \cdot 3NH_3$ (U, 74.2; N, 9.03). It is believed that this compound was obtained in variable composition depending on the amount of ammonia retained in the lattice. The X-ray and infrared spectra were usually ill defined as would be true of an amorphous substance. However, one sample of the insoluble residue, which also contained some silver metal, gave a recognizable powder pattern. The diffraction lines of this sample of diuranate are (given in the order *d* spacings in A and relative intensities followed by the corresponding values for a known preparation): 7.09, 0.30 (7.16, 0.90); 6.13, 0.25 (6.50, 0.90); 3.42, 0.45 (3.46, 1.00); 3.09, 0.25 (3.12, 1.00); 1.99, 0.10 (2.00, 0.50); 1.94, 0.20 (1.93, 0.50). The relative intensities do not agree because silver was present.

The rates of ammonolysis at room temperature of the acetates involved in the study were measured. It was found that silver acetate and ammonium acetate did not produce acetamide over a period of 150 days. Also, silver acetate was reduced electrolytically to ascertain

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whether electron transfer to the silver acetate could produce acetamide. None was found. Uranium(IV) acetate was 50% ammonolyzed in 30 days while both dioxouranium(VI) acetate and ammonium dioxotris(acetato)uranate(VI) required 130 days.

Since the oxidation reaction is much faster than the ammonolysis reaction, it is concluded that the acetamide produced in the oxidation reaction results from acetate involved in oxygen atom transfer to form the dioxouranium (VI) species. Following this, additional acetamide is formed by the ammonolysis of acetate attached to U(VI).

We may now write equations for the reactions involved. For the oxidation reaction we suggest

$$4\mathrm{NH_3} + 2\mathrm{AgC_2H_3O_2} + \mathrm{U(C_2H_3O_2)_4} = \mathrm{(NH_4)_2UO_2(C_2H_3O_2)_4} + 2\mathrm{CH_3CONH_2} + 2\mathrm{Ag} \quad (1)$$

The ammonolysis reaction may be written

$$2\mathrm{(NH_4)_2UO_2(C_2H_3O_2)_4} + 6\mathrm{NH_3} = \mathrm{(NH_4)_2U_2O_7} + 8\mathrm{CH_3CONH_2} + 5\mathrm{H_2O} \quad (2)$$

To account for all of the acetamide formed, we have suggested that the complex $(NH_4)_2UO_2(C_2H_3O_2)_4$ may have been present in solution. There is ample precedence for this kind of complex. The compounds $UO_2(C_2H_3O_2)_2 \cdot 2HC_2H_3O_2 \cdot 2H_2O$,[4] $ZnUO_2(C_2H_3O_2)_4$,[5] and $((CH_3)_4N)_2UO_2(C_2H_3O_2)_4$[5] have all been reported to contain four coordinated acetate groups. Apparently, ammonium acetate is easily lost by this complex to give the tris complex $(NH_4)UO_2(C_2H_3O_2)_3$, which was actually isolated.

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A Study of the Decomposition of Peroxochromic Acid

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Peroxochoromic acid undergoes a first-order decomposition to Cr(III) ion with the liberation of O_2. Several researchers have observed that oxygen evolution continues for a period of time after the blue peroxochromic acid is lost.[1,2] It is interesting to note that those workers who have studied the decomposition reaction have centered their studies on the loss of peroxochromic acid and not on the rate of formation of Cr(III) ion. Since the chromium is undergoing a three-electron change and the peroxide a two-electron change, it is more than likely that one or more intermediates will be present during the decomposition.

The mechanism of this decomposition was studied with the aid of dipicolinic acid (DPA), $C_5H_3N(COOH)_2$, as a chelating agent to interrupt decomposition by stabilizing any intermediate(s).

Experimental Section

Reagents.—H_2O_2 (30%) diluted to 0.933 *M* was used. The H_2O_2 solution was standardized using acidified KI solution and titrating the I_2 liberated with $Na_2S_2O_3$ solution. The $Na_2S_2O_3$ was previously standardized against a mixture of KI and KIO_3. Starch was the indicator in both standardizations.

A 60% solution of reagent grade $HClO_4$ diluted to 1.0 *M* was used. Reagent grade $K_2Cr_2O_7$ was used for all kinetic runs and for the spectrophotometric standardization of the $Cr(ClO_4)_3$ solutions. It was dried overnight at 110–120°.

Sulfate-free $Cr(ClO_4)_3$ was obtained from K & K Laboratories, Inc., and was >99.95% pure. Solutions of $Cr(ClO_4)_3$ were analyzed by oxidizing the Cr(III) ion to $Cr_2O_7^{2-}$ and comparing their absorbancies with reagent grade, acidified $K_2Cr_2O_7$ solutions using a Beckman Model DU spectrophotometer.

The dipicolinic acid used was obtained from K & K Laboratories, Inc., and after recrystallization was >98% pure.

Oxygen Evolution.—The quantity of oxygen liberated and its rate of liberation by the peroxochromic acid decomposition was determined manometrically. The thermostated reaction vessel consisted of a bulb with a movable side arm. The bulb contained acidified potassium dichromate (pH 1), and the side arm contained hydrogen peroxide. Reaction was initiated by turning the jointed side arm so that its contents emptied into the bulb. The concentrations of $K_2Cr_2O_7$ and H_2O_2 were 1.00×10^{-3} and 0.882 *M*, respectively. Runs were made with and without DPA being added to the original reaction mixture. The concentration of DPA was 1.0×10^{-2} *M*. The temperature was 18.7°.

Stoichiometry of the Chelate.—Job's method of continuous variation[3] was used to determine the formula of the chelated intermediate. Absorbancies of the various solutions were measured at 540 mμ using a Beckman Model DU spectrophotometer.

Charge of Chelated Intermediate.—A cation-exchange resin Amberlite IR-120 and an anion-exchange resin Amberlite IRA-400 were used to determine whether the chelated intermediates were positively or negatively charged. The columns were regenerated using a 5% $HClO_4$ solution.

Kinetics of Intermediate Ion Loss.—A 90.0-ml portion of an acidified solution of 1.09×10^{-3} *M* $K_2Cr_2O_7$ and 10.0 ml of 0.933 *M* H_2O_2 solution were mixed to initiate the reaction. The initial pH of the solution was 1.00. After mixing, 5.00-ml aliquot portions were removed from the reaction mixture at designated intervals and added to flasks containing 10.0 ml of 0.0100 *M* DPA. The quantity of DPA used gave a molar ratio for DPA : Cr of 10 : 1. This excess was used to ensure a rapid and complete conversion of the intermediate to the chelated intermediate. Excess hydrogen peroxide and acid were used so that the order of the reaction would be in terms of the intermediate only. Absorbancies of the chelate formed were measured immediately.

Results and Discussion

DPA reacted very slowly with Cr(III) ion from any Cr(III) salt, *i.e.*, $Cr(ClO_4)_3$ or $Cr_2(SO_4)_3$. In order for the chelation to occur rapidly, the solution had to be boiled. The chelation then occurred in <1 min as com-

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