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A Novel Method for the Preparation of Uranium Complexes via Electrolytic Amalgamation

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The synthesis of organometallic complexes, especially in lower oxidation states, has long been of interest, owing to their active involvement in a number of important homogeneous catalytic reactions including metathesis,[1] cyclization,[2] hydrogenation and dehydrogenation, etc.[3] The conventional preparations of these compounds usually involve time-consuming and somewhat tedious chemical procedures.[4–12] Various attempts at improving synthetic methods have been made. Notable among them are the pioneer metal-vapor technique developed by Timms and Skell, which utilizes the high chemical potential of metal atoms by cocondensing them with organic and/or inorganic substrates,[4,5] the preparation of highly reactive metal powders by reducing the respective metal halides with an alkali metal in an inert solvent,[5–8] and active metal slurries generated by cocondensing metals with various solvents.[9–12]

The direct synthesis of the cyclooctatetraene complexes of uranium, thorium, and plutonium by direct reaction of the substrate with the finely divided metal powder (produced via the respective metal hydride) was first achieved by Streitwieser and co-workers.[13] An interesting and significant feature of this method was the apparent catalytic effect of trace mercury. However, the yields are limited, and the method is not applicable for the synthesis of cyclopentadienyl complexes. Recently we have prepared uranium amalgam electrolytically from an aqueous solution. The subsequent thermal decomposition produced a highly active metal powder which reacted with methane, nitrogen, etc.[14] A facile route for organouranium compounds is described here.

Experimental Section

Infrared spectra were obtained with a JASCO A-3 IR spectrophotometer. Proton NMR at 60.0 and 100.0 MHz were recorded on Varian A-60 and Jeol FX-100 spectrometers, respectively. Chemical shifts were measured relative to internal C_6H_6 and Me_4Si. ^{13}C NMR spectra were recorded on a Jeol FX-100 at 25.0 MHz. Chemical shifts were measured relative to internal Me_4Si. ^{19}F NMR spectra were obtained with a Jeol C-60 HL at 56.4 MHz. Chemical shifts were measured relative to internal CCl_3F.

All organic substrates and solvents were distilled prior to use. The starting material, uranium amalgam, was prepared as described elsewhere.[14] The uranium amalgam was washed with dilute HCl, water, and acetone and finally placed in an apparatus designed for the removal of mercury at around 150 °C and 10^{-4} torr. Black, fresh uranium powder was thus obtained.

The organouranium compounds synthesized were first dissolved in 6 M HNO_3 and heated to dryness; the uranium content was determined by potentiometric titration with a 0.1 M standard potassium dichromate solution.[15]

$U(COT)_2$ (Uranium Bis(cyclooctatetraene)). Twenty milliliters of COT was transferred to a flask containing ca. 3.0 g of fresh uranium powder in vacuo at 77 K. The reaction took place immediately after the mixture was warmed to room temperature, and the reaction mixture was stirred for 4 h. The green solution was filtered, and the residue was extracted with benzene. The entire solution was evaporated, and the residue was washed with 5 mL of pentane several times under nitrogen. A yield of 2.5 g (70%) was obtained after drying. No gas evolution was observed during reaction. Anal. Calcd: U, 53.36. Found U, 52.95. Characteristic infrared absorptions (KBr pellet) occur at 670 (s), 700 (s), 745 (s), 778 (w), 900 (s), 1070 (s), 1120 (s), 1280 (vs), 1460 (s), and 3000 (w) cm^{-1}. A visible absorption peak was observed at 616 nm. All spectra are identical with the published data.

Table I. NMR Data of $(CF_3COCHCOCH_3)_4U$

^{19}F: upfield from internal CCl_3F
69 ppm
solvent: $CDCl_3$

^{13}C: downfield from internal Me_4Si
$\delta_{CF_3} = 169.0$ ppm (quartet); $J_{CF_3} = 285$ Hz
$\delta_{*CO} = 144.7$ ppm (singlet)
$J_{CH} = 129.8$ ppm (doublet); $J_{CH} = 169$ Hz
$\delta_{CO} = 159.9$ ppm (singlet)
$\delta_{CH_3} = 61.7$ ppm (quartet); $J_{CH_3} = 122$ Hz
solvent: Me_2SO-d_6 ($(CD_3)_2SO$)

^{1}H: from internal Me_4Si
$\delta_{CH_3} = +9.5$ ppm (upfield)
$\delta_{CH} = -13$ ppm (downfield)
solvent: $CDCl_3$

$U(Cp)_3$ (Uranium Tris(cyclopentadienyl)). Forty milliliters of benzene and 4.5 mL of C_5H_6 were transferred to a flask containing ca. 4.5 g of fresh uranium powder in vacuo at 77 K (the stoichiometry of Cp to U is 2.5), and the mixture was warmed to room temperature and stirred for 8 h. Evolution of hydrogen (confirmed by gas chromatography) was observed during the course of the reaction and found to impede the reaction as the pressure increased. A higher yield was obtained by occasionally releasing the gas. After the reaction mixture turned bronze, the solution was separated from the residue and evaporated and the residue was recrystallized from benzene and dried in vacuo. The yield was 30%. The residue of uranium ignited on exposure to the air. No further analysis on the residue was performed. The same experiments were performed on mixtures with increased Cp/U ratios. Anal. Calcd: U, 54.02. Found: U 54.93. Characteristic infrared spectra absorptions occur at 600 (s), 620 (s), 662 (w), 778/780 (vs), 806 (m), 890 (m), 910 (m), 1014 (s), 1060 (br), 1160 (br), 1440 (m), 1490 (br), and 3097 (w) cm^{-1}, which are in good agreement with the published data.[16] The proton resonance occurs 10.5 ppm upfield from benzene as internal standard.

$U(TFA)_4$ (Uranium Trifluoroacetylacetonate). The procedure was similar to the previous ones. The reaction mixture consisted of 5 mL of HTFA in 20 mL of petroleum ether and 6 g of U powder and was stirred for 1 h and the evolution of hydrogen was observed during the course of reaction. The solution was dried in vacuo after separation under nitrogen; then the yellowish brown crystals (ca. 90% yield, mp 137–138 °C) sublimed. The IR spectrum was identical with the published data.[17] The methyl and methylene proton resonances occur at 9.5 ppm (upfield), −13 ppm (downfield) using Me_4Si as internal standard, and the relative integral intensity ratio of methyl to methylene is 2.8:1; assignments of NMR spectra are shown in Table I. Anal. Calcd: U, 27.65. Found: U, 28.00.

Conclusion

Use of electrolytically produced amalgams as a means of synthesis of organouranium compounds is demonstrated. In all examples the yields are higher than those from conventional methods. Uranium powder obtained from the thermal decomposition of uranium hydride gave lower yields for $U(COT)_2$ and was not feasible for $U(Cp)_3$ and $U(Cp)_4$.[13] The thermal decomposition of uranium hydride takes place above 300 °C, in contrast with 150 °C for the decomposition of the amalgam. The reduced reactivity of the metal powder might be ascribed to the more pronounced sintering effect at higher temperature.

A single product of $U(Cp)_3$ was obtained from a reaction mixture with the Cp/U ratio less than 3. However, with the increased Cp/U ratio, the products were found to be a mixture of $U(Cp)_3$ and $U(Cp)_4$, which were identified by IR.[16,18] Besides the chemical shift observed for $U(Cp)_3$ at 10.5 ppm upfield, an additional resonance occurs at 25.3 ppm upfield (both from benzene as internal standard), which was assigned to be the proton resonance of $U(Cp)_4$.

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Registry No. $U(COT)_2$, 11079-26-8; $U(Cp)_3$, 54007-00-0; $U(TFA)_4$, 32627-13-7.

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Kinetics of Chloride Substitution into Bis(oxalato)platinate(II) Ion

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Kinetic studies on platinum complexes have received new impetus since discovery[1] that certain of these substances exhibit extraordinary biological activity. Oxalato and malonato complexes are among those exhibiting such activity, and where marked differences for analogous complexes are observed, as in the case of $[Pt(en)C_2O_4]$ and [Pt(en)mal],[2] the relative labilities of the carboxylato ligands may be involved.[3] In order to investigate some of these matters we are extending our earlier work[4] on platinum(II) complexes.

We report here on the reactivity of $Pt(C_2O_4)_2^{2-}$ in aqueous chloride media. The solvent is of interest because of its relevance to biologically important fluids, especially blood plasma. Our main observations, which have been for 1 M chloride in the pH range 5–8, are consistent with a simple reaction sequence leading to quantitative production of $PtCl_4^{2-}$.

Some studies were carried out on more strongly acidic solutions (pH <2; 1 M Cl^-). For these conditions a marked oxygen dependence was observed, and even when attempts were made to exclude all dissolved oxygen, complications remained.

In the pH range 5–8 we find no evidence for an influence from dissolved oxygen or for polynuclear species. For these pH conditions the kinetic results are consistent with a sequence of consecutive first-order reactions leading to $PtCl_4^{2-}$. Our results are compared with those obtained by Giacomelli and Indelli[5] for NCS^- substitution into $Pt(C_2O_4)_2^{2-}$.

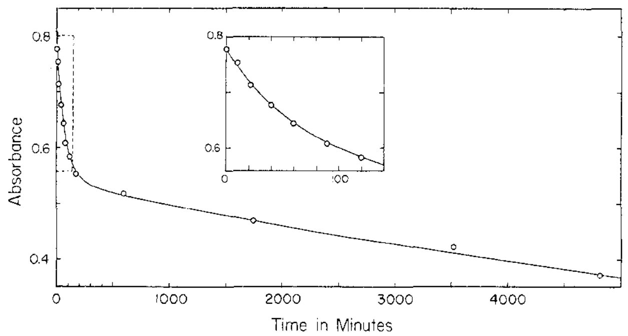

Figure 1. Absorbance vs. time for experiment 1: $[Pt(C_2O_4)_2^{2-}]_0 = 2.00 \times 10^{-4}$ M, [NaCl] = 1.00 M, $T = 35.0$ °C, λ 285 nm. Points are experimental values and the line is calculated from eq 2 with $k_1 = 0.21 \times 10^{-3}\ s^{-1}$, $k_2 = 1.28 \times 10^{-6}\ s^{-1}$, $\epsilon_I = 3850$, and $\epsilon_{III} = 40$. The smaller graph, in insert, is an expansion of the part of the larger graph enclosed within dashed lines.

Experimental Section

Potassium bis(oxalato)platinate(II) dihydrate was prepared by the method of Vèzes[6] and was purified as previously described.[4a] Water was doubly distilled and exhibited negligible UV absorption above 220 nm; other materials were of reagent grade. Phosphate buffers, used for reactions in the pH range 5.5–7.5, were prepared by established procedures.[7]

Kinetic runs were initiated by mixing, at the appropriate temperature, equal volumes of a $K_2[Pt(C_2O_4)_2]$ solution (freshly prepared) with a solution containing chloride (NaCl, and for experiments at low pH, also HCl). For a few runs where $[Cl^-] < 1$ M, $NaClO_4$ was included to maintain constant ionic strength. For reactions in the pH range 5.5–7.5, phosphate buffer, at total phosphate concentrations of up to 10^{-2} M, was generally included, although some experiments were conducted in which the buffer was omitted. In the latter case pH measurements were made at the beginning and completion of reaction. The total platinum(II) concentration in reaction solutions was $(1.0–4.0) \times 10^{-4}$ M while the chloride concentration was 1.00 M in all but a few cases (which are specified). The ionic strength was constant for each run and was always in the range 1.00–1.03 M. Temperatures were held constant to ±0.1 °C.

Progress of the reaction was followed spectrophotometrically by repetitive scanning through the range 220–340 nm, with particular focus on 285 nm (a maximum for $Pt(C_2O_4)_2^{2-}$, where $PtCl_4^{2-}$ absorbs almost negligibly) and on the 235–245-nm region (in which an isosbestic point exists during the earlier stages of reaction). Oxygen was excluded for some experiments by sweeping reactant solutions with nitrogen prior to mixing by syringe techniques.

Results and Discussion

The chloride concentration (usually 1 M) was in all cases in very large excess to the platinum(II) ($(1–4) \times 10^{-4}$ M). For 1 M chloride at pH 5.5–7.5 and 35–65 °C, final spectra were consistent with >98% conversion of $Pt(C_2O_4)_2^{2-}$ to $PtCl_4^{2-}$ in accord with expectations.[8] Replacement of oxalate by chloride undoubtedly involves consecutive steps, and our observations reveal that at least two of these are slow. This feature is illustrated by absorbance vs. time profiles (Figure 1), by nonlinearity of first-order rate plots, and by the absence of an isosbestic point at 242 nm.[9] For this middle pH region the presence or exclusion of oxygen had no apparent effect on the rate or on other aspects of reaction.

The simplest kinetic scheme which can accommodate our observations involves two consecutive first-order processes.

$$\mathrm{I} \xrightarrow{k_1} \mathrm{II} \xrightarrow{k_2} \mathrm{III} \qquad (1)$$

Here I, II, and III are, respectively, $Pt(C_2O_4)_2^{2-}$, an intermediate, and $PtCl_4^{2-}$, while k_1 and k_2 are first-order rate constants. Values of k_1, k_2, and ϵ_{II} (the absorbancy coefficient for the intermediate) were evaluated using a nonlinear least-squares program[10] to minimize differences between observed absorbances (A) at 285 nm (1 cm path) and those