

Plutonium(III)-catalyzed Meerwein–Ponndorf–Verley reactions

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Abstract

The reactivity of Th(IV), U(III), U(IV), Pu(III) and Pu(IV) *iso*-propoxide in the Meerwein–Ponndorf–Verley reduction of ketones by *iso*-propanol have been examined. Plutonium(III) *iso*-propoxide is found to be an effective catalyst for the reduction of a range of substituted aryl-alkyl ketones, while An(IV) *iso*-propoxides (An = Th, U, Pu) are found to be inactive. U(III) was found to oxidize under the reaction conditions to a U(IV) complex, which was also catalytically inactive. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Studies of the reactivity of actinide metals and actinide-containing compounds toward organic-based materials represent an important area of f-element research, since there are many instances in which actinides come into contact with potentially reactive functional groups. During processing operations, plutonium and other actinides are extracted into organic phases by complexants that may possess ketone [1,2], carboxamide [2,3], and phosphoryl functionalities [4,5]. Reactions that degrade or alter these organic species can drastically affect the efficiencies of an extraction, and create unnecessary transuranic (TRU) waste. Actinide-containing complexes also contact organic materials for prolonged periods during disposal; these organic materials include plastics, and fabrics which contain alcohol and acetal functionalities. Catalytic oxidation reactions, including DNA degradation, have also been implicated in the biological effects of Pu [6].

Due to this wide range of interactions, it is important to determine more clearly the reactivity of the actinides.

Detailed studies of actinide reactivity toward organic substrates should facilitate an increase in our predictive capabilities of the way in which actinide-containing compounds will interact with the wide range of materials with which they come into contact. Significant efforts have been made to try to establish reasonable periodic trends for the actinide metals in order to assist in these studies. For example, thorium has been shown to closely resemble a Group IV metal in its reactivity [7], while the late actinides behave in a fashion similar to lanthanides, with a dominant +III oxidation state [8]. The reactivity pathways of the early actinides, however, have proven to be more difficult to predict. This is in large part due to their redox activity, which distinguishes them from the lanthanides, and also their ability to adopt the *trans*-dioxo actinyl ligand geometry $[(O=An=O)^{n+}]$; An = U, $n = 2$; An = Np, Pu, $n = 1, 2$ [9]. Detailed reactivity studies of these early 5f metals should allow a closer comparison of the chemistry of the actinides to that of the lanthanides and transition metals.

We have chosen to explore the chemistry of the early actinides using the Meerwein–Ponndorf–Verley (MPV)

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reduction of ketones. In this reaction, a highly Lewis acidic metal complex containing a secondary alkoxide ligand coordinates a ketone. The close proximity of the alkoxide and the ketone allows a hydride shift, via a cyclic transition state, to interconvert the ketone and alcohol functional groups (Scheme 1). This reaction is reversible, and proceeds to equilibrium; it can be driven towards completion by addition of excess *iso*-propanol. The MPV reaction is usually catalyzed by Lewis-acidic metal alkoxides, such as those of aluminum [10] or the lanthanides [11–14]. Interestingly, zirconocene dihydride has been shown to catalyze this reaction [15], while zirconium *iso*-propoxide behaves only as a stoichiometric reagent [16a]. Immobilization on silica and highly elevated temperatures have been found to be required for zirconium *iso*-propoxide-mediated catalysis [16b].

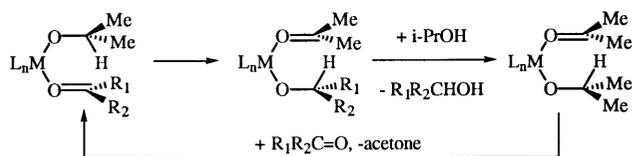
At the outset, we expected that similar reactivity would be seen for An(III) and lanthanide(III) complexes — these were expected to catalyze the MPV reaction. In contrast, An(IV) compounds were not expected to readily catalyze the MPV reaction, by analogy with zirconium *iso*-propoxide. During the course of this study we attempted Meerwein–Ponndorf–Verley reductions using Th(IV), U(III), U(IV), Pu(III) and Pu(IV) complexes, and the results are detailed below.

2. Experimental

2.1. General considerations

All reactions were carried out under an atmosphere of helium in a glovebox. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity 300 spectrometer. Infrared (IR) spectra were recorded on a Nicolet Magna-IR 750 Fourier transform spectrometer. Ultraviolet and visible (UV–Vis) spectra were recorded on a Perkin–Elmer Lambda 19 spectrometer.

Tetrahydrofuran (THF), toluene and hexane were dried and deoxygenated using the Grubbs solvent purification system [17]. Toluene-*d*₈ was degassed in vacuo, and dried by passing through a column of activated alumina. All other reagents are commercially available and were used as received.



Scheme 1.

2.2. MPV experiments

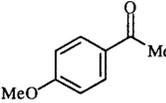
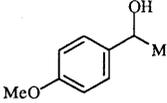
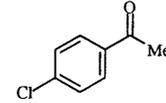
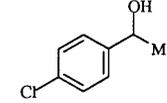
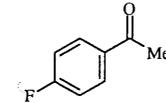
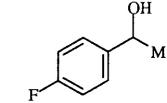
In a typical experiment, a solution of Pu[N(SiMe₃)₂]₃ (0.024 g, 0.033 mmol) in 2-propanol (1.0 g, 16.6 mmol) was added to *p*-methoxyacetophenone (0.090 g, 0.66 mmol) in a helium atmosphere negative pressure glovebox. The reaction was stirred for 24 h, after which the volatiles were removed in vacuo. The residue was extracted into THF and filtered through silica. The solvent was removed to yield an oil (0.089 g, 99% yield) which was determined (by ¹H NMR) to be a mixture of *p*-methoxyacetophenone (43%) and 1-(*p*-methoxyphenyl)ethanol (57%). Reactions using uranium and thorium catalysts were carried out in a standard positive pressure drybox; heating was performed in a Teflon-sealed Schlenk flask.

3. Results and discussion

Since lanthanide tris(amido) complexes are known to be effective precursors for the formation of lanthanide alkoxides via alcoholysis reactions, we employed the analogous An(III) complexes Pu[N(SiMe₃)₂]₃ (**1**) [18] and U[N(SiMe₃)₂]₃ (**2**) [19] as pre-catalysts. In the case of An(IV) alkoxides, the precursor complexes used were the metallacycles An[N(SiMe₃)₂]₂[N(SiMe₃)(SiMe₂CH₂)] (An = Th, U) [20]. The MPV reactions were carried out by adding a solution of 5 mol% of the amido pre-catalyst, dissolved in *iso*-propanol, to the ketone. The reactions were stirred at room temperature for 24 h, after which time the solvent was evaporated, the residue extracted with THF, and the extracts filtered through a short plug of silica to remove residual catalyst. Reactions which showed no formation of product, except for the Pu(IV) reactions, were also run at 90°C for 16 h. The products were then analyzed by ¹H NMR spectroscopy.

The results of the Pu(III) catalyzed MPV reactions are presented in Table 1. The reactions were found to proceed in yields equal to or higher than similar reactions using lanthanide catalysts with equivalent reaction times [12]. Electronic effects were examined by employing 4-substituted acetophenones (entries 1, 4–6). It was found that acetophenone and 4-methoxyacetophenone were both reduced to a greater extent by the Pu(III) catalyst than by lanthanide catalysis, while the reactivity of 4-chloroacetophenone was similar to that seen for samarium [12]. Steric effects were examined using acetophenone, propiophenone, and 2,2-dimethylpropiophenone (entries 1–3). There was essentially no difference in the conversion levels due to steric differences between these substrates, however, both acetophenone and propiophenone proceeded to a greater extent than had been reported for samarium [13]. Aliphatic ketones, represented by cyclohexanone (entry

Table 1
Pu catalysed MPV reactions^a

$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}' \xrightarrow[\text{i-PrOH, 24 h, rt}]{\text{Pu}[\text{N}(\text{SiMe}_3)_2]_3} \text{R}-\text{CH}(\text{OH})-\text{R}'$			
entry	substrate	Product	Conversion
1			91%
2			93%
3			88%
4			57%
5			92%
6			88%
7			100%

^a Conversion refers to the amount of product relative to the starting material.

7), were also smoothly reduced to the same degree as has been reported for Gd and Er-mediated catalysis [13]. Aldehydes, represented by cyclohexanecarboxaldehyde and 4-anisaldehyde, gave complex mixtures which included the esters attributed to Tischenko type disproportionation-coupling reactions [21]. This reaction is known to occur for aldehydes under MPV conditions [22].

Despite the close analogy between uranium(III) and a lanthanide(III) metal center, it was found that the combination of $\text{U}[\text{N}(\text{SiMe}_3)_2]_3$ and *iso*-propanol did *not* catalyze the reduction of ketones, in marked contrast to the high activity of lanthanide *iso*-propoxides in this reaction. Further investigations, however, revealed that the lack of catalytic activity was due to the spontaneous oxidation of U(III) to U(IV) by the *iso*-propanol solvent, and thus the actual catalyst being studied in this case was a uranium(IV), rather than a uranium(III), *iso*-propoxide complex [23]. As confirmation of this fact, it was found that *iso*-propanol solutions of both the U(IV) and U(III) amido precursors were indistinguishable by UV–Vis spectrometry and cyclic voltammetry.

Actinide(IV) *iso*-propoxide complexes did not catalyze the MPV reduction of ketones, even at elevated temperatures in the cases of uranium and thorium. This lack of reactivity could be due to a difference in Lewis acidity between An(III) and An(IV) alkoxides, which we are currently examining. However, the observed differences in reactivity between An(III) and An(IV) *iso*-propoxides may also be a result of markedly different structural properties of the catalytic species involved. Thus a highly oligomeric structure for the metal alkoxide, and a corresponding high coordination number at the metal center, may prevent facile coordination of the ketone and thereby inhibit catalytic activity. Although the structural chemistry of the actinide metals coordinated by bulky aryloxide ligands has been explored in some detail, the nature of simple homoleptic alkoxide complexes of the actinides (e.g. methoxides, ethoxides, *iso*-propoxides etc.) is not well understood [24]. Literature reports describing uranium hexa(*iso*-propoxide) [25], and Lewis base adducts of thorium tetra(*iso*-propoxide) [26] have appeared, but very little is known of the nature of plutonium(III) *iso*-propoxide or uranium(IV) *iso*-propoxide. These materials may contain bridging oxo ligands, as observed for the structurally-characterized lanthanide *iso*-propoxides $\text{Y}_5\text{O}(\text{O}-i\text{-Pr})_{13}$ [27], $\text{Yb}_5\text{O}(\text{O}-i\text{-Pr})_{13}$ [28], $\text{Y}_4\text{PrO}(\text{O}-i\text{-Pr})_{13}$ [29], and $\text{Er}_5\text{O}(\text{O}-i\text{-Pr})_{13}$ [30], and it is perhaps reasonable to draw comparisons between a possible structure for U(IV) *iso*-propoxide and the well characterized cerium(IV) *iso*-propoxide $[\text{Ce}(\text{O}-i\text{-Pr})_4(\text{HO}-i\text{-Pr})_2]_2$ [31].

This report represents our initial efforts to understand the reactivity of the early actinides toward organic substrates. Plutonium(III) *iso*-propoxide shows similar or slightly enhanced reactivity for MPV reductions when compared to lanthanide alkoxide complexes. Unfortunately, the MPV reaction conditions did not allow a comparative study of uranium(III), since this precursor oxidized to uranium(IV) upon dissolution in *iso*-propanol. The An(IV) *iso*-propoxide species do not catalyze the MPV reaction, consistent with assigning reactivity to be analogous to zirconium chemistry under these conditions. However, the relative contributions to catalytic activity of electronic (i.e. oxidation state) changes versus changes in catalyst structure have yet to be determined. Our current efforts are directed towards determining the range of organic transformations which are promoted by the actinide metals, what effect the oxidation state of the metal plays in its reactivity, and what reactivity patterns are common among the redox-active early actinides.

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