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Observations on the Reaction of Uranium Tetrachloride and Dichlorodioxouranium(VI) with Lithium Alkyls*

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Abstract

Both uranium tetrachloride and dichlorodioxouranium(VI) react with lithium alkyls in polar and non-polar solvents to form (presumably) the thermally unstable 'UR_4' and 'UO_2R_2' species respectively, which upon warming to room temperature both decompose by β-hydride elimination (when a β-hydrogen atom is present on the alkyl group). The course of the transformations in such a highly complex, heterogeneous reaction is critically dependent on the state and history of the uranium compound.

Introduction

Interest in organoactinide chemistry has grown rapidly in the past fifteen years [1]. Some of the initial studies on the actinides focused on alkyl and aryl complexes because of the importance of these complexes in organometallic chemistry [2]. Three groups reported independently on the synthesis of the thermally stable alkyl and aryl complexes of the general formula $(\eta^5\text{-}C_5H_5)_3UR$ (R = hydrocarbyl group) [3]. Wachter and Marks reported later on the synthesis and properties of the analogous thorium complexes [4]. Seyam and Marks studied the thermally unstable 'UR_4' species [5] (originally studied during the Manhattan project [6]), which decomposed via β-hydride elimination (when a β-hydrogen atom was present on the R group). This result suggested that these thermally unstable alkyls are coordinatively unsaturated in contrast to the aforementioned thermally stable $(\eta^5\text{-}C_5H_5)_3MR$ complexes, which are presumably coordinatively saturated. The blocking of the β-hydride elimination pathway in $(\eta^5\text{-}C_5H_5)_3$-MR complexes appears to be a major reason for their high thermal stability [3, 4, 7].

In this contribution we highlight recent results from our work in the area of C–H activation (hydrogen abstraction processes) in both reactions of uranium tetrachloride and dichlorodioxouranium(VI) with lithium alkyls.

Experimental

Reaction of Dichlorodioxouranium(VI) with Lithium Alkyls

Dichlorodioxouranium(VI), UO_2Cl_2, reacts with a variety of RLi or RMgCl reagents (R = hydrocarbyl), in polar or non-polar solvents at low temperature to form what we presume to be transitory 'UO_2R_2' species, according to the following equation:

$$UO_2Cl_2 + 2R\text{-}M \xrightarrow[-78\ ^\circ C]{\text{THF or toluene}} \text{'}UO_2R_2\text{'} + 2MCl \qquad (1)$$

M = Li; R = CH_3, n-C_4H_9, t-C_4H_9, C_6H_5
M = MgCl, R = CH_2CH, i-C_3H_7

Upon warming the reaction mixture to room temperature, the 'UO_2R_2' species decomposes to a dark brown solid which is mostly dioxouranium(IV), UO_2. Some of the starting materials (UO_2Cl_2 and RLi or RMgCl) were recovered unchanged. This is apparently due to the heterogeneous nature of this reaction mixture (UO_2Cl_2 is only slightly soluble in polar solvents). This observation is in good agreement with the yield obtained on the gaseous and volatile (liquid or solid) hydrocarbon products.

GC data [8] suggest that there are three pathways available for thermolysis of 'UO_2R_2' which are illustrated in Scheme 1. It was also found that the choice of a given thermolysis pathway does not depend on the type of solvent (polar or non polar), or on the relative amount of RLi or RMgCl, but mainly of the type of hydrocarbyl group (R) (*vide infra*). When R = C_6H_5, the thermolysis path is predominantly reductive elimination [9] of diphenyl, (C_6H_5·C_6H_5). To our knowledge this is the first

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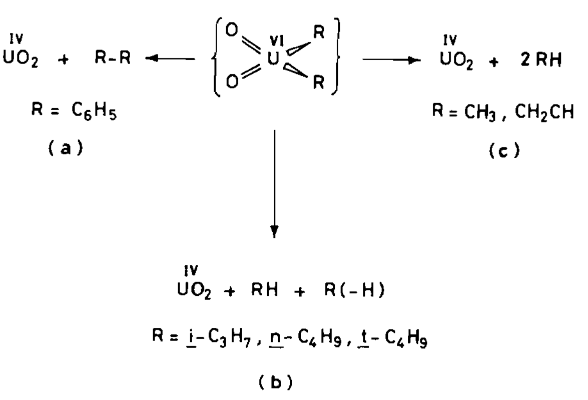

Scheme 1. (a) Reductive Elimination, Coupling, (b) Reductive Elimination, Disproportionation (β-Elimination), and (c) Hydrogen Abstraction [8].

example of a dihydrocarbyl actinide complex which thermally decomposes by reductive elimination (coupling). This is reasonable for uranium(VI) which has accessible lower oxidation states (*e.g.*, U(V), U(IV), Scheme 1(a)).

'UO_2R_2' species (where R = $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, and $t\text{-}C_4H_9$) decompose thermally by path (b) [5] (Scheme 1, *i.e.*, R = $i\text{-}C_3H_7$). Equimolar amounts of propane and propene are obtained and no dimerization product (2,3-dimethylbutane) was formed, which excludes a free radical pathway [10]. Also, for 'UO_2R_2' species, where R = CH_3 or CH_2CH, decomposition occurs via hydrogen abstraction from the surrounding media [5, 11], to form exclusively methane or ethene.

Labelling experiments based on GC/MS analysis of the methane evolved on decomposition of '$UO_2(CH_3)_2$' in toluene-d_8 showed that some of the hydrogen atoms are abstracted from the solvent [8].

Further labelling and X-ray powder diffraction studies are in progress and the results will be discussed elsewhere [12].

Reactions of UO_2Cl_2 with various hydrocarbyl anions, as well as isolation of 'UO_2R_2' species, are areas of continuing investigation [13].

Reaction of Uranium Tetrachloride with Lithium Alkyls

One of the simplest and most important C–H activation processes in catalysis is the β-hydride abstraction process [14]. Although this process is common for many transition metal complexes, it has only been observed for organoactinides under unusual circumstances, *i.e.*, photochemically [15], in unusual coordination environments [16], or where there is a very stable end product [5, 17, 18].

We have reported a brief investigation of the thermally unstable products of the reaction of uranium tetrachloride with lithium alkyl reagents [5] (eqn. 2). The purpose was to ascertain whether

$$UCl_4 + 4RLi \xrightarrow[\text{or ether}]{\text{hydrocarbons}} \text{organic products} + U + 4LiCl \qquad (2)$$

β-hydride elimination might occur in a uranium hydrocarbyl with potential coordinative unsaturation.

The principal goal of this investigation was to determine how, for constant solvent and lithium reagent, the course of eqn. (2) depends on the exact state of the UCl_4 and the reaction conditions. In Table I are compiled data for the gaseous organic products of eqn. (2) as a function of these parameters. For all experiments the distribution of organic products (n-butane:1-butene, isobutane:isobutene) is similar to that reported in eqn. (2) for the longest reaction periods. The nature of the products is evidence that the intermediate uranium hydrocarbyls readily suffer β-hydride elimination. The yields are, however, found to be quite sensitive to the history of the UCl_4 and the agitation procedure. Thus for practical reaction times, yields of butane and butene are significantly below stoichiometric if UCl_4 is employed as obtained from the synthesis, and simple stirring is carried out. These low yields are due to the heterogeneous nature of the conditions and incomplete reaction. Thus, finely pulverizing the UCl_4 and drying it with $SOCl_2$ both increase the hydrocarbon yields substantially*. Furthermore, the use of ultrasonic agitation, which is known to accelerate many types of heterogeneous reactions [19], increases the butane:butene yield to near quantitative. In the case of experiment 4, where the butane:butene yield is not quantitative, the additional equivalents of t-butyl functionality can be readily accounted for as unreacted lithium reagent. Thus, addition of water to the filtrate from the reaction mixture liberates a 43% yield of isobutane.

The nature of the black reaction residue from eqn. (2) was investigated to determine whether residual hydrocarbyls are present and whether, in the case where the organic products indicate quantitative reaction, the expected stoichiometry is obeyed. In regard to the first question, the C, H contents (%) from the residues of experiments 1, 2, and 5 were found to be 2.77, 0.76; 1.68, 0.66; and 4.43, 1.20 respectively, indicating only minor incorporation of carbonaceous products (perhaps ether from

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*In reference 5, a sample of anhydrous UCl_4 from a commercial source was subjected to grinding and drying with $SOCl_2$. This material, perhaps as a result of adventitious contamination by the supplier, appears to have been abnormally reactive.

TABLE 1. Gases Evolved in the $UCl_4 + 4RLi$ Reaction [18].

Experiment Lithium Reagent	UCl_4 Treatment[a]	Time (h)	Agitation	Cumulative Yield RH + R − (H) (%)[b]	Butene:Butane
R = $n\text{-}C_4H_9$	none	153	stirring	20	
		0.7	ultrasound	34	
		105	stirring	44	52:48[c]
R = $n\text{-}C_4H_9$	grinding, $SOCl_2$	110	stirring	48	
		26	ultrasound +		
		9	stirring	77	
		38	ultrasound	90	
		55	ultrasound	90	55:45[c]
R = $t\text{-}C_4H_9$	none	87	stirring	11	
		2.3	ultrasound +		
		33	stirring	28	
		3	ultrasound	30	
		30	stirring	30	56:44[d]
R = $t\text{-}C_4H_9$	$SOCl_2$	90	stirring	38	
		1	ultrasound +		
		24	stirring	52	
		1	ultrasound +		
		48	stirring	60	
		1	ultrasound +		
		38	stirring	63	
		1	ultrasound +		
		24	stirring	63	62:38[d]
R = $t\text{-}C_4H_9$	grinding, $SOCl_2$	118	stirring	58	
		1	ultrasound +		
		9	stirring	68	
		8	ultrasound +		
		37	stirring	81	
		21	ultrasound +		
		59	stirring	96	
		35	ultrasound +		
		47	stirring	98	
		47	ultrasound	98	60:40[d]

[a] None indicates that UCl_4 was employed as obtained from the procedure of ref. 9. [b] Estimated uncertainty: ±5%. [c] 1-Butene: n-butane. Estimated uncertainty in yields: ±3%. [d] Isobutene:isobutane. Estimated uncertainty in yields: ±3%.

the washing). The residue from experiment 5 was found to contain: Li, 6.69; Cl, 33.62; U, 55.20. If eqn. (2) proceeds as written, the stoichiometry of the inorganic residue should be Li_4UCl_4 or Li, 6.81; Cl, 34.78; U, 58.40. If eqn. (2) did not proceed to completion, there would be a deficiency of lithium, since the soluble lithium alkyl would be washed from the residue. Clearly there is no deficiency of lithium.

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