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Further Observations on the Reaction of Uranium Tetrachloride with Simple Lithium Alkyls

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A number of years ago we reported a brief investigation of the thermally unstable products of the reaction of uranium tetrachloride with alkyl lithium reagents [1] (eqn. 1). The purpose of this investigation was to ascertain

$$UCl_4 + 4RLi \xrightarrow[\text{or ether}]{\text{hydrocarbons}} \begin{matrix}\text{organic}\\ \text{products}\end{matrix} + U + 4LiCl \qquad (1)$$

whether β-hydride elimination might occur in a uranium hydrocarbyl with potential coordinative unsaturation. No attempt was made to characterize the intermediate organometallics, nor was any structure or stoichiometric formulation specifically claimed for them (historically such species have been presumed to be tetrahydrocarbyls [2, 3]). Subsequent to this work, several groups have reported the successful use of eqn. 1 to generate finely divided uranium metal for synthetic purposes [4, 5], and evidence has been presented that, under certain conditions [6], more than four alkyl groups may coordinate to uranium. Another group has questioned, for $R = t\text{-}C_4H_9$, whether eqn. 1 actually proceeds to completion as depicted [7].

In hydrocarbon or ether solvents, eqn. 1 is obviously a highly complex, heterogeneous reaction, and the course of the transformation should be critically dependent on the state and history of the UCl_4. During a recent study of 'stabilized' actinide tetrahydrocarbyls [8], the sensitivity of reactions such as eqn. 1 to parameters involving the heterogeneity became apparent and stimulated a brief re-investigation of our earlier work, using improved analytical techniques and a wider range of reaction conditions. We report here, for two representative lithium reagents and the 'innocent' solvent heptane, further observations on eqn. 1 as regards optimization of RLi-derived products and, ultimately, metallic uranium.

Experimental

All chemical manipulations were carried out on a grease-free high vacuum (10^{-4}–10^{-5} torr) line under purest argon, using equipment and techniques described previously [9]. Evolved gases were collected and measured by standard Toepler pump/high vacuum line procedures. The gases were characterized with a Varian 3700 series gas chromatograph, using a 1/8″ × 8′ Poropak QS column, flame ionization detection, and a Hewlett-Packard 3390A electronic integrator. Uranium tetrachloride was prepared by the literature procedure [10] and was transferred in a Vacuum Atmospheres glove box equipped with a HE-193-1 high capacity 'Dri-Train'. Additional treatment of various UCl_4 samples included grinding in a 'wiggle-bug' device for several hours in the glove box and/or refluxing 24 h with thionyl chloride followed by drying at 250 °C/10^{-5} torr for 24 h [1]. Lithium reagents were purchased from Aldrich Chemical Co. and were carefully standardized by the 'double titration' technique [11]. Analytical reagent grade heptane was washed free of olefins and distilled from Na/K. It was then vacuum transferred to a storage bulb containing $U[(CH_3)_5C_5]_2Cl_2$ as a drying agent and used as needed. Ultrasonic agitation of reaction mixtures was performed by lowering the reaction flask into an L. and R. Manufacturing Model 210 ultrasonic cleaning device filled with water. Elemental analyses were performed by Dornis and Kolbe Microanalytical Laboratory, Mülheim a.d. Ruhr, West Germany.

In a typical procedure, the reaction between a weighed UCl_4 sample and a measured volume of lithium reagent was conducted in Schlenk apparatus interfaced to the vacuum line. The solvent (heptane) was condensed directly into the reaction mixture from the vacuum line. In the case of Aldrich $t\text{-}C_4H_9Li$ in pentane, the pentane was evaporated prior to distilling in the heptane. The reactions were begun at $-78°$ with vigorous stirring, and were then allowed to warm to room temperature. Gases were sampled by periodically cooling the reaction mixture in a dry ice slush bath (78°) and pumping the volatiles through a $-195°$ or $-78°$ trap. These gases were transferred to storage bulbs for subsequent analysis. After the reactions were complete, the reaction mixtures were filtered using a fine Schlenk frit directly interfaced to the vacuum line. The solid black residue obtained was washed repeatedly by condensing pentane and diethylether onto it, and was then vacuum dried. In several cases the filtrate from the above operation was treated with water and the evolved gases (if any) were collected by a Toepler pump. The black residue was collected in the glove box for elemental analysis.

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*In reference 1, 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.

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TABLE I. Gases Evolved in the $UCl_4 + 4RLi$ Reaction.

Experiment Lithium Reagent	UCl_4 Treatment[a]	Time (h)	Agitation	Cumulative Yield RH + (RH)−H (%)[b]	Butene:Butane
1 $R = n\text{-}C_4H_9$	none	153	stirring	20	
		0.7	ultrasound	34	
		105	stirring	44	52:48[c]
2 $R = n\text{-}C_4H_9$	grinding, $SOCl_2$	110	stirring	48	
		26	ultrasound +		
		9	stirring	77	
		38	ultrasound	90	
		55	ultrasound	90	55:45[c]
3 $R = t\text{-}C_4H_9$	none	87	stirring	11	
		2.3	ultrasound +		
		33	stirring	28	
		3	ultrasound	30	
		30	stirring	30	56:44[d]
4 $R = t\text{-}C_4H_9$	$SOCl_2$	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]
5 $R = t\text{-}C_4H_9$	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%.

As a check on the quantitation procedure, measured aliquots of the standardized lithium reagent in heptane were hydrolyzed in the aforementioned reaction apparatus and were also collected on the vacuum line. As a check on the ultrasonic agitation procedure, measured amounts of the lithium reagents in heptane were subjected to ultrasonic treatment for various lengths of time and the evolved gases (if any) were collected. Decomposition was found to be less than 3% after 32 h of agitation.

Results

The principal goal of this investigation was to determine how, for constant solvent and lithium reagent, the course of eqn. 1 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. 1 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. 1 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 substantially increase the hydrocarbon yields [12]. Furthermore, the use of ultrasonic agitation, which is known to accelerate many types of heterogeneous reactions [12], 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. 1 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 the washing). The residue from experiment 5 was found to contain: Li, 6.69; Cl, 33.62; U, 55.20. If eqn. 1 proceeds as written, the stoichiometry of the inorganic residue should be Li_4UCl_4 or Li, 6.81; Cl, 34.79; U, 58.40. If eqn. 1 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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