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Thermal Studies of 'Dialkyldioxouranium(VI)'

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Dichlorodioxouranium(VI) reacts with RLi or RMgCl (R = hydrocarbyl) in polar and nonpolar solvents to form (presumably) the thermally unstable 'UO_2R_2' species, which upon warming to room temperature either 1) reductively eliminates R–R leaving UO_2 (R = phenyl), or 2) decomposes by β-hydride elimination to give the corresponding alkane and alkene and UO_2 (when R = i-propyl, n-butyl, and t-butyl), or 3) affords the corresponding alkane (R = methyl) or alkene (R = vinyl) via hydrogen abstraction. Microanalysis, and spectroscopic and gas chromatographic data are discussed.

Introduction

Interest in organoactinide chemistry has grown rapidly in the past decade [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 akyl 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 $(\eta^5\text{-}C_5H_5)_3MR$ complexes appears to be a major reason for their high thermal stability [3, 4, 7]. We wish to report here studies of the thermally unstable 'UO_2R_2' species, where (R = methyl, vinyl, i-propyl, n-butyl, t-butyl, phenyl), in order to better understand the nature of the uranium-to-carbon sigma bond in other uranium oxidation states, and the mechanism by which these presumably coordinatively unsaturated species undergo thermal decomposition.

Experimental

Physical and Analytical Measurements

^1H NMR (60 MHz) spectra were recorded on a Perkin-Elmer R-20B spectrometer. Chemical shifts are reported relative to internal $Si(CH_3)_4$. Samples were prepared either in a glove box or on a high vacuum line. Deuterated aromatic solvents were dried over Na/K alloy, and were degassed by freeze–thaw cycles on a vacuum line. Mass spectra were recorded on a Hewlett-Packard 5985 GC/MS instrument.

Infrared spectra were recorded on Perkin-Elmer 283 or Perkin-Elmer 599B spectrometers and were calibrated with polystyrene film. Samples were prepared in a glove box as mulls using previously dried and degassed Nujol or Fluorolube. Mulls were sandwiched between polished KBr plates contained in an o-ring airtight holder.

Elemental analyses were performed by Dornis and Kolbe Microanalytisches Laboratorium, West Germany.

Gas chromatographic analysis of gaseous and liquid products was performed using a Perkin-Elmer GC column (Porapak QS, 80–100 mesh, 1/8″ diameter, 8′ length), and a Varian 3700 Gas Chromatograph with flame ionization detection and Linear Systems Integrating Recorder.

Materials and Methods

All synthetic procedures were performed in Schlenk-type glassware using normal benchtop Schlenk techniques [8], in Schlenk-type glassware interfaced to a high vacuum (10^{-5}–10^{-6} torr) line, or in a dinitrogen (or argon) filled glove box. Argon and dinitrogen (Matheson, prepurified) were purified further by passage through a supported MnO oxygen removal column [9] and a Davison 4 Å molecular sieve column. Toluene, diethyl ether, tetrahydrofuran, benzene, and pentane (previousy distilled from Na/K benzophenone) were condensed and stored *in vacuo* in bulbs on the vacuum line.

Commercially obtained diethyl ether solutions of $CH_3Li \cdot LiBr$, n-C_4H_9Li in n-hexane, and t-C_4H_9Li in n-pentane (Aldrich), $CH_2{=}CHMgCl$ in THF

TABLE I. Thermolysis Product Data for 'Bis(hydrocarbyl)dioxouranium(VI)'.

RLi	Ratio	Solvent	Decomp.	Decomp.	
R	RLi/UO_2Cl_2		time (h)	Products	Yields (%)[a]
Methyl	2	Ether	15	Methane	61
Methyl	2	Toluene-d_8	20	Methane-d_1	6.5
				Methane	15.2
Methyl	4	Ether	11	Methane	50
Vinyl[b]	2	Ether/THF (1/1)	25	Ethene	69
i-Propyl[b]	2	THF	48	Propane	36
				Propene	35
i-Propyl[b]	4	THF	48	Propane	36
				Propene	37
n-Butyl	2	Toluene/n-hexane (10/1)	28	n-Butane	9
				1-Butene	3
n-Butyl	4	Toluene/n-hexane (5/1)	18	n-Butane	37.8
				1-Butene	4.2
t-Butyl	2	Toluene/n-pentane (10/1)	44	i-Butane	42.8
				i-Butene	14.2
t-Butyl	4	Toluene/n-pentane (5/1)	70	i-Butane	64.3
				i-Butene	31.7
Phenyl	2	THF	72	Benzene	18
				Biphenyl	66

[a] Yield based upon amount of uranyl chloride used. Estimated error, ±0.5%. [b] From Grignard.

(Apache Chemicals), i-C_3H_7MgCl in diethyl ether, and C_6H_5Li in 70:30 benzene:diethyl ether (Alfa) were used without further purification. UO_2Cl_2 (finely divided powder) was prepared according to the literature [10], (99.6% purity) by the vapor phase reacion of dry O_2 with UCl_4 at 300–350 °C. UCl_4 was prepared by the literature procedure [11]. The apparatus used for the reaction of UO_2Cl_2 with RLi or RMgCl in polar or nonpolar solvent was composed of a 15 ml round bottom flask, attached through an intervening stopcock to a 35 ml gas addition bulb which was then attached to a high vacuum line.

Reaction of UO_2Cl_2 with CH_3Li

A 15 ml round bottom flask was charged with 0.19 g (0.56 mmol) of UO_2Cl_2 and a magnetic stirring bar. Diethyl ether (5 ml) was condensed into the flask *in vacuo*, and the stopcock leading to the flask was closed. Next, 0.8 ml $CH_3Li{\cdot}LiBr$ (1.4 *M* in diethyl ether) (1.12 mmol) was syringed into a 35 ml gas addition bulb under a flush of argon and the solvent was removed *in vacuo*. Diethyl ether (5 ml) was condensed into the gas addition bulb *in vacuo*, and the stopcock leading to the high vacuum line was closed. The CH_3Li:LiBr solution was added by opening the stopcock leading to the flask while stirring the UO_2Cl_2–ether mixture at –78 °C. The yellow reaction mixture turned to dark brown while warming to room temperature. After 15 h, the flask was cooled to –78 °C. The gases were then passed through a series of two liquid nitrogen cooled traps and were collected in a calibrated volume via a Toepler pump. The gases collected amounted to 0.68 mmol (61%). The collected gases were analyzed by GC (Table I). Solvent was removed *in vacuo* from the reaction flask, and the dark brown residue was Soxhlet-extracted with diethyl ether (5 ml) to remove unreacted $CH_3Li{\cdot}LiBr$ and LiCl, yielding a dark brown solid (positive halogen flame test). IR (Nujol mull): 960 w, 948 w, 832 w, and 788 w cm^{-1}. IR of UO_2Cl_2 (Nujol mull): 960 s, 849 s, 832 s, and 788 s cm^{-1}. In a separate experiment, 0.10 g (0.28 mmol) of UO_2Cl_2 was reacted with solid $CH_3Li{\cdot}LiBr$ (0.56 mmol) in toluene-d_8 (2 ml) and the gaseous products were collected as described above (yield, 21.7%) and analyzed by GC and mass spectrometry (6.5% CH_3D; 15.2% CH_4).

Reaction of UO_2Cl_2 with CH_2=$CHMgCl$

A 15 ml round bottom flask was charged with 0.19 g (0.56 mmol) of UO_2Cl_2 and a magnetic stirring bar. Diethyl ether (5 ml) was condensed into the flask *in vacuo*, and the stopcock leading to the flask was closed. 0.4 ml of CH_2=CHMgCl (3 *M* in tetrahydrofuran) was syringed into a 35 ml gas addition bulb under a flush of argon. THF (5 ml) was condensed into the gas addition bulb *in vacuo*, and the stopcock leading to the high vacuum line was closed. The CH_2=CHMgCl solution was added via the stopcock leading to the flask while stirring the UO_2Cl_2 mixture at –78 °C. The yellow reaction mixture turned to dark brown while warming to room temperature. After 25 h, the flask was cooled to –78 °C, the gases were then passed through a series of two dry ice-acetone cooled traps and the collected gases amounted to 0.77 mmol (69%). The collected gases were analyzed by GC (Table I). The residue was extracted (Soxhlet) with benzene (5 ml) leaving a dark brown solid (positive halogen flame test). IR (Nujol mull): 960 m, 948 m, 832 m, and 788 m cm^{-1}.

Reaction of UO_2Cl_2 with i-C_3H_7MgCl

To 0.19 g (0.56 mmol) of UO_2Cl_2 in THF (5 ml) was added 0.5 ml of i-C_3H_7MgCl (2.5 *M* in tetrahydrofuran) while stirring at –78 °C (*vide supra*). After 48 h, the gases collected amount to 71% (0.79 mmol). *Anal.* of the dark brown solid. Found: C, 8.18; H, 1.11, which corresponds to ($UO_2C_{2.03}H_{3.28}$). The collected gases were analyzed by GC (Table I). The residue was extracted (as described above) leaving a dark brown solid (positive halogen flame test). IR (Nujol mull): 960 m, 948 m, 832 m, 778 m, cm^{-1}. IR (Fluorolube mull): 2960 sh, 2920w 2860 sh, cm^{-1}. IR of diethyl ether extract (Nujol mull): 1030 s, 918 w, 880 m, 665 w cm^{-1}, and ^1H NMR (C_6D_6): δ 1.90 (6H, d).

Reaction of UO_2Cl_2 with n-C_4H_9Li

To 0.19 g of UO_2Cl_2 (0.56 mmol) in toluene (5 ml) was added 0.4 ml of n-C_4H_9Li (1.6 *M* in n-hexane) while stirring at –78 °C (as described above). After 28 h, the gases collected amounted to 12% (0.13 mmol), and were analyzed by GC (Table I). Solvent was removed *in vacuo*, and the dark brown residue was Soxhlet extracted (as described above) leaving a yellowish brown solid. IR (Nujol mull): 930 s, 810 s,br, 665 s cm^{-1}. IR (Fluorolube mull); 2950 sh, 2922 vw, 2850 vw cm^{-1}.

Reaction of UO_2Cl_2 with t-C_4H_9Li

To 0.19 g of UO_2Cl_2 (0.56 mmol) in toluene (5 ml) was added 0.8 ml of t-C_4H_9Li (1.5 *M* in n-pentane) while stirring at –78 °C (as described above). After 44 h, the gases collected amounted to 57% (0.63 mmol), and were analyzed by GC (Table I). Solvent was removed *in vacuo*, and the dark brown residue was Soxhlet-extracted with n-pentane, then with diethyl ether to remove unreacted t-C_4H_9Li and LiCl respectively, leaving a dark brown solid (positive halogen flame test). IR (Nujol mull): 1018 w, 948 m, 825 sh, 800 s, 665 s cm^{-1}. IR (Fluorolube mull): 2950 sh, 2922 vw, 2860 vw cm^{-1}. *Anal.* Found: C, 2.56; H, 0.53, which corresponds to ($UO_2C_{0.59}H_{1.46}$).

Reaction of UO_2Cl_2 with C_6H_5Li

To 0.10 g of UO_2Cl_2 in THF (5 ml) was added 0.2 ml of C_6H_5Li (2 *M* in 70:30 benzene:ether) in THF (5 ml) while stirring at –78 °C (benzene–ether solvents were removed *in vacuo* as described above). After 72 h, the solvent was trap-to-trap distilled leaving a dark brown residue from which colorless crystals were obtained by sublimation at 30 °C *in vacuo*. Characterization (by m.p. (68.5–69.2) and ^1H NMR (in C_6D_6)): δ 7.06 (4H, t) and 7.36 (6H, m) revealed this material to be biphenyl ($C_6H_5 \cdot C_6H_5$; 66% yield). ^1H NMR of liquid distillate (THF): δ 7.15 (s), which was identical to a reference sample of benzene in THF. Yield = 18%. The dark brown residue was washed (Soxhlet) with benzene and diethyl ether to give a dark brown solid. IR (Nujol mull): 830 sh, 800 s,br, 665 m cm^{-1}. IR (Fluorolube mull): 2950 vw, 2920 vw, 2850 vw cm^{-1}. *Anal.* Found: C, 5.63; H, 1.6, which corresponds to ($UO_2Cl_{1.36}H_{4.80}$).

Reaction of UO_2Cl_2 with excess RLi or RMgCl

To 0.19 g of UO_2Cl_2 (0.56 mmol) in 5 ml solvent was added R–Li or RMgX (2.4 mmol) as described above, and gaseous products were collected and amounted to 50% (0.56 mmol) when R = CH_3; 73% (0.82 mmol) when R = i-C_3H_7; 42% (0.47 mmol) when R = n-C_4H_9; 96% (1.08 mmol) when R = t-C_4H_9; and a black brown solid was obtained (as described above).

For R = CH_3, IR (Nujol mull): 960 w, 948 w, 832 w, 788 w cm^{-1}. R = i-C_3H_7, IR (Nujol mull): 960 w, 948 w, 832 w, 788 w cm^{-1}. R = n-C_4H_9, IR (Nujol mull); 830 sh, 800 m, 665 s cm^{-1}; IR (Fluorolube mull): 2950 sh, 2920 vw, 2850 vw cm^{-1}. R = t-C_4H_9, IR (Nujol mull): 610 vw, 495 vw cm^{-1}; IR (Fluorolube mull): 2960 sh, 2920 vw, 2850 vw cm^{-1}.

Results and Discussion

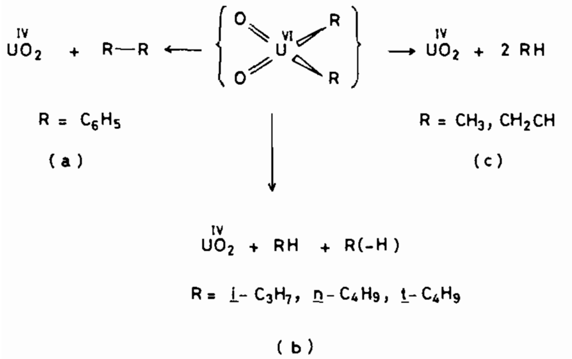
Dichlorodioxouranium(VI), UO_2Cl_2, reacts with a variety of RLi or RMgCl reagents (R = hydrocarbyl), in polar or nonpolar solvents at low temperature to form what we presume to be transitory 'UO_2R_2' species, according to the following equation.

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

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 (giving an infrared spectrum identical to an authentic UO_2 sample) with residual hydrocarbon as is evidenced by elemental analysis and infrared spectroscopy, and gaseous, or liquid and solid hydrocarbon products. Infrared and ^1H NMR data as well as analytical data (Experimental section) showed that some of the starting materials (UO_2Cl_2 and RLi or RMgCl) were recovered unchanged (infrared bands at: 960 s, 948 s, 832 s, and 788 s cm^{-1} are due to UO_2Cl_2 and 1030 s, 918 w, 880 m, 665 w cm^{-1} are due to *e.g.*, i-C_3H_7MgCl). 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 of the gaseous and volatile (liquid or solid) hydrocarbon products.

Gas chromatographic data are summarized in Table I. GC data suggest that there are three pathways available for thermolysis of 'UO_2R_2' which are illustrated in Scheme I. It was also found that the choice of a given thermolysis pathway does not depend on the type of solvent (polar or nonpolar), or on the relative amount of RLi or RMgCl, but mainly on the type of hydrocarbyl group (R) (*vide infra*). When R = C_6H_5, the thermolysis path is predominantly reductive elimination [12] of diphenyl, ($C_6H_5{\cdot}C_6H_5$). To our knowledge this is the first 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 I(a)).



Scheme I. (a) Reductive Elimination, Coupling, (b) Reductive Elimination, Disproportionation (*β*-Elimination), and (c) Hydrogen Abstraction.

'UO_2R_2' species (where R = i-C_3H_7, n-C_4H_9, and t-C_4H_9) decompose thermally by path (b) [5] (Scheme I, *i.e.*, (R = i-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 [13]. Also, for 'UO_2R_2' species, where R = CH_3 or CH_2CH, decomposition occurs via hydrogen abstraction from the surrounding media [5, 14] to form exclusively methane or ethene, respectively.

Labeling 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.

Further labeling and X-ray powder diffraction studies are in progress and the results will be discussed elsewhere [15].

Reactions of UO_2Cl_2 with various other hydrocarbyl anions as well as isolation 'UO_2R_2' species are areas of continuing investigation [16].

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