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OBSERVATIONS ON THE THERMAL DECOMPOSITION OF SOME URANIUM(IV) TETRAALKYLS

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Summary

The thermally unstable products of the reactions 4 RLi + UCl_4 (R = various alkyl groups), presumed to be uranium tetraalkyls, decompose readily at room temperature in ethereal or hydrocarbon solvents. When R contains a β-hydrogen, comparable quantities of alkane (R—H) and alkene (R—H-H_2) are produced along with trace amounts of the dimer, R—R. This result indicates that uranium alkyl compounds readily decompose via β-hydrogen elimination under the appropriate circumstances (coordinative unsaturation). When a β-hydrogen is not present, the alkane, R—H, is the major product. That stereochemistry is retained at the α-carbon atom of the 2-*cis*- and 2-*trans*-2-butenyl compounds suggests that 2-butenes are not formed from free $R^{\cdot}$ radicals.

Considerable synthetic effort both prior to and during the Manhattan project was directed toward the synthesis of volatile uranium alkyl compounds such as tetraethyluranium, $U(C_2H_5)_4$, for possible use in isotope separation. These attempts were singularly unsuccessful, and it was evident that such compounds were at best only transient intermediates which rapidly decomposed at ambient temperatures and defied isolation [1]. Recently, it was shown [2] that the appropriate choice of ligands allows the synthesis and isolation of a large number of uranium alkyl and aryl compounds, (eqn. 1).

$$(C_5H_5)_3U\text{—}Cl + RLi \rightarrow (C_5H_5)_3U\text{—}R + LiCl \qquad (R = \text{alkyl or aryl}) \qquad (1)$$

Most of these complexes possess rather high thermal stability**, and this prompted a study [2c] of the thermolysis products and the rate of thermolysis as a function of R to better understand those factors which stabilize uranium—carbon σ bonds. The most surprising conclusion of this mechanistic investigation [2c] was that the commonly observed β-hydrogen elimination reaction [3,4] (eqn. 2) is not important for the thermal decomposition of $(C_5H_5)_3U$—R compounds. Instead, stereospecific intramolecular abstraction of a cyclopentadienyl

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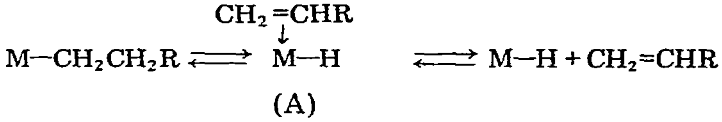
** For example, at 97° the R = n-butyl compound has a half-life of over 1000 h in toluene solution, if there is rigorous exclusion of air and moisture.



$$\mathrm{M{-}CH_2CH_2R} \rightleftarrows \underset{\text{(A)}}{\overset{\overset{\mathrm{CH_2{=}CHR}}{\downarrow}}{\mathrm{M{-}H}}} \rightleftarrows \mathrm{M{-}H + CH_2{=}CHR} \qquad (2)$$

ring hydrogen takes place. It was suggested [2a,c] that inability to suffer β-elimination was a significant stabilizing factor for a number of the compounds, and that this inability might be due to partial or complete coordinative saturation of the uranium(IV) ion. This would render an intermediate [3] such as (A) prohibitively high in free energy. In order to test this idea, and to ascertain whether reluctance to suffer β-elimination might be an intrinsic property of all uranium—carbon σ bonds, we have undertaken a study of the decomposition of the presumed [1] UR_4 compounds. Here, coordinative saturation is far less probable.

Experimental

All operations were performed with rigorous exclusion of air and moisture. All glassware was oven-dried or, when possible, was flamed under high vacuum. Solvents were distilled from sodium/potassium alloy benzophenone immediately prior to use. Commercial anhydrous uranium tetrachloride was finely pulverized, refluxed overnight with thionyl chloride, and then dried at 250°/ 10^{-3} mm for 24 h. Lithium reagents were commercially available or were synthesized and standardized as previously described [2c].

Thermolysis experiments

These were performed in two kinds of vessels, the results being identical. In the first, uranium tetrachloride was weighed into an NMR tube in a glove box. The tube was capped with a serum stopper, and outside the glove box, hexane or diethyl ether was added by syringe. The tube was next cooled to —78° and a carefully measured volume of lithium reagent added by syringe. The resulting mixture (usually dark brown or dark green) was vigorously agitated and then allowed to warm to room temperature. Decomposition began immediately, with the formation of a black precipitate. After an appropriate time interval, samples of the gas above the solution were withdrawn with a gas syringe and were analyzed gas chromatographically. The liquid phase was trap-to-trap (—196°) distilled and was also analyzed by gas chromatography. Yields were determined from control samples prepared with known quantities of hydrocarbons. Aliquots of the lithium reagents were hydrolyzed with degassed water and organic products examined by gas chromatography. The second thermolysis procedure involved decomposing reaction mixtures prepared in ampules which could be sealed with Teflon needle valves. This prevented possible gas leakage or chemical reaction involving the serum stopper. Gas samples were withdrawn by syringe through a septum in the sidearm leading to the valve from the outside. Liquid samples were analyzed after trap-to-trap distillation. Yields were calibrated as above. In several cases, the black thermolysis residue was isolated, washed with hexane, studied by infrared spectroscopy, and submitted for elemental analysis.

Instrumental measurements

Infrared spectra were recorded with Beckman IR-5 and IR-12 spectrophotometers on mulls prepared with dry, degassed Nujol in a glove box. When the spectra had been recorded, samples were routinely exposed to air and spectra retaken, to ascertain the effect of air and moisture on the sample. PMR spectra were recorded on a Perkin—Elmer Hitachi R20-B spectrometer operating at 0.6, 6.0, and 18.0 KHz, sweep widths, or on a Bruker HFX-90 spectrometer. Temperatures were measured with a Wilmad thermometer.

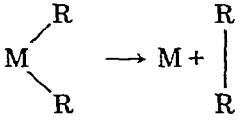
Gas chromatographic analyses were performed on a Barber—Colman Series 5000 instrument with flame ionization detection. Columns employed were a 1/8" × 8' Porapak Q-S (96—110°) and a 1/8" × 16' 15% tris(cyanoethoxy)propane on Chromosorb W (27°). We thank Mrs. L. Kao for helpful advice.

Results and discussion

Many data are at hand from the study of thermolysis mechanisms involving both transition metal [3,4] and main group [5] organometallics. The β-elimination mechanism (eqn. 2) is one of the most securely established processes, and is sometimes accompanied by metal hydride reduction of a second molecule of metal alkyl (eqn. 3) [4a]. Thus, the presence of nearly equimolar quantities of alkane and alkene in thermolysis products or the presence of alkene and a metal hydride is taken to be indicative of β-elimination. Homolytic scission (eqn. 4) would also produce alkene (from radical disproportionation [6a]) and alkane (from radical disproportionation [6a] and solvent hydrogen atom abstraction [6b]) but also $(RCH_2CH_2)_2$ in large quantities (from radical dimerization*). In addition to the above pathways, reductive elimination (eqn. 5) has also been observed [7]. Finally, a number of cases (including $(C_5H_5)_3U—R$ compounds [2a,c]) have been identified which involve hydrogen abstraction from another coordinated ligand to produce R—H [2c,5,8]. Hence, it is possible to identify a number of thermal decomposition pathways simply by product analysis.

$$M—H + M—CH_2CH_2R \rightarrow 2\,M + CH_3CH_2R \qquad (3)$$

$$M—CH_2CH_2R \rightarrow M^{\cdot}\ {}^{\cdot}CH_2CH_2R \rightarrow \text{products} \qquad (4)$$



(5)

Table 1 presents thermolysis product yield data, determined gas chromatographically, for the products of reaction 6. As has been observed previously,

$$UCl_4 + 4\,RLi \xrightarrow[\text{diethyl ether}]{\text{hexane or}} [UR_4] \rightarrow \text{products} + U \qquad (6)$$

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* Radical dimerization to disproportionation ratios are typically ~ 10 for primary alkyl radicals [6a].

TABLE 1

THERMOLYSIS PRODUCT DATA FOR URANIUM ALKYL COMPOUNDS

RLi R	Ratio RLi/UCl_4	Solvent	Decomp. time (h)	Decomp. temp. (°C)	Decomp. products and	yields (%)[a]
n-Butyl	4.0	n-Hexane	1	25	n-Butane	23.6
					1-Butene	5.6
					Octane	0.4
n-Butyl	4.0	n-Hexane/ether (1/1)	1	25	n-Butane	31.5
					1-Butene	7.4
					Octane	0.5
n-Butyl	4.0	n-Hexane	120	25	n-Butane	49.0
					1-Butene	46.0
					Octane	1.4
n-Butyl	2.0	n-Hexane	120	25	n-Butane	49.0
					1-Butene	47.0
					Octane	1.4
Methyl	4.0	Ether	1	25	Methane	38.8
					Ethane	1.2
Methyl	4.0	Ether	96	25	Methane	98.3
					Ethane	0.7
Methyl[b]	4.0	Ether	96	25	Methane	98.0
					Ethane	0.7
Methyl	4.0	n-Hexane	48	55	Methane	98.0
					Ethane	0.7
2-*cis*-2-Butenyl[c]	4.0	Ether	1	25	*cis*-2-Butene	48.5
					trans-2-Butene	11.5
2-*cis*-2-Butenyl[c]	4.0	Ether	24	25	*cis*-2-Butene	80.8
					trans-2-Butene	19.2
2-*trans*-2-Butenyl	4.0	Ether	1	25	*trans*-2-Butene	60.0
					cis-2-Butene	0.0
2-*trans*-2-Butenyl	4.0	Ether	24	25	*trans*-2-Butene	98.0
					cis-2-Butene	2.0
Isopropyl[d]	4.0	THF	1	25	Propane	32.0
					Propene	8.0
Isopropyl[d]	4.0	THF	96	25	Propane	73.0
					Propene	26.0
					Methane	0.7
					Ethane	0.3
Tert-butyl	4.0	n-Pentane	1	25	Isobutane	31.4
					Isobutene	8.6
Tert-butyl	4.0	n-Pentane	96	25	Isobutane	77.0
					Isobutene	22.0
Neopentyl	4.0	Ether	96	25	Neopentane	98.0

[a] Yield based upon amount of lithium reagent used. Estimated error, ± 0.5%. [b] An equimolar quantity of 2,2'-bipyridine was added after allowing the UCl_4 and CH_3Li to react for 2 h at —35°. [c] 80% *cis*-2-butenyl, 20% *trans*-2-butenyl. [d] From Grignard.

thermal decomposition of these mixtures commences immediately on warming to room temperature. In all cases investigated, the product distribution is relatively insensitive to solvent but does change somewhat with decomposition time. Yields based upon starting reagents eventually approach 100% after several days. The sluggishness in the rate of product formation may be due to the heterogeneous nature of the initial reaction (uranium tetrachloride is insoluble in hexane and diethyl ether) since yields were increased somewhat by finely pulverizing the uranium tetrachloride, increasing the decomposition time, and by gently warming the reaction mixture. The most important feature of Table 1 is that both alkane and alkene are observed in the decomposition of a number of the alkyl compounds. In no case is a significant amount of the dimer, R—R, observed. This is a clear indication that uranium alkyls can decompose by β-H elimination (eqns. 2 and 3), through in several cases the excess of R—H suggests that another mechanism may also be operative.For the methyl, neopentyl, and evidently also the butenyl compounds, this elimination cannot occur, and only the corresponding R—H product is observed (rather than the dimer, R—R [7,9]). The source of the hydrogen is apparently the solvent. The retention of stereochemistry in the 2-butenes suggests that free 2-butenyl radicals are not involved [9,2c].

In a number of cases, the PMR spectra of the decomposing reaction mixtures were examined at room temperature. In no case was chemically induced dynamic nuclear polarization [10] observed. This is further evidence that free radicals are not involved in these reactions, however it is recognized that the presence of paramagnetic uranium(IV) species in solution might reduce the spin—lattice relaxation times of polarized products to a point where CIDNP was quenched [11].

Due to high thermal instability, it has not been possible to investigate the molecularity or structures of the presumed UR_4 species in detail. By analogy to known cyclopentadienyl, $(\eta^5\text{-}C_5H_5)_4U$ [12], and amido, $[(C_2H_5)_2N]_4U$ [1a], compounds, a discrete four-connected, monomeric geometry involving uranium seems reasonable. Tetrabenzylzirconium has a similar structure [13], and some tetraalkyl transition metal complexes are known [3a]. However, in the present case, it is impossible to rigorously exclude halide or solvent coordination, though the latter does not influence thermolysis product distribution (Table 1). The PMR spectrum (—30°) of a "$U(CH_3)_4$" sample prepared by ether removal in vacuo at —50°, and extraction with cold toluene-d_8 shows, besides traces of ether, an isotropically shifted singlet at $\tau \approx 32.7$ ($lw_{1/2} \sim 50$ Hz). If the complex is assumed to be tetrahedral, there should be no dipolar (pseudocontact) contribution to the observed shift [14]. That the observed contact shift is then to high field is in qualitative agreement with results for $(C_5H_5)_3UCH_3$ [2c].

The intractable dark residues remaining after thermolysis were collected in several instances, washed with hexane, and dried under high vacuum. Elemental analyses of residues from both partial and complete reaction-decompositons revealed only traces of carbon (ca. 0.8%) and hydrogen (ca. 0.3%). No stable organometallic results from the UR_4 species, in contrast to the $(C_5H_5)_3U$—R system [2c]. Far infrared spectra of the residues as Nujol mulls were featureless, except for a vibration at 250 cm^{-1}, which was only significant in the partially decomposed samples. This is apparently due to a four-valent uranium chloride (UCl_4: ν(U—Cl) 254 cm^{-1} [15]; UCl_6^{2-}: ν 253—259 cm^{-1} [15]) rather than to a reduced ($RbUCl_4 \cdot 5H_2O$: ν 230 cm^{-1} [16]) or oxidized ($UO_2Cl_4^{2-}$: ν 270 cm^{-1} [15]) species.

The thermal stabilization of titanium tetraalkyls by coordination of chelating bases [17] led us to add 2,2'-bipyridine to "$U(CH_3)_4$" solutions. No appreciable stabilization was detected either visually or in product yield data (Table 1). No new features were observed in the PMR spectrum, except those due to free 2,2′-bipyridine. In all probability, uranium(IV) is too hard an acid to interact strongly with such a soft base.

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