

## Communications

### Pyrolytic Transformation of Metal Alkoxides to Oxides: Mechanistic Studies. Pyrolysis of Homoleptic Titanium Alkoxides

Homoleptic metal alkoxides are of considerable interest as precursors to metal oxides. Both thermolytic and hydrolytic methods have been employed for the conversion to the corresponding oxides.<sup>1</sup> As an example of the former procedure, oxide films have been created by the exposure of metal alkoxide vapors to hot surfaces.<sup>2</sup> Little, however, is known concerning the mechanistic steps involved in the thermal decomposition of metal alkoxides.<sup>3</sup> This contrasts with extensive mechanistic information that is available for the decomposition of the corresponding metal alkyl species.<sup>4</sup> Herein, we report the preliminary results of our study on the high-temperature, vapor-phase, decomposition of a series of titanium alkoxides, Ti(OR)<sub>4</sub> (R = CH<sub>2</sub>CH<sub>3</sub> (1), CH(CH<sub>3</sub>)<sub>2</sub> (2), C(CH<sub>3</sub>)<sub>3</sub> (3), CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub> (4), CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub> (5)). Our study provides the first understanding of how the decomposition mode varies with the nature of the alkoxy ligand. The decomposition of Ti(OR)<sub>4</sub><sup>5</sup> in the vapor phase was per-

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- While the lower titanium alkoxides associate in solution,<sup>3c</sup> all are presumably monomeric in the gas phase like the corresponding zirconium analogues.<sup>6</sup>
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Table I. Products Formed upon Flash Vacuum Pyrolysis of Ti(OR)<sub>4</sub>

compd	temp, °C	products <sup>a</sup>
Ti(OEt) <sub>4</sub>	550	C <sub>2</sub> H <sub>4</sub> CH <sub>3</sub> CHO (10%), CH <sub>3</sub> CH <sub>2</sub> OH (58%), (CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> O (32%)
	700	C <sub>2</sub> H <sub>4</sub> CH <sub>3</sub> CHO (33%), CH <sub>3</sub> CH <sub>2</sub> OH (38%), (CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> O (29%)
Ti(O-iPr) <sub>4</sub>	550	CH <sub>3</sub> CH=CH <sub>2</sub> CH <sub>3</sub> COCH <sub>3</sub> (11%), (CH <sub>3</sub> ) <sub>2</sub> CHOH (87%), [(CH <sub>3</sub> ) <sub>2</sub> CH] <sub>2</sub> O (2%)
	700	CH <sub>3</sub> CH=CH <sub>2</sub> , (CH <sub>3</sub> ) <sub>2</sub> CHOH (100%)
Ti(O-tBu) <sub>4</sub>	550	(CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub> , (CH <sub>3</sub> ) <sub>3</sub> COH (100%)
	700	(CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub> , (CH <sub>3</sub> ) <sub>3</sub> COH (100%)
Ti(OCH <sub>2</sub> CMe <sub>3</sub> ) <sub>4</sub>	550	CH <sub>3</sub> CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> , (CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub> CHO (trace), (CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> OH (100%)
	550	

<sup>a</sup> Aldehyde + alcohol + ether = 100%. Because of high volatility, the yield of olefins could not be precisely determined.

formed by using the flash vacuum pyrolysis technique<sup>7</sup> at a pressure of approximately 10<sup>-2</sup> mm of Hg. Pyrolyses at 550 and 700 °C were carried out in glass and quartz tubes, respectively. The inorganic product obtained was amorphous TiO<sub>2</sub> containing small amounts of carbon and hydrogen (typical analysis: C, 4.0%; H, <0.5%). When the amorphous TiO<sub>2</sub> was annealed at 750 °C in oxygen, rutile was formed as judged by the X-ray powder diffraction pattern. The organic products formed were collected in a liquid-N<sub>2</sub> trap. They were identified and quantified by using <sup>1</sup>H NMR, <sup>13</sup>C NMR, GC, and GC-MS techniques. In some instances <sup>1</sup>H-<sup>13</sup>C NMR correlations were performed in order to distinguish between different isomeric molecules. The alcohols and ethers derived from the pyrolysis of **5** were further characterized by comparison of their retention times with those of authentic samples.

Since the pyrolysis was carried out under a dynamic vacuum, the organic products formed were removed quickly, thus preventing secondary reactions. In control experiments, the product alcohols

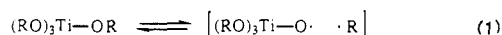
(7) Brown, R. F. C. *Pyrolytic Methods in Organic Chemistry*; Academic: New York, 1980.

were passed over the residual TiO<sub>2</sub> under pyrolytic conditions. With the exception of neopentyl alcohol, no significant dehydration was observed. Thus, our study differs from that reported earlier by Bradley.<sup>3d</sup> Since the latter was done under static vacuum, the alcohol formed underwent dehydration to generate water, which, in turn, caused hydrolysis of the M-OR bonds. As a result, an autocatalytic decomposition of the metal alkoxide ensued.

Table I summarizes our decomposition data. On the basis of these, the following conclusions may be drawn.

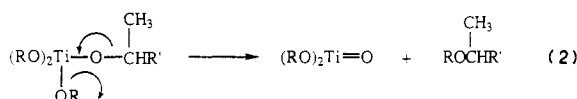
The complete absence of any products arising from the scission of the C<sub>α</sub>-C<sub>β</sub> bond rules out the formation of alkoxy radicals, RO<sup>•</sup>. This fragmentation mode is known to be particularly facile for tertiary and secondary alkoxy radicals.<sup>8</sup>

The pyrolysis of the cyclopropylcarbinyl alkoxide derivative, **5**, led to the formation of significant amounts of the ring-opened allylcarbinyl products. At the same time, no cyclobutyl derivative was observed. This product distribution supports at least the *transient* formation of the radical, R<sup>•9</sup> (eq 1) but argues against

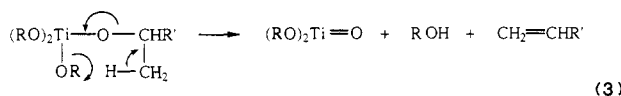


the formation of the corresponding carbocation, R<sup>+</sup>.<sup>10</sup> Also note that the formation of carbocation by charge separation in the gas phase is unlikely due to the absence of solvent stabilization of the charged species. However, *free* radicals *do not* appear to be the intermediates in the product formation since the pyrolysis of **4** did not yield dineopentane, neopentane, and/or 1,1-dimethylcyclopropane. These products were obtained from dineopentyl magnesium and dineopentyl oxalate<sup>11</sup>—compounds that are expected to yield the neopentyl free radical upon flash vacuum pyrolysis.

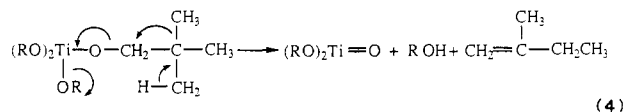
The R-O bond of at least one alkoxide ligand must remain unbroken during ether formation, since it is unlikely that ethers arise by the termolecular combination of two hydrocarbyl radicals with one oxygen atom. Therefore, the formation of diallylcarbinyl ether implies that the homolysis of the R-O bond in **5** (eq 1) occurs in a step that is separate from those involved in ether formation (eq 2).



A further feature of the pyrolysis that emerges upon examination of the product distribution is that, with the exception of **4**, the ratio of alcohol to ether formed increases markedly on going from primary (**1** and **5**) to secondary (**2**) to tertiary (**3**) alkoxide, i.e., with increasing steric crowding at the α-carbon. This observation is most easily explained by a mechanism encompassing eqs 2 and 3. Both involve nucleophilic attack by an incipient

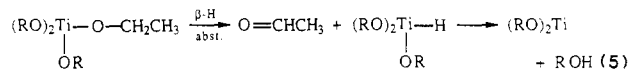


alkoxide ion. As the α-carbon becomes less accessible, attack on the β-hydrogen becomes more prevalent. Steric crowding at the α-carbon also causes the hydrogen atoms of the β-methyl group to approach the oxygens of the neighboring alkoxide groups. Note that the allylcarbinyl derivatives obtained from **5** arise through an additional radical-induced ring-opening step<sup>9</sup> (eq 1). Although the neopentoxide derivative, **4**, is a primary alkoxide, it appears to undergo decomposition mainly by attack on the γ-hydrogen (eq 4). However, this is not surprising since models show that these hydrogens are quite close to the neighboring alkoxide oxygens. The skeletal rearrangement shown in eq 4 was previously



invoked to explain the formation of 2-methylbutenes by the dehydration of neopentyl alcohol on alumina.<sup>12</sup> Again, the intermediacy of a discrete carbocation is unlikely due to the lack of solvent stabilization in the gas phase.

Significant quantities of carbonyl compounds are formed during the pyrolysis of **1** and **2**. Since alkoxide radicals are not involved (*vide supra*), these are presumably formed by a β-hydrogen abstraction step (eq 5). Facile β-hydrogen abstraction from metal



alkoxides has been reported previously.<sup>3b</sup> Note that eq 5 involves a net 2e<sup>-</sup> reduction of titanium (from +4 to +2). Hence the oxidation level of the metal in the titanium oxide derived from **1** should be lower than that derived from an alkoxide lacking β-hydrogens (e.g., **3**). We are currently examining this possibility. If the conclusion is valid, it opens up the interesting possibility of varying the oxidation level of the metal in oxides by the proper choice of the precursor alkoxide complexes.

In conclusion, our study allows, for the first time, the delineation of the multitude of mechanistic steps involved in the thermal decomposition of metal alkoxides.

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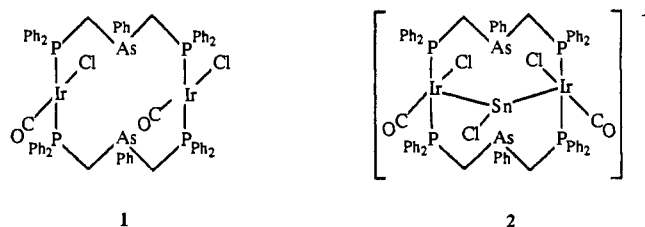
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### Metal Ions as Ligands: Complexation of Tin(II) Chloride by the Bidentate Ligand [Ir<sub>2</sub>(CO)<sub>2</sub>Cl<sub>2</sub>(Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>]

We have reported that the metallamacrocyclic **1**, Ir<sub>2</sub>(CO)<sub>2</sub>Cl<sub>2</sub>(μ-dpma)<sub>2</sub>, reacts with a variety of transition-metal ions and main-group ions to form complexes in which metal ions are bound to the center of the cavity.<sup>1</sup> For transition metals, this



invariably involves bonding to the two arsenic donors with possible additional bonding to the iridium ions, the halide ligands, or the carbonyl groups. A few main-group ions (Sn<sup>II</sup>, Pb<sup>II</sup>, Tl<sup>I</sup>) bind to **1**, but the structural information suggests that bonding is exclusively through the iridium ions, as shown in **2**.<sup>2,3</sup> Metal-

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