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Preliminary communication

A KINETIC STUDY OF THE THERMAL DECOMPOSITION OF PENTABENZYLTANTALUM

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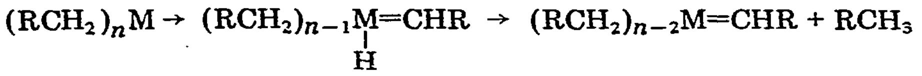
Summary

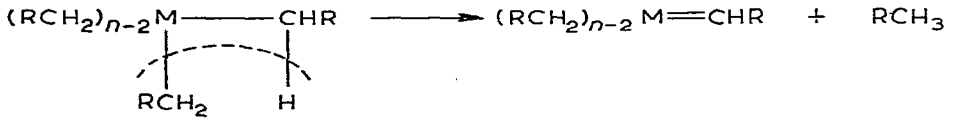
The thermal decomposition of $(C_6H_5CH_2)_5Ta$ occurs by an intramolecular hydrogen transfer, not by an intermolecular free-radical chain reaction.

The mechanism of the thermal decomposition of transition metal alkyls is currently a subject of lively interest [1, 2]. This is particularly true for compounds in which the well-known β-hydride elimination [1, 2] cannot occur because the alkyl groups contain only α-hydrogens. That such compounds may decompose by an analogous α-hydride elimination has been recognized only comparatively recently [1, 2]. According to this mechanism an α-H is transferred to the metal to form an alkylidene hydride which subsequently eliminates a molecule of alkane (eq.1). An alternative mechanism involves transfer of hydrogen to the α-carbon of an adjacent ligand. This is generally referred to as an intramolecular α-H abstraction.



$$(RCH_2)_nM \rightarrow (RCH_2)_{n-1}\underset{\substack{|\\ H}}{M}{=}CHR \rightarrow (RCH_2)_{n-2}M{=}CHR + RCH_3 \qquad (1)$$

$(R = H, C_6H_5, (CH_3)_3C, \text{etc.})$



(2)

Still another mechanistic possibility is a free-radical chain reaction with an in-

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termolecular α-H abstraction, the chain being initiated either by homolysis of an M—CH_2R bond or by adventitious impurities (e.g., O_2) (eq.3).

$$RCH_2\cdot + (RCH_2)_nM \rightarrow RCH_3 + [(RCH_2)_{n-1}M\dot{C}HR] \qquad (3)$$

$$[(RCH_2)_{n-1}M\dot{C}HR] \rightarrow RCH_2\cdot + (RCH_2)_{n-2}M{=}CHR$$

In an earlier study of the decomposition of pentabenzyltantalum [3] it was found that $(C_6H_5CH_2)_5Ta$ decomposed about 3 times as rapidly as $(C_6H_5CD_2)_5Ta$ at 60°C in benzene. This isotope effect cannot, of course, be used to distinguish between the three mechanisms outlined above. The free-radical chain was tentatively eliminated because little bibenzyl (the expected product of chain termination) was formed. However, this conclusion is not incontrovertable because the chain might be long and very little bibenzyl would be produced if reaction 1 were fast. The free-radical chain decomposition of pentabenzyltantalum therefore remained a distinct mechanistic possibility which we have now investigated by such classical techniques as the effect of radical initiators and traps on the rate and kinetics of the reaction and "cross" product studies.

The decomposition of $(C_6H_5CH_2)_5Ta$ in C_6D_6 at 40°C was monitored by FT NMR for 12 h or more. Rates determined from the decrease in the $(C_6H_5CH_2)_5Ta$ benzyl resonance (δ 2.5 ppm) and from the increase in the $C_6H_5CH_3$ benzylic resonance (δ 2.15 ppm) were identical, with ca. 2.6 mol of toluene being formed per mol of pentabenzyltantalum decomposed. No $C_6H_5CH_2D$ was found in this reaction system. The tantalum remains in an involatile red-brown organic gum and the overall process can be represented as:

$$2(C_6H_5CH_2)_5Ta \rightarrow 5C_6H_5CH_3 + (C_6H_5CH{=})_5Ta_2$$

Over the 2—3 half-lives which were followed, all decompositions occurred with "clean" first order kinetics. The overall rate constants k_0, obtained in some of

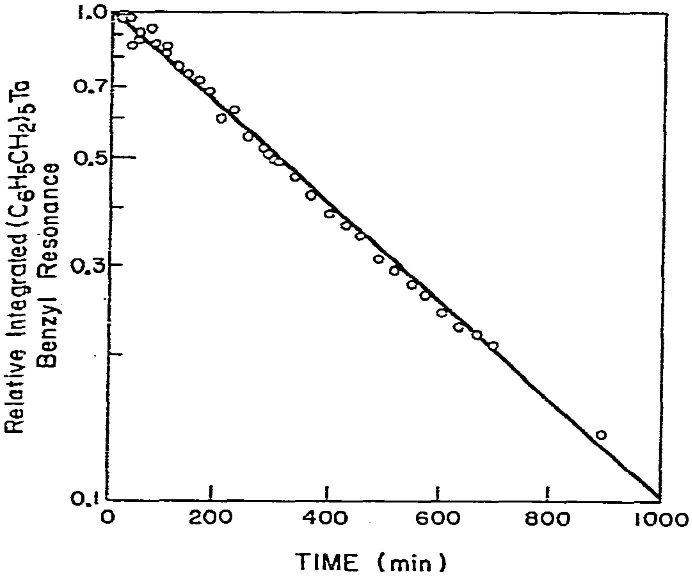

Fig. 1. Integrated areas of the benzyl signals at various times during the decomposition of a 5.1 × 10^{-2} *M* solution of $(C_6H_5CH_2)_5Ta$ in C_6D_6 at 40°C.

TABLE 1

KINETIC DATA FOR THE DECOMPOSITION OF $(C_6H_5CH_2)_5Ta$ IN C_6D_6 AT 40°C

$[(C_6H_5CH_2)_5Ta]$ × 10^2 (M)	k_o × 10^5 (s^{-1})	[Added reagent] × 10^2 (M)	R_i × 10^8 ($M\ s^{-1}$)
1.1	3.8		
5.1	3.9		
9.6	4.3		
10.4	2.9	[TPB] 1.2	15
10.4	4.3	[TPB] 3.3	42
9.6	3.6	[AIBN] 2.3	1.4
11.7	3.6	[Galvinoxyl] 0.2[a]	
9.0	4.4	$[(C_6H_5CD_2)_5Ta]$ 6.1	
5.9	3.5	$[(C_6H_5CD_2)_5Ta]$ 10.8	

[a] Immediately destroyed.

our experiments are listed in Table 1. No NMR signal (15 ppm range) which could be attributed to $(C_6H_5CH_2)_3Ta{=}CHC_6H_5$ was ever observed.

Although k_o is not as reproducible as might be wished, it is clear that k_o is independent of the initial concentration of $(C_6H_5CH_2)_5Ta$. This rules out a free-radical chain initiated by homolysis of a $Ta{-}CH_2C_6H_5$ bond. Furthermore, the general constancy of k_o militates against an initiation by "adventitious" impurities. However, the clinching evidence against a free-radical chain was the failure of 2,2,3,3-tetraphenylbutane (TPB) to accelerate the decomposition. At 40°C this compound provides a thermal source of 1,1-diphenylethyl radicals and these radicals will be only slightly less active hydrogen atom abstracting agents than benzyl radicals.

$$(C_6H_5)_2C(CH_3)C(CH_3)(C_6H_5)_2 \rightarrow 2(C_6H_5)_2\dot{C}CH_3 \qquad (\text{Rate} = R_i)$$

This means that the 1,1-diphenylethyl radicals should be capable of initiating the chain decomposition of pentabenzyltantalum if this decomposition can occur by a radical chain process. Since there was no increase in k_o in the presence of TPB we must conclude that pentabenzyltantalum does not decompose by a free-radical chain under the present experimental conditions.

A number of other experiments, though individually less definitive, all reinforce the conclusion that pentabenzyltantalum does not decompose by a radical chain mechanism. Thus, k_o was unaffected by the initiator azobisisobutyronitrile, AIBN. The free radical inhibitor, Galvinoxyl, was shown by ESR to be rapidly destroyed by the pentabenzyltantalum. The products of this reaction did not affect the subsequent rate of decomposition of the pentabenzyltantalum. No ESR signal could be observed when pentabenzyltantalum was decomposed in the cavity of an ESR spectrometer, nor were signals obtained when the decomposition was carried out in the presence of potential spin traps, such as 1,1-diphenylethylene and 2,4,6-tri-*t*-butylnitrosobenzene. No CIDNP signal was observed when the compound was decomposed at 100°C in the probe of an NMR spectrometer.

Only one piece of evidence was obtained which could support a radical chain. Decomposition of a mixture of $(C_6H_5CH_2)_5Ta$ and $(C_6H_5CD_2)_5Ta$ in C_6D_6 at

40°C* gave both $C_6H_5CH_3$ and $C_6H_5CH_2D$, the latter compound being identified by the high field line of the CH_2 triplet. The yield of $C_6H_5CH_2D$ increased with an increase in the relative concentration of $(C_6H_5CD_2)_5Ta$. In view of the overwhelming evidence against a radical chain decomposition, we interpret this result in terms of a relatively rapid intermolecular ligand exchange, rather than as the intermolecular deuterium abstraction reaction:

$$C_6H_5CH_2\cdot + (C_6H_5CD_2)_5Ta \rightarrow C_6H_5CH_2D + (C_6H_5CD_2)_4Ta\dot{C}DC_6H_5$$

We have eliminated the radical chain thermal decomposition of pentabenzyltantalum from mechanistic consideration. It is going to be much more difficult to distinguish between the α-hydride elimination and the intramolecular α-H abstraction mechanisms [3]. However, a process analogous to that suggested for the thermal decomposition of some 5-coordinate neopentyl-substituted tantalum compounds [4] seems most likely, viz., the trigonal bipyramidal pentabenzyltantalum decomposes by the transfer of a relatively acidic proton from an equatorial benzyl to an apical, and relatively nucleophilic, benzylic carbon atom.

References

1 P.J. Davidson, M.F. Lappert and R. Pearce, Chem. Rev., 76 (1976) 219 and ref. cited.
2 R.R. Schrock and G.W. Parshall, Chem. Rev., 76 (1976) 243 and ref. cited.
3 R.R. Schrock, J. Organometal. Chem., 122 (1976) 209.
4 R.R. Schrock and J.D. Fellmann, J. Amer. Chem. Soc., in press.

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[*] Under these conditions decomposition of the individual compounds showed that $(C_6H_5CH_2)_5Ta$ decomposed almost ten times as fast as $(C_6H_5CD_2)_5Ta$.