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Thermal Decomposition of Vanadium Tetrachloride in Hydrocarbon Solvents

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Vanadium tetrachloride (VCl_4, **1**), which is soluble in hexane, provides a convenient starting material for vanadium chemistry;[1] **1** is also used as a catalyst component for the solution Ziegler polymerization of olefins. We have discovered that solutions of **1** in alkane solvents slowly decompose on standing in the dark to form precipitates of vanadium trichloride (VCl_3, **2**). This study examines the rate of decomposition as a function of temperature and in the presence of olefins.

Results

The decomposition is conveniently monitored by visible spectroscopy at 412 nm ($\log \epsilon = 3.46$): the only chromophore in these solutions is **1**. The rate of decomposition is accelerated by heating or in the presence of light. This paper examines the decomposition process and the rates in alkane solvents at temperatures between 0 and 95 °C.

The decomposition of pure **1** is shown in eq 1. The rate of decomposition is slow, and an independent study[3] of the kinetics of decomposition showed the reaction is first order in **1**; half-lives are found to be 12.4 h at 150 °C, 295 h at 100 °C and 3×10^6 h at 20 °C.

$$VCl_4(g) = VCl_3(s) + 0.5Cl_2(g) \qquad (1)$$

$$\Delta G = -12.15 \text{ kcal/mol at } 25\ ^\circ\text{C}^2$$

The decompositions of **1** in *n*-hexane, cyclohexane, and 2,2,4-trimethylpentane (isooctane) solutions follow a different stoichiometry. Further, the reaction is faster (by a factor of 700–8000) than that of pure **1**. **2** is the only isolated vanadium product in all cases (Table I). Quantitative yields of **2** are obtained when the decomposition is carried to completion. Very little chlorine (less than 2%) is evolved during the reaction. Analysis of other products from two decompositions at temperatures of 60 and 75 °C is reported in Table II, which lists all products appearing in greater than 2% yield. In both cases, nearly half of the stoichiometric amount of chlorine appears as HCl. Chlorination of the solvent accounts for a majority of the other products. We note that in case of the decomposition in *n*-hexane, several other C_6 chlorides were also seen at less than 1.5% yield. These materials presumably occur by halogen substitution on the isomers of *n*-hexane (principally 2- and 3-methylpentane and 2,3-dimethylbutane), which are also present in the solvent system as contaminants. The formation of olefins (2- and 3-hexenes) is surprising, and we speculate that they are formed by the loss of hydrogen atom from a $C_6H_{13}^•$ free radical formed by the attack of $Cl^•$ on the hexanes.

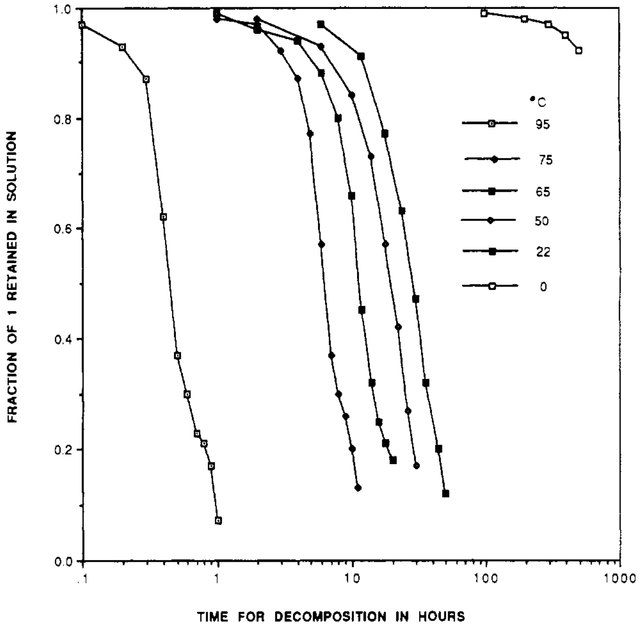

Figure 1. Decomposition Data for Solutions of **1** at Temperatures between 0 and 95 °C.

The results for the rate of decomposition of **1** in alkane solvents are summarized in Table III, which compares the time required for the half-decomposition of pure **1** and **1** in solution at several temperatures. These decompositions were all conducted in the dark: the decomposition of **1** under typical photochemical conditions is rapid at room temperature with complete degradation in 20 h at 22 °C. We note that the solution decompositions do not follow first-order kinetics: they are catalyzed by the decomposition products. The time for the decomposition of the first 10% of **1** is 5–7 times that needed for the decomposition of a similar amount of material during the later stages of the reaction. This acceleration in the rate of decomposition is shown in Figure 1, which plots the extent of decomposition of **1** as a function of reaction time.

We find that the acceleration in the rate of decomposition is principally due to the presence of precipitated **2**. In a diagnostic experiment, **2** precipitated from a decomposition experiment is washed with hexane and added to a fresh solution of **1**. The composition of the mixture is the same a 50% decomposed solution of **1** in the experiments reported in Figure 1: duplicate experiments at 65 °C show the initial rate of decomposition of this mixture to be 69 ± 7% of the 50% decomposed solution. This is much faster than the initial rate of decomposition of **1**. We note that commercially available **2** (Aldrich) does not have a significant catalytic effect on the decomposition of **1**.

Changing the solvent system leads to changes in the rate of decomposition; however, since the reaction is autocatalytic, the largest differences are in the initial stages (first 10%) of the reaction. Our results are shown in Table IV. The presence of tertiary hydrogen on the solvent leads to a slow increase in the rate of decomposition at 65 °C. The difference between the times needed for *n*-hexane and 2,4-dimethylpentane is about 40%. Much smaller differences are observed between *n*-hexane, cyclohexane, and isooctane; in these common alkane solvents, temperature is the dominant factor in controlling the rate of reaction. We note that the rate in isooctane is perceptibly faster. Decomposition conducted in perdeuteriocyclohexane is about 1.9 times slower than that in cyclohexane at the same temperature. Aromatic solvents are not considered in this study since they form dark red complexes[1] with **1** in solution. We have not attempted to fit this decomposition data to any simple kinetic scheme though we do speculate later on a possible pathway for the reaction.

Burfield[4] has shown that **1** rapidly forms insoluble adducts with olefins at low temperatures (−30 to −78 °C). These adducts have the molecular formula of $VCl_n{\cdot}x$(olefin) where $n = 3$ or slightly less and $x = 1–2$. Vanadium(3+) compounds similar to these materials (by elemental analysis: Table I) are formed during the decomposition of **1** in alkane solvents at 65 °C in the presence of a 20-fold excess of the following olefins: ethylene, 1-octene, and bicyclo[2.2.1]hept-2-ene (norbornene). In all of these copounds the V/Cl molar ratio is constrained within a narrow range

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Table I. Analytical Results for the Insoluble Products of Decomposition of **1**

		chem anal. %					
solvent	olefin	V	Cl	C	H	V/Cl	V/olefin[a]
isooctane	none	32.0	67.0	0.6	...	1/3.01	
cyclohexane	none	32.1	67.3	0.1	...	1/3.01	
hexane	none	31.7	67.6	0.9	0.1	1/3.06	
hexane	cyclooctene	31.2	63.9	1.9	0.15	1/2.94	1/0.03
hexane	ethylene	6.15	12.0	69.1	11.9	1/2.81	1/48
hexane	1-octene	13.8	25.1	53.1	8.71	1/2.62	1/2.08
hexane	norbornene	7.99	15.1	69.6	8.39	1/2.71	1/4.17

[a] V/olefin ratio is calculated from the vanadium and carbon analytical ratio.

Table II. Alkane-Soluble Products of Decomposition of **1** in Solution

temp, °C	solvent	decompn products[a]
60	*n*-hexane	HCl (52%) 2-chlorohexane (10%) 3-chlorohexane (8.7%) 1-chlorohexane (1.2%) hex-3-ene (7.0%) hex-2-ene (4.1%)
75	cyclohexane	HCl (59%) chlorocyclohexane (22%) cyclohexene (5.2%)

[a] Results are the average of three decompositions at 60 °C and two at 75 °C. Numbers in parentheses are the mol % yield compared to the original amount of **1**.

Table III. Time for the Half-Decomposition of **1** in Solution and in Neat Liquid

	VCl_4 in soln		pure VCl_4[a]
temp, °C	solvent	*t*, h	*t*, h
0	hexane	5×10^3 (est)	4×10^7
22	hexane	2.9×10^2	2×10^6
50	hexane	20	4.5×10^4
60	hexane	12	1.0×10^4
75	cyclohexane	6	4.2×10^3
95	isooctane	1.1	9.1×10^2

[a] Data for decomposition of pure **1** is extrapolated from ref 4.

Table IV. Reaction Times for the First 10% Decomposition of **1** at 65 °C

solvent	*t*,[a] h	solvent	*t*,[a] h
n-hexane	5.6	cyclohexane-d_{12}	11.1
2,4-dimethylpentane	3.4	isooctane	5.0
cyclohexane	5.7		

[a] Results are the average of two experiments that did not differ by more than 8%.

Table V. Products of Decomposition of **1** at 65 °C in *n*-Hexane Solution in the Presence of a 10-Fold Molar Excess of Olefin

olefin	solvent	decomposition products
1-octene	hexane	HCl (22%) 2-chlorooctane (15%) 1-chlorooctane (2.1%) 3-chlorooct-1-ene (28%) 2-chlorohexane (2.4%) 3-chlorohexane (3.5%)
cyclooctene	hexane	HCl (17%) chlorocyclooctane (31%) 3-chlorocyclooctane (19%) 2-chlorohexane (3.0%) 3-chlorohexane (4.5%)

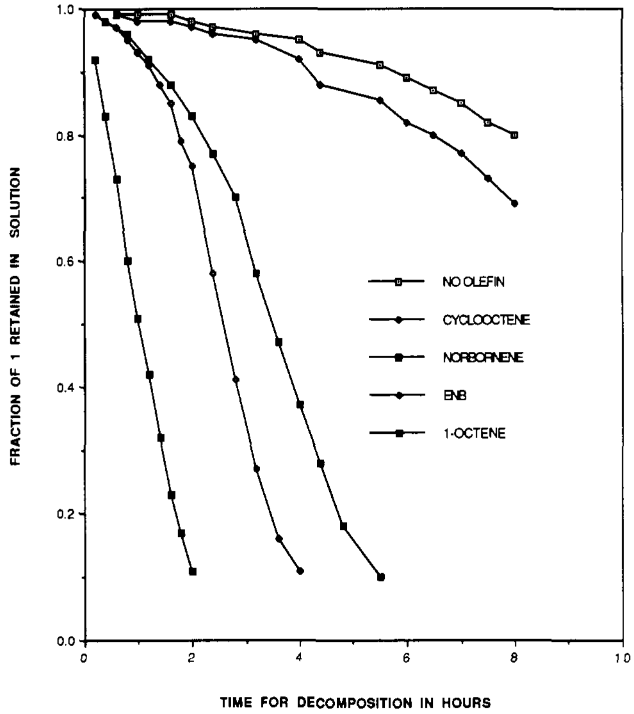

Figure 2. Decomposition data for **1** in hexane at 65 °C at a **1**/olefin ratio of 0.5.

between 1/3 and 1/2.6 while the V/olefin molar ratio is about 1/2.1 for the decomposition reactions in the presence of 1-octene. We observed that the V/Cl stoichiometry is greater than the 1/3 ratio for all reactions in the presence of olefins: this mirrors the observations of Burfield. Solid products from the decomposition in presence of cyclooctene are almost pure **2** with very little coordinated olefin. Reaction products formed in the presence of ethylene and norbornene apparently violate the V/olefin stoichiometry; however, we were able to isolate a significant amount of hexane-insoluble polyethylene and polynorbornene from these solids. These polymers contaminate the vanadium products. Hexane-soluble products of the reaction are the following: very little chlorine is evolved; less than half of the available chlorine appears as HCl while a substantial fraction of the chlorine appears as the product of solvent and olefin chlorination. Olefin chlorination appears to be predominantly at the allylic position (Table V).

The presence of olefins increases the solution decomposition rate of **1**; this is shown in Figure 2. Cyclooctene and similar internal olefins (e.g. 2-octene) have little efect on the rate of decomposition. More highly substituted olefins are inert toward accelerating the decomposition of **1**. Norbornene and 1-octene, which are more accessible olefins, increase the rate of decomposition of **1**. We note that the reaction with ethylene is very rapid at room temperature. The effect of diolefins (e.g. 5-ethylidene-2-norbornene, ENB) is the sum of the effect of the constituent olefin functionalities.

We were not able to isolate any possible adduct of olefins and **1**. Solutions of **1** in the presence of norbornene or 1-octene are intensely colored with a broad absorption maxima in the visible spectra at 380 nm. The dark red solutions are unstable and degrade during workup to insoluble V(3+) compounds. These observations parallel those of Burfield.[4] Dilute solutions of these mixtures have a absorption at 412 nm, characteristic of **1**. We believe that these solutions contain unstable adducts of **1** and the olefin; the formation equilibrium constant for these adducts must be small to account for the differences in visible spectra between concentrated and dilute solutions.

Discussion

We believe that the decomposition of **1** in the absence of olefin occurs by a reversible loss of chlorine atoms as in (2). The free

$$VCl_4(g) \rightleftharpoons VCl_3(s) + Cl^\bullet \qquad (2)$$

$$\Delta G = 13.05 \text{ kcal/mol at } 25\ ^\circ C^{2,6}$$

energy change is estimated from published data.[2,6] UV light or high temperatures accelerate the forward process. The presence of solvents, particularly those with reactive tertiary or allylic hydrogens, leads to more efficient scavenging of $Cl^\bullet$ free radicals, thereby promoting the decomposition. However perdeuterio solvents are less efficient than the corresponding protonated solvents in reacting with $Cl^\bullet$ because of the deuterium isotope effect—hence, the use of cyclohexane-d_{12} is less effective at promoting decomposition. The increase in the rate of decomposition in the presence of olefins is explained by the formation of a unstable adduct $VCl_4 \cdot x$(olefin), which then rapidly decomposes to the corresponding insoluble VCl_3 product by loss of a chlorine atom. This is parallel to the reaction of **1** with Lewis bases.[1,5] The explanation is consistent with our observation that easily coordinated olefins such as ethylene and 1-octene have the greatest effect on the decomposition rate. Alternate schemes for the reduction of **1** such as direct chlorination of the allylic hydrogen of the olefin by **1** are not supported by the data; thus, 2-octene with five allylic hydrogens is less effective than 1-octene with two and ethylene with none.

The most important conclusion in this study has been the need to invoke the presence of chlorine atoms in the reaction mixture in order to understand the product distribution and the kinetics. The presence of chlorine radicals is supported by the formation of solvent chlorination products (with preference for the allylic or tertiary positions) as well as the formation of polyethylene in the ethylene assisted decomposition. Further support for this scheme is provided by our observation that free radical chlorinators (CCl_4, for example) in solution retard[7] the decomposition of **1**. Alternate reactions such as 1, which do not require the formation of chlorine atoms, will account for most of the reaction products but do not explain the increase in the decomposition rate in the presence of solvents nor the dependence of this rate on the reaction medium.

Experimental Section

VCl_4 was obtained from Stratcor, Niagara Falls, NY, or from Metaux Speciaux S.A., Paris, France: both of these samples contained less than 4% of chlorine. No difference in the decomposition rates or products was noted between these samples. *n*-Hexane was obtained from Phillips Petroleum and contained 5–7% of isomers, principally 2- and 3-methylpentane, 2,3-dimethylbutane, and cyclohexane. Cyclohexane and isooctane were obtained from Burdick and Jackson. All solvents were purified to 2 ppm of moisture and oxygen prior to use. All other chemicals were obtained from Aldrich Chemical Co.

Decomposition of **1** was conducted in a thermostated reaction vessel; temperature control was obtained with a Neslab 610 constant-temperature bath with an accuracy of ±2 °C. UV–vis spectra were obtained on a Perkin-Elmer Lambda 7 spectrophotometer at ambient temperature between 300 and 700 nm. GC, GC-MS, and elemental analysis were performed internally.

Polyethylene and polynorbornene formed during decomposition were isolated by extracting the solid residue with dilute (7%) HCl and then drying the polymer in a vacuum oven. The polymer was identified by IR spectroscopy.

Decomposition Experiment. The decomposition experiment was conducted by dissolving 10 mL (18.2 g) of **1** in 1 L of the solvent under nitrogen at the reaction temperature. The olefin, if necessary, is added at this stage. The thermostated reaction mixture was protected from light, and samples of the solution were syringed out through a in-line filter at predetermined intervals and introduced into a 0.1-mm-pathlength quartz UV–vis solution cell under nitrogen. Spectra were obtained at ambient temperature, and interference from solid precipitates in the reaction vessel was not observed. All of the spectra had a single absorption with a maxima at 412 nm. All data reported in this paper have been normalized by the initial absorption of the solution at 412 nm: this eliminates scatter in the data due to the variation in the real concentration of **1** or inaccuracies of dilution and transfer. We estimate that the extent of this variation is about 5%. These data correspond to the fraction of **1**, compared to the initial amount, left in solution at any stage of the decomposition and are reported as such. Evolved HCl was removed by slowly bubbling a stream of nitrogen through the reaction mixture, followed by absorption into a measured volume of 0.1 M NaOH. Other organic decomposition products were measured by GC or GC–MS analysis after the decomposition of **1** was complete. Experiments in deuteriocyclohexane were conducted at the same concentration of **1** but in a volume of 20 mL of liquid in appropriately scaled equipment.

Vanadium Oxidation State. Insoluble vanadium residues from the decomposition were removed by filtration under a nitrogen atmosphere, washed with hexane, and dissolved at 0 °C in deaerated 1 M HCl. Clear solutions were obtained in 1 h. Visible spectra of these solutions showed a broad absorption centered at 580 nm for V(3+). All solid decomposition residues were found to contain V(3+) as the only oxidation state.

Photochemical Experiments. Photochemical decomposition was conducted in a vented quartz reactor containing 100 mL of a 1% v/v hexane solution of **1**. The sample was irradiated at 22 °C with a 150-W high-pressure mercury lamp. Onset of decomposition was rapid, with the walls of the reactor being coated with a dark layer of **2**. Complete decomposition was observed in 20 h.

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^{1}H NMR Hyperfine-Shifted Resonances from the Exchange-Coupled Fe_4S_4–Siroheme of the Assimilatory Sulfite Reductase from *Desulfovibrio vulgaris* (Hildenborough)

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Introduction

^{1}H NMR spectroscopy is a powerful probe of structure and mechanism in biochemical studies of proteins and enzymes.[1,2] In the presence of a paramagnetic prosthetic group, hyperfine-shifted resonances can be observed outside of the normal diamagnetic envelope and so provide a probe of active-site environment.[3–5] There have been several studies of heme proteins (predominantly on myoglobins and a variety of *c*-type cytochromes),[6] cobalt-substituted proteins,[3] HiPIP's, and ferredoxins,[7,8] in which the protons on chromophores and residues ligating the paramagnetic center have been assigned. These resonances can subsequently be used to monitor the magnetic and electronic properties of metal ions (by variable-temperature experiments) or to identify neighboring ionizable residues (by pH titration).

The understanding of the interactions of electronically coupled metal ions is of importance in traditional coordination chemistry, materials science, and biological chemistry (in particular metalloredox proteins). In the latter case, both electron transfer and redox chemistry are of relevance. Many metalloenzymes possess

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