Table III. Values of Rate Constants and Equilibrium Constants for $RCr([15]aneN_4)(H_2O)^{2+}$ Complexes in H_2O at 25 °C

R	$k_{col}/10^7$ L mol^{-1} s^{-1}	$k_{hom}/10^{-4}$ s^{-1} [a]	log (K/L mol^{-1})
$^{\bullet}CH(CH_3)_2$	8.5	5.0	11.23
$^{\bullet}CH_2C_6H_5$	19	1.24	12.19

[a] Reference 14.

Table IV. Values of log K for Organochromium and Organonickel Complexes

R	$(H_2O)_2$-CrL^{2+}	Cr-$(H_2O)_6^{2+}$ [a]	*RRRR*-$[Ni([14]aneN_4)^{2+}]$ [b]
$^{\bullet}CH(CH_3)_2$	11.23	11.87	3.49
$^{\bullet}CH_2C_6H_5$	12.19	10.52	
$^{\bullet}CH(CH_3)OH$		10.96	
$^{\bullet}CH_2OCH_3$		>13.8	6.82

[a] References 7, 13, and 14. [b] Reference 10.

have expected a faster reaction of the macrocyclic complex, since it is the better reducing agent ($E° = -0.58$ V vs -0.41 V for $Cr(H_2O)_6^{2+}$).

An important point is that the analogous reactions of the $Ni([14]aneN_4)^{2+}$ complexes *do* show a significant rate reduction along the series $^{\bullet}CH_3 > ^{\bullet}C_2H_5 > ^{\bullet}CH(CH_3)_2$. The present results show that this cannot be attributed to an effect of the macrocycle. As suggested before,[9,10] the large reactivity ratios in the case of $Ni([14]aneN_4)^{2+}$ are due to the change in coordination number and the fact that the organonickel complexes readily homolyze, since they have such weak metal–carbon bonds. Also a kinetic "leveling effect" may come into play for the six-coordinate cobalt(II) and chromium(II) complexes because colligation occurs with ligand interchange. Such an effect would be absent for the four-coordinate molecule. Solvent exchange is itself not limiting (note $k_{ex} = 7 \times 10^9$ s^{-1} for $Cr(H_2O)_6^{2+}$);[41] rather, we suggest a competition between radical and solvent for the coordination site.

Equilibrium. The opposing reactions of colligation and homolysis, as in eq 2, constitute a chemical equilibrium, with an equilibrium constant $K = k_{col}/k_{hom}$. Values in the $(H_2O)_2CrL^{2+}$ series are available for two R groups, as summarized in Table III.[13,14]

The similarity of the two equilibrium constants merely reflects the few compounds whose homolysis rates fall in a measurable region. Complexes with R groups such as CH_3, C_2H_5, CH_2OH and so on are much less prone to homolyze and therefore have much larger values of K. These very substantial differences in K_f are, therefore, due to the variation in k_{hom}, since the k_{col} values do not change with R. That is, variations in the strengths of the chromium–carbon bonds are contained entirely in the dissociation rates and not in those for bond formation. This is sensible, which is what makes the trend for nickel so remarkable in that rates in both directions show substantial and opposing effects.[9,10]

The rate of equilibration in eq 2 is controlled by the composite constant $k_{col}[(H_2O)_2CrL^{2+}] + k_{hom}$. Under all conditions the first term is much larger than the second and equilibrium established very rapidly, since k_{col} values are so large. Of course when a scavenger is added, the reaction, now controlled by k_{hom}, occurs slowly.

It is instructive to examine the equilibrium constants for several organometals. Values of log K are given in Table IV.

The organonickel complexes are much less stable than the organochromium complexes. This is certainly not surprising, because nickel(III) is more strongly oxidizing than chromium(III). The small values of K_f for nickel may contribute to the fact that *both* of its components, k_{col} and k_{hom}, vary with R.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82.

Registry No. $MV^{\bullet +}$, 25239-55-8; $(H_2O)_2Cr([15]aneN_4)^{2+}$, 70835-04-0; $(CH_2OH)Cr([15]aneN_4)H_2O^{2+}$, 98737-23-6; $(CH(CH_3)OH)Cr([15]aneN_4)H_2O^{2+}$, 98737-26-9; $(CH_2OCH_3)Cr([15]aneN_4)H_2O^{2+}$, 137007-15-9; CH_3OH, 67-56-1; C_2H_5OH, 64-17-5; $(CH_3)_2O$, 115-10-6; CH_3, 2229-07-4; CH_2CH_3, 2025-56-1; $CH_2C_2H_5$, 2143-61-5; $CH(CH_3)_2$, 2025-55-0; $CH_2C_3H_7$, 2492-36-6; $CH(CH_3)C_2H_5$, 2348-55-2; $CH_2CH(CH_3)_2$, 4630-45-9; c-C_5H_9, 3889-74-5; $CH_2C(CH_3)_3$, 3744-21-6; CH_2OCH_3, 16520-04-0; CH_2Cl, 6806-86-6; CH_2Br, 16519-97-4; CH_2Ph, 2154-56-5.

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Kinetics and Mechanism of the Oxidation of Hexaaquavanadium(II) Ions by Alkyl Radicals

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Received June 21, 1991

The title reaction produces vanadium(III) ions and the corresponding hydrocarbons. The kinetics were studied by laser flash photolysis with the use of the paraquat radical ion as a kinetic probe. Results are reported for 11 radicals, consisting of primary alkyl radicals (substituted and unsubstituted) and secondary and aralkyl radicals. The rate constants are remarkably insensitive to the nature of the radical, lying in the range $(1-6) \times 10^5$ L mol^{-1} s^{-1}. The solvent kinetic isotope effects comparing $V(H_2O)_6^{2+}$ in H_2O with $V(D_2O)_6^{2+}$ in D_2O was determined for $^{\bullet}CH_3$, $k_H/k_D = 3.0$. Of several mechanisms considered, we prefer one in which the radical attacks at a trigonal face of $V(H_2O)_6^{2+}$. This leads to electron transfer and a transient $(H_2O)_6VR^{2+}$ intermediates, the protonolysis of which yields the observed alkane.

Introduction

The reduction of alkyl radicals by transition-metal complexes has been reported for such reagents as $Cr(H_2O)_6^{2+}$,[1] $Co(N_4mac)^{2+}$,[2] $Ni(cyclam)^+$,[3] $Ti(H_2O)_6^{3+}$,[4] and Cu_{aq}^+.[5] It has been reported that generation of $^{\bullet}CH_3$ in the presence of $V(H_2O)_6^{2+}$

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yields methane.[6] This certainly indicates a direct reaction between V^{2+} and $^{\bullet}CH_3$, in that the latter by itself gives exclusively ethane. The rate constant for the reduction of $^{\bullet}C_2H_5$ by V^{2+} was estimated as $\sim 6 \times 10^5$ L mol^{-1} s^{-1} from product ratios in competition experiments.[7] The metal complexes listed, other than V^{2+}, react with $R^{\bullet}$ by a "colligation" process. That is, they capture the radical forming stable or transient organometals. The reactions of $V(H_2O)_6^{2+}$ are necessarily different, in that formation of a six-coordinate organovanadium complex is prohibited by the low rate of ligand substitution.

The reactions of two aliphatic radicals, $^{\bullet}C(CH_3)_2OH$ and $^{\bullet}CH(CH_3)OC_2H_5$, with V^{2+} were studied by more direct methods based on the competitive inhibition of the homolysis of the corresponding $(H_2O)_5CrR^{2+}$ complexes.[8] These radicals were found to oxidize V^{2+} with rate constants of 2.1×10^5 and 5.9×10^4 L mol^{-1} s^{-1} (25 °C, 0.2–1.0 M H^+).

None of the situations referred to provides an experimental means by which the kinetics of other than a few aliphatic radicals can be explored. For example, the method[8] based on CrR^{2+} complexes is limited to a few special cases where these complexes decompose primarily by a homolytic pathway. Thus we sought a general method, recognizing from the few rate constants available that the reactions were likely to be fairly slow. Any "direct" method—that is, one in which a burst of the radical is generated in the presence of V^{2+}—will need to contend with the $R^{\bullet} + R^{\bullet}$ self-reactions, which are generally characterized by second-order rate constants $2k_d \sim 2 \times 10^9$ L mol^{-1} s^{-1}. That is the case with the flash-photolytic method used here.

We have turned to a method[9] whereby alkyl radicals are generated by photolysis of organocobalt complexes, $RCo(dmgH)_2OH_2$ and $RCo([14]aneN_4)H_2O^{2+}$. Since these complexes do not react with V^{2+}, the components are thermally stable together. Because the absorbance changes attending the oxidation of V^{2+} by $R^{\bullet}$ are very small, a second reaction was introduced as a kinetic probe. This is the reaction between $R^{\bullet}$ and the methyl viologen radical cation ($PQ^{\bullet+}$), which occurs at a known rate.[9] Because $PQ^{\bullet+}$ has a strong absorption in the visible region (λ 600 nm, ϵ 1.37×10^4 L mol^{-1} cm^{-1}), its consumption upon reaction with $R^{\bullet}$ can easily be monitored over time. The major reactions occurring are summarized in eqs 1–4.

$$RCo(dmgH)_2OH_2 \xrightarrow{h\nu} Co(dmgH)_2OH_2 + R^{\bullet} \quad (1)$$

$$R^{\bullet} + V(H_2O)_6^{2+} \xrightarrow{H^+} RH + V(H_2O)_6^{3+} \quad (k_V) \quad (2)$$

$$R^{\bullet} + R^{\bullet} \rightarrow R_2 + (RH + R_{-H}) \quad (k_d) \quad (3)$$

$$R^{\bullet} + PQ^{\bullet+} \rightarrow \text{adduct} \quad (k_{PQ}) \quad (4)$$

Experimental Section

Solutions of VO^{2+} in aqueous perchloric acid were prepared from $VOSO_4 \cdot xH_2O$, which was adsorbed onto Dowex 50W-X4 cation-exchange resin. After the rinsing of sulfate ions from the column, VO^{2+} was eluted with 2 M $HClO_4$. The concentration of VO^{2+} was determined spectrophotometrically (ϵ_{760} 17.5 L mol^{-1} cm^{-1}), and that of H^+ by difference from the total [H^+] after ion exchange and that displaced by VO^{2+}. Solutions of $V(H_2O)_6^{2+}$ were produced by reduction over zinc amalgam and were used shortly thereafter because of the slow oxidation of V^{2+} by perchlorate ions. The accurate value of [V^{2+}] was determined from the absorbance at 850 nm, ϵ 3.22 L mol^{-1} cm^{-1}.

The compound 1,1′-dimethyl-4,4′-bipyridinium dichloride, $PQCl_2$, was recrystallized one or two times from methanol. Solutions of PQ^{2+} were reduced to $PQ^{\bullet+}$ over amalgamated zinc. The radical was removed from the zinc and stored only a short time before use. Concentrations were determined spectrophotometrically. Solutions of V^{2+} and $PQ^{\bullet+}$ were handled with the rigorous exclusion of air.

Organocobalt complexes $RCo(dmgH)_2L$ (L = C_5H_5N, H_2O) and $RCo([14]aneN_4)H_2O^{2+}$ ([14]aneN_4 = 1,4,8,11-tetraazacyclotetradecane) were prepared as in the literature.[9,10] If necessary, the compounds were recrystallized. Solutions were not exposed to light. The reaction solutions were thoroughly purged with argon, since the reagents themselves as well as the alkyl radicals react with oxygen.

Kinetics. The laser flash photolysis experiments were performed on an apparatus built from the published description.[11] The energy of the laser pulse is 250 mJ, and the pulse width is 0.6 μs. The dye used was LD 490 (Exciton). The reaction solutions were made up to contain V^{2+} (1–6 × 10^{-2} M), $PQ^{\bullet+}$ (5–38 μM), and $RCo(dmgH)_2OH_2$ or $RCo([14]aneN_4)H_2O^{2+}$ (10–50 μM) at low [H^+] (0.01–0.03 M). The laser flash, which used 490-nm emissions, was sufficient to produce $R^{\bullet}$ at ~0.6–4 μM. The analyzing light was from a tungsten iodide source, which was focused onto the fluorescence cuvette at the point where the laser beam impinged at right angles to it. The reaction progress was monitored by following the decrease in absorption at 600 nm due to consumption of $PQ^{\bullet+}$. The transient signal was captured by a Nicolet 2090 digitizing oscilloscope. From there, it was transferred to an Apple IIe computer. The voltage (transmittance) signal was converted to absorbance, and the absorbance–time data were fit to a first-order expression, $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_\psi t)$. Between two and four laser shots were taken for a given cell. In each, the absolute values of the initial and final absorbances were recorded to determine $[PQ^{\bullet+}]_{av}$ in that shot.

Results

In the absence of V^{2+}, the radicals branch between self-reaction (eq 3) and addition to $PQ^{\bullet+}$ (eq 4). The rate of $R^{\bullet}$ consumption is given by eq 5. With $[PQ^{\bullet+}]_0 \gg [R^{\bullet}]_0$, the former can be taken

$$-d[R^{\bullet}]/dt = 2k_d[R^{\bullet}]^2 + k_{PQ}[R^{\bullet}][PQ^{\bullet+}] \quad (5)$$

as an approximate constant. Also, the self-reaction term makes a rather small contribution to eq 3, usually 10% or less. Thus, as justified before,[9] the rate of radical loss can be approximated as a first-order kinetic process, with k_ψ given by

$$k_\psi = 2k_d[R^{\bullet}]_{av} + k_{PQ}[PQ^{\bullet+}]_{av} \quad (6)$$

The reaction is monitored by the consumption of $PQ^{\bullet+}$. The initial and final absorbances afford two values of $[PQ^{\bullet+}]$, the average of which is used in eq 6. This is not ideal; it would be preferable to monitor $[R^{\bullet}]$ itself, or product buildup, but no suitable, intense absorptions are available. It should be noted that the experimental rate constant for $PQ^{\bullet+}$ loss is not simply that for eq 4; in addition, the rate constant for eq 3 contributes.[12]

According to eq 5, the value of the experimental rate constant should vary linearly with $[PQ^{\bullet+}]$, provided $[R^{\bullet}]_{av}$ remains about constant in the series of determinations. The nonzero intercepts should correspond to $2k_d[R^{\bullet}]_{av}$. These rate constants are all known, $2k_d \sim 2 \times 10^9$ L mol^{-1} s^{-1} for most alkyl radicals. The change in $[PQ^{\bullet+}]$ allows an estimate of $[R^{\bullet}]_0$ according to

$$[R^{\bullet}]_0 = k_\psi(\Delta[PQ^{\bullet+}])/k_{PQ}[PQ^{\bullet+}]_{av} \quad (7)$$

This is done iteratively, since k_{PQ} starts out as being unknown, but the procedure quickly converges. With $[R^{\bullet}]_{av} = [R^{\bullet}]_0/2$, the calculated intercept is always near that measured. The agreement is usually no better than ±20%, however, since the experiment

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(12) That is because $R^{\bullet}$ is the limiting reagent, and the loss of $PQ^{\bullet+}$ responds to all the pathways by which $R^{\bullet}$ disappears, whether or not $PQ^{\bullet+}$ is consumed. That is to say, with $[R^{\bullet}]_t = [R^{\bullet}]_0 \exp(-k_\psi t)$, substitution into the equation $-d[PQ^{\bullet+}]/dt = k_{PQ}[R^{\bullet}][PQ^{\bullet+}]$ gives the result $[PQ^{\bullet+}]_t = [PQ^{\bullet+}]_\infty + C\exp(-k_\psi t)$, where $C = k_{PQ}[PQ^{\bullet+}]_{av}[R^{\bullet}]_0/k_\psi$. The approximation by which the second-order term is treated by a first-order approximation has already been considered.[9,11] It is allowable because the self-reaction makes a relatively small contribution to the overall rate. Its validity was also demonstrated by using simulated values of absorbances, obtained by numerical integration of the rate equations. [Barshop, B. A.; Wrenn, R. F.; Frieden, C. *Anal. Biochem.* **1983**, *130*, 134.] This method allows one to calculate a value of k_{PQ} which is close to that used in creating the simulation.

Table I. Summary of the Rate Constants (L mol^{-1} s^{-1})[a] for the Reactions of Carbon-Centered Radicals with $PQ^{\bullet +}$ and $V(H_2O)_6^{2+}$

radical	$k_{PQ}/10^9$	$k_V/10^5$
CH_3	1.5 (±0.1)	6.2 (±0.2)
	1.3 (±0.1)[b]	2.1 (±0.3)[b]
C_2H_5	1.0 (±0.1)	4.3 (±0.3)
$CH(CH_3)_2$	1.5 (±0.1)	2.4 (±0.1)
$CH_2CH(CH_3)_2$	1.2 (±0.1)	3.5 (±0.1)
$CH_2C_6H_5$	1.5 (±0.1)	1.2 (±0.1)
CH_2Cl	1.2 (±0.1)	1.5 (±0.1)
CH_2Br	2.1 (±0.1)	3.1 (±0.1)
1-C_3H_7	1.2 (±0.1)	2.4 (±0.1)
1-C_4H_9	1.1 (±0.1)	2.5 (±0.1)
$CH_2C(CH_3)_3$	0.97 (±0.2)	3.5 (±0.1)
c-C_5H_9	1.2 (±0.1)	~1
$^{\bullet}C(CH_3)_2OH$		2.1[c]
		0.36[b,c]
$^{\bullet}CH(CH_3)OC_2H_5$		0.59[c]

[a] At 23 ± 1 °C, with $[H^+] = 0.01$–0.03 M. Typical concentrations are $[R^{\bullet}]_0 = 0.6$–4 μM and $[PQ^{\bullet +}] = 10$–60 μM. The uncertainties shown for k_V are from the least-squares fit to eq 8 and do not reflect the errors in the constituent rate constants; values of k_V are probably reliable to only ±15%. [b] In D_2O. [c] Reference 8.

is designed such that the k_d term is relatively minor. Moreover, using an "average value" for $[R^{\bullet}]$ is clearly a rough approximation. The slopes of plots of k_ψ vs $[PQ^{\bullet +}]$ give the value of k_{PQ}. The results are summarized in Table I. Most of the values were determined in earlier work,[9] and they agree well. Indeed, this redundant work was not done to redetermine these rate constants but to provide the exact values by which to correct the observed rate constants in experiments with V^{2+} added under the precise conditions of these measurements.

With $V(H_2O)_6^{2+}$ present, reaction 2 occurs to some extent. The concentration of V^{2+} must be adjusted to the point where its reaction becomes a substantial contribution, yet the probe reaction must still occur enough that a sizable absorbance decrease can be observed. As it turns out, values of k_V are sufficiently low that rather high $[V^{2+}]$ must be used. Fortunately, V^{2+} ions have only weak absorptions and can thus be tolerated even at high concentrations. In these experiments, the observed rate constant, $k_{\psi,V}$, now contains a third term, $k_V[V^{2+}]$. It is evaluated by subtracting from $k_{\psi,V}$ a correction for the other two paths obtained from the vanadium-free experiments.

$$k_{corr} = k_V[V^{2+}] = k_{\psi,V} - 2k_d[R^{\bullet}]_{av} - k_{PQ}[PQ^{\bullet +}]_{av} \quad (8)$$

Typical plots of k_{corr} vs $[V^{2+}]$ are shown in Figure 1. The lines pass within experimental error of the origin, as predicted by the model. The slopes of the lines define k_V, values of which are given in Table I.

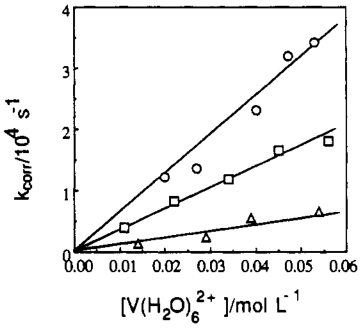

Figure 1. Plot of the first-order rate constant, after correction for the contributions of the $R^{\bullet} + R^{\bullet}$ self-reaction and the reaction of $R^{\bullet}$ with $PQ^{\bullet +}$ (eq 8), against the concentration of $V(H_2O)_6^{2+}$. Data are shown for R = CH_3 (circles), $CH_2C(CH_3)_3$ (squares), and $CH_2C_6H_5$ (triangles).

Experiments for $^{\bullet}CH_3$ were also done for $V(D_2O)_6^{2+}$ in D_2O. There is an appreciable isotope effect, with $k_V = 2.1 \times 10^5$ L mol^{-1} s^{-1} as compared to 6.2×10^5 in H_2O.

The hydrocarbon products were determined for $R^{\bullet} = {}^{\bullet}CH_3$, $^{\bullet}C_2H_5$, and c-$C_5H_9^{\bullet}$ in the absence of $PQ^{\bullet +}$. Without V^{2+}, $^{\bullet}CH_3$ yields only C_2H_6, as expected; with 0.055 mol L^{-1} V^{2+} only CH_4 is seen. Similarly, for $^{\bullet}C_2H_5$, the distribution of products (C_2H_6, C_2H_4, n-C_4H_9) in the absence of V^{2+} was as reported earlier[13a] for the self-reaction of $^{\bullet}C_2H_5$. The R_2 dimer may also result from $R^{\bullet}$ + RCo^{III},[13b] but this is not important aside from R = CH_3. With 0.055 mol L^{-1} V^{2+} present, the percentage of ethane rises to 63%. Also, with c-$C_5H_9^{\bullet}$, cyclopentane rises to 83% (with V^{2+}), as compared to 50% (V^{2+} absent). That the alkane yields are not quantitative simply reflects the competition between reactions 2 and 3.

Discussion

We have previously considered[8] what the mechanism might be of reactions in which $V(H_2O)_6^{2+}$ is oxidized by aliphatic radicals. These new data and other recent results allow us now to consider the matter more fully. There are a number of points to be raised, particularly whether the reaction consists of a so-called "colligation"[14] reaction. That is, whether it entails a coupling of an odd electron of V^{2+} and $R^{\bullet}$, akin to coupling of $R^{\bullet} + R^{\bullet}$.

A colligation mechanism is responsible for the reactions of $R^{\bullet}$ with quite a number of other complexes. The list includes $Cr(H_2O)_6^{2+}$,[9] $(H_2O)_2Cr([15]aneN_4)^{2+}$,[16] $(H_2O)_2Co([14]aneN_4)^{2+}$,[15] Co(corrin) (=Vitamin B_{12r}) and several other macrocyclic Co(II) complexes.[15] Complexes with nta ligands of Co, Fe, and Mn have been examined, as have a variety of Cu complexes.[17] Also, the four-coordinate complexes $Ni([14]aneN_4)^{2+}$ and Cu^+_{aq} react with $R^{\bullet}$ in a colligation reaction.[2d,5,18] In all of these complexes, an alkylmetal is formed. In the first group the product is a six-coordinate complex, L_5M–R, formed such that one molecule of solvent is lost *concurrently*. (It cannot be lost prior to $R^{\bullet}$ colligation, in view of the high energy of a putative ML_5 intermediate.)

The limitation in the case of $V(H_2O)_6^{2+}$ arises because its rate of exchange with solvent molecules is relatively slow, 90 ± 20 s^{-1}.[19] Indeed, this barrier is the usual limit of ligand-substitution processes, a two-electron step. Electron-transfer reactions are limited similarly, evidently because the bridging ligand must also substitute for a water molecule. Clearly, with $k_V = 10^5$–10^6 L mol^{-1} s^{-1}, simple inner-sphere substitution does not occur.

We raise in passing a matter considered in earlier work dealing with the reaction between $(H_2O)_5CrCH(CH_3)_2^{2+}$ and O_2.[20] One of the chain-propagating steps is

$$CrCH(CH_3)_2^{2+} + (CH_3)_2CHO_2^{\bullet} \rightarrow (CH_3)_2CHOOCr^{2+} + {}^{\bullet}CH(CH_3)_2 \quad (9)$$

This reaction is much faster than the rate of substitution of the water molecule trans to the alkyl group. We suggested that the single-electron entering "ligand" might be able to engage in rapid substitution, in that the nonbonding orbitals are half-filled. Perhaps the same suggestion could be applied to the reaction of $V(H_2O)_6^{2+}$ with $R^{\bullet}$. There is no real evidence in support of that suggestion, however, and until a real test in this system or another can be devised, we do not put it forward as a real contender.

Of more substance is a different type of colligation reaction, in which no ligand is displaced. This would result in a seven-coordinate organovanadium cation (eq 10), whose hydrolysis (eq

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11) would yield the observed alkanes.

$$V(H_2O)_6^{2+} + R^{\bullet} \rightarrow (H_2O)_6VR^{2+} \tag{10}$$

$$(H_2O)_6VR^{2+} + H^+ \rightarrow V(H_2O)_6^{3+} + RH \tag{11}$$

There is now ample evidence, both crystallographic and kinetic, for the existence of stable seven-coordinate vanadium(III) complexes with polycarboxylate and water molecules as ligands.[21,22] Structurally, then, the scheme in eqs 10 and 11 is plausible. These are the issues we raise in considering whether it is likely. First, there is very little systematic variation in rate constant with variation of the radical. Would not bulkier radicals be expected to react more slowly by this mechanism, given that they would experience repulsion from the coordinated water molecules, and also that the α-carbon atom would need to begin to assume tetrahedral bond angles in the transition state? The answer is probably, no. Reactions in which Cr(II) and Co(II) complexes react with alkyl radicals show very small variations in rate with the bulk of the alkyl radical, yet the same considerations apply there. Second, there is the magnitude of the H/D kinetic isotope effect, which amounts to a factor of 3 in favor of $V(H_2O)_6^{2+}$ in H_2O versus $V(D_2O)_6^{2+}$ in D_2O. This may not be out of line for the mechanism suggested by eqs 10 and 11. The accumulative effects of many small secondary isotope effects of uninvolved water molecules, and the solvent isotope itself, seem more than ample to account for the experimental value.

Related to the mechanism of eqs 10 and 11 is the suggestion made earlier[23] for the reaction between $V(H_2O)_6^{2+}$ and O_2.[24] Here, it is imagined that O_2 approaches a trigonal face of $V(H_2O)_6^{2+}$, toward which the singly occupied t_{2g} orbitals point. Electron transfer to oxygen occurs, yielding a seven-coordinate V^{3+}–O_2^- complex, which undergoes further reactions. This is entirely equivalent to eqs 10 and 11. As pointed out,[23] such a scheme blurs the distinction between inner-sphere and outer-sphere mechanisms.

There is still another variant in this scheme. Consider that the $V(H_2O)_6^{2+}$–$R^{\bullet}$ interaction might be an equilibration and that the rate-controlling step is the solvolysis of the species so formed.[25] This mechanism is shown as follows:

$$V(H_2O)_6^{2+} + R^{\bullet} \rightleftarrows (H_2O)_6VR^{2+} \tag{12}$$

$$(H_2O)_6VR^{2+} + H_2O \rightarrow V(H_2O)_6^{3+} + RH + OH^- \tag{13}$$

In this case, $k = K_{12}k_{13}$ provided equilibrium in eq 12 lies to the left. The kinetic isotope effect would be accounted for by k_{13}. The only kinetic test would be that k should be $[V^{2+}]$-dependent over a narrower concentration range: $k = K_{12}k_{13}/(1 + K_{12}[V^{2+}])$. The low rate constants encountered in this system preclude application of this test, however. There appears to be no other kinetic test that could distinguish this from eqs 10 and 11, because of their close similarity.

We should also mention a mechanism involving hydrogen atom abstraction from a coordinated water molecule. This can be written as shown:

$$V(H_2O)_6^{2+} + R^{\bullet} \rightarrow (H_2O)_5VOH^{2+} + RH \tag{14}$$

$$(H_2O)_5VOH^{2+} + H^+ \rightleftarrows V(H_2O)_6^{3+} \tag{15}$$

There is relatively little to support this scheme. Once suggested as a scheme for electron exchange, e.g., between $Fe(H_2O)_6^{2+}$ and $(H_2O)_5FeOH^{2+}$, it has been largely discredited in favor of an inner-sphere (OH-bridged) transition state because the entire series of $(H_2O)_5FeX^{2+}$ complexes react analogously. Despite this, it may of course still provide a pathway for alkyl radicals to react. If so, the k_H/k_D value of 3 is surprisingly small. It could be accommodated in this scheme only if the primary kie were substantially offset by an opposing secondary kie. Because the solvent, the five incidental water molecules and the perhaps-reactive water molecule cannot be labeled separately, this point cannot be checked experimentally. Although we earlier[8] favored this mechanism, it.was more for a lack of alternatives than for an abundance of convincing evidence. Even now, we do not rule it out. But the alternative that now presents itself (eqs 10 and 11) seems more appealing in that it is supported by structural confirmation of seven-coordinate vanadium(III) and by the fast V^{2+}–O_2 reaction, where the H atom analogue is not feasible.

The production of the alkane as the exclusive product at high $[V^{2+}]$ is consistent with the values of k_V found, since the $R^{\bullet}$ self-reactions are then relatively unimportant. Both of the suggested mechanisms would yield RH as the product and are thus compatible on those grounds. The seven-coordinate scheme, eqs 10 and 11 (or 12 and 13), seems the most likely. Further substantiation of it will need to await a method to detect the $(H_2O)_6VR^{2+}$ intermediate, assuming it lives long enough.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82.

Registry No. $V(H_2O)_6^{2+}$, 15696-18-1; CH_3, 2229-07-4; C_2H_5, 2025-56-1; $CH(CH_3)_2$, 2025-55-0; $CH_2CH(CH_3)_2$, 2348-55-2; $CH_2C_6H_5$, 2154-56-5; CH_2Cl, 6806-86-6; CH_2Br, 16519-97-4; 1-C_3H_7, 2143-61-5; 1-C_4H_9, 2492-36-6; $CH_2C(CH_3)_3$, 3744-21-6; c-C_5H_9, 3889-74-5; D_2, 7782-39-0.

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(25) We are grateful to a reviewer for this suggestion.