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# $^{51}V$ NMR and EPR Study of Reaction Kinetics and Mechanisms in $V_2O_5$ Gelation by Ion Exchange of Sodium Metavanadate Solutions

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$V_2O_5$ gels have several potential uses in electronics and catalysis, but the rate and mechanism of the synthesis remain poorly understood. $^{51}V$ NMR spectra show the consumption of the dioxovanadium cation ($V^VO_2^+$) to form vanadate polymers in solution. The only other vanadium(V) species in solution, decavanadic acid, acts primarily as a source of dioxovanadium cations for the polymerization. The oxovanadium cation ($V^{IV}O^{2+}$) may act as an initiator for the polymerization reaction with the dioxovanadium cation. The pH remains constant throughout this process, suggesting that hydrolysis of the polymer furnishes hydronium ions. $^{51}V$ MAS NMR of the resulting sol indicates that the vanadium environment in the polymer is similar to that of the dioxovanadium cation. These results confirm some aspects of models previously proposed.[1,2]

## Introduction

Though the chemistry of $V_2O_5$ sols and gels has been studied recently, it is not yet clear how to engineer the processing of these materials.[3–8] Though a model has been proposed to relate the characteristic ribbon structure of the gel to vanadate solution chemistry,[1,2] it is useful to experimentally test the model through the use of $^{51}V$ NMR and EPR.

From a modeling standpoint, the most straightforward processing procedure is to acidifying a solution of metavanadate salt with an ion-exchange resin.[4–6] Alternative procedures include addition of mineral acid to vanadate solutions,[9] hydrolysis of alkoxides,[10] or addition of molten $V_2O_5$ to water,[11] but the ion exchange method is particularly attractive since it introduces no new components and it results in gelation that is slow enough for NMR analysis. Insights from published work on vanadate chemistry and on $^{51}V$ NMR[12–28] allow us to identify the species present as gelation occurs and to test a kinetic model that can be used in process design, optimization and control.

A previously proposed model suggests that vanadium(V) exchanges between tetrahedrally coordinated, unchanged vanadium(V) monomers, decavanadate anions, and octahedrally coordinated, uncharged monomers as shown in (a) and (b).[1,2]

$$V^VO(OH)_3 \Leftrightarrow V^VO_2(OH)_2^- + H^+ \qquad \text{(a)}$$

$$xV^VO_2(OH)_2^- + (10-x)V^VO(OH)_3 \Leftrightarrow [V^V_{10}O_{28}H_{6-x}]^{x-} + 12H_2O \qquad \text{(b)}$$

According to this model, if $x = 0$ in reaction (b), water molecules should become better nucleophiles than the tetrahedral $V^VO(OH)_3$. Under these conditions, water attacks the latter to form the octahedrally coordinated species $V^VO(OH)_3(H_2O)_2$ as shown in (c). It is thought

$$V^VO(OH)_3 + 2H_2O \Leftrightarrow V^VO(OH)_3(H_2O)_2 \qquad \text{(c)}$$

that this condition should be satisfied at pH values less than the point of zero charge, i.e., at pH < 2. A sequence of olation and oxolation reactions between the $V^VO(OH)_3$-

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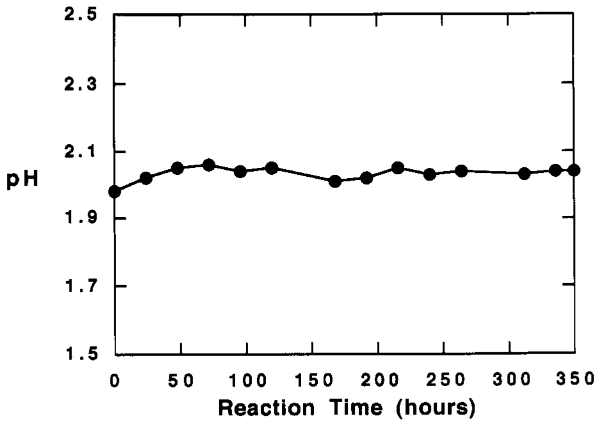

**Figure 1.** Solution pH with reaction time.

$(H_2O)_2$ molecules would then build the characteristic ribbon structure of the polymer.[1,2]

In this paper, we present $^{51}V$ NMR and EPR evidence that confirms some features of this proposed model. We also propose new features that help to explain both the rate of gelation and the ribbon morphology of the gel.

## Experimental Section

Gels were prepared by acidifying 0.1, 0.2, and 0.4 M sodium metavanadate solutions (initial pH = 8).[4-6] A column of Dowex 50W X-2 50–100-mesh ion-exchange beads was prepared for each procedure by charging it with hydrochloric acid and washing it with deionized, distilled water. Typical concentrations of chlorine and sodium in the effluent solutions, as tested by atomic absorption spectroscopy, were only $8.1 \times 10^{-5}$ and $1.2 \times 10^{-5}$ M, respectively.

$^{51}V$ NMR solution spectra were acquired at 131.487 MHz on a GE 500 NMR spectrometer using a 90° pulse width of 12 $\mu$s, a relaxation delay of 0.5 s, a spectral width of 60 kHz, and 256 transients/spectrum. $^{51}V$ NMR chemical shifts were referenced to an external sample of vanadium oxytrichloride, $VOCl_3$ (0 ppm). Liquid samples of different age were prepared by acidifying at different times prior to acquisition of the $^{51}V$ NMR spectra. The spectra of differently aged samples were acquired on the same day without retuning or changing spectrometer parameters.

MAS NMR experiments of the sols were performed by spinning the aged sols in a $Si_3N_4$ rotor at 10 kHz in a Doty MAS probe using spectral widths of 60–100 kHz and 10 000 transients. The pulse width and relaxation delay remained unchanged for both liquid and MAS NMR, and external quantitative referencing was used.

Electron paramagnetic resonance spectra were acquired on a Bruker ESP 300 at a frequency of 9.66 GHz. The spectral width used was 3400 G.

## Results

The starting 0.1 M metavanadata salt solution is light yellow and has a pH of ~8. After ion exchange, the effluent solution has darkened to orange and the pH has been reduced to ~2. As the effluent ages, the pH remains almost constant (Figure 1). Brown colloidal particles are formed after 1 day, and a dark red viscous sol is formed after 6 days. This time is reproducible provided that complete exchange is achieved and contamination by chloride anions is avoided. Solutions with concentrations of 0.2 and 0.4 M vanadate behave similarly, but they form the sol at a much faster rate.

$^{51}V$ solution NMR spectra are shown in Figure 2 for the 0.1 M vanadate solution; all spectra are plotted on the same scale. The spectrum of the effluent solution ($t = 0$) initially shows several peaks. The three peaks at −426, −512, and −531 ppm are assigned to the decavanadate anion undergoing fast proton exchange in the acidic solution.[17,25] From potentiometric studies on aqueous vanadates, the dominant form of the decavanadate anion present at this concentration and pH is the diprotonated form of the decavanadate anion (decavanadic acid),[13] which is probably what these peaks correspond to. The peak at −545 ppm is assigned to the dioxovanadium cation based on refs 18 and 19 and by comparison with the spectrum of a dilute vanadate solution at a pH ~ 0, which should contain only the dioxovanadium cation.[13]

The assignment of peaks at −523 and −537 ppm is more problematic. They disappear from the spectra at the same rate and have chemical shifts close to shifts previously reported for the triprotonated form of the decavanadate anion at this pH, ($H_3V_{10}O_{28}^{3-}$).[18,19] While other reports have been unable to distinguish between the di- and triprotonated forms of the decavanadate anion in pure aqueous solution due to rapid exchange with protons,[17,25] such exchange phenomena may be highly dependent on concentration and solvent.[29] We note that in this study the vanadate concentrations are much higher than in one previous work,[17] and, in another, it was also reportedly not possible to form stable solutions at similar concentrations without precipitation; after precipitation, the remaining decavanadate anion in solution was subject to rapid proton exchange, which prevented the different protonated forms from being distinguished by $^{51}V$ NMR.[25] The downfield resonance reported for $H_3V_{10}O_{28}^{3-}$ is not observed in Figure 2 since it undergoes rapid, mutual site exchange in aqueous solution, but the two upfield resonances seem unaffected by this.[25] The ion-exchange procedure is thus apparently able to form a metastable solution before precipitation occurs.

Figure 3 shows the distribution of the vanadium(V) in the various species over the course of 300 h. Three distinct processes are observed: (1) The species tentatively identified as the triprotonated devacanadate anion disappears from solution at day 1. That the signal intensity lost fails to appear elsewhere in the solution NMR spectra leads us to believe that this vanadium becomes incorporated in the visible precipitates that have been formed at this point. (2) Dioxovanadium cation is consumed in 4 days to form more visible polymers, and, at the same time, a broad peak appears at −547 ppm. The decananadic acid concentration, though, remains constant until the dioxovanadium cation concentration has decreased to ~0.005 M. (3) When the concentration of the dioxovanadium cation has fallen sufficiently, the decavanadic acid concentration, then decreases. The bulk of the decavanadic acid is consumed rapidly (within 5 days), but, after this, the consumption rate slows.

To confirm that the broad peak in the liquid $^{51}V$ spectrum corresponds to the polymer, a magic angle spinning (MAS) spectrum was collected with a 0.1 M $V_2O_5$ sol aged for 1 month (Figure 4).[30,31] The peak reappearring at −547 ppm must correspond to $V^V$ in the polymer. Ninety percent of the vanadium is incorporated into the polymer, and the remainder is in unreacted $H_2V_{10}O_{28}^{4-}$. This

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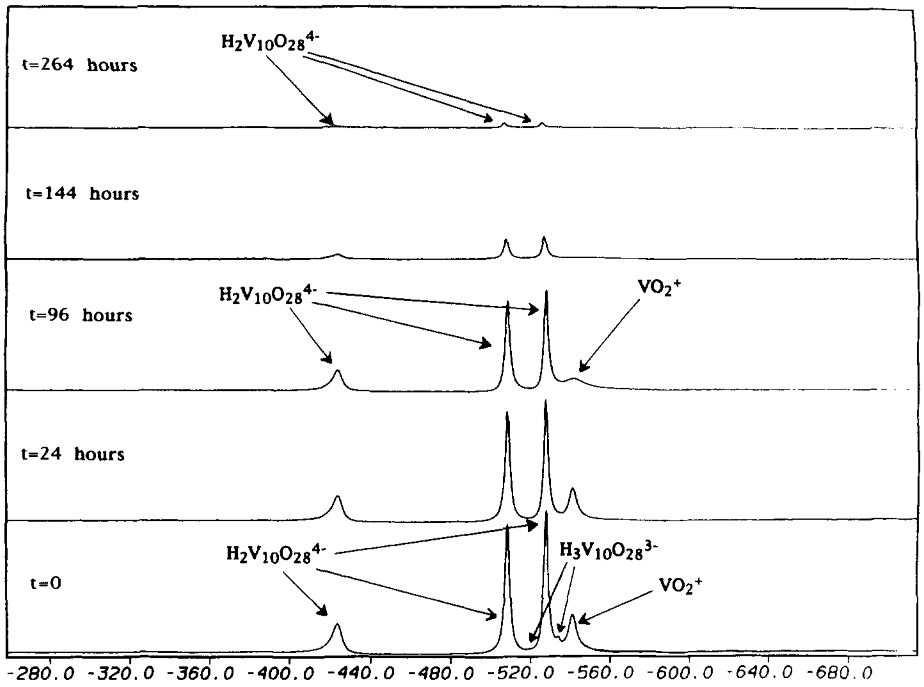

*Intensities of successive spectra referred to sample at t=0.

**Figure 2.** $^{51}$V NMR spectra of reacting solution.

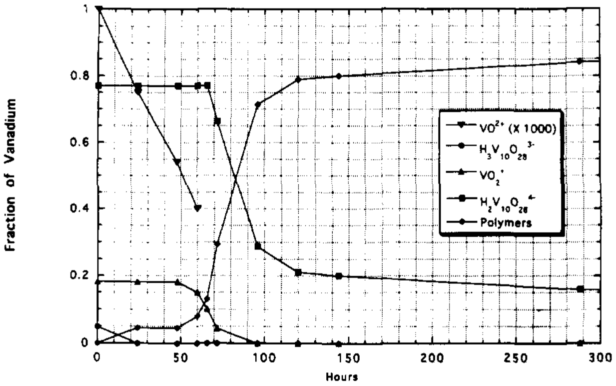

**Figure 3.** Species distribution with time.

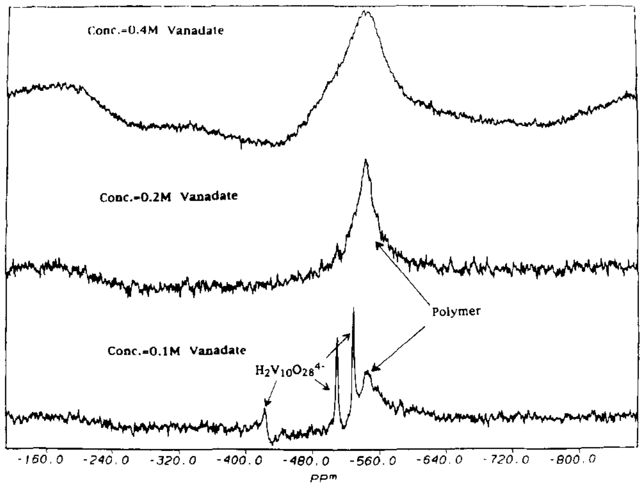

**Figure 4.** $^{51}$V MAS NMR spectra of $V_2O_5$ sols.

distribution is consistent with the results from solution NMR spectra (Figure 2). Since one would not expect quadrupolar broadening to be completely averaged by ordinary MAS, the line width in the solution spectrum must be due only to inefficient averaging of chemical shift and dipole interactions, as would be expected for polymers, and *not* to an increase in the asymmetry of the vanadium(V) site. We deduce then that chemical environment of the vanadium(V) in the polymer is symmetric, similar to the environment in the dioxovanadium cation.[30,31] MAS NMR of the 0.2 and 0.4 M vanadate sols (Figure 4) were similar to the 0.1 M sol spectrum except that they show no unreacted decavanadate species.

EPR spectra of the reacting solutions both before and after gelation are consistent with previous EPR studies of such sols at both ambient and low temperatures.[4,32-35] The EPR spectra shown in Figure 5 display the characteristic eight line spectrum produced by the coupling of the unpaired electron of the vanadium(IV) with the spin = $^7/_2$ vanadium nucleus.[36] The initial concentration was determined by calibration with a standard solution of $V^{IV}O(SO_4)$ and was only 0.001 M. The vanadium(IV) species is probably the oxovanadium cation, $V^{IV}O^{2+}$, which is formed by a redox reaction of the dioxovanadium cation with the ion-exchange resin.[4-6,36] No significant amount of vanadium(V) is reduced to vanadium(IV) during aging. However, as the solution gels, the spectrum collapses to a single, central line due to delocalization of electrons. The concentration of $V^{IV}O^{2+}$ decreases rapidly until the concentration measurement becomes unacceptably imprecise below ~0.0004 M during the same time period as the dioxovanadium cation consumption. Note that the presence of the vanadium(IV) should not significantly broaden the $^{51}$V NMR patterns because vanadium(IV) constitutes only 1% of the total vanadium in solution.

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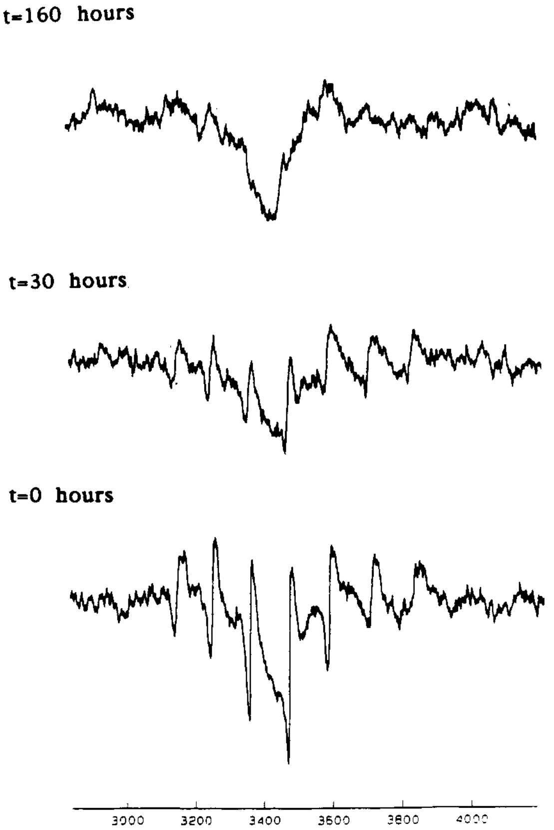


**Figure 5.** EPR spectra of reacting solution.

## Discussion

About 80% of the vanadium in the effluent from the ion-exchange column is initially incorporated into the decavanadate anions. Most of the remaining vanadium nuclei are in dioxovanadium cations. A species previously identified as the triprotonated form of the decavanadate anion, $H_3V_{10}O_{28}{}^{3-}$, is also present,[18,19] and its rapid disappearance coincides with the formation of the first visible solids.

The formation of the vanadate polymers in solution coincides with the consumption of the dioxovanadium cation in solution. As in previous models, the decavanadate anion (in both tri- and diprotonated forms) is shown to act only as a source of monomers for the polymerization process.[1,2] The solution NMR spectra for the gelation process does not indicate the formation of any monomeric species in solution other than the dioxovanadium cation, so this is the only possibility for the monomeric building block in the polymerization process.

The equilibrium between decavanadic acid and the dioxovanadium cation

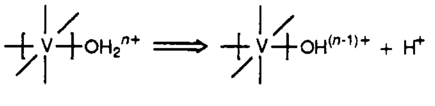
$$H_2V^{V}{}_{10}O_{28}{}^{4-} + 14H^+ \Leftrightarrow 10V^{V}O_2{}^+ + 8H_2O \qquad (d)$$

has been investigated by Rossoti and Rossoti,[37] from whose results we calculate that the equilibrium concentration of the dioxovanadium cation in the solution should be ~0.005 M. Thus, the dioxovanadium cation is initially supersaturated (~0.01 M). However, the decavanadic acid concentration does not appear to increase, apparently since the reverse of reaction (d) is very slow.[37] When the concentration of the dioxovanadium cation drops below ~0.005 M, though, the decavanadic acid decomposes rapidly by the forward reaction (d).

For reaction (d) to proceed, though, a large number of hydronium ions are required. Since there is no corresponding rise in pH (Figure 1), hydrolysis of one of the vanadate species must occur to supply the needed protons. One possibility may be the hydrolysis of the dioxovanadium cation by reaction (e). However, $^{51}V$ NMR fails to

$$VO_2(H_2O)_4{}^+ \Rightarrow H^+ + VO_2(OH)(OH_2)_3 \qquad (e)$$

detect any such distinct neutral species in aqueous solution at any vanadate concentration.[18-20] Moreover, reaction (e) would require charge transfer from a solvated water to an empty d-orbital on the vanadium,[1,2,13] while, due to the cis arrangement of the double bonded oxygens in the dioxovanadium cation, no empty d orbitals exist.[36,38] Another possibility is hydrolysis of the polymer:



$$-V-OH_2{}^{n+} \Longrightarrow -V-OH^{(n-1)+} + H^+ \qquad (f)$$

By this reaction the polymer can act as a buffer (consistent with Figure 1) while providing hydronium ions for reaction (d). The slowing of the consumption of the decavanadic acid between day 4 and 5 might be explained by reaction (f). When the concentration of the dioxovanadium cation becomes depleted, the formation of polymers from dioxovanadium cations slows. If the polymer were to provide protons for the decavanadic acid decomposition, the low polymerization rate might subsequently limit the rate at which the devacanadic acid can decompose. At 0.1 M vanadate, the sols still contain unreacted decavanadic acid at 1 month for both the liquid and MAS spectra (Figures 2 and 4). MAS spectra of sols formed from higher concentrations in Figure 4, though, show no unreacted decavanadic acid. We propose that at 0.1 M, the amount of polymer formed is too low to provide a sufficient number of hydronium ions while maintaining a pH of 2.

$^{51}V$ NMR and EPR spectra show consumption of the $V^{V}O_2{}^+$ and $V^{IV}O^{2+}$ cations in the same period of time. The reaction of $V^{V}O_2{}^+$ and $V^{IV}O^{2+}$ to form mixed valence dimers has been confirmed in acidic conditions with a number of different solvents.[40-43] This dimerization might initiate the polymerization process as the dioxovanadium cation reacts with the mixed valence dimer in a chain propagation scheme.[44] However, from Figure 3, it is clear that the polymerization of the dioxovanadium cation does not start immediately. This indicates that the dimerization reaction to initiate the polymerization is much slower than the following polymerization reaction. Note that during the dimerization period ($t < 4$ days), the dioxovanadium cation concentration is nearly constant because only a very small portion of it is consumed in dimerization with the very dilute $V^{IV}O^{2+}$ cation.

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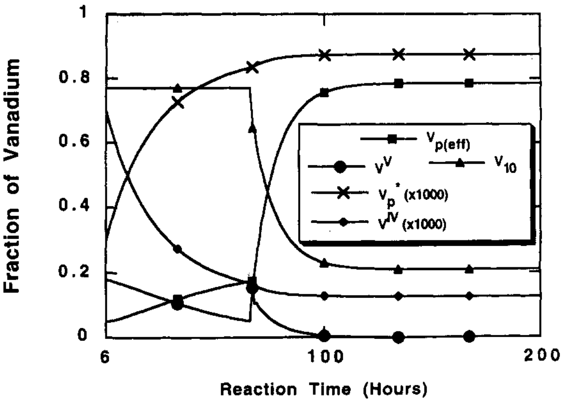

**Figure 6.** Simulated species distribution.

The decavanadic acid concentration remains unaffected as long as the dioxovanadium cation concentration is supersaturated, so it apparently acts only as a source of dioxovanadium cations; this is in agreement with previous models.[1,2] None of the previously proposed $V^V$ intermediates in these models are observed.[1,2] Previous NMR studies have also failed to detect any such species.[18-20]

If each vanadium unit in the polymer can produce one hydronium ion as shown in reaction (f), the polymer repeat unit might be $VO_2(OH)(OH_2)_2$, a charge-balanced formula which can result from the linear polymerization of the dioxovanadium cation followed by the hydrolysis reaction of (f). This proposed mechanism is consistent with a previous report of the polymerization of dioxovanadium cation in acidic solutions to form linear vanadate species.[39]

The MAS $^{51}V$ NMR spectra show that the vanadium environment of the polymer is similar to that in the dioxovanadium cation; the chemical shift differs by only 1–2 ppm. Apparently, the $V^V$ in the polymer are still in an octahedral coordination.[15,27,28] However, the chemical shift is quite different from that of crystalline vanadium pentoxide.[45]

To summarize, all of the above evidence is consistent with the following chain-propagation polymerization scheme:

$$V_{10} + 14H^+ \xrightarrow{k_{dec}} 10V^V + 8H_2O \tag{A}$$

$$V^V + V^{IV} \xrightarrow{k_d} V_p^* \tag{B}$$

$$V_p^* + V^V \xrightarrow{k_p} V_p + V_p^* \tag{C}$$

$$V_p \xrightarrow{k_h} V_h + H^+ \tag{D}$$

where $V_{10} = H_2V^V{}_{10}O_{28}{}^{4-}$, $V^V = VO_2{}^+$, $V^{IV} = V^{IV}O^{2+}$, $V_p$ = vanadium site in the polymer, $V_p^*$ = reactive sites on vanadium polymer, $V_{hp}$ = hydrolyzed polymer, $k_{dec}$ = decomposition rate constant, $k_d$ = dimerization rate constant, $k_p$ = polymerization constant, and $k_h$ = hydrolysis rate constant (neither coordinated water molecules nor charges are indicated). This scheme is somewhat different in its quantitative implications than that previously proposed.[1,2]

If chain propagation is assumed to occur exclusively at the reactive end, and the reactivity of this site is assumed to be independent of the chain length,[44] balances for each detected site can be written:

$$d[V^{IV}]/dt = -k_d[V^{IV}][V^V] \tag{1}$$

$$d[V^V]/dt = -k_d[V^{IV}][V^V] - k_p[V_p^*][V^V] + 10k_{dec}[H^+][V_{10}] \tag{2}$$

$$d[V_{10}]/dt = -k_{dec}[H^+][V_{10}] \tag{3}$$

$$d[V_{p(eff)}]/dt = k_p[V_p^*][V^V] \tag{4}$$

$$d[V_p^*]/dt = k_d[V^{IV}][V^V] \tag{5}$$

In formulating these rate expressions, several reasoned assumptions are made:

(a) The reverse of reactive (A) to form decavanadic acid does not occur to any appreciable extent.

(b) In accordance with a classical chain propagation mechanism, the concentration of reactive sites on the polymer is equal to the concentration of the initiating oxovanadium cation.[44]

(c) The unhydrolyzed and hydrolyzed sites on the polymer cannot be distinguished by $^{51}V$ NMR, so the balance for $V_{p(eff)}$ does not distinguish between the two sites. In addition, the initially accumulated amount of polymer is hydrolyzed during the start of the decavanadic acid decomposition, and the hydrolysis of the polymerized dioxovanadium cation occurs immediately to supply protons for the continuing devacanadic acid decomposition. Thus, all of the $V_p$ is either all unhydrolyzed at $t <$ 72 h and all hydrolyzed at $t >$ 72 h.

(d) The rate law for the polymerization of the dioxovanadium cation follows mass action kinetics, so it is first order in both the monomer and the amount of reactive sites.[44]

(e) In accord with refs 46 and 47, the rate of decanavadic acid decomposition is first order in $[H^+]$, meaning that the first nucleophilic attack by $H^+$ is rate limiting. This is consistent with the absence of any decomposition intermediates. Since the concentration of protons was constant, it was included in the rate constant to yield the rate law $k'_{dec}[H_2V_{10}O_{28}{}^{4-}]$.

These equations are consistent with the observed data, and the integrated solutions are shown in Figure 6. This can then be compared to the NMR and EPR data in Figure 3. Rate constants were evaluated by fitting data from 6 to 200 h with initial conditions consistent with the spectra presented. Both the initial conditions and rate constants are shown in Table 1. Since concentrations determined by EPR and NMR are accurate to ~10% and 5%, respectively, the rate constants are reported with only two significant figures.

The rate constant $k_d$ was determined from the EPR data shown in Figure 3 and is somewhat smaller than suggested by $^{17}O$ NMR relaxation techniques.[48] The rate constants $k_{p_a}$ and $k_{p_b}$ indicate that after hydrolysis the polymer may be much more reactive for polymer growth. The slow consumption of the decavanadic acid after 120 h results from the slowed polymerization of the dioxo-

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**Table 1. Initial Concentrations and Rate Constants**

| variable | value |
|---|---|
| $[V^{IV}]_0$ | 0.0001 M |
| $[V^{V}]_0$ | 0.018 M |
| $[V_{10}]_0$ | 0.0077 M |
| $[V_{p(eff)}]_0$ | 0.005 M |
| $[H^+]_0$ | 0.01 M |
| $[V_{p^*}]_0$ | 0.0003 M |
| $k_d$ | 2 L·(mol h$^{-1}$) |
| $k_{p^a}$ ($t < 72$ h) | 28 L·(mol h$^{-1}$) |
| $k_{p^b}$ ($t > 72$ h) | 500 L·(mol h$^{-1}$) |
| $k'_{dec}$ | 0.046 h$^{-1}$ |

vanadium cation as its concentration is depleted, but nearly 80% of the vanadate in solution has been polymerized by this time. The rate constant $k'_{dec}$ is much lower than the value of 0.43 h$^{-1}$ predicted by Kepert.[46,47] This lower value may result from the previously discussed rate-limiting effects on the formation of the polymer chain in solution.

## Conclusions

Previously proposed models for this system have been based on the formation of neutral monomers from the decavanadic acid, which then polymerize to form the gel ribbons.[1,2] This study confirms that the decavanadate species does indeed act as the source of vanadate monomers for the polymerization but detects no neutral monomer. Moreover, our results are consistent with the chain polymerization of the dioxovanadium cation to form linear polymers. The polymerization seems to be initiated by the dioxovanadium cation–oxovanadium cation dimerization. Decavanadate anions continue to supply dioxovanadium cations for the chain polymerization, but this requires hydrolysis of the polymer already formed. A kinetic model based on these observations provides qualitative agreement with the data presented here. The mechanism of rearrangement and assembly into the two-dimensional ribbons from these linear polymers still remains in question.[1,2]

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