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

by

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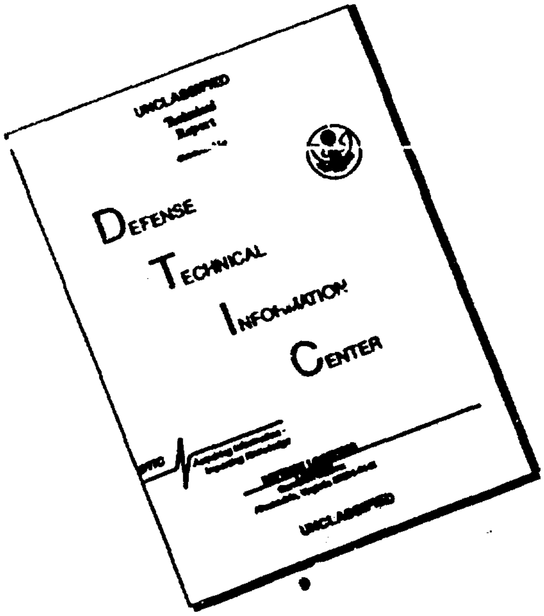

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13. ABSTRACT (*Maximum 200 words*)

V_2O_5 gels produced by sol-gel methods have several potential uses in electronics and catalysis, but the rate and mechnaism of the synthesis remain poorly understood. Recent results disagree with models previously proposed. ^{51}V NMR spectra show that the initial reactions involve the consumption of the dioxovanadium cation ($V^VO_2^+$). The only other vanadium (V) species in solution, decavanadic acid, actos only as a source of dioxovanadium cations for the polymerization through a dimerization reaction with the dioxovanadium cation. Hydrolysis of the polymer allows further decavanadic acid decomposition to the dioxovanadium cation by furnishing protons. ^{51}V MAS NMR of the resulting colloidal suspensions indicates that the vanadium environment in the polymer is similar to that of the dioxovanadium cation.

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Abstract

V_2O_5 gels produced by sol-gel methods have several potential uses in electronics and catalysis, but the rate and mechanism of the synthesis remain poorly understood. Recent results disagree with models previously proposed. ^{51}V NMR spectra show that the initial reactions involve the consumption of the dioxovanadium cation ($V^{V}O_2^{+}$). The only other vanadium(V) species in solution, decavanadic acid, acts only as a source of dioxovanadium cations for the polymerization. The oxovanadium cation ($V^{IV}O^{2+}$) acts as an initiator for the polymerization through a dimerization reaction with the dioxovanadium cation. Hydrolysis of the polymer allows further decavanadic acid decomposition to the dioxovanadium cation by furnishing protons. ^{51}V MAS NMR of the resulting colloidal suspensions indicates that the vanadium environment in the polymer is similar to that of the dioxovanadium cation.

Introduction

Though the chemistry of V_2O_5 sols and gels has been studied, it is not yet clear how to engineer their processing to produce desired properties[1-6]. The relationship between the characteristic ribbon structure of the gel and vanadate solution chemistry remains unclear[1-6]. Our goal is to determine what chemical steps control the rate and mechanism of development of this intriguing gel microstructure through the use of ^{51}V NMR and EPR.

From a modeling standpoint, the most straightforward processing procedure is to acidify a solution of metavanadate salt with an ion exchange resin[2]. Alternative procedures include addition of mineral acid to vanadate solutions[7], hydrolysis of alkoxides[8], or addition of molten V_2O_5 to water[9]. The ion exchange method, though, is attractive for study as it introduces no new components and it causes slow enough gelation for NMR analysis. Using insights from work on vanadate chemistry and ^{51}V NMR in aqueous solution[10-25], we can identify the species present as gelation occurs and monitor reactions among them in order to build a kinetic model that can be used in process design, optimization and control.

A previously proposed model involves a tetrahedrally coordinated, uncharged vanadium(V) monomer, which exchanges with both decavanadate anions and an octahedrally coordinated, uncharged monomer as shown in (a) and (b)[26,27]:

$$V^{V}O(OH)_3 \Leftrightarrow V^{V}O_2(OH)_2^{-} + H^{+} \tag{a}$$

$$x\,V^{V}O_2(OH)_2^{-} + (10\text{-}x)V^{V}O(OH)_3 \Leftrightarrow [V^{V}{}_{10}O_{28}H_{6-x}]^{x-} + 12\,H_2O \tag{b}$$

$$V^{V}O(OH)_3 + 2\,H_2O \Leftrightarrow V^{V}O(OH)_3(H_2O)_2 \tag{c}$$

According to this model, if $x=0$ in reaction (b), it is presumed that water molecules become better nucleophiles than the tetrahedral $V^{V}O(OH)_3$, so water attacks the latter to form the octahedrally coordinated species $V^{V}O(OH)_3(H_2O)_2$ as in reaction (c). It is thought that this occurs near the point of zero charge, i.e., at pH=2; a sequence of olation and oxolation reactions between the $V^{V}O(OH)_3(H_2O)_2$ molecules then builds the characteristic ribbon structure of the polymer[26,27]. The rate limiting step of the polymerization, then, is thought to be an olation reaction between the octahedral monomers[26,27].

Gelation via ion exchange is remarkably slow (requiring up to months in dilute solutions), even though the supposedly rate limiting olation reaction is currently thought to be quite fast[26,27]. For that reason we are especially interested in what other rate limiting step could hinder polymerization.

Experimental

Gels were prepared by acidifying 0.1M, 0.2M, and 0.4M sodium metavanadate solutions (initial pH=7)[2,3,4]. A column of Dowex 50W X-2 50-100 mesh ion exchange beads was charged with hydrochloric acid, washed with deionized, distilled water, and then used for acidifying the solutions. Typical concentrations of chlorine and sodium in the solution were only 8.1×10^{-5} and 1.2×10^{-5} M, respectively, as tested by atomic absorption spectroscopy.

^{51}V NMR spectra were referenced to an external sample of vanadium oxy-trichloride, $VOCl_3$ (0 ppm). ^{51}V NMR spectra were acquired at 131.487 MHz on a GE 500 NMR spectrometer using a pulse width of 12 μs, a relaxation delay of 0.5 s, a sweep width of 60 kHz, and 256 scans per spectrum for liquid samples. MAS NMR experiments were performed using a high speed 5mm Doty probe utilizing a Si_3N_4 rotor spinning at 10 kHz with the pulse width and relaxation delay unchanged. Sweep widths of 60-100 kHz were used in MAS experiments and, due to the small sample size, up to 10,000 scans were acquired per spectrum to improve the signal to noise ratio. Electron paramagnetic resonance spectra were acquired on a Bruker ESP 300 with a sweep width of 3400 Gauss.

Results

The starting 0.1M metavanadate salt solutions are light yellow in color and have pH=7. With passage through the ion exchange column, these solutions darken to orange and the pH is reduced to ~2. As the effluent ages, the pH remains almost constant (Figure 1), and brown colloidal particles are formed (Figure 2). After 6 days, a dark, red viscous sol is formed. Solutions using the higher concentrations of 0.2 and 0.4M vanadate behave similarly but form the sol at a much faster rate.[Insert Figures 1 and 2]

^{51}V solution NMR spectra are shown in Figure 3 for the 0.1M vanadate concentration. The spectrum of the initial effluent solution (t=0) shows the presence of several peaks. Three peaks at -426 ppm, -512 ppm, and -531 ppm are assigned to the diprotonated form of the decavanadate anion (decavanadic acid) at pH=2 based on references 15 and 17. The peak at -545 ppm is assigned to the dioxovanadium cation based on these references and also by comparison with the chemical shift of a freshly prepared dioxovanadium cation solution (pH=0). The remaining small peaks at -523 and -537 ppm disappear from the spectra within 7 hours (Figure 4), indicating that the species they represent are not stable at these conditions. These two shifts are close to those previously reported for the triprotonated form of the decavanadate anion; $H_3V_{10}O_{28}^{3-}$[17]. The third peak at -424 to -427 ppm associated with this species may be obscured. This species was shown to be unstable in aqueous conditions at low pH where it disproportionated into the dioxovanadium cation[17-23].

Figure 5 shows a distribution of the vanadium(V) in the various species over two months. Three distinct processes are observed over the time required for gelation.

1) The triprotonated decavanadate anion disappears from solution (Figure 4), and this coincides with the first colloidal particles observed in solution at day 1.

2) Dioxovanadium cation is consumed by 4 days to form more colloidal particles, and a broad peak appears at -547 ppm. During this time, the decavanadic acid concentration remains nearly constant.

3) After the concentration of the dioxovanadium cation is decreased to one half of its initial concentration, the decavanadic acid concentration starts to decrease. The bulk of the decavanadic acid is consumed by 5 days, but then the remainder is consumed more gradually.

To confirm that the broad peak corresponds to the polymer, magic angle spinning (MAS) was performed on a 0.1M sample aged for one month[28,29]. The spectrum is shown in Figure 6. The reappearing peak at -547 ppm corresponds to V^{V} in the polymer. Ninety percent of the vanadium originally present in the sample is now incorporated into this peak. MAS was also performed on 0.2M and 0.4M vanadate gels (Figure 7). While the solution spectra at these concentrations were similar to the 0.1M vanadate spectra (Figure 3), the MAS spectra show no decavanadate species; the broad peak at -547 ppm, though, is still present. Since one would not expect quadrupolar broadening to be so completely averaged by ordinary MAS, we deduce then that chemical environment of the vanadium(V) in the polymer is symmetric and similar to that of vanadium(V) in the dioxovanadium cation[28,29].

Vanadium(IV) has been examined by EPR at both ambient and low temperatures; both ENDOR and X-Band techniques have been used[2,30,31,32,33]. Our EPR spectra of the vanadium(IV) species both before and after gelation agree with these studies. The EPR spectra shown in Figure 8 display the characteristic eight line spectrum for an unpaired electron coupling with the spin=7/2 vanadium nucleus[34]. The initial concentration is approximately 0.001M as determined by comparison to a standard solution of $V^{IV}O(SO_4)^+$. With aging, though, the EPR spectrum collapses to a single, central line due to delocalization of electrons as the solution gels. Note that the vanadium(IV) spectrum is converted during the same period that the dioxovanadium cation is consumed.

Discussion

About eighty percent of the vanadium in the effluent solutions is initially incorporated in the decavanadate anions. The triprotonated form of the decavanadate anion is initially present, but is highly unstable[17]. Its disappearance coincides with the formation of the first colloids in solution. The diprotonated decavanadate anion and the dioxovanadium cation remain in solution. The equilibrium between the decavanadic acid and the dioxovanadium cation in reaction (d) has been investigated by Rossoti and Rossoti[35]:

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

Using their reported equilibrium constant, the equilibrium concentration for the dioxovanadium cation under the present conditions should be ~0.005M. Even though the dioxovanadium cation is initially at supersaturated concentration, no decavanadic acid is formed by the reverse of reaction (d); this is consistent with previous reports that this reaction is very slow[35].

When the concentration of dioxovanadium cation drops below 0.005M, though, the decavanadic acid decomposition is rapid. The break-up of the decavanadic acid, though, requires a large number of hydronium ions. Since the concentration of decavanadic acid drops precipitously without a corresponding rise in pH, a hydrolysis reaction must be occurring to supply the needed protons.

$$\text{unhydrolyzed polymer} \Leftrightarrow \text{hydrolyzed polymer} + H^+ \qquad \text{(e)}$$

If reaction (e) is fast, the pH is maintained.

After the steep drop in concentration of the decavanadic acid from day 4 to 5, a more gradual decrease persists as shown in Figure 5. The slowdown might be due to the following reaction limitations. The consumption of dioxovanadium cation and triprotonated decavanadate anion from t=0 to t=4 days allows a reserve of unhydrolyzed polymer to be built up in solution. This reserved provides reaction (d) with hydronium ions for a short time. After the hydrolysis of all the accumulated polymer is exhausted, though, the rate of decomposition of the decavanadic acid decreases. Polymerization of the dioxovanadium cation still continues, though. If the polymer hydrolysis (e) is a fast reaction, the decomposition of the decavanadic acid now depends largely on the polymerization rate of the dioxovanadium cation.

It has been shown that the presence of the vanadium(IV) species in solution is needed for polymerization to occur[3,4]. This vanadium(IV) species is identified as the oxovanadium cation, formed by a reaction of the following type[34,36].

$$4V^{V}O_2^{+} + 4H^{+} \Leftrightarrow O_2 + 4V^{IV}O^{2+} + 2H_2O \qquad (f)$$

The oxidation half-cell reaction could occur by oxidation of either water, as shown, or of the ion-exchange beads used. 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[37,38,39,40,41,42].

^{51}V NMR and EPR spectra show a simultaneous consumption of the $V^{V}O_2^{+}$ and $V^{IV}O^{2+}$ cations. That delocalization of the unpaired electron of the vanadium(IV) species occurs at the same time as the consumption of the dioxovanadium cation consumption suggests that the initial reactants in the polymerization process are in fact the dioxovanadium cation and this vanadium(IV) species. The simultaneous appearance of colloidal particles and disappearance of the dioxovanadium cation indicates that the dioxovanadium cation, not the decavanadate anion, acts as the reactant for polymerization. The polymers apparently then act as a source of the hydronium ions for the decomposition of the decavanadic acid. The decavanadic acid apparently acts only as a source of dioxovanadium cations for the polymerization-gelation process.

None of the previously proposed tetrahedrally coordinated V^V intermediates are observed[26,27]. The MAS ^{51}V NMR spectra show that the vanadium environment of the polymer in solution is similar to that in the dioxovanadium cation. The chemical shift is only 1-2 ppm away from that of the dioxovanadium cation, indicating that the V^V are still in octahedral coordination[13]. The chemical shift is quite different from that of the crystalline form of vanadium pentoxide[43].

All of the above evidence is consistent with the following chain propagation polymerization scheme.

$$V_{10} + 14H^+ \xrightarrow{k_{dec}} 10V^V + 8\,H_2O \qquad (A)$$

$$V^V + V^{IV} \xrightarrow{k_d} V_p{}^* \qquad (B)$$

$$V_p{}^* + V^V \xrightarrow{k_p} V_p + V_p{}^* \qquad (C)$$

$$V_p \xrightarrow{k_h} V_h + H^+ \qquad (D)$$

Neither coordinated water molecules nor charges are indicated, and 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. This scheme is quite different from those previously proposed[26,27].

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 species can be written:

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

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

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

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

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

In formulating these rate expressions, several assumptions have been made:

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

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

c) The vanadium sites in the unhydrolyzed and hydrolyzed polymers can not be distinguished by ^{51}V NMR, so the rate law for $V_{p(eff)}$ also does not differentiate between the two polymers. In addition, the initial 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 decavanadic acid decomposition. V_p is either all unhydrolyzed, as at $t < 72$ hours, or all hydrolyzed at $t > 72$ hours, as reaction 2) activates and consumes all available protons from the unhydrolyzed polymer. Both forms of the polymer do not co-exist in solution for more than a short period time at the start of the decavanadic acid decomposition, and so both are represented by $V_{p(eff)}$ in the rate laws.

d) The rate law for the polymerization of the dioxovanadium cation is first order in both the monomer and the amount of reactive sites[44].

e) In accordance with references 45 and 46, the rate of decavanadic acid decomposition is first order in $[H^+]$, meaning that the first nucleophilic attack of H^+ is rate limiting. The decomposition of decavanadic acid was assumed to follow a rate expression of $k_{dec}[H^+][H_2V_{10}O_{28}^{4-}]$. As the decomposition reaction (A) occurs, the hydrolysis of the polymer will occur quickly to maintain the pH at 2; the polymer is acting as a buffer. Since the hydrolysis of the polymer seems to be extremely fast, no pH dependence on the rate of (e) can be observed. The concentration of protons was included in the rate constant to yield the rate law $k'_{dec}[H_2V_{10}O_{28}^{4-}]$.

f) $[H^+]$ is constant, as dictated by the buffer reaction (D),

Rate constants were evaluated by fitting data from 6 to 200 hours with initial conditions consistent with the spectra presented:

1) $[V^{IV}]=0.0001$ M

2) $[V^{V}] = 0.018$ M

3) $[V_{10}] = .0077$ M

4) $[V_{p(eff)}] = 0.005$ M

5) $[H^+] = 0.01$ M

6) $[V_p{}^*] = 0.0003$ M

The rate constants found were:

$k_d = 2$ liter(mole-hr)$^{-1}$

$k_p = 28.4$ liter(mole-hr)$^{-1}$ for t < 72 hours, 500 liter(mole-hr)$^{-1}$ for t > 72 hours

$k'_{dec} = 0.0458$ hr^{-1}

Integrated solutions using these parameters are shown in Figure 9.[Insert Figure 9]

The rate constant k_d was determined from the from the EPR data shown in Figure 8. It is somewhat smaller than suggested by ^{17}O NMR relaxation techniques[47].

The rate constant, k_p, is 28.4 liter(mole-hr)$^{-1}$ before the start of the rapid decomposition of the decavanadic acid. The polymer at this point in the gelation is unhydrolyzed. After the start of the decavanadic acid decomposition, the effective rate constant of the polymerization reaction must increase to 500 liter(mole-hr)$^{-1}$ to be consistent with the observation that there is no accumulation of dioxovanadium cation in solution. This indicates that after hydrolysis the polymer is more reactive towards polymerization of the dioxovanadium cation. This is supported by the observed autocatalytic ability of the reacted sol to accelerate gelation in unreacted solutions[4]. The initial decomposition of the decavanadic acid will also consume all of the accumulated, unhydrolyzed polymer in solution, so the polymerization becomes controlled by this new polymerization rate constant. The new rate constant also explains the precipitous drop in decavanadic acid concentration seen in Figure 5. The slow consumption of the decavanadic acid in solution after 120 hours as the reaction sequence becomes rate-limited by the polymerization of dioxovanadium cation to supply protons for decavanadic acid decomposition. Nearly 80% of the vanadate in solution has been polymerized by this time.

The rate constant, k'_{dec}, determined for this reaction is 0.0458 hr^{-1}. It is much lower than the value of 0.432 hr^{-1} predicted by Kepert in solutions close to these sols in pH and ionic strength[45,46]. This lower value may result from the rate-limiting effect of the formation of the polymer chain in solution. This rate limitation is overcome at the higher vanadate concentrations of 0.2 and 0.4M as shown in the MAS spectra in Figure 7 but effects on coating quality and material properties are unknown. The absence of decavanadic acid in these gels means that a stoichiometric amount of protons needed for decavanadic acid decomposition is being obtained by the polymer hydrolysis. This would suggest a repeat unit of $(VO_2(OH)(OH_2)_2)$ in the hydrolyzed polymer.

Conclusions

Gelation of V_2O_5 solutions by ion exchange acidification is governed by a number of reactions. The amount of oxovanadium cation produced is a major limiting factor. Without it to initiate the polymerization process, no consumption of dioxovanadium cation can occur other than the very slow process of decavanadic acid reformation. Later steps in the process are limited by the production of dioxovanadium cation from the decomposition of decavanadic acid, which is in turn limited by production of protons from the newly polymerized dioxovanadium cations. Only a small amount of dioxovanadium cation must be present in solution for equilibrium of reaction (d) to be established after the initial sharp drop in decavanadic acid concentration. However, polymerization of dioxovanadium cations continues slowly beyond this point; preventing equilibrium from being established and aiding in the continuing decomposition of the decavanadic acid.

These results do not support previously proposed models for this system. The mechanism of rearrangement and assembly into the two-dimensional ribbons from the linear polymers still remains in question[26,27].

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References

1. Livage, J., Chem. Mater., 1991, **3**, p. 578.

2. Gharbi, N., Sanchez, C., Livage, J., Lemerle, J., and Lefebvre, J., Inorg. Chem., 1982, **21**, p. 2758.

3. Lemerle, J., Nejem, L., Lefebvre, J., J. Inorg. Nucl. Chem., 1980, **42**, p. 17

4. Lemerle, J., Nejem, L., and Lefebvre, J., J. Inorg. Nucl. Chem., 1981, **43**(11), p. 2683.

5. Livage, J., and Legendre, J.J., J. Coll. Int. Sci., 1982, **94**, p. 75.

6. Legendre, J., Aldebert, P., Baffier, and Livage, J., J. Coll. Int., 1982, **94**, p. 84.

7. Zocher, H., and Jacobsohn, K., Koll. Beih., 1929, **28**, p. 167

8. Sanchez, C., Nabavi, M., and Taulelle, F., "Better Ceramics through Chemistry III", MRS Proceedings 121, Brinker, C.J., Clark, D.E., and Ulrich, D.R., editors, Pittsburgh, 1988, p. 96.

9. Muller, E., Z. Chem. Ind. Kolloide, 1911, **8**, p. 302

10. Pope and Dale, Q. Rev. Chem. Soc., 1968, **22**, p. 527

11. Mesmer, R.E., and Baes, C.F., "The Hydrolysis of Cations", John Wiley and Sons, New York, 1976, p. 195.

12. Kepert, L., "The Early Transition Metals", John Wiley and Sons, New York, 1972. p.181.

13. Howarth, O.W., and Richards, R.E., J. Chem. Soc., 1965, p. 864.

14. Pope, M.T., and O'Donnell, S.E., J.C.S. Dalton, 1976, p. 2290.

15. Howarth, O.W., and Jarrold, M., J.C.S. Dalton, 1978, p. 503.

16. Pettersson, L., Hedman, B., Andersson, I., and Ingri, N., Chem. Scr., 1983, **22**, p. 254.

17. Pettersson, L., Hedman, B., Andersson, I., Hedman, B., Chem. Scr., 1985, **25**, p. 309.

18. Heath, E., and Howarth, O.W., J.C.S. Dalton, 1981, p. 1105.

19. Klemperer, W.G., and Shum, W., J. Am.Chem.Soc., 1977, **99**, p. 3544.

20. Kazanskii, L.P., and Špitsyn, V.I., Dokl. Phys. Chem., 1975, p. 721.

21. Besecker, C.J., Klemperer, W.G., Maltbie, D.J., and Wright, D.A., Inorg. Chem., 1985, **24**, p. 1027.

22. Day, V.W., Klemperer, W.G., and Maltbie, D.J. J. Am. Chem. Soc., 1987, **109**, p. 2991

23. Harrison, A.T., and Howarth, O.W., J.C.S. Dalton, 1985, p. 1953.

24. Rehder, D., Bull. Mag. Res., 1982, **4**(1), p. 33.

25. Howarth, O.W., Prog. NMR Spec., 1990, **22**, p.453.

26. Livage, J., Henry, M., and Sanchez, C., Prog. Solid State Chem., 1988, **18**(4), p. 259.

27. Henry, M., Jolivet, J.P., and Livage, J., Structure and Bonding, 1992, **77**, p. 154.

28. Harris, R.K., "Nuclear Magnetic Resonance Spectroscopy", Wiley & Sons, New York, 1986, p. 144.

29. Fyfe, C., "Solid State NMR for Chemists", Wiley & Sons, London, 1983, p. 139.

30. Barboux, P., Gourier, D., and Livage, J., J. Coll. Surf., 1984, **11**, p. 119.

31. Sanchez, C., Babonneau, F., Morineau, R., Livage, J., and Bullot, J., Phil. Mag. B, 1983, **3**, p. 279

32. Sanchez, C., Henry, M., Grenet, J.C., Livage, J., J. Phys. C: Solid State, 1982, **15**, p. 7133

33. Sanchez, C., Livage, J., Tougne, P., Legrand, A. P., Magnetic Resonance in Colloids and Interface Science, eds. Fraissard, J., and Resing, H., Reidel, Dordrecht Press, 1980, p. 559.

34. Cotton, F.A., and Wilkinson, G., Advanced Inorganic Chemistry, Wiley & Sons, 5th ed., 1988, p. 671.

35. Rossotti, F.J.C., and Rossotti, H., Acta Chem. Scand., 1956, **10**(6), p. 957.

36. Milazzo, G., and Caroli, S., "Tables of Standard Electrode Potentials", John Wiley and Sons, New York, 1978, p. 215.

37. Madic, C., Begun G.M., Hahn, R.L., Launay, J.P., and Thiessen, W.E., Inorg. Chem., 1984, **23**, p. 469.

38. Nishizawa, M., Hirotsu, S., Ooi, S., and Saito, K., J. Chem. Soc. Chem. Comm., 1979, p. 707.

39. Nishizawa, M., and Saito, K., Inorg. Chem., 1980, **19**, p. 2284

40. Babonneau, F., Sanchez, C., Livage, J., Launay, J.P., Daoudi, M., and Jeannin, Y., Nouveau. J. De Chimie, 1982, **6**(7-8), p. 353.

41. Madic, C., Begun, G.M., Hahn, L., Launay, J.P., and Theissen, W.E., Inorg. Chem., 1984, **23**, p. 469.

42. Hibbert, R.C., Logan, N., Howarth, O.W., J.C.S. Dalton, 1986, p. 369.

43. Nabavi, M., Taulelle, F., Sanchez, C., and Verdaguer, M., J. Phys. Chem. Solids, 1990, **51**, p. 1375.

44. Rodriguez, R., "Principles of Polymeric Systems", John Wiley and Sons, New York, 1983, p. 73.

45. Clare, B.W., Kepert, D.L., and Watts, D.W., J. C. S. Dalton Trans., 1973, p. 2476.

46. Clare, B.W., Kepert, D.L., and Watts, D.W., J. C. S. Dalton Trans., 1973, p. 2479.

47. Wuthrich, K., and Connick, R.E., Inorg. Chem., 1967, **6**(3), p. 583.

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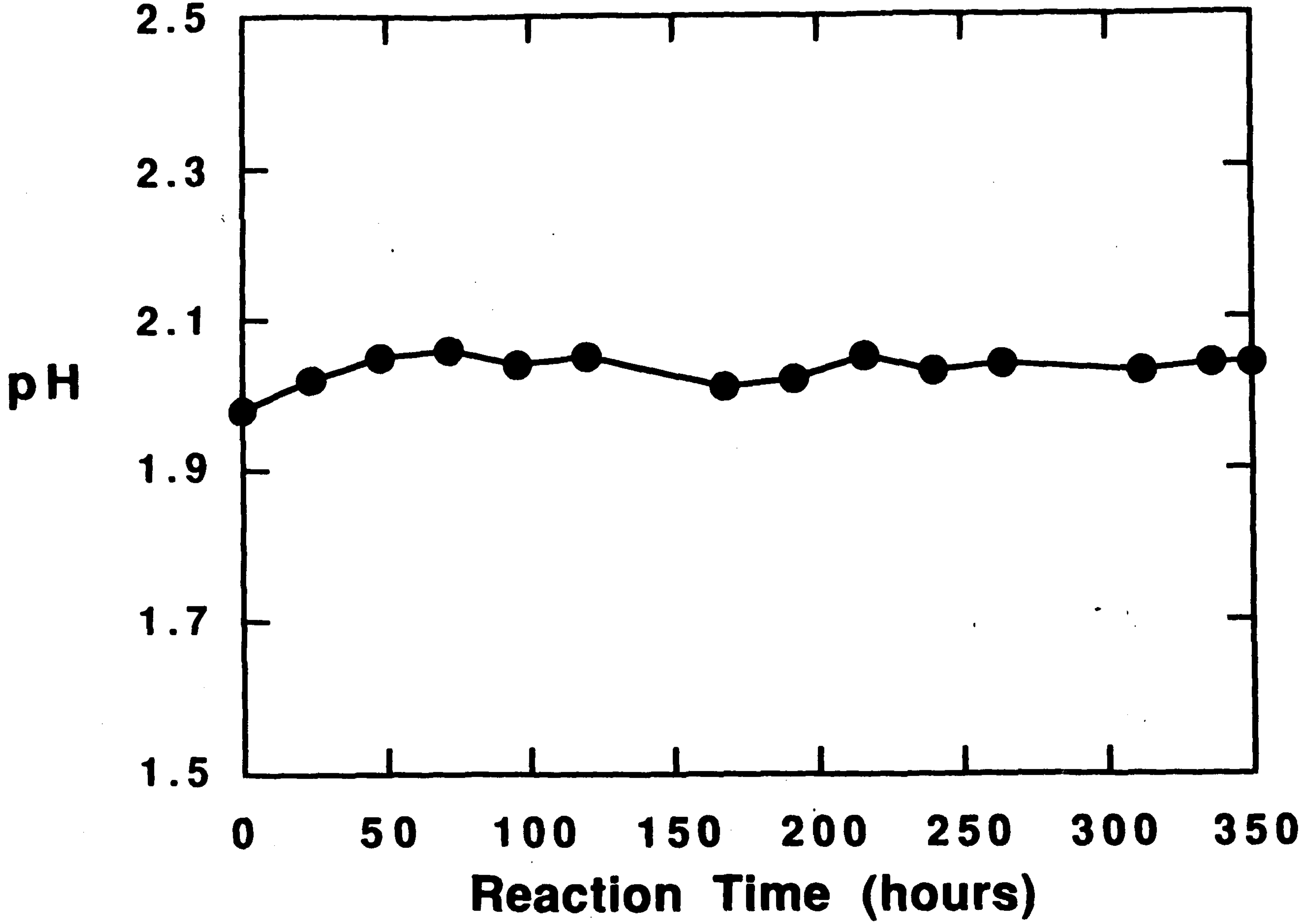

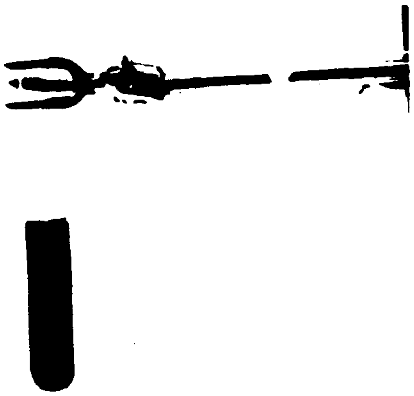

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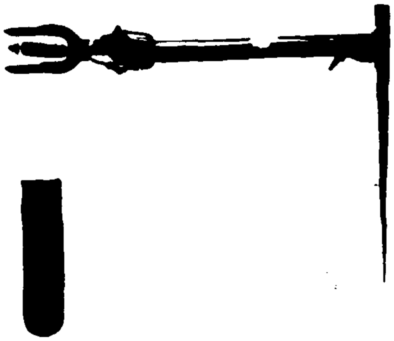

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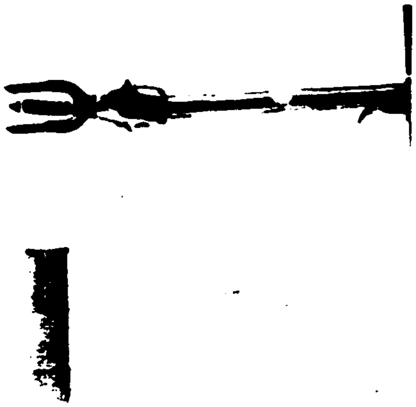

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Figure 2. Development of V_2O_5 Sol

Figure 3. ^{51}V Solution NMR Spectra of Reacting Sol

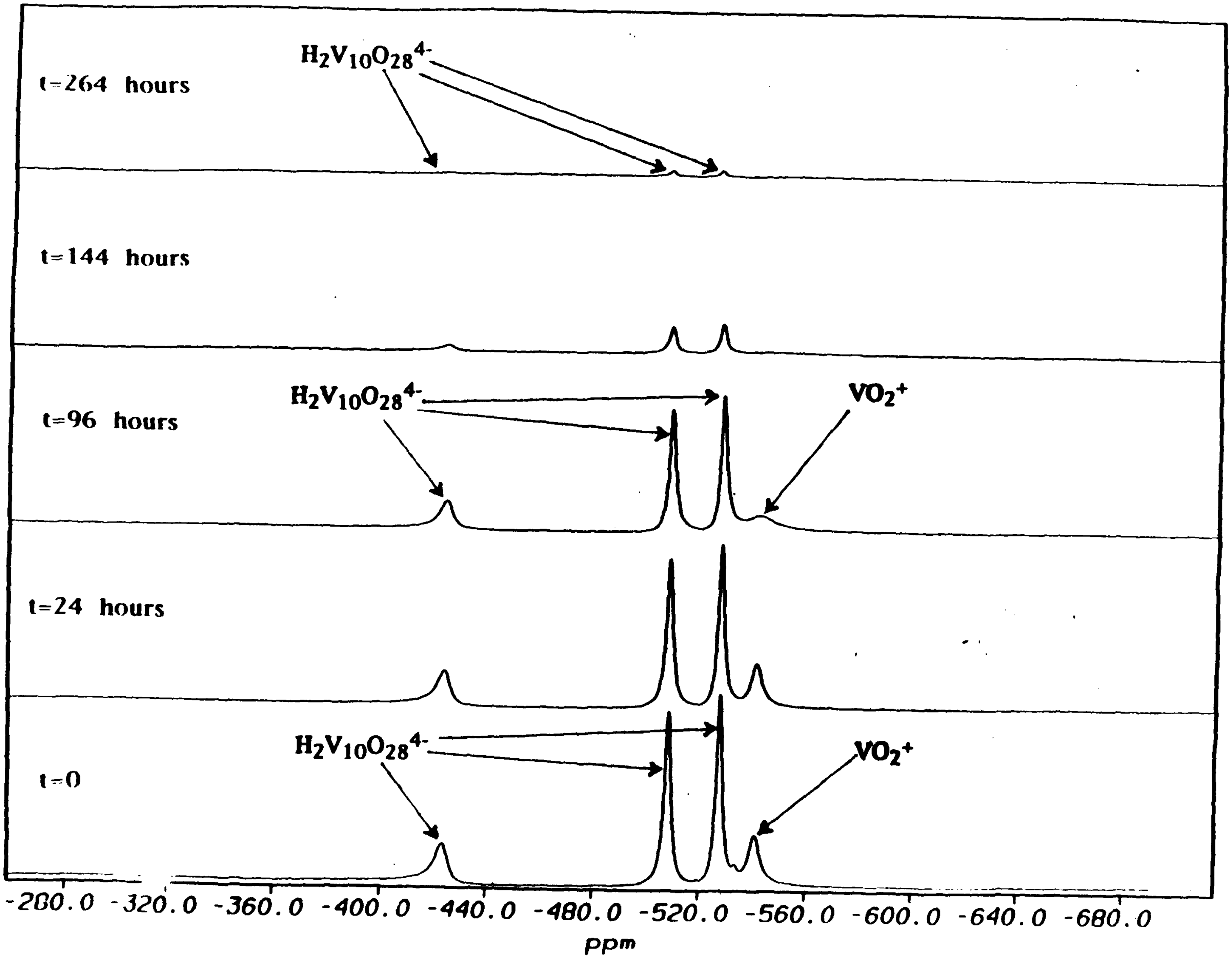


Figure 4. ^{51}V Solution NMR Spectra of Initial Reacting Solution

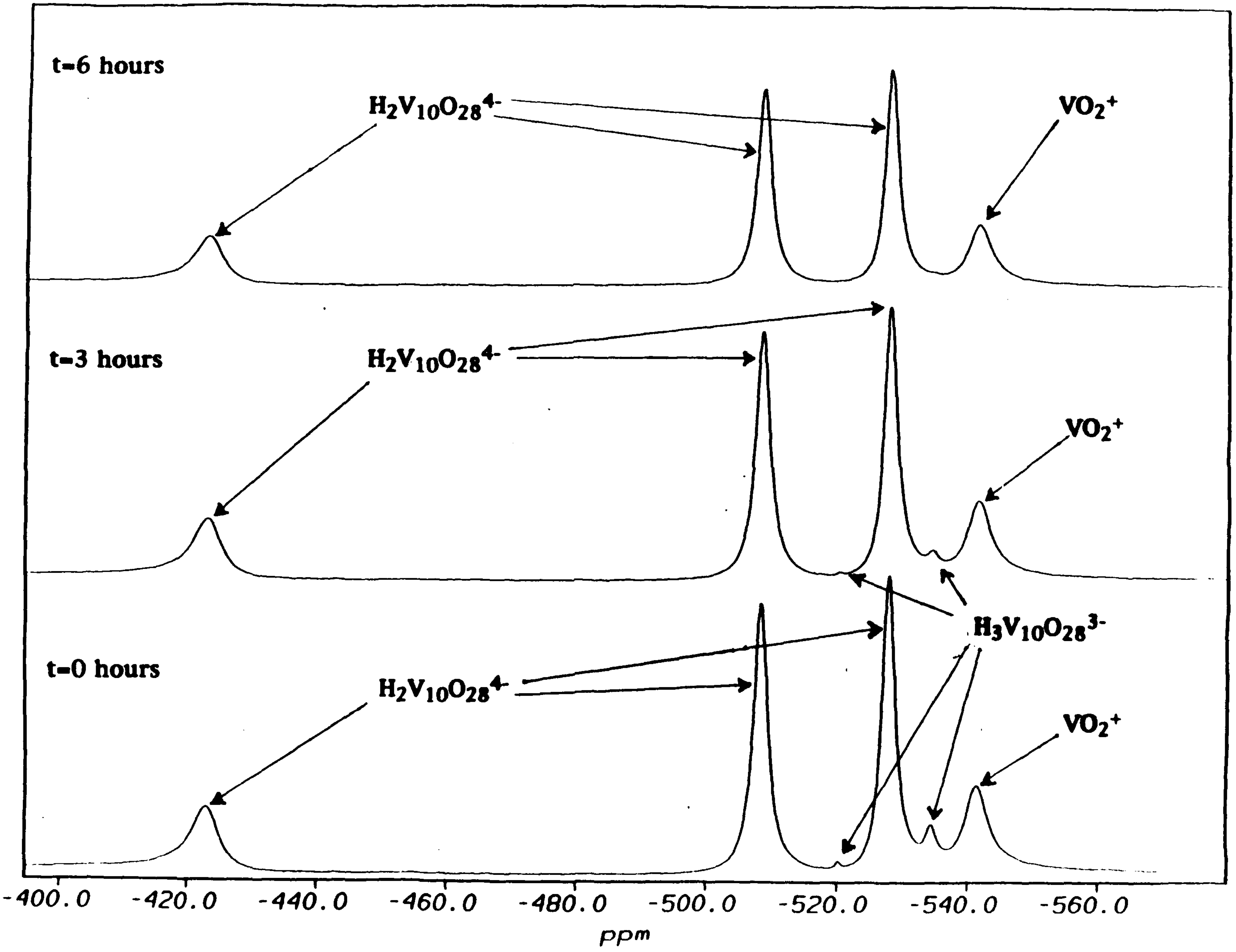


Figure 5. Species Distribution with Time

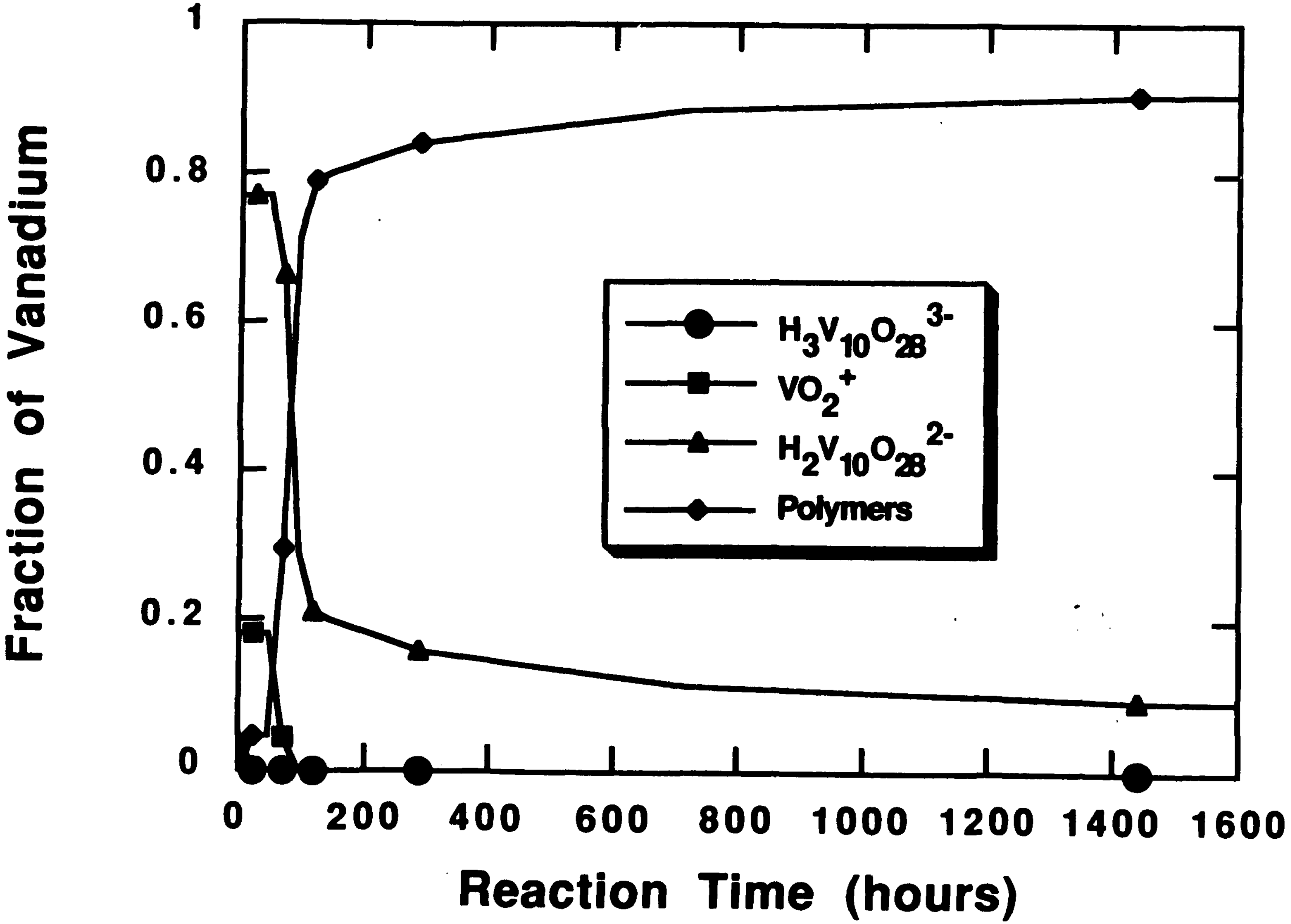


Figure 6. ^{51}V MAS NMR Spectrum of V_2O_5 Sol (t=720 hours)

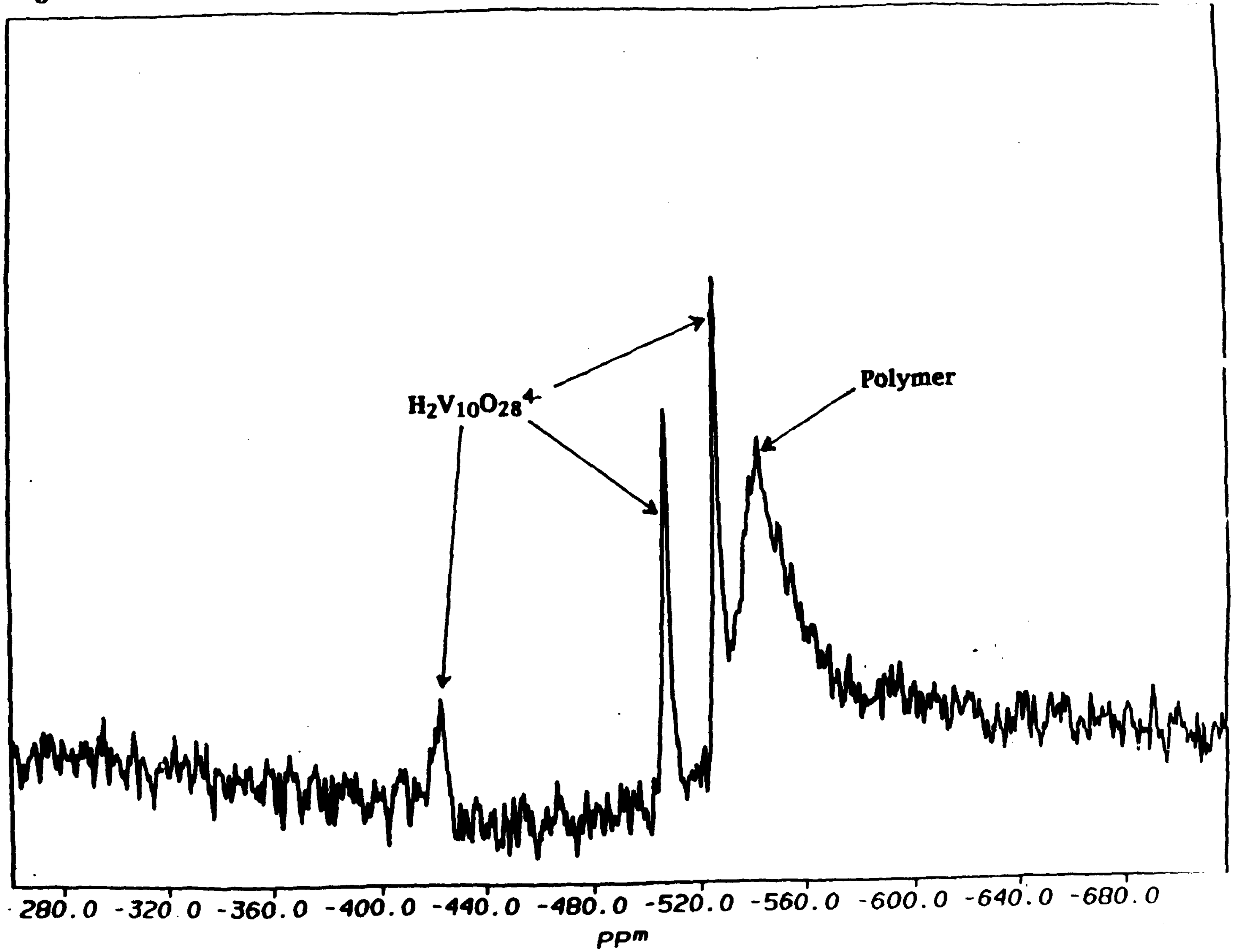


Figure 7. Comparative ^{51}V MAS NMR Spectra of Different Sols

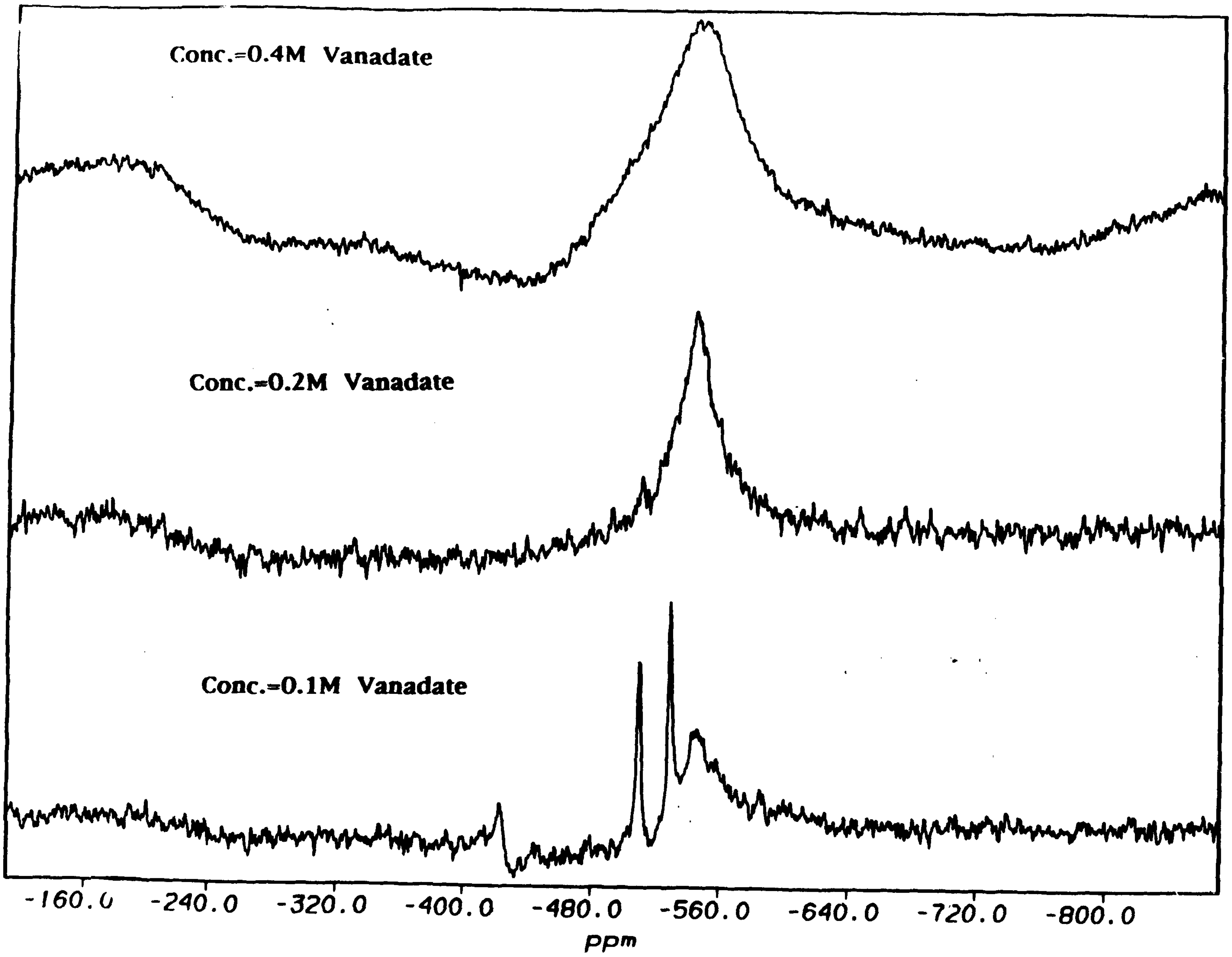
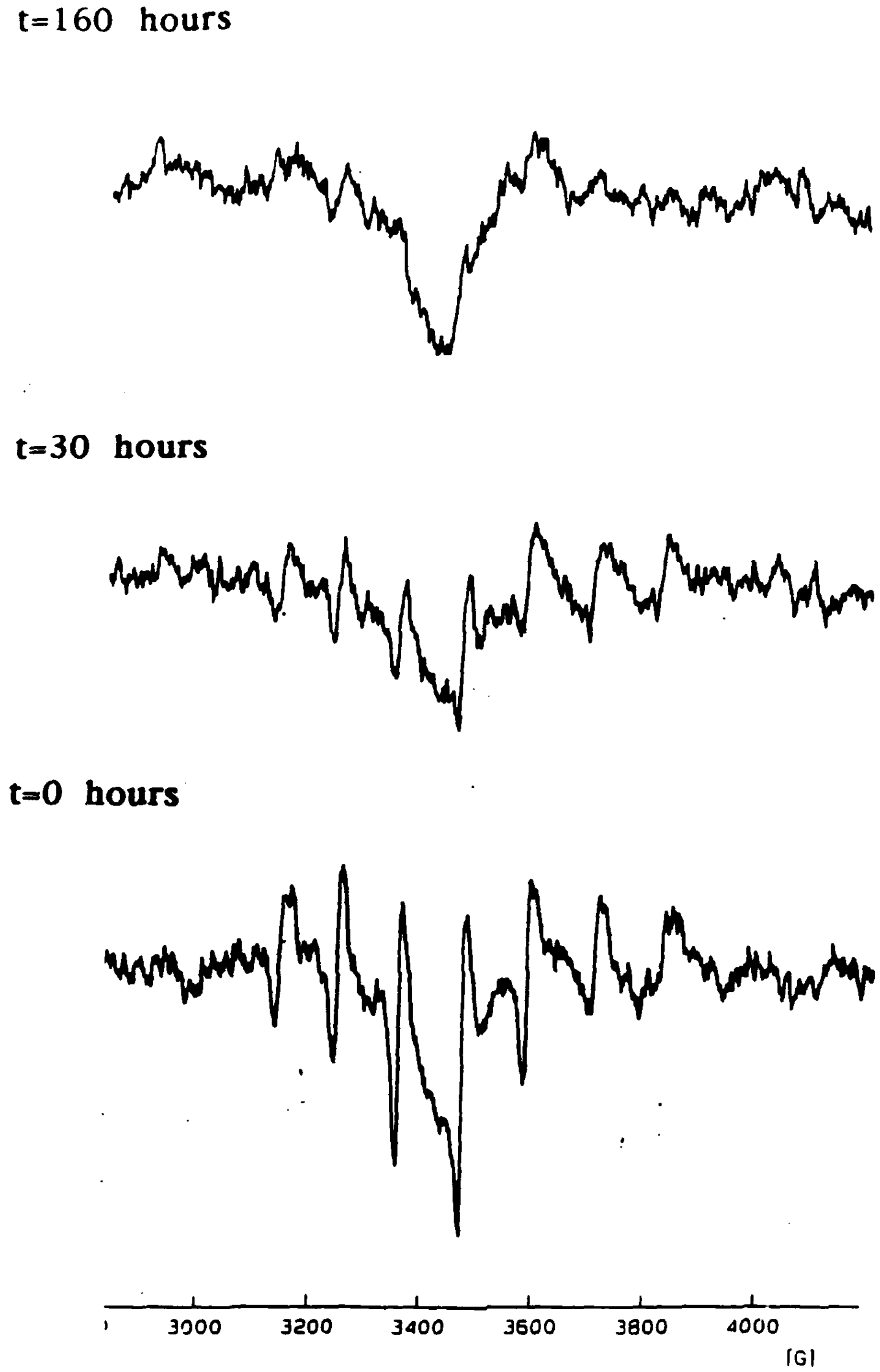


Figure 8. EPR Spectra of Reacting Solution



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