Redox Polymerization of Acrylonitrile by V⁵ /Propane-1,2-diol System in Aqueous Sulfuric Acid

B. C. Singh[a]; T. R. Mohanty[a]; P. L. Nayak[a]

[a] Department of Chemistry, Ravenshaw College, Cuttack, India

PLEASE SCROLL DOWN FOR ARTICLE

Redox Polymerization of Acrylonitrile by V^{5+}/Propane-1,2-diol System in Aqueous Sulfuric Acid

B. C. SINGH, T. R. MOHANTY, and P. L. NAYAK

Department of Chemistry
Ravenshaw College
Cuttack-3, India

ABSTRACT

The kinetics of polymerization of acrylonitrile by the redox system V^{5+}—propane-1,2-diol in aqueous sulfuric acid at 40 to 50°C were studied. The rate of polymerization, V^{5+} disappearance, and chain lengths of polyacrylonitrile were measured. The kinetics are consistent with the formation of an intermediate complex between the diol and the oxidant whose decomposition leads to the initiating radical. A suitable kinetic scheme has been proposed and the various rate and energy parameters were evaluated.

INTRODUCTION

The kinetics of the oxidation of glycols by quinquevalent vanadium in acid solutions had been the subject of a number of publications [1-3].

Waters and colleagues [1] reported that acid solutions of quinqueva-
lent vanadium oxidize α-glycols with the production of free radicals,
and the immediate color changes indicate that glycol-vanadium
complexes are formed. The use of redox systems for the initiation
of polymerization has been frequently reported in the literature [4-10],
but those involving V^{5+}-glycol reducing agent systems have not been
employed. The system ethylene glycol-chromic acid has been used as
a redox initiator for the polymerization of acrylonitrile [11]. The
results of the kinetics of polymerization of acrylonitrile by V^{5+}-
propane-1, 2-diol (PD) in sulfuric acid at 40 to 50°C are reported in
this paper. From the experimental observations, a suitable reaction
scheme is suggested and the kinetic parameters are evaluated.

EXPERIMENTAL

Acrylonitrile (American Cyanamid) was washed with 5% NaOH,
dilute H_2SO_4, and finally with water and dried over anhydrous $CaCl_2$.
Ammonium metavanadate (AR), propane-1, 2-diol (AR), ethane-1, 2-
diol (AR), butane-1, 4-diol (Fluka), sodium bisulfate (Riedel), and
sulfuric acid (~18 M; AR Basynth, India) were used. Water, distilled
thrice over alkaline permanganate and deionized by passing through a
column of Biodeminrolit resin (Permutit Co., U.K.), was used to
prepare all solutions. Nitorgen used for deaeration of the experimental
system was purified by passing through several column's of Fieser's
solution, a column of saturated lead acetate solution, and finally a wash
bottle containing distilled water.

Preparation of V(V) stock solutions, their estimations, etc. have
been described before [8, 9]. The polymerization reactions were
heterogeneous, with polymer precipitating continuously. Rates of
polymerization were obtained gravimetrically, while rates of
oxidant consumption were obtained by vanadometry on reaction mixtures
arrested by addition of excess standard ferrous sulfate solution.
Polymer samples were crystallized by dissolving in dimethylformamide
and reprecipitating in cold methanol. Intrinsic viscosities for the
polymer solutions were determined viscometrically, and the $\overline{M}_v$

values were evaluated by using the Mark-Houwink equation as given by
Stockmayer and Cleland [12].

RESULTS AND DISCUSSION

Rates of oxidant consumption $-d[V(V)]/dt$ were first order with
respect to $[V(V)]$ and $[PD]$. Plots of $(-d[V(V)]/dt)^{-1}$ vs $[PD]^{-1}$

were linear with the intercept on the rate axis showing Michaelis-Menten kinetics for complex formation. The reaction is catalyzed for sulfuric acid and perchloric acid; the catalysis by sulfuric acid is more than perchloric acid for the same molar concentrations.

Acrylonitrile was polymerized in aqueous solutions at 40, 45, and 50°C in sulfuric acid in the presence of the redox system ammonium metavanadate—propane-1, 2-diol. A typical time-conversion curve at 45°C is shown in Fig. 1. Acrylonitrile was also polymerized under identical conditions as propane-1, 2-diol in the presence of a number of primary and secondary alcohols and glycols. There is an induction period involved in all cases except pinacol, and the point of appearance of turbidity in the reaction solution is taken as the starting point of polymerization. The induction period and R_p for different redox systems are reported in Table 1.
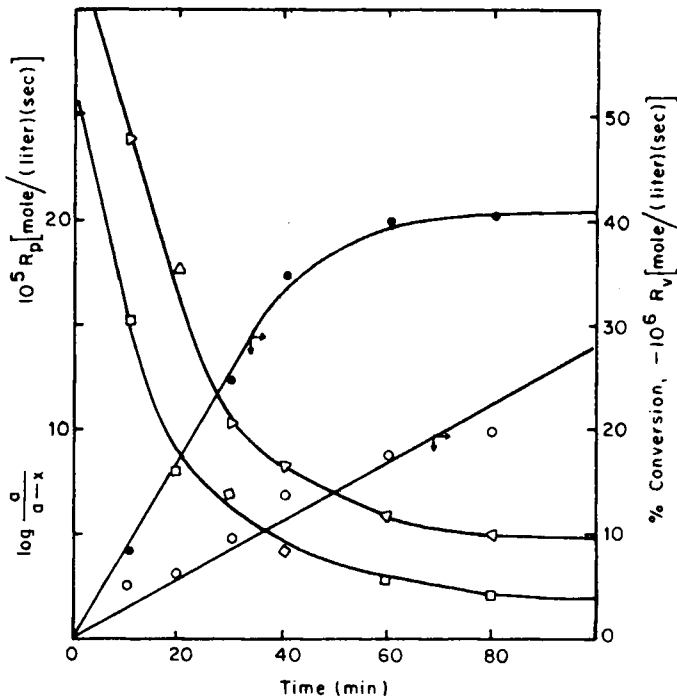

FIG. 1. Variation of rate with time at 45°C. $[V^{5+}]$ = 0.025 M, $[H^+]$ = 3.9 M, $[M]$ = 0.603 M, μ = 4 M, and $[PD]$ = 2 M. (O) $\log a/(a - x)$ vs time, ($\triangle$) R_p vs time, ($\square$) $-R_v$ vs time, and (●) % of conversion vs time.

TABLE 1. Polymerization of Acrylonitrile by Various V^{5+}-Alcohol Systems

Alcohol	Concentration (mole/liter)	Induction period (min)	Initial rate $R_p \times 10^5$ mole/(liter)(sec)
Propane-1, 2-diol[a]	2	13	6.14
Ethane-1, 2-diol[a]	2	8	9.265
Butane-1, 4-diol[a]	2	10	4.685
Isopropyl alcohol[a]	2	10	1.48
sec-Butyl alcohol[a]	2	26	0.2625
n-Butanol[a]	2	11	2.3505
Pinacol[b]	0.6	Nil	2.43
Cyclohexanol[c]	0.0818	5	5.75

[a]Reaction conditions: $[V^{5+}] = 0.03$ M; $[H_2SO_4] = 2.5$ M; $[AN] = 0.75$ M; temperature $= 45°C$; $\mu = 2.6$ M.
[b]Reaction conditions: $[V^{5+}] = 2.729 \times 10^{-2}$ M; $[H_2SO_4] = 0.375$ M; $[AN] = 1.05$ M; temperature $= 30°C$; $\mu = 0.4$ M.
[c]Reaction conditions: $[V^{5+}] = 5.625 \times 10^{-2}$ M; $[H_2SO_4] = 4$ M; $[AN] = 1.05$ M; temperature $= 50°C$; $\mu = 4.2$ M.

The polymerization takes place without any induction period in the case of pinacol. This can be explained by the remarkable oxidation rate of pinacol compared with that of other alcohols [13]. The reason for the faster oxidation of pinacol by C—C bond fission are 1) the inductive effect of the two methyl groups which will operate so as to increase the stability constant K of the more methylated diol complexes, and 2) the stability of the 2-hydroxy-2-propanol radical formed by the oxidation. Hence the complex breaks up quickly to produce the free radical which initiates polymerization.

Rate of Polymerization: R_p

The rate of polymerization R_p increased with an increase in the monomer concentration (0.23 to 0.825 M). The plots of R_p vs $[M]^2$ were linear, passing through the origin (Fig. 2), and therefore the
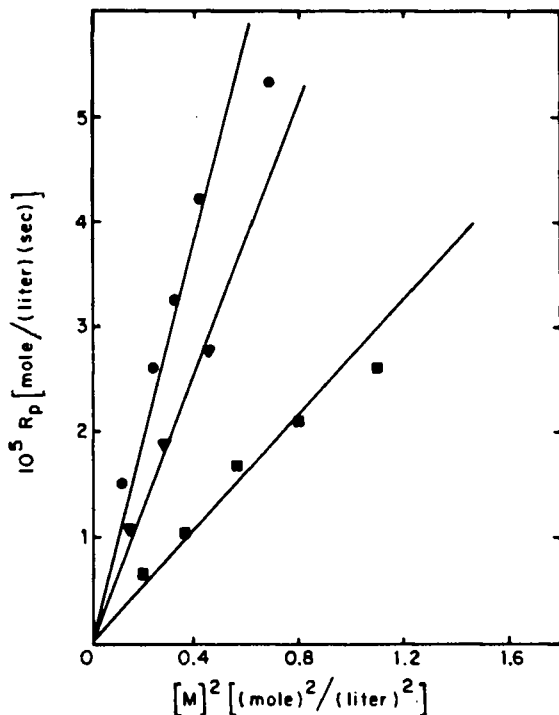
FIG. 2. Variation of R_p with $[M]^2$. $[H^+]$ = 2.325 $\underline{M}$, μ = 2.4 $\underline{M}$, ($\bullet$)
$[V^{5+}]$ = 0.0125 $\underline{M}$, $[PD]$ = 2.0 $\underline{M}$, 45°C; ($\blacktriangle$) $[V^{5+}]$ = 0.05 $\underline{M}$, $[PD]$ =
1.6 $\underline{M}$, 45°C; and ($\blacksquare$) $[V^{5+}]$ = $\overline{0}$.044 $\underline{M}$, $[PD]$ = 1.7 $\underline{M}$, 40°C.

order with respect to $[M]$ was 2. The rate data were inversely pro-
portional to $[V^{5+}]$ $(1.875 \times 10^{-2}$ to 9.375×10^{-2} $\underline{M})$, the $1/R_p$ vs
$[V^{5+}]$ plot being linear with the intercept on the ordinate (Fig. 3).
The rate also increased linearly with an increase of propane-1, 2-
diol concentration (1.33 to 2.8 $\underline{M}$), and linear plots of log R_p vs log
$[PD]$ with unit slopes as well as R_p vs $[PD]$ plots with zero inter-
cepts (Fig. 4) indicated that the order with respect to $[PD]$ was
unity. The increase of rate with an increase of $[HSO_4^-]$ may be under-
stood in terms of equilibrium

$$V(OH)_3^{2+} + HSO_4^- \rightleftharpoons V(OH)_3(HSO_4)^+$$
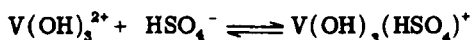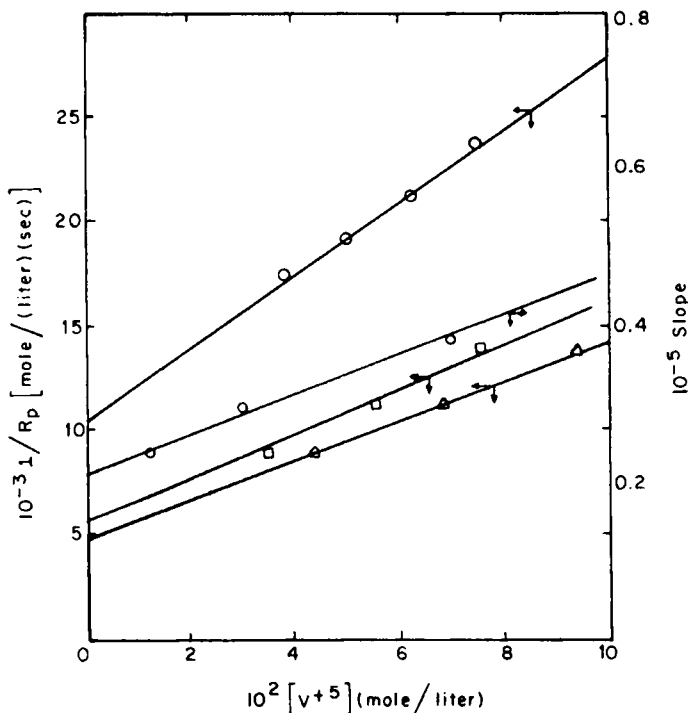
FIG. 3. Variation of $1/R_p$ with $[V^{5+}]$. $[H_2SO_4] = 2.925$ $\underline{M}$, $[M] =$ 0.754 $\underline{M}$, $\mu = 3.0$ $\underline{M}$, $[PD] = 2.0$ $\underline{M}$, (O) 40°C, ($\triangle$) 45°C, and ($\square$) 50°C. (●) Variation of slope vs $[V^{5+}]$.

The species $V(OH)_3(HSO_4)^+$ is a more powerful oxidant than $V(OH)_3^{2+}$. This also indicates that the bisulfate complexes of V^{5+} were more effective initiators or less effective terminators. R_p increased with an increase of $[H_2SO_4]$ (1.35 to 6.75 M). Anions such as SO_4^{2-} and Cl^{-1} at constant μ and $[H^+]$ decreased the rate, probably due to formation of the inactive complexes $V^{5+}....SO_4^{2-}$ (or Cl^-). R_p increased with μ when $ZnSO_4$ and sodium perchlorate were used to adjust the ionic strength, and this increasing rate may be understood in terms of the salts catalyzing the propagation step since Bamford and co-workers [14] pointed out that salts such as LiCl and LiNO$_3$ formed complexes with the polar monomer acrylonitrile, which would catalyze the propagation step. An increase in R_p due to an increase
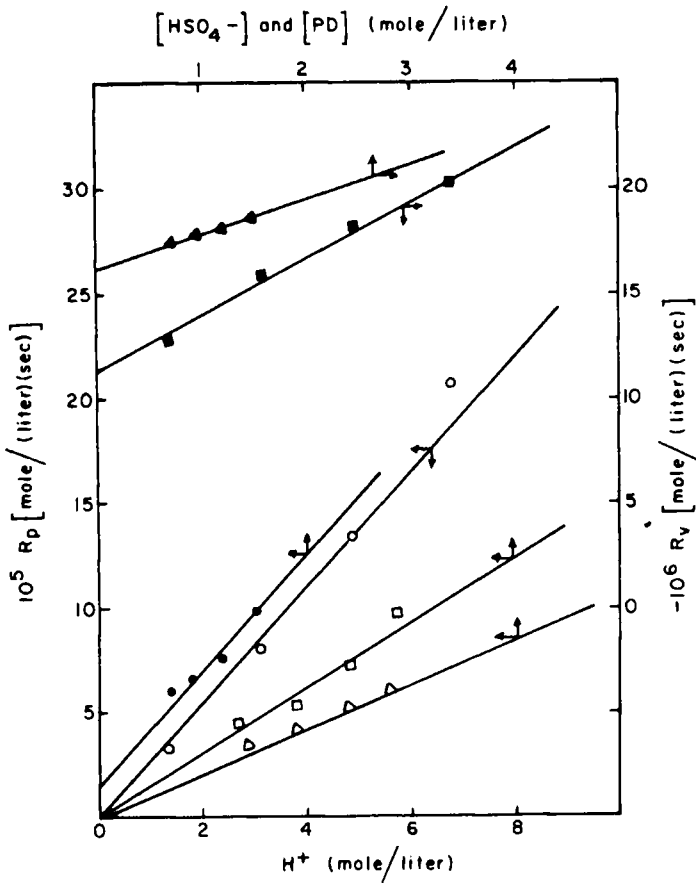
FIG. 4. Variation of R_p and $-R_v$ with $[H_2SO_4]$, $[HSO_4^-]$, and $[PD]$. (○) R_p vs $[H_2SO_4]$: $[V^{5+}] = 0.0375$ $\underline{M}$, $[PD] = 1.32$ $\underline{M}$, and $[M] = 0.53$, at 45°C. (△) R_p vs $[PD]$: $[V^{5+}] = 0.0125$ $\underline{M}$, $[H^+] = 2.5$ $\underline{M}$, $\mu = 2.6$ $\underline{M}$, and $[M] = 0.754$ $\underline{M}$ at 45°C. (□) R_p vs $[PD]$: $[V^{5+}] = 0.03$ $\underline{M}$, $[H^+] = 2.5$ $\underline{M}$, $\mu = 2.6$ M, and $[M] = 0.754$ M at 45°C. (●) R_p vs $[HSO_4^-]$: $[V^{5+}] = 0.0375$ $\underline{M}$, $[H^+] = 2.5$ $\underline{M}$, $[PD] = 2$ $\underline{M}$, and $[M] = 0.754$ $\underline{M}$ at 40°C. (▲) $-R_v$ vs $[HSO_4^-]$: $[V^{5+}] = 0.0375$ $\underline{M}$, $[H^+] = 2.5$ M, $[PD] = 2$ $\underline{M}$, $[M] = 0.754$ M at 40°C. (■) $-R_v$ vs $[H_2SO_4]$: $[V^{5+}] = 0.0375$ $\underline{M}$, $[PD] = 1.32$ $\underline{M}$, and $[M] = 0.53$ $\underline{M}$ at 45°C.

in μ was also observed in the polymerization of acrylonitrile by the redox systems cyclohexanone/V^{5+} [8], tartaric acid/V^{5+} [9], and thiourea/V^{5+} [15], and by Santappa and co-workers [16] in the polymerization of acrylonitrile initiated by Co^{3+}.

Rate of V^{5+} Disappearance ($-R_V$)

Monomer concentration had no effect on rate. An increase in $[V^{5+}]$ (1.875 to 9.375 $\times$ 10^{-2} $\underline{M}$) increased the rate, and the first-order dependence of the rate on $[V^{5+}]$ was concluded from the linear plots of $-R_V$ vs $[V^{5+}]$. The nondependence of the rate on $[M]$ was also observed in the case of other redox systems: V^{5+}-cyclohexanone [8], V^{5+}-tartaric acid [9], V^{5+}-thiourea [15], and V^{5+}-pinacol [17]. An increase in the concentration of propane-1,2-diol (1.33 to 2.8 $\underline{M}$) increased the rate; $-R_V$ vs $[PD]$ plots (Fig. 5) were linear, showing the order with respect to propane-1,2-diol to be unity. An increase in $[H_2SO_4]$ (1.35 to 6.74 $\underline{M}$) increased the rate, the plot of $-R_V$ vs $[H_2SO_4]$ being linear with an intercept on the ordinate, and the corresponding slope being 1.75. Similar observations were noted by Mehrotra [3] with a slope of 2.2 in the case of propane-1,3-diol. Plots of $-R_V$ vs Hammett acidity function, H_0, and activity of water as reported by Bunnett [18] for different concentrations of acid were linear. An increase in $[HSO_4^-]$ (0.7 to 1.4 $\underline{M}$) increased the rate, indicating that the bisulfate complex of V(V) was also active. An increase in ionic strength (2.5 to 4.0 $\underline{M}$) also increased the rate.

Chain Length

The chain length n of the polyacrylonitrile decreased with an increase of $[V^{5+}]$, and n values were found to be directly proportional to $[M]$.

Reaction Mechanism and Rate Law

The polymerization of acrylonitrile in aqueous media initiated by quinquevalent vanadium ion in the presence of propane-1,2-diol shows characteristic features of heterogeneous polymerization. The reaction system, though homogeneous before initiation of polymerization, becomes heterogeneous as soon as polymerization starts due to the insolubility of the polymer in the aqueous phase.
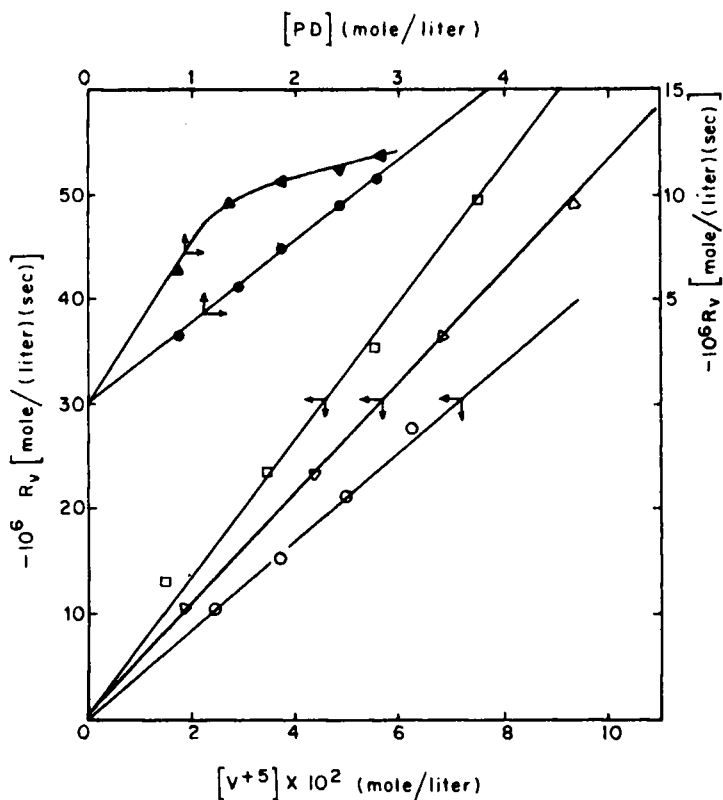
FIG. 5. Variation of $-R_v$ with $[V^{5+}]$ and $[PD]$. $-R_v$ vs $[V^{5+}]$: $[H_2SO_4] = 2.925$ M, $\mu = 3.0$ M, $[M] = 0.754$ M, and $[PD] = 2$ M, at (O) 40°C, ($\triangle$) 45°C, and ($\square$) 50°C. $-R_v$ vs $[PD]$ at 45°C: $[V^{5+}] = 0.0375$ M, $[H^+] = 2.5$ M, $\mu = 2.6$ M, $[M] = 0.754$ M, ($\bullet$) $[V^{5+}] = 0.0125$ M, and ($\blacktriangle$) $[V^{5+}] = 0.05$ M.

From the proportionalities obtained between the measurable parameters and the variables, the following reaction scheme is suggested involving initiation by organic free radicals produced by the interaction of V^{5+} with propane-1, 2-diol and termination by V^{5+} ion. Termination of vinyl polymerization by metal ions is now well recognized [16, 19].

Primary Radical Production:

$$PD + VO_2^+ \underset{fast}{\overset{K^I}{\rightleftharpoons}} \quad complex_I \xrightarrow[slow]{k_1} \quad R\cdot + V(IV)$$

$$PD + V(OH)_3^{2+} \underset{fast}{\overset{K^{II}}{\rightleftharpoons}} complex_{II} \xrightarrow[slow]{k_2} \quad R\cdot + V(IV) + H_3O^+$$

$$PD + VO\cdot OH^{2+} \overset{K^{III}}{\rightleftharpoons} complex_{III} \xrightarrow{k_3} \quad R\cdot + V(IV) + H^+ \tag{1}$$

$$PD + V(OH)_3HSO_4^+ \underset{fast}{\overset{K^{IV}}{\rightleftharpoons}} complex_{IV} \xrightarrow[slow]{k_4}$$

$$R\cdot + V(IV) + H_2SO_4 + H_2O$$

where

$$VO_2^+ + H_3O^+ \overset{K_1}{\rightleftharpoons} V(OH)_3^{2+}$$

$$V(OH)_3^{2+} + HSO_4^- \overset{K_2}{\rightleftharpoons} V(OH)_3HSO_4^+$$

$$VO_2^+ + H^+ \overset{K_3}{\rightleftharpoons} VO\cdot OH^{2+}$$
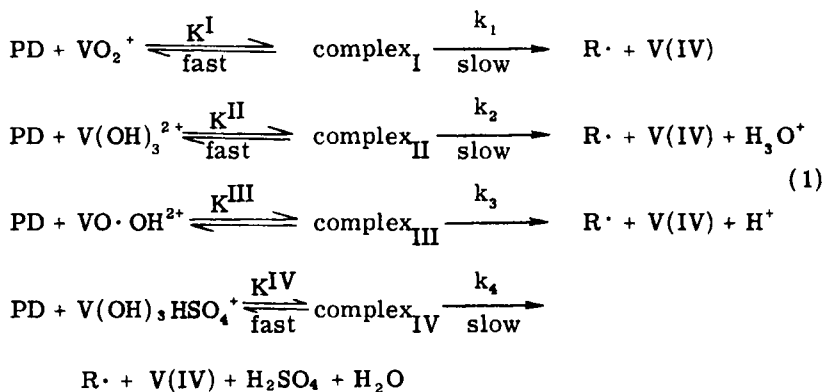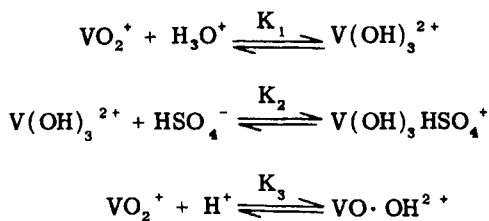
In the presence of a monomer, the free radical R· starts the chain reaction:

Initiation:

$$R\cdot + M \xrightarrow{k_i} RM\cdot \tag{2}$$

Propagation:

$$RM\cdot + M \xrightarrow{k_p} RM_2^\cdot$$

$$RM_{n-1}^\cdot + M \xrightarrow{k_p} RM_n^\cdot \tag{3}$$

Linear Termination by V^{5+}:

$$RM_n^{\cdot} + VO_2^+ \xrightarrow{\ k_{t_1}\ } \text{polymer} + V(IV)$$

$$RM_n^{\cdot} + V(OH)_3^{2+} \xrightarrow{\ k_{t_2}\ } \text{polymer} + V(IV) \qquad (4)$$

$$RM_n^{\cdot} + VO\cdot OH^{2+} \xrightarrow{\ k_{t_3}\ } \text{polymer} + V(IV)$$
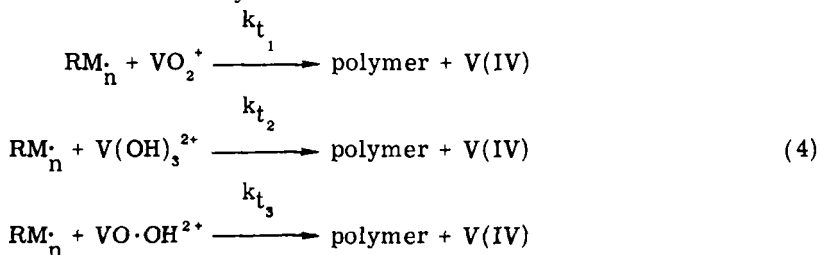
Reaction of the Primary Radical with V^{5+}:

$$\left. \begin{array}{l} R\cdot + VO_2^+ \xrightarrow{\ k_{0_1}\ } \\[6pt] R\cdot + V(OH)_3^{2+} \xrightarrow{\ k_{0_2}\ } \\[6pt] R\cdot + VO\cdot OH^{2+} \xrightarrow{\ k_{0_3}\ } \end{array} \right\} \text{products} + V(IV) \qquad (5)$$
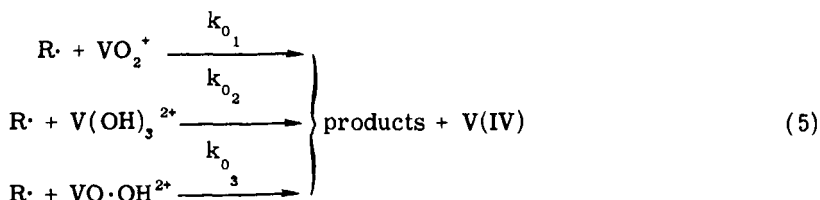
Here M represents the monomer, RM· is the radical formed by the reaction of primary radicals with monomer, and $RM_n^{\cdot}$ represents the growing polymer radical.

Taking into account of the above reaction scheme and applying steady-state assumption to both [R·] and [M·] separately, possible expressions for R_p, $-R_v$, and chain length n were derived:

$$R_p = (k_p/k_t)k'[PD][M]^2 / \{[M] + (k_0/k_i)[V^{5+}]\} \qquad (6)$$

$$-R_v = 2k'[PD][VO_2^+] \qquad (7)$$

where

$$k' = k_1 K^I + k_3 K_3 K^{III}[H^+]$$

$$k_1 K^I + K_1 K^{II} k_2 [H_3O^+]$$

$$k_1 K^I + K^{IV} k_4 K_1 K_2 [H_3O^+][HSO_4^-]$$

$$k_t = k_{t_1},\ k_{t_2},\ \text{or}\ k_{t_3}$$

$$k_0 = k_{0_1}, \ k_{0_2}, \ \text{or} \ k_{0_3}$$

$$n = (k_p/k_t)[M]/[V^{5+}] \tag{8}$$

The dependence of R_p on $[M]^2$ and $[PD]$, of $1/R_p$ on $[V^{5+}]$ and $1/[PD]$, of $-R_v$ on $[PD]$ and $[V^{5+}]$, and not on $[M]$, all of which were observed, favored the above scheme.

The other modes of termination—mutual termination and primary radical termination—were discounted on the basis that the expressions for R_p, $-R_v$, and n involved proportionalities which were not experimentally realized. In the case of mutual termination, the expressions involved proportionalities such as $[M]^{3/2}$, $[V^{5+}]^{1/2}$, $[PD]^{1/2}$ for R_p, $[V^{5+}]^2$ for $-R_v$, $[PD]^{-1/2}$ for n and in the case of primary radical termination, the expressions involved terms like $1/[M]$ for $-R_v$, $[M]^2$, $1/[PD]$ for n, and R_p involved no $[V^{5+}]$ and $[PD]$ terms.

Evaluation of Rate Constants: k_p/k_t and k_0/k_i

The values of k_p/k_t and k_0/k_i were evaluated from Eq. (6) by plotting $1/R_p$ vs $[V^{5+}]$. Taking the reciprocal of the rate expression for R_p (Eq. 6) and rearranging gives

$$\frac{1}{R_p} = \frac{k_t}{k_p k'[PD][M]} + \frac{k_t(k_0/k_i)[V^{5+}]}{k_p k'[PD][M]^2} \tag{9}$$

Plots of $1/R_p$ vs $[V^{5+}]$ according to the above equation were linear (Fig. 3), and (k_0/k_i) values were obtained from (slope/intercept) $\times$ $[M]$, and k_p/k_t values were obtained from reciprocal of (intercept) $\times$ $k'[PD][M]$.

Alternately, k_0/k_i and k_p/k_t values were evaluated from the linear plot of $1/R_p$ vs $1/[PD]$, whose slope would be

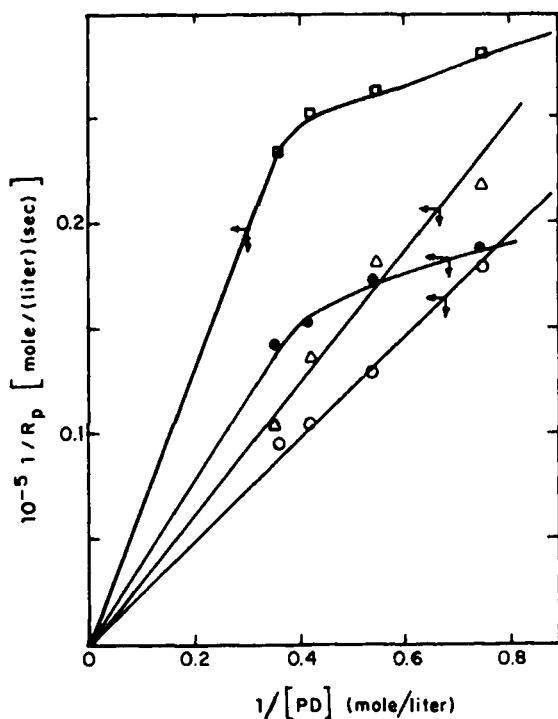$$\frac{k_t}{k_p} \ \frac{(k_0/k_i)[V^{5+}]}{k'[M]^2} + \frac{k_t}{k_p k'[M]}$$

FIG. 6. Variation of $1/R_p$ with $1/[PD]$ $[H_2SO_4] = 2.5\ \underline{M}$, $\mu = 2.6\ \underline{M}$, $[M] = 0.754\ \underline{M}$, 45°C, (○) $[V^{5+}] = 0.0125\ \underline{M}$, (△) $[V^{5+}] = 0.03\ \underline{M}$, (□) $[V^{5+}] = \overline{0}.05\ \underline{M}$, and (●) $[V^{5+}] = 0.07\ \overline{\underline{M}}$.

At different $[V^{5+}]$, $[PD]$ was varied, and hence different plots of $1/R_p$ vs $1/[PD]$ were obtained (Fig. 6). The slopes of these plots were then plotted against $[V^{5+}]$ (Fig. 3) to resolve the composite term into two. The slope and intercept of this latter plot were equal to $(k_t/k_p)\{(k_0/k_i)/k'[M]^2\}$ and $\{(k_t/k_p)k'[M]\}$, respectively; k_0/k_i from plots of (slope/intercept)$[M]$ and k_p/k_t from (1/intercept) $\{(1/k')[M]\}$ were evaluated, and the values obtained by the above two methods were compared (Table 2).

Activation Parameters

The values of k', (k_p/k_t), and (k_0/k_i) at 40, 45, and 50°C have

TABLE 2. Values of the Rate Parameters in the Polymerization
Acrylonitrile (AN) Initiated by the System Propane-1, 2-diol/V^{5+}

Temper-ature (°C)	$k' \times 10^3$ (liter/(mole)(sec))			k_p/k_t		k_0/k_i	
	From log $a/(a - x)$ vs time	From $-R_v$ vs [V(V)]	From $-R_v$ vs [$\overline{PD}$]	From $1/R_p$ vs [PD]	From $1/R_p$ vs [V^{5+}]	From $1/R_p$ vs $1/$[PD]	From $1/R_p$ vs [V^{5+}]
40	-	4.5	-	-	1.08	-	20.11
45	5.29	5.5	5.6	0.6002	0.5076	16.08	15.87
50	-	6.5	-	-	0.2945	-	14.03

been utilized in the computation of the activation parameters by plot-
ting them against $1/T$.

The value of E', $E_p - E_t$, and $E_0 - E_i$ were computed to be 8.30,
-6.90, and -22.60 kcal/mole. Further, the value of E_p for acrylo-
nitrile in water has been reported by Dainton et al. [20] to be 4.1
kcal/mole. Using this value for E_p, E_t has been calculated to be
11.00 kcal/mole. The corresponding entropy of activation for k',
(k_p/k_t), and (k_0/k_i) were evaluated to be -49.60, -80.50, and -109.90
cal/(mole)(°K), respectively.

REFERENCES

[1] J. S. Littler, A. I. Mallet, and W. A. Waters, J. Chem. Soc.,
    1960, 2761.
[2] R. N. Mehrotra, J. Chem. Soc., B, 1968, 1123.
[3] R. N. Mehrotra, Ibid., 1970, 1722.
[4] V. S. Ananthanarayanan and M. Santappa, J. Appl. Polym. Sci.,
    9, 2437 (1965).
[5] K. Jijee, M. Santappa, and V. Mahadevan, J. Polym. Sci., A-1,
    4, 377 (1966).
[6] R. S. Konar and S. R. Palit, J. Indian Chem. Soc., 38, 481
    (1961).
[7] E. A. S. Cavell and A. C. Meeks, Polymer, 8, 79 (1967).
[8] T. R. Mohanty, B. C. Singh, and P. L. Nayak, Makromol. Chem.,
    175, 2345 (1974).

[9] T. R. Mohanty, B. C. Singh, and P. L. Nayak, Accepted for publication, J. Polym. Sci., Polym. Chem. Ed., In Press.
[10] S. K. Saha and A. K. Choudhury, J. Polym. Sci., A-1, 9, 79 (1971).
[11] S. Viswanathan and M. Santappa, Ibid., 9, 1685 (1971).
[12] W. H. Stockmayer and R. C. Cleland, J. Polym. Sci., 17, 473 (1955).
[13] J. S. Littler and W. A. Water, J. Chem. Soc., 1959, 1299.
[14] C. H. Banford, A. D. Jenkins, and R. Johnston, J. Polym. Sci., 31, 393 (1966).
[15] B. C. Singh, Ph.D. Thesis, Utkal University, India, 1974.
[16] K. Jijie, M. Santappa, and V. Mahadevan, J. Polym. Sci., A-1, 4, 393 (1966).
[17] S. Saccubai and M. Santappa, Proc. Indian. Acad. Sci., 71, 111 (1970).
[18] J. F. Bunnett, J. Amer. Chem. Soc., 83, 4956 (1961).
[19] T. R. Mohanty, Ph.D. Thesis, Utkal University, India, 1974.
[20] F. S. Dainton and R. S. Eaton, J. Polym. Sci., 39, 313 (1959).