**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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**To cite this Article** Varaprasad, D. V. P. R. and Mahadevan, V.(1983) 'Aqueous Redox Polymerization of Acrylonitrile Initiated by Systems Based on Tervalent and Tetravalent Vanadium in Combination with N-Bromosuccinimide as the Oxidant', Journal of Macromolecular Science, Part A, 19: 5, 781 — 795

**To link to this Article: DOI:** 10.1080/00222338308069458

**URL:** http://dx.doi.org/10.1080/00222338308069458

J. MACROMOL. SCI.–CHEM., A19(5), pp. 781-795 (1983)

# Aqueous Redox Polymerization of Acrylonitrile Initiated by Systems Based on Tervalent and Tetravalent Vanadium in Combination with N-Bromosuccinimide as the Oxidant

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## ABSTRACT

The kinetics of polymerization of acrylonitrile (AN) initiated by the systems V(IV)/N-bromosuccinimide (NBS) and V(III)/NBS have been investigated in aqueous acid media in the 25-35°C range. Evidence for Michaelis-Menten kinetics is obtained from oxidation data with the system V(IV)/NBS. Rates of polymerization varied as $[AN]^{3/2}$, $[NBS]^{1/2}$, and $[V^{n+}]^{1/2}$, where $n = 3$ or 4. The retardation of oxidation as well as polymerization by increasing $[H^+]$ results from protonation of NBS which inhibits complexation. A mechanism involving formation of a complex between the reductant metal ion and oxidant followed by its reaction with AN to generate initiating radicals, coupled with mutual termination of growing radicals, accounts for the kinetics of polymerization.

0022-233X/83/1905-0781$3.50/

## INTRODUCTION

The use of N-bromosuccinimide (NBS) as an oxidant is well documented [1-3]. It has also been used as the photoinitiator for vinyl polymerization [4]. At around 100°C the homolytic fission of NBS yielded fragments which accelerated the polymerization of MMA while with styrene the effect is opposite [5]. It has been shown [6] that equimolar amounts of NBS and organic peroxides such as cumene hydroperoxide are useful as polymerization initiators at temperatures less than normally employed. Combination of NBS with reducing metal ions yields useful redox systems for vinyl polymerization. Otsu et al. [7, 8] have reported that the system Ni(0)/NBS showed excellent activity for MMA, weak activity for styrene, and none at all toward vinyl acetate. Banthia and Palit [4] have shown that the redox systems involving metal ions such as Fe(II), Cu(I), Ti(III), and V(IV) in combination with NBS are good initiators for polymerization. Polymerization proceeds through radical intermediates, and the initiation is considered to be effected by the succinimide radical. With the V(IV)/NBS redox system it has been reported that the rates of polymerization increase with the pH of the medium, and this has been attributed to a coagulating effect which brings down the number of polymer particles, thereby affecting the rate of polymerization. However, no systematic investigation of the oxidation of metal ions by NBS has been carried out. This paper deals with the kinetics of oxidation of oxovanadium(IV) by NBS and polymerization of acrylonitrile using the systems V(IV)/NBS and V(III)/NBS in aqueous perchloric and sulfuric acid media.

## EXPERIMENTAL

All reagents used were of AnalaR grade. Water doubly distilled over alkaline permanganate in an all-glass still was used throughout. Vanadyl perchlorate solutions were prepared according to the method of Jones and Larsen [9]. The free acid content of the stock solutions was estimated by ion exchange. Stock solutions of vanadium(IV) were estimated by titration against permanganate [10]. Ammonium vanadium(III) sulfate was prepared according to the method of Palmer [11], and stock solutions of vanadium(III) were estimated by the method of Ramsey et al. [12]. Ionic strength was maintained constant by the addition of $NaClO_4$. NBS was twice recrystallized from water and dried in vacuo (mp 179-180°C). Acrylonitrile was freed from inhibitor and distilled under diminished pressure.

Initial rates of oxidation were measured by monitoring the absorbance due to $VO^{2+}$ at 770 nm. A Carl Zeiss DMR 21 model recording spectrophotometer equipped with thermostatted cell compartments was used for this purpose. All the reactants except $VO^{2+}$ were taken in a 4-cm quartz cell and thermostatted at the required temperature.

The required amount of separately thermostatted $VO^{2+}$ stock solution was then added, and after rapid mixing, recording of absorbance commenced. Rates of oxidation (-d[V(IV)]/dt) were obtained from the slopes of the absorbance versus time plots using the appropriate extinction coefficient for $VO^{2+}$ in the two acid media, whose values are 14.3 $dm^3 mol^{-1} cm^{-1}$ in $HClO_4$ and 15.6 $dm^3 mol^{-1} cm^{-1}$ in $H_2SO_4$. All polymerizations were quenched by the addition of $NaBrO_3$ solution and the rates followed gravimetrically. Viscosity measurements were carried out in DMF medium at 30°C, and the average degrees of polymerization were calculated using the relationship [13]

$$\log \overline{P}_n = 3.118 + 1.316 \log [\eta]_{int}$$

## RESULTS AND DISCUSSION

Kinetics of oxidation of $VO^{2+}$ by NBS were investigated in both aqueous $HClO_4$ and $H_2SO_4$ media. Stoichiometry of this reaction was found to be 2 mol of $VO^{2+}$ per mol of NBS. The initial rates of oxidation (-d[V(IV)]/dt) varied as the first power of the V(IV) concentration (Table 1). Plots of rates versus [NBS] at fixed [$H^+$] and ionic strength are shown in Fig. 1. It is evident that oxidation is retarded by increasing the $H^+$ ion concentration. Increasing the ionic strength of the medium also showed a decreasing effect on rates (Table 2). Figure 2 depicts two sets of Lineweaver-Burk plots, viz., $(rate)^{-1}$ versus $[NBS]^{-1}$ at different initial [$H^+$]. The common intercepts in

TABLE 1. Variation of -d[V(IV)]/dt with [V(IV)]

| (a) [V(IV)] × $10^3$ mol $dm^{-3}$ | (b) Rate × $10^5$ mol $dm^{-3} s^{-1}$ | (b) [V(IV)] × $10^3$ mol $dm^{-3}$ | (b) Rate × $10^5$ mol $dm^{-3} s^{-1}$ |
|---|---|---|---|
| 2.55 | 0.34 | 2.41 | 0.51 |
| 3.39 | 0.42 | 3.62 | 0.76 |
| 4.61 | 0.59 | 4.79 | 1.03 |
| 6.42 | 0.81 | 6.01 | 1.27 |
| 7.36 | 0.93 | 7.18 | 1.53 |

(a) [$HClO_4$] = 0.75 mol $dm^{-3}$; [NBS] = 1.69 × $10^{-2}$ mol $dm^{-3}$; ionic strength = 1.87 $dm^{-3}$; 25°C.

(b) [$H_2SO_4$] = 0.73 mol $dm^{-3}$; [NBS] = 1.71 × $10^{-2}$ mol $dm^{-3}$; ionic strength = 1.83 mol $dm^{-3}$; 30°C.

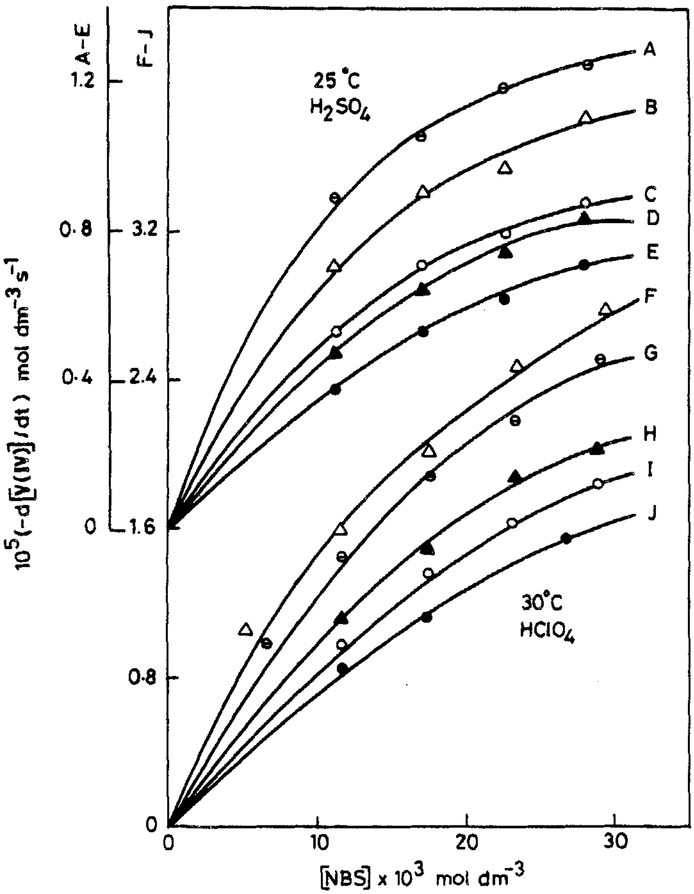

FIG. 1. Plots of -d[V(IV)]/dt vs [NBS]. Lines (A)-(E): [V(IV)] = 5.93 × $10^{-3}$ M; [$H_2SO_4$] = (A) 0.364 M, (B) 0.728 M, (C) 1.092 M, (D) 1.455 M, (E) 1.819 M; 25°C. Lines (F)-(J): [V(IV)] = 6.12 × $10^{-3}$ M; [$HClO_4$] = (F) 0.376 M, (G) 0.746 M, (H) 1.12 M, (I) 1.49 M, (J) 1.86 M; 30°C.

these plots suggest for $H^+$ the role of competitive inhibitor in the mechanism of oxidation. The following sequence of reactions accounts for the observed kinetics.

$$NBS + H^+ \overset{K}{\rightleftharpoons} NBSH^+ \qquad (i)$$

$$\text{NBS} + \text{V(IV)} \overset{K_1}{\rightleftharpoons} \text{complex} \qquad \text{(ii)}$$

$$\text{Complex} \xrightarrow{k_r} \text{R}^{\bullet} + \text{Br}^- + \text{V(V)} \qquad \text{(iii)}$$

$$\text{R}^{\bullet} + \text{V(IV)} \xrightarrow{\text{fast}} \text{R}^- + \text{V(V)} \qquad \text{(iv)}$$

V(IV) and V(V) represent predominant species in solution and $R^{\bullet}$ is the succinimidyl radical. The retarding effect of added $H^+$ could also be due to equilibria such as

$$(\text{in } HClO_4) \qquad VO^{2+}(aq) \rightleftharpoons VOOH^+ + H^+ \qquad \text{(v)}$$

$$(\text{in } H_2SO_4) \qquad VO^{2+}(aq) + HSO_4^- \rightleftharpoons VOSO_4 + H^+ \qquad \text{(vi)}$$

The $pK_a$ of $VO^{2+}(aq)$ being of the order of 6 [14], under the experimental conditions ($[H^+]$ = 0.3 to 1.8 M) the Equilibrium (v) lies well to the left and in $H_2SO_4$ medium the most predominant species is $VOSO_4$. Besides, the kinetics would be different if changes in $H^+$ ion concentration affect the rates through equilibria such as (v) and (vi). Steps (i)-(iv) lead to the following rate law:

$$-d[V(IV)]/dt = \frac{2k_r K_1 [V(IV)]_T [NBS]_T}{1 + K[H^+] + K_1[NBS]_T} \qquad (1)$$

where $[V(IV)]_T$ and $[NBS]_T$ represent the total concentrations. Data in Figs. 1 and 2 substantiate Eq. (1). The slopes of these plots (Fig. 2)

TABLE 2. Effect of Varying Ionic Strength on $-d[V(IV)]/dt$

| | | | | | | |
|---|---|---|---|---|---|---|
| Ionic strength ($mol\ dm^{-3}$) | 0.58 | 0.66 | 0.82 | 0.98 | 1.14 | 1.30 |
| Rate × $10^5$ $mol\ dm^{-3}\ s^{-1}$ | 2.94 | 2.88 | 2.56 | 2.24 | 2.08 | 1.60 |
| Temperature 30°C | $[V(IV)] = 6.3 \times 10^{-3}\ mol\ dm^{-3}$<br>$[NBS] = 1.39 \times 10^{-2}\ mol\ dm^{-3}$<br>$[H_2SO_4] = 0.48\ mol\ dm^{-3}$ | | | | | |

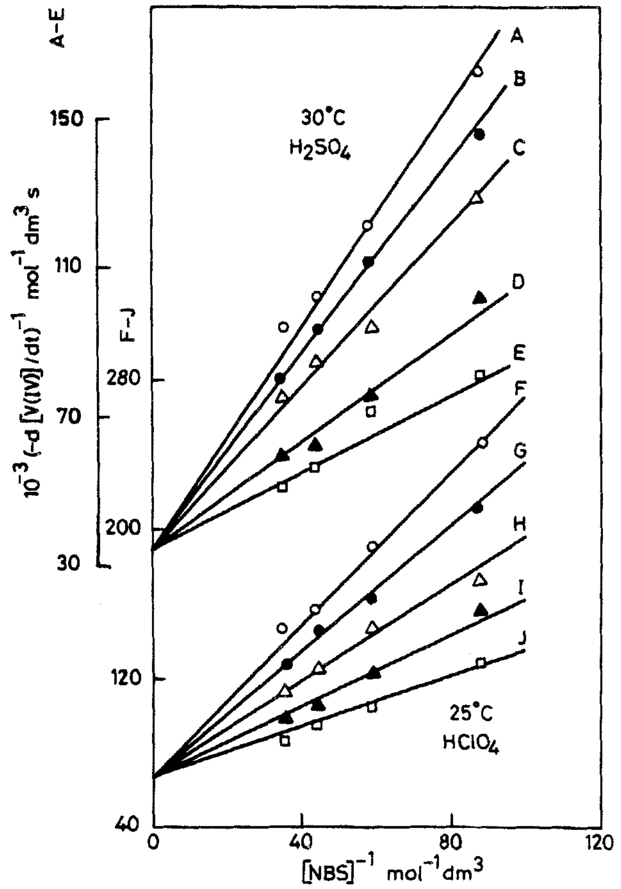

FIG. 2. Plots of $(-d[V(IV)]/dt)^{-1}$ vs $[NBS]^{-1}$. Lines (A)-(E): $[V(IV)] = 5.93 \times 10^{-3}$ M; $[H_2SO_4]$ = (A) 1.82 M, (B) 1.459 M, (C) 1.096 M, (D) 0.732 M, (E) 0.369 M; 30°C; ionic strength = 1.84 M. Lines (F)-(J): $[V(IV)] = 6.45 \times 10^{-3}$ M; $[HClO_4]$ = (F) 1.86 M, (G) 1.496 M, (H) 1.123 M, (I) 0.75 M, (J) 0.377 M; 25°C; ionic strength = 1.87 M.

can in turn be plotted versus $[H^+]$ (Fig. 3) and we can estimate K, $K_1$, and $k_r$. The collected data appear in Table 3. The values of the protonation equilibrium constant are the same in the two acid media. Complexation between reactants occurs with negative enthalpy and

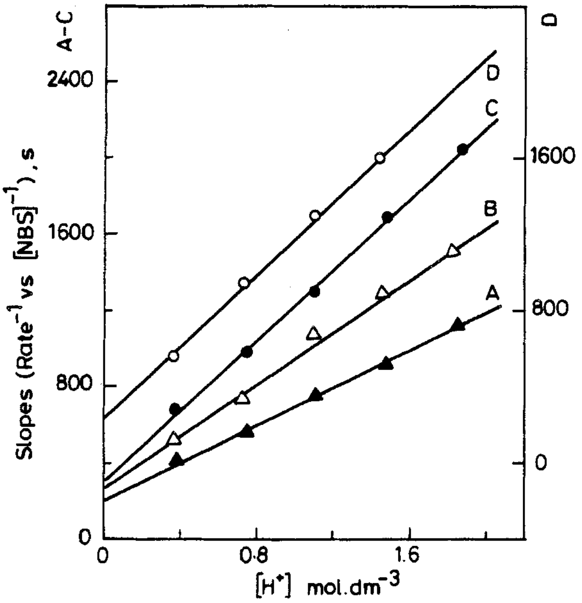

FIG. 3. Plots of slopes (rate$^{-1}$ vs [NBS]$^{-1}$) vs [H$^+$]. Lines (A) and (C): $HClO_4$ medium at 30 and 25°C, respectively. Lines (B) and (D): $H_2SO_4$ medium at 30 and 25°C, respectively.

TABLE 3. Mean Values of Rate and Thermodynamic Parameters for Oxidation

| Medium | Temperature (°K) | $10^3 k_r$ ($s^{-1}$) | $E_a$ (kJ/mol) | $K_1$ ($dm^3$/mol) | $\Delta H_1$ (kJ/mol) | $\Delta S_1$ (J/mol/deg) | K ($dm^3$/mol) |
|---|---|---|---|---|---|---|---|
| $HClO_4$ | 298 | 1.19 | 169.9 | 222.8 | -129.0 | -388.3 | 3.2 |
| | 303 | 3.69 | | 94.3 | | | 2.1 |
| $H_2SO_4$ | 298 | 1.33 | 91.7 | 295.3 | -114.7 | -337.6 | 3.8 |
| | 303 | 2.45 | | 137.6 | | | 2.8 |

entropy changes. The activation energy for the electron transfer process is larger in $HClO_4$, which could be due to the difference in the species of $VO^{2+}$ involved in Step (ii). The formation constants are larger in $H_2SO_4$ medium, again due to the nature of $VO^{2+}$ species involved. The coordination of NBS to the metal ion is most probably through the carbonyl group which is also the site of protonation.

Other mechanisms that may be envisaged are 1) a radical path for the breakdown of NBS followed by reaction of one or both the fragments with $VO^{2+}$, and 2) a heterolytic fission of NBS due to the high acidities employed, followed again by a reaction of one of the fragments with $VO^{2+}$.

However, since the rates of oxidation depend on [V(IV)] (Table 1), the breakdown of NBS cannot be the rate-determining step. The other alternative is a mechanism involving a rapid equilibrium such as

Mechanism I:

$$\mathrm{NBS} \rightleftharpoons \mathrm{R}^{\bullet} + \mathrm{Br}^{\bullet}$$

$$\mathrm{R}^{\bullet} + \mathrm{V(IV)} \xrightarrow{\text{slow}} \mathrm{R}^{-} + \mathrm{V(V)}$$

and/or

$$\mathrm{Br}^{\bullet} + \mathrm{V(IV)} \xrightarrow{\text{slow}} \mathrm{Br}^{-} + \mathrm{V(V)}$$

Mechanism II:

$$\mathrm{NBS} \rightleftharpoons \mathrm{R}^{-} + \mathrm{Br}^{+}$$

$$\mathrm{Br}^{+} + \mathrm{V(IV)} \xrightarrow{\text{slow}} \mathrm{Br}^{\bullet} + \mathrm{V(V)}$$

$$\mathrm{Br}^{\bullet} + \mathrm{V(IV)} \xrightarrow{\text{slow}} \mathrm{Br}^{-} + \mathrm{V(V)}$$

However, the decrease in rates with increasing $H^+$ would not result from either of these mechanisms. Also, homolysis of NBS requires temperatures much higher than those employed in this study [5]. Mechanism I would require an order in NBS equal to 1/2, while Mechanism II requires a first power dependence. However, what is observed is a variable order ranging from 1 to 0. A combination of Mechanisms I and II depending on the acidity of the medium might account for most of the data provided the rate and equilibrium constants of the heterolytic path are considerably lower than those associated with the corresponding steps in the homolytic mechanism. But as

TABLE 4. Percentage Conversion of Polymer with Time

| (a) Time (min) | (a) % Conversion | (b) Time (min) | (b) % Conversion |
|---|---|---|---|
| 1 | 1.4 | 5 | 11.4 |
| 3 | 13.6 | 10 | 21.6 |
| 5 | 18.1 | 15 | 26.8 |
| 7 | 33.5 | 20 | 30.2 |
| 10 | 40.2 | 25 | 33.3 |
| 15 | 51.7 | 30 | 37.4 |

(a) [V(III)] = $1.02 \times 10^{-2}$ mol dm$^{-3}$; [NBS] = $8.71 \times 10^{-3}$ mol dm$^{-3}$; [AN] = 1.02 mol dm$^{-3}$; [$H_2SO_4$] = 0.65 mol dm$^{-3}$; 30°C.

(b) [V(IV)] = $1.01 \times 10^{-2}$ mol dm$^{-3}$; [NBS] = $8.76 \times 10^{-3}$ mol dm$^{-3}$; [AN] = 1.02 mol dm$^{-3}$; [$H_2SO_4$] = 0.61 mol dm$^{-3}$; 30°C.

detailed earlier, a complexation equilibrium involving reactants, with $H^+$ functioning as a competitive inhibitor, seems most appropriate. This mechanism is also favored due to the lower temperatures empolyed. The kinetics of oxidation of vanadium(III) could not be investigated in isolation due to the concurrent oxidation of the V(IV) formed.

## POLYMERIZATION KINETICS

With both the redox systems V(IV)/NBS and V(III)/NBS, only acrylonitrile was polymerized in the temperature range 25 to 35°C. Polymerization kinetics using the V(IV)/NBS system were studied in both aqueous $HClO_4$ and $H_2SO_4$ media while the system V(III)/NBS was investigated in $H_2SO_4$ medium only. The system V(III)/NBS was more efficient than the system V(IV)/NBS as a redox initiator (Table 4). This can be ascribed to the less negative redox potential of the V(III)/V(IV) couple (-0.3 V versus SHE) compared to the V(IV)/V(V) couple (-1.0 V versus SHE). Both the redox systems exhibited similar kinetic features. Rates of polymerization varied as $[AN]^{3/2}$, $[NBS]^{1/2}$ (Fig. 4), and $[V^{n+}]^{1/2}$ (n = 3 or 4) (Fig. 5). Rates decreased with increasing acidity (Table 5). Thus a common mechanism would account for the results. The 3/2 order in [AN] can result from a reaction between monomer and the 1:1 complex between reactants, generating secondary radicals ($X^{\bullet}$) which are the sole initiators. In addition to Steps (i)-(iv) proposed for the oxidation we can include the following steps in the overall mechanism.

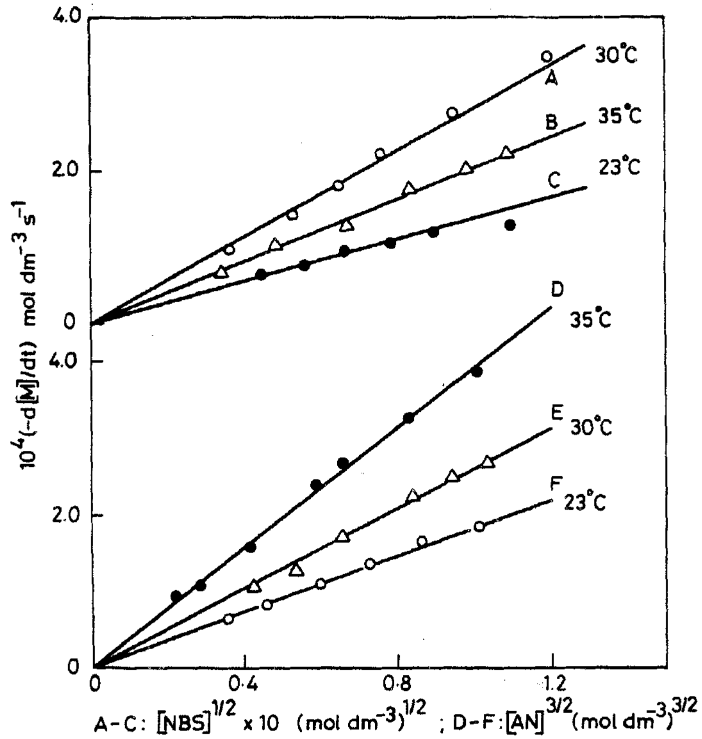

FIG. 4. Plots of -d[M]/dt vs [NBS]$^{1/2}$ and [AN]$^{3/2}$. [$HClO_4$] = 0.55 M (A, E); [$H_2SO_4$] = 0.567 M (B, D); and 0.085 M (C, F); $10^4$ [V(III)] = 8.02 M (C, F); $10^2$ [V(IV)] = 1.47 M (A), 1.03 M (B), 1.36 M (D), 1.18 M (E); $10^3$ [NBS] = 7.04 M (D), 6.85 M (E), 3.74 M (F).

$$\text{Complex} + \text{M} \xrightarrow{k_x} \text{X}^\bullet + \text{products} \qquad \text{(vii)}$$

$$\text{X}^\bullet + \text{M} \xrightarrow{k_i} \text{X–M}^\bullet \qquad \text{(viii)}$$

$$\text{X–M}^\bullet + \text{M} \xrightarrow{k_p} \text{X–M–M}^\bullet,\ \text{etc.} \qquad \text{(ix)}$$

$$\text{X–M}_n{}^\bullet + \text{X–M}_n{}^\bullet \xrightarrow{k_t} \text{polymer} \qquad \text{(x)}$$

With the primary radicals (R$^\bullet$) being effectively reduced by the metal

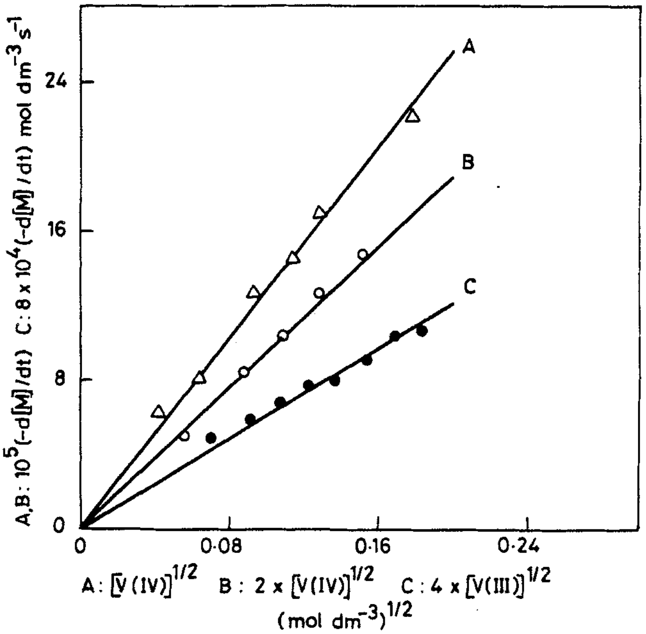

FIG. 5. Plots of -d[M]/dt vs $[V(IV)]^{1/2}$ and $[V(III)]^{1/2}$. Line (A): 35°C; $[H_2SO_4]$ = 0.567 M; [AN] = 0.634 M; [NBS] = $5.1 \times 10^{-3}$ M. Line (B): 30°C; $[HClO_4]$ = 0.55 M; [AN] = 0.855 M; [NBS] = $8.15 \times 10^{-3}$ M. Line (C): 23°C; $[H_2SO_4]$ = 0.085 M; [AN] = 0.608 M; [NBS] = $3.51 \times 10^{-3}$ M.

ion, and X' being much less reactive toward metal ion compared to monomer, we can derive the following rate law:

$$\frac{-d[M]}{dt} = \frac{k_p(k_x K_1[V^{n+}]_T^{1/2}[NBS]_T)^{1/2}[AN]^{3/2}}{(2k_t)^{1/2}(1 + K[H^+] + K_1[NBS]_T)^{1/2}}$$

At very large [NBS] the order in [NBS] should tend to zero. However, in the range of NBS employed, a strict half power dependence was observed. Also, in accordance with the above rate law, rates decreased with increasing $[H^+]$ (Table 5). These results offer an alternate explanation to that suggested by Banthia and Palit [4] involving coagulation. Increasing $[H^+]$ results in a decrease of the 1:1 complex whose interaction with monomer generates the initiating radicals, thus causing a decrease in the rate.

TABLE 5. Variation of $-d[M]/dt$ with $[H^+]$

| (a) $[H_2SO_4]$ mol dm$^{-3}$ | (a) Rate × $10^4$ mol dm$^{-3}$ s$^{-1}$ | (b) $[HClO_4]$ mol dm$^{-3}$ | (b) Rate × $10^4$ mol dm$^{-3}$ s$^{-1}$ | (c) $[H_2SO_4]$ mol dm$^{-3}$ | (c) Rate × $10^4$ mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|---|---|
| 0.039 | 5.44 | 0.068 | 1.99 | 0.152 | 1.54 |
| 0.108 | 4.43 | 0.187 | 1.84 | 0.261 | 1.43 |
| 0.175 | 4.16 | 0.306 | 1.76 | 0.402 | 1.37 |
| 0.312 | 3.49 | 0.483 | 1.68 | 0.531 | 1.31 |
| 0.583 | 3.21 | 0.721 | 1.51 | 0.702 | 1.24 |
| 0.855 | 3.01 | 0.958 | 1.36 | 0.981 | 1.16 |
| 1.127 | 2.81 | - | - | 1.201 | 1.09 |

(a) 23° C; $[V(III)] = 3.88 \times 10^{-3}$ mol dm$^{-3}$; $[NBS] = 5.32 \times 10^{-3}$ mol dm$^{-3}$; $[AN] = 1.02$ mol dm$^{-3}$.
(b) 30°C; $[V(IV)] = 1.22 \times 10^{-2}$ mol dm$^{-3}$; $[NBS] = 5.93 \times 10^{-3}$ mol dm$^{-3}$; $[AN] = 0.764$ mol dm$^{-3}$.
(c) 30° C; $[V(IV)] = 1.33 \times 10^{-2}$ mol dm$^{-3}$; $[NBS] = 7.51 \times 10^{-3}$ mol dm$^{-3}$; $[AN] = 0.634$ mol dm$^{-3}$.

TABLE 6. Mean Values of Rate and Thermodynamic Parameters for Polymerization

| Medium | Temperature (°K) | $10^5$ $k_x$ ($dm^3$ $mol^{-1}$ $s^{-1}$) | $E_a$ (kJ/mol) | $\Delta H^\ddagger$ (kJ/mol) | $\Delta S^\ddagger$ (J/deg/mol) |
|---|---|---|---|---|---|
| $HClO_4$ | 303 | 1.84 | 157.3 | 154.9 | 175.1 |
| | 308 | 5.07 | | | |
| $H_2SO_4$ | 303 | 1.37 | 96.8 | 94.2 | -27.2 |
| | 308 | 2.55 | | | |

In the case of the V(IV)/NBS system, from the data on oxidation (Table 3) and polymerization (Figs. 4 and 5), the values of $k_x$ can be estimated using the literature data [15] on the ratio $k_p/k_t^{1/2}$. The collected data appear in Table 6 together with thermodynamic parameters. The values of $k_x$ are larger in $HClO_4$ medium which is due to a difference in the $VO^{2+}$ species involved in complexation. The activation energy is also smaller in $H_2SO_4$ medium, and the reaction is associated with negative entropy of activation which suggests a crowded transition state for the reaction of monomer with the redox complex. The complete mechanism involving Steps (i)-(iv) and (vii)-(x) yields the following rate law for oxidation in the presence of monomer:

$$\frac{-d[V^{n+}]}{dt} = \frac{(2k_r + k_x[M])[V^{n+}]_T[NBS]_T}{1 + K[H^+] + K_1[NBS]_T}$$

The dependence of $-d[V^{n+}]/dt$ on [AN] could not be confirmed spectrophotometrically due to heterogeneous polymerization conditions.

In the absence of any significant termination by primary or secondary radicals and linear termination by metal ions, the average degrees of polymerization are given by

$$\overline{P}_n = \frac{k_p[M]^{1/2}\,(1 + K[H^+] + K_1[NBS]_T)^{1/2}}{(2k_tk_x)^{1/2}[V^{n+}]_T^{1/2}[NBS]_T^{1/2}}$$

TABLE 7. Variation of $\overline{P}_n$ with [AN], [NBS], [V(IV)], and [$H^+$]

| (a) [AN] mol $dm^{-3}$ | $\overline{P}_n$ | (b) $10^3$ [NBS] mol $dm^{-3}$ | $\overline{P}_n$ | (c) $10^2$ [V(IV)] mol $dm^{-3}$ | $\overline{P}_n$ | (d) 10 [$H^+$] mol $dm^{-3}$ | $\overline{P}_n$ |
|---|---|---|---|---|---|---|---|
| 0.506 | 1870 | 1.47 | 8447 | 0.43 | 5631 | 1.87 | 3573 |
| 0.608 | 3012 | 4.40 | 8155 | 0.86 | 5245 | 3.06 | 3921 |
| 0.709 | 3638 | 5.87 | 6111 | 2.15 | 4159 | 4.83 | 4470 |
| 0.810 | 5542 | 11.74 | 3856 | 2.58 | 3358 | 9.58 | 5720 |
| 0.912 | 6555 | - | - | 3.44 | 2189 | - | - |

(a) 29°C; [V(III)] = $1.05 \times 10^{-3}$ mol $dm^{-3}$; [NBS] = $3.0 \times 10^{-3}$ mol $dm^{-3}$; [$H_2SO_4$] = 0.085 mol $dm^{-3}$.

(b) 30°C; [V(IV)] = $1.47 \times 10^{-2}$ mol $dm^{-3}$; [AN] = 0.855 mol $dm^{-3}$; [$HClO_4$] = 0.55 mol $dm^{-3}$.

(c) 35°C; [NBS] = $5.1 \times 10^{-3}$ mol $dm^{-3}$; [AN] = 0.634 mol $dm^{-3}$; [$H_2SO_4$] = 0.567 mol $dm^{-3}$.

(d) 30°C; [V(IV)] = $1.22 \times 10^{-2}$ mol $dm^{-3}$; [NBS] = $5.93 \times 10^{-3}$ mol $dm^{-3}$; [AN] = 0.761 mol $dm^{-3}$.

Data in Table 7 support the above expression. $\overline{P}_n$ decreased with increasing $[V^{n+}]_T$ and $[NBS]_T$ and increased with increasing [AN] and $[H^+]$.

## ACKNOWLEDGMENT

Financial assistance by C.S.I.R., New Delhi, is gratefully acknowledged.

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Accepted by editor August 20, 1982
Received for publication September 14, 1982