Redox Polymerization of Acrylonitrile: Kinetics of the Reaction Initiated by the Redox System 1-Propanol—Chromic Acid

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ABSTRACT

The kinetics of the aqueous polymerization of acrylonitrile initiated by the chromic acid–1-propanol redox system was investigated under a nitrogen atmosphere. The rates of polymerization and the disappearance of Cr(VI) were measured. Chromic acid alone did not initiate the polymerization under deaerated and undeaerated conditions. Water-miscible organic solvents and neutral salts depress both the rate and the conversion. On the basis of the experimental observations of the dependence of the rate of polymerization R_p and the rate of disappearance of Cr(VI)-R_m on various variables, a suitable kinetic scheme was proposed and various rate and energy parameters evaluated.

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*Dedicated to Prof. M. Santappa, FNA.

INTRODUCTION

Certain transition metals in their higher valence states coupled with easily reducible organic substrates act as potential initiators [1-9] for the redox polymerization of vinyl monomers. In this laboratory, we have earlier reported [10-13] the various initiating systems involving quinquevalent vanadium ion coupled with several organic substrates. Chromic acid has been used for the oxidation of large number of organic substrates [14] and the mechanisms for such steps have been lucidly explained by various authors in the past three decades. The use of chromic acid redox systems for initiating vinyl polymerization has not been well explored. Kolthoff and Meehan [15] have reported the emulsion copolymerization of styrene and butadiene in presence of chromic acid. In this present communication, we report a detailed study on the aqueous polymerization of acrylonitrile initiated by the chromic acid–1-propanol reducing agent system. From the experimental observations, a suitable reaction scheme has been suggested, and the kinetic parameters were evaluated.

EXPERIMENTAL

Acrylonitrile (American Cyanamid Co.) was washed with 5% NaOH, dilute H_3PO_4, and finally with water and dried over anhydrous $CaCl_2$. Chromic acid solutions were prepared by dissolving chromium trioxide (BDH, AR) in distilled water. Perchloric acid (E. Merck, G. R. 60%), 1-propanol (AR), propane-1,2-diol, cyclopentanol (AR), cyclohexanol (AR), cycloheptanol (AR), sodium perchlorate (Riedel), and sulfuric acid ($\sim$ 18 $\underline{M}$; AR Basynth, India) were used. Water distilled over alkaline permanganate and deionized by passing through a column of Biodeminrolit resin (Permutit Co., U. K.) was used to prepare all solutions. Nitrogen used for deaeration of the experimental system was purified by passing through several columns of Fieser's solution, a column of saturated lead acetate solution, and finally a wash bottle containing distilled water. Cr(VI) was estimated either by titrimetry (for Cr(VI) $> 5 \times 10^{-4}$ mole/liter) or spectrophotometry (for Cr(VI) $< 5 \times 10^{-5}$ mole/liter).

For oxidation experiments, a three-necked glass vessel fitted with ground glass joints was used. The reaction was stopped by addition of excess ferrous ammonium sulfate solution; the unreacted ferrous was estimated by cerimetry. For polymerization experiments, a Pyrex glass tube (100 ml) fitted with B_{24} ground joint head, through

which two glass tubes were fused, was used. The reaction mixture, containing the reducing agent, the monomer, and the acid was de-aerated for 20-30 min. The reaction was carried out for 30 min, after which it was stopped by addition of an excess Fe(II) solution; the precipitated polymer was filtered, washed repeatedly with water, and dried to a constant weight at 60°C in a vacuum oven. The rate of polymerization was calculated from the weight of polymer obtained. From the filtrate, the change in [Cr(VI)] was followed by estimating the unreacted [Fe(II)] either by titration against standard Ce(IV) solution or spectrophotometry after addition of o-phenanthroline and measuring the optical density of ferrous-o-phenanthroline complex at λ = 510 nm and reference to a previously calibrated plot of optical density vs [Fe(II)]. From the changes in [Cr(VI)], the rate of Cr(VI) disappearance, $-R_m$, was computed.

The molecular weights $\overline{M}_w$ of the purified polymers were determined by viscometry by using the appropriate Mark-Houwink relationship. The viscosities of polymer solutions (0.1%) were determined in an Ubbelohde-type suspended-level dilution viscometer in DMF at 30°C by using the relationship [16]:

$$[\eta] = 3.335 \times 10^{-4} \, \overline{M}_w^{0.72}$$

RESULTS AND DISCUSSION

The polymerization of acrylonitrile was carried out in aqueous solutions at 40, 45, and 50°C in perchloric acid, sulfuric acid, and nitric acid in presence of the redox system; chromic acid–1-propanol. A typical set of time-conversion curves for 40°C at various 1-propanol (PR) concentrations (0.136-0.408 $\underline{M}$) and at constant [Cr(VI)] (5.6515 × 10^{-3} $\underline{M}$) are shown in Fig. 1. Acrylonitrile was also polymerized under identical conditions as mentioned above in the presence of other alcohols like 1-propanol, 1,2-propanediol, 1,4-butanediol, cyclopentanol, cyclohexanol, and cycloheptanol. The results are recorded in Table 1, which shows that under identical conditions, the order of reactivity of alcohols is: 1-propanol > 1,2-propanediol > cycloheptanol > cyclohexanol > 1,4-butanediol > cyclopentanol.

Rate of Polymerization R_p

The rate of polymerization R_p increased with an increase in the monomer concentration (0.6032-1.2064 $\underline{M}$). The fact that the plots of
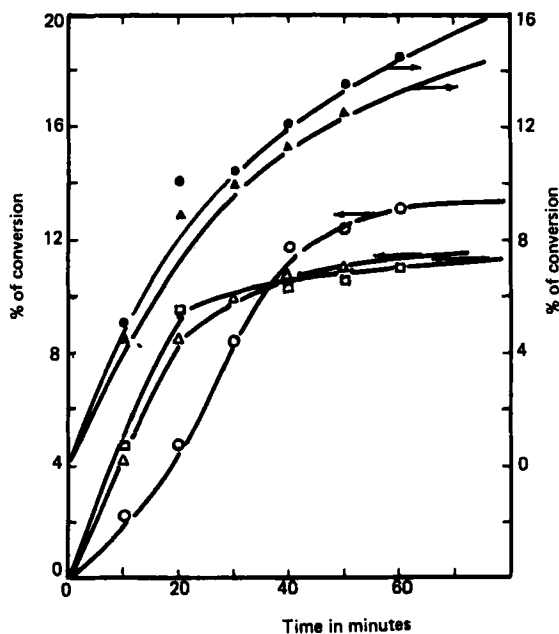
FIG. 1. Variation of rate with time (in perchloric acid): (a) at
$40°C$, ($\circ$) [PR] = 0.136 M, ($\square$) [PR] = 0.272 M, ($\triangle$) [PR] = 0.408
M, (b) at [PR] = 0.272 M, ($\bullet$) $45°C$ ($\blacktriangle$) $50°C$. [Cr(VI)] = 5.6515
$\times 10^{-3}$ M; [H$^+$] = 0.7692 M; μ = 0.8 M; [AN] = 0.7539 M.

$\log R_p$ versus $\log$ [AN] gave slopes varying from 1.2 to 1.6 (Fig. 2)
and that the rate decreased with the increase in [Cr(VI)] indicated
the termination to be of a linear type. The terminating species might
be either Cr(VI) or Cr(IV), but the latter, on the basis of interaction
of two unstable species of low concentration of Cr(IV) + M· (the
monomer radical), seemed very unlikely. The plots of $[AN]^2/R_p$
versus [AN] were found to be linear (Fig. 2).

Rate Dependence on Activator Concentration

The initial rate of polymerization and limiting conversion were
found to increase with an increase of activator concentration (Fig. 1).

TABLE 1. Polymerization of Acrylonitrile by Various Cr(VI)–Alcohol Systems at 40° C[a]

Alcohol	Alcohol concn (mole/liter)	Induction period (min)	Initial rate, $R_p \times 10^5$ (mole/liter-sec)
1-Propanol	0.1366	1	3.50
1,2-Propanediol	0.1366	2	2.80
Cycloheptanol	0.1366	5	1.48
Cyclohexanol	0.1366	2.5	1.39
1,4-Butanediol	0.1366	2	1.37
Cyclopentanol	0.1366	8	0.591

[a]Reaction conditions: $[Cr(VI)]$ = 0.00539 mole/liter; $[HClO_4]$ = 0.7051 mole/liter; $[AN]$ = 0.7539 mole/liter; μ = 2 mole/liter.

This might be due to an increase in the rate of generation of the primary radicals which initiate polymerization. An enhancement in the rate of polymerization would, therefore, be expected at higher concentrations of 1-propanol (PR). However, at higher concentrations of PR, the initial rate as well as the limiting conversion decreases. This might be due to the accompanying changes in polarity of the system. Similar observations were noted by Misra and co-workers [17] and Palit and co-workers [18-20] for permanganate–oxalic acid redox systems.

The rate of polymerization increased linearly with [n-propanol], the plot of R_p versus [PR] is linear (Fig. 5). Further, the plot of log R_p versus log [PR] is linear with unit slopes indicating the dependence of R_p on the first power of [PR] (Fig. 3). This may be understood in terms of linear termination by Cr(VI).

A similar explanation has been advanced by Katai and co-workers [21] for Ce(IV)-initiated polymerization.

The additional evidence for a linear termination was that R_p varied inversely with $[Cr(VI)]$, the plots of $1/R_p$ versus $[Cr(VI)]$ being linear (Fig. 4).
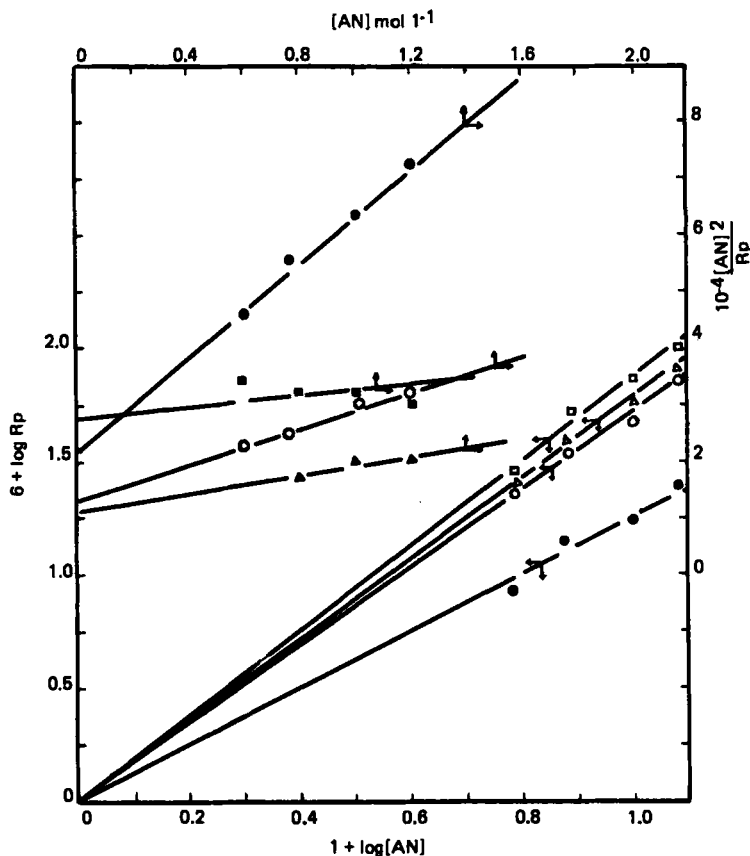
FIG. 2. Variation of rate with monomer. (a) Plot of $(1 + \log [AN])$ vs. $(6 + \log R_p)$ at different temperatures: ($\circ$) 40° C, ($\square$) 45° C, ($\triangle$) 50° C; $[H^+] = 0.641 \underline{M}$, $[Cr(VI)] = 5.6515 \times 10^{-3} \underline{M}$, $\mu = 0.8 \underline{M}$, $[PR] = 0.136 \underline{M}$. (b) Plot of $(1 + \log [AN])$ vs. $(6 + \log R_p)$ at ($\bullet$) $[Cr(VI)] = 4.617 \times 10^{-3} \underline{M}$; $[H^+] = 0.641 \underline{M}$, $\mu = 0.799 \underline{M}$, $[PR] = 0.04197 \underline{M}$, 40° C. (c) Plot of $[AN]^2 / R_p$ vs. $[AN]$ at various temperatures: ($\circ$) 40° C, ($\blacksquare$) 45° C, ($\triangle$) 50° C; $[H^+] = 0.641 \underline{M}$, $[Cr(VI)] = 5.6515 \times 10^3 \underline{M}$, $\mu = 0.8 \underline{M}$, $[PR] = 0.136 \underline{M}$. (d) Plot of $[AN]^2 / R_p$ vs. $[AN]$ at ($\bullet$) $[Cr(VI)] = 4.617 \times 10^{-3} \underline{M}$, $[H^+] = 0.641 \underline{M}$, $\mu = 0.799 \underline{M}$, $[PR] = 0.04197 \underline{M}$, 40° C.
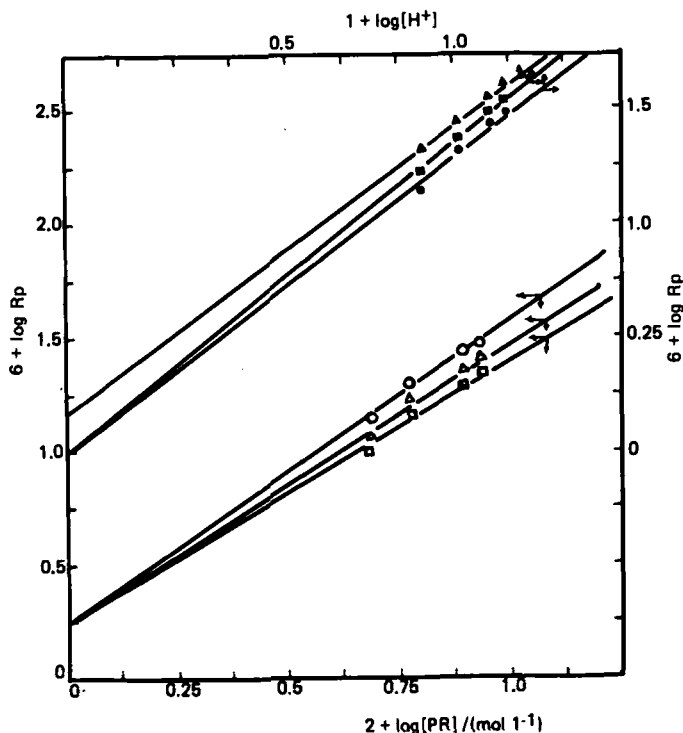
FIG. 3. (a) Variation of rate with substrate at different $[Cr(VI)]$, as plots of $(2 + \log [PR])$ vs. $(6 + \log R_p)$ (lower curves): ($\circ$) $[Cr(VI)]$ $= 5.6515 \times 10^{-3}$ $\underline{M}$, ($\square$) $[Cr(VI)] = 4.617 \times 10^{-3}$ $\underline{M}$, ($\triangle$) $[Cr(VI)]$ $= 0.65195 \times 10^{-3}$ $\underline{M}$; $[H^+] = 0.7052$ $\underline{M}$, $\mu = 0.8$ $\underline{M}$, $[AN] = 0.7539$ $\underline{M}$, $45°$ C. (b) Variation of rate with acid at different temperatures, as plots of $(1 + \log [H^+])$ vs. $(6 + \log R_p)$: ($\bullet$) $40°$ C, ($\blacktriangle$) $45°$ C, ($\blacksquare$) $50°$ C; $[Cr(VI)] = 5.15 \times 10^{-3}$ $\underline{M}$, $[PR] = 0.0612$ $\underline{M}$, $[AN] = 0.7539$ $\underline{M}$.

Variation of Rate with $[H^+]$

The initial rate of polymerization and the limiting conversion (Fig. 5) increases with increase of perchloric acid and sulfuric acid concentration. The plots of R_p versus $[H^+]$ as well as $\log R_p$ versus $\log [H^+]$ were linear (Figs. 3 and 5). R_p values were highest in
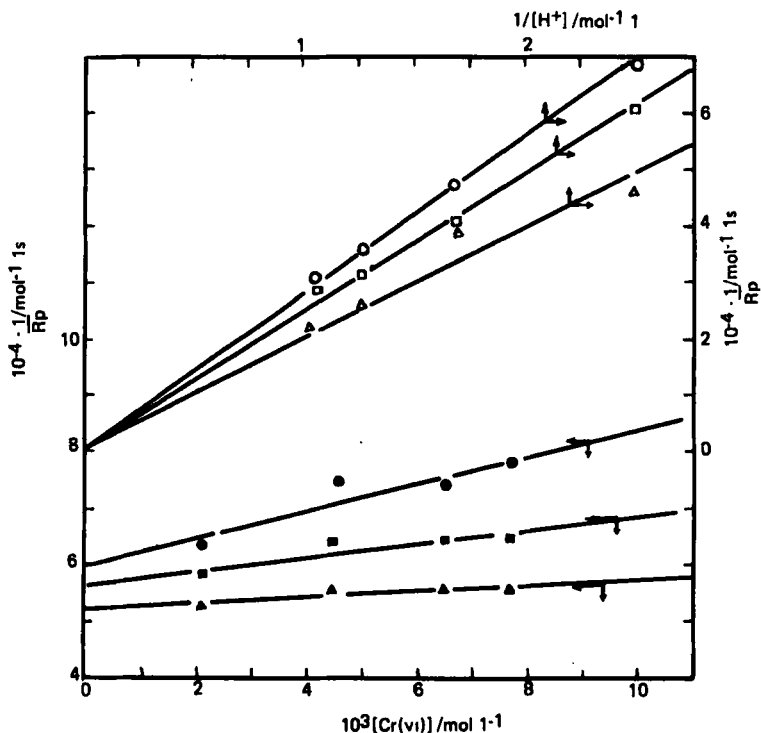
FIG. 4. (a) Variation of rate with [Cr(VI)] at different tempera-
tures, as plots of $1/R_p$ vs. [Cr(VI)]: (•) 40° C, (▲) 45° C, (■) 50°C;
[H$^+$] = 0.7052 $\underline{M}$, μ = 0.8 $\underline{M}$, [AN] = 0.7539 $\underline{M}$, [PR] = 0.0612 $\underline{M}$. (b)
Variation of rate with acid at different temperatures, as plots of
$1/R_p$ vs. $1/[H^+]$: (○) 40° C, (□) 45° C, (△) 50 °C; [Cr(VI)] = 5.15
× 10^{-3} $\underline{M}$, [PR] = 0.0612 $\underline{M}$, [AN] = 0.7539 $\underline{M}$.

HClO$_4$ medium and decreased in the order HClO$_4$ > H$_2$SO$_4$ > HNO$_3$.
The acid anions probably complex with monochromate ion, reducing
the oxidizing power of the latter, as pointed out by Stewart and Lee
[22] for the variation of oxidation rates of isopropyl alcohol.

Variation of Rate with Cr(VI)

The plots of $1/R_p$ versus [Cr(VI)] were linear (Fig. 4). This is
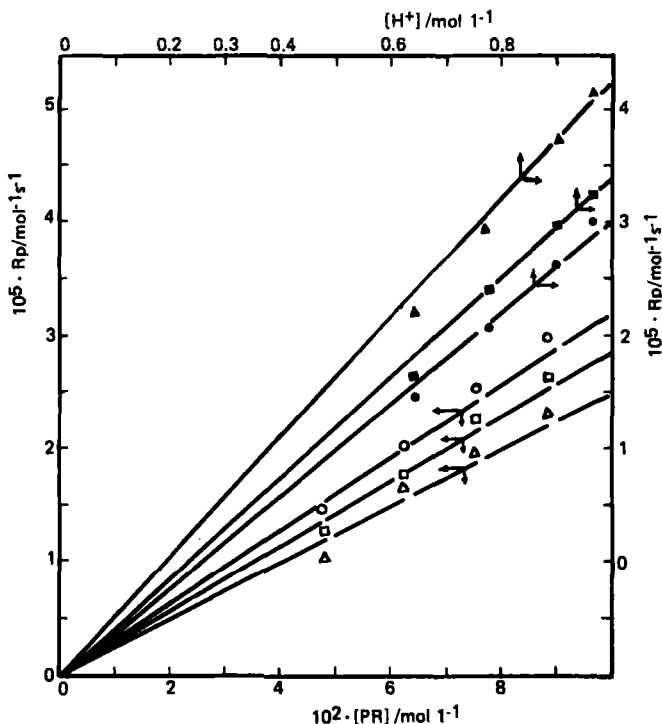additional evidence for linear termination.

FIG. 5. (a) Variation of rate with substrate, as plots of $[PR]$ vs. R_p: ($\circ$) $[Cr(VI)]$ = 5.6515×10^{-3} $\underline{M}$, ($\square$) $[Cr(VI)]$ = 6.5195×10^{-3} $\underline{M}$, ($\triangle$) $[Cr(VI)]$ = 4.617×10^{-3} $\underline{M}$; $[H^+]$ = 0.7052 $\underline{M}$, μ = 0.8 $\underline{M}$, $[AN]$ = 0.7539 $\underline{M}$, $45°C$. (b) Variation of rate with acid at different temperatures, as plots of $[H^+]$ vs. R_p: ($\bullet$) $40°C$, ($\blacktriangle$) $45°C$, ($\blacksquare$) $50°C$. $[Cr(VI)]$ = 5.15×10^{-3} $\underline{M}$, $[AN]$ = 0.7539 $\underline{M}$, $[PR]$ = 0.0612 $\underline{M}$.

Effect of Organic Solvents

The introduction of water-miscible organic solvents like methanol, acetone, or dioxane, tends to depress the initial rate as well as the limiting conversion (Fig. 6). Similar observations have also been made by several other workers [18, 19]. This behavior can be interpreted by assuming that the water-miscible organic solvents can perform three functions: (a) decrease the area of shielding of a strong hydration layer in an aqueous medium, resulting in the termination of the growing chain, (b) increase of the regulated rate of production of primary radicals, which renders the termination rate
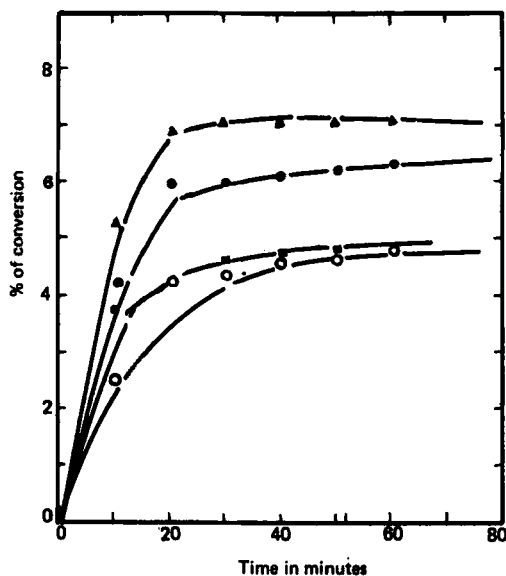
FIG. 6. Variation of rate with time (effect of water-soluble sub-
stance), as plots of time vs. % conversion: (▲) 5% acetone, (●) 5%
dioxane, (■) 5% methyl alcohol, (○) 5% acetic acid; [Cr(VI)]
= 5.6515×10^{-3} $\underline{M}$, [H^+] = 0.7692 $\underline{M}$, μ = 0.8 $\underline{M}$, [AN] = 0.7539 $\underline{M}$,
[PR] = 0.272 $\underline{M}$, 45° C.

relatively fast compared to the growing rate, in accordance with the
view of Kern and co-workers [23]; (c) decrease the rigidity of the
interchain hydrogen bonding interlocking the polymer chain, thereby
increasing the tendency of mutual termination of polymer chain.

From all these facts, a decrease in degree and rate of polymeri-
zation is expected with the addition of water-miscible organic
solvents; whatever the reason may be, it appears that organic
solvents cause the formation of low molecular weight polymers.

Effect of Inorganic Salts

The addition of a neutral salt such as Na_2SO_4 reduces both the
initial rate of polymerization and the maximum conversion to a con-
siderable extent. This might be due to the ionic dissociation of the

added electrolyte, which interferes with the usual polymerization reaction, resulting in the premature termination of the growing polymer chains.

Introduction of manganous sulfate in small amounts into the polymerization system brings about an increase, both in the rate and the limiting conversion. This can be explained by considering the fact that the disproportionation reaction occurs between Cr(VI) and Mn(II), producing the highly reactive Mn^{3+} ions in the system at a rapid rate. A similar argument has been advanced by us [24] in the chromic acid oxidation of aromatic ketones. The trivalent manganese ions thus formed react rapidly with the organic substrate (n-propanol) in solution, producing free radicals which most probably propagate the polymerization reaction at a comparatively faster rate. Misra and co-workers [18] put forward similar observations for permanganate-tartaric acid redox systems.

R_p remained unaffected by initially added Cr(III) at constant ionic strength μ, which excluded equilibria of the type [25]

$$Cr(III) + Cr(V) \rightleftharpoons 2\ Cr(IV)$$

The addition of even small amounts of cerous perchlorate decreased R_p. The retardation of rate of oxidation of substrates by Cr(VI) in the presence of cerous salts noticed by many workers [26] was attributed to the removal of reactive intermediate chromium species.

An increase in the ionic strength of the medium at constant $[H^+]$ increased R_p (Fig. 7), in keeping with the observations with other metal ions. The increase in R_p may be due either to a salt effect in the propagation step or an increase in the rate of oxidation with μ.

Rate of Disappearance of Chromium (VI) - R_m

The rate of disappearance of Cr(VI) was dependent on the first power of $[Cr(VI)]$. The pseudo first-order rate constant k_{obs}, remained almost constant for a wide range of $[Cr(VI)]$. Further, $-R_m$ was found to be independent of monomer concentration, indicating that Cr(VI) was not directly involved in the initiation. This is very much similar to the observation of Rocek et al. [27, 28] that when cyclobutanol was present in the oxidation of V(V) by Cr(VI),
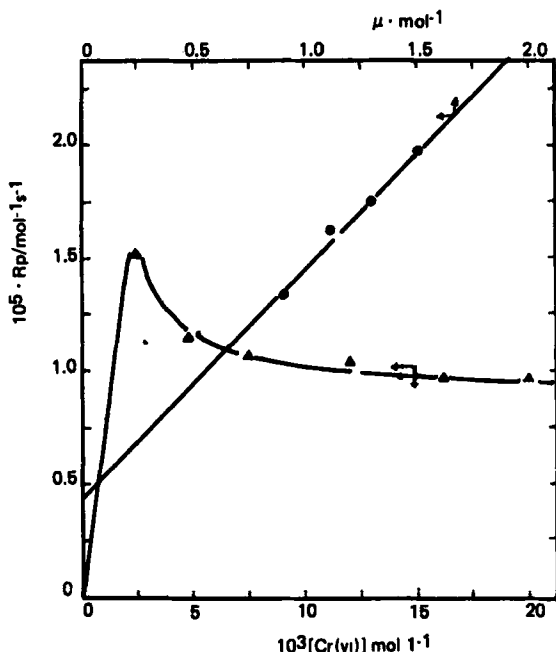
FIG. 7. Variation of rate with (•) ionic strength as plot of R_p vs. μ at $[Cr(VI)] = 6.5195 \times 10^{-3}$ $\underline{M}$, $[H^+] = 0.7052$ $\underline{M}$; (▲) effect on rate of initially added chromous chloride, as plot of R_p vs. $[Cr(III)]$, at $[Cr(VI)] = 5.775 \times 10^{-3}$ $\underline{M}$, $[H^+] = 0.7692$ $\underline{M}$. For both curves: $[AN] = 0.7539$ $\underline{M}$, $[PR] = 0.0612$ $\underline{M}$, 40° C.

$-R_m$ was unaffected, despite extensive oxidation of cyclobutanol. The value of k_{obs} decreased with added Cl^-. Such an inhibition in rate observed in the oxidation of alcohols and phosphoric acid was attributed to the participation of the weaker oxidant, CrO_3Cl^- in oxidations [14].

REACTION MECHANISM AND RATE LAW

Chromic acid alone was found to be not effective as initiator of the vinyl polymerization. Preliminary experiments carried out with chromic acid and acrylonitrile in perchloric acid medium under
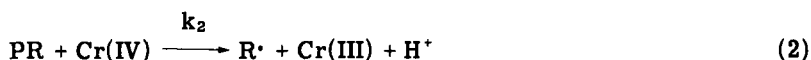
deaerated conditions showed that no polymerization took place and there was no decrease in $[Cr(VI)]$.

Of various possible reaction schemes examined, that involving initiation by $Cr(VI)$ or $R^{\cdot}$ and termination by $Cr(VI)$ satisfied the experimental results. The active oxidizing agent is the acid chromate ion, $HCrO_4^{-}$.

Reaction of acid chromate ion with the reducing agent PR:

$$HCrO_4^{-} + PR + H^{+} \xrightarrow{k_1} Cr(IV) + products \tag{1}$$
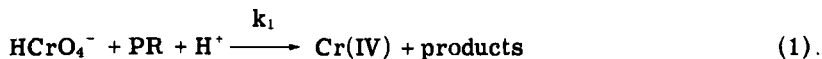
Reaction of tetravalent chromium with PR:

$$PR + Cr(IV) \xrightarrow{k_2} R^{\cdot} + Cr(III) + H^{+} \tag{2}$$

Reaction of the primary radical $R^{\cdot}$ with $Cr(VI)$:

$$R^{\cdot} + Cr(VI) \xrightarrow{k_3} Cr(V) + product \tag{3}$$

Reaction of $Cr(V)$ to $Cr(III)$ by reacting with PR:

$$PR + Cr(V) \longrightarrow products + Cr(III) \tag{4}$$

Initiation of polymerization by reaction of a primary radical with monomer:

$$R^{\cdot} + M \xrightarrow{k_i} M^{\cdot} \tag{5}$$

Initiation of the polymerization by reaction of $Cr(IV)$ with the monomer:

$$Cr(IV) + M \xrightarrow{k_i'} M^{\cdot} + Cr(III) + H^{+} \tag{6}$$

Propagation:

$$M^{\cdot} + M \xrightarrow{k_p} M_2^{\cdot}$$
$$\vdots$$
$$M^{\cdot}_{n-1} + M \xrightarrow{k_p} M_n^{\cdot} \tag{7}$$
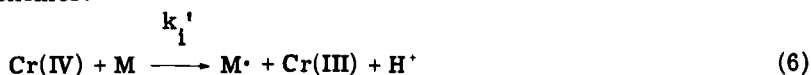
Termination of the polymerization:

$$M_n^{\cdot} + Cr(VI) \xrightarrow{\ k_t\ } M_n + Cr(V) + H^+ \tag{8}$$
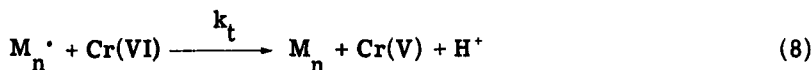
By considering Eq. (5) for the initiation and making the usual steady-state assumptions for the free radicals and unstable intermediates, we have:

$$R_p = \frac{k_p k_1 k_i [AN]^2 [PR][H^+]}{k_t \{ k_3 [Cr(VI)] + k_i [AN] \}} \tag{9}$$

which rearranges to:

$$\frac{[AN]^2}{R_p} = \frac{k_t k_3 [Cr(VI)]}{k_p k_1 k_i [PR][H^+]} + \frac{k_t [AN]}{k_p k_1 [PR][H^+]} \tag{10}$$

Then

$$-R_m = 2k_1 [Cr(VI)][PR][H^+] \tag{11}$$

The chain length is given by

$$n_i = k_p [AN] / k_t [Cr(VI)] \tag{12}$$

The facts that Cr(VI) alone neither oxidized nor polymerized AN discounted the reaction between Cr(VI) and monomer as the radical-producing step. Initiation of polymerization of AN by the system Cr(VI) + PR in acid media and reduction of Cr(VI) suggested that the possible radical production steps might be Cr(VI) + PR or Cr(V) + PR or Cr(IV) + PR. On the basis of the reasonable assumption that Cr(VI) is a two-electron oxidant, step (1) of the kinetic scheme

is predominant, the reaction Cr(IV) + PR rather than Cr(V) + R [Eq. (4) in the kinetic scheme] appears as a plausible radical production step. Another possible reaction for radical production might be between Cr(VI) and the product in Eq. (1) of the kinetic scheme. Mosher and Driscoll [29] have predicted the polymerization of AN in the Cr(VI) oxidation of phenyl tert-butyl alcohol was due to the production of radicals from the reaction between Cr(IV) and the product. But under the present experimental conditions with large [PR], it is likely that the reaction Cr(IV) + product might be discounted. Another possible radical production reaction is Cr(IV) + M [Eq. (6) in the kinetic scheme]. If reaction (6) in preference to reaction (5) were to take place, the expressions (9)-(11) would be identical, except for the replacement of k_i by k_i' in Eqs. (9) and (10). In the presence of an

organic substrate, the reaction between Cr(IV) and PR would take place in preference to that between Cr(IV) and monomer, and hence Eq. (6) could be neglected. Hence the species responsible for the radical production might be Cr(IV) and not Cr(V). The recent work of Rocek et al. [27, 28] also showed that Cr(IV) and not Cr(V) oxidized cyclobutanol.

Evaluation of the Rate Constants

The values of k_1 in the presence of the monomer and in its absence, were obtained from the plots of k_{obs} versus [PR] (where k_{obs} is the pseudo first-order rate constant). The composite rate constants k_{t2}/k_p and k_3/k_i (Table 2) for the system were obtained from the slopes and intercepts, respectively; of plots of $[AN]^2/R_p$ versus [AN] (Fig. 2).

Activation Parameters

The values of k_1, k_t/k_p, and k_3/k_i at 45 and 50° C were utilized in the computation of the activation parameters by plotting them against 1/T. The values of E_1, $(E_t - E_p)$, and $(E_3 - E_i)$ were computed to be 13.40 and 26.70, and 25.80 kcal/mole, respectively. Further, the value of E_p for acrylonitrile in water has been reported by Dainton et al. [30] to be 4.1 kcal/mole. For this value for E_p, E_t

TABLE 2. Values of the Rate Parameters in the Polymerization of
Acrylonitrile (AN) Initiated by the System Cr(VI)–1-Propanol

Temp ($^\circ$C)	$k_1 \times 10^3$ (mole^{-1}-sec^{-1})[a]	$k_t/k_p \times 10^{-1}$[b]	$(k_3/k_1) \times 10^3$	
			From [AN]^2/R$_p$ vs. [AN]	From 1/R$_p$ vs. [Cr(VI)]
40	17.38	0.5754	—	
45	23.90	1.29	4.92	4.86
50	33.11	2.77	6.21	6.19

[a]From oxidation.
[b]From plots of [AN]^2/R$_p$ vs. [AN].

is calculated to be 30.80 kcal/mole. The corresponding entropies of
activation for k_1, (k_t/k_p), and (k_3/k_1), were computed to be -27.10,
+28.10, and +9.40 cal/$^\circ$K-mole, respectively.

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