

VINYL POLYMERIZATION

III. Polymerization of Acrylamide Initiated by Cobaltic Ions in Aqueous Solution

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ABSTRACT

Polymerization of Acrylamide initiated by cobaltic ions in aqueous solution at 15° C. and 20° C. in HClO_4 and H_2SO_4 media have been studied. Kinetics have been followed by determining the rate of cobaltic ion disappearance as well as monomer disappearance with variations in cobaltic, monomer and hydrogen ion concentrations, temperature, ionic strength, etc. Besides polymer reaction it has been observed that side reactions like water oxidation and monomer oxidation also contribute to rate of cobaltic ion disappearance. Certain anomalous results in H_2SO_4 medium have been observed. A reaction scheme involving CoOH^{2+} and Co^{3+} as initiators in HClO_4 and H_2SO_4 media respectively and mixed termination—mutual and linear—has been suggested. Certain rate parameters involving rate constants for initiation, propagation, termination and the corresponding activation energies have been evaluated.

INTRODUCTION

STUDIES on the kinetics of polymerization of acrylamide (A.Am.) especially in aqueous solution have been few even though the soluble nature of polyacrylamide in water offers decided advantages for such studies. Dainton and co-workers^{1, 2} as well as Toppet and co-workers³ and others⁴ have reported polymerization of A.Am. photo-initiated by Fe^{3+} OH^- , H_2O_2 , eosin, riboflavin, etc., in aqueous solution. X- and γ -ray-initiated polymerizations^{5, 6} of the monomer in aqueous solution have been reported. Red-ox systems, chlorate-sulfite;⁷ persulfate-metabisulfite;⁸ ceric nitrate-3 chloro-1-propanol,^{9a} etc., have also been employed as initiators in the thermal polymerization of the monomer. Mino, Kaizermann and Rasmussen^{9a} have pointed out the efficacy of ceric ion-reducing agent system for initiation and have suggested^{9b} the unique preference of polyacrylamide radicals to react with carbon radicals. Waters and co-workers^{9c} have utilised this interesting

property of polyacrylamide radicals to arrive at conclusions with regard to precursor species in the oxidation of alcohols by cobaltic ions. We have studied thermal polymerization of A.Am. in aqueous perchloric and sulfuric acid solutions initiated by cobaltic ions in the temperature range 15–20° C. Experimental results together with discussion with regard to nature of initiation and termination for the polymerization reactions; oxidations of water and monomer as side reactions, etc., are presented in the following sections.

EXPERIMENTAL

Reagents.—Acrylamide (American cyanamid product) recrystallised from A.R. chloroform has been used. Acids—perchloric and sulfuric—are reagent, grade type from Baker and Adamson or E. Merck or Basynth Chemicals (Calcutta). The bisulfate, bicarbonate and the iodide of potassium are A.R. type.

Preparations.—Double distilled and deionized (with Bioderminolit-mixed bed ion exchange resin) water has been used for preparing the solutions, etc. Sodium perchlorate used for adjustment of ionic strength has been prepared by neutralization of A.R. sodium carbonate with A.R. perchloric acid. Cobaltous perchlorate has been prepared by fuming A.R. cobaltous nitrate with A.R. HClO_4 and crystallizing the former from acid solution. Cobaltic perchlorate¹⁰ has been prepared by the anodic oxidation of ~0.1 M cobaltous perchlorate in 5–6 M HClO_4 at 0° C. and stored at –10° C. Cobaltic sulfate prepared^{11, 12} in a solid form by anodic oxidation of saturated solution of cobaltous sulfate—(T.T. English) in 10.0 N sulfuric acid is dissolved in 4–6 N sulfuric acid precooled to –10° C. and stored at the latter temperature. All the cobaltic solutions have been prepared and used immediately.

Estimations.—Total cobalt content has been estimated by the method of Latinen and Burdett.¹³ Co^{3+} has been estimated by running aliquots of Co^{3+} stock solution into known excess of standard Fe^{2+} and backtitrating the unreacted latter with Ce^{4+} either by potentiometry or by titrimetry with Ferroin as the indicator. The acid content of cobaltic stock solution has been determined by warming an aliquot and titrating with standard alkali using Bromocresol green as indicator, allowance being made for the acid generated during the decomposition reaction



The monomer concentration, [M], has been estimated by the usual bromometric method.

Polymerization.—Polymerization has been conducted in a pyrex test-tube (8" long, 1.5" diameter) fitted with B-24 socket and cone; inlet and outlet tubes being fused to the latter for deaeration. A solution containing monomer, free acid and the appropriate sodium salt is taken in this test-tube and thoroughly deaerated by flushing with oxygen-free nitrogen for about one half hour. Cobaltic stock solution is then added and the outlet tube is then closed with a rubber gasket. The reaction is run for about 20-30 minutes in a thermostat. The reaction is quenched by addition of excess Fe^{2+} . $[\text{Co}^{3+}]$ and the residual monomer concentration are estimated from aliquots withdrawn or from experiments conducted in duplicate. From these, the rate of cobaltic ion disappearance, $-\text{R}_{\text{co}}$, and the rate of monomer disappearance, $-\text{R}_M$, have been computed.

RESULTS AND DISCUSSION

A.Am. polymerizes rapidly in the presence of Co^{3+} at 15°C ; the steady state being attained in about 10-15 minutes with $\text{Ca} 50\%$ consumption of monomer. Lower temperatures usually have induction periods which can always be detected by absence of turbidity when few ml. of the reaction mixture is added to ethanol.

(A) $-\text{R}_{\text{co}}$.—(a) A linear variation of $-\text{R}_{\text{co}}$ with initial $[\text{M}]$ at constant acidity and ionic strength has been observed in HClO_4 (Fig. 1, A, B, C) as well as H_2SO_4 medium (Fig. 1, D, E, F). These plots have considerable intercepts on the Y-axis and point to the existence of side reactions, water, monomer oxidations, etc., all of which must be independent of $[\text{M}]$. The magnitude of the intercept for the reaction in HClO_4 is greater than the blank rate (without monomer) under identical conditions; while that in H_2SO_4 approximately corresponds to the blank rate at lower $[\text{Co}^{3+}]$. If the blank rate is taken as representing water oxidation rate it follows that in HClO_4 medium there may be other side reactions (apart from water oxidation) and monomer oxidation reaction has to be identified as such a major side reaction. That monomer oxidation reaction being independent of $[\text{M}]$ in Co^{3+} -monomer systems has also been realised by Bawn and Sharp¹⁴ under slightly different experimental conditions. The existence of monomer oxidation as a side reaction and the latter being independent of $[\text{M}]$ and directly proportional to $[\text{Co}^{3+}]$ but inversely proportional to $[\text{H}^+]$ in the polymerization of Methyl methacrylate initiated by cobaltic ions in aqueous HClO_4 system has also been inferred by us¹⁵ from the kinetic data and proved experimentally by rate of monomer disappearance (bromometry) being greater than the rate of polymerization (gravimetry). Such an experimental confirmation

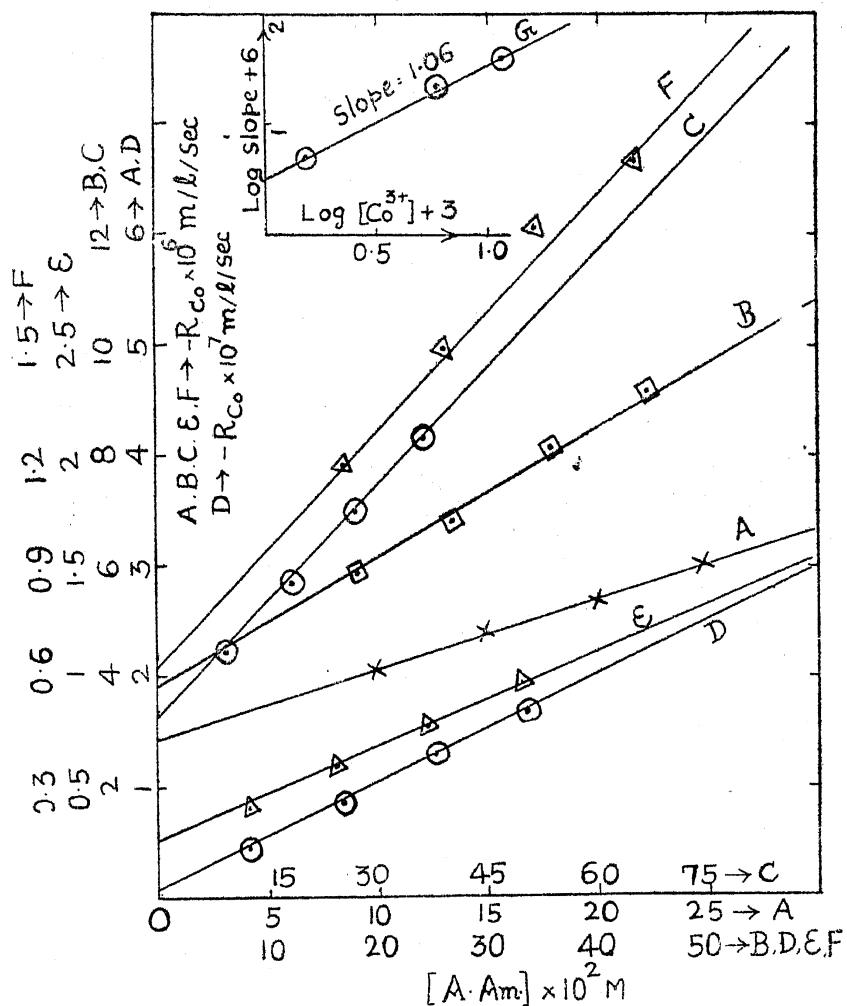


FIG. 1. Variation of $-R_{Co}$ with $[A.Am.]$ at $(H^+): 1.0 M$; $\mu: 1.2 M$; A, B, C: $HClO_4$ medium; D, E, F: H_2SO_4 medium. A: $[Co^{3+}]: 8.726 \times 10^{-8} M$; Temp.: $15^\circ C$; B: $[Co^{3+}]: 12.53 \times 10^{-8} M$, Temp.: $15^\circ C$; C: $[Co^{3+}]: 10.25 \times 10^{-8} M$ Temp.: $20^\circ C$; D: $[Co^{3+}]: 1.511 \times 10^{-8} M$, Temp.: $15^\circ C$; E: $[Co^{3+}]: 5.824 \times 10^{-8} M$, Temp.: $15^\circ C$; F: $[Co^{3+}]: 4.856 \times 10^{-8} M$, Temp.: $20^\circ C$; G: log slope (of R_{Co} vs. $[A.Am.]$ in H_2SO_4) vs. log $[Co^{3+}]$ at $15^\circ C$

could not be achieved in the polymerization of A.Am. because of the difficulty of accurately estimating the rate of polymerization in this case. That the monomer oxidation as a side reaction is less pronounced in H_2SO_4 than in $HClO_4$ has been observed in the polymerization of methyl methacrylate also as it is of acrylamide.

(b) Plots of $-R_{Co}$ vs. $[Co^{3+}]$ (Fig. 2, A and B) in $HClO_4$ medium are linear upto $[Co^{3+}] \approx 2 \times 10^{-2} M$ beyond which deviations from linearity probably due to water oxidation reaction becoming preponderant, occur. On the other hand in the range of $[Co^{3+}] < 2 \times 10^{-2} M$ water oxidation

is negligible in HClO_4 but significant in H_2SO_4 medium. Blank rates in H_2SO_4 have therefore been subtracted from $-R_{\text{co}}$ in H_2SO_4 and the orders

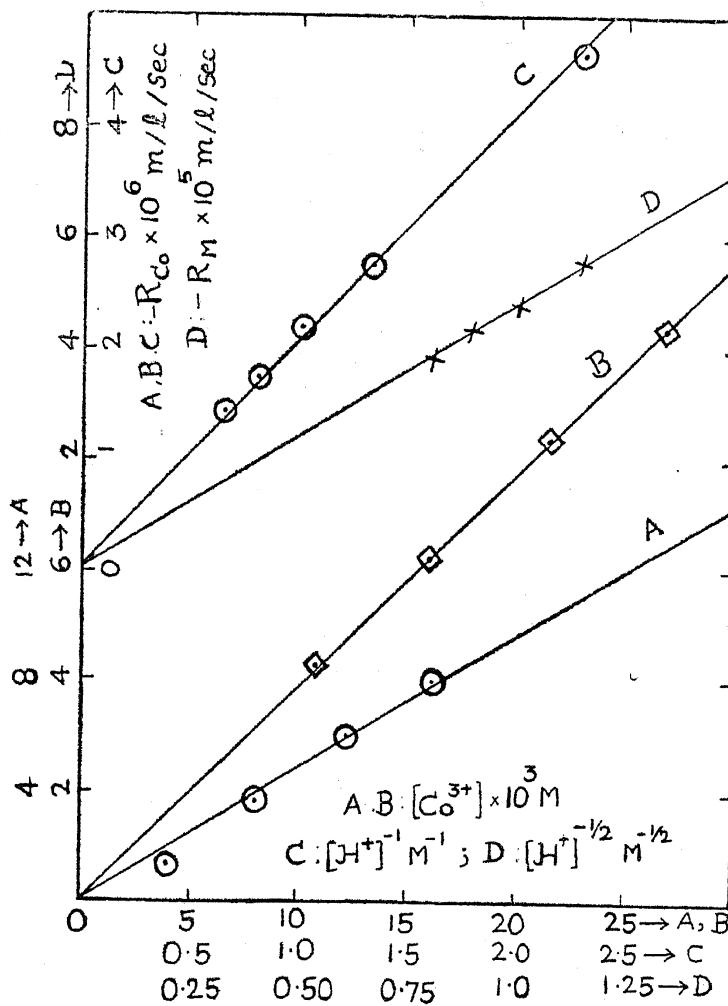


FIG. 2. Variation of $-R_{\text{co}}$ with $[\text{Co}^{3+}]$ and $[\text{H}^+]$ and variation of $-R_M$ with $[\text{H}^+]$ in HClO_4 medium. A and B: $-R_{\text{co}}$ vs. $[\text{Co}^{3+}]$ at $[\text{H}^+]$: 1.2 M , μ : 1.5 M ; A at [A.Am.]: 0.115 M , Temp.: 20° C. ; B at [A.Am.]: 0.2598 M , Temp.: 15° C. ; $-R_{\text{co}}$ vs. $[\text{H}^+]^{-1}$; $[\text{Co}^{3+}]$: $8.196 \times 10^{-8} \text{ M}$, [A.Am.]: 0.149 M , μ : 1.7 M , Temp.: 15° C. ; D: $-R_M$ vs. $[\text{H}^+]^{-0.5}$, conditions same as C.

of $[\text{Co}^{3+}]$ with respect to these corrected $-R_{\text{co}}$ have still been found to be varying from 2.3 to 1.4 (Fig. 3, A, B, C, D, E, F), the higher order obtaining at $[\text{M}] < 3 \times 10^{-2} \text{ M}$ and lower orders for $[\text{M}] > 3 \times 10^{-2} \text{ M}$. However, the order of $[\text{Co}^{3+}]$ for the polymerization part of $-R_{\text{co}}$ has been found to be unity, the log-log plot of slope (of $-R_{\text{co}}$ vs. $[\text{M}]$) vs. $[\text{Co}^{3+}]$ (Fig. 1, G) yielding a slope of unity. Participation of complexes of the type $(\text{Co} - \text{O} - \text{Co})^{4+}$ or $(\text{Co} - \text{SO}_4 - \text{Co})^{4+}$ as initiators leading to higher orders of $[\text{Co}^{3+}]$ should be discounted because of unfavourable experimental

conditions for the existence of the former. Under the circumstances we are forced to the conclusions that the blank rate (water oxidation) and rates for side reactions (water oxidation + monomer oxidation) in the polymer reaction are not accurately comparable and higher orders of $[Co^{3+}]$ in $-R_{co}$ (corrected) must be traced to orders of $[Co^{3+}]$ higher than unity in the monomer oxidation rate in H_2SO_4 medium, leading to overall order 2-1.4 for $[Co^{3+}]$ in $-R_{co}$.

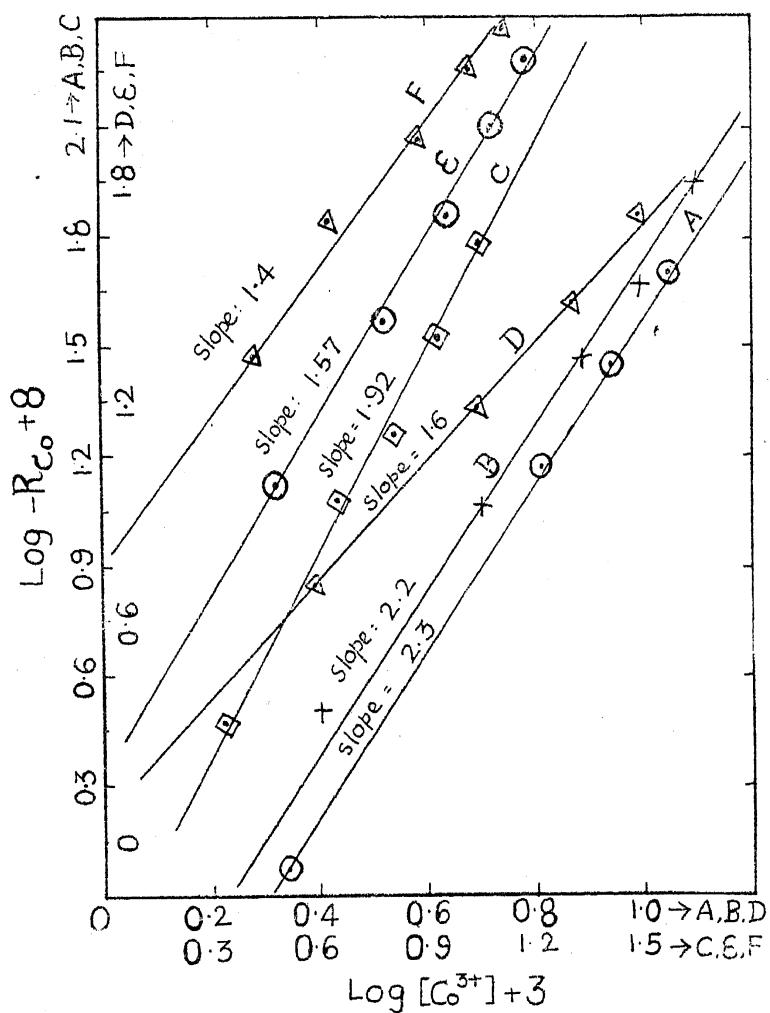


FIG. 3. $\log -R_{C_0}$ vs. $\log [Co^{3+}]$ in H_2SO_4 medium at different initial $[A.Am.]$; $[H^+]: 1.0 M$; $\mu: 1.2 M$, Temp.: $15^\circ C$; A: $1.791 \times 10^{-2} M$; B: $2.891 \times 10^{-2} M$; C: $3.582 \times 10^{-2} M$; D: $4.818 \times 10^{-2} M$; E: $9.635 \times 10^{-2} M$; F: $16.44 \times 10^{-2} M$.

(c) Plot of $-R_{Co}$ vs. $[H^+]^{-1}$ (Fig. 2, C) being linear with no intercept in $HClO_4$ medium and $-R_{Co}$ being independent of $[H^+]$ in H_2SO_4 argue in favour of $CoOH^{2+}$ in the former and Co^{3+} in the latter as initiators under conditions of mutual termination observed in this work.

(d) $-R_{Co}$ values are unaffected by changes in total ionic strength of the medium. For a fivefold increase in μ (0.5 to 2.5 M) the rates are increased hardly to 2% indicating the absence of salt effects.

(e) Initially added Co^{2+} , $[Co^{3+}]/[Co^{2+}] = 0.1$ have no effect on $-R_{Co}$ values.

(B) $-R_M$.—(a) Plots of $-R_M$ are strictly proportional to $3/2$ powers of $[M]$ in both acid media (Fig. 4, A, B, C, D, E).

On the assumption that monomer consumption for oxidation is small compared with that for polymerization and the former being independent of $[M]$, order of $3/2$ for $[M]$ may confidently be assumed to belong to the polymer reaction.

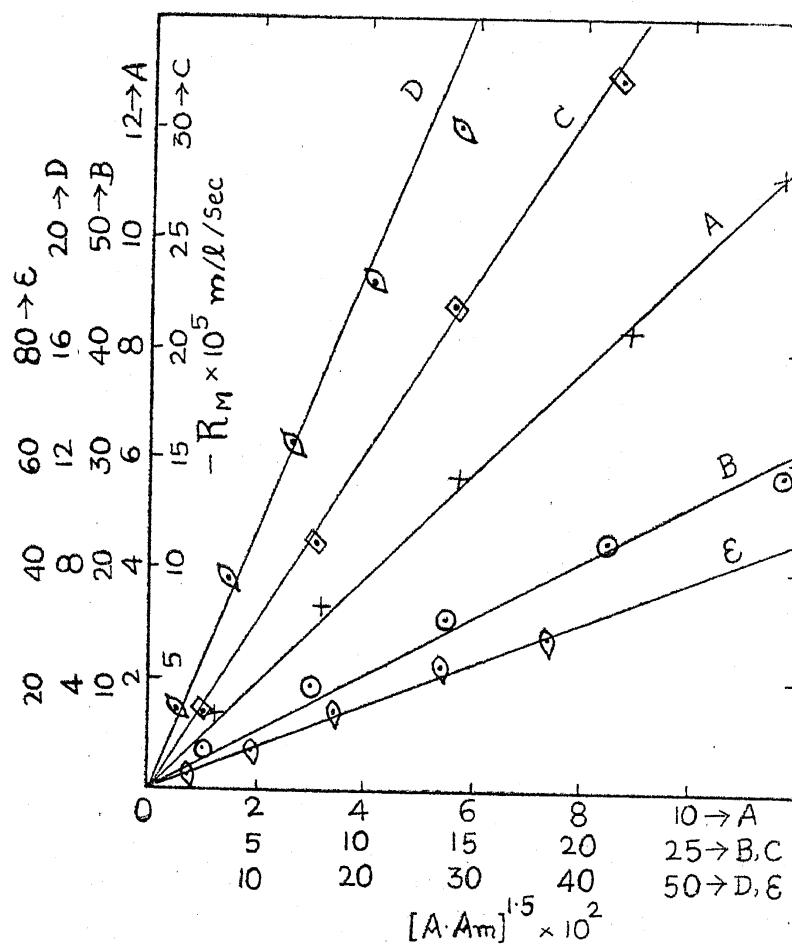


FIG. 4. Variation of $-R_M$ with $[Co^{3+}]$. A, B, C, D, E: $-R_M$ vs. $[Co^{3+}]^{0.5}$ at $[H^+]$: 1.2 M, μ : 1.5 M, Temp.: 15°C. in $HClO_4$ medium. A: [A.Am.]: 0.0866 M; B: [A.Am.]: 0.149 M; C: [A.Am.]: 0.223 M; D: [A.Am.]: 0.2598 M; E: [A.Am.]: 0.5244 M. F, G: $-R_M$ vs. $[Co^{3+}]$ in H_2SO_4 medium at $[H^+]$: 1.0 M, μ : 1.2 M; Temp.: 15°C.; F: [A.Am.]: 1.023×10^{-2} M, G: [A.Am.]: 2.891×10^{-2} M.

(b) Effect of Co^{3+} on $-\text{R}_M$ in both acids reveal certain interesting aspects. In HClO_4 medium plots of $-\text{R}_M$ vs. $[\text{Co}^{3+}]^{0.5}$ pass through the origin when $[\text{M}] < 0.2 \text{ M}$. For $[\text{M}] > 0.2 \text{ M}$, the square root dependence of $[\text{Co}^{3+}]$ is still obeyed but the plots leave successively larger intercepts on the Y-axis and for $[\text{M}] > 0.5 \text{ M}$ the plot is parallel to X-axis and has largest intercept (Fig. 5, A, B, C, D, E). $3/2$ powers of $[\text{M}]$ and 0.5 powers of $[\text{Co}^{3+}]$ emphasize the importance of mutual type of termination. The intercepts on the Y-axis suggest linear type of termination also. This type of mixed termination is in strong contrast to exclusive linear type of termination by Co^{3+} or CoOH^{2+} observed in the polymer-

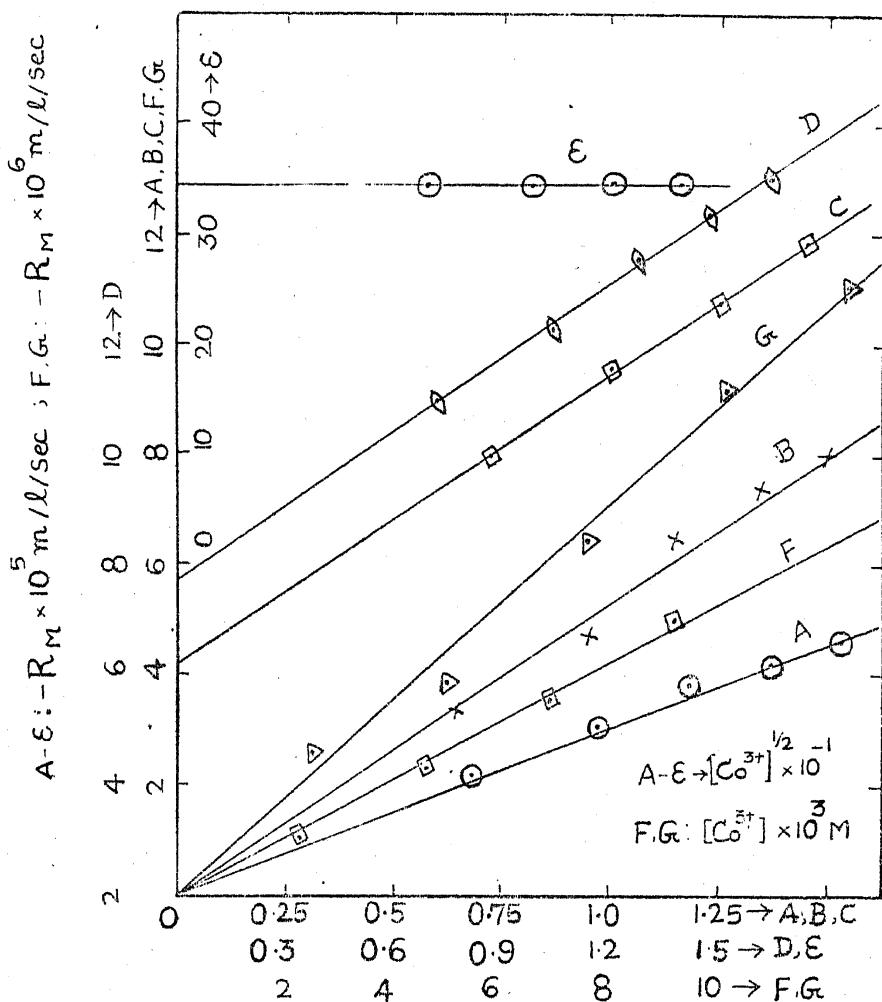


FIG. 5. Variation of $-\text{R}_M$ with $[\text{A.Am.}]$. $[\text{H}^+]$: 1.0 M ; μ : 1.2 M ; A, B, C: $-\text{R}_M$ vs. $[\text{A.Am.}]^{1.5}$ in HClO_4 medium. D, E: $-\text{R}_M$ vs. $[\text{A.Am.}]^{1.5}$ in H_2SO_4 medium. A: $[\text{Co}^{3+}]$: $8.726 \times 10^{-3} \text{ M}$; Temp.: 15° C ; B: $[\text{Co}^{3+}]$: $12.53 \times 10^{-3} \text{ M}$, Temp.: 15° C ; C: $[\text{Co}^{3+}]$: $10.25 \times 10^{-3} \text{ M}$, Temp.: 20° C ; D: $[\text{Co}^{3+}]$: $4.856 \times 10^{-3} \text{ M}$, Temp.: 20° C ; E: $[\text{Co}^{3+}]$: $11.77 \times 10^{-3} \text{ M}$, Temp.: 15° C .

ization of methyl methacrylate, methyl acrylate and acrylonitrile monomers initiated by cobaltic ions.¹⁵ Under conditions $[M] > 0.5$ M of exclusive linear termination in the polymerization of A.Am. there is rapid consumption of Co^{3+} and a detailed investigation of dependence of $-\text{R}_M$ on $[M]^2$ is not therefore easy. In H_2SO_4 medium results of $-\text{R}_M$ with $[\text{Co}^{3+}]$ are still more anomalous. At $[M] < 3 \times 10^{-2}$ M, $-\text{R}_M$ is found to depend on first power of $[\text{Co}^{3+}]$ (Fig. 5, F, G). For higher $[M]$, $-\text{R}_M$ is independent of $[\text{Co}^{3+}]$ suggesting linear termination. But the strict 3/2 order for $[M]$ in $-\text{R}_M$ indicates clearly that termination by mutual combination of radicals is predominant. However, values of $[M]$ as low as 3×10^{-2} M, have not been used in experiments on variation of $[M]$ to evaluate the order w.r.t. $[M]$ in polymerization. It is highly probable that at such low $[M]$, monomer consumption by oxidation is predominant.

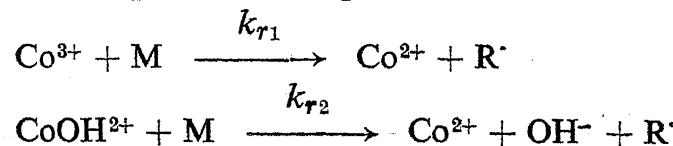
(c) Plot of $-\text{R}_M$ vs. $(\text{H}^+)^{-0.5}$ under conditions $[M] < 0.3$ M in HClO_4 medium is linear and is devoid of an intercept (Fig. 2, D) on the Y-axis which shows that CoOH^{2+} species are the active entities. Also such a dependence of $-\text{R}_M$ on $(\text{H}^+)^{-0.5}$ indicates that only mutual termination is significant. On the other hand in H_2SO_4 medium $-\text{R}_M$ values are independent of $[\text{H}^+]$ in conformity with the earlier conclusions drawn under A (c), viz., in polymerization of A.Am. in H_2SO_4 medium Co^{3+} ions are the active species.

(d) In both acid media the effect of added salt, NaClO_4 in HClO_4 and HSO_4^- in H_2SO_4 , is negligible, there being only 10% increase in $-\text{R}_M$ values for a fivefold increase in ionic strength. This also emphasizes the fact that species like CoSO_4^{2-} present in preponderate quantities in H_2SO_4 medium need not necessarily be the active species as initiators. Waters and his associates¹⁶ have drawn similar conclusions in their studies on oxidation of Diethylketone by Co^{3+} .

(e) $-\text{R}_M$ values are unaffected by initially added cobaltous ions.

(C) *Kinetic Scheme.*—The experimental results outlined above may conveniently be explained on the basis of the following reaction scheme:

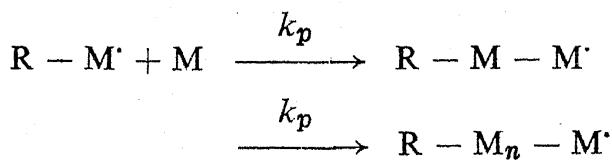
(a) Radical production steps:



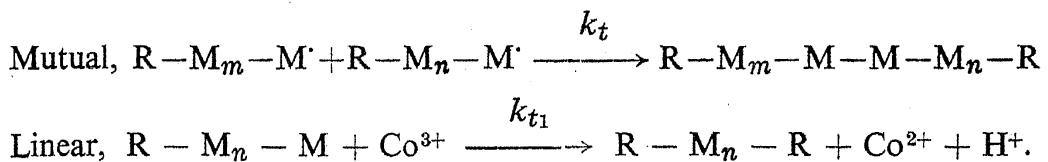
(b) Initiation:



(c) Propagation:



(d) Termination:



(D) *Rate equations*: Assuming the usual stationary state kinetics for micro and macroradicals and that k_p and k_t are independent of chain-length, the polymerization parts of rate equations may be derived.

$$\begin{aligned}
 -R_{Co} = & \frac{K_1 k_{r_2} [Co^{3+}] [M]}{[H^+]} + \frac{k_w [Co^{3+}]^{1.5}}{[H^+]} \\
 & + \frac{k_m [Co^{3+}]}{[H^+]} \text{ (HClO}_4 \text{ medium).}
 \end{aligned} \quad (1)$$

The first term on R.H.S. of equation (1) refers to polymerization part, K_1 is the hydrolytic constant for $Co^{3+} + H_2O \rightleftharpoons CoOH^{2+} + H^+$.

The second and third terms refer to water oxidation and monomer oxidation respectively and k_w and k_m are the rate constants for oxidation of water and monomer respectively. In H_2SO_4 medium the first term of $-R_{Co}$ may be replaced by $k_{r_1} [Co^{3+}] [M]$; in the second term, power of $[Co^{3+}]$ is 1.5 or 2; 1.5 at $[Co^{3+}] < 4 \times 10^{-3} M$ and 2 at $[Co^{3+}] > 4 \times 10^{-3} M$ while in the third term it is an unknown variable "Y".

The rate laws for water oxidation in various acids have been obtained from kinetics of water oxidation studied under the same conditions as for polymerization experiments.

$$-R_M = \frac{k_p}{k_t^{\frac{1}{2}}} \left\{ \frac{K_1 k_{r_2} [Co^{3+}]}{[H^+]} \right\}^{\frac{1}{2}} [M]^{3/2} + k_2 [M]^2 \text{ (HClO}_4 \text{ medium.}) \quad (2)$$

The first term refers to mutual termination and the second to linear termination.

$$-R_M = \frac{k_{r_1}^{\frac{1}{2}} \cdot k_p [M]^{3/2}}{k_t^{\frac{1}{2}} [Co^{3+}]^x} + k_2 [M]^2 \dots H_2SO_4 \text{ medium} \quad (3)$$

$x = 1$ for $[M] < 3 \times 10^{-2} M$ and $x = 0$ for higher $[M]$.

(E) *Evaluation of rate constants.*—From slopes of plots $-R_{Co}$ vs. [M] (Fig. 1) k_{r1} in H_2SO_4 medium and k_{r2} in $HClO_4$ have been evaluated. From slopes of $-R_M$ vs. $[M]^{3/2}$ (Fig. 4) and substitution of known k_{r1} or k_{r2} values, values of $k_p/k_t^{1/2}$ have been computed in the two acid media. Values of $k_p/k_t^{1/2}$ and k_m in $HClO_4$ medium have also been evaluated from slopes of plots $-R_M$ vs. $[Co^{3+}]^{0.5}$ (Fig. 5) and $-R_{Co}$ vs. $1/[H^+]$ respectively. All the rate constants with activation energies are given in Tables I a and I b.

TABLES OF RATE CONSTANTS

TABLE I a

 $HClO_4$ medium

$k_{r2} \text{ lm}^{-1} \text{ sec.}^{-1}$	$k_m \times 10^4$ from $-R_{Co}$ vs. $1/[H^+]$	$k_p \left[\frac{k_{r2}}{k_t} \right]^{1/2}$	$k_p/k_t^{1/2} \text{ lm}^{-1/2} \text{ sec.}^{-1/2}$	$E k_{r2}$ K. cals./mole	$E_p - \frac{1}{2} E_t$
15° C. 20° C.	..	15° C. 20° C.	15° C. 20° C.		
0.089	0.124	1.263 at 15° C.	0.095 ^a 0.153	0.323 ^{a,b} 0.435	10.91 10.34
..	0.098 ^b
..	0.141 ^c ..	0.463 ^c
..	0.108 ^d ..	0.356 ^d
..	0.058 ^e ..	0.191 ^e
..	0.040 ^f ..	0.132 ^f

a, evaluated from $-R_M$ vs. $[A.Am.]^{1.5}$ plots; *b*, from $-R_M$ vs. $[H^+]^{-0.5}$ plot; *c, d, e, f*, from $-R_M$ vs. $[Co^{3+}]^{0.5}$ plots at $[A.Am.]$: 0.087 M, 0.149 M, 0.223 M and 0.259 M respectively.

TABLE I b

 H_2SO_4 medium

$k_{r1} \times 10^4 \text{ lm}^{-1} \text{ sec.}^{-1}$	$k_p/k_t^{1/2} \times k_{r1}^{1/2} \times 10^2$	$*k_p/k_t^{1/2} \text{ lm}^{-1/2} \text{ sec.}^{-1/2}$	$E k_{r1}$ K. cals./mole
15° C. 20° C.	15° C. 20° C.	15° C. 20° C.	
1.67	3.20	2.142 ^a 1.511 ^d	1.659 0.839
..	..	1.201 ^b 1.353 ^e	0.930 0.756
..	..	0.710 ^c ..	0.550 ..

a, b, c, d, e at initial $[Co^{3+}]$: 1.511×10^{-3} M, 5.824×10^{-3} M, 11.77×10^{-3} M, 4.856×10^{-3} M and 6.006×10^{-3} M respectively.

* values evaluated from $-R_M$ vs. $[A.Am.]^{1.5}$ plots.

$k_p/k_t^{\frac{1}{2}}$ values in H_2SO_4 have to be treated with caution because they have been evaluated assuming the theoretical $[Co^{3+}]^{0.5}$ dependence on $-R_M$ even though this has not been realised experimentally. The decreasing trend of $k_p/k_t^{\frac{1}{2}}$ values in H_2SO_4 medium and of those evaluated from $-R_M$ vs. $[Co^{3+}]^{0.5}$ in $HClO_4$ reflect the simultaneous occurrence of both mutual and linear types of terminations. The occurrence of linear termination by metal ions in the polymerization of A.Am. is now well recognised.^{17, 18, 9a} In polymerization initiated by cobaltic ions there is an unmistakable evidence for the occurrence of mutual type of termination also.

In conclusion, we wish to state that our kinetic results do not favour initiation of polymerization by OH^- radicals produced in the water oxidation by Co^{3+} ions. If OH^- radicals were to initiate, $-R_M$ should have varied as $[M]$ and $-R_c$ independent of $[M]$. Our experimental results are contrary to these expectations.

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REFERENCES

1. Dainton, F. S. and Tordoff, M. *Trans. Farad. Soc.*, 1957, **53**, 666.
2. ——— ... *Ibid.*, 1957, **53**, 499-511.
3. Toppet, S., Delzenne, G. and Smets, G. *J. Polym. Sci.*, 1964, **2**, Part A, 1539-48.
4. Oster, G. K., Oster, G. and Prati, G. *J. Amer. Chem. Soc.*, 1957, **79**, 595-98.
5. Schulz, R., Renner, G., Henglein, A. and Kern, W. *Makromol. Chem.*, 1954, **12**, 20-34.
6. (a) Collinson, E., Dainton, F. S. and McNaughton, G. S. *Trans. Farad. Soc.*, 1957, **53**, 476-88, 489-98.
(b) Dainton, F. S., Collinson, E. and Armstrong *Ibid.*, 1959, **55**, 1375.
7. Suen, T. J., Yunjen, Janet. V. Lockwood *J. Polym. Sci.*, 1958, **31**, 481.
8. Rodriguez, F. and Givey, R. D. *Ibid.*, 1961, **55**, 713.
9. (a) Mino, G., Kaizerman, S. and Rasmussen, E. *Ibid.*, 1959, **38**, 393.
(b) ——— ... *J. Amer. Chem. Soc.*, 1959, **81**, 1494.

(c) Hoare, D. G. and Waters, W. A. *J. Chem. Soc.*, 1964, p. 2554.

10. Hargreaves, G. and Sutcliffe, L. H. *Trans. Farad. Soc.*, 1955, **51**, 786.

11. Swann, S. and Xanthakos, T. S. *J. Amer. Chem. Soc.*, 1931, **53**, 400.

12. Bawn, C. E. H. and White, A. G. *J. Chem. Soc.*, 1951, p. 331.

13. Latinen, H. A. and Burdett, L. W. *Analyt. Chem.*, 1951, **23**, 1268.

14. Bawn, C. E. H. and Sharp, J. A. *J. Chem. Soc.*, 1957, p. 1866.

15. Jijie, K., Santappa, M. and Mahadevan, V. *J. Polym. Sci.* 1966, **A1**, 4, pp. 377-406.

16. Hoare, D. G. and Waters, W. A. *J. Chem. Soc.* 1962, p. 971.

17. Collinson, E. and Dainton, F. S. *Nature*, 1956, **177**, 1224.

18. Dainton, F. S., Collinson, E., Smith, D. R., Trudel, G. J. and Tazuke, S. *Disc., Farad. Soc.*, 1960, **29**, 188.