VINYL POLYMERIZATION

IV. Co^{3+}–Tert. butylalcohol Red-ox System

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Abstract

The effect of tert. butyl alcohol on the polymerization of Methylmethacrylate initiated by cobaltic ions in aqueous perchloric acid medium was tried.   Rates of cobaltic ion disappearance and rates of polymerization were measured with variables, [M], [A], [Co^{3+}], [H$^+$], etc. at constant ionic strength.   From the experimental results it was concluded that at low [A], initiation and termination of polymerization was by Co^{3+} species. At higher [A], initiation was still by Co^{3+} species but termination was found to change over to mutual type.   At very high [A], Co^{3+} + tert. butyl alcohol reaction was found to function as a red-ox system for polymerization of monomer.   An appropriate kinetic scheme was proposed and the various rate constants under different [A] regions evaluated.

Introduction

Reported studies on the kinetics of vinyl polymerization initiated by red-ox system are numerous though metal ion-reducing agent systems have been used to a very limited extent. Ce^{4+}–3, chloro 1-propanol[1], Ce^{+4}–ethylene glycol[2] are examples of the latter type.   Studies on initiation of vinyl polymerization by metal ions only, like Ce^{4+},[3] Co^{3+},[4] etc., confined solely to our laboratory have now been extended to include red-ox systems with Co^{3+} or Ce^{4+} as oxidising agent with a view to gain an insight into the nature of active species in the systems involving these ions.   The results of polymerization of Methylmethacrylate initiated by the red-ox system, Co^{3+}–tert. butyl alcohol (T.B.A.) in perchloric acid are reported and the nature of initiation and termination are discussed in this paper.

Experimental

(*a*) *Reagents.*—Tert. butyl alcohol, a B.D.H.; A.R. product was fractionally distilled and the middle fraction (b.p. 82·4° C.; 760 mm. of Hg)

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was used for the experiments. The details for purification of Methylmetha-crylate (M.M.A.) (Rohm and Haas product) and preparation of cobaltic perchlorate, etc., are same as reported in the previous paper.[5]

(b) *Polymerization and rate measurements.*—Polymerization was con-ducted in long pyrex tube ($8'' \times 1''$) fitted with B-24 sockets. The tube was closed by means of a B-24 cone to which were fused nitrogen inlet and outlet tubes. Reaction mixtures consisting of the requisite quantities of monomer, alcohol, free acid and sodium perchlorate thermostated at $15° \pm 0·1°$ C. were deaerated with oxygen-free nitrogen for 20–30 minutes. Nitrogen was passed through wash bottles containing appropriate concentration of monomer and alcohol before bubbling through the reaction mixture. At the end of the deaeration period, Co^{3+} was added and the system was sealed under nitrogen. Reactions were usually carried out for 20–25 minutes in a thermostat at $15 \pm 0·1$ °C. The course of polymerization was arrested by addition of known excess of Fe^{2+}. Rates of polymerization were followed by gravimetry (of weight of the polymer precipitated after arresting the reac-tion and addition of water) while Co^{3+} was estimated from the filtrates by means of back titration of unreacted Fe^{2+} with standard Ce^{4+} using Ferroin as indicator. Chainlengths of poly (methylmethacrylate) were determined viscometrically making use of the equation[6]

$$\text{``} n \text{''} = 2·81 \times 10^3 [\eta]^{1·32}$$

where: $[\eta]$ intrinsic viscosity and " n " chainlength of the polymer.

RESULTS AND DISCUSSION

The system Co^{3+}-T.B.A. was found to be highly reactive and con-sequently experiments, using this system for polymerization, were carried out at 15° C. at an acidity of 2M which facilitated convenient rate measure-ments. Polymerization was found to be very rapid at higher alcohol concen-trations $[A] \gtrsim 20 \times 10^{-2}$ M.

(a) *Rates of Cobaltic Ion Disappearance,* $- R_{co}$:

(i) A linear variation of $- R_{co}$ with monomer concentration $[M]$, with intercepts on the ordinate (Fig. 1, A–D) were observed up to $[A] \approx 60 \times 10^{-2}$ M; for $[A] > 60 \times 10^{-2}$ M, rates were practically constant with changes in $[M]$ (Fig. 1, E). At higher $[A]$, probably Co^{3+} species were consumed predomi-nantly for oxidation of alcohol rather than of monomer leading to polymeri-zation. The intercepts represent rates of oxidation of alcohol, the magnitude

of these intercepts being approximately equal to the blank rates (without monomer) under indentical conditions. This indicated that side reactions such as water oxidation, monomer oxidation not leading to polymerization, etc., were not significant in the presence of T.B.A. On the other hand, our studies on kinetics of polymerization of M.M.A. in the absence of T.B.A. by Co^{3+} (aq) system[7] have shown the occurrence of these side reactions along with oxidation of monomer leading to polymerization.
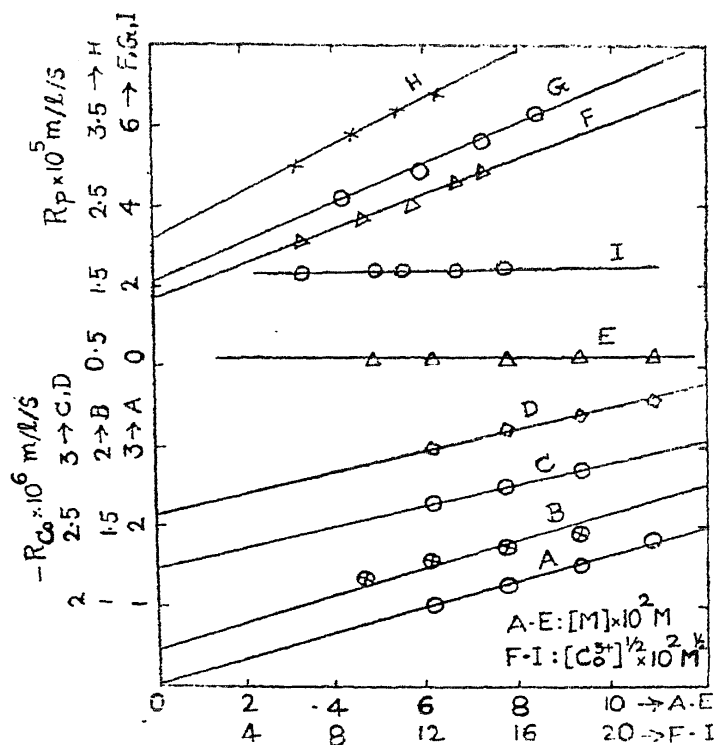

FIG. 1. Effect of [M] on $- R_{Co}$ and effect of $[Co^{3+}]$ on R_p.

A–E Plots of $- R_{Co}$ vs. [M] at various [A] at $[H^+]$: 2·0 M; μ: 2·3 M and Temp. 15° C. A: [T.B.A.] $= 0 \times 10^{-2}$ M; $[Co^{3+}]$: 11·37 $\times 10^{-3}$ M; B: [T.B.A.]: 12 $\times 10^{-2}$ M $[Co^{+3}]$: 7·914 $\times 10^{-3}$ M; C: (T.B.A.]: 21 $\times 10^{-2}$ M, $[Co^{3+}]$: 11·37 $\times 10^{-3}$ M; D: [T.B.A.]: 30 $\times 10^{-2}$ M; $[Co^{+3}]$: 10·45 $\times 10^{-3}$ M and E: [T.B.A.] $= 100 \times 10^{-2}$ M; $[Co^{3+}]$: 11·45 $\times 10^{-3}$ M; F–I: Plots of R_p vs. $[Co^{3+}]^{\frac{1}{2}}$ at [T.B.A.]: 100 $\times 10^{-2}$ M, 150 $\times 10^{-2}$ M, (40–80) $\times 10^{-2}$ M and 8 $\times 10^{-2}$ M respectively, all at [M]: 9·353 $\times 10^{-2}$ M, $[H^+]$: 2·0 M, μ: 2·3 M and temp. 15° C.

(ii) A strict first power dependence of $- R_{co}$ on $[Co^{3+}]$ has been observed (Fig. 2, A–D) for [A] $= 1 \times 10^{-2}$ to 200×10^{-2} M.

(iii) $- R_{co}$ also varied directly as [A] (Fig. 2, E–G) with a break in linearity at [A] $\gtrsim 50 \times 10^{-2}$ M. The decreased $- R_{co}$ at higher [A] may be understood in terms of observation of Hoare and Waters[8] who proposed a sequence of six steps for the mechanism of oxidation of T.B.A. by cobaltic perchlorate under conditions of $[Co^{3+}] < [A]$; the products being CH_3OH, CH_3, $COCH_3$, $HCHO$ and $HCOOH$, etc., and stoichiometry, $\triangle$ Alcohol/

$\triangle$ Co^{3+} = 1:6. For [A] $\gg$ [Co^{3+}], the stoichiometry tended to drop to a limiting value 1:2. The change in stoichiometry was explained on the basis of the first four steps of the sequence only occurring, leading to the products methanol and acetone. Plots of $- R_{co}$ vs. [A] left intercepts on the ordinates (Fig. 2, E–G) which indicated the consumption of Co^{3+} for oxidation of monomer leading to polymerization. A break in the linearity of the plot $- R_{co}$ vs. [A] was observed at [A] $\gtrsim$ 50×10^{-2} M in the blank (absence of monomer) also; the blank plot left no intercept on the ordinate.

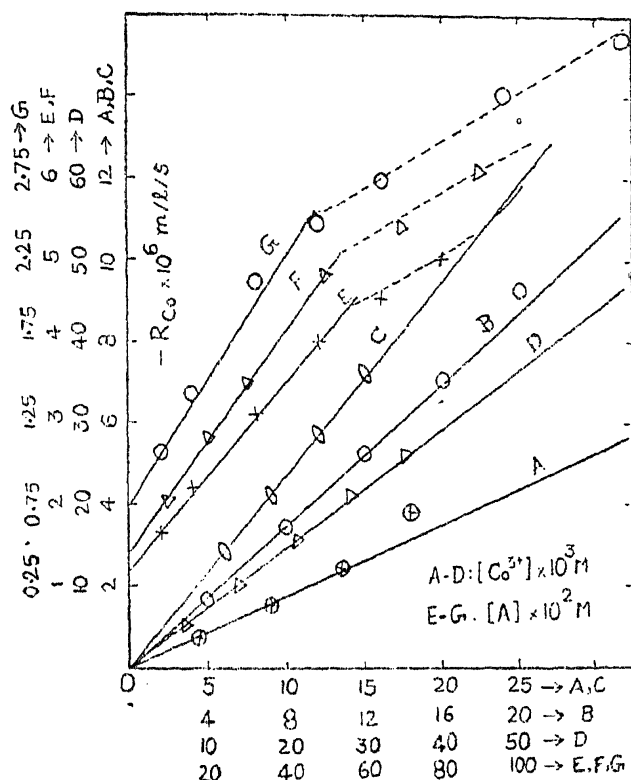Fig. 2. Effect of [Co^{3+}] and [A] on $- R_{co}$.

A–D plots of $- R_{Co}$ vs. [Co^{3+}] at [M]: 9·353×10^{-2} M; [H^{+}]: 2·0 M; μ = 2·3 M; Temp. 15° C. and [T.B.A.]: 8×10^{-2} M, 64×10^{-2} M, 80×10^{-2} M and 150×10^{-2} M respectively. E–G: Plots of $- R_{Co}$ vs. [A] at [M]: 9·353×10^{-2} M, [H^{+}]: 2·0 M, μ: 2·3 M, Temp. 15° C. and [Co^{3+}]:. 10·3×10^{-3} M, 12·01×10^{-3} M and 6·325×10^{-3} M respectively.

(iv) An inverse dependence of $- R_{co}$ with [H^{+}] (Fig. 3, A, B, E) was observed both in the higher as well as lower [A] regions and plots of $- R_{co}$ vs. [H^{+}]$^{-1}$ (Fig. 3, A, B) or $k_{obs.}$ vs. 1/[H^{+}] (Fig. 3, E) ($k_{obs.}$ was obtained from slopes of plots of $- R_{co}$ vs. [Co^{3+}] at fixed [A] and [M] but different [H^{+}]) were found to leave intercepts on the Y-axis which indicated the existence of acid independent reaction paths in polymerization reaction. This is possible only if Co^{3+} (aq) ions are one of the initiating species. However, our experiments[9] on oxidation of T.B.A. by Co^{3+} under identical conditions

as well as those of Waters *et al.*,[10] have shown that the oxidation of alcohol consists only of an acid dependent path arising from the $CoOH^{2+}$ species taking part in the reaction sequence. Hence, the linear portion of the plot of $- R_{co}$ *vs.* $1/[H^+]$ may comprise of the rate constant due to alcohol oxidation and probably due to the reaction $CoOH^{2+} +$ Monomer leading to polymerization of the latter.

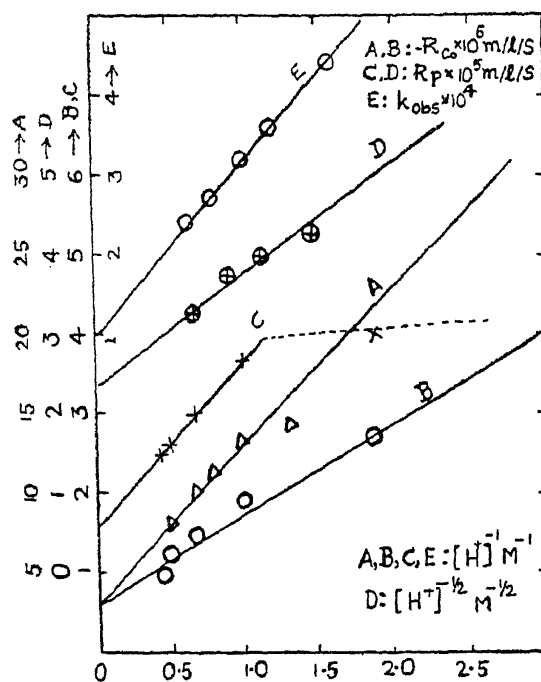FIG. 3. Effect of $[H^+]$ on R_p and $- R_{co}$ at $[M]$: $9 \cdot 353 \times 10^{-2}$ M; μ: $2 \cdot 3$ M, Temp. 15° C. A and B: $- R_{co}$ *vs.* $1/[H^+]$ At [T.B.A.]: 64×10^{-2} M, $[Co^{3+}]$: $15 \cdot 02 \times 10^{-3}$ M. B: [T.B.A.]: 9×10^{-2} M, $[Co^{3+}]$: $9 \cdot 873 \times 10^{-3}$ M. C and D: R_p *vs.* $1/[H^+]$ and R_p *vs.* $1/[H^+]^{\frac{1}{2}}$ respectively, conditions same as B and A respectively. E: k_{obs}. *vs.* $1/[H^+]$ at [T.B.A.]: 21×10^{-2} M.

(b) Rates of Polymerization, R_p:

(i) The variation of R_p with $[M]$ was found to depend on the $[A]$ used and three types of variations were observed. At an initial $[A] < 20 \times 10^{-2}$ M, a strict square dependence of R_p on $[M]^2$ was realized (Fig. 4, A) which showed the occurrence of linear termination. At $[A] = 20 \times 10^{-2}$ M $- 60 \times 10^{-2}$ M, R_p varied as $[M]^{3/2}$ (Fig. 4, B) suggestive of mutual type of termination. The transition from linear to mutual type of termination is understandable in view of increased rate of T.B.A. $+ Co^{3+}$ reaction and consequent depletion of the latter for linear termination. At still higher $[A]$, $> 60 \times 10^{-2}$ M, R_p varied linearly with $[M]$ (Fig. 4, C, D) which meant initiation exclusively from radicals produced from alcohol oxidation. The observed independence of $- R_{co}$ on $[M]$ in this region of high $[A]$ mentioned under $- R_{co}$ also supports this conclusion. It is highly probable that under the

conditions of $[A] \gg [M]$, oxidation of alcohol and initiation of polymerization by the radicals from alcohol are more important.
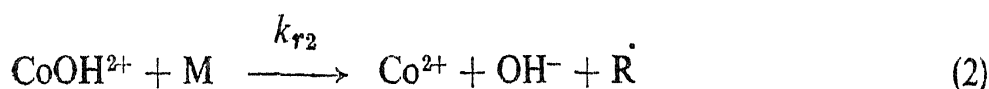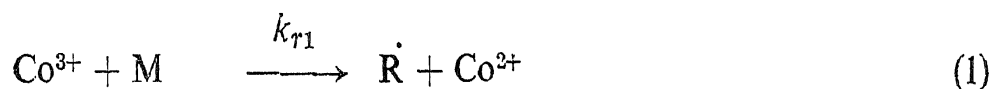
(ii) In the low $[A]$ region, R_p values were independent of $[Co^{3+}]^{\frac{1}{2}}$ (Fig. 1, I). This coupled with the observed dependence of R_p on $[M]^2$ in this region of $[A]$, points to preferential linear termination. At medium $[A]$, $> 20 \times 10^{-2}$ M, plots of R_p *vs.* $(Co^{3+})^{\frac{1}{2}}$ were linear (Fig. 1, F–H) with intercepts on the ordinates, the magnitudes of the intercepts being appreciable at $[A] = 40$–80×10^{-2} M and decreasing for $[A] = 100$–150×10^{-2} M. The half power dependence of R_p on $[Co^{3+}]^{\frac{1}{2}}$ clearly indicates the mutual type of termination, irrespective of the mode of initiation, *i.e.*, by Co^{3+} species and or radicals derived from alcohol. If the intercepts on the Y-axis of the R_p *vs.* $[Co^{3+}]^{\frac{1}{2}}$ plots are an indication of occurrence of linear termination, it is then evident that at small $[A]$ preponderant linear termination occurs, while at high $[A]$, mutual termination appears to take precedence over linear termination. In addition to this one half power dependence on $[Co^{3+}]$, a strict 3/2 order for $[M]$ with R_p at $[A] = 20$–60×10^{-2} M and a first order at $[A] > 60 \times 10^{-2}$ M indicate the occurrence of mutual termination under conditions of predominant initiation by Co^{3+} species in the former and by alcohol radicals in the latter. However, linear termination does occur in this region of medium and high $[A]$, though to a small extent.

(iii) Further support for the above conclusions was gained from the effect of $[A]$ on R_p. R_p *vs.* $[A]$ variations depended on $[A]$ being low, medium or high. At lower $[A] < 20 \times 10^{-2}$ M there was little if insignificant rise in R_p values with $[A]$ and therefore it may be concluded that Co^{3+} species are the effective initiators. Oxidation of monomer (leading to polymerization) and oxidation of T.B.A. may be concurrent reactions under the conditions of low $[A]$, the rate for the former being much greater than for the latter. The magnitudes of intercepts observed in $- R_{co}$ *vs.* $[M]$ plots (corresponding to oxidation of the alcohol) and $- R_{co}$ *vs.* $[A]$ plots (corresponding to oxidation of monomer) also lend support to such a view. At medium $[A]$, $> 20 \times 10^{-2}$ M, plots of R_p *vs.* $[A]^{\frac{1}{2}}$ (Fig. 4, E, F) were linear with intercepts on the ordinate, the linearity due to initiation by alcohol radicals and mutual termination while the intercept refers to initiation by cobaltic ions. For initiation by alcohol radicals and linear termination, a direct variation of R_p with $[A]$ is expected, but this is highly unlikely in view of the rapidity of the $Co^{3+} + $ T.B.A. reaction and consequent depletion of Co^{3+} for termination. At $[A] > 120 \times 10^{-2}$ M, the rates were again practically constant with increase in $[A]$, probably due to inhibition by acetone, a product of oxidation of T.B.A. at such high $[A]$.

FIG. 4. Effect of [M] and [A] on R_p at [H$^+$]: 2·0 M, Temp. 15° C.

A: R_p vs. [M]^2 at low [A].   B: R_p vs. [M]$^{3/2}$ at [A]: 21×10^{-2} M and [Co^{3+}]: $11 \cdot 37 \times 10^{-3}$ M. C, D: R_p vs. [M] at [A]: 100×10^{-2} M and 64×10^{-2} M and [Co^{3+}]: $11 \cdot 45 \times 10^{-3}$ M and $13 \cdot 17 \times 10^{-3}$ M respectively. E, F: R_p vs. [A]$^{\frac{1}{2}}$ at [Co^{3+}]: $12 \cdot 01 \times 10^{-3}$ M and $6 \cdot 325 \times 10^{-3}$ M. respectively. and [M]: $9 \cdot 353 \times 10^{-2}$ M.

(iv) The effect of [H$^+$] on R_p also supports the above conclusions. At low [A], where linear termination is predominant, plots of R_p vs. $1/$[H$^+$] were linear for high acidities and flat for low acidities, with intercepts on the ordinate (Fig. 3, C), the latter indicating the presence of acid independent path. The flat portion of the curve is explicable by the fact that at lower acidities, initiation and termination involve CoOH^{2+} species. The linear portion is due to initiation by CoOH^{2+} species, and termination by Co^{3+} ions. This behavior is analogous to that observed in the absence of alcohol under identical conditions. At higher [A], where mutual termination is predominant, R_p varied as $1/$[H$^+$]$^{\frac{1}{2}}$ (Fig. 3, D) as required under these conditions.

(c) *Chainlengths, " n ":*

Evaluation of chain lengths of the polymer samples by viscometry showed that extremely short chains were formed. However the results are of qualitative interest only. At low [A] $< 20 \times 10^{-2}$ M, " n " values varied directly as [M] and inversely as [Co^{3+}] and independent of [H$^+$] which supports the conclusions drawn—initiation by Co^{3+} and CoOH^{2+} species and termination by Co^{3+} ions.
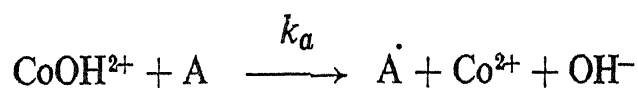
REACTION SCHEME

The foregoing experimental results and conclusions can be adequately explained on the basis of the following reaction scheme:
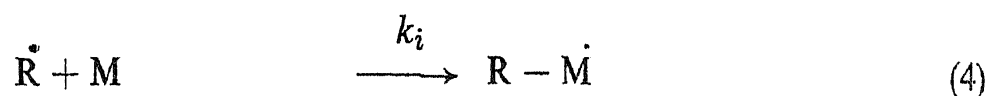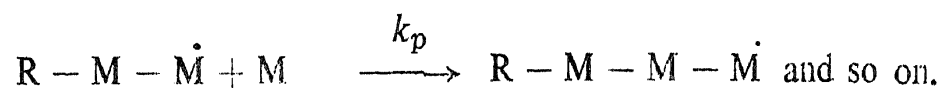
Radical Production:

$$Co^{3+} + M \xrightarrow{k_{r1}} \dot{R} + Co^{2+} \tag{1}$$

$$CoOH^{2+} + M \xrightarrow{k_{r2}} Co^{2+} + OH^- + \dot{R} \tag{2}$$

if

$$Co^{3+} + H_2O \underset{K_1}{\rightleftharpoons} CoOH^{2+} + H^+$$

$$CoOH^{2+} + A \xrightarrow{k_a} \dot{A} + Co^{2+} + OH^-$$

$$\dot{A} + M \xrightarrow{k_{r3}} \dot{R} \tag{3}$$

(Structures and configurations of $\dot{R}$ in (1), (2) and (3) may be different.)

Initiation:

$$\dot{R} + M \xrightarrow{k_i} R - \dot{M} \tag{4}$$

Propagation:

$$R - \dot{M} + M \xrightarrow{k_p} R - M - \dot{M} \tag{5}$$

$$R - M - \dot{M} + M \xrightarrow{k_p} R - M - M - \dot{M} \text{ and so on.}$$

Termination:

Mutual;

$$R - \dot{M}_n + R - \dot{M}_m \xrightarrow{k_{t1}} R - M_{m+n} - R \tag{6}$$

Linear;

$$R - \dot{M}_n + Co^{3+} \xrightarrow{k_{t2}} P + Co^{2+} + H^+. \tag{7}$$
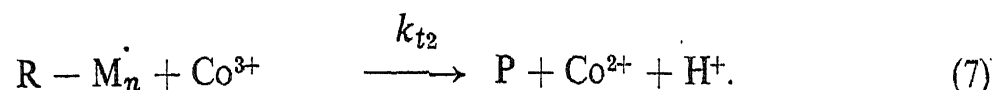
On the basis of usual assumptions for stationary state concentrations of radicals, etc., the following rate laws may be derived.

At low [A], considering steps 1, 2, 4, 5 and 7 for polymerization,

$$- R_{co} = 2 \left[k_{r1} + \frac{K_1 k_{r2}}{[H^+]} \right] [Co^{3+}] \, [M] + \frac{K_1 k_a [Co^{3+}] \, [A]}{[H^+]} \qquad (8)$$

(the second term on R.H.S. corresponds to oxidation of alcohol)

$$R_p = \frac{k_p}{k_{t_2}} \left\{ k_{r1} + \frac{K_1 k_{r2}}{[H^+]} \right\} [M]^2 \qquad (9)$$

$$\text{`` } n \text{ ''} = \frac{k_p}{k_{t_2}} \cdot \frac{[M]}{[Co^{3+}]} . \qquad (10)$$

At medium [A], considering steps 1, 2, 4, 5 and 6 for polymerization and including oxidation of alcohol for rate of cobaltic ion disappearance.

$$- R_{co} = \left[k_{r1} + \frac{K_1 k_{r2}}{[H^+]} \right] [Co^{3+}] \, [M] + \frac{K_1 k_a [A] \, [Co^{3+}]}{[H^+]} \qquad (11)$$

$$R_p = \frac{k_p}{k_{t1}^{\frac{1}{2}}} \left[k_{r1} + \frac{K_1 k_{r2}}{[H^+]} \right]^{\frac{1}{2}} [Co^{3+}]^{\frac{1}{2}} \, [M]^{3/2} \qquad (12)$$

$$\text{`` } n \text{ ''} = \frac{k_p}{k_{t1}^{\frac{1}{2}}} \frac{[M]^{\frac{1}{2}}}{\left\{ \left[k_{r1} + \frac{K_1 k_{r2}}{[H^+]} \right] [Co^{3+}] \right\}^{\frac{1}{2}}} . \qquad (13)$$

At high [A] considering steps 3, 4, 5 and 6

$$- R_{co} = \frac{K_1 k_a [Co^{3+}] \, [A]}{[H^+]}$$

$$R_p = \frac{k_p}{k_{t1}^{\frac{1}{2}}} \frac{\{ K_1 k_a [Co^{3+}] \, [A] \}^{\frac{1}{2}} [M]}{[H^+]^{\frac{1}{2}}}$$

$$\text{`` } n \text{ ''} = \frac{k_p}{k_{t1}^{\frac{1}{2}}} \frac{[H^+]^{\frac{1}{2}} [M]}{\{ K_1 k_a [A] \, [Co^{3+}] \}^{\frac{1}{2}}} .$$

RATE CONSTANTS

(a) From slopes of plots of $- R_{co}$ vs. [M], the values of

$$\left[k_{r1} + \frac{K_1 k_{r2}}{[H^+]} \right]$$

under conditions of linear as well as mutual terminations have been evaluated.

(*b*) From initial slopes of the plots of $- R_{co}$ *vs.* [A], the rate constant $K_1 k_a$ for alcohol oxidation has been computed. From the intercept,

$$\left[k_{r1} + \frac{K_1 k_{r2}}{[H^+]} \right]$$

has been evaluated and found to agree well with that from (*a*).

(*c*) Values of $K_1 k_{r2}$ [M] $+ K_1 k_a$ [A] have been evaluated from slopes of plots of $- R_{co}$ *vs.* $1/[H^+]$ or $k_{obs.}$ *vs.* $1/[H^+]$. It is not possible to evaluate $K_1 k_{r2}$ from known values of $K_1 k_a$ [A], ($\approx 10^{-4}$), since the magnitude of $K_1 k_{r2}$ [M] is 10^{-6} and therefore insignificant compared to the value for the former. From intercepts on the ordinates of the plots at low [A] region, k_{r1} was calculated.

(*d*) From slopes of plots of R_p *vs.* $[M]^2$, R_p *vs.* $[M]^{3/2}$ and R_p *vs.* [M] after substitution of the appropriate quantities and constants, k_p/k_{t2}, $k_p/k_{t1}^{\frac{1}{2}}$ etc., values were computed.

(*e*) According to the conclusions drawn, slopes of plots of $- R_{co}$ *vs.* [Co^{3+}] should yield $K_1 k_a$ at high [A]. Values evaluated from these plots agree well with those from *b* and *c* thus supporting the conclusion that initiation is by radical from alcohol at high [A]. At lower [A], slopes of $- R_{co}$ *vs.* [Co^{3+}] yield either

$$\frac{K_1 k_a [A]}{[H^+]} + 2 \left\{ k_{r1} + \frac{K_1 k_{r2}}{[H^+]} \right\}$$

or the factor 2 being absent in the second term. The experimental and calculated values under these conditions are listed in Table I.

CONCLUSION

From the foregoing results and discussion it is evident that cobaltic ions are very powerful initiators of vinyl polymerization so that even in the presence of a reducing agent, the thermal polymerization occurs independently. The rate of initiation by Co^{3+} species is far greater than that by radicals from oxidation of alcohol. However, Co^{3+} + T.B.A. functions as a true red-ox system for polymerization when [A] $\gg$ [M].

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TABLE I

	Low [A] $< (20 \times 10^{-2} M)$	Medium [A] $(20–60) \times 10^{-2} M$	High [A] $> 60 \times 10^{-2} M$
$\left\{ k_{r1} + \dfrac{K_1 k_{r2}}{[H^+]} \right\} \times 10^4$	*6·945 at [A] : O M 5·530 6·870†	*6·048	..
$k_{r1} \times 10^4$	.. 5·654	..	..
$K_1 k_a \times 10^3$	.. 1·144[a]	1·144[a]	1·091[b] 1·114[c]
k_p/k_{t2}	.. 4·808	..	..
$k_p/k_{t1}^{\frac{1}{2}}$	..	·3823‡	0·1872‡
Composite slope $\times 10^4$ from—R_{co} vs. [Co³⁺] plots	1·760 (observed) 1·625 (calculated) at [A] : 8×10⁻² M & [M] : 9·353 × 10⁻² M	3·498 (observed) 2·877 (calculated) at [A] : 40×10⁻² M & [M] : 9·353 × 10⁻² M.	..

* from —R_{Co} vs. [M] plots.

† from intercepts of —R_{Co} vs. [A] plots.

‡ The disparity in values is probably due to occurrence of linear termination also, under conditions of medium [A], as well as initiation by $\overset{\cdot}{A}$ to some extent.

[a] from — R_{Co} vs. [A] plots.

[b] from — R_{Co} vs. [Co³⁺].

[c] from — R_{Co} vs. 1/[H]⁺ plots.

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