VINYL POLYMERIZATION

IV. Co\textsuperscript{3+}-Tert. butyl alcohol 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\textsuperscript{3+}], [H\textsuperscript{+}], etc. at constant ionic strength. From the experimental results it was concluded that at low [A], initiation and termination of polymerization was by Co\textsuperscript{3+} species. At higher [A], initiation was still by Co\textsuperscript{3+} species but termination was found to change over to mutual type. At very high [A], Co\textsuperscript{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\textsuperscript{4+} - 3, chloro 1-propanol\textsuperscript{1}, Ce\textsuperscript{4+}-ethylene glycol\textsuperscript{2} are examples of the latter type. Studies on initiation of vinyl polymerization by metal ions only, like Ce\textsuperscript{4+},\textsuperscript{3} Co\textsuperscript{3+},\textsuperscript{4} etc., confined solely to our laboratory have now been extended to include red-ox systems with Co\textsuperscript{3+} or Ce\textsuperscript{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\textsuperscript{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)
was used for the experiments. The details for purification of Methylmethacrylate (M.M.A.) (Rohm and Haas product) and preparation of cobaltic perchlorate, etc., are same as reported in the previous paper.²

(b) Polymerization and rate measurements.—Polymerization was conducted in long pyrex tube (8"×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 $15^\circ \pm 0.1^\circ$ 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, Co³⁺ 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 Fe²⁺. Rates of polymerization were followed by gravimetry (of weight of the polymer precipitated after arresting the reaction and addition of water) while Co³⁺ was estimated from the filtrates by means of back titration of unreacted Fe²⁺ with standard Ce⁴⁺ using Ferroin as indicator. Chainlengths of poly (methylmethacrylate) were determined viscometrically making use of the equation³

\[
"n" = 2.81 \times 10^3 [\eta]^{1.32}
\]

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

RESULTS AND DISCUSSION

The system Co³⁺–T.B.A. was found to be highly reactive and consequently experiments, using this system for polymerization, were carried out at $15^\circ$ C. at an acidity of 2M which facilitated convenient rate measurements. Polymerization was found to be very rapid at higher alcohol concentrations $[A] \geq 20 \times 10^{-2}$ 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 Co³⁺ species were consumed predominantly for oxidation of alcohol rather than of monomer leading to polymerization. The intercepts represent rates of oxidation of alcohol, the magnitude
of these intercepts being approximately equal to the blank rates (without monomer) under identical 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\textsuperscript{3+} (aq) system\textsuperscript{7} have shown the occurrence of these side reactions along with oxidation of monomer leading to polymerization.

![Graph showing effect of [M] on -R_co and effect of [Co\textsuperscript{3+}] on R_p.]

**Fig. 1.** Effect of [M] on -R_co and effect of [Co\textsuperscript{3+}] on R_p.

A–E Plots of -R_co vs. [M] at various [A] at [H\textsuperscript{+}]: 2·0 M; \( \mu \): 2·3 M and Temp. 15\textdegree{}C. A: [T.B.A.] = 0 × 10\textsuperscript{-4} M; [Co\textsuperscript{3+}]: 11·37 × 10\textsuperscript{-3} M; B: [T.B.A.]: 12 × 10\textsuperscript{-2} M [Co\textsuperscript{3+}]: 7·914 × 10\textsuperscript{-8} M; C: [T.B.A.]: 21 × 10\textsuperscript{-2} M, [Co\textsuperscript{3+}]: 11·37 × 10\textsuperscript{-8} M; D: [T.B.A.]: 30 × 10\textsuperscript{-2} M; [Co\textsuperscript{3+}]: 10·45 × 10\textsuperscript{-3} M and E: [T.B.A.]: 100 × 10\textsuperscript{-3} M; [Co\textsuperscript{3+}]: 11·45 × 10\textsuperscript{-3} M; F–I: Plots of R_p vs. [Co\textsuperscript{3+}]\textsuperscript{4} at [T.B.A.]: 100 × 10\textsuperscript{-2} M, 150 × 10\textsuperscript{-2} M, (40–80) × 10\textsuperscript{-2} M and 8 × 10\textsuperscript{-2} M respectively, all at [M]: 9·353 × 10\textsuperscript{-2} M, [H\textsuperscript{+}]: 2·0 M, \( \mu \): 2·3 M and temp. 15\textdegree{}C.

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

(iii) -R_co also varied directly as [A] (Fig. 2, E–G) with a break in linearity at [A] > 50 × 10\textsuperscript{-2} M. The decreased -R_co at higher [A] may be understood in terms of observation of Hoare and Waters\textsuperscript{8} who proposed a sequence of six steps for the mechanism of oxidation of T.B.A. by cobaltic perchlorate under conditions of [Co\textsuperscript{3+}] < [A]; the products being CH\textsubscript{3}OH, CH\textsubscript{2}, COCH\textsubscript{3}, HCHO and HCOOH, etc., and stoichiometry, \( \triangle \) Alcohol/
For $[A] \gg [\text{Co}^{3+}]$, 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 $-R_{\text{co}}$ vs. $[A]$ left intercepts on the ordinates (Fig. 2, E–G) which indicated the consumption of $\text{Co}^{3+}$ for oxidation of monomer leading to polymerization. A break in the linearity of the plot $-R_{\text{co}}$ vs. $[A]$ was observed at $[A] \approx 50 \times 10^{-2}$ M in the blank (absence of monomer) also; the blank plot left no intercept on the ordinate.

![Graph](image_url)

**Fig. 2.** Effect of $[\text{Co}^{3+}]$ and $[A]$ on $-R_{\text{co}}$. A–D plots of $-R_{\text{co}}$ vs. $[\text{Co}^{3+}]$ at $[M]$: 9.353 $\times 10^{-2}$ M; $[\text{H}^+]$: 2.0 M; $\mu = 2.3$ M; Temp. 15°C and T.B.A.: 8 $\times 10^{-2}$ M, 64 $\times 10^{-2}$ M, 80 $\times 10^{-2}$ M and 150 $\times 10^{-2}$ M respectively. E–G: Plots of $-R_{\text{co}}$ vs. $[A]$ at $[M]$: 9.353 $\times 10^{-2}$ M, $[\text{H}^+]$: 2.0 M, $\mu = 2.3$ M, Temp. 15°C and $[\text{Co}^{3+}]$: 10.3 $\times 10^{-2}$ M, 12.01 $\times 10^{-2}$ M and 6.325 $\times 10^{-2}$ M respectively.

(iv) An inverse dependence of $-R_{\text{co}}$ with $[\text{H}^+]$ (Fig. 3, A, B, E) was observed both in the higher as well as lower $[A]$ regions and plots of $-R_{\text{co}}$ vs. $[\text{H}^+]^{-1}$ (Fig. 3, A, B) or $k_{\text{obs}}$ vs. $1/[\text{H}^+]$ (Fig. 3, E) ($k_{\text{obs}}$ was obtained from slopes of plots of $-R_{\text{co}}$ vs. $[\text{Co}^{3+}]$ at fixed $[A]$ and $[M]$ but different $[\text{H}^+]$) 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 $\text{Co}^{3+}$ (aq) ions are one of the initiating species. However, our experiments on oxidation of T.B.A. by $\text{Co}^{3+}$ under identical conditions
as well as those of Waters et al.,\textsuperscript{10} have shown that the oxidation of alcohol consists only of an acid dependent path arising from the CoOH\textsuperscript{2+} species taking part in the reaction sequence. Hence, the linear portion of the plot of $- R_{co} \text{ vs. } 1/[H^+]$ may comprise of the rate constant due to alcohol oxidation and probably due to the reaction CoOH\textsuperscript{2+} + Monomer leading to polymerization of the latter.

![Graph showing the effect of $[H^+]$ on $R_p$ and $- \Delta R_{co}$ at $[M]$: \(9 \times 353 \times 10^{-8} M\); $\mu$: 2.3 M, Temp. 15\(^\circ\) C. A and B: $- R_{co} \text{ vs. } 1/[H^+]$ at [T.B.A.]: 54x10\textsuperscript{-8} M, [Co\textsuperscript{2+}]: 15-02x10\textsuperscript{-8} M. B: [T.B.A.]: 9x10\textsuperscript{-8} M, [Co\textsuperscript{2+}]: 9-73x10\textsuperscript{-8} M. C and D: $R_p$ vs. 1/[H\textsuperscript{+}] and $R_{co}$ vs. 1/[H\textsuperscript{+}] respectively, conditions same as B and A respectively. E: $k_{obs}$ vs. 1/[H\textsuperscript{+}] at [T.B.A.]: 21x10\textsuperscript{-8} M.](image)

**(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] < 20x10\textsuperscript{-8} M, a strict square dependence of $R_p$ on [M]\textsuperscript{2} was realized (Fig. 4, A) which showed the occurrence of linear termination. At [A] = 20x10\textsuperscript{-8} M — 60x10\textsuperscript{-8} M, $R_p$ varied as [M]\textsuperscript{3/4} (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\textsuperscript{2+} reaction and consequent depletion of the latter for linear termination. At still higher [A], > 60x10\textsuperscript{-8} 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 \( [\text{Co}^{3+}] \) (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. \( (\text{Co}^{3+})^4 \) were linear (Fig. 1, F–H) with intercepts on the ordinates, the magnitudes of the intercepts being appreciable at \([A] = 40–80 \times 10^{-2} \) M and decreasing for \([A] = 100–150 \times 10^{-2} \) M. The half power dependence of \( R_p \) on \([\text{Co}^{3+}]^4 \) clearly indicates the mutual type of termination, irrespective of the mode of initiation, *i.e.*, by \( \text{Co}^{3+} \) species and or radicals derived from alcohol. If the intercepts on the Y-axis of the \( R_p \) vs. \([\text{Co}^{3+}]^4 \) 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 \([\text{Co}^{3+}]\), a strict 3/2 order for \([M]\) with \( R_p \) at \([A] = 20–60 \times 10^{-2} \) M and a first order at \([A] > 60 \times 10^{-2} \) M indicate the occurrence of mutual termination under conditions of predominant initiation by \( \text{Co}^{3+} \) 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 \( \text{Co}^{3+} \) 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. \([A]^4 \) (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 \( \text{Co}^{3+} + \text{T.B.A.} \) reaction and consequent depletion of \( \text{Co}^{3+} \) 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 \([A]\).
A: $R_p$ vs. $[M]$ at low $[A]$.  B: $R_p$ vs. $[M]^{0.5}$ at $[A]: 2.1 \times 10^{-3}$ M and $[Co^{3+}]: 11.37 \times 10^{-8}$ M.  
C, D: $R_p$ vs. $[M]$ at $[A]: 100 \times 10^{-8}$ M and $44 \times 10^{-8}$ M and $[Co^{3+}]: 11.45 \times 10^{-8}$ M and $13.17 \times 10^{-8}$ M respectively.  E, F: $R_p$ vs. $[A]$ at $[Co^{3+}]: 12.01 \times 10^{-8}$ M and $6.325 \times 10^{-8}$ M respectively and $[MJ]: 9.353 \times 10^{-8}$ 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$^{3+}$ species. The linear portion is due to initiation by CoOH$^{3+}$ 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 $1/[H^+]^{1/2}$ (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 $[A] < 20 \times 10^{-8}$ 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$^{3+}$ species and termination by Co$^{3+}$ ions.
Vinyl Polymerization—IV

REACTION SCHEME

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

Radical Production:

\[
\begin{align*}
\text{Co}^{3+} + M & \xrightarrow{k_{r1}} \dot{R} + \text{Co}^{2+} \\
\text{CoOH}^{3+} + M & \xrightarrow{k_{r2}} \text{Co}^{2+} + \text{OH}^- + \dot{R}
\end{align*}
\]

if

\[
\begin{align*}
\text{Co}^{3+} + \text{H}_2\text{O} & \xleftarrow{K_1} \text{CoOH}^{3+} + \text{H}^+ \\
\text{CoOH}^{3+} & \xrightarrow{k_a} \dot{A} + \text{Co}^{2+} + \text{OH}^- \\
\dot{A} + M & \xrightarrow{k_{r3}} \dot{R}
\end{align*}
\]

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

Initiation:

\[
\dot{R} + M \xrightarrow{k_i} R - M
\]

Propagation:

\[
\begin{align*}
R - \dot{M} + M & \xrightarrow{k_p} R - M - \dot{M} \\
R - M - \dot{M} + M & \xrightarrow{k_p} R - M - M - \dot{M} \text{ and so on.}
\end{align*}
\]

Termination:

Mutual;

\[
R - M_n^* + R - M_m^* \xrightarrow{k_{t1}} R - M_{m+n} - R
\]

Linear;

\[
R - M_n^* + \text{Co}^{3+} \xrightarrow{k_{t2}} P + \text{Co}^{2+} + \text{H}^+.
\]

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,

\[ -R_{co} = 2 \left[ k_{r1} + \frac{K_1 k_{r2}}{[H^+]} \right] [Co^{3+}] [M] + \frac{K_2 k_d [Co^{3+}] [A]}{[H^+]} \]  

(8)

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

\[ R_p = \frac{k_p}{k_{t2}} \left\{ k_{r1} + \frac{K_1 k_{r2}}{[H^+]} \right\} [M]^2 \]  

(9)

\[ "n" = \frac{k_p}{k_{t2}} \cdot \frac{[M]}{[Co^{3+}]} \]  

(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.

\[ -R_{co} = \left[ k_{r1} + \frac{K_1 k_{r2}}{[H^+]} \right] [Co^{3+}] [M] + \frac{K_2 k_d [A] [Co^{3+}]}{[H^+]} \]  

(11)

\[ R_p = \frac{k_p}{k_{t1}^{\frac{1}{2}}} \left[ k_{r1} + \frac{K_1 k_{r2}}{[H^+]} \right]^{\frac{1}{2}} [Co^{3+}]^{\frac{1}{2}} [M]^{\frac{3}{2}} \]  

(12)

\[ "n" = \frac{k_p}{k_{t1}^{\frac{1}{2}}} \cdot \frac{[M]^{\frac{1}{2}}}{\left\{ k_{r1} + \frac{K_1 k_{r2}}{[H^+]} [Co^{3+}] \right\}^{\frac{1}{2}}} \]  

(13)

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

\[ -R_{co} = \frac{K_2 k_d [Co^{3+}] [A]}{[H^+]} \]  

\[ R_p = \frac{k_p}{k_{t1}^{\frac{1}{4}}} \left\{ K_2 k_d [Co^{3+}] [A] \right\}^{\frac{1}{2}} [M]^{\frac{1}{2}} \]  

\[ "n" = \frac{k_p}{k_{t1}^{\frac{1}{4}}} \cdot \frac{[H^+]}{\left\{ K_2 k_d [A] [Co^{3+}] \right\}^{\frac{1}{2}}} \]  

(RATE CONSTANTS)

(a) From slopes of plots of \(-R_{co}\) vs. [M], the values of \(k_{r1} + \frac{K_1 k_{r2}}{[H^+]}\) under conditions of linear as well as mutual terminations have been evaluated.
(b) From initial slopes of the plots of \( -R_c \) vs. [A], the rate constant \( k_1k_a \) for alcohol oxidation has been computed. From the intercept,

\[
\left[ k_{r1} + \frac{K_1k_{r2}}{[H^+]} \right]
\]

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

(c) Values of \( K_1k_{r2} [M] + K_1k_a [A] \) have been evaluated from slopes of plots of \( -R_c \) vs. \( 1/[H^+] \) or \( k_{obs} \) vs. \( 1/[H^+] \). It is not possible to evaluate \( K_1k_{r2} \) from known values of \( K_1k_a [A] \), \(( \approx 10^{-4} \)\), since the magnitude of \( K_1k_{r2} [M] \) 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, \( k_p/k_{15} \), \( k_p/k_{13} \), etc., values were computed.

(e) According to the conclusions drawn, slopes of plots of \( -R_c \) vs. [Co^{3+}] should yield \( K_1k_a \) 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 \( -R_c \) vs. [Co^{3+}] yield either

\[
\frac{K_1k_a[A]}{[H^+]} + 2 \left( k_{r1} + \frac{K_1k_{r2}}{[H^+]} \right)
\]

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].
K. JIREE AND M. SANTAPPA

**Table I**

<table>
<thead>
<tr>
<th>Low [A] ( &lt; (20 \times 10^{-2} \text{ M}) )</th>
<th>Medium [A] ( (20-60) \times 10^{-2} \text{ M} )</th>
<th>High [A] ( &gt; 60 \times 10^{-2} \text{ M} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \left{ k_{r1} + \frac{K_{1}k_{r2}}{[H^+]^{2}} \right} \times 10^{4} ) *6·945 at [A]: O M *6·048</td>
<td>( 5·530 )</td>
<td>( 6·870 ) †</td>
</tr>
<tr>
<td>( k_{r1} \times 10^{4} )</td>
<td>( 5·654 )</td>
<td>( \ldots )</td>
</tr>
<tr>
<td>( K_{1}k_{a} \times 10^{3} )</td>
<td>( 1·144^{(a)} )</td>
<td>( 1·144^{(a)} )</td>
</tr>
<tr>
<td>( k_p/k_{t2} )</td>
<td>( 4·308 )</td>
<td>( \ldots )</td>
</tr>
<tr>
<td>( k_p/k_{t1,2} )</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
</tr>
<tr>
<td>Composite slope ( \times 10^{4} )</td>
<td>1·760 (observed)</td>
<td>3·498 (observed)</td>
</tr>
<tr>
<td>from—Rc0 vs. [Co³⁺] plots</td>
<td>( 1·625 ) (calculated)</td>
<td>( 2·877 ) (calculated)</td>
</tr>
<tr>
<td>at [A]: ( 8 \times 10^{-2} )</td>
<td>at [A]: ( 40 \times 10^{-2} )</td>
<td>( M + [M]: 9·353 )</td>
</tr>
<tr>
<td>( M + [M]: 9·353 \times 10^{-2} \text{ M} )</td>
<td>( M + [M]: 9·353 \times 10^{-2} \text{ M} )</td>
<td></td>
</tr>
</tbody>
</table>

\* from —Rc0 vs. [M] plots.
† from intercepts of —Rc0 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 A to some extent.

\( ^{(a)} \) from —Rc0 vs. [A] plots.
\( ^{(b)} \) from —Rc0 vs. [Co³⁺].
\( ^{(c)} \) from —Rc0 vs. 1/[H⁺] plots.

**References**


S. and Evans, M. G.


W. A.


W. A.