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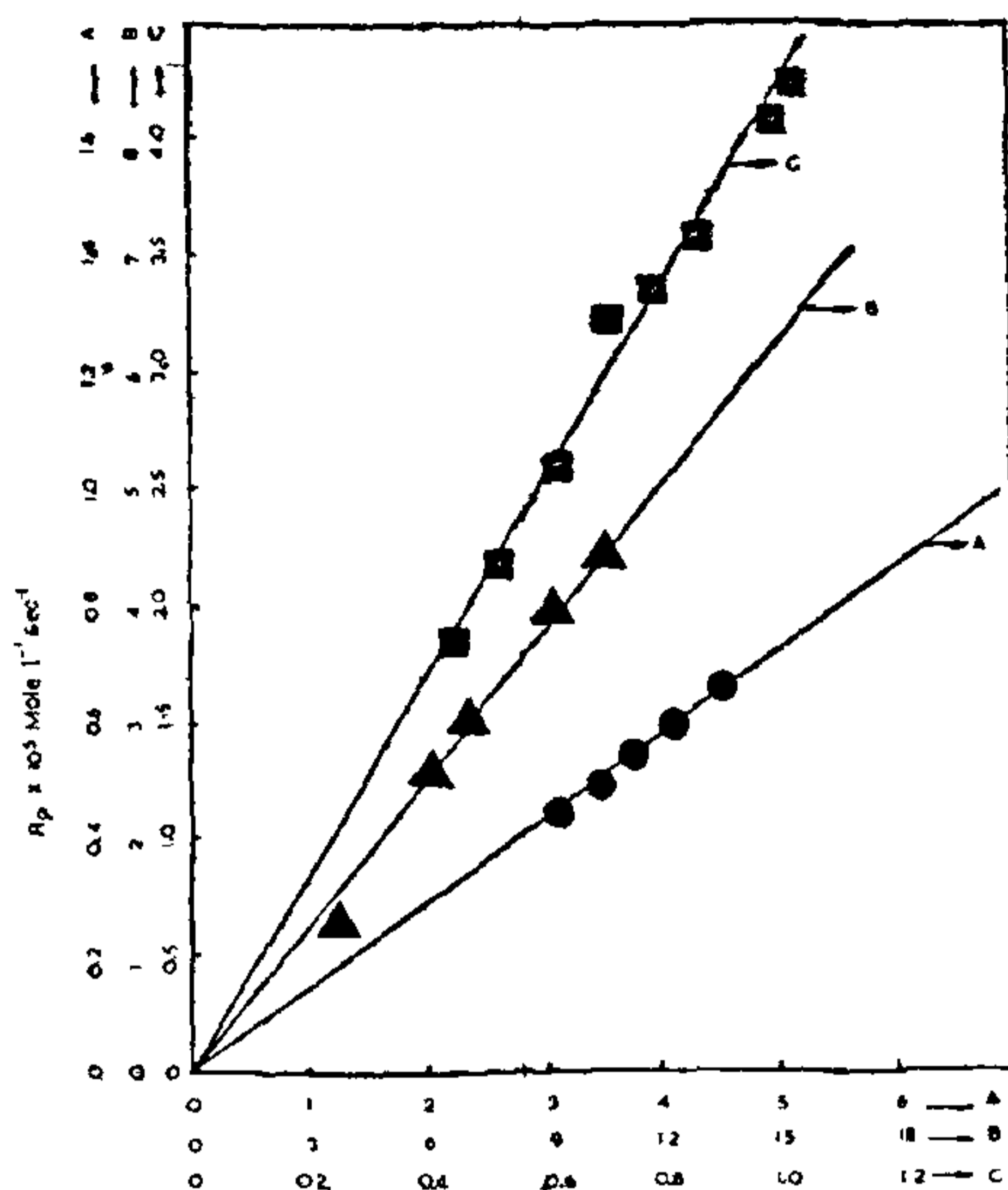
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CERIUM(IV)-BENZYL ALCOHOL REDOX SYSTEM FOR ACRYLONITRILE POLYMERIZATION

NUMEROUS reducing agents like alcohols¹, aldehydes^{2,3} acids⁴ have been used in combination with Ce(IV) for aqueous vinyl polymerization. In all these systems, the primary initiation species is the radical produced from the substrate by oxidation with Ce(IV). Literature survey on vinyl polymerization reveals that benzyl alcohol has not been used as a reducing agent in combination with Ce(IV) for vinyl polymerization. The oxidation⁵⁻⁷ of benzyl alcohol by Ce(IV) has been shown to proceed through the formation of intermediate radical $C_6H_5CH_2O\cdot$ which subsequently decomposes to give the product benzaldehyde. In this communication we report the studies on thermal polymerization of acrylonitrile (AN) at 20° C in nitric acid medium by the redox system Ce(IV)-benzyl alcohol (BA).

The polymerization experiments were conducted in the dark under deaerated conditions at constant pH (pH=1.7) and ionic strength, $\mu = 0.2$ M. The [ANt] was varied from 0.45 to 1.05 M [Ce(IV)] from 1×10^{-4} to 1×10^{-3} M, [BA] from 2×10^{-4} to 2×10^{-3} M. The rate of polymerization was followed gravimetrically and that of Ce(IV) disappearance by titrimetry.

The following are some of the salient features of the polymerization reaction. The steady state was attained in about 15 minutes. The rate of polymerization (R_p) was directly proportional to [AN] and to the square roots of [Ce(IV)] and [BA] (Fig. 1). The first order dependence of R_p on [AN] observed here, is a rare occurrence since orders 1.5 and 2 were reported for Ce(IV) initiated vinyl polymerization reactions¹⁻⁴. $-R_{Ce(IV)}$, namely the rate of Ce(IV) disappearance, was individually proportional to first powers of [Ce(IV)] and [BA]. There was no polymerization in

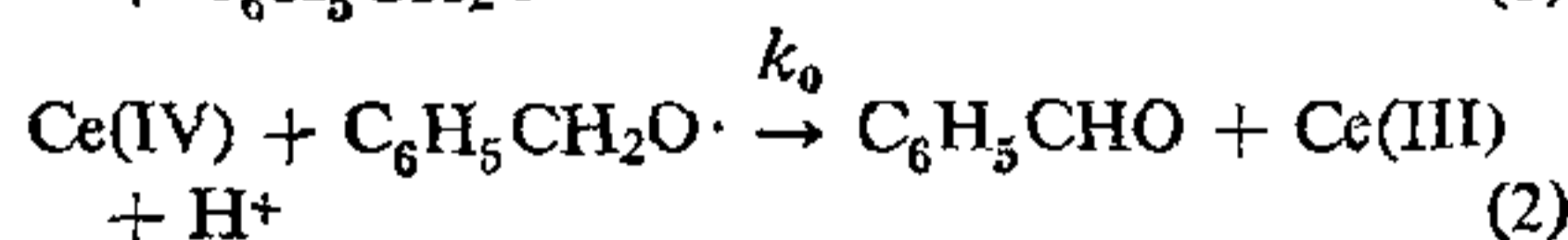
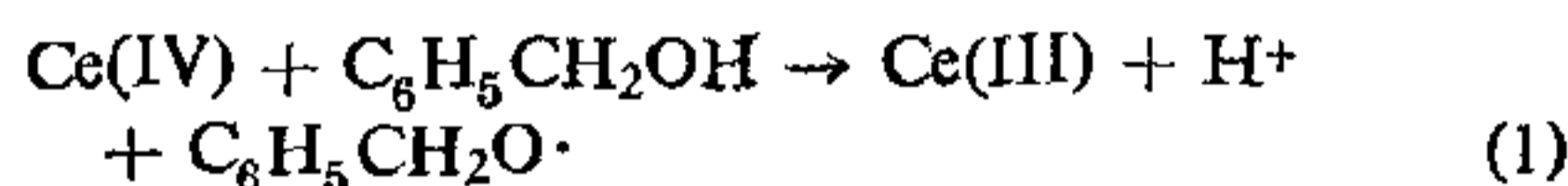


$$A = [BA]^{0.5} (\text{Mole. l}^{-1})^{0.5} \times 10^2; \quad B = [Ce(IV)]^{0.5} (\text{Mole. l}^{-1})^{0.5} \times 10^2; \quad C = [AN] (\text{Mole. l}^{-1})$$

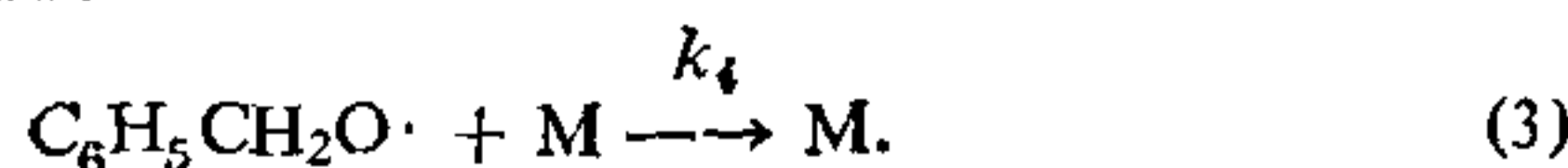
FIG. 1. Plots of rates of polymerization against (A) square root of benzyl alcohol concentration, (B) square root of ceric ion concentration, (C) acrylonitrile concentration.

the absence of benzyl alcohol under the present experimental conditions.

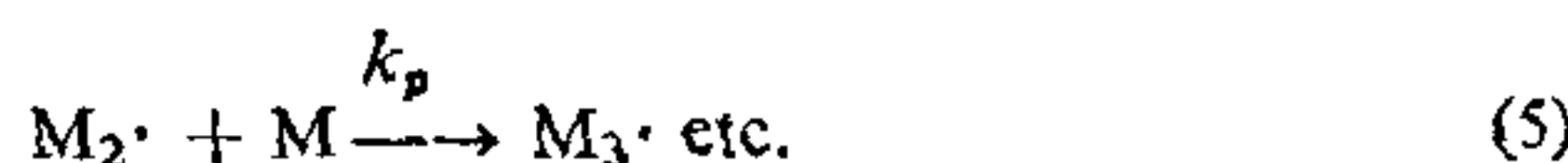
Our results lead to the following conclusions: 1. Under the present experimental conditions, namely 20° C, oxidation of water by Ce(IV) producing $OH\cdot$ and the initiation of vinyl polymerization by Ce(IV) do not occur. 2. The reaction $Ce(IV) +$ benzyl alcohol produces the free radical $C_6H_5CH_2O\cdot$ which may partly be oxidised by Ce(IV) to give the products (eqn. 2).



and partly reacts with the monomer initiating polymerization.



This is followed by the usual propagation steps.



The growing polymer chains get terminated by the mutual annihilation of polymer radicals as evidenced by the dependence of rate of polymerization over square roots of [Ce(IV)] and [BA].



Mutual type of termination proposed by us seems to be a rate occurrence since in most cases termination of polymer radical by Ce(IV) was reported to be predominant^{1, 2, 8}. Similar mutual type combination of polymer chains was observed in the case of Ce(IV)-malonic acid initiated polymerization of methyl acrylate⁴ and also Ce(IV)-acetaldehyde initiated polymerization of acrylonitrile³. Termination by Ce(IV) in our case would give a kinetic dependence of [AN]², [BA] and [Ce(IV)]⁻¹ on R_p and hence inconsistent with our observed results.

Assuming the stationary state kinetics for free radicals and under the conditions $k_t [AN] \gg k_0 [Ce(IV)]$, the following rate expressions are derived:

$$R_p = k_p/k_t^{1/2} [AN] [Ce(IV)]^{1/2} [BA]^{1/2} \quad (I)$$

$$-R_{Ce(IV)} = k_r [Ce(IV)] [BA] \quad (II)$$

The overall activation energy was evaluated as 13.25 K.cals mole⁻¹, which is of the same order as that obtained for Ce(IV)-acetaldehyde initiated polymerization of acrylonitrile³. The second order rate constant $k_p/k_t^{1/2}$, evaluated from plots of $-R_{Ce(IV)}$ against [Ce(IV)] and [BA] agreed well and was equal to 7.5 lit. mole⁻¹ sec⁻¹. The value of the rate constant $k_p/k_t^{1/2}$ was evaluated as 0.0113 lit^{-1/2}. mole^{1/2}. sec^{-1/2} which compares well with that reported in the literature for acrylonitrile polymerization^{3, 8-10}.

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HEXAAQUOCOBLTIC ION AS THE ACTIVE SPECIES OF Co(III)

STUDIES involving Co(III)^{1,2} indicate that the hydroxopentaaquocobaltic ion is more active than the hexaaquocobaltic ion. The general explanation¹ offered to this point, is the greater ease of conversion of Co(III) from the low spin form ($t_{2g}^5 e_g^1$) in the case of [Co(OH)(H₂O)₅]²⁺ since a preliminary or subsequent step involving purely a multiplicity change should be considered in reactions involving Co(III) besides the normal rate-determining step in any oxidation reaction. Actually, evidence for spin-state conversion has been provided in a very fast reaction, namely the oxidation of Fe²⁺(aq.) by Co(III)³. But a careful analysis of oxidations by Co(III) indicates that there are certain reactions wherein Co(H₂O)₆³⁺ is the only active species of Co(III). A striking feature of these reactions is that all of them occur by bonded mechanism.

Even though Co(III) has a very high redox potential⁴ capable of oxidising the substrate by non-bonded mechanism, the lability of the complex, Co(H₂O)₆³⁺ is in favour of a bonded mechanism. But the chemistry of Co(III) is not rich in evidence for complex formation preceding electron transfer from substrate to Co(III) unlike the other one-electron oxidants, V(V)¹ and Ce(IV)⁵. Of the very large number of oxidations investigated with Co(III), only a few reactions exhibited evidence for complex formation and it is indeed surprising that Co(H₂O)₆³⁺ is the active oxidant in all these instances. These reactions are summarised in Table I.

In all the reactions summarized in Table I, only Co(H₂O)₆³⁺ has been the active species and the rate laws correspond to

$$\frac{1}{k} = \frac{1}{k_t} + \frac{(H^+)}{k_t K (\text{substrate})} \quad (1)$$

and/or

$$\frac{1}{k} = \frac{1}{k_t} + \frac{1}{k_t K (\text{substrate})} \quad (2)$$

where k is the pseudo-first-order rate constant, k_t is the rate constant for the disproportionation of the complex and K is equilibrium constant for complex formation. On the contrary, [Co(OH)(H₂O)₅]²⁺ as the active oxidant yielding the rate law,

$$\frac{1}{k} = \frac{(H^+)}{k_t K_1} + \frac{(H^+)}{k_t K_1 K (\text{substrate})} \quad (3)$$