Aqueous Polymerization of Acrylonitrile by Ce(IV) – Diacetone Alcohol Redox System

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Introduction

In the oxidation of diacetone alcohol (DAA) by Co(III) in aqueous perchloric acid medium, Santappa et al.(5) assumed the formation of 1:1 complex between the substrate and oxidant prior to oxidation to a radical and acetone. DAA–Mn(III) redox system has been used as an initiator for the polymerization of acrylonitrile (2). Various reducing agents such as alcohols (4,8) aldehydes (9,1) malonic acid (11) acetophenone(7) etc., have been used in combination with Ce(IV) for aqueous polymerization in which primary initiating species is the radical produced by the oxidation of the substrate. In this work we report some of our results on the oxidation of DAA by Ce(IV) in the dilute H_2SO_4 medium and the polymerization of acrylonitrile (AN) initiated by the Ce(IV)–DAA redox system at 45°C in order to understand i) the mechanism of oxidation ii) the nature of initiating radical and iii) mode of termination in the polymerization.

Experimental

All the chemicals used in this work were of the BDH (Analar) grade. The monomer was purified by distilling at low pressure under nitrogen atmosphere. The method adopted for following the rates of oxidation of DAA in the absence of monomer was the same as reported for other substrates (6).

The polymerization experiments were conducted in the dark under deaerated conditions, at constant ionic strength. The [AN] was varied from 0.3 to 0.9 M, [Ce(IV)] from 2×10^{-3} to 8×10^{-3} M, [DAA] from 2×10^{-2} to 8×10^{-2} M. The rate of polymerization was followed gravimetrically and that of Ce(IV) disappearance titrimetrically. Determination of chain lengths (n) of poly (Acrylonitrile) (0.1% solution in dimethylformamide) was carried out viscometrically. The relevant Mark-Houwink equation due to Stockmeyer and Cleland (10)

used was

$$[\eta] = 2.43 \times 10^{-4}[M_v]^{0.75} \text{ at } 25°C$$

where $[\eta]$ = intrinsic viscocity and$[M_v]$ = viscocity average molecular weight.
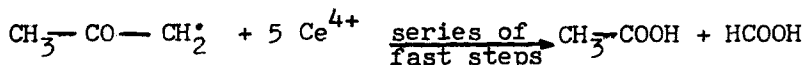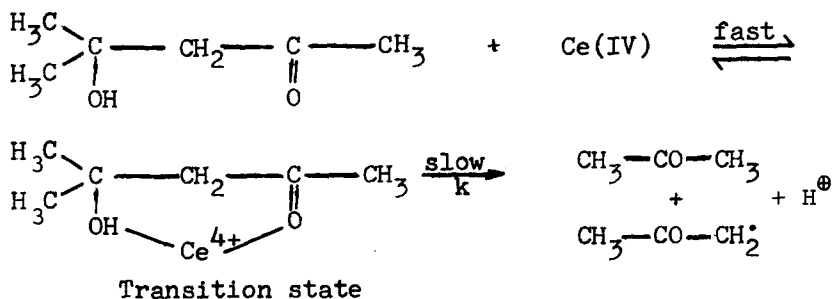
Results and discussion

Oxidation

The kinetics of oxidation of DAA by Ce(IV) in sulphuric acid medium showed the following features. The rate of oxidation was proportional to the first power of$[Ce(IV)]$and first power of$[DAA]$giving an overall order of two (fig. 1 A,B). The stoichiometry of the reaction was 6 moles of Ce(IV) to one mole of DAA and the reaction products as identified by the TLC were acetone, acetic acid and formic acid. The rate of oxidation decreased with increase in$[H^+]$when the ionic strength was not constant. But at constant ionic strength the rates increased considerably with increase in$[H^+]$. For example under the conditions viz.$[Ce(IV)]$= 0.003 M,$[DAA]$= 0.05 M, temp. = 45°C, the rate constant values (k x 10^3 min.$^{-1}$) at$[H^+]$=1.00, 2.00, 2.50, 3.00 M are 0.153, 2.687, 4.722, 6.010 respectively. At constant$[H^+]$increase in$[HSO_4^-]$decreased the rate constant value (k x 10^3 min.$^{-1}$) from 0.422 at$[HSO_4^-]$= 1.0 to 0.23 at$[HSO_4^-]$= 2.40 M.

The fact that there was no complex formation in sulphuric acid medium between the substrate and oxidant and the inhibition due to HSO_4 shows that the reactive species is $Ce(SO_4)_2$. This is also in accordance with the observation of previous workers in the oxidation of alcohols and other substrates by Ce(IV) (3,6).

Since no complex formation is observed, we assume the course of the reaction to be as follows:

Transition state

$$CH_3-CO-CH_2^{\cdot} + 5 Ce^{4+} \xrightarrow[\text{fast steps}]{\text{series of}} CH_3-COOH + HCOOH$$

The inhibition by added sulphuric acid or bisul-
phate could be due to the removal of the reactive spe-
cies as

$$Ce\ (SO_4)_2 + HSO_4^- \rightleftharpoons HCe\ (SO_4)_3^-$$
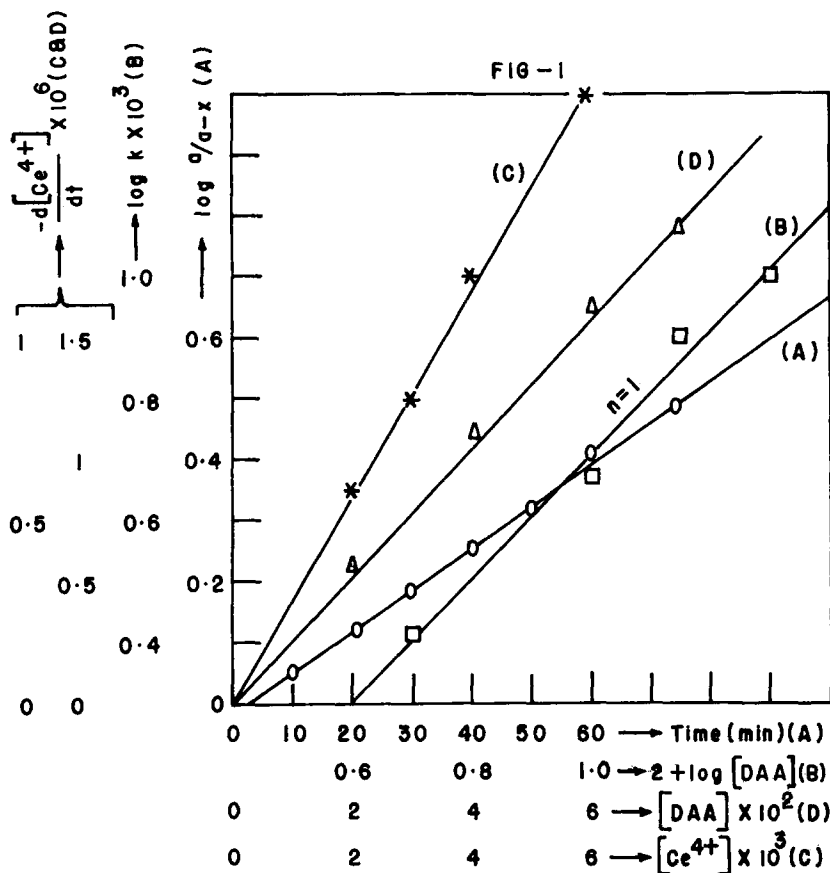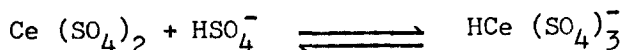
Fig. 1(A) Plot of time Vs log a/a-x ;[Ce(IV)]x 10^3 =
3.00 M; [DAA] x 10^2 = 5.00 M;[H$^+$]= 1.00 M
temp. 45°C.

1(B) Plot of 2 + log k Vs 2 + log [DAA]; Other
conditions are same as above.

1(C) Plot of [Ce(IV)] x 10^3 Vs -R$_{Ce(IV)}$ x 10^6;
[Ce(IV)]x 10^3 = 2.00 to 8.00 M ;[DAA]x 10^2 =
5.00 M; [M]= 0.60 ;[H$^+$]= 1.25 M; temp.=45°C

1(D) Plot of[DAA]x 10^2 Vs -R$_{Ce(IV)}$ x 10^6 other
conditions are same as in 1(C).

The accelerating effect of the hydrogen ions when the ionic strength was constant, can be explained by assuming the following equilibria.

$$Ce\ (SO_4)_2 \quad \rightleftharpoons \quad Ce\ (SO_4)^{2+} + SO_4^{2-}$$

$$Ce\ (SO_4)^{2+} + H_2O \quad \rightleftharpoons \quad Ce\ (OH)\ (SO_4)^+ + H^+$$
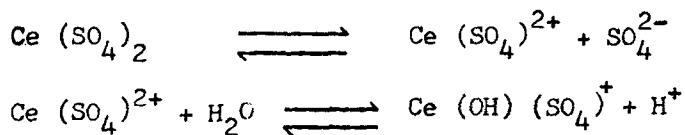
considering all the above equilibria the rate law comes out to be

$$- \frac{d\,[Ce^{4+}]}{dt} = \frac{k[Ce^{4+}][DAA]}{[H_2\,SO_4]}$$

which explains well all the kinetic data obtained.

Polymerization

Above study on Ce(IV) oxidation of DAA indicates that oxidation proceeds through a free radical mechanism. Evidence for the free radical intermediate has been provided by the induced polymerization of acrylonitrile. In the absence of DAA the polymerization was extremely slow. The nature of the initiating radical has been confirmed by infra-red spectrum of poly (acrylonitrile) formed which showed the typical absorption peak of the $>C = O$ group at 1712 cm^{-1}.

Rate dependence on [DAA]

The rate of polymerization increased with increase in[DAA]. This is attributed to the greater yield of the initiating radicals by increasing the concentration of DAA. Linear plot of log R_p against log [DAA]with slope of 0.5 (fig.2A) indicated that the order with respect to [DAA] to be 0.5. Plot of $-R_{Ce(IV)}$ Vs [DAA] was also linear as expected (fig.1D).

Rate dependence on[Ce(IV)]

The rate of polymerization was found to be proportional to[Ce(IV)]$^{0.5}$ as can be seen from the slope of the plot of log R_p Vs log [Ce(IV)] (fig.2B). Such an observation can be explained by considering the termination mechanism to be of mutual type. Several instances are known where linear termination by Ce(IV) was also proposed by previous workers(8). In the present work, the R_p instead of decreasing with increase in [Ce(IV)]increased progressively, and this observation certainly rules out the possibility of linear termination.

The first order dependence of rate of ceric dis-
appearance on[Ce(IV)]was clear from the linear plot of
-$R_{Ce(IV)}$ Vs[Ce(IV)] passing through the origin (fig.1C).

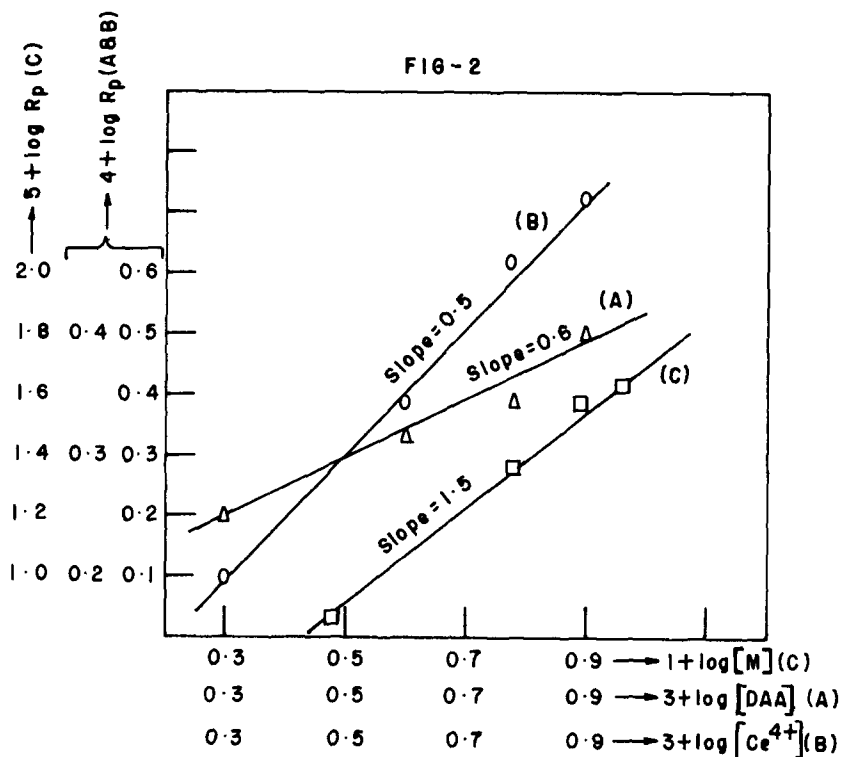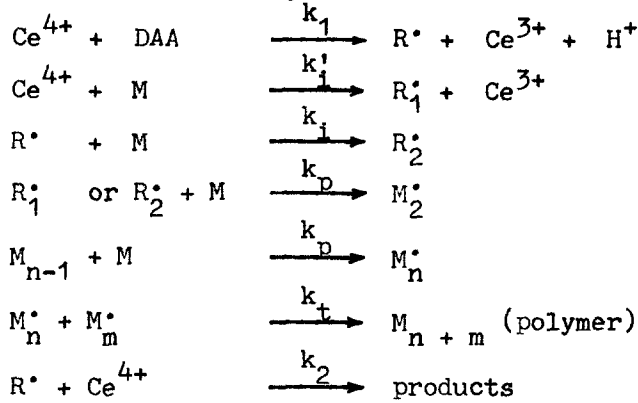Fig.2A Plot of 2 + log [DAA]Vs 4 + log R_p;
[Ce(IV)]x 10^3 = 5.00 M; [M]= 0.65 M ;[H+]=1.25 M
temp. = 45°C; (B) Plot of 3 + log[Ce(IV)]Vs
4 + logR_p other conditions are same as above.
(C) Plot of 1 + log[M] Vs 5 + logR_p; other con-
ditions are same as above.

Rate dependence on [Monomer]

The rate of polymerization increased progressively
with increase in [M] and the plot of logR_p Vs log[M]was
linear with a slope of 1.5 indicating the order with
respect to[M]to be 1.5 (fig.2C).

The increase in monomer concentration did not prod-
uce appreciable effect on the rate of ceric disappear-
ance. The effect of[H+] at constant ionic strength
and[HSO4]were the same as in the absence of monomer.

From the above results the following mechanism may be proposed for the polymerization.

$$Ce^{4+} + DAA \xrightarrow{k_1} R^{\bullet} + Ce^{3+} + H^{+}$$

$$Ce^{4+} + M \xrightarrow{k_i'} R_1^{\bullet} + Ce^{3+}$$

$$R^{\bullet} + M \xrightarrow{k_i} R_2^{\bullet}$$

$$R_1^{\bullet} \text{ or } R_2^{\bullet} + M \xrightarrow{k_p} M_2^{\bullet}$$

$$M_{n-1} + M \xrightarrow{k_p} M_n^{\bullet}$$

$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow{k_t} M_{n+m} \quad \text{(polymer)}$$

$$R^{\bullet} + Ce^{4+} \xrightarrow{k_2} \text{products}$$

where $R^{\bullet}$ is the radical $CH_3 - CO - CH_2^{\bullet}$ derived from the DAA during oxidation and M represents monomer molecule.

Applying steady state principle we can arrive at the following rate expression for the rate of polymerization

$$R_p = \frac{k_p[M]^{3/2}[Ce^{4+}]^{\frac{1}{2}}}{k_t^{\frac{1}{2}}} \left(\frac{k_i k_1 [DAA]}{k_2[Ce^{4+}] + k_i[M]} + k_i' \right)^{\frac{1}{2}}$$

and for the ceric disappearance the expression is

$$- \frac{d[Ce^{4+}]}{dt} = [Ce^{4+}]\left(k_1 [DAA] + k_i' [M]\right)$$

Neglecting the small contribution of Ce(IV) to the polymerization i.e. k_i' term, the expression for chain lengths can be written as

$$n = \frac{k_p [M]^{\frac{1}{2}}}{k_t^{\frac{1}{2}}} \left(\frac{k_2[Ce^{4+}] + k_i[M]}{k_i k_1 [Ce^{4+}] [DAA]} \right)^{\frac{1}{2}}$$

The chain lengths of the polymers were found to decrease with increasing concentration of both Ce(IV) and DAA (Table - 1A,B). This is attributed to increase in radical concentration which prevents increase of the chain length. Increase in monomer concentration increases the chain length of the polymer (Table - 1C). All these results are in confirmity with the above expression for chain lengths.

TABLE - 1

Effect of [Ce^{4+}], [DAA] and [M] on chain lengths

A) Effect of [Ce^{4+}] on chain length:

[Ce^{4+}] x 10^3 mol. lit^{-1}	2.00	4.00	6.00	8.00
Chain length x 10^{-3}	5.264	4.109	3.452	3.031

B) Effect of [DAA] on chain length:

[DAA] x 10^2 mol. lit^{-1}	2.00	4.00	6.00	8.00
Chain length x 10^{-3}	7.071	3.999	2.042	0.366

C) Effect of [M] on chain length:

[M] x 10 mol. lit^{-1}	3.041	6.083	7.600	9.120
Chain length x 10^{-3}	0.366	3.770	5.745	8.431

The value of the composite constants i.e. $k_p^2 k_1/k_t$ and k_2/k_i were evaluated from the expression for R_p by plotting $[M]^2/R_p^2$ Vs $1/[M]$. Neglecting the k_i term and squaring and taking reciprocal of the equation for R_p we get

$$\frac{[M]^2}{R_p^2} = \frac{k_t k_2}{k_1 k_i k_p^2 [M][DAA]} + \frac{k_t}{k_1 k_p^2 [Ce^{4+}][DAA]}$$

from which $k_p^2 k_1/k_t$ value was obtained from reciprocal of the product of intercept x [Ce(IV)] x [DAA] and k_2/k_i value was obtained from (slope/intercept) x [Ce(IV)].

Abstract

The kinetics of oxidation of DAA by Ce(IV) in dilute sulphuric acid medium has been studied and the reaction was found to obey a second order rate law. This DAA - Ce(IV) redox system has been used for the polymerization of acrylonitrile and the rate of polymerization was found to be proportional to [Ce(IV)]$^{0.5}$, [DAA]$^{0.5}$ and [M]$^{1.5}$. Based on these results a probable mechanism for initiation and termination has been proposed. The chain lengths of the polymers were found to increase with [M] and decrease with both [Ce(IV)] and [DAA].

References

1. K.AHMED RIAZ, L.V.NATARAJAN, and Q.ANWARUDDIN:
   Makromol. Chem., 179, 1193 (1978)
2. N.GANGADEVI and V.MAHADEVAN: Curr.Sci., 39,
   37 (1970)
3. T.J.HARDWICK and E.ROBERTSON: Can.J.Chem., 29,
   818, 828 (1951)
4. A.A.KATAI, V.K.KULSHRESTHA, and R.H.MARCHISSAULT:
   J.Polym.Sci., Part-C No.2, 403 (1963)
5. A.MEENAKSHI, and M.SANTAPPA: Indian J.Chemistry,
   8, 467 (1970)
6. S.S.MUHAMMAD, and B.SETHURAM: Acta. Chem.Hung.,
   46, 115 (1965)
7. ROUT ANURADHA, R.P.SWOYAM, M.NIGAMANANDA,
   SINGH BAISHNAB, and M.SANTAPPA: J.Polym.Sci.,
   16, 391 (1978)
8. K.SAJJAD, Q.ANWARUDDIN and L.V.NATARAJAN: Curr.
   Sci., 48, 156 (1979)
9. M.SANTAPPA and V.S.ANANTHANARAYAN: Proc.Indian
   Acad.Sci., A62, 150 (1965)
10. W.H.STOCKMAYER and R.C.CLELAND: J.Polym.Sci.,
    17, 473 (1955)
11. S.V.SUBRAMANIAN and M.SANTAPPA: Curr.Sci.,
    35, 437 (1966)