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Efficiency of Ceric Ions for Oxidation and Polymerization—A Review

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1. INTRODUCTION

Cerium(IV) ions are versatile reagents for the oxidation of numerous functional groups in organic synthesis, as well as in transition metal chemistry. They are also employed [1] to achieve nitration, hydroxylation, rearrangement, addition of carbonyl compounds to 1,3-dienes, homolytic malonylation of aromatic hydrocarbons, alkoxyiodination, nitratoiodination, and more. Most of these transformations open up a broad applicability due to their mild reaction conditions, fast conversions, and convenient work-up procedures.

The use of ceric ion as an oxidant for organic substrates gained prominence as an analytical reagent; this subject has been reviewed by G. F. Smith [2]. Later, an inherent interest developed in this subject, and two additional reviews on ceric ion oxidation of organic compounds appeared [3, 4]. Most of the reactions involve a direct oxidation of the organic compound by cerium(IV). However, some indirect oxidations are also considered in which cerium(IV) produces an active oxidant.

2. CHEMISTRY OF CERIUM

Cerium is a member of Group III A of the periodic table, commonly referred to as rare earth metals, lanthanons, or lanthanides. It has two common oxidation states: 3+ (cerous, Ce(III)) and 4+ (ceric, Ce(IV)). Cerous compounds resemble other trivalent lanthanons, but ceric compounds are like the elements titanium, zirconium, and thorium. The oxidation potential for the reaction.

$$Ce^{3+} \rightleftarrows Ce^{4+} + e^-$$

depends on the nature of the medium. Values of E^0_{298} are reported to be between −1.28 and −1.70 V [5]. The electrode potential for the reaction,

$$Ce(s) \rightleftarrows Ce^{3+} + 3e^-$$

is +2.335 V on the hydrogen scale.

Principal advantages of employing Ce^{4+} as an oxidizing agent are [6]

1. There is only one oxidation state, Ce^{3+}, to which the Ce^{4+} ion is reduced, and the redox potential of the Ce^{4+}/Ce^{3+} couple is high.
2. It is a very powerful oxidizing agent and, as mentioned above, one could alter the intensity of its oxidizing power by suitable choice of the medium.
3. Oxidation by Ce^{4+} proceeds in one step:

$$Ce^{4+} + e^- \rightleftarrows Ce^{3+}$$

4. Acid solutions of Ce^{4+} ion are extremely stable. Solutions can be kept for an indefinite period of time without any change in their concentration.
5. Ce^{4+} solutions could be employed, even in the presence of chloride ion, for oxidations that must be carried out by the use of excess reagent at elevated temperatures. However, chloride ion becomes oxidized when the solution is boiled.

3. OXIDATION STUDIES USING CERIC ION

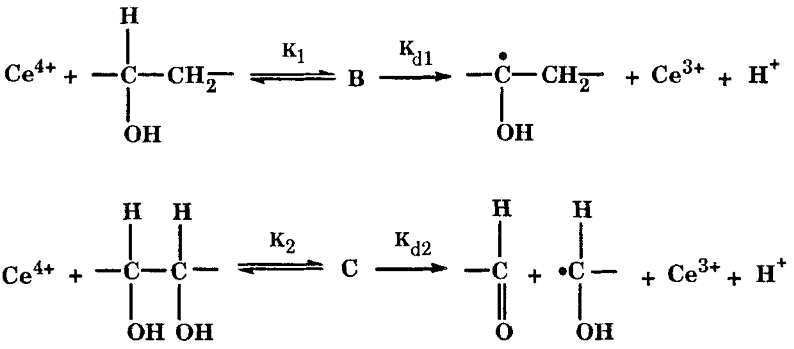
The present review article is limited to the oxidation of simple organic substrates and a few functional polymers. The oxidation of several organic substrates by Ce^{4+} was reviewed by Richardson in 1965 [7]. In most of the homogeneous oxidation of substrates by Ce^{4+}, the formation of an intermediate complex has been found to be an important prerequisite [8].

3.1. Oxidation of Alcohols

A theory for specific oxidation of bidentate ligands such as 1,2-glycols and related compounds has been developed based on the oxidation of acetone by selenious acid and trivalent manganese oxalate [9]. These reactions have been believed to involve the formation of a coordination complex between the oxidant and substrate, the unimolecular decomposition of which has been found to be the rate-determining step.

Duke and Bremer have studied the oxidation of 2,3-butane diol by ceric perchlorate in perchloric acid medium [8] to test the above theory and have observed that the intermediate complex formed disproportionated slowly. Further studies on the oxidation of 2,3-butane diol by ceric nitrate in nitric acid medium [10] have revealed that the mechanism is analogous to the oxidation of the diol by ceric perchlorate. In the same way, the oxidation of ethanol by ceric perchlorate proceeded via the formation of an intermediate complex of Ce^{4+} and ethanol that subsequently disproportionated unimolecularly [11]. It has been shown further that the scheme suggested for ethanol is also applicable to *n*-butanol [12].

Mino, Kaizerman, and Rasmussen have studied the oxidation of poly(vinyl alcohol) (PVA) [13] and 3-chloro-1-propanol [14] by ceric nitrate and inferred that the free radicals produced in the redox process could initiate the polymerization of acrylamide (AAm) and other vinyl monomers. In the case of PVA, free radicals are produced from two types of complexes, alcohol complex and the glycol complex, as shown in Scheme 1, where B and C are alcohol and glycol complexes, respectively.



SCHEME 1.

Muhammad and Sethuram have reported their results on the oxidation of isopropanol and secondary butanol by ceric nitrate in nitric acid medium [15] with a view to get evidence for the reactive species. They reported few experimental results in perchloric and sulfuric acid media for comparative purposes.

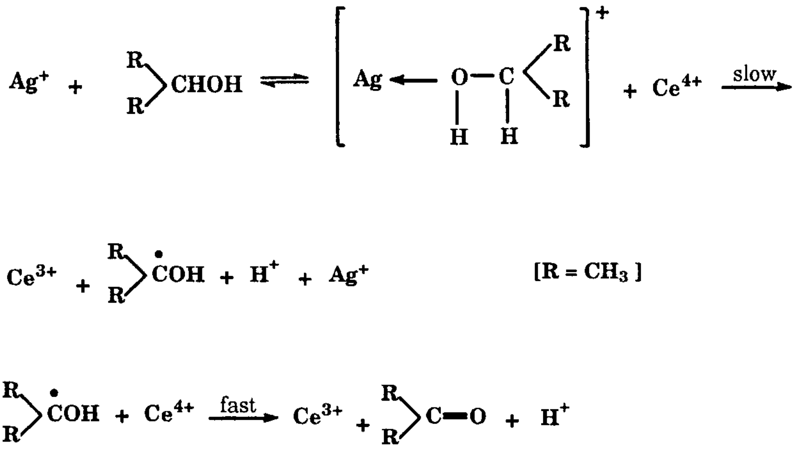
The oxidation of pinacol by ceric sulfate in both the presence and absence of AAm has been studied by Mino, Kaizerman, and Rasmussen [16]. In the absence of AAm, no evidence for complex formation between ceric sulfate and pinacol has been found. The overall order was found to be two and one molecule of acetone formed for every ceric ion consumed. The kinetics of oxidation of methanol, ethanol, isopropanol, *n*- and isobutanols, and benzyl alcohol (PA) by $KMnO_4$ and $Ce(SO_4)_2$ has been studied in the temperature range 20°C to 70°C; the overall order was found to be two in all these cases [17]. The oxidation of alcohols by ceric sulfate has been found to be slow and was attributed to the high energy barrier for the reaction. Further, the activation energies for the oxidation of alcohols by ceric sulfate have been correlated with dipole moments of the former. In the oxidation of glycerol by ceric sulfate in sulfuric acid medium [18], $Ce(SO_4)^{2+}$ was assumed to be the reactive species. The reaction was found to be bimolecular without the formation of any intermediate complex. Interestingly, the same system in perchloric acid medium proceeded via the formation of a complex between Ce^{4+} and glycerol.

Muhammad and Rao have not obtained any evidence for the formation of an intermediate complex [19] in the oxidation of methanol by $Ce(SO_4)_2$. Studies on the oxidation of benzyl alcohol by Ce^{4+} in perchloric acid medium have also revealed no complex formation [20]. Similar observations have been made for Ce^{4+}-ethylene glycol system in sulfuric acid medium by Katai, Kulshrestha, and Marchessault [21].

The kinetics of oxidation of *n*-propanol, allyl alcohol, cyclohexanol, and benzyl alcohol by ceric nitrate has been studied in nitric acid medium [22] in the temperature range 10°C to 35°C. The oxidation reactions of *n*-propanol, allyl alcohol, and cyclohexanol proceeded through the formation of Ce^{4+}-alcohol complex, whereas, in the case of benzyl alcohol, such a complex could not be detected. This could be attributed to the $-I$ effect of the phenyl group, which prevents the complex formation.

The kinetics of oxidation of α-phenyl ethyl alcohol by ceric ions [23] has been investigated by Venkatasubramanian and Balasubramanian. It has been observed that α-phenyl ethyl alcohol formed a complex with Ce^{4+} (in spite of the phenyl group on the secondary carbon atom). Trahanovsky, Young, and Brown have studied the oxidation of benzyl and related alcohols by Ce^{4+} and compared it with other modes of oxidation [24]. It has been concluded that Ce^{4+} oxidation is often the method of choice for oxidizing benzyl and related alcohols to their corresponding aldehydes on a synthetically useful scale.

The kinetics of oxidation of ethyl and benzyl alcohols by ceric sulfate in sulfuric acid and sulfuric-acetic acid mixtures have been studied by Saiprakash and Sethuram with a view to find out the state of Ce^{4+} ions in the reaction medium [25]. The active form of Ce^{4+} during the oxidation of the above alcohols in both media has been suggested to be the neutral $Ce(SO_4)_2$. These authors have also studied the kinetics of Ag^+-catalyzed oxidation of isopropyl alcohol by ceric sulfate in sulfuric acid medium [26]. The change in the order of the reaction with respect to [alcohol], from unity in the absence of Ag^+ to 0.44 in the presence of Ag^+, has been explained in terms of complex formation between Ag^+ and alcohol, shown in Scheme 2.



SCHEME 2.

The kinetics of oxidation of isopropyl alcohol to acetone and to formic acid by ceric sulfate in sulfuric acid medium has been studied [27] in both the presence and absence of mercuric chloride. It has been observed that, in both these cases, mercuric chloride catalyzes the reaction.

The oxidation studies of a series of cyclic alcohols and glycols (*cis*- and *trans*-1,2-cyclopentanediols, *cis*- and *trans*-1,2-cyclohexanediols, *trans*-2-methoxy-cyclohexanol and cyclohexanol) by Ce^{4+} have been made in perchloric acid and in mixed sulfuric and perchloric acid media [28]. Definite evidence for the formation of Ce^{4+} complexes has been obtained with *cis*- and *trans*-1,2-cyclohexanediols, *trans*-2-methoxy cyclohexanol, and cyclohexanol in perchloric acid medium. *Cis*- and *trans*-1,2-cyclopentanediols and *trans*-2-methoxy cyclopentanediol followed second-order kinetics, probably with either a direct oxidation mechanism or with a complex formed in low concentration.

The kinetics of oxidations of 1,3-propane, 1,3-butane, 1,4-butane, 1,5-pentane, and 1,6-hexane diols and 3-methoxybutan-1-ol have been studied by Prakash, Mehrotra, and Kapoor [29]. They have reported that 1,3- and 1,4-diols formed chelate complexes, whereas 1,5- and 1,6-diols, as well as 3-methoxy-butan-1-ol, acted as unidentate ligands in the oxidation process.

Nagarajan, Srinivasan, and Venkata Rao have studied and reported the kinetics of oxidation of a macromolecule, poly(ethylene glycol) (PEG) by ceric sulfate in sulfuric acid with a view to find out any difference in oxidation of monomeric and polymeric analogues [30]. The first-order dependence of the rate on Ce^{4+} concentration is indicated by the linearity in the plot of log (optical density change) [$\log(\Delta OD)$] against time t (Fig. 1). The oxidation of PEG proceeded without the formation of a stable intermediate complex, as evidenced by the Michaelis–Menton plot. Further, from the absorption spectra of CS and a CS–PEG mixture (Fig. 2), it could be seen that, on the addition of PEG, there was no shift in the absorption maxima of Ce^{4+}. Both these observations indicate that there is no complex formation between Ce^{4+} and PEG during the oxidation. The order with respect to the concentration of PEG and ceric sulfate has been found to be one, and the overall order is two. It has been observed that the oxidation of PEG proceeded faster than that of ethylene glycol. Further, the rate increased with an increase in the molecular weight of PEG (Table 1). These observations could be attributed to cage formation. It has been observed that the addition of vinyl monomer to the Ce^{4+}–PEG redox system results in the polymerization of the vinyl monomer [31], which indicates that free radicals are produced during the redox reaction. The formation of intermediate free radicals has been substantiated by electron spin resonance (ESR) spectroscopy using a spin trapping technique [32]. The ESR spectrum (Fig. 3) showed three lines of equal intensities, and the coupling constant was found to be 5.5×10^{-4} T. This macromolecular oxidation, proceeding via

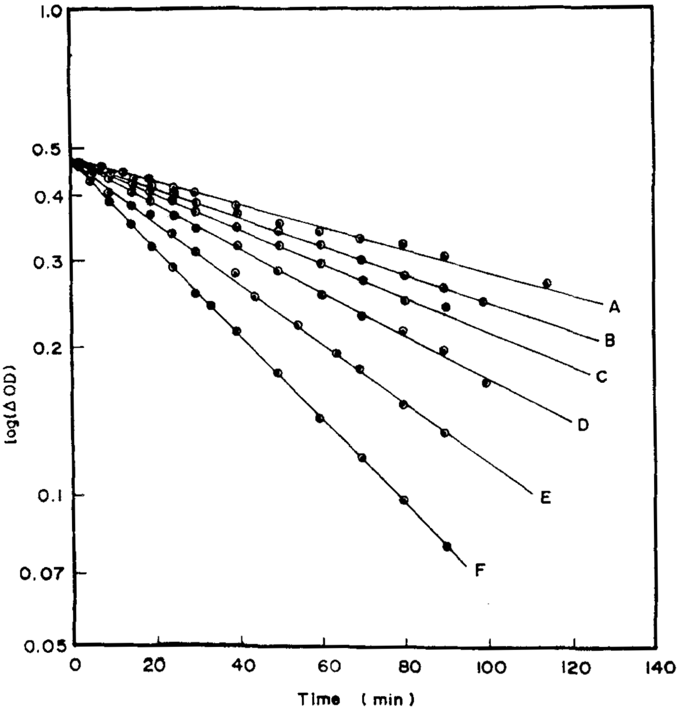
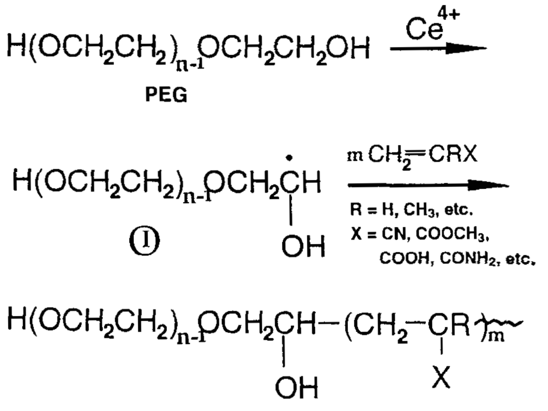


FIG. 1. First-order plots for the variation of PEG concentration: (A) $[CE^{4+}]$ = 1.5×10^{-4} M, $[H^+] \times 0.1$ M, $\mu = 1.05$ M, temperature = 299 K, [PEG] = 1×10^{-3} M; (B) 2×10^{-3} M; (C) 4×10^{-3} M; (D) 6×10^{-3} M; (E) 8×10^{-3} M; and (F) 10×10^{-3} M.



SCHEME 3.

a macroradical intermediate *I*, is used for the selective synthesis of block copolymers by us [33, 34] (Scheme 3). The macroradical *I*, in the absence of any vinyl monomer, is further oxidized to yield a long-chain aldehyde [35, 36].

3.2 Oxidation of Aldehydes and Ketones

The studies on the oxidation of formaldehyde by Ce^{4+} in perchloric and sulfuric acid media [37] have been based on the assumption that $H_2Ce(SO_4)_3$ and $H_4Ce(SO_4)_4$ are involved in sulfuric acid medium. The oxidative kinetics of benzaldehyde by Ce^{4+} ion [38] has been studied in aqueous sulfuric acid medium. The oxidative cleavage has not shown the existence of any kinetically detectable transition complex.

The studies on the oxidation of organic compounds [39] have revealed that the active form of the ceric ion is either $\{HCe(SO_4)_3OH\}^{2-}$ or $\{H_2Ce(SO_4)_3\text{-}OH\}^-$. In the oxidation of acetone by ceric nitrate [40], the first step has been assumed to be the acid-catalyzed enolization of acetone followed by slow attack of a hydrolyzed ceric species, $Ce(OH)^{3+}$ on the enol to form

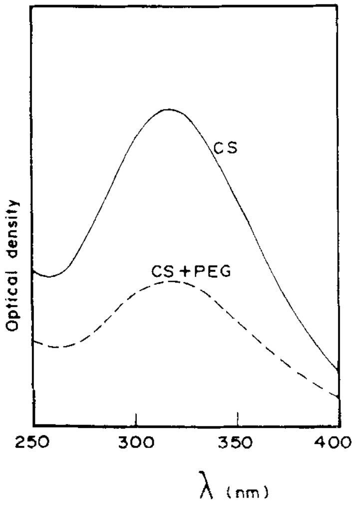


FIG. 2. Absorption spectra of ceric sulfate before (____) and after (---------) mixing with PEG.

TABLE 1

Effect of Molecular Weight of PEG on the Pseudo-First-Order Rate Constant

Molecular weight of PEG	$t_{1/2}$ (min)	k × 10^4 $(s)^{-1}$
200	230.00	0.502
300	222.00	0.520
400	48.50	2.381
600	13.00	8.885
4000	1.80	64.167
6000	0.60	192.500
9000	0.48	240.625

[PEG] = 3.33×10^{-3} M, [Ce^{4+}] = 0.67×10^{-4} M, [H^+] = 0.33 M, μ = 1.05 M, temperature = 26°C

acetol. It has also been pointed out that the acetone could form an acetonate anion that might be attacked by the ceric species. Venkatakrishnan and Santappa have investigated the oxidation of acetone and methyl ethyl ketone by ceric perchlorate [41] and concluded that an intermediate complex has been formed that on disproportionation gives a free radical.

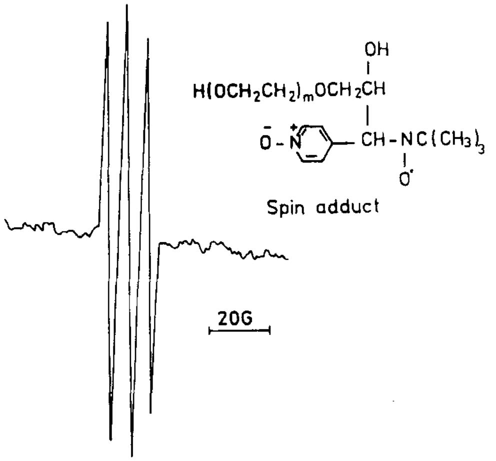


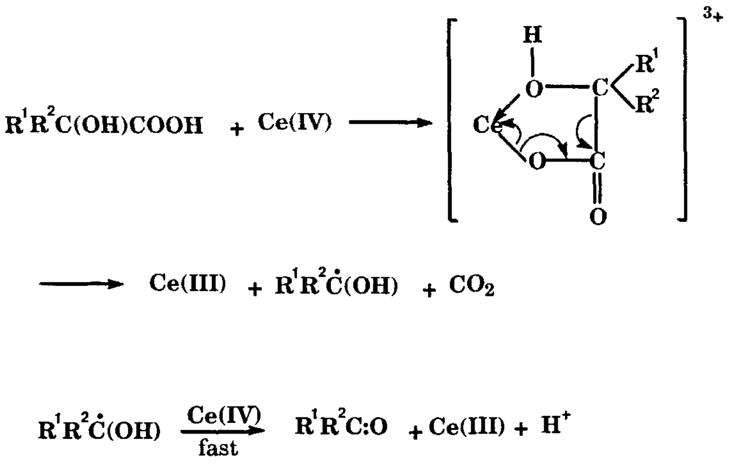
FIG. 3. ESR spectrum of the system Ce^{4+}/PEG/POBN at room temperature, with [Ce^{4+}] = 3.65×10^{-3} M, [PEG] = 1.67×10^{-3} M, [POBN] = 5.15×10^{-3} M, and [H^+] = 0.1 M.

3.3 Oxidation of Acids and Other Organic Compounds

The kinetics of oxidation of oxalic acid by ceric sulfate [42] has been studied based on the principle of concentration cells. Dodson and Black, from their work on the oxidation of oxalate ions by ceric sulfate, found that the overall order of the reaction was two [43]. Later, from spectrophotometric studies of Ce^{4+}-oxalate reaction in sulfuric acid medium [44], a mechanism involving the formation of a transient intermediate complex was proposed. This accounted for the observed variation in reaction rate with the nature and concentration of solvent anions. The oxidation of mandelic and α-hydroxybutyric acids by Ce^{4+} in aqueous sulfuric acid medium has been studied at several temperatures [45]. The oxidation was found to be first order with respect to both Ce^{4+} and organic acid.

Arcoleo et al. have studied the kinetics of Ce^{4+} oxidation of mandelic acid [46] in aqueous sulfuric acid solutions and in H_2SO_4-MClO$_4$ (M^+ = H^+, Li^+, and Na^+) and H_2SO_4-MHSO$_4$ (M^+ = Li^+, Na^+, and K^+) mixtures. The type of cation used did not affect the activation parameters significantly.

The redox reaction of α-hydroxy carboxylic acids by Ce^{4+} in perchloric acid medium proceeded via an inner sphere mechanism [47] (Scheme 4).

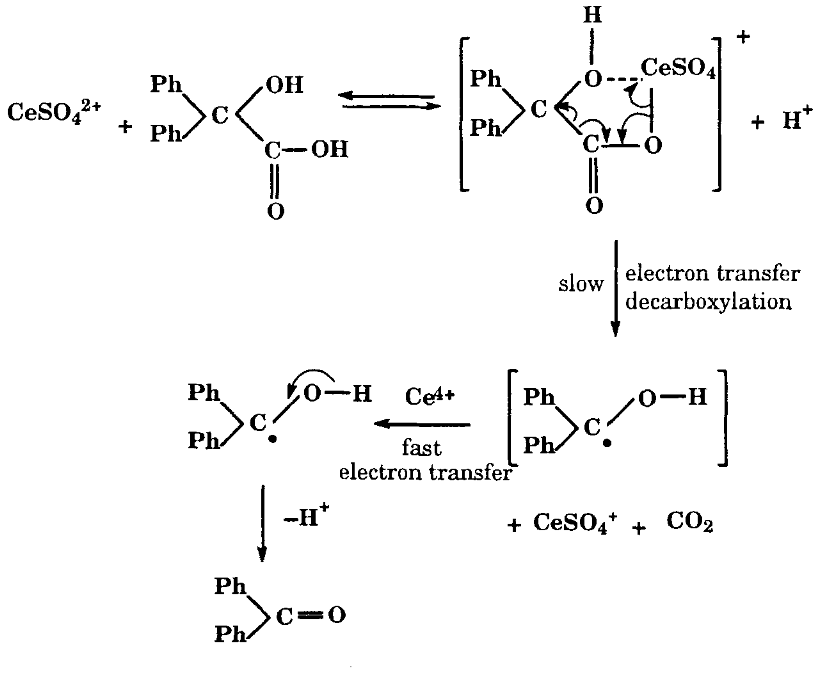


SCHEME 4.

The oxidation of lactyl lactic acid by Ce^{4+} in aqueous sulfuric-acetic acid medium at 35 °C was studied by Saxena [48]. The oxidative cleavage did not show the existence of any detectable transition complex.

The kinetics of oxidation of benzilic acid to benzophenone by Ce^{4+} was studied in several media using the stopped-flow technique [49]. In $HClO_4$-Na_2SO_4-$NaClO_4$ medium, $Ce(SO_4)^{2+}$ was found to be the kinetically pertinent species. Scheme 5 portrays a preliminary Ce(IV)-benzilic acid complex formation followed by a rate-determining intramolecular electron transfer simultaneous with C—C bond fission and liberation of CO_2.

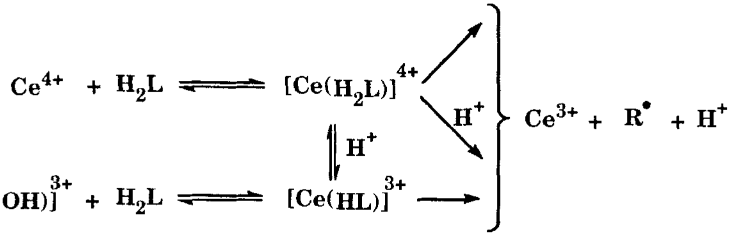
Studies on the kinetics and mechanism of oxidation of *N*-benzyliminodiacetic acid with Ce^{4+} in perchloric and sulfuric acid media have been reported [50]. The Ce^{4+}-mediated decarboxylation of *N*-benzyliminodiacetic acid produced benzaldehyde, formaldehyde, dimethylamine, benzylmethylamine, and *N*-benzylglycine.



SCHEME 5.

The oxidations of four α-keto acids (glyoxylic, pyruvic, phenylglyoxylic, and 2-oxybutyric acids) by Ce^{4+} in H_2SO_4-$NaHSO_4$ and H_2SO_4-$HClO_4$ solutions were studied by Sarac [51], who concluded that $Ce(SO_4)^{2+}$ is the most reactive species.

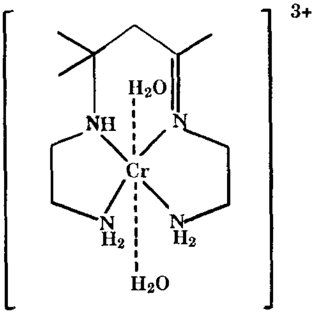
The oxidation of malonic acid (H_2L) proceeds via an inner-sphere mechanism [52]. A notable feature of the reaction is that, while at low temperatures there is kinetic and spectroscopic evidence for intermediate complex formation, at higher temperatures (30–35 °C) the reaction order changes to unity with respect to the reductant concentration (Scheme 6).



SCHEME 6.

The oxidation of hypophosphorous acid by Ce^{4+} in aqueous nitric acid medium [53] has shown a first-order dependence on both $[Ce^{4+}]$ and $[H^+]$ and an order less than unity on $[H_3PO_2]$. Detailed studies on the oxidation of lactic acid [54], mandelic acid [55], pyruvic acid [56], tartaric acid [57], oxalic acid [58], citric acid [59], glycolic acid [60], hyponitrous acid [61], butanoic acid [62], thiodiglycolic acid [63], diphenyl diselenide [64], and some naphthalene derivatives [65] involving the formation of an activated complex between Ce^{4+} and the substrate have also been reported.

Saffir and Taube have investigated the kinetics of oxidation [66] of captive oxalates $[(NH_3)_5Co(C_2O_4)]^+$. The kinetics and mechanism of Ce^{4+} oxidations of Cr(III) complexes of a series of macrocyclic (or pseudomacrocyclic) ligands with [14]-membered intraligand ring sizes (Scheme 7) have been investigated by Nair, Ramasami, and Ramaswamy [67]. The observed kinetic parameters have been explained in terms of changes brought about by the macrocyclic ligands on the Cr(III)–Cr(IV) redox potentials and in specific rates for Cr(IV)–Cr(V) conversion.



SCHEME 7.

4. VINYL POLYMERIZATIONS INVOLVING CERIC ION

The thermal and photochemical reactions entailing quadrivalent cerium ion for vinyl polymerization in aqueous solutions have been the subject of extensive research. Ceric ions are effective both by themselves [68] as well as in association with organic substrates [69, 70] as redox systems for initiating vinyl polymerization. The most striking feature of the redox process from a practical point of view is that it enables polymerizations to be performed at a substantially faster rate than conventional methods. Also, it enables polymerizations to be conducted at lower temperatures. Because of these features, this technique has considerable value in polymer synthesis. The role of ceric ion in redox-initiated vinyl polymerization has been discussed extensively [71].

4.1. Alcohols as Reducing Agents

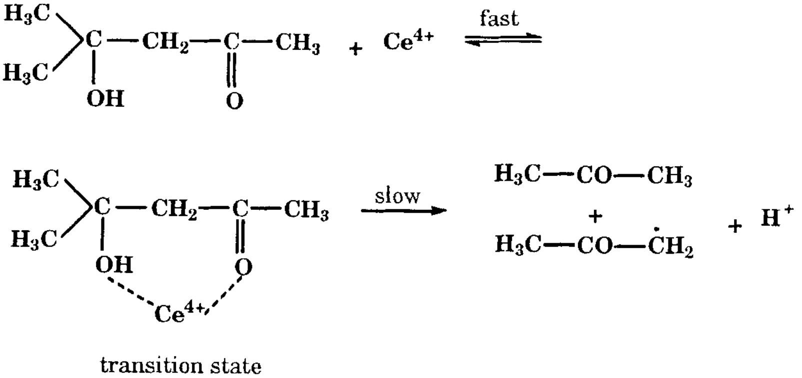
Coutinho, Guimareaes, and Gomes studied the polymerization of methyl methacrylate (MMA) initiated by a Ce^{4+}-methanol redox system in aqueous nitric acid medium [72] and obtained poly(methyl methacrylate) (PMMA) chains containing the alcohol residue. The polymerization of styrene in benzene catalyzed by a ceric salt containing *n*-dodecyl benzene sulfonic ion and ethyl alcohol [73] has been reported. The kinetics of AAm polymerization employing ceric ammonium nitrate and 2-chloroethanol was studied by Gupta and Behari [74]; it was observed that ceric ion alone is incapable of initiating the AAm polymerization.

Polymerization of MMA initiated by ceric ammonium nitrate in combination with isopropyl and isobutyl alcohols in aqueous nitric acid medium [75] has been characterized by homogeneous kinetics at the early stages of polymerization. The polymerization of AAm initiated by ceric nitrate and 3-chloro-1-propanol [14] has been studied by Mino et al.; they reported that, in the absence of a reducing agent, the rate of polymerization of AAm initiated by ceric nitrate is negligible. Polymerization of AAm initiated by a ceric ion–pinacol redox system [76] yielded polyacrylamide (PAAm) with one ceric atom in its molecule, possibly due to the termination by Ce^{4+}.

Katai, Kulshrestha, and Marchessault speculated the possibility of using ethylene glycol as a reducing agent [77]. It has been observed that the amount of polyacrylonitrile (PAN) formed in the absence of glycol is by no means negligible, and that the ratio of rates of polymerization of comparable systems in the presence and absence of alcohol has been found to be about three.

Diacetone alcohol (DAA) has been coupled with Ce^{4+} for the polymerization of acrylonitrile (AN) [78], and the rate of polymerization has been found to be proportional to $[Ce^{4+}]^{0.5}$, $[DAA]^{0.5}$, and $[M]^{1.5}$. The redox reaction is schematically represented in Scheme 8.

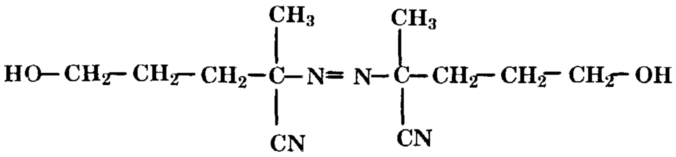
Similarly the polymerization of AN by CE^{4+}-benzyl alcohol (BA) redox system [79] indicated the dependence of rate of polymerization on [AN], $[Ce^{4+}]^{0.5}$, and $[BA]^{0.5}$. No polymerization has been observed in the absence of BA under the experimental conditions.



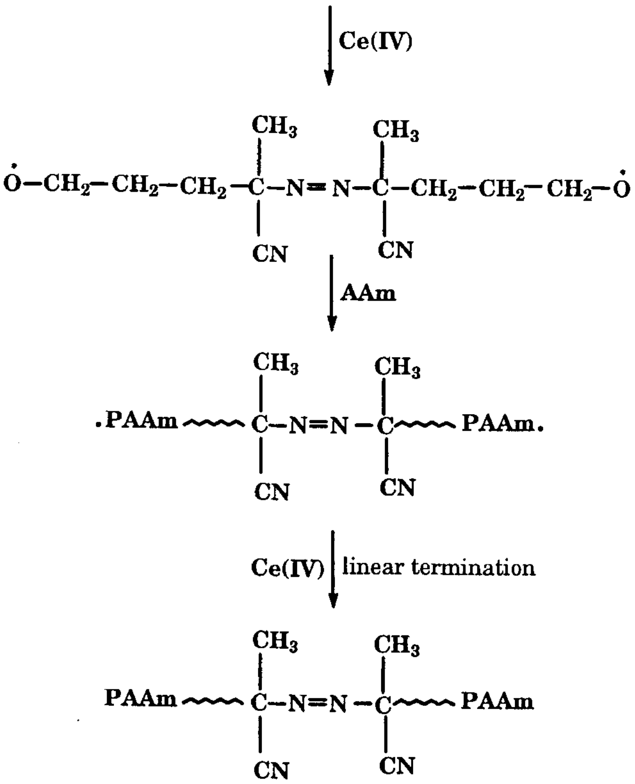
SCHEME 8.

The polymerization of AN initiated by Ce^{4+} and 1,2-propane diol (R) in aqueous sulfuric acid medium [80] has been studied in the temperature range 30°C to 40°C. The rate of polymerization has been found to be proportional to $[AN]^2$, $[R]$, and $[Ce^{4+}]$, and the rate of ceric ion disappearance has been proportional to $[R]$ and $[Ce^{4+}]$. Acrylamide has been polymerized by Ce(IV)-4,4′-azobis(4-cyanopentanol) (ACP) [81] redox pair in aqueous nitric acid under nitrogen atmosphere. The rate of polymerization was proportional to $[M]^2$, [ACP], and $[Ce(IV)]^{-1}$. The reaction proceeded as shown in Scheme 9.

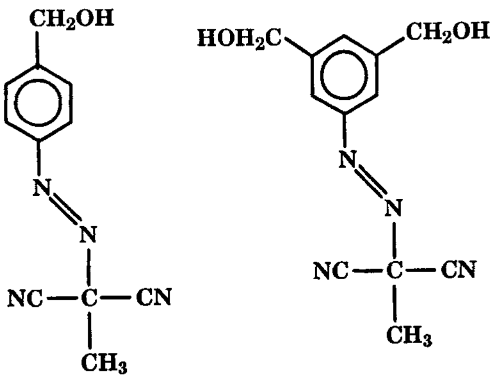
2-Methoxy ethanol (methyl cellosolve) has been employed with ceric ions for the polymerization of MMA, and a detailed kinetic analysis has been made [82]. Recently, hydroxy-containing, thermolabile azo compounds (Scheme 10) have been used in conjunction with Ce(IV) for the polymerization of AAm [83].



$$HO{-}CH_2{-}CH_2{-}CH_2{-}\underset{CN}{\overset{CH_3}{C}}{-}N{=}N{-}\underset{CN}{\overset{CH_3}{C}}{-}CH_2{-}CH_2{-}CH_2{-}OH$$



SCHEME 9.



SCHEME 10.

Nagarajan and Srinivasan have reported [69, 84] the kinetic and mechanistic features of tetravalent cerium-poly(ethylene glycol) (PEG molecular weight 6000) redox-couple-initiated block copolymerization of acrylonitrile (M) in aqueous acidic medium in the temperature range 35 °C to 60 °C. The block copolymerization behavior, as a function of $[Ce^{4+}]$, [PEG], $[M]$, $[H^+]$, $[SO_4^{2-}]$, as well as temperature, have been studied. The overall rate of polymerization R_p, the rate of disappearance of Ce^{4+} R_{Ce}, and the number average molecular weight $\overline{M}_n$ have been determined from gravimetry, cerimetry, and gel permeation chromatography, respectively. The R_p was found to be dependent on $[M]^2$ and [PEG], as indicated from the log-log plots (Fig. 4), and independent of both $[Ce^{4+}]$ and $[H^+]$. The R_{Ce} was found to be directly proportional to $[Ce^{4+}]$, [PEG] (Fig. 5), and $[H^+]$, and independent of $[M]$. Both R_p and R_{Ce} were found to be retarded on adding sulfate ions, while an increase of temperature accelerated the rates. The $\overline{M}_n$ of the block copolymer has been found to depend on $[Ce^{4+}]$, [PEG], $[M]$, and $[H^+]$, as well as on temperature. A plausible reaction scheme has been derived and suitable kinetic expressions have been evaluated based on these observations.

Similar kinetic studies were also made by changing the metal ion, such as with the system Mn(III)-PEG-AN [70], as well as by changing the vinyl monomer, as with the systems Ce^{4+}-PEG-MMA [85] and Ce^{4+}-PEG-AAm [86]. It was found that all these systems follow the same kinetic pattern, and it has been concluded that this could be a model study for the system M^{n+}-PEG-vinyl monomer. Thus, by varying the temperature and concentration of the components of the redox system, it is possible to control the rate of polymerization and the molecular weight of the resulting polymer.

4.2. Aldehydes, Ketones, or Acids as Reducing Agents

Polymerizations of MA, AN, and MMA in perchloric acid medium initiated by the ceric perchlorate/formaldehyde redox couple [87] have been studied by Subramanian and Santappa. The initiation of polymerization was found to be by both Ce^{4+} ions and the primary radical produced from the redox reaction of ceric perchlorate and formaldehyde. Only with MMA, the initiation by Ce^{4+} was found to be negligible compared to that by primary radicals.

The radical polymerization of AAm initiated by a ceric ion/1,3-diketone compound, that is, 3-phenylmethyl-2,4-pentanedione system, and grafting of AAm onto macromolecules having 1,3-diketone pendant groups using ceric ion as an initiator have been studied by Qiu, Zhao, and Dong [88].

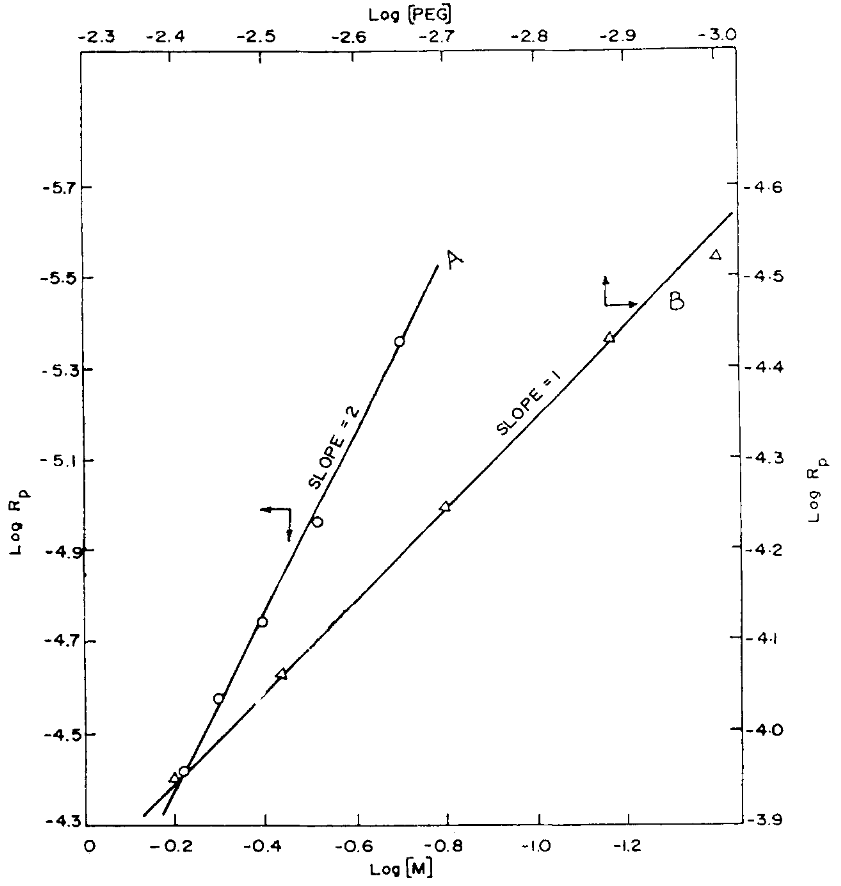


FIG. 4. Log-log plots for the dependences of R_p on $[M]^2$ (A) and [PEG] (B): (A) $[CE^{4+}] = 3.46 \times 10^{-3}$ M, $[H^+] = 0.1$ M, $\mu = 1.05$ M, [PEG] $= 4 \times 10^{-3}$, temperature = 308 K, time = 60 min; (B) $[Ce^{4+}] = 3.46 \times 10^{-3}$ M, $[H^+] = 0.1$ M, $\mu = 1.05$ M, $[M] = 0.7$, temperature = 308 K, time = 30 min.

They have proposed a mechanism (Scheme 11) based on electron paramagnetic resonance (EPR) and kinetic studies, and the formation of graft copolymer has been confirmed by x-ray photoelectron spectroscopy (XPS) spectra, Fourier transform infrared (FTIR) spectra, and photomicrographs. Erbil et al. studied the polymerization of AAm [89] initiated with Ce(IV) in the presence of methionine, phenylalanine, serine, and aspartic acid and

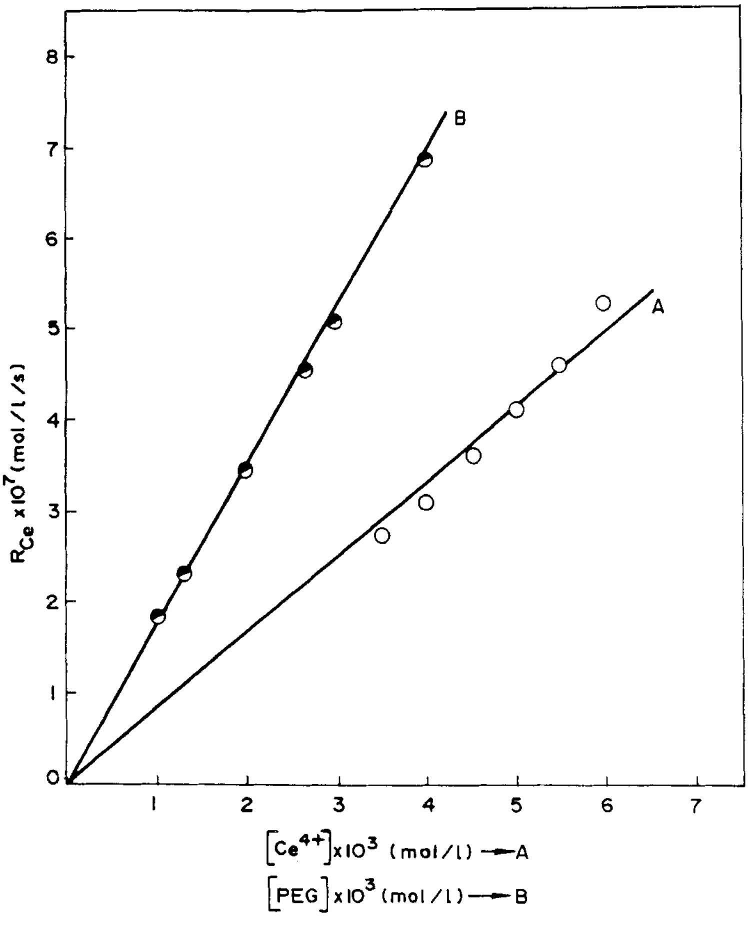
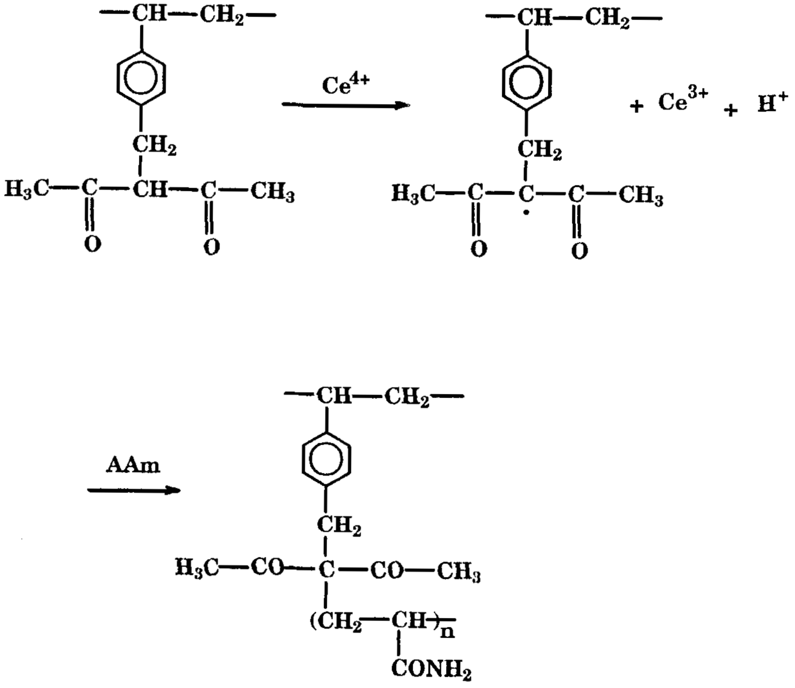


FIG. 5. (A) Plot of R_{Ce} against [Ce^{4+}], with [M] = 0.6 M, [H^+] = 0.2 M, μ = 1.05 M, [PEG] = 4 × 10^{-3}, temperature = 308 K, time = 30 min; (B) plot of R_{Ce} against [PEG], with [Ce^{4+}] = 3.46 × 10^{-3} M, [H^+] = 0.1 M, μ = 1.05 M, [M] = 0.7, temperature = 308 K, time = 30 min.

established the presence of carboxy end groups in the resulting polymers by both conductometric titration and FTIR techniques.

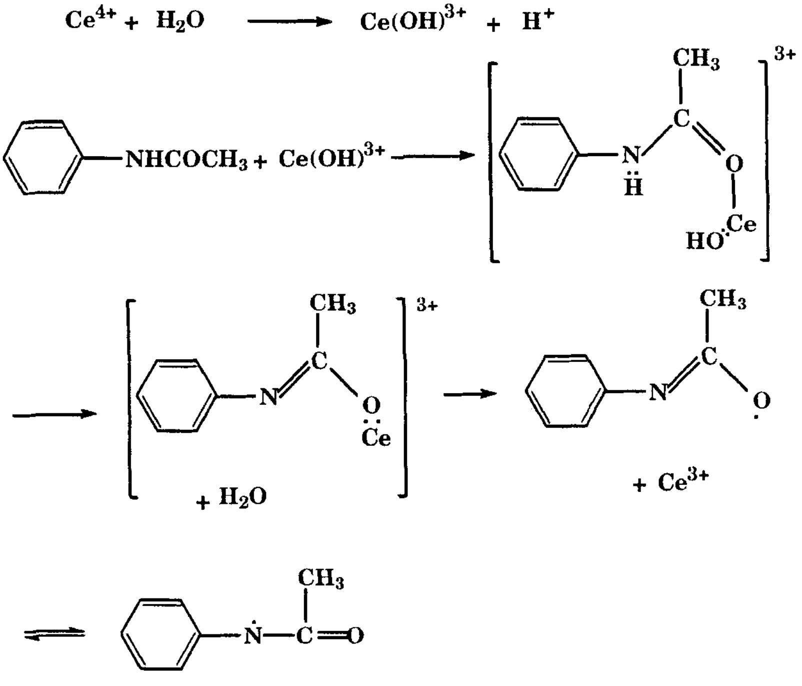
Several papers dealing with ceric ion-acid redox systems have appeared in the literature. The acids employed are malonic acid [90], malic acid [91], tartaric acid [92], glycolic acid [93], citric acid [94] amino acids [95], nitrilotriacetic acid [96], polyaminocarboxylic acids [97], and so on.



SCHEME 11.

4.3. Other Reducing Agents

The use of thiourea as one of the components of a redox system for vinyl polymerization has been reported by Pramanick, Chatterjee, and Sarkar [98]. The compounds of acyl acetanilide such as 2-benzoylacetanilide, acetoacetanilide, *o*-acetoacetotoluidide, and *o*-acetoacetanisidide have been coupled with Ce^{4+} as redox initiators for radical polymerization of AAm [99]. Qiu has also reviewed the vinyl polymerization initiated by the redox systems [100] Ce(IV)/acetanilide, Ce(IV)/alkyl phenylcarbamate, Ce(IV)/4-methoxysuccinyl-toluidine, Ce(IV)/aliphatic aldehyde, Ce(IV)/aromatic aldehyde, and Ce(IV)/diketone systems. In the case of acetanilide, the redox reaction is proposed to proceed as shown in Scheme 12.



SCHEME 12.

The effect of various substituted amines on the polymerization of AN initiated by ceric ammonium sulfate [101] has been studied in aqueous solution at 30°C. It has been found that the secondary and tertiary amines considerably increased the rate of polymerization, whereas the primary amines appeared to have no effect at all. Thioacetamide has been used as a reducing agent with Ce^{4+} for the polymerization of AN in aqueous sulfuric acid medium [102]. The reactivity of thioacetamide has been compared with other amides and the order of reactivity has been found to be

thioacetamide > succinamide > acetamide > formamide

Chelating-type reductants have also been employed with ceric ion for vinyl polymerization. The redox pairs consisted of Ce^{4+} or several first-row transition metals and chelating agents of amino acids, dibasic acids, or diamine [103].

Other reducing agents reported are EDTA [104], cotton cellulose [105], D-glucose [106], maltose [107], cellobiose [108], sorbose [109], and so on.

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