Asian Journal of Chemistry Vol. 1, No. 4 (1989), 318-327

Kinetic and Analytical Studies of Oxidation of Poly (Vinyl Alcohol) with Ammonium Hexanitratocerate (IV) in Nitric Acid Medium

B. MADHAVA RAO* and U. R. CHOUDHARI

Department of Chemistry
Visvesvaraya Regional College of Engineering
Nagpur 440 011, India.

Kinetics of oxidation of poly (vinyl alcohol) is extensively studied to evaluate the thermodynamic parameters and the formation constant (K_f) of the intermediate complex and furthermore to achieve the optimal conditions for analytical determination of poly (vinyl alcohol) in commercially available poly (vinyl alcohol) sample through an established stoichiometry. Second order rate constants obtained in these investigations are utilised to correlate the effects of variation of poly (vinyl alcohol) as a monomer, [Ce(IV)], [H^+], $^{a}NO_3^-$ and added [Ce(III)]. The mechanism of oxidation of poly (vinyl alcohol) involves the formation of a transitory cyclic complex, followed by disproportionation of the complex. The disproportionation of the intermediate complex is the rate determining step. The values for K_f, $\Delta E^{\neq}$, $-\Delta H^{\neq}$, $\Delta F^{\neq}$, $\Delta S^{\neq}$ and log A are found to be 15.77 lit. mole^{-1}, 14.34 Kcal mole^{-1}, 13.92 Kcal mole^{-1}, -1.606 Kcal mol^{-1} and 41.57 e.u. and 4.5×10^8 sec^{-1} respectively.

INTRODUCTION

Makoto Shiraishi *et al*[1] studied the degradation of poly (vinyl alcohol) in hot aqueous alkali and observed the change in the carbonyl content of polymer. They have also noticed that the polymer cleared at all C = C groups. Schlaefer[2] in his study of oxidation of poly (vinyl alcohol) by ammonium dichromate noticed the photosensitivity of chromium(IV) poly (vinyl alcohol) layer and further established the oxidation takes place with the splitting of C–C bonds, Samvelyam *et al.*[3] in the study of oxidation of poly (vinyl alcohol) observed that the initial rate of oxidation of poly (vinyl alcohol) is first order in $K_2S_2O_8$ and half order in alcohol at 20–80°C and further the reaction is independent of pH and presence of oxygen.

Okhrimanko and Smirnov[4] have extracted poly (vinyl alcohol) with ethanol as solvent and followed its oxidative degradation with potassium bromate through viscosity and functional group measurements. A kinetic study of silver ion catalysed oxidation of poly (vinyl alcohol) by aqueous $K_2S_2O_8$ was carried out by Beileryan *et al.*[5] and they noticed that the rate of oxidation was accelerated by Ag^+, while Co^{++} and Cu^{++} have little effect. They proposed a radical oxidation mechanism in the above oxidation reaction. In the IR study of thermal oxidative degradation of poly (vinyl alcohol), Karodenko *et al.*[6] showed that the oxidation was accompanied through the formation of ester bridges and carboxyl groups. In the oxidation of poly (vinyl alcohol) by aqueous $KMnO_4$, Makoto *et al.*[7] observed the inhibitory effect of sodium dodecyl sulphate and concluded the interaction between poly (vinyl alcohol) and sodium dodecyl sulphate resulting in the negative charge on poly (vinyl alcohol) which repelled the MnO_4^- ion from other oxidation. Ikada Yoshito *et. al.*[8] carried out the oxidation of poly (vinyl alcohol) by potassium persulphate and found that poly (vinyl alcohol) acts as a free radical in the graft copolymerisation of methyl methacrylate-vinyl alcohol graft copolymer.

Trakhtenbery *et al.*[9] have examined the graft polymerisation of poly (vinyl alcohol) with acrylic compounds in presence of ammonium persulphate and the interaction was followed by IR spectroscopy. A mechanism involving the interaction of functional groups of poly (vinyl alcohol) and acrylic compounds was suggested. In the photo oxidation of poly (vinyl alcohol) Auki *et al.*[10] showed that the amounts of carbonyl groups formed decreases in the order aldehyde > ketone > acid > ester and the rate expression for assumed mechanism was: rate $= B(1 - e^{-\lambda t})$ where A and B are constants and t is time. Bate and Shanks[11] carried out the oxidative scission of poly (vinyl alcohol) by 30% H_2O_2 solution at 25°C. The reaction is first order and occurs through oxidative cleavage of 1,2 glycol units in the chain and a first order cleavage that followed the formation of oxidised sites along the chain.

In the oxidation of poly (vinyl alcohol) by NaOCl, Huang *et al.*[12] observed that the oxidation is highly sensitive to pH of the medium and the reaction time. The highest conversion of —OH group to ketone was 83% at pH 5.4 with a reaction time of 1 hr. Further they noticed that with high percentage conversion, the polymer existed mostly in the enol keto form instead of the diketone. In their next publication[13] they showed that the oxidised poly (vinyl alcohol) to (polyhydroxy ketone from NaOCl the oxidation undergoes biodegradation faster than the unoxidised poly (vinyl alcohol). Hypochlorite oxidation of (poly alcohols) like cellulose starch and certain gums has been studied extensively[14–18]. The oxidation of poly (vinyl alcohol) has, however, not been investigated in detail, though a few studies have been reported[19–21].

Ogiwara and Uchiyama[22,23] observed an initial rapid chain cleavage in the oxidation of poly (vinyl alcohol) by cerium(IV). The rate and the extent of rapid oxidative cleavage by cerium(IV) increased with an increase in carbonyl content.

Cerium(IV) species in nitric acid medium differs from those in $HClO_4$ and H_2SO_4 media and further much more complicated due to hydrolysis, dimerisation, complex formation with the nitrate ion and hydroxyl ion and association of cerium(IV) with cerium(III) as well as cerium(III) nitrate association.

EXPERIMENTAL

The materials employed were of highest purity available (AR, E merk, G.R. grade etc.). A 0.1N Ce(IV) solution was prepared in 1.0N nitric acid and was further standardized by standard Fe(II). A 0.1% PVA solution (*ca.* 0.05M PVA solution as a monomer) was prepared by dissolving requisite amount of PVA (Amrut Industrial Products, Thana, Bombay)

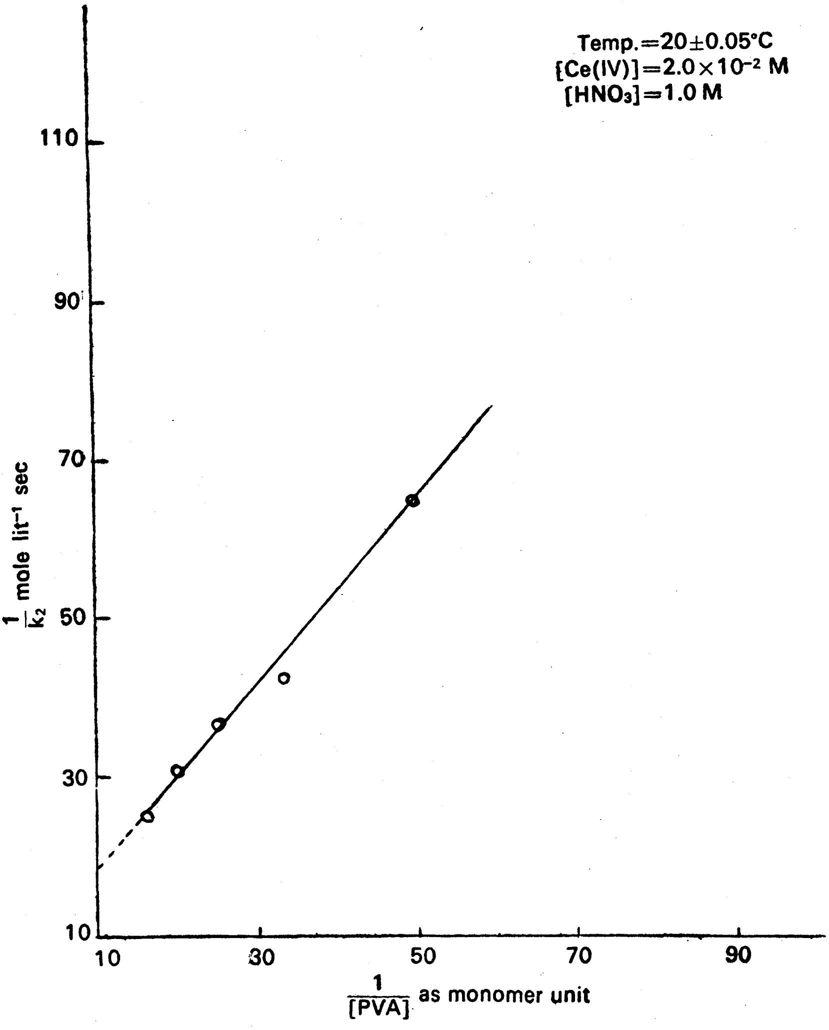
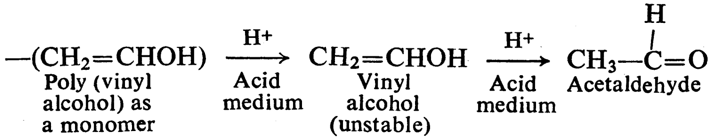
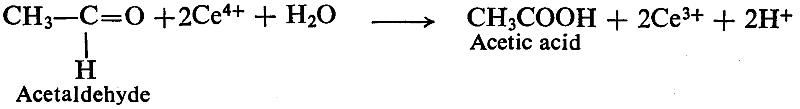


Fig. 1. Poly (vinyl alcohol)-Ce(IV) reaction in 1M nitric acid medium, Data of Fig. 2 plotted assuming a 1 : 1 poly (vinyl alcohol)-Ce(IV) complex intermediate.

in conductivity water. Further this solution was standardised through an oxidimetric procedure using Ce(IV) nitrate in 0.5N HNO_3 medium. Stoichiometry of the reaction between Ce(IV) and PVA has been established for the experimental conditions employed as well as for 1, 2 and 3 hrs. of the reaction. In every case it was found that one mole of PVA considering as monomer requires 2.0 equivalents of Ce(IV) for oxidation to acetic acid as shown below.



$$\underset{\substack{\text{Poly (vinyl}\\\text{alcohol) as}\\\text{a monomer}}}{-(CH_2{=}CHOH)} \xrightarrow[\substack{\text{Acid}\\\text{medium}}]{H^+} \underset{\substack{\text{Vinyl}\\\text{alcohol}\\\text{(unstable)}}}{CH_2{=}CHOH} \xrightarrow[\substack{\text{Acid}\\\text{medium}}]{H^+} \underset{\text{Acetaldehyde}}{CH_3-\overset{\displaystyle H}{\overset{|}{C}}{=}O} \tag{1}$$



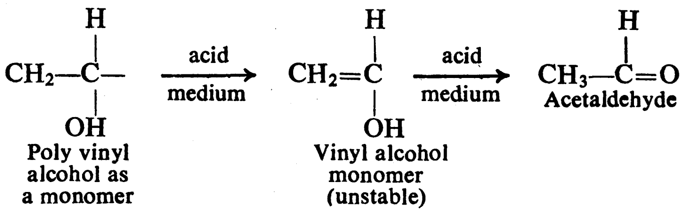
$$\underset{\text{Acetaldehyde}}{CH_3-\underset{\displaystyle H}{\underset{|}{C}}{=}O} + 2Ce^{4+} + H_2O \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + 2Ce^{3+} + 2H^+ \tag{2}$$

The progress of the reaction was followed by arresting the reaction mixture in a known excess of Fe(II) and back-titrating the unreacted Fe(II) with standard Ce(IV) sulphate solution (*ca* 0.025N).

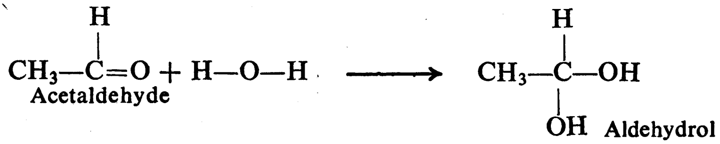
The reaction follows simple second order kinetics under the conditions $[Ce(IV)] \simeq [PVA \text{ as monomer}]$. A plot of $1/(a - x)$ vs. time t is linear indicating the total order is two. At different [Ce(IV)] and [PVA], the plot $\frac{2.303}{(a-b)} \log \frac{(a-x)}{(b-x)}$, time t is also linear indicating first order dependence each in [Ce(IV)] and [PVA as monomer]. As is observed in the linear plot, Figure 1 ($1/k_2$ vs. 1/[PVA]) the rate increases with increase in [PVA], under the experimental conditions viz. $Ce(IV) = 2.0 \times 10^{-2}$ M, $HNO_3 = 1.0M$ at $20 \pm 0.05°C$. From the intercept and slope of this linear plot, the stability constant of 1 : 1 (Ce(IV)–PVA) complex has been evaluated at the above conditions, $K_f = 15.77$ lit. $mole^{-1}$.

RESULTS AND DISCUSSION

The reaction involves the formation of a prior complex between Ce(IV) and monomer of PVA which decomposes by the second order type of kinetics. The low value for formation constant (K_f) may be due to the formation of unstable vinyl monomer which at once isomerises into acetaldehyde. Acetaldehyde on hydration with water followed by complexation with the reactive $(CeOH)^{3+}$ species yields an intermediary complex of the type as shown in equation (4). This intermediary complex on further oxidation with excess Ce(IV) yields finally acetic acid with a C–H bond cleavage. Under the employed experimental conditions acetic acid has no noticeable oxidation with excess Ce(IV).

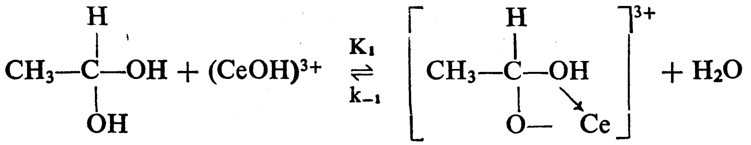


$$\underset{\text{Poly vinyl alcohol as a monomer}}{CH_2-\overset{H}{\underset{OH}{C}}-} \xrightarrow[\text{medium}]{\text{acid}} \underset{\text{Vinyl alcohol monomer (unstable)}}{CH_2=\overset{H}{\underset{OH}{C}}} \xrightarrow[\text{medium}]{\text{acid}} \underset{\text{Acetaldehyde}}{CH_3-\overset{H}{C}=O} \qquad (1)$$

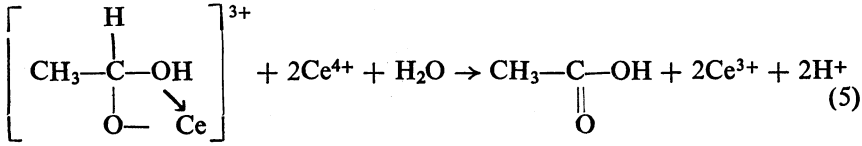


$$\underset{\text{Acetaldehyde}}{CH_3-\overset{H}{C}=O} + H-O-H \longrightarrow CH_3-\overset{H}{\underset{OH}{C}}-OH \ \text{Aldehydrol} \qquad (2)$$

$$Ce^{4+} + H_2O \rightleftharpoons (CeOH)^{3+} + H^+ \qquad (3)$$

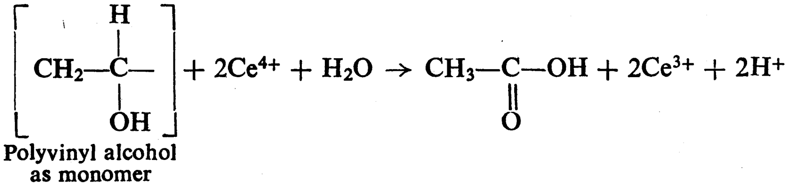


$$CH_3-\overset{H}{\underset{OH}{C}}-OH + (CeOH)^{3+} \underset{k_{-1}}{\overset{K_1}{\rightleftharpoons}} \left[\begin{array}{c} H \\ | \\ CH_3-C-OH \\ | \quad \searrow \\ O- \quad Ce \end{array} \right]^{3+} + H_2O \qquad (4)$$



$$\left[\begin{array}{c} H \\ | \\ CH_3-C-OH \\ | \quad \searrow \\ O- \quad Ce \end{array} \right]^{3+} + 2Ce^{4+} + H_2O \rightarrow CH_3-\underset{O}{\underset{\|}{C}}-OH + 2Ce^{3+} + 2H^+ \qquad (5)$$

The stoichiometric equation may finally be written as



$$\underset{\text{Polyvinyl alcohol as monomer}}{\left[CH_2-\overset{H}{\underset{OH}{C}}- \right]} + 2Ce^{4+} + H_2O \rightarrow CH_3-\underset{O}{\underset{\|}{C}}-OH + 2Ce^{3+} + 2H^+ \qquad (6)$$

The rate of oxidation decreases with increase of Ce(IV) i.e. decreased by about half of its original value 9.16×10^{-3} lit. mole^{-1} sec^{-1} at 2.0×10^{-2}M [Ce(IV)] to 4.50×10^{-3} lit. mole^{-1} sec^{-1} at 4.0×10^{-2}M [Ce(IV)] at 20 ± 0.05°C [HNO_3] = 1.0M and [PVA as monomer] = 1×10^{-2}M; while the initial rate proportionately increases i.e. 6.46×10^{-5} lit.$^{-1}$ sec^{-1} at 2.0×10^{-2}M [Ce(IV)] to 14.12×10^{-5} lit.$^{-1}$ sec^{-1} at 4.0×10^{-2}M [Ce(IV)]. Such an accelerating effect in the initial rate may be due to the availability of kinetically reactive Ce(IV) species viz. $(CeOH)^{3+}$ in the reaction mixture. In the study of the effects of [H^+] on the second order rate constant, Figure 2, it is observed that there is a continuous proportional retarding effect on the rate constant as the concentration of nitric acid increases from 1.0 to 6.0M. This observation is in agreement with that of Duke and Forist[24].

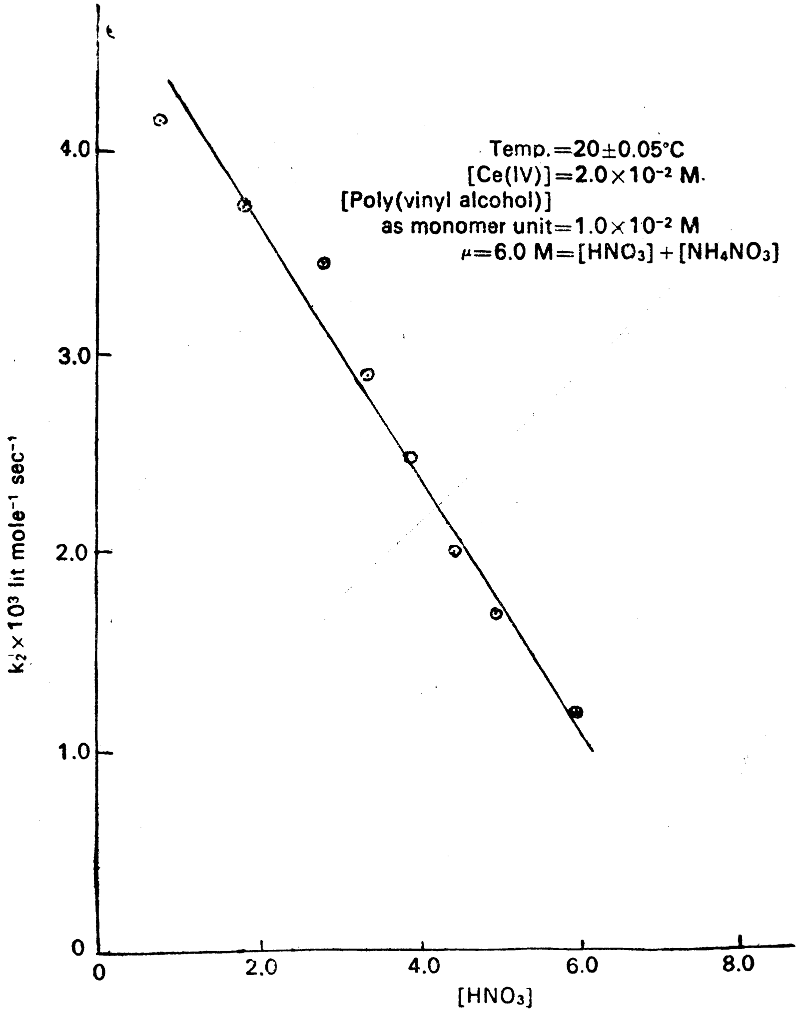


Fig. 2. Poly (vinyl alcohol)—Ce(IV) reaction in nitric acid medium. Effect of varying [HNO_3] on second order rate constant.

The rate of oxidation decreases proportionately with the activity of added nitrate ion (Figure 3). The added nitrate ion may complex with the reactive $(CeOH)^{3+}$ species and converting it into less reactive species viz. $[Ce(OH^-)(NO_3^-)]^{2+}$ and $[Ce(OH^-)(NO_3^-)_2)^+$. Such observations were also made by Shorter[25]. The activity data were taken from Landolt-Bornstein Tabellen Vol. III (1936). The marginal retardation effect of added Ce(III) (Figure 4) may be due to the association of reactive $(CeOH)^{3+}$ with Ce(III) which consequently decreases the total concentration of reactive $(CeOH)^{3+}$ species. Such instances of association of reac-

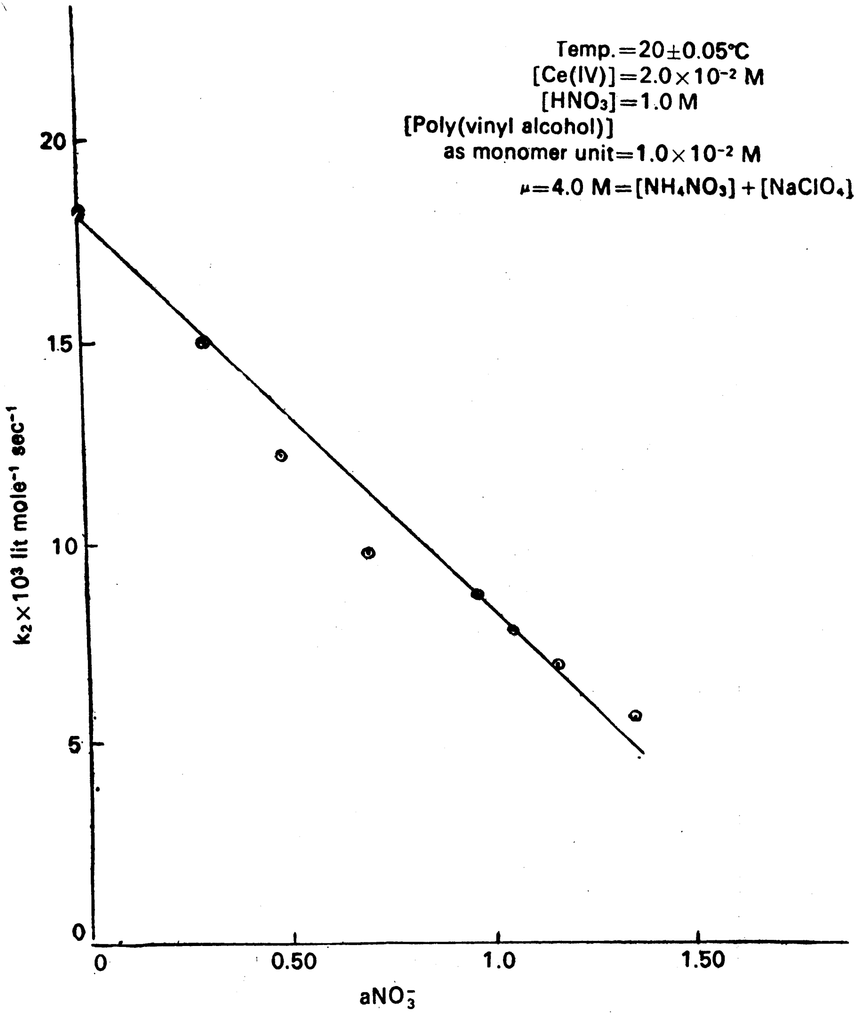


Fig. 3. Poly (vinyl alcohol)-Ce(1V) reaction in 1M nitric acid medium. Effect of varying $^{a}NO_3$ on second order rate constant.

tive Ce(IV) species with Ce(III) were already established by Yost *et al.*[26] and also separately by Blaustein and Gryder[27]. Comparatively lower values for thermodynamic parameters viz. $\Delta E^{\neq} = 14.34$ Kcal. mole^{-2} $-\Delta H^{\neq} = 13.92$ Kcal. mole^{-1} $\Delta F^{\neq} = -1.606$ Kcal. mole^{-1}, $\Delta S^{\neq} = 41.57$ e.u. and frequency factor log $A = 4.5 \times 10^{8}$ sec^{-1} respectively obtained in these investigations necessarily show that the reaction proceeds through a prior intermediary complex which further reacts with excess of Ce(IV) to form finally acetic acid with a C-H bond cleavage.

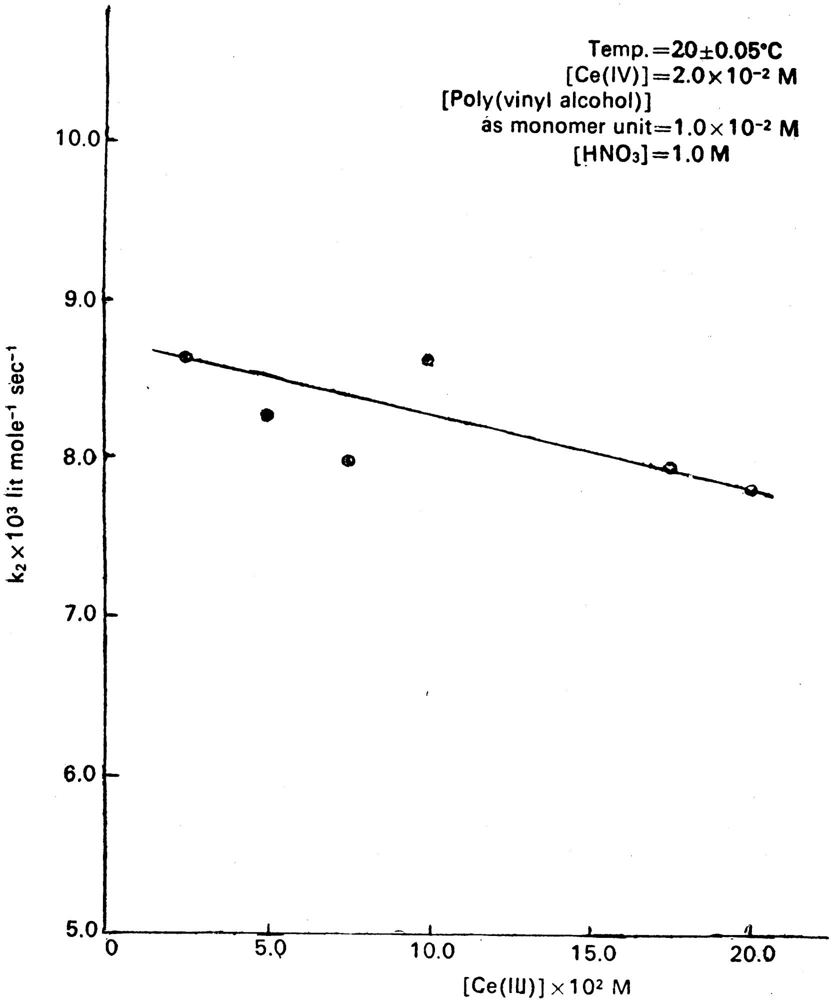


Fig. 4. Poly (vinyl alcohol)—Ce(IV) reaction in 1M nitric acid medium. Effect of variation of [Ce(III)] on second order rate constant.

OXIDIMETRIC DETERMINATION OF POLY (VINYL ALCOHOL) WITH AMMONIUM HEXANITRATOCERATE (IV)

Recommended Procedure

Transfer an aliquot of 0.1% poly (vinyl alcohol) solution (*ca* 0.05M as poly (vinyl alcohol) monomer unit) containing 5.0–20.0 mg of poly (vinyl alcohol) as a monomer to an Erlenmeyer flask provided with a leakproof stopper. Add 2.5–3.0 times known excess of cerium(IV) nitrate solution required for complete oxidation and further add a requisite volume of 1.0N nitric acid to maintain overall 0.5N nitric acid concentration. From the above kinetic studies, it is evident that the rate of oxidation of poly (vinyl alcohol) is very much facilitated at lower concentrations of nitric acid (*ca* 0.5N). The reaction mixture should be left out at 50 ± 5°C at least for $\frac{1}{2}$ hr. for complete oxidation to acetic acid. As discussed earlier the number of equivalents of cerium(IV) required per mole of poly (vinyl alcohol) is 2.0. From this stoichiometry the factor worked out is as follows:

1 ml of 0.1N Ce(IV) consumed $\equiv$ 2.2 mg of PVA as monomer unit.

A large number of determinations are carried out utilising the above stoichiometry at 50 ± 5°C for $\frac{1}{2}$ hr. In all these determinations the unused Ce(IV) was back titrated with standard Fe(II) to a ferroin indicator end point as well as potentiometric end point. These determinations are in a narrow error range of −0.1 to +0.5N.

ACKNOWLEDGEMENT

The authors are grateful to Dr. G. N. Garud, Principal, Visvesvaraya Regional College of Engg., Nagpur and Prof. V. Ramachandra Rao, Professor of Chemistry. VRCE, Nagpur, for their constant encouragement and helpful attitude in providing facilities in pursuit of this research work.

REFERENCES

1. Shiraishi Makoto and Matsumoto Masakazu, *Kobunshi Kagaku*, **19**, 722 (1962).
2. K. Schlaepfer, *Schweiz Arch Angew, Wiss Tech.* (Ger.), **31**, 154 (1965).
3. A. L. Samvelyam, O. A. Chaltykyan and N. M. Belieryan, *Dokh. Akad. Nauk. Arm. S.S.R.*, **43**, 22 (1966).
4. I. S. Okhrimenko and G. N. Smirnov, *Zh. Prikl. Khim.*, **40**, 2531 (1967).
5. N. M. Beileryan, R. P. Meliksetyun and O. A. Chaltykyan, *Vysokomol Soedin*, Ser. B, **12**, 416 (1970).
6. G. D. Korodenko, B. N. Naruzullaey, S. N. Karimov and A. G. Aleksandrov, *Tr. Kafedry Fiz. Tevred Tela Probl. Lab. Fiz. Prochnostipulim Todzh. Univ.* (1970). 22–8 (Russ.) From *Ref. Zh. Khim.*, 1971, Abstr. No. 10 S 170.
7. T. Makoto and O. Makoto, *Kobunshi Kagaku*, **30**, 456 (1973).
8. Yoshito Ikada, Yashuko Nishizaki and Ichiro Sakurada, *J. Polym. Sci. Polym. Chem. Ed.*, **12**, 1829 (1974).
9. S. I. Trakhtenbery and E. K. Kovalyuk, *Zh. Prikh. Khim.* (Leningrad), **48**, 182 (1975).
10. H. Auki, M. Uehara and T. Suzuki, *Zairy*, **27**, 1141 (1978) (Japan).
11. J. S. Sate and R. A. Shanks, *J. Polymer. Sci.*, *Polym. Chem. Ed.*, **17b**, 1867 (1979).
12. S. J. Huang, E. Quinga and I. F. Wang, *Org. Coat. Appl. Polym. Sc. Proc.*, **46**, 345 (1981).
13. ———, *Poly. Sci. Technol.* (Plenum), **21** (Modif. Polym.), 75 (1983).

14. J. A. Radley, Starch and Its Derivatives, Chapman and Hall Ltd., London (1968).

15. R. L. Whistler and Paschall, Editor, Starch, Chemistry and Technology, Vol. II, Academic Press Inc., New York (1967).

16. K. F. Paten, "Kinetics and mechanism of oxidation of starch with hypochlorite", Ph.D. thesis, Gujarat Univ. (1970).

17. C. Birtwell, D. A. Clibberns and B. P. Ridge, *J. Text. Inst.*, **16**, T. 13 (1925).

18. J. Schmorak and M. Lewin, *J. Polym. Sci.*, (A-1) **1**, 2601 (1963).

19. Shiraish Makoto and Matsumeto Masakazu, U.S. Pat. 3052, 662 (to Kurashiki Rayon Co. Ltd., Japan) (Sept. 1962), *Chem. Abstr.*, **58**, 594 (1964).

20. ———, *Kogyo Kagaku Zasshi*, **65**, 1430 (1962); *Chem. Abstr.*, **58**, 5496 (1964).

21. C. A. Finch, Polyvinyl Alcohol, Text, Edited by C. A. Finch, Wiley Publ., p. 561 (1973).

22. Y. Ogiwara and M. Uchiyama, *J. Polym. Sci.*, (A-1) **7**, 147 (1969).

23. ———, op. cit., (A-1) **8**, 641 (1970).

24. F. R. Duke and A. A. Forist, *J. Amer. Chem. Soc.*, **71**, 2790 (1949).

25. J. Shorter, *J. Chem. Soc.*, 1870 (1962).

26. D. M. Yost, H. Russel and C. S. Garner. The Rare Earth Elements and Their Compounds, John Wiley, New York, p. 5 (1947).

27. B. D. Blaustein and J. N. Gryder, *J. Amer. Chem. Soc.*, **79**, 540 (1957).

[*Received*: 18 December 1988; *Accepted*: 27 March 1989]. AJC—52