Mechanism of Oxidation of Esters by Ce^{4+} in Absence & Presence of Ag(I): A Kinetic Study

M. ANAND RAO, B. SETHURAM & T. NAVANEETH RAO*

Department of Chemistry, Osmania University, Hyderabad 500007

Kinetics of oxidation of aliphatic esters such as methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl and isobutyl acetates by Ce^{4+} in H_2SO_4 medium has been studied both under uncatalysed and Ag^+-catalysed conditions. The rate laws obtained for uncatalyzed and Ag^+ catalysed reactions are $k_0''[Ce^{4+}][ester]$ and $k''K[Ce^{4+}][ester][Ag^+]/1+K[ester]+K[Ag^+]$ respectively. A mechanism has been suggested for both the reactions, in which Ce^{4+} attacks the ester in a rate-determining step. The products obtained are HCHO, CO_2 and the aldehyde or ketone corresponding to the alcohol moiety.

OXIDATION of a variety of compounds like alcohols, aldehydes and ketones by Ce^{4+} have been extensively studied[1-5]. It is reported that esters could be oxidized using oxidants like acid permanganate[6], aqueous Br_2^7, Cr(VI)[8] and V(V)[9]. Two routes have been suggested for the oxidation of esters: (i) direct oxidation of the ester, and (ii) hydrolysis followed by the oxidation of alcohol. In the present work, we have undertaken the oxidation of some aliphatic esters by Ce^{4+} to understand which one of the two possible mechanisms is more likely when Ce^{4+} is the oxidant. It is observed that in the presence of Ag^+ ions the rate increased considerably and hence, the oxidation of esters by Ce^{4+} in the presence of Ag^+ has also been carried out to find out whether the presence of Ag^+ ion will result in a change in the mechanism of oxidation as also the mechanism of catalysis.

Materials and Methods

All the chemicals used were of extra pure quality and the kinetics was followed by estimating the unreacted Ce^{4+} at regular time intervals by volumetric analysis. The method of evaluating the rates, orders and other kinetic parameters are same as in our earlier paper[2].

Product analysis — The products of oxidation, HCHO, CO_2 and the corresponding aldehydes or ketones from the alcohol moiety were identified by their characteristic tests[10,11] as well as by TLC analysis of their 2,4-DNP derivatives. Aldehydes were estimated gravimetrically as their 2,4-DNP derivatives.

Stoichiometry — It was found that one mole of ester required six moles of Ce^{4+} to form one mole of aldehyde or ketone in the absence or presence of Ag^+.

Results and Discussion

Under the conditions $[Ce^{4+}]\ll[ester]$, the order in $[Ce^{4+}]$ was unity for all esters studied in the absence

or presence of Ag^+. The plots of log $(a/a-x)$ versus time (Figs 1 and 2, curve A) [where '*a*' and $(a-x)$ are respectively the concentrations of Ce^{4+} at zero and time t were linear passing through the origin from the slope of which the psuedo-first order rate constants (k') were evaluated. The order in [ester] in the absence of Ag^+ was found to be unity (Fig. 1B) from the slope of the linear plot of log k' versus log [ester]. However, it was found to be fractional (Fig. 2B) in the presence of Ag^+. The increase in $[Ag^+]$ increased the rate and the order in $[Ag^+]$ was also found to be fractional (Fig. 2C). The plot of $1/k'$ versus 1/[ester] was also linear with no intercept indicating no complex formation (Fig. 1C) in the absence of Ag^+. The increase in $[SO_4^{2-}]$ or $[HSO_4^-]$ decreased the rate of oxidation and increase in $[H^+]$ increased the rate [from $k' = 6 \cdot 0 \times 10^{-3}$ sec^{-1} $(1 \cdot 0M$ $H^+)$ to $12 \cdot 5 \times 10^{-3}$ sec^{-1} $(2 \cdot 0M$ $H^+)]$ at constant $[HSO_4^-]$ in the absence of Ag^+. Similar trends were observed in the presence of Ag^+. This indicates that neutral $Ce(SO_4)_2$ is probably the reactive species as observed in our earlier studies[2]. Ag^{2+}-substrate was detected by the formation of bipyridyl complex. Induced polymerization of acrylamide indicated the production of free radicals in the system. The reactions were studied in the temperature range (40-60°) to evaluate the activation parameters.

Oxidation of esters in the absence of Ag^+ — If hydrolysis followed by oxidation of alcohol were to be the probable mechanism of oxidation of ester, the rate of oxidation of ester in the limit could at best be equal to the rate of hydrolysis but never exceed it. The rate of oxidation of ester by Ce^{4+} was found to be several times greater (Table 1) than the rate of hydrolysis under otherwise similar conditions indicating direct oxidation of the ester by the oxidant. Another point in favour of the above contention is that only one aldehyde is possible if oxidation occures after hydrolysis[12]. Also formation of CO_2 cannot be explained by this mechanism. Hence, a mechanism in which Ce^{4+}
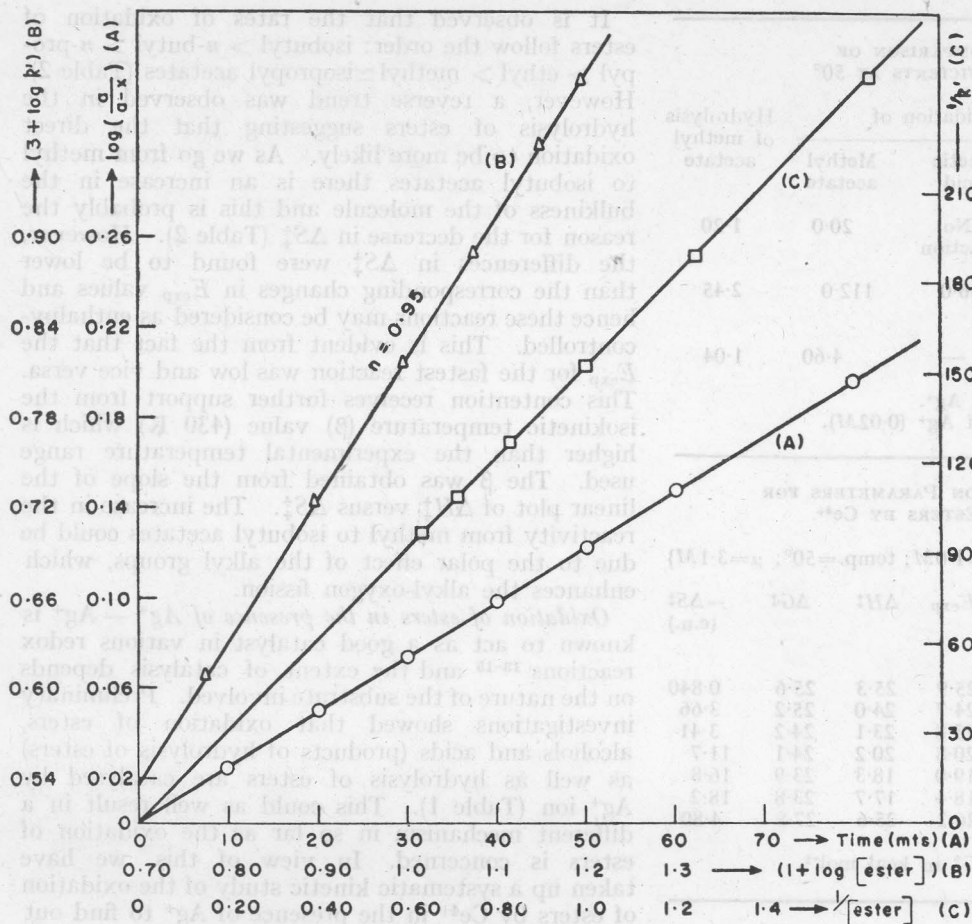
It is observed that the rates of oxidation of esters follow the order: isobutyl > n-butyl ≈ propyl ≈ ethyl ≈ methyl ≈ isopropyl acetates (Table 2). However, a reverse trend was observed in the hydrolysis of esters suggesting that the direct oxidation is more likely. As we go from methyl to isobutyl acetates there is an increase in the bulkiness of the molecule and this is probably the reason for the decrease in ΔS‡ (Table 2).

the differences in ΔS‡ were found to be lower than the corresponding changes in E_a, values and hence these reactions may be considered entropy controlled. This is evident from the fact that the E_a for the fastest reaction was low and vice-versa. This criterion receives further support from the isokinetic temperature (β) value (430 K) which is higher than the experimental temperature range used. The β was obtained from the slope of the linear plot of ΔH‡ versus ΔS‡. The increase in reactivity from n-butyl to isobutyl acetate could be due to the polar effect of the alkyl groups, which enhances the alkyl-oxygen fission.

Oxidation of esters in the presence of Ag⁺. — Ag⁺ is known to act as a good catalyst in various redox reactions[13,14] and the extent of catalysis depends on the nature of the substrate involved. The present investigations showed the oxidation of esters, alcohols and acids (products of hydrolysis of esters) as well as hydrolysis of esters catalysed by Ag⁺ ion (Table 1). This could as well result in a different mechanism in so far as the oxidation of esters is concerned. In view of this, we have taken up a systematic kinetic study of the oxidation of esters by Ce⁴⁺ in the presence of Ag⁺, to find out whether the presence of Ag⁺ ion will result in a change in the mechanism of oxidation as also the intermediates involved in the process. The general mechanism of Ag⁺-catalysed redox reactions involving Ce⁴⁺ and organic substrates has now been recognised[13] and is shown in Scheme 2.

From a comparison of the catalytic coefficients $[k_c = A_0 - A_0']/A_0']$ and k_0' are the bimolecular rate constants in the presence and absence of Ag⁺ respectively), it is found that the catalytic coefficient for oxidation of ester is much greater than that of hydrolysis (Table 1). This indicates that the route of direct oxidation is more likely even in the presence of Ag⁺. The products obtained and the stoichiometry of the reaction were same in the Ag⁺-catalysed oxidation of esters. The rate law obtained in the presence of Ag⁺ is similar to that which was obtained in the case of other esters[13], viz. change in the order in [ester] from unity (in the absence of Ag⁺) to fractional (in the presence of Ag⁺) (Figs. 1B and 2B) and

attacks the ester directly in the rate-determining step. In the present case, the fission of R—O bond appears more likely than C—C bond fission and this is supported by the rate constant which were found to be approximately the same for methyl acetate and ethyl acetate but different for ethyl acetate and any higher ester of acetic acid (Table 2). Based on the above experimental observations, the mechanism outlined in Scheme 1 appears to be the most probable.

Axes (Fig. 1):
- (A) $(3 + \log k')$ (B) — $\log\left(\frac{a}{a-x}\right)$ (A)
- Time (mts) (A)
- $(1 + \log$ [ester]$)$ (B)
- $1/$[ester] (C)

$$H_3C\text{-}COO\text{-}R + Ce^{4+} \xrightarrow[\text{slow}]{k_1} H_3C\text{-}COO^{\cdot} + R^{\cdot} + Ce^{3+}$$

$$H_3C\text{-}COO^{\cdot} \longrightarrow H_3C^{\cdot} + CO_2$$

$$H_3C^{\cdot} + Ce^{4+} \xrightarrow[\text{fast}]{} H_3C^{+} + Ce^{3+}$$

$$H_3C^+ \longrightarrow H_3C\text{-}OH + H^+ + Ce^{3+}$$

$$H_3C\text{-}OH + 2Ce^{4+} \xrightarrow[\text{fast}]{} HCHO + 2H^+ + 2Ce^{3+}$$

$$R^{\cdot} + Ce^{4+} \xrightarrow[\text{fast}]{} R\text{-}OH + H^+ + Ce^{3+}$$

$$R\text{-}OH + 2Ce^{4+} \xrightarrow[\text{fast}]{} R'CHO + 2H^+ + 2Ce^{3+}$$

Scheme 1

(where R is any alkyl group and R′ is similar to R with one carbon atom less). From the above mechanism, the rate law comes out to be —d[Ce⁴⁺]/dt = k[Ce⁴⁺][ester]. The products obtained for the various esters by this method would be the corresponding aldehydes and acids and this is generally observed in the present investigations.

Axes (Fig. 2):
- (2 + log k′) (A), $\log\left(\frac{a}{a-x}\right)$ (A)
- 1/[methyl acetate] (D)
- (2 + log k′) (C), 1/k′ (D)
- time in min (A)
- (+ log [methyl acetate]) (B)
- (2 + log [Ag⁺]) (C)

$$S + Ag^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{(adduct)}^+$$

$$\text{(adduct)}^+ + Ce^{4+} \overset{k_2}{\longrightarrow} \text{(adduct)}^{2+} + Ce^{3+}$$

$$\text{(adduct)}^{2+} \longrightarrow R^{\cdot} + H^+ + Ag^+ + \cdots$$

$$R^{\cdot} + Ce^{4+} \xrightarrow[\text{fast}]{} \text{products} + Ce^{3+}$$

Scheme 2

261

TABLE 1 — COMPARISON OF
CATALYTIC COEFFICIENTS AT 50°

	Ce⁴⁺ oxidation of			Hydrolysis of methyl acetate
	Methanol	Acetic acid	Methyl acetate	
$*10^4 \times k_0''$ (litre mol⁻¹ sec⁻¹)	56.0	No reaction	20.0	1.20
$\dagger 10^4 \times k''$ (litre mol⁻¹ sec⁻¹)	500.0	56.0	112.0	2.45
$(k'' - k_0'')/k_0''$	7.93	—	4.60	1.04

*In absence of Ag⁺.
†In presence of Ag⁺ (0.02M).

TABLE 2 — ACTIVATION PARAMETERS FOR
OXIDATION OF ESTERS BY Ce⁴⁺

$\{[Ce^{4+}] = 2.0 \times 10^{-3}M; [H_2SO_4] = 1.0M; temp. = 50°; \mu = 3.1M\}$

Ester	$10^4 \times k_0''$ (litre mol⁻¹ sec⁻¹)	E_{exp}	$\Delta H\ddagger$	$\Delta G\ddagger$	$-\Delta S\ddagger$ (e.u.)
Methyl acetate	1.47	25.9	25.3	25.6	0.840
Ethyl acetate	3.87	24.7	24.0	25.2	3.66
Ethyl formate	3.78	23.8	23.1	24.2	3.41
n-Propyl acetate	14.1	20.8	20.2	24.1	11.7
n-Butyl acetate	17.0	19.0	18.3	23.9	16.8
Isobutyl acetate	21.4	18.4	17.7	23.8	18.2
Isopropyl acetate	1.12	26.2	25.6	27.8	4.80

E_{exp}, $\Delta H\ddagger$ and $\Delta G\ddagger$ in kcal mol⁻¹.

attacks the ester directly in the rate-determining step is envisaged. In this case, the fission of R—O bond appears more likely than C—C bond fission and this is supported by the rate constants which were found to be approximately the same for ethyl formate and ethyl acetate but different for ethyl acetate and any other ester of acetic acid (Table 2). Based on the above experimental observations, the mechanism outlined in Scheme 1 appears to be the most probable.
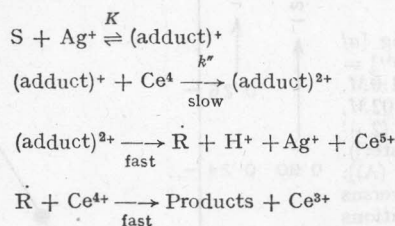
$$H_3C-COOR + Ce^{4+} \xrightarrow[slow]{k''} H_3C-CO\dot{O} + R^+ + Ce^{3+}$$

$$H_3C-CO\dot{O} \xrightarrow{fast} H_3\dot{C} + CO_2$$

$$H_3\dot{C} + Ce^{4+} \xrightarrow[fast]{HOH} H_3COH + H^+ + Ce^{3+}$$

$$H_3COH + 2Ce^{4+} \xrightarrow{fast} HCHO + 2H^+ + 2Ce^{3+}$$

$$R^+ \xrightarrow[fast]{HOH} ROH + H^+$$

$$ROH + 2Ce^{4+} \xrightarrow{fast} R'CHO + 2H^+ + 2Ce^{3+}$$
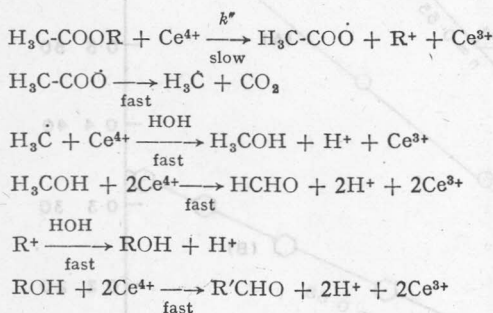
Scheme 1

(where R is any alkyl group and R' is similar to R with one carbon atom less). From the above mechanism, the rate law comes out to be $-d[Ce^{4+}]/dt = k'[Ce^{4+}][ester]$. The products obtained for the various esters as well as observed rate law, and the stoichiometry of the reaction confirm the proposed mechanism.

It is observed that the rates of oxidation of esters follow the order: isobutyl > n-butyl > n-propyl > ethyl > methyl ≃ isopropyl acetates (Table 2). However, a reverse trend was observed in the hydrolysis of esters suggesting that the direct oxidation to be more likely. As we go from methyl to isobutyl acetates there is an increase in the bulkiness of the molecule and this is probably the reason for the decrease in $\Delta S\ddagger$ (Table 2). However, the differences in $\Delta S\ddagger$ were found to be lower than the corresponding changes in E_{exp} values and hence these reactions may be considered as enthalpy-controlled. This is evident from the fact that the E_{exp} for the fastest reaction was low and vice versa. This contention receives further support from the isokinetic temperature (β) value (430 K) which is higher than the experimental temperature range used. The β was obtained from the slope of the linear plot of $\Delta H\ddagger$ versus $\Delta S\ddagger$. The increase in the reactivity from methyl to isobutyl acetates could be due to the polar effect of the alkyl groups, which enhances the alkyl-oxygen fission.
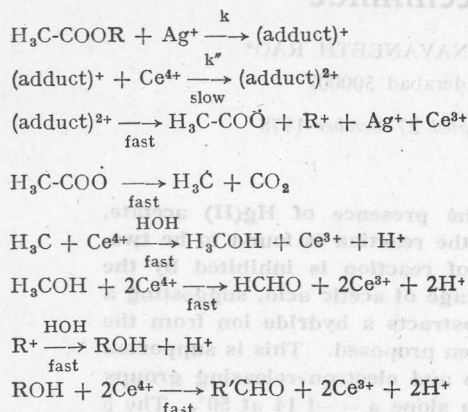
Oxidation of esters in the presence of Ag⁺ — Ag⁺ is known to act as a good catalyst in various redox reactions [13-15] and the extent of catalysis depends on the nature of the substrate involved. Preliminary investigations showed that oxidation of esters, alcohols and acids (products of hydrolysis of esters) as well as hydrolysis of esters are catalysed by Ag⁺ ion (Table 1). This could as well result in a different mechanism in so far as the oxidation of esters is concerned. In view of this, we have taken up a systematic kinetic study of the oxidation of esters by Ce⁴⁺ in the presence of Ag⁺ to find out whether the presence of Ag⁺ ion will result in a change in the mechanism of oxidation as also the mechanism of catalysis. The general mechanism of Ag⁺ catalysis in redox reactions involving Ce⁴⁺ and organic substrate (S) have now been recognized[13-15] and is shown in Scheme 2.

$$S + Ag^+ \xrightleftharpoons{K} (adduct)^+$$

$$(adduct)^+ + Ce^4 \xrightarrow[slow]{k''} (adduct)^{2+}$$

$$(adduct)^{2+} \xrightarrow{fast} R + H^+ + Ag^+ + Ce^{5+}$$

$$R + Ce^{4+} \xrightarrow{fast} Products + Ce^{3+}$$

Scheme 2

From a comparison of the catalytic coefficients $[(k'' - k_0'')/k_0'']$ (where k'' and k_0'' are the bimolecular rate constants in the presence and absence of Ag⁺, respectively), it is found that the catalytic coefficient for the oxidation of ester is much greater than that of hydrolysis (Table 1). This indicates that the route of direct oxidation is more likely even in the presence of Ag⁺. The products obtained and the stoichiometry of the reaction were same as in the uncatalysed oxidation of esters. The rate law obtained in the presence of Ag⁺ is similar to what has been obtained in the case of other substrates[13-15], viz. change in the order in [ester] from unity (in the absence of Ag⁺) to fractional (in the presence of Ag⁺) (Figs. 1B and 2B) and

fractional order in $[Ag^+]$ (Fig. 2C). Since Ag^{2+} was also detected in the reaction mixture, we invoke a similar mechanism as has been proposed for the oxidation of isopropyl alcohol, for the oxidation of ester also. The mechanism of oxidation of ester in the presence of Ag^+ may be written as shown in Scheme 3.

$$H_3C-COOR + Ag^+ \xrightarrow{k} (adduct)^+$$

$$(adduct)^+ + Ce^{4+} \xrightarrow[slow]{k''} (adduct)^{2+}$$

$$(adduct)^{2+} \xrightarrow{fast} H_3C-CO\ddot{O} + R^+ + Ag^+ + Ce^{3+}$$

$$H_3C-CO\ddot{O} \xrightarrow{fast} H_3\dot{C} + CO_2$$

$$H_3C + Ce^{4+} \xrightarrow[fast]{HOH} H_3COH + Ce^{3+} + H^+$$

$$H_3COH + 2Ce^{4+} \xrightarrow{fast} HCHO + 2Ce^{3+} + 2H^+$$

$$R^+ \xrightarrow[fast]{HOH} ROH + H^+$$

$$ROH + 2Ce^{4+} \xrightarrow{fast} R'CHO + 2Ce^{3+} + 2H^+$$

<p align="center">Scheme 3</p>

From the above mechanism, the rate equation comes out to be,

$$-\frac{2 \cdot 303 d \log [Ce^{4+}]}{dt} = k' = \frac{k''K[ester][Ag^+]}{1 + K[ester] + K[Ag^+]} \quad ...(1)$$

where k' is the observed psuedo-first order rate constant, k'' is the bimolecular rate constant for the slow step, and K the formation constant of the adduct. Equation (1) accounts for the first order dependence of rate on $[Ce^{4+}]$ (Fig. 2A) and fractional order dependence of rate on $[Ag^+]$ and $[ester]$ (Figs. 2C & 2B) obtained experimentally. Taking reciprocals of Eq. (1), we get

$$\frac{1}{k'} = \frac{1}{[ester]} \left[\frac{1}{k''K[Ag^+]} + \frac{1}{k''} \right] + \frac{1}{k''[Ag^+]} \quad ...(2)$$

From Eq. (2), it is clear that the plot of $1/k'$ versus $1/[ester]$ at constant $[Ag^+]$ should be linear. Such plots were obtained in the present work for all the esters studied (Fig. 2D). From the intercept and slope values the bimolecular rate constants for the slow step (k'') and formation constant of the adducts (K) were evaluated (Table 3).

The increase in reactivity from methyl to *n*-butyl could be due to the polar effect of the alkyl groups which enhances the alkyl-oxygen fission. The increase in the electron density on alkyl-oxygen also favours the formation of Ag^+-ester adduct as is evident from the trends in K values (Table 3).

TABLE 3 — ACTIVATION PARAMETERS FOR THE Ag⁺-CATALYSED OXIDATION OF ESTERS BY Ce⁴⁺ IN H_2SO_4 MEDIUM

{$[Ce^{4+}] = 2 \cdot 0 \times 10^{-3} M$; $[H_2SO_4] = 1 \cdot 0 M$; $[Ag^+] = 0 \cdot 02 M$; temp. $= 50°$; $\mu = 3 \cdot 1 M$}

Ester	$k'' \times 10^2$ (litre mol⁻¹ sec⁻¹)	K_{exp} (litre mol⁻¹)	E_{exp}	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$-\Delta S^{\ddagger}$ (e.u.)
Methyl acetate	1·72	1·34	22·0	21·4	21·7	0·928
Ethyl acetate	3·78	6·86	21·3	20·7	21·3	1·86
Ethyl formate	3·56	6·60	21·0	20·4	21·2	2·47
n-Propyl acetate	6·41	18·0	17·3	16·7	19·8	9·59
Isopropyl acetate	4·63	13·6	18·4	17·8	20·5	8·36
n-Butyl acetate	9·05	23·8	16·5	15·9	19·6	11·4
Isobutyl acetate	8·05	20·0	17·1	16·5	19·7	9·91

E_{exp}, $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ in kcal mol⁻¹.

Acknowledgement

References

1. MUHAMMAD, S. S. & RAO, K. V., *Bull. chem. Soc. Japan*, **36** (1963), 943, 949.
2. MUHAMMAD, S. S. & SETHURAM, B., *Acta chim. hung.*, **46** (1965), 115, 125.
3. HARGREAVES, G. & SUTCLIFFE, L. M., *Trans. Faraday Soc.*, **51** (1955), 1105.
4. CONANT, J. B. & ASTON, J. G., *J. Am. chem. Soc.*, **50** (1928), 1783.
5. PANIGRAHI, G. P. & MISHRA, P. K., *Indian J. Chem.*, **14A** (1976), 579.
6. SUBBA RAO, P. V., *Z. phys. Chem.*, **246** (1971), 352.
7. DENO, N. C. & POTTER, N. H., *J. Am. chem. Soc.*, **89** (1967), 3555.
8. RADHAKRISHNAMURTHI, P. S. & BEHERA, T. C., *J. Indian chem. Soc.*, **46** (1969), 92.
9. RADHAKRISHNAMURTHI, P. S. & PATI, S. C., *J. Indian chem. Soc.*, **46** (1969), 847.
10. FEIGL, F., *Spot tests in organic analysis* (Elsevier, London), 1966, 435, 414.
11. VOGEL, A. I., *A text book of macro and semi-micro qualitative inorganic analysis* (Orient Longmans, New Delhi), 1967, 326.
12. WILLARD, H. H. & YOUNG, P., *J. Am. chem. Soc.*, **52** (1930), 132.
13. SAIPRAKASH, P. K. & SETHURAM, B., *Indian J. Chem.*, **11** (1973), 246.
14. SRIVASTAVA, S. P. & HAMBIR SINGH, *Indian J. Chem.*, **14A** (1976), 667.
15. ADINARAYANA, M., SETHURAM, B. & NAVANEETH RAO, T., *Curr. Sci.*, **44** (1975), 581.