Kinetics and Mechanism of the Oxidation of Hypophosphite with *N*-Chlorotoluene-*p*-sulphonamide (Chloramine T) catalysed by Osmium(VIII) in Alkaline Solution

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The kinetics of osmium(VIII)-catalysed oxidation of hypophosphite, $H_2PO_2^-$, with chloramine T (cat, *N*-chlorotoluene-*p*-sulphamide) was studied by estimating the latter iodometrically. The rate law (i) holds for $[OH^-] = 0.02–0.142$, $[H_2PO_2^-] = 0.001–0.02$, and $[Os_{VIII}] = 1 \times 10^{-5}$ to 1×10^{-4} mol dm^{-3} where K_1 is defined by equation (ii), K_2 and K_3 are the equilibrium formation constants

$$\gtrsim\frac{d[cat]}{dt} = \frac{k_1K_2[cat][Os^{VIII}][H_2PO_2^-]}{1 + K_1[OH^-] + K_2[H_2PO_2^-] + K_1K_3[OH^-][H_2PO_2^-]} \qquad (i)$$

$$[OsO_3(OH)_3]^- + OH^- \xrightleftharpoons{K_1} [OsO_4(OH)_2]^{2-} + H_2O \qquad (ii)$$

of complexes $[OsO_3(OH)_3(H_2PO_2)]^{2-}$ and $[OsO_4(OH)_2(H_2PO_2)]^{3-}$ respectively and the former reacts with chloramine T. The values of k_1, K_1, K_2 and K_3 were calculated to be 16.6 ± 0.5 dm^3 mol^{-1} s^{-1}, 37.6 ± 2, 175 ± 6.0 and 130 ± 5.0 dm^3 mol^{-1} at 45 °C and I = 1.0 mol dm^{-3} respectively.

The kinetic study of the oxidation of hypophosphite with chloramine T (cat, *N*-chlorotoluene-*p*-sulphonamide) is interesting in view of the little known chemistry of hypophosphorous acid in alkaline media.[1] The oxidation of hypophosphorous acid with carboxylato-bound chromium(V) and reduction of cobalt(III)-co-ordinated phosphite and hypophosphite with $[Ru(NH_3)_6]^{2+}$, Eu^{2+}, V^{2+} and Cr^{2+} have recently been reported[1] in solutions. So far as the oxidation of hypophosphorous acid in acidic media is concerned, a large number of reactions[2–5] exhibits rate independence of the concentration of the substrate. However, reactions[6] in alkaline media do not behave analogously. Nevertheless, studies with non-metallic oxidants both in acidic and alkaline media are surprisingly scanty.

Further, the alkaline chemistry of chloramine T is not well defined despite a large volume of research in recent years.[7] The reason is, probably, the slow reactions of the oxidant in alkaline media. Moreover, osmium(VIII) has frequently been employed as a catalyst[8–11] in chloramine T reactions in alkaline media, and its catalytic role is still not well established.

These observations prompted us to undertake a kinetic study of the present reaction, with the following aims: to define more precisely the chloramine T species which partake in the redox system in alkaline media, and secondly, since chloramine T is not expected to form an intermediate complex with hypophosphite, to explore the other options that are available to the substrate for oxidation in the presence of osmium(VIII).

Experimental

Material.—Solutions of chloramine T were prepared by dissolving the sodium salt of *N*-chlorotoluene-*p*-sulphonamide (E. Merck) in twice distilled water. These solutions were stored in brown glass bottles blackened from the outside to eliminate photochemical decomposition. They were standardized iodometrically.[12,13] The sodium salt of hypophosphorous acid (Riedel) and NaOH (E. Merck) were used as received. Osmium tetraoxide (Johnson Matthey) was dissolved in 0.5 mol dm^{-3} NaOH and analysed iodometrically. Solutions of osmium(VIII) are quite stable[14] >0.3 mol dm^{-3} in NaOH provided they are kept refrigerated. Other chemicals were either of AnalaR or guaranteed reagent grade.

Doubly distilled water was used throughout the study, the second distillation being from alkaline permanganate solution in an all-glass assembly. Corning glass vessels blackened from the outside were employed for the reaction mixtures to ensure the kinetics of the reaction was free from any photochemical effects.

Spectrophotometric work was carried out on a UV spectrophotometer. The solutions of Os^{VIII} show a broad maximum between 320 and 360 nm. However, no change in spectrum was observed for $[OH^-] > 0.1$ mol dm^{-3} and cat concentrations ranging from 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3}.

Procedure.—The reaction vessels containing all ingredients except chloramine T were immersed in a water-bath thermostatted at 45 ± 0.1 °C unless stated otherwise. The reactions were usually initiated by adding a known volume of chloramine T solution to reaction mixtures containing all other reaction components. However, the order of addition did not affect the kinetics. The progress of the reaction was monitored by estimating unreacted chloramine T iodometrically[12,13] at different intervals of time. The iodine liberated by osmium(VIII) was accounted for in subsequent calculations of concentrations.

The reported slow reaction[15] between iodine and phosphorous acid in acid concentration (≈ 1.0 mol dm^{-3}) employed in iodometric analysis did not occur even over 1 h at ambient temperature. Initial rates were computed by the plane-mirror method.[16] Pseudo-first-order rate constants were also calculated wherever reaction conditions permitted. Reproducibility was better than ±6%.

Results

Stoichiometric determinations were carried out for reactions with excess of chloramine T (henceforth written as cat) over hypophosphite. These reactions were allowed to proceed for 2–3 h at 50 °C and the excess of cat was estimated iodometrically. The results collected in Table 1 conform to the stoichiometry as represented by equation (1) (R = *p*-$MeC_6H_4SO_2$).

$$RNCl^- + H_2PO_2^- \xrightarrow{H_2O} RNH_2 + HPO_3^{2-} + HCl \quad (1)$$

Chloramine T *and Osmium*(VIII) *Dependences.*—The concentration of chloramine T was varied in the range (5.0–40.0) × 10^{-4} mol dm^{-3} at constant concentrations of $[H_2PO_2^-] = 1.0 \times 10^{-2}$, $[Os^{VIII}] = 1.0 \times 10^{-4}$, $[OH^-] = 4.15 \times 10^{-2}$ and ionic strength (I) = 1.0 mol dm^{-3} (adjusted by the addition of sodium perchlorate). A plot of the initial rate against the concentration of chloramine T yielded a straight line passing through the origin. This indicates an order of one with respect to the oxidant concentration. Pseudo-first-order plots were also constructed for reactions where $[cat] < 10\,[H_2PO_2^-]$. The rate constants calculated from these plots were constant and independent of the initial concentrations of cat.

Similarly, the concentration of osmium(VIII) was varied from 1.0×10^{-5} to 1.0×10^{-4} mol dm^{-3} at fixed concentrations of $[cat] = 3.0 \times 10^{-3}$, $[H_2PO_2^-] = 5.0 \times 10^{-3}$ and $[OH^-] = 4.15 \times 10^{-2}$ mol dm^{-3} at I = 1.0 mol dm^{-3}. A plot of the initial rate against the concentration of osmium(VIII) also yielded a straight line passing through the origin, indicating an order of one with respect to the catalyst concentration.

Table 1 Stoichiometric results for the reaction of chloramine T and hypophosphite in the presence of osmium(VIII) as catalyst in alkaline media $[Os^{VIII}] = 1.0 \times 10^{-4}$, $[OH^-] = 4.15 \times 10^{-2}$ and I = 1.0 mol dm^{-3} (adjusted with sodium perchlorate)

$10^3[cat]$	$10^3[H_2PO_2^-]$	$10^3[cat]$ consumed	$\Delta[cat]/\Delta[H_2PO_2^-]$
	mol dm^{-3}		
3.0	2.0	1.9	0.95
4.0	2.0	1.85	0.93
5.0	3.0	2.80	0.93
6.0	4.0	3.85	0.96

Hypophosphite Dependence.—The concentration of hypophosphite was varied from 1.0×10^{-3} to 2.0×10^{-2} mol dm^{-3} at fixed concentrations of the other reaction components. The rate initially increases and then tends to a limiting value with increasing hypophosphite concentration. A plot of $1/k'$ *versus* $[H_2PO_2^-]^{-1}$ (k' is the observed second-order constant) yielded a straight line with non-zero intercept at three different concentrations of hydroxide ion. Such behaviour conforms to the empirical rate equation (2), where a' and b' are constants.

$$-\frac{d[cat]}{dt} = \frac{a'[H_2PO_2^-][Os^{VIII}][cat]}{1 + b'[H_2PO_2^-]} \quad (2)$$

Results are given in Table 2.

Hydroxide Ion Dependence.—The concentration of hydroxide ion was varied from 0.02 to 0.1 mol dm^{-3} at three different hypophosphite concentrations and fixed concentrations of other reaction ingredients at I = 1.0 mol dm^{-3} (adjusted by the addition of sodium perchlorate). The rate decreases with increasing hydroxide concentration. A plot of $1/k'$ *versus* $[OH^-]$ yielded a straight line with non-zero intercept. Results are collected in Table 2.

Effect of Toluene-p-*sulphonamide.*—The concentration of toluene-*p*-sulphonamide when varied from 0.001 to 0.01 mol dm^{-3} at fixed concentrations of other reaction components did not result in any change in rate. This observation rules out the possibility of any equilibrium involving toluene-*p*-sulphonamide preceded by the rate-determining step.

Effect of Chloride Ion.—The concentration of chloride ion was varied from 0.05 to 0.2 mol dm^{-3} at constant concentrations of other reaction ingredients. However, the rate of the reaction remained unchanged. It is worth noting that chloride ion catalyses a large number of chloramine T reactions including those with hypophosphite and phosphite in acidic media.[17] This

Table 2 Observed and calculated values of k' in the osmium(VIII)-catalysed oxidation of hypophosphite with cat. $[cat] = 3.0 \times 10^{-3}$, $[Os^{VIII}] = 1.0 \times 10^{-4}$ and I = 1.0 mol dm^{-3}, 45 °C

(*a*) $[OH^-]$ = 0.022 mol dm^{-3}											
$10^2[H_2PO_2^-]$/mol dm^{-3}		0.1	0.2	0.3	0.4	0.5	0.6	0.8	1.0	1.5	2.0
k'/dm^3 mol^{-1} s^{-1}	exptl.	1.5	2.4	3.4	3.9	4.2	5.1	5.7	6.3	6.7	7.2
	calc.	1.4	2.4	3.3	3.9	4.5	5.0	5.7	6.2	7.2	7.8
(*b*) $[OH^-]$ = 0.042 mol dm^{-3}											
$10^2[H_2PO_2^-]$/mol dm^{-3}		0.1	—	0.3	—	0.5	0.6	0.8	1.0	—	2.0
k'/dm^3 mol^{-1} s^{-1}	exptl.	0.97	—	2.4	—	2.9	3.3	3.9	4.2	—	5.3
	calc.	0.98	—	2.3	—	3.3	3.6	4.1	4.6	—	5.7
(*c*) $[OH^-]$ = 0.062 mol dm^{-3}											
$10^2[H_2PO_2^-]$/mol dm^{-3}		0.1	0.2	0.3	0.4	0.5	0.6	—	1.0	—	2.0
k'/dm^3 mol^{-1} s^{-1}	exptl.	0.83	1.5	1.9	2.1	2.3	2.5	—	3.3	—	4.2
	calc.	0.76	1.4	1.8	2.2	2.5	2.8	—	3.6	—	4.5
(*d*) $10^3[H_2PO_2^-]$ = 5.0 mol dm^{-3}											
$10^2[OH^-]$/mol dm^{-3}		2.2	3.2	4.2	5.2	6.2	7.2	10.2			
k'/dm^3 mol^{-1} s^{-1}	exptl.	4.2	3.6	2.9	2.6	2.2	2.1	1.7			
	calc.	4.5	3.8	3.2	2.8	2.5	2.3	1.8			
(*e*) $10^2[H_2PO_2^-]$ = 1.0 mol dm^{-3}											
$10^2[OH^-]$/mol dm^{-3}		2.2	4.2	6.2	8.2	10.2	14.2				
k'/dm^3 mol^{-1} s^{-1}	exptl.	6.3	4.2	3.3	2.8	2.3	1.8				
	calc.	6.2	4.6	3.6	3.0	2.5	1.9				
(*f*) $10^2[H_2PO_2^-]$ = 2.0 mol dm^{-3}											
$10^2[OH^-]$/mol dm^{-3}		2.2	4.2	6.2	8.2	10.2	14.2				
k'/dm^3 mol^{-1} s^{-1}	exptl.	7.2	5.3	4.2	3.3	3.1	2.2				
	calc.	7.8	5.7	4.5	3.7	3.2	2.5				

Calculated k' values were obtained by substituting the values of the constants k_1 = 16.6 dm^3 mol^{-1} s^{-1}, K_1 = 37.6 dm^3 mol^{-1}, K_2 = 175 dm^3 mol^{-1} and K_3 = 130 dm^3 mol^{-1} at 45 °C in rate equation (15).

difference in chloride-ion catalysis indicates that the reactive species of cat in the two media are different.

Discussion

Chloramine T is reported[18,19] to be a strong electrolyte in aqueous solutions [equation (3)]. However, equilibria (4)–(7)[19–22] have been reported in acidic media. In view of the fact that the kinetic order with respect to [cat] is one, and the rate of reaction is unaffected by toluene-*p*-sulphonamide, the equilibria (5) and (6) do not exist. Equilibrium (7) conforms to hydroxide-ion catalysis contrary to the hydroxide-ion dependence observed in the reference reaction. If calculations based on the decinormal solutions of cat made by Bishop and Jennings[18] are any guide, the concentration of RNHCl is negligibly small as compared to that of $RNCl^-$.

$$\mathrm{RNClNa} \rightleftharpoons \mathrm{RNCl^-} + \mathrm{Na^+} \qquad (3)$$

$$\mathrm{RNCl^-} + \mathrm{H^+} \rightleftharpoons \mathrm{RNHCl} \qquad (4)$$

$$\mathrm{2RNHCl} \rightleftharpoons \mathrm{RNCl_2} + \mathrm{RNH_2} \qquad (5)$$

$$\mathrm{RNHCl} + \mathrm{H_2O} \rightleftharpoons \mathrm{HOCl} + \mathrm{RNH_2} \qquad (6)$$

$$\mathrm{HOCl} \rightleftharpoons \mathrm{OCl^-} + \mathrm{H^+} \qquad (7)$$

Chloride-ion catalysis[7] in reactions of cat has been explained through an interaction of RNHCl and Cl^- producing an intermediate $RNHCl^{\delta+} \cdots Cl^{\delta-}$. However, no such interaction is known between $RNCl^-$ and Cl^-.[13]

Thus the effect of Cl^- on the rate of the reaction of cat and substrate in acidic and alkaline media can be considered to be important evidence in distinguishing between RNHCl and $RNCl^-$ species. Apart from this effect, the rate of the reaction is also retarded by hydroxide ion and if these two observations are coupled with the first-order dependence with respect to [cat], $RNCl^-$ is believed to be the only reactive species of cat.

Hypophosphorous acid is monobasic and as such $H_2PO_2^-$ is the most likely species of the acid in alkaline media. This species has also been considered to be reactive in other reactions.[1,6] Since the hydroxide-ion dependence is complex it cannot be linked with hypophosphite in a similar way to that reported[6] in the reaction of H_3PO_2 with hexacyanoferrate(III). The species $H_3PO_3^{2-}$ and HPO_2^{2-} reported in the reaction[23] of hypophosphite with RuO_4^- can also not be considered based on similar arguments.

Osmium tetraoxide yields a red solution of $[OsO_4(OH)_2]^{2-}$ in strongly alkaline solution.[24] However, a dilute alkaline solution of OsO_4 converts $[OsO_4(OH)_2]^{2-}$ into $[OsO_3(OH)_3]^-$ in agreement with the results reported by Sauerbrum and Sandell.[25] Since the rate decreases with increasing hydroxide-ion concentration, all the species subsequent to $[OsO_3(OH)_3]^-$ must be less reactive. Furthermore, an intense brown-red colour appeared in the reaction mixture on mixing solutions of hypophosphite and osmium(VIII) at < 10 °C, whereas mixtures of Os^{VIII} or $H_2PO_2^-$ with cat did not yield any colour change. The spectral analysis of the $H_2PO_2^-$–Os^{VIII} system is too difficult. It is worth mentioning that chelate formation between cat and osmium(VIII) has been reported in the oxidation of α-hydroxy acids[8] without adducing any kinetic or spectral evidence. The kinetic results for the reference study, however, do not support this observation.

Sisley and Jordan[26] recently reported the complexation between $Co^{III}(NH_3)_5$ and $H_2PO_2^-$ with the metal centre being O- rather than P-bound. Moreover, both P-bound hydrogens in $H_2P(O)OH$ are retained in the ligation, similar to singly P-bound hydrogen in $HP(O)(OH)_2$. Thus the co-ordination to Co^{III} leaves only one accessible acidic centre in phosphite and none in hypophosphite. The reaction of Os^{VIII} with P^I in the light of these observations is suspected to proceed through an oxygen-bridged intermediate arising from hypophosphite rather than Os^{VIII}. If it is assumed that the loss of the OH^- group is affected in ligation by $H_2PO_2^-$, a more complex hydroxide-ion dependence should have been observed.

Thus considering the experimental observations, *viz.* first order with respect to [cat] and $[Os^{VIII}]$ respectively, complex dependence on $[H_2PO_2^-]$, and inverse dependence on hydroxide-ion concentration, a reaction mechanism comprising steps (8)–(12) can be suggested. The corresponding rate law is (13) or (14) where k' is the observed second-order rate constant. Since the limiting rate is not attained even at higher concentrations of $[OH^-]$, the contribution of step (12) as compared to step (11) can be neglected. This reduces rate law (14) to (15). A plot of $1/k'$ *versus* $[H_2PO_2^-]^{-1}$ yields a straight line with non-zero intercept. The intercept and slope calculated from the plot are equal to $(K_2 + K_1K_3[OH^-])/k_1K_2$ and $(1 + K_1[OH^-])/k_1K_2$ respectively. Further plots of the intercept *versus* $[OH^-]$ and slope *versus* $[OH^-]$ yielded the values of k_1 and K_1 as 16.6 ± 0.05 $dm^3\ mol^{-1}\ s^{-1}$ and 37.6 ± 2.0 $dm^3\ mol^{-1}$ respectively. However, K_1 agrees with the value reported[27] earlier (42.5 ± 6.0 $dm^3\ mol^{-1}$) under almost identical experimental conditions. Further analysis of rate constants from equation (15) was made by plotting $1/k'$ *versus* $[OH^-]$ at three different hypophosphite concentrations. The intercept and slope calculated from the plot are equal to $(1 + K_2[H_2PO_2^-])/k_1K_2[H_2PO_2^-]$ and $(K_1 + K_1K_3[H_2PO_2^-])/k_1K_2[H_2PO_2^-]$ respectively.

$$[\mathrm{OsO_3(OH)_3}]^- + \mathrm{OH^-} \xrightleftharpoons{K_1} [\mathrm{OsO_4(OH)_2}]^{2-} + \mathrm{H_2O} \qquad (8)$$

$$[\mathrm{OsO_3(OH)_3}]^- + \mathrm{H_2PO_2^-} \xrightleftharpoons{K_2} [\mathrm{OsO_3(OH)_3(H_2PO_2)}]^{2-} \qquad (9)$$

$$[\mathrm{OsO_4(OH)_2}]^{2-} + \mathrm{H_2PO_2^-} \xrightleftharpoons{K_3} [\mathrm{OsO_4(OH)_2(H_2PO_2)}]^{3-} \qquad (10)$$

$$[\mathrm{OsO_3(OH)_3(H_2PO_2)}]^{2-} + \mathrm{RNCl^-} \xrightarrow[\mathrm{H_2O}]{k_1} [\mathrm{OsO_3(OH)_3}]^- + \mathrm{HPO_3^{2-}} + \mathrm{RNH_2} + \mathrm{HCl} \qquad (11)$$

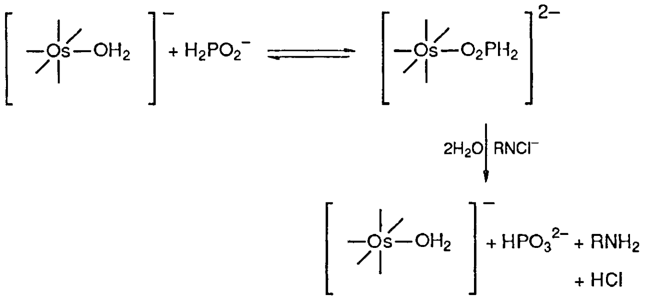
$$[\mathrm{OsO_4(OH)_2(H_2PO_2)}]^{3-} + \mathrm{RNCl^-} \xrightarrow[\mathrm{H_2O}]{k_2} [\mathrm{OsO_4(OH)_2}]^{2-} + \mathrm{HPO_3^{2-}} + \mathrm{RNH_2} + \mathrm{HCl} \qquad (12)$$

$$-\frac{d[\mathrm{cat}]}{dt} = \frac{[\mathrm{cat}][\mathrm{Os^{VIII}}][\mathrm{H_2PO_2^-}](k_1K_2 + k_2K_1K_3[\mathrm{OH^-}])}{1 + K_1[\mathrm{OH^-}] + K_2[\mathrm{H_2PO_2^-}] + K_1K_3[\mathrm{OH^-}][\mathrm{H_2PO_2^-}]} \qquad (13)$$

$$k' = \frac{[\mathrm{H_2PO_2^-}](k_1K_2 + k_2K_1K_3[\mathrm{OH^-}])}{1 + K_1[\mathrm{OH^-}] + K_2[\mathrm{H_2PO_2^-}] + K_1K_3[\mathrm{OH^-}][\mathrm{H_2PO_2^-}]} \qquad (14)$$

$$k' = \frac{k_1K_2[\mathrm{H_2PO_2^-}]}{1 + K_1[\mathrm{OH^-}] + K_2[\mathrm{H_2PO_2^-}] + K_1K_3[\mathrm{OH^-}][\mathrm{H_2PO_2^-}]} \qquad (15)$$

Further plots of the intercept *versus* $[H_2PO_2^-]^{-1}$ and slope



Scheme 1

versus $[H_2PO_2^-]^{-1}$ gave straight lines. The values of K_2 and K_3 obtained from these plots were 175 ± 6.0 and 130 ± 5.0 dm^3 mol^{-1} respectively at $I = 1.0$ mol dm^{-3} and 45 °C. Thus these graphically derived values of k_1, K_1, K_2 and K_3 were substituted in rate equation (15) to recalculate the values of k'. The calculated and experimental values of k' collected in Table 2 are in agreement, bearing in mind the complications encountered in the system. Moreover, the presumption, made earlier, as to the contribution of the second term in the numerator of rate law (15) is justified in the light of the agreement between the calculated and experimental values.

The visual and kinetic evidence substantiates the complexation between osmium(VIII) and $H_2PO_2^-$. However, the first order dependence on [cat] indicates a ternary activated complex comprising all three components, *viz.* Os^{VIII}, cat and $H_2PO_2^-$. Such an activated complex, being highly bulky and disorganized, ruptures upon the intramolecular electron transfer from the substrate to the oxidant. The reaction events can be represented as shown in Scheme 1. A similar pattern for catalysis by $[OsO_4(OH)_2]^{2-}$ species can also be envisaged. It appears that the electron-deficient metal centre, being coordinated through oxygen to the hypophosphite anion, exposes the latter for external attack by $RNCl^-$ in a preferential manner.

References

1 S. K. Ghosh, R. N. Bose, K. Laali and E. S. Gould, *Inorg. Chem.*, 1986, **25**, 473; D. E. Linn, jun. and E. S. Gould, *Inorg. Chem.*, 1987, **26**, 3442.
2 K. S. Gupta and Y. K. Gupta, *J. Chem. Soc. A*, 1970, 256.
3 S. K. Mishra and Y. K. Gupta, *J. Inorg. Nucl. Chem.*, 1967, **29**, 1643.
4 J. H. Espenson and E. E. Binsu, *Inorg. Chem.*, 1966, **5**, 1365.
5 A. D. Mitchell, *J. Chem. Soc.*, 1920, **117**, 1322; 1921, **119**, 1266; 1922, **121**, 1924; 1923, **123**, 629; R. O. Griffith and A. Michlown, *Trans. Faraday Soc.*, 1934, **30**, 530; 1940, **36**, 752; P. Hayword and D. M. Yost, *J. Am. Chem. Soc.*, 1949, **71**, 915.
6 D. Mohan, V. K. Chhabra and Y. K. Gupta, *J. Chem. Soc., Dalton Trans.*, 1975, 1737.
7 M. M. Campbell and G. Johnson, *Chem. Rev.*, 1978, **78**, 65; B. Singh, A. J. Samant and B. B. L. Saxena, *Tetrahedron*, 1982, **38**, 2591; M. M. Olmstead and P. P. Power, *Inorg. Chem.*, 1986, **25**, 4057.
8 K. V. Uma and S. P. Mayanna, *J. Catal.*, 1980, **61**, 65; S. P. Mushran, M. C. Agrawal and B. Prasad, *J. Chem. Soc. B*, 1971, 1712.
9 S. P. Mushran, R. Sanehi and M. C. Argarwal, *Z. Naturforsch., Teil B*, 1972, **27**, 1161.
10 R. Sanehi, M. C. Agarwal and S. P. Mushran, *Indian J. Chem.*, 1974, **12**, 311.
11 L. Bhatt, P. D. Sharma and Y. K. Gupta, *J. Chem. Soc., Dalton Trans.*, 1984, 2653.
12 K. Bottger and W. Z. Bottger, *Anal. Chem.*, 1927, **70**, 225.
13 E. Bishop and V. J. Jennings, *Talanta*, 1961, **8**, 697.
14 P. Norkus and S. Stulgiens, *Zh. Anal. Khim.*, 1968, **23**, 443.
15 A. D. Mitchell, *J. Chem. Soc.*, 1923, **123**, 2241.
16 M. Latshaw, *J. Am. Chem. Soc.*, 1925, **47**, 793.
17 L. Bhatt, P. Parasher and P. D. Sharma, *Bull. Assoc. Kinet. India*, 1988, **1**, 10.
18 E. Bishop and V. J. Jennings, *Talanta*, 1958, **1**, 197.
19 J. C. Morris, J. A. Salazar and M. A. Wineman, *J. Am. Chem. Soc.*, 1948, **70**, 2036.
20 T. Higuchi, K. Ikeda and A. Hussain, *J. Chem. Soc. B*, 1967, 546; 1968, 1031.
21 F. G. Soper, *J. Chem. Soc.*, 1924, 1899.
22 V. R. S. Rao, D. Venkappayya and G. Arvamudan, *Talanta*, 1970, **17**, 770.
23 S. J. Paton and C. J. Brubaker, jun., *Inorg. Chem.*, 1973, **12**, 1402.
24 W. P. Griffith, *J. Chem. Soc.*, 1964, 245.
25 R. D. Sauerbrum and F. B. Sandell, *J. Am. Chem. Soc.*, 1953, **75**, 4170.
26 M. J. Sisley and R. B. Jordan, *Inorg. Chem.*, 1987, **26**, 273.
27 D. Mohan and Y. K. Gupta, *J. Chem. Soc., Dalton Trans.*, 1977, 1085.

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