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# Kinetics and Mechanism of Osmium(VIII) Catalyzed Oxidation of Uric Acid with *N*-Chloro-*p*-toluenesulfonamide (Chloramine-T) in Alkaline Medium

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The kinetics of oxidation of uric acid ($UaH_2$) by chloramine-T (CAT) studied in the presence of osmium(VIII) in alkaline medium conform to a rate law (i)

$$\frac{-d[CAT]}{dt}=\{k_1+k_2K_2[OH^-]+k_3K_2K_3[Os(VIII)][OH^-]\}[CAT]_T[UaH_2]_T, \tag{i}$$

where $K_2$ and $K_3$ are second dissociation constant of uric acid and formation constant of an intermediate complex respectively. Osmium(VIII) catalyzes the reaction intramolecularly via redox cycle of Os(VIII)/Os(VI).

The kinetics of oxidation of various organic compounds with sodium salt of *N*-chloro-*p*-toluenesulfonamide (chloramine-T) have been reported extensively both in acidic and alkaline media.[1] The reagent has also been widely employed in analytical determinations of a large number of organic and inorganic compounds.[2] Also, the catalytic role of osmium(VIII) in chloramine-T reactions of some hydroxy acids,[3] aldehydes,[4] and ketones[5,6] have been reported in alkaline medium. However, neither osmium(VIII) nor chloramine-T alone is an effective oxidant in such reactions: hence a complex of the two was considered to be the potential oxidant. It was based on the hydride ion abstracting capacity of the complex. The complex structure indicates lowering of electron density around the nitrogen atom and that results in weakening of N–Cl bond. Such a proposition increases the hydride ion abstracting capacity of chloramine-T. The catalytic action of osmium(VIII) in oxidations of benzaldehydes,[7] cyclic alcohols and diols[8] in alkaline medium has similarly been explained. However, oxidations of benzyl alcohol[9] and some of primary alcohols[10] with chloramine-T in the presence of osmium(VIII) exhibit different kinetic features. Such observations prompted us to undertake the title reaction from three view points:

Firstly, the role of osmium(VIII) in probing the reaction events of oxidation of uric acid will be interesting in gaining more about the chemistry of uric acid.

Secondly, the osmium(VIII) complexes are not, yet, well established, the proposed study is expected to help in highlighting this features.

Thirdly, chloramine-T has been reported to be an analytical reagent in the determination of uric acid; however, analytical conditions are not well defined. The title study will help in defining the analytical conditions for determination of uric acid precisely and gainfully in aqueous solutions and biochemical systems.

## Experimental

Uric acid (henceforth written as $UaH_2$) was used as received and the details of its solution in aqueous medium are given elsewhere. Sodium salt of *N*-chloro-*p*-toluenesulfonamide was employed for solution of chloramine T (hereafter written as CAT). However, CAT solutions were stored in brown colored glass bottles to check the photolight decomposition. Chloramine-T solutions were standardized iodometrically.[11] All other chemicals were either of AnalaR or guaranteed reagent grade.

Doubly distilled water was used, second distillation being from alkaline potassium permanganate in an all glass assembly.

The reactions were carried out by taking reagents in separate bottles thermostated at desired temperature with an accuracy of ±0.1 °C unless indicated otherwise. The reagents were mixed rapidly minimizing error in measurements of initial time readings. The kinetics were monitored by quenching aliquot samples (5 cm³) in an excess of KI (ca. 20%) in $H_2SO_4$ (ca. 1 mol dm$^{-3}$), the liberated iodine was titrated against thiosulfate solution using starch as an indicator. A few reactions were also carried out in bottles blackened from the outside to check the effect of photolight on the rate; however, rates remained unchanged. The reactions were studied in initial stages (<50%). Rate measurements in triplicate were reproducible to within ±5%.

Initial rates were computed[12] by the plane mirror method. Pseudo first order and second order plots were also made wherever reaction conditions permitted.

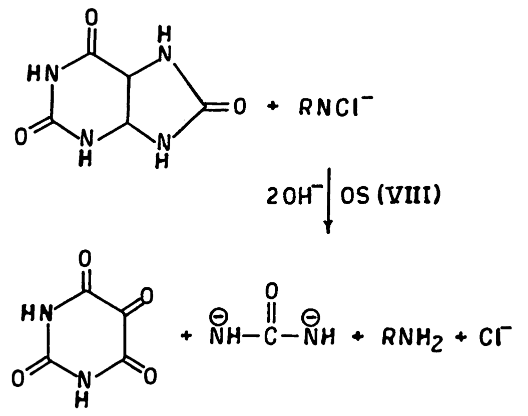
**Stoichiometry.** The reaction of uric acid with chloramine-T in alkaline medium is slow. However, it is appreciably catalyzed by osmium(VIII). The stoichiometry of the reac-

Table 1. Stoichiometric Results for the Reaction of Chloramine-T and Uric Acid in Alkaline Medium[a)]

| $10^3$ [CAT] / mol dm$^{-3}$ | $10^3$ [$UaH_2$] / mol dm$^{-3}$ | $\Delta$[CAT] / $\Delta$[$UaH_2$] |
|---|---|---|
| 1.82 | 1.00 | 1.07 |
| 2.73 | 1.00 | 1.05 |
| 3.65 | 2.00 | 1.00 |
| 4.56 | 2.00 | 0.99 |
| 6.38 | 2.00 | 1.00 |
| 9.12 | 2.00 | 1.10 |

a) [Os(VIII)]=1.0×10$^{-4}$ mol dm$^{-3}$, [OH$^-$]=0.1 mol dm$^{-3}$, temp=45 °C.

tion (Table 1) determined with CAT in excess over uric acid in the presence of osmium(VIII) conforms to Eq. 1.



(1)

Attempts were unsuccessful in detecting products of the reaction spectrally owing to the interference caused by chloramine-T and its reduction product. However, qualitative tests confirm alloxan and urea. Furthermore, similar stoichiometry has been reported earlier[13] too. Since the monomer methyl methacrylate added in the reaction mixture did not polymerize, the possibility of any involvement of free radicals is also ruled out.

## Results

**Chloramine-T Dependence.** The concentration of chloramine-T was varied in the range $0.64\times10^{-3}$ to $4.55\times10^{-3}$ mol dm$^{-3}$ at fixed concentrations of $[\mathrm{UaH_2}]=$ 0.025 and 0.01 mol dm$^{-3}$ respectively, $[\mathrm{Os(VIII)}]=1.0\times10^{-4}$ mol dm$^{-3}$ and $[\mathrm{OH^-}]=0.1$ mol dm$^{-3}$. Pseudo first order rate constants were calculated and these were found to be independent of initial concentrations of chloramine-T (Table 2).

**Uric Acid Dependence.** The concentration of uric acid was varied from $3.0\times10^{-3}$ to $2.0\times10^{-2}$ mol dm$^{-3}$ at three different concentrations of CAT viz., $9.4\times10^{-4}$, $1.4\times10^{-3}$, and $2.34\times10^{-3}$ mol dm$^{-3}$ respectively fixing concentrations of $[\mathrm{Os(VIII)}]=1.0\times10^{-4}$ mol dm$^{-3}$ and $[\mathrm{OH^-}]=0.1$ mol dm$^{-3}$. Typical pseudo first order rate constants ($k_1$) calculated for reactions where conditions permitted, show proportionate increase with increase in concentration of uric acid. Moreover, second order plots between $\log[\mathrm{CAT}]_t/[\mathrm{UaH_2}]_t$ or $\log[\mathrm{UaH_2}]_t/[\mathrm{CAT}]_t$ versus time (where $[\mathrm{CAT}]_t$ and $[\mathrm{UaH_2}]_t$ are the concentrations of chloramine-T and uric acid at any time '$t$') yield the second order rate constants in agreement with those calculated from pseudo first order rate constants (Table 2).

Furthermore, stoichiometric plots of $1/[\mathrm{CAT}]_t$ versus time were also made (Fig. 1), the second order rate constants derived from these plots also agree with those calculated from pseudo first order and second order plots (Table 2). Such an agreement also supports the earlier determined stoichiometry.

**Osmium(VIII) Dependence.** The concentration of

Table 2. Pseudo-First Order Rate Constants and Second Order Rate Constants in the Reaction of Chloramine-T and Uric Acid in Alkaline Medium[a]

| $10^3$ [CAT] mol dm$^{-3}$ | $10^2$ [UaH$_2$] mol dm$^{-3}$ | $10^4\,k$ s$^{-1}$ | $10^2\,k'$ dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| 0.69 | 2.5 | 2.00 | 0.82 |
| 0.91 | 2.5 | 2.04 | 0.82 |
| 1.36 | 2.5 | 2.04 | 0.82 |
| 1.82 | 2.5 | 2.04 | 0.82 |
| 2.28 | 2.5 | 2.04 | 0.82 |
| 0.64 | 1.0 | — | 0.82 |
| 0.91 | 1.0 | — | 0.84 |
| 1.36 | 1.0 | — | 0.84 |
| 1.82 | 1.0 | — | 0.83 |
| 2.28 | 1.0 | — | 0.83 |
| 2.73 | 1.0 | — | 0.83 |
| 3.19 | 1.0 | — | 0.82 |
| 3.65 | 1.0 | — | 0.83 |
| 4.12 | 1.0 | — | 0.82 |
| 4.55 | 1.0 | — | 0.82 |
| 2.34 | 3.0 | — | 0.84 |
| 2.34 | 4.0 | — | 0.83 |
| 2.34 | 5.0 | — | 0.82 |
| 2.34 | 6.0 | — | 0.82 |
| 2.34 | 7.0 | — | 0.82 |
| 2.34 | 8.0 | — | 0.82 |
| 2.34 | 10.0 | — | 0.82 |
| 2.34 | 15.0 | — | 0.84 |
| 2.34 | 20.0 | — | 0.82 |
| 0.94 | 15.0 | 1.24 | 0.82 |
| 0.94 | 25.0 | 1.64 | 0.82 |
| 0.94 | 30.0 | 2.50 | 0.83 |
| 1.34 | 15.0 | 1.23 | 0.82 |
| 1.34 | 20.0 | 1.66 | 0.83 |
| 1.34 | 25.0 | 2.10 | 0.84 |

a) $[\mathrm{Os(VIII)}]=1.0\times10^{-4}$ mol dm$^{-3}$, $[\mathrm{OH^-}]=0.1$ mol dm$^{-3}$, temp=45 °C.

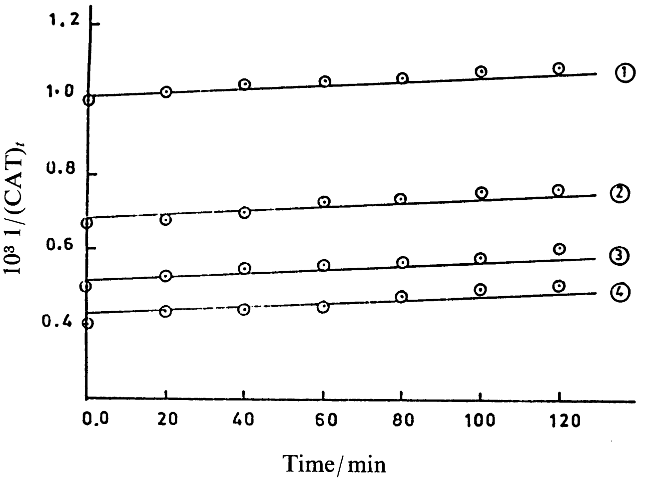


Fig. 1. Second order plots for stoichiometric concentrations.
$[\mathrm{Os(VIII)}]=1.0\times10^{-4}$ mol dm$^{-3}$, $[\mathrm{OH^-}]=0.10$ mol dm$^{-3}$, [CAT]=[U.A.]=①, $1.0\times10^{-3}$ mol dm$^{-3}$; ②, $1.5\times10^{-3}$ mol dm$^{-3}$; ③, $2.0\times10^{-3}$ mol dm$^{-3}$; ④, $2.5\times10^{-3}$ mol dm$^{-3}$.

osmium(VIII) was varied from $1.0\times10^{-5}$ to $1.0\times10^{-4}$ mol dm$^{-3}$ at fixed concentrations of [CAT]$=1.87\times10^{-3}$ mol dm$^{-3}$, [$UaH_2$]$=2.5\times10^{-2}$ mol dm$^{-3}$ and [$OH^-$]$=0.1$ mol dm$^{-3}$. The plot of pseudo first order rate constants ($k$) against the concentration of osmium(VIII) yields a straight line with non-zero intercept suggesting simultaneous occurrence of catalyzed reaction (Fig. 2).

**Hydroxide Ion Dependence.** Hydroxide ion concentration was varied from 0.1 to 1.0 mol dm$^{-3}$ at fixed concentrations of [CAT]$=1.82\times10^{-3}$ mol dm$^{-3}$, [$UaH_2$]$=2.0\times10^{-2}$ mol dm$^{-3}$, $I=1.0$ mol dm$^{-3}$ (adjusted by sodium nitrate), at three different Os(VIII) concentrations viz.: $0.5\times10^{-4}$, $1.0\times10^{-4}$, and $2.0\times10^{-4}$ mol dm$^{-3}$ respectively, and also at three temperatures viz: 40, 45, and 50 °C respectively. Second order rate constant increases with increasing concentration of hydroxide ion (Table 3).

**Effect of Sodium Nitrate.** The concentration of sodium nitrate was varied from 0.1 to 1.0 mol dm$^{-3}$ at fixed concentrations of [CAT]$=2.73\times10^{-3}$ mol dm$^{-3}$, [$UaH_2$]$=1.0\times10^{-2}$ mol dm$^{-3}$, [Os(VIII)]$=1.0\times10^{-4}$ mol dm$^{-3}$ and [$OH^-$]$=0.1$ mol dm$^{-3}$. The rate of the reaction decreases with increase in concentration of sodium nitrate (Table 4).

**Effect of *p*-Toluenesulfonamide (PTS).** The effect of PTS on the rate was studied in the range $1.0\times10^{-3}$ to $1.0\times10^{-2}$ mol dm$^{-3}$ at fixed concentrations of [CAT]$=1.8\times10^{-3}$ mol dm$^{-3}$, [$UaH_2$]$=2.0\times10^{-2}$ mol dm$^{-3}$ and [$OH^-$]$=0.1$ mol dm$^{-3}$ in presence of osmium(VIII) i.e. $1.0\times10^{-4}$ mol dm$^{-3}$. However, rate of the reaction remains unchanged.

**Effect of Chloride Ion Concentration.** The chloride ion concentration was varied from $1.0\times10^{-3}$ to $1.0\times10^{-2}$ mol dm$^{-3}$ at fixed concentrations of [CAT]$=1.87\times10^{-3}$ mol dm$^{-3}$, [$UaH_2$]$=2.0\times10^{-2}$ mol dm$^{-3}$ and [$OH^-$]$=0.1$ mol dm$^{-3}$. The rate of the reaction remains unchanged with the changing concentration of chloride ion.

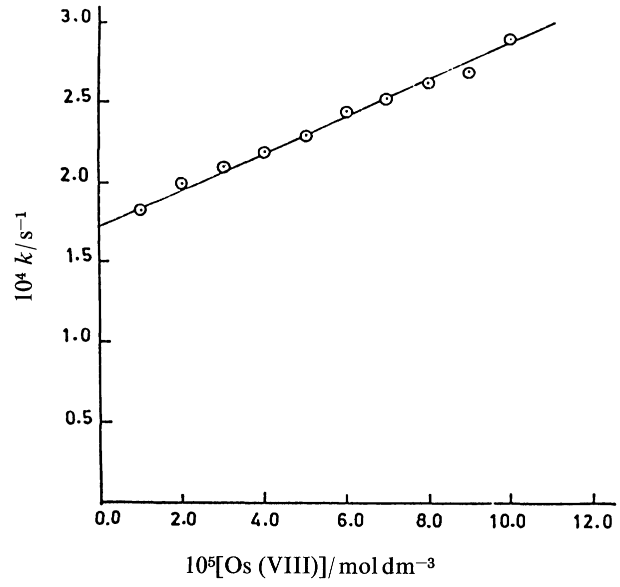


Fig. 2. Relation between pseudo first order rate constant ($k$) and the concentration of osmium(VIII). [CAT]$=1.87\times10^{-3}$ mol dm$^{-3}$, [U.A.]$=2.5\times10^{-2}$ mol dm$^{-3}$, [$OH^-$]$=0.10$ mol dm$^{-3}$, temp=45 °C.

**Uncatalyzed Reaction—Chloramine-T and Uric Acid Dependence.** The concentration of chloramine-T was varied from $9.12\times10^{-4}$ to $1.82\times10^{-3}$ mol dm$^{-3}$ at fixed concentrations of [$UaH_2$]$=2.5\times10^{-2}$ mol dm$^{-3}$ and [$OH^-$]$=0.1$ mol dm$^{-3}$. Similarly the concentration of uric acid was varied from $1.5\times10^{-2}$ to $3.0\times10^{-2}$ mol dm$^{-3}$ under pseudo first order conditions keeping constant concentrations of [CAT]$=1.36\times10^{-3}$ mol dm$^{-3}$ and [$OH^-$]$=0.1$ mol dm$^{-3}$ at 45 °C. Pseudo first order rate constants calculated in CAT variation are independent of the initial concentrations of CAT whereas they exhibit proportionate increase with the increasing concentration of uric acid. Further, the second order rate constants ($k''$) derived in these variations agree fairly well (Table 5).

**Hydroxide Ion Dependence.** Hydroxide ion concen-

Table 3. Calculated and Experimental Second Order Rate Constants in Hydroxide Ion Variation[a)]

| $10^4$ [Os(VIII)] | [$OH^-$] | $k'_{exp}$ | $k'_{calcd}$ |
|---|---|---|---|
| mol dm$^{-3}$ | mol dm$^{-3}$ | dm$^3$ mol$^{-1}$ s$^{-1}$ | dm$^3$ mol$^{-1}$ s$^{-1}$ |
| 0.5 | 0.20 | 7.3 | 7.1 |
| | 0.40 | 9.5 | 9.6 |
| | 0.60 | 12.4 | 12.1 |
| | 0.80 | 14.5 | 14.6 |
| | 1.00 | 16.6 | 17.1 |
| 1.0 | 0.10 | 7.0 | 6.3 |
| | 0.20 | 8.3 | 7.9 |
| | 0.30 | 9.6 | 9.6 |
| | 0.40 | 10.4 | 11.2 |
| | 0.50 | 12.0 | 12.9 |
| | 0.60 | 14.0 | 14.6 |
| | 0.80 | 17.2 | 17.9 |
| | 1.00 | 21.1 | 21.3 |
| 2.0 | 0.20 | 11.3 | 9.6 |
| | 0.40 | 15.9 | 14.6 |
| | 0.60 | 19.5 | 19.6 |
| | 0.80 | 23.0 | 24.6 |
| | 1.00 | 26.8 | 29.7 |

a) [CAT]$=1.8\times10^{-3}$ mol dm$^{-3}$, [$UaH_2$]$=2.0\times10^{-2}$ mol dm$^{-3}$, temp=45 °C.

Table 4. Effect of Ionic Strength[a)]

| [$NaNO_3$] | $10^7$ (i.r.) |
|---|---|
| mol dm$^{-3}$ | mol dm$^{-3}$ s$^{-1}$ |
| 0.10 | 7.55 |
| 0.20 | 6.88 |
| 0.40 | 5.88 |
| 0.60 | 4.55 |
| 0.80 | 3.55 |
| 1.00 | 2.66 |

a) [$UaH_2$]$=1.0\times10^{-2}$ mol dm$^{-3}$, [CAT]$=2.73\times10^{-3}$ mol dm$^{-3}$, [Os(VIII)]$=1.0\times10^{-4}$ mol dm$^{-3}$, [$OH^-$]$=0.1$ mol dm$^{-3}$, temp=45 °C.

Table 5. Second Order Rate Constants in Uncatalyzed Reaction[a)]

| $10^3$ [CAT] mol dm$^{-3}$ | $10^2$ [$UaH_2$] mol dm$^{-3}$ | $k''$ dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|
| 1.36 | 1.5 | 0.40 |
| 1.36 | 2.0 | 0.41 |
| 1.36 | 2.5 | 0.42 |
| 1.36 | 3.0 | 0.42 |
| 0.91 | 2.5 | 0.40 |
| 1.59 | 2.5 | 0.41 |
| 1.82 | 2.5 | 0.41 |

a) [$OH^-$]=0.1 mol dm$^{-3}$, temp=45 °C.

tration was varied from 0.2 to 1.0 mol dm$^{-3}$ at fixed concentrations of [CAT]=$1.82\times10^{-3}$ mol dm$^{-3}$, [$UaH_2$]=$2.5\times10^{-3}$ mol dm$^{-3}$ and 45 °C. Pseudo first order rate constant increases with increasing concentration of hydroxide ion.

## Discussion

Chloramine-T is known to be a reagent of vital importance in analytical,[2)] synthetic,[1)] and biochemistry.[2)] Different forms of CAT governed by equilibria[14)] Eqs. 2—7 are known to be present in acid and alkaline media.

$$\mathrm{RNClNa} \rightleftarrows \mathrm{RNCl^- + Na^+} \tag{2}$$

$$\mathrm{RNCl + H^+} \rightleftarrows \mathrm{RNHCl} \tag{3}$$

$$\mathrm{2RNHCl} \rightleftarrows \mathrm{RNCl_2 + RNH_2} \tag{4}$$

$$\mathrm{RNHCl + H_2O} \rightleftarrows \mathrm{RNH_2 + HOCl} \tag{5}$$

$$\mathrm{RNHCl + OH^-} \rightleftarrows \mathrm{RNH_2 + OCl^-} \tag{6}$$

$$\mathrm{HOCl} \rightleftarrows \mathrm{H^+ + OCl^-} \tag{7}$$

where R=$p$-$CH_3C_6H_4SO_2$.

Since the reaction is first order with respect to CAT, the possibility of $RNCl_2$ to be the reactive species of CAT is ruled out. Had RNHCl disproportionated, the order with respect to CAT would have been found to be two. Furthermore, rate independence of $p$-toluenesulfonamide ($RNH_2$) also eliminates reactivity of both $RNCl_2$ and HOCl. Further, rate is not affected by $Cl^-$ ion concentration; hence $RNCl^-$ might be the reactive species of CAT. The chloride ion effect also corroborates that neither chloride ion catalysis nor inhibition has been found in reactions where $RNCl^-$ is considered to be the predominantly reactive species of chloramine-T.[14)] Since hydroxide ion catalyzes the reaction, $OCl^-$ as governed by Eq. 6 might be the reactive species. However, such a possibility of $OCl^-$ being the reactive species of CAT is also ruled out on the premise that rate is not affected by $p$-toluenesulfonamide. Thus, $RNCl^-$ appears to be the reactive species of chloramine-T. Also, hydroxide ion dependence is not related to chloramine-T species.

Uric acid is imidazo[4,5-*d*]pyrimidine-2,5,7-triol ($UaH_2$) and its dissociation is reported[15)] to be governed by equilibria (8) and (9).

$$\mathrm{UaH_2} \rightleftarrows \mathrm{UaH^- + H^+} \tag{8}$$

$$\mathrm{UaH^-} \rightleftarrows \mathrm{Ua^{2-} + H^+} \tag{9}$$

Thus the predominant and reactive species of uric acid are $UaH^-$ and $Ua^{2-}$, and $Ua^{2-}$ is more reactive than $UaH^-$ in view of the observed hydroxide ion dependence.

Osmium tetraoxide is known[16)] to yield a red solution of $OsO_4(OH)_2^{2-}$ in strong alkaline solution. However, dilution of the solution ensues conversion of $OsO_4(OH)_2^{2-}$ into $OsO_3(OH)_3^-$ species well in agreement with the results reported by Sauerbrum and Sandell.[17)] Since rate of the reaction increases with increase in hydroxide ion concentration and does not tend towards a limiting value, the species $OsO_4(OH)_2^{2-}$ in all probability should be the only reactive species of Os(VIII).

The spectral observations of reaction mixtures do not indicate any complexation of CAT with uric acid or osmium(VIII). Kinetic observations also subscribe to this. However, weak complexation between uric acid and osmium (VIII) can not be ruled out completely only on the premise that it is not indicated. Nevertheless, we fail to ascertain any evidence of complexation between osmium(VIII) and uric acid either kinetically or spectrophotometrically.

The complexation between Os(VIII) and $\alpha$-hydroxy acids in oxidation of $\alpha$-hydroxy acids with chloramine-T appears to be speculative.[3)] Considering these observations, a mechanism in consonance with the experimental observations, can be suggested as follows:

$$\mathrm{UaH^- + OH^-} \overset{K_2}{\rightleftarrows} \mathrm{Ua^{2-} + H_2O} \tag{10}$$

$$\mathrm{UaH^- + RNCl^-} \overset{k_1}{\rightleftarrows} \mathrm{Products} \tag{11}$$

$$\mathrm{Ua^{2-} + RNCl^-} \xrightarrow{k_2} \mathrm{Products} \tag{12}$$

$$\mathrm{Ua^{2-} + OsO_4(OH)_2^{2-}} \overset{K_3}{\rightleftarrows} \mathrm{X} \tag{13}$$

$$\mathrm{X + RNCl^-} \xrightarrow{k_3} \mathrm{Products} \tag{14}$$

This mechanism leads to rate law (15)

$$-\frac{d[\mathrm{CAT}]}{dt}=\frac{(k_1+k_2K_2[\mathrm{OH^-}]+k_3K_2K_3[\mathrm{Os(VIII)}][\mathrm{OH^-}])[\mathrm{RNCl^-}]_\mathrm{T}[\mathrm{Ua^{2-}}]_\mathrm{T}}{1+K_2[\mathrm{OH^-}]} \tag{15}$$

where $[RNCl^-]_T$ and $[Ua^{2-}]_T$ are the gross analytical concentrations of chloramine-T and uric acid.

Since $K_2[OH^-]\ll1$, Eq. 15 changes to Eqs. 16 or 17

$$-\frac{d[\mathrm{CAT}]}{dt}= (k_1+k_2K_2[\mathrm{OH^-}]+k_3K_2K_3[\mathrm{Os(VIII)}][\mathrm{OH^-}])[\mathrm{RNCl^-}]_\mathrm{T}[\mathrm{Ua^{2-}}]_\mathrm{T} \tag{16}$$

or

$$k'=k_1+k_2K_2[\mathrm{OH^-}]+k_3K_2K_3[\mathrm{Os(VIII)}]\,[\mathrm{OH^-}], \tag{17}$$

where $k'$ is the observed second order rate constant. A plot of $k'$ versus $[\mathrm{OH}^-]$ from Eq. 17 was made at three concentrations of osmium(VIII) that yielded a straight line with non-zero intercept. A typical plot is given in Fig. 3. The value of $k_1$ was calculated from the intercept to be $(4.6\pm0.02)\times10^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 45 °C and $I$=1.0 mol dm$^{-3}$ in agreement with the value $(4.1\pm0.02)\times10^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 45 °C and $I$=1.0 mol dm$^{-3}$ obtained from uncatalyzed reaction. However, gradient ($G$) of the straight line (Fig. 2) from Eq. 17 can be represented by Eq. 18.

$$G=k_2K_2+k_3K_2K_3\,[\mathrm{Os(VIII)}]. \qquad (18)$$

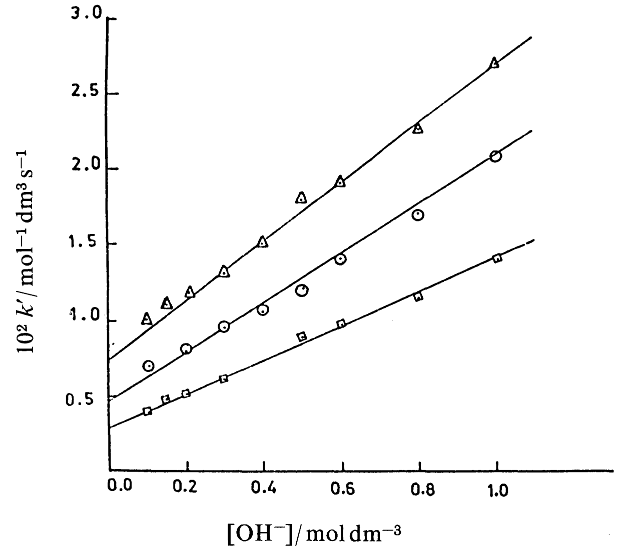


Fig. 3. Relation between observed second order rate constant and $[\mathrm{OH}^-]$.
[U.A.]=$2.0\times10^{-2}$ mol dm$^{-3}$, [CAT]=$1.8\times10^{-3}$ mol dm$^{-3}$, [Os(VIII)]=$1.0\times10^{-4}$ mol dm$^{-3}$, temp=△, 50 °C; ⊙, 45 °C; ⊡, 40 °C.

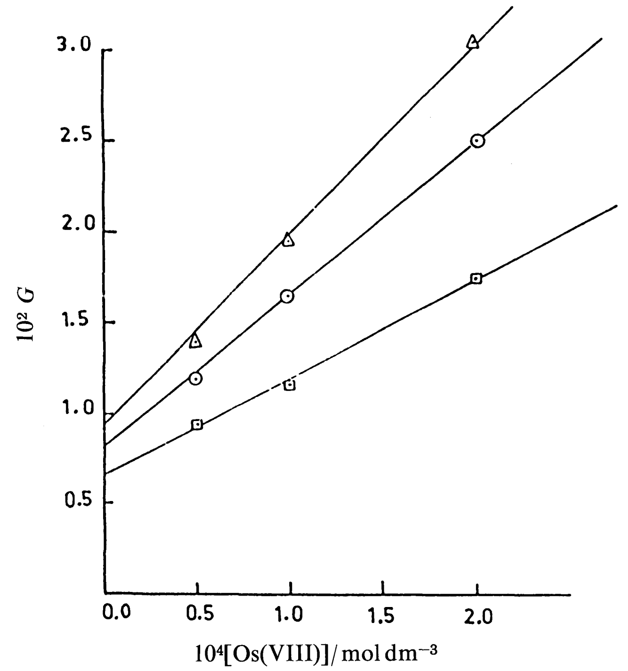


Fig. 4. Relation between gradient ($G$) and [Os(VIII)]. Temp=△, 50 °C; ⊙, 45 °C; ⊡, 40 °C.

Further, the plot of gradient ($G$) versus [Os(VIII)] also yielded a straight line with non-zero intercept (Fig. 4). $k_2K_2$ was calculated from the intercept to be $6.5\times10^{-3}$, $8.3\times10^{-3}$, and $9.5\times10^{-3}$ s$^{-1}$ at 40, 45, and 50 °C respectively and $I$=1.0 mol dm$^{-3}$. Similarly slope of the line yielded the value of $k_3K_2K_3$ to be $5.5\times10^{-1}$, $8.4\times10^{-1}$, and $10.5\times10^{-1}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 40, 45, and 50 °C respectively and $I$=1.0 mol dm$^{-3}$.

The composite values of $k_1$, $k_2K_2$, and $k_3K_2K_3$ were further substituted in rate Eq. 17. The values of $k'_{\mathrm{calcd}}$ were found in agreement with $k'_{\mathrm{exp}}$ values in hydroxide ion variation at 45 °C and three different concentrations of osmium(VIII) (Table 4). These results support our earlier assumption of hydroxide ion dependence relation with uric acid only.

So far as the role of osmium(VIII) as a catalyst is concerned, the complexation of catalyst and substrate is an essentiality in the transition state to provide a ternary configuration. The latter brings Os(VIII)/Os(VI) redox cycle intramolecularly during the transfer of electron from substrate to the oxidant.

A similar ternary transition complex has been reported[18] in Os(VIII) catalyzed oxidation of phosphinic acid with chloramine-T in alkaline medium. Since such a transition state would be bulky, its rupture to the end products should be a facile process.

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