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Kinetics and Mechanism of Oxidation of Quinol by Mercuric Nitrate in *Ac*OH—H_2O—HNO_3 Medium

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The kinetics of oxidation of quinol by mercuric nitrate in presence of *Ac*OH—H_2O—HNO_3 mixture has been investigated in order to find the active species of mercuric nitrate involved in the oxidation in this medium. The order of reaction both with respect to quinol and Hg(II) is found to be one. The reaction rate slightly increases with the increase in $[HNO_3]$ and the decrease of the dielectric constant of the medium. The reaction rate retards on addition of KNO_3. There is no evidence for complex formation between quinol and Hg(II). These results suggest that $HgNO_3^+$ might be the active species in this medium. A probable mechanism involving a two electron transfer in the rate determining step has been suggested. The produced *p*-benzoquinone does not exist in free state but forms a stable (1 : 1) complex with mercuric nitrate which has been characterized by TLC and IR studies.

(Keywords: Kinetics; Mechanism; Oxidation)

*Kinetik und Mechanismus der Oxidation von Chinol mit Quecksilbernitrat in Ac*OH—H_2O—HNO_3

Es wurde die Kinetik der Oxidation von Chinol mit Quecksilbernitrat in Gegenwart einer Mischung aus *Ac*OH—H_2O—HNO_3 untersucht, um die aktive Species bei der Oxidation in diesem Medium aufzuklären. Die Reaktionsordnung ist sowohl bezüglich des Chinols als auch des Hg(II)-Ions erster Ordnung. Die Reaktionsgeschwindigkeit erhöht sich leicht mit der HNO_3-Konzentration und auch mit abfallender Dielektrizitätskonstante des Mediums. Die Reaktionsgeschwindigkeit sinkt mit dem Zusatz von KNO_3. Es ist keinerlei Hinweis auf eine Komplexbildung zwischen Chinol und Hg(II) festzustellen. Die Resultate der Untersuchungen legen $HgNO_3^+$ als aktive Spezies nahe. Es wird ein möglicher Mechanismus mit einem Zweielektronen-Transfer im geschwindigkeitsbestimmenden Schritt vorgeschlagen. Das dabei produzierte *p*-Benzochinon existiert nicht in freier Form, sondern es bildet einen stabilen 1 : 1-Komplex mit Quecksilbernitrat; dieser Komplex wurde mittels TLC und IR charakterisiert.

Introduction

Kinetic investigations of organic compounds by Hg(II) have not received much attention so far, probably because organic compounds are readily mercurated by mercuric ions[1] and because of its low redox potential [Hg(II)/Hg(O) = 0.85 V]. Earlier the kinetics of oxidation of organic compounds by mercury involving two electron transfer process have been studied[2–9] in acidic media. However, in these oxidation-reactions Hg(O) could not be ordinarily obtained as one of the reaction products. In continuation of our earlier work[10, 11] we report in the present paper the kinetics and mechanism of oxidation of quinol by mercuric nitrate in $AcOH—H_2O—HNO_3$ medium and formation of a new bridged complex.

Materials and Methods

Nitric acid, gl. acetic acid, silver nitrate, potassium thiocyanate, potassium nitrate, sodium acetate, perchloric acid (A.R., B.D.H.), sodium perchlorate (E. Merck), quinol (m.p. 171 °C), mercuric nitrate (S. Merck) and ferric alum (A.R., T. Baker) were used. Mercuric nitrate was dissolved in HNO_3 of known strength and its concentration was determined by titrating against standard potassium thiocyanate using ferric alum as an indicator. Freshly prepared standard solution of quinol in 20% $AcOH$ was taken in a 50 ml flask and 50 ml mercuric nitrate solution was taken in another flask, fitted with a two way stopper (N_2 atmosphere). The two flasks were placed in a thermostat maintained at ± 0.1 °C accuracy.

After 0.5 h both the reactants were mixed. The rate of oxidation was followed by quenching 5 ml aliquots of the reaction mixture in a known excess (10 ml) standard potassium thiocyanate solution at definite time intervals and unreacted KCNS was estimated against standard solution of $AgNO_3$ using ferric alum as an indicator[9, 12, 13]. From the titre values and first order integrated equation, k_1 values have been evaluated.

Results and Discussion

Under the pseudo conditions, $[QH_2] \gg [Hg(II)]$ and at constant ionic strength, μ (by adding $NaClO_4$), the order of reaction with respect to Hg(II) has been determined and found to be unity. Calculated mean k_1 values have been given in Table 1, column 2.

The reaction in a particular run does not proceed beyond 50–55% as *p*-benzoquinone produced forms a complex with remaining Hg(II). Under these conditions, the effective concentration of Hg(II) might be changing with time.

To avoid the effect of products the initial rate constant $k_0\,(= x/t)$ at $x = 0$ has been calculated from the cuts on the y-axis of the linear plots (Fig. 1) of x/t against x by extrapolation[14]. Hence,

$$k_1 = \frac{k_0 S}{2C\,V} \tag{1}$$

Table 1. *Effect of varying [Oxidant] on the reaction rate.* $[QH_2] = 20.0 \cdot 10^{-2} M$; $[HNO_3] = 0.55\,M$; $[AcOH] = 20\%$; $\mu = 0.58\,M$; Temp. = 35 °C

$[Hg(NO_3)_2]$ $M \cdot 10^3$	$k_1 \cdot 10^5$ s^{-1}	$\frac{k_0 \cdot S}{2CV} = k_1 \cdot 10^5$; s^{-1}
10.0	26.44	26.00
5.0	15.51	15.33
3.3	12.51	12.62
2.5	10.41	10.66

Table 2. *Effect of varying [Quinol] on the reaction rate.* $[Hg(NO_3)_2] = 10.0 \cdot 10^{-3} M$; $[HNO_3] = 0.55\,M$; $[AcOH] = 20\%$; $\mu = 0.58\,M$

$[QH_2]$ $M \cdot 10^2$	$k_1 \cdot 10^5$ s^{-1}	$\frac{k_1}{[QH_2]} \cdot 10^4$
	Temperature = 20 °C	
33.33	15.51	4.75
25.00	12.54	5.05
20.00	10.46	5.23
10.00	5.49	5.49
8.33	4.44	5.31
6.66	3.51	5.27
4.16	2.49	5.98
	Temperature = 25 °C	
20.00	13.03	6.51
10.00	7.52	7.52
8.33	6.24	7.49
	Temperature = 30 °C	
33.33	33.32	9.99
25.00	26.51	10.60
20.00	20.60	10.30
10.00	10.43	10.43
8.33	8.79	10.55
6.66	7.17	10.76
4.16	4.42	10.62
	Temperature = 35 °C	
20.00	26.44	13.22
10.00	13.66	13.66
8.33	11.49	13.78
6.66	10.54	15.81
5.00	6.86	13.72
4.16	5.43	13.03

where S is the strength of $AgNO_3$, V the volume of aliquot taken and C the concentration of mercuric nitrate. The k_1 values (Table 1, column 3) in each case have been calculated from equation (1) and the calculated values are nearly the same as obtained by above method, showing thereby that the rates of oxidation are not affected by complex formation. It is due to fact that at any instant complexed Hg(II) is replaced by KCNS which results in a constant concentration of Hg(II) during the progress of the reaction.

Table 3. *Effect of varying the* AcOH—H_2O *ratio.* $[QH_2] = 20.0 \cdot 10^{-2} M$; $[Hg(NO_3)_2] = 10.0 \cdot 10^{-3} M$; $[HNO_3] = 0.55 M$; $\mu = 0.58 M$; Temp. = 35 °C

[AcOH] % (v/v)	$k_1 \cdot 10^5$ s^{-1}
10	23.58
15	24.46
20	26.44
30	27.66
40	29.41

It may be noted that k_1 remains constant in a particular set of the reaction but decreases with the decrease in the concentration of the oxidant[15]. This decrease in k_1 values appears to be due to involvement of other species of either mercuric nitrate (loc. cit.) or the hydrolysed species $HgOH^+$ as mercury has a tendency to hydrolyse. The equilibria[16] involved are given as:

$$Hg(II) + H_2O \rightleftharpoons HgOH^+ + H^+; \quad K_h^{298} = 10^{-3.5} \tag{2}$$

$$HgOH^+ + H_2O \rightleftharpoons Hg(OH)_2 + H^+; \quad K_h^{298} = 10^{-2.7} \tag{3}$$

The data in Table 2 show that the reaction rate decreases gradually with the decrease in the concentration of quinol. The ratios $k_1/[QH_2]$ are fairly uniform in each set, confirming the first order dependence of the rate on [quinol].

With the decrease in dielectric constant of the medium (maintained by the addition of varying volume percentage of gl. AcOH in AcOH—H_2O mixture) the reaction rate was found to increase slightly (Table 3). This indicates that the reaction is of the ion-dipole type, possibly a positively charged species is involved in accordance with *Amis*'s treatment[17].

The reaction rate slightly increases (from $20.60 \cdot 10^{-5} s^{-1}$ to $29.50 \cdot 10^{-5} s^{-1}$) with the increase in concentration of HNO_3 (from

0.55 *M* to 1.05 *M*) at [QH_2] = $20.0 \cdot 10^{-2}$ *M*; [$Hg(NO_3)_2$] = $10.0 \cdot 10^{-3}$ *M*; [*Ac*OH] = 20%; μ = 1.08 *M*; temp. = 30 °C. On the other hand the reaction rate decreases with increase in the KNO_3 concentration (Fig. 2). The reaction rate is not affected by the addition of sodium perchlorate (from 0.2 *M* to 1.0 *M*), whereas it decreases with increase in the concentration of sodium acetate. However, at 1 *M* sodium acetate the reaction mixture immediately becomes dark red and shining grey Hg(O) precipitated out.

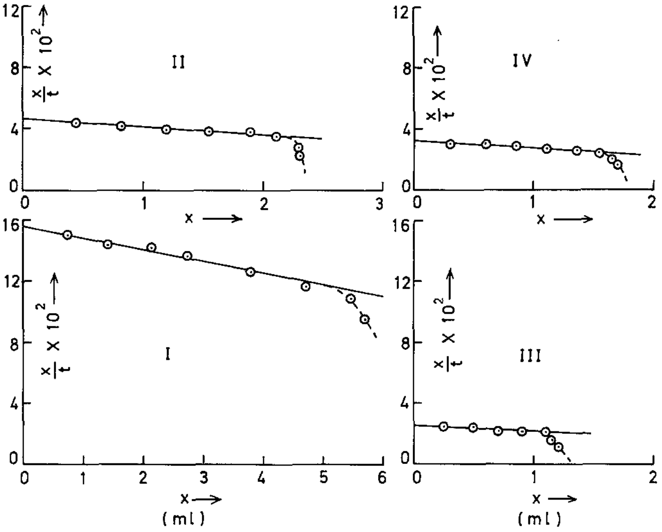


Fig. 1. Plots of *x*/*t* versus *x*. Temperature = 35 °C; [QH_2] = $20.0 \cdot 10^{-2}$ *M*; [HNO_3] = 0.55 *M*; [*Ac*OH] = 20%; I. [$Hg(NO_3)_2$] = $10.0 \cdot 10^{-3}$ *M*; II. [$Hg(NO_3)_2$] = $5.0 \cdot 10^{-3}$ *M*; III. [$Hg(NO_3)_2$] = $3.3 \cdot 10^{-3}$ *M*; IV. [$Hg(NO_3)_2$] = $2.5 \cdot 10^{-3}$ *M*

The reactions have been studied in the temperature range 20–35 °C (Table 2) and from log k_1 vs. $1/T$ plots the activation energy was found to be 45.47 kJ mol^{-1}. The other activation parameters calculated were: $\Delta H^{\neq} = 42.93$ kJ mol^{-1}; $\Delta F^{\neq} = 91.39$ kJ mol^{-1}; $\Delta S^{\neq} = -159.9$ JK^{-1} mol^{-1} and k_r ($= k_1/[QH_2]$) at 30 °C = $10.43 \cdot 10^{-4}$ mol^{-1} l s^{-1}. The observed negative entropy of activation is due to solvation of the activation complex which becomes more polar than the reactants leading to a decrease in entropy.

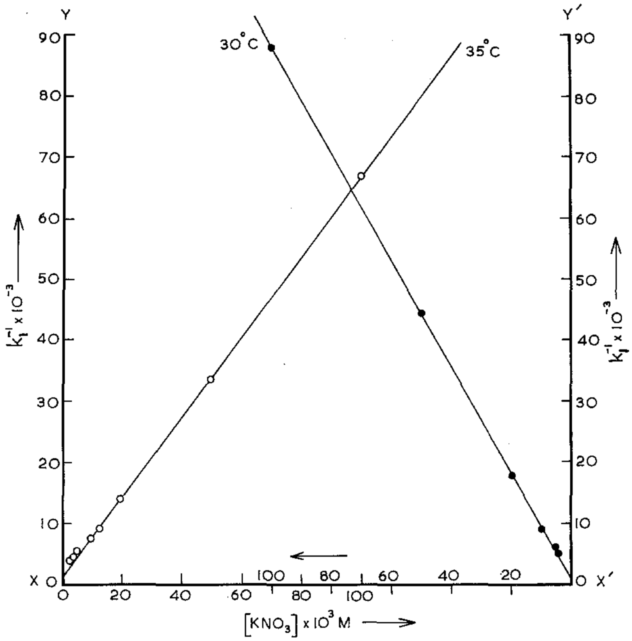


Fig. 2. Plots of k_1^{-1} versus $[KNO_3]$. $[QH_2] = 20.0 \cdot 10^{-2} M$; $[Hg(NO_3)_2] = 10.0 \cdot 10^{-3} M$; $[AcOH] = 20\%$; $[HNO_3] = 0.55 M$

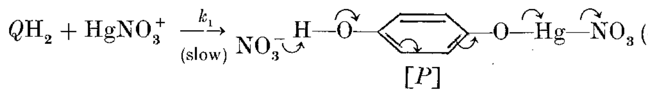
Mechanism of Oxidation

Electrophilic substitutions are generally acid catalysed reactions. Mercury is a soft *Lewis* acid and its co-ordination from O atom leads to an unstable complex. Mercuric nitrate is highly soluble in nitric acid. However, in aqueous systems, it exists[16] in the form of either Hg^{2+}—NO_3^- or $HgNO_3^+$. The log K_1 is about 0.30. There is some evidence for its existence as $Hg(NO_3)_3^-$ and $Hg(NO_3)_4^{2-}$. Polymeric oxonium ions in basic mercuric compounds of the general formula, $Hg(OH)_a^{a+}$ $(XO_3^-)_a$ are also reported in the literature[18].

The linear plot between observed $1/k_1$ and $1/[QH_2]$ passing through origin indicates that no complex is formed between Hg(II) and quinol prior to the oxidation step. According to our experimental findings, it is appropriate to neglect Hg(II) and $Hg(NO_3)_2$ being reactive species because the reaction rate decreases proportionately contrary to the increase in the concentration of NO_3^- ions. The increase in the velocity constant with the increase in the percentage of gl. acetic acid in acetic acid—water mixture or decrease in the dielectric constant gives only a suitable choice that the positive specie $HgNO_3^+$ and dipolar molecule

$Q\mathrm{H}_2$ interacts slowly. As a result of two electron transfer they are converted into Hg(O) and *p*-benzoquinone. The *p*-benzoquinone produced further reacts with remaining mercuric nitrate and forms a (1 : 1) stable complex.

The reaction sequence in presence of solvent i.e., at low dielectric constant of the medium and fixed $[\mathrm{HNO_3}]$ is shown as:



(4)

$$[P] \xrightarrow[\text{(fast)}]{k_2} \mathrm{Hg(O)} + Q + \text{other products} \tag{5}$$

$$Q + \mathrm{Hg(NO_3)_2} \xrightarrow[\text{(fast)}]{k_3} \underset{\text{(stable complex)}}{[Q\text{———————}\mathrm{Hg(NO_3)_2}]} \tag{6}$$

The rate of disappearance of Hg(II) is given by step (4),

$$-\frac{\mathrm{d}\,[\mathrm{Hg(II)}]}{\mathrm{d}t} = k_1\,[Q\mathrm{H_2}]\,[\mathrm{HgNO_3^+}] \tag{7}$$

The intermediate $[\mathrm{HgNO_3^+}]$ can be evaluated by considering the following two types of the equilibria as:

$$\mathrm{Hg(II)} + \mathrm{NO_3^-} \overset{K_1^*}{\rightleftharpoons} \mathrm{HgNO_3^+} \tag{8}$$

$$\mathrm{HgNO_3^+} + \mathrm{NO_3^-} \overset{K_2^*}{\rightleftharpoons} \mathrm{Hg(NO_3)_2} \tag{9}$$

where K_1^* and K_2^* are the equilibrium constants. From equations (8) and (9),

$$\begin{aligned}[\mathrm{Hg(II)}]_{Total} &= [\mathrm{Hg(II)}] + [\mathrm{HgNO_3^+}] + [\mathrm{Hg(NO_3)_2}] \\ &= [\mathrm{HgNO_3^+}]\left[\frac{1}{K_1^*(\mathrm{NO_3^-})} + 1 + K_2^*\,(\mathrm{NO_3^-})\right]\end{aligned} \tag{10}$$

neglecting the small factor $1/K_1^*\,(\mathrm{NO_3^-})$, the equation (10) reduces to:

$$[\mathrm{Hg(II)}]_T = [\mathrm{HgNO_3^+}]\,[1 + K_2^*\,(\mathrm{NO_3^-})] \tag{11}$$

on substituting the value of $[\mathrm{HgNO_3^+}]$ in eq. (7) the expression becomes:

$$-\frac{\mathrm{d}\,[\mathrm{Hg(II)}]}{\mathrm{d}t} = \frac{k_1\,[Q\mathrm{H_2}]\,[\mathrm{Hg(II)}]_T}{[1 + K_2^*(\mathrm{NO_3^-})]} \tag{12}$$

The derived rate law (12) satisfies our observed kinetics. The equation (12) further suggests that:

$$\frac{1}{-\frac{d[\mathrm{Hg(II)}]}{dt}} = \frac{1}{[k_1]_{obs}} = \frac{1}{k_1[QH_2][\mathrm{Hg(II)}]_T} + \frac{K_2^*(\mathrm{NO_3^-})}{k_1[QH_2][\mathrm{Hg(II)}]_T} \quad (13)$$

and hence the rate should decrease with the addition of NO_3^- ions and the plot between $[1/k_1]_{obs}$ and $[KNO_3]$ must be linear with a cut on the y-axis which has been practically obtained (Fig. 2).

The results obtained are well supported by the work of *Navaneeth Rao*[9], *McKillop*[19], and *Patai*[7].

There exists an equilibrium[20] between various states of mercury as:

$$\mathrm{Hg(O)} + \mathrm{Hg^{2+}} \overset{K}{\rightleftharpoons} \mathrm{Hg_2^{2+}}$$

for which $E^0_{298} = +0.056\,\mathrm{V}$ and $K_{298} = 79$.

However, under our experimental conditions Hg_2^{2+} has not been detected at any stage[7]. The Hg(O) produced settles down (below 0.5 *M* HNO_3) on the bottom of the reaction vessel due to its heavy weight and does not affect the reaction velocity.

Products and Analysis

The *p*-benzoquinone produced does not exist in free state but forms a complex with mercuric nitrate which has been identified by the identical R_f values (Table 4) as that of seperately prepared [$Hg(NO_3)_2$—*p*-benzoquinone] complex by spraying dithizone[21]; the absence of free *p*-benzoquinone has been confirmed by spraying 1% potassium permanganate[22] in 1% H_2SO_4 solution on TLC plates.

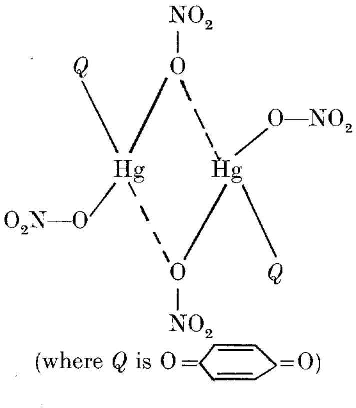
Such a complex is not reported in literature. Hence for comparison, ethanolic solutions of equimolar quantities of *p*-benzoquinone and mercuric nitrate were mixed together. After 2 days, yellowish brown cystals separated out which darkened on drying. The sparingly soluble (ca. 0.05%) crystals in water (specific conductance = $2.35 \cdot 10^{-4}\,\mathrm{ohm^{-1}\,cm^{-1}}$ at 30 °C) do not melt on heating but decompose. The elemental analysis shows that it contains 23.03% of Hg and 3.53% of N_2 as compared to their theoretical values 23% and 3.2% respectively required for a 1 : 1 complex. *Van't Hoff* factor and NMR could not be recorded because of the insolubility of the complex (less than 0.1%) in common organic solvents.

However, the IR spectrum shows the presence of co-ordinated *p*-benzoquinone by a distinct shift of the strong absorption due to $\nu\,C=O$ from $1\,640\,\mathrm{cm^{-1}}$ in the free ligand to $1\,595\,\mathrm{cm^{-1}}$ in the complex.

Table 4. *R_f values of* [$Hg(NO_3)_2$-*p-benzoquinone*] *complex*

Reagents and solvents	Reactants without Hg(II)	Reaction mixture	Prepared complex	*p*-Benzo-quinone
Barton Reagent *Bz*:*EtOAc* (1:3)	0.57	0.57	—	—
Bz:Dioxane:*Ac*OH (9:2.5:4)	0.70	0.70	—	—
Dithizone *Bz*:*EtOAc* (1:3)	—	0.30	0.30	—
Bz:Dioxane:*Ac*OH (9:2.5:4)	—	0.84	0.84	—
$KMnO_4$ *Bz*:$CHCl_3$ (1:1)	—	—	—	0.41

The presence of bands at 1 560 (ν_4), 1 285 (ν_1), 1 010 (ν_2), 790 (ν_6), and 755 cm^{-1} (ν_3/ν_5) indicates the existence of bicovalently bonded nitrate groups in the complex which is further supported by the observed poor specific conductance ($2.35 \cdot 10^{-4}$ ohm^{-1} cm^{-1}). Thus, a tetrahedral structure of the complex with bridging nitrate groups[23] in the dimeric molecule may be proposed as



which is supported by the nuclear-quadrupole resonance study[24] of oxygen donor (*p*-benzoquinone) and mercuric chloride acceptor (1:1) dimeric complexes.

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