

# Kinetics of Oxidation of Quinol by Mercuric Perchlorate in Perchloric Acid Medium

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The kinetics of oxidation of quinol by mercuric perchlorate have been studied in perchloric acid medium. The order of reaction both with respect to quinol and Hg(II) has been found to be unity. The rate of reaction decreases with increase in the concentration of perchloric acid. The reaction rate decreases on addition of sodium acetate due to formation of different reacting species whereas on addition of NaIO<sub>4</sub> it increases due to primary salt effect. The mechanism of the reaction has been suggested on the basis of two electron transition of Hg(II). The effect of solvent and temperature has also been discussed. The produced *p*-benzoquinone does not exist in free state but forms stable (1:1) complex with mercuric perchlorate which has been characterized by tlc and ir studies.

THE kinetics of oxidation of formic acid<sup>1,2</sup> and ketones<sup>3,4</sup> by mercuric compounds have been studied in acidic medium. The results in the case of formic acid indicate that the reaction is first order in each of the oxidant and formic acid and inversely first order in H<sup>+</sup> ion. Mechanism has been suggested by two equivalent reduction of the metal ion by electron transfer from the coordinated HCOO<sup>-</sup> ion, coupled with proton transfer to a water molecule. However, in these oxidation reactions Hg(O) could not be ordinarily obtained as one of the reaction products. In continuation of our earlier work on sugar oxidation<sup>5,6</sup>, we report here the kinetics and mechanism of oxidation of quinol by mercuric perchlorate in perchloric acid medium and formation of a new bridged complex.

## Experimental

Mercuric perchlorate, prepared by dissolving yellow mercuric oxide (A.R., B.D.H.) in perchloric acid (A.R., B.D.H.), silver nitrate, potassium thiocyanate, sodium acetate (A.R., B.D.H.), quinol (m.p. 171°) and ferric alum (S. Merck) were used. The reactions have been studied with respect to Hg(II). Ionic strength has been maintained constant by adding sodium perchlorate. Freshly prepared standard solution of quinol in conductivity water was taken in a 50 ml flask and 50 ml mercuric perchlorate in perchloric acid were taken in another flask, filled with a two way stopper (N<sub>2</sub> atmosphere). The two flasks were placed in a thermostat maintained at ± 0.1° accuracy.

After half an hour both the reactants were mixed. A 5 ml aliquot was taken out and poured in excess (10 ml) standard potassium thiocyanate solution at different intervals of times. The excess of potassium thiocyanate was titrated against standard silver nitrate solution using ferric alum as an

indicator<sup>7,20</sup>. From the titre values and first order integrated equation, *k*<sub>1</sub> values have been evaluated.

## Results and Discussion

Under the pseudo conditions, [QH<sub>2</sub>] >> [Hg(II)], the order of reaction with respect to Hg(II) has been determined and found to be unity. Calculated mean *k*<sub>1</sub> values have been given in Table 1, column 2.

TABLE 1—EFFECT OF VARIATION OF [OXIDANT] ON THE REACTION RATE

[QH<sub>2</sub>] = 10.0 × 10<sup>-2</sup> M; [HClO<sub>4</sub>] = 0.25 M; μ = 0.28 M; Temp. = 30°

[Hg(ClO <sub>4</sub> ) <sub>2</sub> ] M × 10 <sup>2</sup>	<i>k</i> <sub>1</sub> × 10 <sup>4</sup> sec <sup>-1</sup>	<i>k</i> <sub>0</sub> × S 2C × V = <i>k</i> <sub>1</sub> × 10 <sup>4</sup> , sec <sup>-1</sup>
10.0	1.784	1.750
5.0	2.614	2.600
3.3	3.147	3.175
2.5	3.692	3.950

The reaction in a particular run, does not proceed beyond 50-55% as *p*-benzoquinone produced forms complex with the 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*<sub>0</sub>(=x/t) at x=0 has been calculated from the intercepts on the y-axis of the linear plots of  $\frac{x}{t}$  against x by extrapolation<sup>8</sup>. Hence,

$$k_1 = \frac{k_0 \times S}{2C \times V} \quad (1)$$

where S is the strength of AgNO<sub>3</sub>, V the volume of aliquot taken and C the concentration of mercuric perchlorate. The *k*<sub>1</sub> 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 may be noted that  $k_1$  remains constant in a particular set of reaction but increases with a decrease in the concentration of the oxidant<sup>9,10</sup>.

The summarized results in Table 2 show that the reaction rate decreases gradually with a decrease in the concentration of quinol. The ratios  $\frac{k_1}{[QH_2]}$  are fairly uniform in each set confirming the first order dependence of the rate on [quinol].

TABLE 2—EFFECT OF VARYING [QUINOL] ON THE REACTION RATE

$[Hg(ClO_4)_2] = 10.0 \times 10^{-3} M$ ;  $[HClO_4] = 0.25 M$ ;  $\mu = 0.28 M$

$[QH_2]$ $M \times 10^3$	$k_1 \times 10^5$ $sec^{-1}$	$\frac{k_1}{[QH_2]} \times 10^5$
Temp. 20°		
14.2	13.50	0.95
10.0	9.206	0.92
8.3	7.507	0.90
6.6	6.394	0.96
5.0	4.525	0.90
Temp. 25°		
14.2	20.36	1.43
10.0	13.58	1.35
8.3	11.57	1.39
6.6	9.206	1.39
5.0	6.582	1.31
Temp. 30°		
20.0	35.41	1.77
14.2	24.64	1.73
10.0	17.34	1.73
8.3	14.60	1.75
6.6	11.53	1.74
5.0	8.601	1.72
Temp. 35°		
14.2	38.70	2.72
10.0	27.67	2.76
8.3	22.55	2.71
6.6	17.45	2.64
5.0	13.80	2.76

The data in Table 3, show that the reaction rate decreases with increase in the  $HClO_4$  concentration. Further, the rate of reaction increases on addition of  $NaClO_4$  and  $\log k_1$  varies with ionic strength ( $\mu$ ) due to primary salt effect involving two neutral molecules or a neutral molecule and an ion. However,  $\log k_1$  drops significantly (from  $15.36 \times 10^{-5} sec^{-1}$  to  $6.58 \times 10^{-5} sec^{-1}$ ) with an increase in the concentration of added  $CH_3COONa$  (from 0.0  $M$  to 0.2  $M$ ) at  $[QH_2] = 10.0 \times 10^{-3} M$ ;  $[Hg(ClO_4)_2] = 10.0 \times 10^{-3} M$ ;  $[HClO_4] = 0.50 M$ ; temp. = 30°.

**Effect of solvent:** The reactions have been studied at different dielectric constants of the medium by varying weight percentage of dioxane in dioxane-water mixture<sup>11</sup> at two different temperatures.

TABLE 3—EFFECT OF VARIATION OF  $[HClO_4]$  ON THE REACTION RATE

$[QH_2] = 10.0 \times 10^{-3} M$ ;  $[Hg(ClO_4)_2] = 10.0 \times 10^{-3} M$ ;  $\mu = 1.20 M$ , Temp. = 30°

$[HClO_4]$ $M$	$k_1 \times 10^5$ $sec^{-1}$
1.17	12.42
1.00	13.10
0.50	16.47
0.33	17.90
0.25	18.90
0.20	20.45

The present reactions are between dipolar molecule and positive ion. According to Amis<sup>12</sup>, the reaction rate should increase with a decrease in dielectric constant of the medium. However, the observed rate of reaction decreases with the decrease in dielectric constant of medium. The linear plots (Fig. 1), with slight deviation at low dielectric constant, of  $\log k_1$  vs  $(D-1)/(2D+1)$  with positive slopes<sup>12</sup> and of  $\log k_1$  vs  $1/D$  with negative slopes<sup>12</sup> indicate dipole-dipole interaction. The contradictory results obtained are due to decrease in dissociation<sup>14</sup> of quinol and formation of ion-pairs [such as  $HgOH^+ClO_4^-$ ,  $Hg^{2+}(ClO_4^-)_2$  and  $HgOH^+OH^-$ ] with the decrease in dielectric constant of the medium.

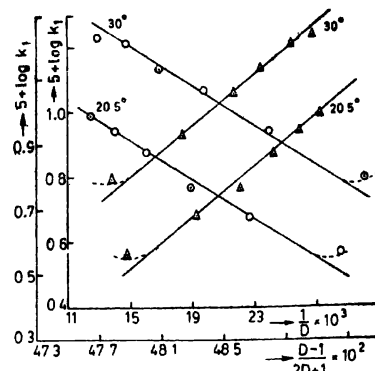


Fig. 1

○—○ Plots of  $\log k_1$  vs  $1/D$ ;

Δ—Δ Plots of  $\log k_1$  vs  $(D-1)/(2D+1)$ ;

$[QH_2] = 10.0 \times 10^{-3} M$

$[Hg(ClO_4)_2] = 10.0 \times 10^{-3} M$

$[HClO_4] = 0.25 M$

**Activation parameters:** The activation parameters have been evaluated from  $\log k_1$  vs  $\frac{1}{T}$  plots (Table 2) as :

$k_r$ ( $sec^{-1} \cdot mol^{-1}$ )	$E_a$ ( $kJ \cdot mol^{-1}$ )	$\Delta H^\ddagger$ ( $kJ \cdot mol^{-1}$ )	$\Delta S^\ddagger$ ( $JK^{-1} \cdot mol^{-1}$ )	$\Delta F^\ddagger$ ( $kJ \cdot mol^{-1}$ )
$13.58 \times 10^{-5}$	50.07	47.57	-139.5	89.17

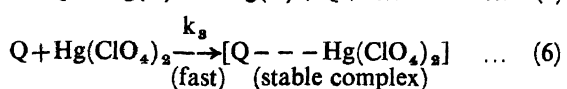
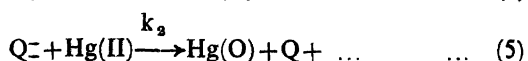
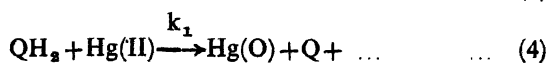
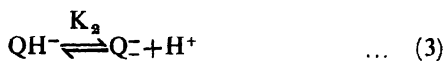
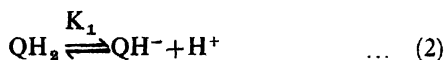
$k_r = k_1/[QH_2]$ ;  $\Delta H^\ddagger = E_a - RT$

$[QH_2] = 10.0 \times 10^{-3} M$ ;  $[Hg(ClO_4)_2] = 10.0 \times 10^{-3} M$ ;  
 $[HClO_4] = 0.25 M$ ;  $\mu = 0.28 M$ , temp. = 25°.

The observed negative entropy of activation is due to solvation of activation complex which becomes more polar than the reactants leading to a decrease in entropy.

**Mechanism of oxidation:** From the foregoing discussion it is concluded that the first stage is oxidation and the next is complexation. When oxide of Hg(II) is dissolved in  $\text{HClO}_4$ , the species  $\text{Hg(II)}$  is formed. However, the equilibria are interpreted in terms of the species<sup>1,5</sup>  $\text{Hg(II)}$ ,  $\text{HgOH}^+$  and  $\text{Hg(OH)}_2$ .

The quinol in aqueous solution i.e. at high dielectric constant of medium dissociates ( $K_1 > K_2$ ) and forms dianion<sup>1,6</sup>. The linear plot of observed  $1/k_1$  against  $1/[\text{QH}_2]$  passing through origin indicates that no complex is formed between  $\text{Hg(II)}$  and  $\text{QH}_2$  prior to oxidation step. Thus,  $\text{QH}_2$  and  $\text{Hg(II)}$  interact slowly, and as a result of two electron transfer they are converted into  $\text{Hg(O)}$  and *p*-benzoquinone. The *p*-benzoquinone produced further reacts with the remaining mercuric perchlorate and forms (1 : 1) stable complex. The reaction sequence is shown as :



Scheme 1

On the basis of Scheme 1, the final rate expression comes out to be :

$$-\frac{d[\text{Hg(II)}]}{dt} = [k_1 + \frac{k_2 K_1 K_2}{[\text{H}^+]^2}] [\text{Hg(II)}] [\text{QH}_2]_T \quad \dots (7)$$

$\text{QH}_2$  is largely unionized in acid solutions and hence at fixed acid concentration this expression becomes :

$$-\frac{d[\text{Hg(II)}]}{dt} = k' [\text{Hg(II)}] [\text{QH}_2]_T \quad \dots (8)$$

$$\text{where } k' = \left[ k_1 + \frac{k_2 K_1 K_2}{[\text{H}^+]^2} \right]$$

The derived rate law (8) satisfies our observed first order kinetics both with respect to  $\text{QH}_2$  and  $\text{Hg(II)}$ . At varying concentration of  $\text{H}^+$  ions and in the presence of a large excess of  $\text{QH}_2$ , the experimentally determined first order velocity constant  $[k_1]_{\text{obs}}$  is given by,

$$[k_1]_{\text{obs}} = \left[ k_1 + \frac{k_2 K_1 K_2}{[\text{H}^+]^2} \right] [\text{QH}_2]_T \quad \dots (9)$$

and it should thus show a linear dependence on  $1/[\text{H}^+]^2$  with a non-zero intercept at  $1/[\text{H}^+]^2 \rightarrow 0$ .

However, the linear plot with slight deviation and small slope (Fig. 2; curve 1) of  $k_1$  against  $1/[\text{HClO}_4]^2$  with a non-zero intercept at  $1/[\text{H}^+]^2 \rightarrow 0$ , indicates that the reaction rate is largely independent of  $[\text{H}^+]$  with a small component inhibited by  $\text{H}^+$  ions, showing thereby that unionized quinol plays dominant role in the rate determining step.

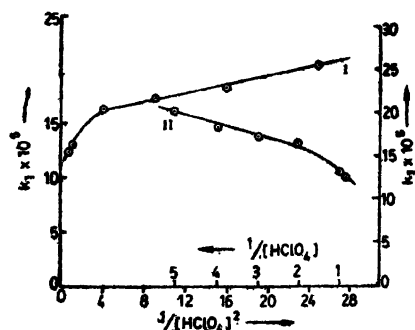
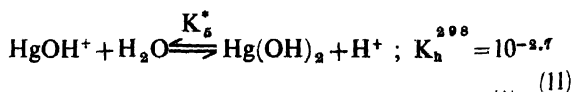
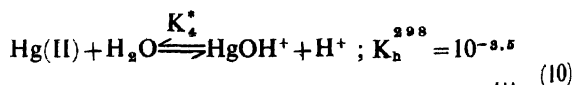
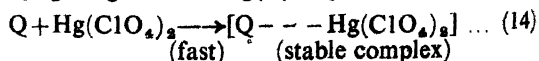
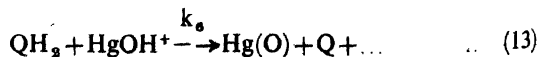
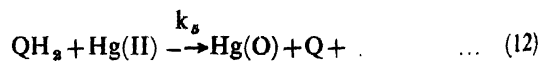


Fig. 2. Plots of  $k_1$  vs  $1/[\text{HClO}_4]^2$  and  $1/[\text{HClO}_4]$   
Temperature =  $30^\circ$ ;  $[\text{QH}_2] = 10.0 \times 10^{-3} \text{ M}$ ;  
 $[\text{Hg(ClO}_4)_2] = 10.0 \times 10^{-3} \text{ M}$ .

Thus, it is concluded that both hydrolysed and unhydrolysed species of mercury take part in the reaction. The involvement of hydrolysed species is expected as mercury tends to hydrolyse in aqueous solution. The equilibria<sup>1,7</sup> involved are given as :



Holding the degree of hydrolysis constant, as long as hydrolysis involves only mono nuclear specie, the equilibria (10) becomes prominent. Ignoring the role of dissociated specie of quinol, the following most probable steps may be proposed for the rate determining process :



Scheme 2

Then,

$$-\frac{d[\text{Hg(II)}]}{dt} = k_5 [\text{QH}_2] [\text{Hg(II)}] + k_6 [\text{QH}_2] [\text{HgOH}^+] \quad \dots (15)$$

$$[\text{HgOH}^+] = \frac{K_4^* [\text{Hg(II)}] [\text{H}_2\text{O}]}{[\text{H}^+]} \quad \dots (16)$$

and hence equation (15) becomes :

$$-\frac{d[\text{Hg(II)}]}{dt} = \left[ k_s + \frac{K_4^* k_6 [\text{H}_2\text{O}]}{[\text{H}^+]} \right] [\text{QH}_2][\text{Hg(II)}] \quad \dots (17)$$

The total mercury concentration is :

$$[\text{Hg(II)}]_T = [\text{Hg(II)}] + [\text{HgOH}^+] \quad \dots (18)$$

$$\text{and, } [\text{Hg(II)}] = \frac{[\text{Hg(II)}]_T}{\left[ 1 + \frac{K_4^* [\text{H}_2\text{O}]}{[\text{H}^+]} \right]} \quad \dots (19)$$

on substituting the value of  $[\text{Hg(II)}]$  in eq. (19), the final rate expression becomes :

$$-\frac{d[\text{Hg(II)}]}{dt} = \frac{[k_s[\text{H}^+] + K_4^* k_6 [\text{H}_2\text{O}]] [\text{QH}_2] [\text{Hg(II)}]_T}{[[\text{H}^+] + K_4^* [\text{H}_2\text{O}]]} \quad \dots (20)$$

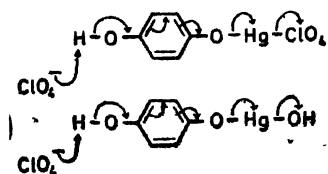
If  $[\text{H}^+] \gg K_4^* [\text{H}_2\text{O}]$ , then the factor  $K_4^* [\text{H}_2\text{O}]$  may be neglected. Hence equation (20) reduces to :

$$-\frac{d[\text{Hg(II)}]}{dt} = \left[ k_s + \frac{K_4^* k_6 [\text{H}_2\text{O}]}{[\text{H}^+]} \right] [\text{QH}_2][\text{Hg(II)}]_T \quad (21)$$

The derived rate expressions (20) and (21) show first order dependence of the rate on oxidant and  $\text{QH}_2$  and inhibiting action of  $\text{H}^+$  ions. The graph of  $[k_1]_{\text{obs}} \text{ vs } 1/[\text{H}^+]$  has been plotted [Fig 2; curve II] and instead of a straight line, a complex, non-linear curve has been obtained possibly due to involvement of  $\text{Hg(OH)}_2$ . Under these circumstances the modified rate expression would be

$$-\frac{d[\text{Hg(II)}]}{dt} = \left[ k_s + \frac{K_4^* k_6 [\text{H}_2\text{O}]}{[\text{H}^+]} + \frac{K_4^* K_5^* k_7 [\text{H}_2\text{O}]^2}{[\text{H}^+]^2} \right] [\text{QH}_2][\text{Hg(II)}]_T$$

which also satisfies the observed kinetics. The intermediate interactions are shown as



The results obtained are well supported by the work of Baxendale<sup>18</sup>, Halpern<sup>2</sup> and Singh and coworkers<sup>19</sup>.

Further, on addition of  $\text{CH}_3\text{COONa}$ , the reaction rate decreases. This may be due to conversion of the more reactive species of mercury into the less reactive species<sup>20</sup>,  $\text{Hg(OAc)}_2$ , supported by the observed linear plot (Fig. 3; curve II) between  $[\text{rate}]^{-1}$  and  $[\text{CH}_3\text{COONa}]^2$  with an intercept on y axis ( $6.50 \times 10^8$ ) which fairly agrees with the  $[\text{rate}]^{-1} = 1/15.36 \times 10^{-8} = 6.51 \times 10^8$ , in absence of added  $\text{CH}_3\text{COONa}$ . The deviation at latter part of the curves may be due to complexity of the buffer action of  $\text{CH}_3\text{COONa}$ .

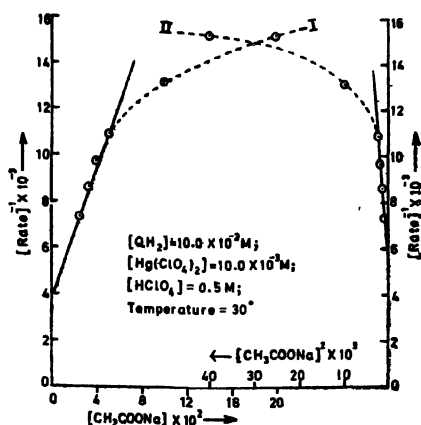
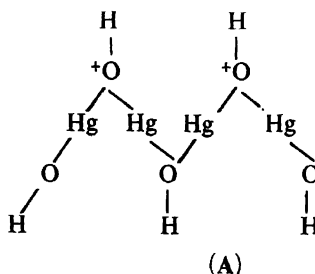
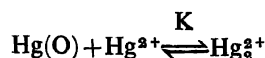


Fig. 3. Effect of  $\text{CH}_3\text{COONa}$  on reaction rate.

The observed enhancement in the reaction rate with the dilution of the oxidant remains to be explained. Such observations in ceric redox system<sup>10</sup> has been explained by dimer formation of hydrolysed species of ceric. The polymeric oxonium ion (structure A) in basic mercuric compounds of the general formula,  $\text{Hg(OH)}_2^+ (\text{XO}_3^-)_2$  are reported in literature<sup>21</sup> and this may be reviewed as an alternative possibility and be included in any comprehensive account of the overall nature of the oxidising species.



There exist an equilibrium<sup>22</sup> between various states of mercury as :



for which,  $E_{298}^0 = +0.056 \text{ V}$  and  $K_{298} = 79$ . However, under our experimental conditions  $\text{Hg}_2^{2+}$  state has not been detected at any stage<sup>23</sup>.

The  $\text{Hg(O)}$  produced settles down at the bottom of the reaction vessel due to its weight and does not affect the reaction rate.

**Product and analysis :** The *p*-benzoquinone produced does not exist in free state, but forms a complex with  $\text{Hg(ClO}_4)_2$  which has been identified by the identical  $R_f$  values (Table 4) as that of prepared  $[\text{Hg(ClO}_4)_2 \cdot \text{p-benzoquinone}]$  complex by spraying dithizone<sup>24</sup> on tlc plates.

Such complex was not reported in the past. Hence for comparison, ethanolic solutions of equimolar quantities of *p*-benzoquinone and mercuric perchlorate were mixed together. After 2 days, a

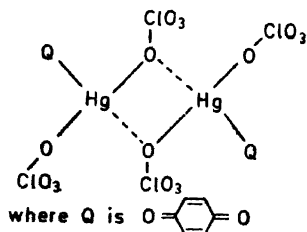
TABLE 4— $R_f$  VALUES OF  $[\text{Hg}(\text{ClO}_4)_2\text{-}p\text{-BENZOQUINONE}]$  COMPLEX

Compound	$R_f \times 10$ (cm)
Reaction product	5.7
Prepared complex	5.7
Solvent, EtAc : Bz :: 1 : 1	

yellowish brown crystal separated out which darkened on drying. The sparingly water soluble crystals (sp. cond. =  $8.4 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$  at  $30^\circ$ ) do not melt on heating but decomposed and contain 40.4% of Hg as compared to theoretical value of 39.5% required for 1 : 1 complex.

The expected broad ir absorption due to  $\nu_s$  absorption of the isolated perchlorate group<sup>25,26</sup> undergoes distinct splitting giving rise to three absorptions at 1140, 1120 and 1080  $\text{cm}^{-1}$ , indicating reduced symmetry<sup>27</sup> and presence of two types of perchlorate groups. The data thus support the tetrahedral structure of the complex with bridging perchlorate groups in the dimeric molecule in which terminal  $\text{ClO}_4^-$  groups are also present.

The presence of coordinated  $p$ -benzoquinone is clearly indicated by a distinct shift of the strong absorption due to  $\nu_{\text{C=O}}$  absorption from 1640  $\text{cm}^{-1}$  in the free ligand to 1600  $\text{cm}^{-1}$  in the complex. Thus, the structure may be proposed as



which is supported by the nuclear quadrupole resonance study<sup>28</sup> of oxygen donor ( $p$ -benzoquinone) and mercuric chloride acceptor (1 : 1) dimeric complexes.

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