Oxidation of Glycine using Rhodium (III)-catalyst by bromate in acidic medium

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ABSTRACT

The kinetics of Rhodium(III) catalysed oxidation of glycine in an acidified solution of KBrO3 in the presence of Hg(OAc)2 as a scavenger, has been studied in temperature range of 30–45°C. The rate is first order in Rh(III) but zero order with respect to bromate. The rate decreases with increasing concentration of H+ ion, showing negative effect, while positive effect is exhibited w.r.t. substrate (glycine) and AcOH. The influence of Hg(OAc)2, ionic strength and Cl– ion on the rate was found to be insignificant. A suitable mechanism in conformity with the kinetic observations has been proposed and the rate law is derived on the basis of obtained data. The various thermodynamic parameters were calculated from rate measurements at 30, 35, 40 and 45°C, respectively.

Keywords: bromate, catalysis, oxidation, Rhodium(III), acidified potassium bromate.

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Aims and Background:

Potassium bromate has been used to oxidize various compounds [1–4]. Little attention has been paid, however, to the reactivity of $KBrO_3$ in the presence of catalyst [5,6] and no investigation has so far been reported on the catalytic role of Rhodium(III) chloride with potassium bromate as an oxidant in acidic medium. This fact prompted us to undertake the present investigation, namely oxidation of glycine by acidified $KBrO_3$ in the presence of Rh(III) chloride as a catalyst and mercuric acetate as a scavenger for bromide ion.

Experimental:

Materials: A number of aqueous solutions containing known concentrations of E. merck glycine, potassium bromate (BDH, AR), sodium perchlorate and $Hg(OAc)_2$ were prepared in triply distilled water. We used $HClO_4$ to generate H^+ ions. We prepared also $RhCl_3$ solution coming from the Sigma Chemical Company with HCl of known concentration. All other chemicals were of analytical grade. The reaction vessels were all painted black to prevent any undesired photochemical reaction.

All reagents and the substrate were pre-heated at 35 ± 0.1 ºC in order to arrive at equilibrium. The reaction vessel was rapidly loaded with a preset amount of $KBrO_3$ at identical temperature. A sample of the mixture was taken during the reaction to test for KBrO3 with iodometry and starch to determine when the reaction was complete.

Results and Discussion: This was done by equilibrating the reaction mixture that had an excess of potassium bromate over glycine (in several ratios) to 50 °C for 48 hours.

Product analysis showed that there was an excess of bromate in all reactions and it turned out that the stoichiometric ratio was 1 mol of bromate to 1 mol of glycine. Analysis of products confirmed that the product of the reaction is indeed aldehyde. The general reaction can be written as (1):

$$NH2–CH2–COOH + BrO^{3-} + H^+ \rightarrow HCHO + NH_3 \uparrow + CO_2 \uparrow + 2BrO_2^-$$

(Glycine)

(Formaldehyde)

The kinetic studies of glycine oxidation were conducted at different concentrations of the starting reagents (see table 2). It was shown that with increasing concentration of substrate, that is [substrate], the rate of reaction indicated by (-dc/dt) increased. In the case of bromate, the value of (–dc/dt) was constant for all tested concentrations which indicates 0 order kinetics in respect to $KBrO_3$. Reduction of perchloric acid concentration has displayed the opposite effect as illustrated in the (Fig.1), (Fig.2) and (Fig.3). The rate measurement were taken at 30-45°C and specific rate constants were used to draw a plot of log(-dc/dt) versus 1/T, which is linear (Fig4.). The reactive species of Rh(III) chloride is Rh^{3+}.

Table 1: Effect of variation of $HClO_4$, $[Hg(OAc)_2]$, KCl at 35 ^{0}C

$HClO_4$ x 10^3M	KCl x 10^3M	$[Hg(OAc)_2]$ x 10^3M	(dc/dt) x 10^7 [$ML^{-1}s^{-1}$]
0.83	1.00	1.25	0.28
1.00	1.00	1.25	0.23
1.33	1.00	1.25	0.20
1.66	1.00	1.25	0.19
4.00	1.00	1.25	0.18
8.00	1.00	1.25	0.14
1.00	1.00	1.25	0.23
1.00	1.25	1.25	0.23
1.00	1.66	1.25	0.26
1.00	2.50	1.25	0.21
1.00	5.00	1.25	0.24
1.00	1.00	0.83	0.20
1.00	1.00	1.00	0.22
1.00	1.00	1.33	0.26
1.00	1.00	1.66	0.24
1.00	1.00	2.00	0.25
1.00	1.00	4.00	0.20

[Glycine] = 1.00 x10^{-2} M, [Rhodium(III)] = 11.25x10^{-5} M, $[HClO_4]$ = 1.00x10^{-3} M.

Table 2: Effect of variation of oxidant, glycine, Rh (III) at 35 ^{0}C

[Oxidant] x 10^3M	[Substrate] x 10^2M	[Rh(III)] x 10^{-5} M	(dc/dt) x 10^7 [$ML^{-1}S^{-1}$]
0.83	1.00	11.25	0.25
1.00	1.00	11.25	0.23
1.35	1.00	11.25	0.26
1.66	1.00	11.25	0.24
2.5	1.00	11.25	0.22
5.00	1.00	11.25	0.20
1.00	0.83	11.25	0.19
1.00	1.25	11.25	0.23
1.00	2.50	11.25	0.55
1.00	4.00	11.25	0.88
1.00	5.00	11.25	0.94
1.00	8.00	11.25	1.33
1.00	1.00	5.62	0.14
1.00	1.00	11.25	0.23
1.00	1.00	16.87	0.30
1.00	1.00	22.50	0.41
1.00	1.00	28.12	0.52
1.00	1.00	33.74	0.62

$[Hg(OAc)_2]$ = 1.25 x 10^{-3} M, [KCl] = 1.00 x 10^{-3} M, $[HClO_4]$ = 1.00 x 10^{-3} M.

Table 3: activation parameter for the oxidation of Glycine

Parameter	Temperature ^{0}C	Glycine
K_1 x 10^4 s^{-1}	30	0.87
K_1 x 10^4 s^{-1}	35	1.30
K_1 x 10^4 s^{-1}	40	1.79
K_1 x 10^4 s^{-1}	45	2.41
log*A* ($KJmol^{-1}$)	-	6.95231
ΔE^* ($KJmol^{-1}$)	35	42.31
ΔG^* ($KJmol^{-1}$)	35	76.09265
ΔH^* ($KJmol^{-1}$)	35	66.37159
ΔS^* ($JK^{-1}mol^{-1}$)	35	-24.824332

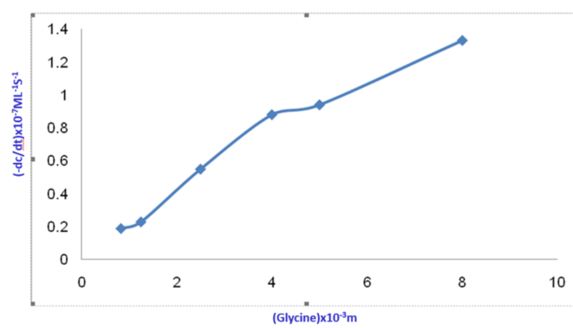


Fig.1 Plot between (-dc/dt) and glycine for the oxidation of glycine at 35 ºC

[Glycine] = 1.00 x10^{-2}M, [Rhodium] = 11.25x10^{-5}M, $[HClO_4]$ = 1.00x10^{-3}M,

[Hg(OAc)] = 1.25 x 10^{-3} M.

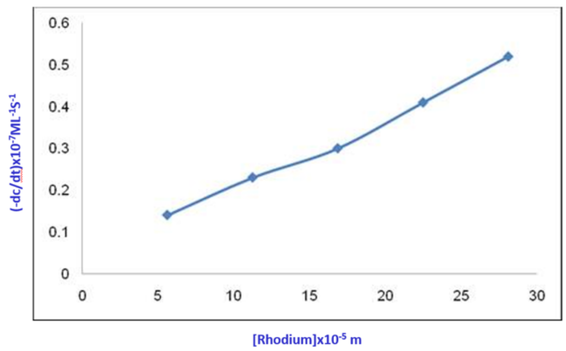


Fig.2 Plot between (-dc/dt) and Rhodium for the oxidation of glycine at 35 ºC
[Glycine] = 1.00 x10^{-3}M, [Rhodium(III)]= 11.25 x 10^{-5} M, $[HClO_4]$ = 1.00 x 10^{-3} M.

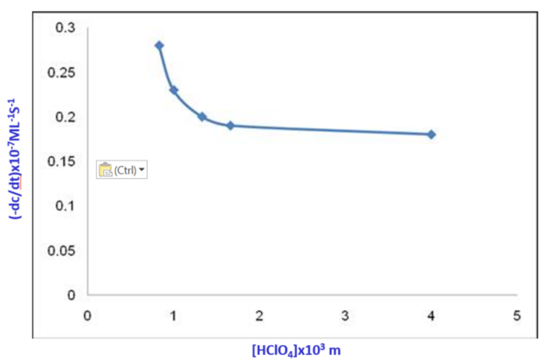


Fig.3 Plot between (-dc/dt) and $HClO_4$ for the oxidation of glycine at 35 ºC
[Glycine] = 1.00 x10^{-3}M, [Rhodium] = 11.25x10^{-5}M, $[HClO_4]$ = 1.00x10 $^{-3}$M,
$[Hg(OAc)_2]$ = 1.25 x 10^{-3}M.

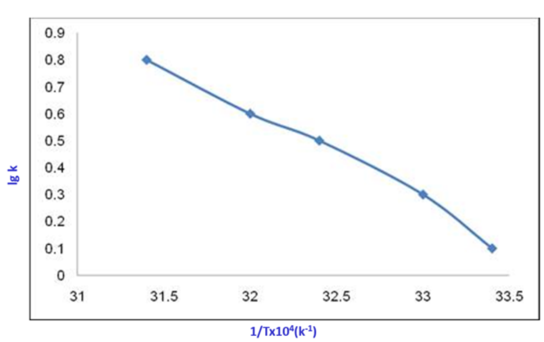
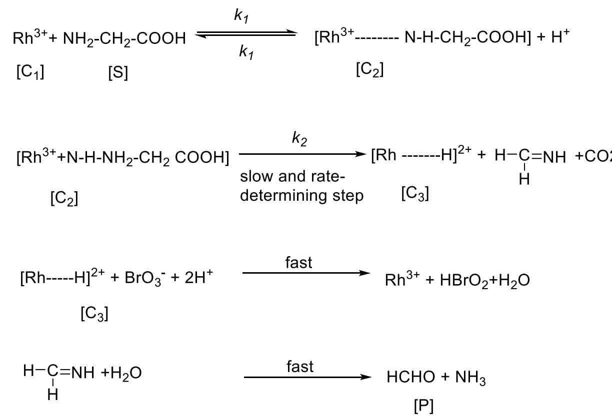


Fig.4 Plot between log k and 1/T for the oxidation of glycine, $[KBrO_3]$ = 1.00 x 10^{-3} M, $[Hg(OAc)_2]$ = 1.25 x 10^{-3}M, [KCl] = 1.00 x 10 $^{-3}$M, [Glycine] = 1.00x10^{-2} M, [Rh(III)] = 11.25 x 10^{-5} M, $[HClO_4]$ = 1.00x10^{-3}M.

On the basis of the above data the following reactions are suggested. Rh^{3+} is used for $RhCl_3$, for convenience. C_1 and C_2 are the intermediate complexes formed during the course of the reactions:



where [S] is glycine and [P] – formaldehyde.

Formation of hydride ion $[Rh\text{---}H]^{2+}$ of rhodium is well known [10]. Considering the above slow steps and applying steady-state treatment with a reasonable approximation, the rate law may be written in terms of consumption of $[BrO_3^-]$ as follows:

$$-\frac{d[BrO_3^-]}{dt} = k_2[C_2]$$

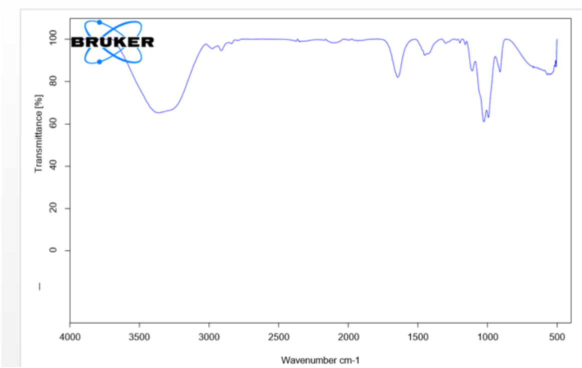
OR

$$-\frac{d[BrO_3^-]}{dt} = \frac{k_1\, k_2\, [S]\, [Rh(III)]_T}{k_{-1}\, [H^+] + k_1\, [S]}$$

Where $[Rh(III)]_T = C_1 + C_2$

Product Analysis: Formaldehyde is the main product in the oxidation of Glycine was identified by the help of chromatography (TLC), conventional (spot test) Method and also through 2,4 dinitro phenyl hydrazine (DNPH) derivative (Brady's test). The functional group - CHO also confirmed by Tollens reagent and Schiff base. The nature of Formaldehyde further confirmed by the IR spectrum 2720 -2820 cm- due to(C-H) stretching, 1720 cm- due to (C=O) stretching ,1450 cm- due to (CH_2) Bending and 1100 cm- due to out of plane (CH_2) bending. Various combinations, bands and overtones of these fundamental vibrations are also observed in the IR spectrum. The position and intensity of absorption band can be influenced by the physical state like (gas liquid and solid) of the formaldehyde sample. Similarly, ammonia was identified by the Nessler's reagent and CO_2 was qualitatively detected by bubbling nitrogen gas through acidified reaction mixtures and passing the liberated gas through tube containing lime water.

Conclusions: These results indicate that the reaction rate is doubled as the concentration of the catalyst [Rh(III)] is doubled. The rate law is in conformity with all kinetic observations and the mechanistic steps proposed are also logical in view of the fact that the influence of ionic strength is almost negligible. Moreover, the high positive ΔG^* values indicate a very much solvated transition state, but such high negative values of ΔS^* give the possibility of an activation complex with a limited mobility. Thus, from this study the conclusion drawn is that the reactive species of $KBrO_3$ and Rh(III) chloride in acidic medium are BrO_3^- and Rh^{3+} respectively.



IR Spectrum of Main Product Formaldehyde

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