



International Journal of ChemTech Research CODEN(USA): IJCRGG ISSN : 0974-4290 Vol.4, No.4, pp 1615-1618, Oct-Dec 2012

Kinetics Of Oxidation Of Acetanilide And Benzanilide By Cr (Vi) In Aqueous Acetic Acid – H₂so₄ Medium

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Abstract: Kinetics of oxidation of acetanilide and benzanilide by Cr(VI) in aqueous acetic acid-sulphuric acid mixture reveals that the kinetic orders are fractional in [substrate], first order in [oxidant] and first order in [H⁺] till 0.5M leading to second order in higher concentrations for acetanilide. Benzanilide exhibits first order in [substrate] till 0.005M leading to independent of [substrate] at higher concentrations, first order in [oxidant] and second order in [H⁺]. These results are rationalized by a mechanism involving complex formation with different Cr(VI) species. The complex in a series of fast reactions yields azobenzene as the product in both the cases.

Key Words: kinetics, oxidation, anilides, chromic acid, acid medium.

Introduction:

A survey of literature shows that reports on the oxidation of anilides by oxidants like Mn(VII) and Cr(VI) are scanty¹⁻⁵. Hence this investigation deals with oxidation of acetanilide and benzanilide by Cr(VI) in aqueous acetic acid - sulphuric acid mixtures with a view to establish whether it is direct oxidation of anilides or whether it is oxidation of the hydrolytic products of anilides.

Experimental:

Chromium (VI) trioxide (Chromic acid): Qualigens – ExcelaR grade was prepared in doubly distilled water and used as stock solution.

Acetanilide: Qualigens – SQ grade was used without further purification.

Benzanilide: Qualigens – ExcelaR grade was used without further purification.

All other chemicals, acids and solvents used in these investigations were of analytical reagent grade.

Kinetic Method: Aliquots in the reaction mixture were analysed by iodometric method. 5.0 ml of the reaction mixture containing chromic acid was pipetted out at various intervals of time into a mixture of iodate free potassium iodide solution containing dilute sulphuric acid (4N) in a carbon dioxide atmosphere. The liberated iodine was titrated against standard thiosulphate solution to the disappearance of the blue starch-iodine end point.

Stoichiometry and product analysis:

Stoichiometry has been found to be 3:2 as per the following equation

 $2CrO_3 \rightarrow Cr_2O_3 + 3(O)$

 $2C_6H_5NHCOCH_3 + 2(O) \rightarrow 2C_6H_5N=NC_6H_5 + 2CH_3COOH$

The products are azobenzene and acetic acid in case of acetanilide and azobenzene while benzoic acid and azobenzene in case of benzanilide.

Azobenzene has been identified by its physical constant melting point 68° C.

Results And Discussion:

Kinetics of oxidation of acetanilide and benzanilide by Cr (VI) in aqueous acetic acid medium in the presence of H_2SO_4 have been investigated. The kinetic results are given below

Acetanilide:

Dependence on oxidant: The reaction is first order in oxidant as evidenced by linear plots of log(a-x) vs time. In addition the constancy in the first order rate constants of different concentrations of the oxidant establishes firmly that it is first order in oxidant (Table-I).

Dependence on substrate: The reaction rate increases with increase in the concentration of substrate (Table-I). A plot of log k vs log [S] yielded fractional slope. This proves that the reaction is fractional order in substrate.

Dependence on acid: The first order rate constants increase with the concentration of substrate. There is unit order dependence on H^+ till 0.5M and later it exhibits second order dependence at higher concentrations of H^+ (Table-I).

Effect of varying solvent proportion: The reaction rate increases with increase in the

percentage of solvent. A plot of log k vs 1/D shows linearity (Table-I).

<u>Benzanilide:</u>

Dependence on oxidant: The reaction is first order in oxidant as evidenced by linear plots of log(a-x) vs time. The first order rate constants (Table-II) are constant in a wider range of concentration of oxidant confirming first order nature on oxidant.

Dependence on substrate: The reaction rate increases at lower concentrations of substrate. A plot of log k vs log[S] yield unit slope. At higher concentrations of H^+ the kinetic rate is independent of concentration of substrate (Table-II).

Dependence on acid: The dependence on acid is two in the concentration range of 1.0 - 2.0M (Table-II). A plot of log k vs log [H⁺] yields a line of slope of two confirming second order dependence on acidity.

Effect of varying solvent proportion: The reaction rate increases with increase in the percentage of solvent. A plot of log k vs 1/D shows linear dependence on solvent percentage (Table-II)

Concentration of	Concentration of	k x 10 ⁴ (sec ⁻¹)
Non variant	Variant	
[Acetanilide] = 0.1M	0.00012M	3.40
$[H_2SO_4] = 0.5M$	0.00025M	3.55
AcOH = 50%	0.00050M	3.20
Temp. = 60° C		
$[CrO_3] = 0.00025M$	0.05M	2.33
$[H_2SO_4] = 0.5M$	0.10M	3.55
AcOH = 50%	0.20M	6.00
Temp. = 60° C		
[Acetanilide] = 0.1M	0.25M	1.38
$[CrO_3] = 0.00025M$	0.50M	3.55
AcOH = 50%	0.75M	5.40
Temp. = 60° C	1.00M	6.50
	1.50M	8.20
[Acetanilide] = 0.1M	25%	2.31
$[CrO_3] = 0.00025M$	50%	3.55
$[H_2SO_4] = 0.5M$	75%	6.80
Temp. $= 60^{\circ}$ C		
	Concentration of Non variant [Acetanilide] = 0.1M $[H_2SO_4] = 0.5M$ AcOH = 50% Temp. = 60^0C $[CrO_3] = 0.00025M$ $[H_2SO_4] = 0.5M$ AcOH = 50% Temp. = 60^0C [Acetanilide] = 0.1M $[CrO_3] = 0.00025M$ AcOH = 50% Temp. = 60^0C [Acetanilide] = 0.1M $[CrO_3] = 0.00025M$ AcOH = 50% Temp. = 60^0C [Acetanilide] = 0.1M $[CrO_3] = 0.00025M$ $H_2SO_4] = 0.5M$ Temp. = 60^0C	Concentration of Non variant Concentration of Variant [Acetanilide] = 0.1M 0.00012M $[H_2SO_4] = 0.5M$ 0.00025M AcOH = 50% 0.00050M Temp. = 60^0C 0.05M [CrO_3] = 0.00025M 0.05M $[H_2SO_4] = 0.5M$ 0.10M AcOH = 50% 0.20M Temp. = 60^0C 0.20M [Acetanilide] = 0.1M 0.25M [CrO_3] = 0.00025M 0.50M AcOH = 50% 0.75M Temp. = 60^0C 1.00M [Acetanilide] = 0.1M 25% [CrO_3] = 0.00025M 50% [Acetanilide] = 0.1M 25% [CrO_3] = 0.00025M 50% [Acetanilide] = 0.1M 25% [CrO_3] = 0.00025M 50% [H_2SO_4] = 0.5M 75% Temp. = 60^0C 75%

TABLE - I : Effect of variation of various constituents on reaction rate of Acetanilide

Variant	Concentration of Non variant	Concentration of Variant	k x 10 ⁴ (sec ⁻¹)
CrO ₃	[Benzanilide] = 0.01M	0.00012M	1.59
	$H_2SO_4 = 1.5M$	0.00025M	1.60
	AcOH = 50%	0.00050M	1.62
	Temp. = 60° C		
Benzanilide	$[CrO_3] = 0.00025M$	0.00125M	0.41
	$H_2SO_4 = 1.5M$	0.00250M	0.75
	AcOH = 50%	0.00500M	1.59
	Temp. = 60° C	0.00750M	1.55
		0.01000M	1.60
H_2SO_4	[Benzanilide] = 0.01M	1.0M	0.74
	$[CrO_3] = 0.00025M$	1.5M	1.60
	AcOH = 50%	2.5M	4.30
	Temp. = 60° C		
AcOH	[Benzanilide] = 0.01M	50%	1.60
	$[CrO_3] = 0.00025M$	60%	2.89
	$[H_2SO_4] = 1.5M$	70%	5.28
	Temp. = 60° C		

TABLE - II : Effect of variation of various constituents on reaction rate of Benzanilide

Nature of chromium species and sequence of reactions: Cr (VI) can be any of the following forms in oxidation reactions H₂CrO₄ + H⁺ \rightarrow HCrO₃⁺ + H₂O

 $HCrO_3^+ + H^+ \rightarrow H_2CrO_3^{++}$

Dependence on the [acid] in the range used shows that any of the above species may be participating in the present investigation. It appears that monocationic and dicationic species are both relevant due to the observance of first order dependence on H^+ and second order dependence on H^+ .

The sequence of reactions can be pictured as follows:

$H_2CrO_4 + H^+$	K :	$HCrO_3^+ + H_2O$
$H_2CrO_4 + 2H^+$	ζ_1	$H2CrO_{3}^{++} + H_{2}O$
C ₆ H ₅ NHCOCH ₃ +HCrO	$\overline{\mathbf{N}_3^+}$ K	Complex C_1
C ₆ H ₅ NHCOCH ₃ +H ₂ CrO	O_3^{++} K	Complex C_2
Complex C ₁	k	$C_6H_5N COCH_3 + Cr(V) + H^+$
Complex C ₂	k_1	$-C_6H_5N COCH_3 + Cr(V) + H^+$
$C_6H_5N^{\bullet}COCH_3 + H_2O$	fast	$\sim C_6H_5NH + AcOH$
$C_6H_5NH + Cr(V)$	fast	$\sim C_6H_5NH + Cr(IV)$
$C_6H_5NH + C_6H_5NH^{\bullet}$	fast	$\bullet C_6H_5NH - NH - C_6H_5$
$C_6H_5NH-NH-C_6H_5\\$	fast	$C_6H_5N = N - C_6H_5$
Cr(V)	fast	Cr(III) + Cr(II)
Cr(II) + Cr(IV)	fast	Cr(III)

Scheme – I Rate = k C₁ =
$$\frac{kK_2K[H_2CrO_4][H^+][S]}{1+k_2[S]}$$

Scheme – II Rate
$$= k_1 C_2 = \frac{k_1 K_1 K_3 [S] [H_2 CrO_4] [H^+]^2}{1 + k_3 [S]}$$

These two rate laws in combination easily explain the fractional order on [acetanilide], first order in oxidant and first order in [H⁺] leading to second order in [H⁺] at higher concentrations. The observed orders in benzanilide system are first order in substrate leading to independent of [substrate] at higher concentrations, first order in oxidant and second order in $[H^+]$ which are accounted by the combination of the two rate equations. Finally the rate law is as follows cumulatively. _

Rate

$$\frac{kK_2K[H_2CrQ_4][H^+][S]}{1+K_2[S]} + \frac{k_1K_1K_3[S][H_2CrQ_4][H^+]^2}{1+K_3[S]}$$

An alternative mechanism leading to formation of benzalehyde and azobenzene in a previous study ⁴ is unlikely for the following reasons.

Nitrogen which is more basic in character can only take up protons from the water molecule which is the hydrolysing agent. Consequently the OH⁻ goes to carbonyl group which is polarized with fractional positive charge on carbon. Hence the mechanism postulated is unlikely though the kinetic observations are quite reasonable.

The mechanism postulated for this study involving the formation of $C_6H_5 - N - COCH_3$ as a slow step which later decomposes in series of steps to give corresponding carboxylic acid and azobenzene explain all kinetic observations and concurs with product study.

Thus the products are benzoic acid and azobenzene in case of benzanilide while acetic acid and azobenzene in case of acetanilide.

Comparison of rates in acetanilide and **benzanilide:** Though the experimental conditions are at variance, it is still possible to compare the reactivity of acetanilide and benzanilide in an approximate manner by extrapolating the values at equal concentrations. Rate constants of acetanilide and benzanilide are 6.9 x 10^{-4} sec⁻¹ and 1.6 x 10^{-4} sec⁻¹ respectively. It is obvious that rate of abstracting hydrogen from benzanilide is much more difficult due to presence of two phenyl rings which cause steric hindrance. This steric factor is not present in acetanilide and hence losing hydrogen is much easier in case of acetanilide compared to benzanilide in the presence of oxidant. It may be added that the reaction is proceeding through a radical mechanism as quantum of retardation observed is not phenomenal. The reaction is not proceeding through ionic pathway as cation formation will result in larger differential reactivity. This is additional evidence for radical formation in the oxidation process.

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