

KINETICS AND MECHANISM OF THE OXIDATION OF FORMAMIDE, ACETAMIDE, BENZAMIDE AND 4-NITROBENZAMIDE BY TRICHLOROISOCYANURIC ACID (TCCA) IN ACETIC ACID-SODIUM ACETATE BUFFER MEDIUM

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The kinetics of oxidation of formamide, acetamide, benzamide and 4-nitrobenzamide by trichloroisocyanuric acid (TCCA) in acetic acid-sodium acetate buffer medium have been studied. The reaction is first order in oxidant (TCCA) and fractional order in the substrate. The reaction is pH dependent i.e., the rate increases linearly with the increase in acetate ion concentration. The effect of solvent composition has been investigated. Effect of temperature on the reaction kinetic has been studied and different thermodynamic parameters are computed. A suitable mechanism is discussed on the basis of observed-kinetic data. The rate law is given by,

$$-\frac{d[\text{TCCA}]}{dt} = \frac{k_2 k_1 [\text{A}] [\text{TCCA}]_T}{1 + k_1 [\text{A}]}$$

where, $A \Rightarrow$ Amide, $k_1 \Rightarrow$ Forward rate constant for complex formation, $k_2 \Rightarrow$ Rate constant for decomposition of complex.

Key Words: Kinetics & Mechanism; Oxidation; Formamide; Acetamide; Benzamide and 4-Nitrobenzamide; Trichloroisocyanuric Acid (TCCA); Acid Medium

Introduction

Trichloroisocyanuric acid has been used as an oxidant, for oxidising a number of organic substrates like unsaturated acids¹, benzaldehyde and substituted benzaldehydes^{2,6}, diols and cyclanols³, benzhydrol and *p*-chlorobenzhydrol⁴, substituted toluenes and hydrocarbons⁵, aliphatic alcohols⁷, aromatic amines⁹, acetanilide and substituted acetanilides⁸, phenylacetic acid⁹, aldoses⁷ and ketones⁹. Acid amides have been subjected to oxidation by a number of oxidants like Thallium(III)¹¹, Silver(II), Cobalt(III) and Manganese(III)¹⁰, PIA¹², Potassium permanganate¹³, peroxodisulphate^{14,15,16} and peroxides¹⁷.

A survey of literature reveals that there is no report on oxidation of amides by trichloroisocyanuric acid (TCCA). The kinetics of oxidation of formamide, acetamide, benzamide and 4-nitrobenzamide by trichloroisocyanuric acid have been studied in acetic acid-sodium acetate buffer medium.

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Experimental

Formamide (E. Merck) was distilled before use. Acetamide (E. Merck), Benzamide (BDH, Glaxo Laboratories) and 4-nitrobenzamide (synthesized according to standard procedure has been given by A.I. Vogel in Text book of practical Organic Chemistry) were used as such. Trichloroisocyanuric acid (TCCA) was of AnalaR (Fluka) grade. Standard iodometric procedure was adopted in estimating unreacted TCCA.

The progress of the reaction was carried out by withdrawing aliquots (5ml each) of the reaction mixture at regular intervals of time and quenched by pouring into large excess of acidified KI solution and the liberated iodine titrated against standard thiosulphate solution. The results were reproducible within $\pm 3\%$. The pH of the solution was noted, before and after the experiment is over.

Results and Discussion

Effect of Varying [Oxidant] on the Reaction Rate

The dependence of the reaction rate on the oxidant concentration (disappearance of [TCCA]) has been determined by studying the reaction at different initial oxidant concentrations. The order of the reaction with respect to oxidant was found to be unity as indicated by the good linearity in the plots of log titrated value versus time (Fig. 1). The pseudo first order rate constants are fairly independent of the initial concentration of TCCA (Table I).

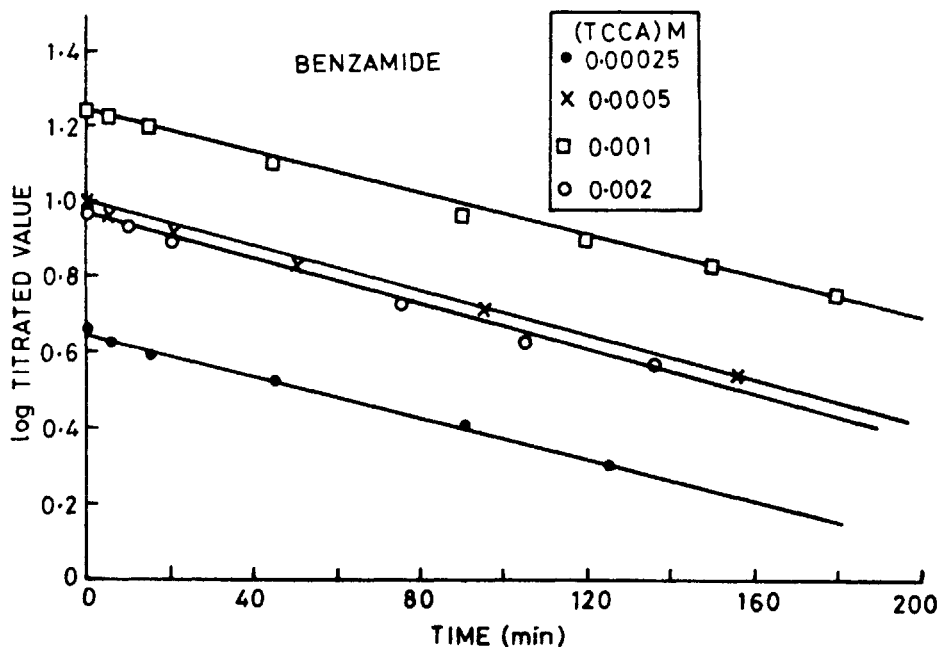


Fig 1 Log titrated value vs time

Table I

$\frac{10^2 \times M}{[S][TCCA]}$	[AcONa]M	pH	AcOH% (v/v)	Temp. °C	$10^4 \times k_t s^{-4}$				
					Formamide	Acetamide	Benzamide	*4-Nitro- benzamide	
Effect of varying [Oxidant]									
1.0									
	0.025	1.0	4.6	5	40	6.2	0.80	1.00	1.7
	0.05					6.7	1.04	1.09	2.1
	0.1					6.3	0.90	1.10	2.0
	0.2					6.3	0.90	1.00	1.8
Effect of varying [Amide]									
0.25	0.05	1.0	4.6	5	40	4.5			1.0
	0.5					5.9	0.92	0.83	1.3
	1.0					6.7	1.04	1.09	2.1
	2.0					7.8	1.10	1.18	2.4
	4.0						1.20	1.30	
Effect of varying [AcONa]									
1.0	0.05	0.2	3.8		40		0.48	0.31	
		0.4	4.1				0.71	0.57	
		0.8	4.3				0.95	0.91	
		1.0	4.6				1.04	1.09	
Effect of varying AcOH % (v/v)									
1.0	0.05	1.0		5	40	6.7	1.04	1.09	
				10		6.2	0.68	0.64	
				20		4.1	0.38	0.44	
				30					3.1
				40					2.1
				50					1.0
Effect of temperature									
1.0	0.05	1.0		5	35	3.8	0.60	0.50	1.1
					40	6.7	1.04	1.09	2.1
					45	10.5	1.90	2.10	3.1

*AcOH = 40% (v/v), pH = 3.5

Effect of Varying Substrate Concentration on Reaction Rate

The effect of change in substrate concentration on the reaction rate has been studied by varying the initial substrate concentration for different amides. The rate of reaction increases on increasing the substrate concentration (Table I).

The plots of $\log k_1$ vs. $\log[S]$ are linear with a slope less than unity (Fig. 2), for all compounds studied. This observation reveals that fractional order dependence on substrate. Such dependence on substrate has been earlier reported in the oxidation of aliphatic and cyclic ketones by periodate¹⁸; Ru(III) catalysed oxidation of unsaturated acids by TCCA¹; and bromination of acetanilides by N-Bromoacetamide (NBA)¹⁹.

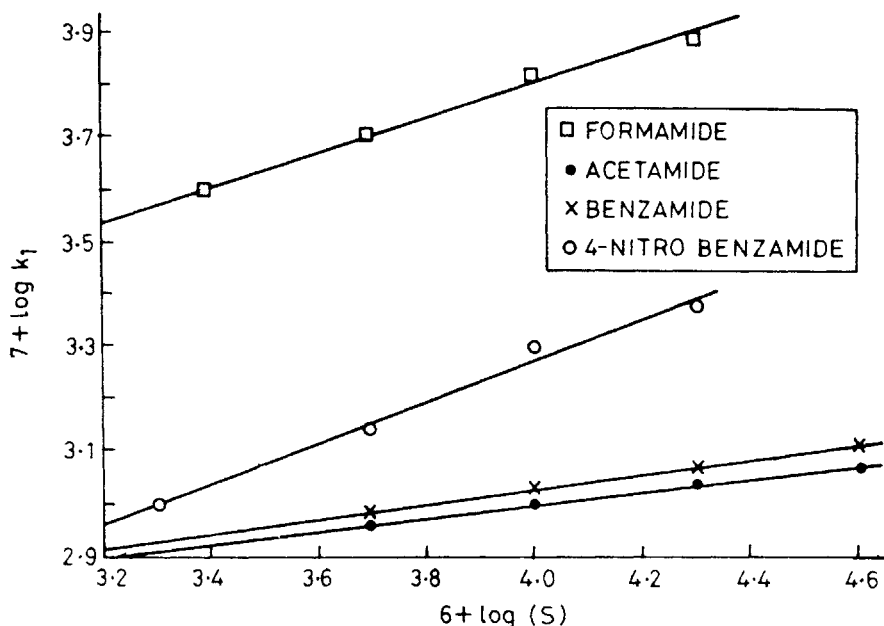


Fig 2 $\log K_1$ vs $\log[S]$

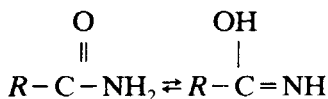
Effect of Sodium Acetate on Reaction Rate

In order to investigate the effect of *pH* the reaction was carried out at different concentrations of sodium acetate. With increase in the acetate ion concentration, the reaction rate increases (Table I). However, the plots of $\log k_1$ vs. $\log[\text{OAc}^-]$ are linear pointing to a marginal effect of OAc^- ions.

Effect of Solvent Composition on Reaction Rate

The effect of change in the solvent composition on the reaction rate has been determined by varying the proportion of acetic acid in the reaction mixture. It has been observed that by increasing the acetic acid content a decrease in the rate of reaction (Table I). The plots of $\log k_1$ vs. $1/D$ are linear for all the substrates studied.

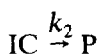
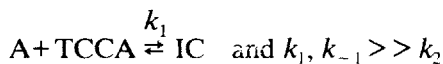
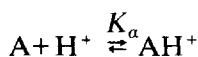
The amides have prototropic interconversion as:



Under present experimental environment, the concentration of protonated substrate (AH^+) is very small in compare to free substrate concentration (as the amides are very weak bases); complexation between amide and oxidant is most probably with the enolised form of the substrate^{10,11}. Also the order of reaction with respect to substrate is fractional. This typical behaviour of reaction kinetics involve an intermediate complex formation prior to the slow step^{20,9}. At constant concentration of amide and from plots of $1/V$ vs. $1/[\text{TCCA}]_T$ and with known values of k_1 , k_2 have been evaluated for different amides which are as follows:

	$k_2, \text{s}^{-1} \times 10^4$
Formamide	7.33
Acetamide	0.85
Benzamide	1.27
4-NO ₂ benzamide	2.47

The following mechanism is suggested:



where A \Rightarrow Amide, IC \Rightarrow Intermediate Complex,
P \Rightarrow Product, V \Rightarrow Rate of reaction.

The following general rate law has been derived by taking TCCA and HOCl as the active species.

Now,

$$[\text{A}]_T = [\text{A}] + [\text{AH}^+] \quad \dots \text{ (i)}$$

and

$$[\text{AH}^+] = K_a[\text{A}][\text{H}^+] \quad \dots \text{ (ii)}$$

Substituting the value of $[\text{AH}^+]$ in equation (i) from equation (ii),

$$[\text{A}]_T = [\text{A}] + K_a[\text{A}][\text{H}^+]$$

or

$$[\text{A}]_T = [\text{A}]\{1 + K_a[\text{H}^+]\}$$

$$\text{or } [A] = \frac{[A]_T}{1 + K_a [H^+]} \quad \dots \text{ (iii)}$$

$$[IC] = k_1[A][TCCA] \quad \dots \text{ (iv)}$$

$$\begin{aligned} [TCCA]_T &= [TCCA] + [IC] = [TCCA] + k_1[A][TCCA] \\ &= [TCCA]\{1 + k_1[A]\} \end{aligned}$$

$$\text{or } [TCCA] = \frac{[TCCA]_T}{1 + k_1[A]} \quad \dots \text{ (v)}$$

$$\text{and } V = k_2[IC] \quad \dots \text{ (vi)}$$

Now putting the value of $[A]$ and $[TCCA]$ in eq. (iv), also assuming magnitude of K_a to be very small^{11,23},

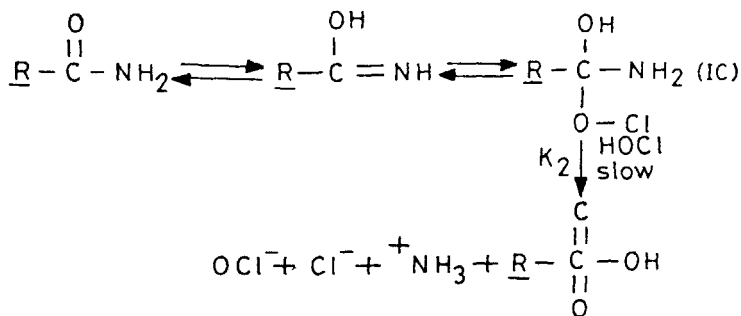
$$[IC] = \frac{k_1[A][TCCA]_T}{1 + k_1[A]}$$

Now

$$V = \frac{k_2 k_1 [A] [TCCA]_T}{1 + k_1 [A]}$$

The above rate law explains all the observed kinetic order.

Mechanism



Acknowledgement

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