Asian Journal of Chemistry Vol. 7, No. 3 (1995), 681–684

NOTE

Kinetics of Chloramine-T Oxidation of *p*-Hydroxy Benzoic Acid in Perchloric Acid: A Mechanistic Study

U.S. PANDEY* and NAWAL KISHORE ROY
Department of Chemistry
H.D. Jain College, Ara (Bihar), India

Kinetic results in chloramine-T oxidation of *p*-hydroxy benzoic acid in perchloric acid have been reported. First order kinetics with respect to each of chloramine-T, *p*-hydroxy benzoic acid (*p*-HBA) and H^+ ions has been observed. Zero effect of variation of ionic strength of the medium on the rate of the reaction has been obtained,. Successive addition of *p*-toluene suphonamide (PTS) did not influence the reaction rate. A suitable mechanism in conformity with observed kinetic results has been proposed.

Chloramine-T[1–3] has earlier been used as oxidant both in acidic and alkaline medium in oxidation of many organic compounds. It has not been, so far, used as oxidant in oxidation of *p*-hydroxy benzoic acid in acidic solution. In the present communication, an attempt has been made to study the kinetics and mechanism of oxidation of *p*-hydroxy benzoic acid by acidic solution of chloramine-T.

Chemistry of N-halogeno compunds[4] has been recently probed in order to explore its oxidative potential. None has, so far, paid attention to reveal the oxidative kinetic feactures of the reaction involving chloramine-T as oxidant and *p*-hydroxy benzoic acid as reducing agent. This prompted us to undertake the present investigation which constitutes the study of kinetics and mechanism of chloramine-T oxidation of *p*-hydroxy benzoic acid in perchloric acid medium.

All the reagents used were of the highest purity available. An aqueous solution of chloramine-T (E. Merck) was checked by estimating it iodometrically. Perchloric acid (E. Merck) was used as a source of H^+ ions and sodium perchlorate (E. Merck) was used for varying ionic strength of the medium. E. Merck (Germany) sample of *p*-toluene sulphonamide was used to observe its effect on the rate of the reaction. The solution of *p*-hydroxy benzoic acid (BDH) was prepared in 50% A.R. (BDH) methanol of 90% purity.

The reaction stills were blackened from outside to avoide any photo-chemical reaction. The kinetic procedure followed was the same as reported in the previous publication[5]. The reaction was studied for 60% of the reaction.

The estimation of unreacted chloramine-T from different sets of experiments with various chloramine-T to *p*-hydroxy benzoic acid ratios showed consumption of two moles of chloramine-T per mole of *p*-hydroxy benzoic acid and accordingly the following equation could be formulated:

$$2TsNNaCl + OHC_6H_4COOH + H_2O \rightarrow 2TsNH_2 + C_6H_4O_2 + 2NaCl + CO_2 \quad (1)$$

TsNNaCl is chloramine-T in which Ts stands for $CH_3C_6H_4SO_2$—, Ts NH_2 is *p*-toluene sulphonamide(PTS) and OHC_6H_4COOH is *p*-hydroxy benzoic acid. The product *p*-benzoquinone ($C_6H_4O_2$) was confirmed by conventional spot tast[6].

The kinetics of oxidation of *p*-hydroxy benzoic acid (*p*-HBA) by chloramine-T (CAT) in perchloric acid medium was investigated at several initial concentrations of reactants (Table 1). The first order kinetics with respect to CAT is evident from the kinetic data of Table 1. The linear relationship between k_1 (first order rate constant) and [*p*-HBA] or [$HClO_4$] confirms first order dependence on *p*-HBA and $HClO_4$. Table 2 contains the data on effect of variation of ionic strength of the medium and addition of *p*-toluene sulphonamide (PTS) on the rate of the reaction. Negligible effect of variation of ionic strength of the medium and addition of PTS was observed. The solvent composition effect was studied by addition of methanol 50% (v/v) and data obtained indicate zero effect on the rate of the reaction (Table-2). The measurements at different temperatures gave the value of energy of activation (E_a) as 16.65 k cal/mol.

TABLE-1
EFFECT OF VARIATION OF [REACTANTS] ON THE RATE AT 45°C (UNLESS OTHERWISE STATED) METHANOL = 50% (v/v)

[CAT] × 10^4 M	[*p-HBA*] × 10^2 M	[$HClO_4$] × 10^2	$k_1 \times 10^5$ sec^{-1}
8.00	1.00	2.00	4.72
10.00	1.00	2.00	4.74
12.00	1.00	2.00	4.72
16.00	1.00	2.00	4.68
20.00	1.00	2.00	4.70
10.00	1.20	2.00	3.26
10.00	1.50	2.00	3.84
10.00	1.80	2.00	4.76, 3.58[a]
10.00	2.40	2.00	6.48
10.00	3.00	2.00	7.86
10.00	1.80	1.00	2.36
10.00	1.80	1.25	2.96
10.00	1.80	1.50	3.58
10.00	1.80	2.00	4.76
10.00	1.80	2.00	6.08
10.00	1.80	2.00	7.08
10.00	1.80	2.00	7.60[b], 9.82[c]

Temp. 40°C (a), 50° (b) and 55 (c)°C

TABLE-2
EFFECT OF VARIATION OF IONIC STRENGTH (μ) AND SOLVENT EFFECT AND ADDITION OF PARA TOLUENE SULPHONAMIDE (PTS) ON THE REACTION RATE AT 45°C [CAT] = 10.00×10^{-4}, [*p*-HBA] = 2.40×10^{-2} M and [$HClO_4$] = $2{,}00 \times 10M^{-2}$

$\mu \times 10^2$M	[PTS] $\times 10^{-4}$M	Methanol % (v/v)	$k_1 \times 10^5$ sec^{-1}
2.00	—	—	6.46
4.00	—	—	6.50
6.00	—	—	6.53
8.00	—	—	6.54
12.00	—	—	6.48
10.00[a]	—	—	2.36
10.00[a]	0.00	—	2.38
10.00[a]	2.00	—	2.35
10.00[a]	4.00	—	2.36
10.00[a]	6.00	—	2.34
10.00[a]	10.00	—	4.76
10.00[b]	—	0.00	4.73
10.00[b]	—	10.00	4.72
10.00[b]	—	20.00	4.72
10.00[b]	—	30.00	4.75
10.00[b]	—	40.00	4.74

a → $HClO_4 = 10.00 \times 10^3$ M and b → *p*-HBA = 1.80×10^{-2} M

In aqueous solution chloramine-T ionises as $TsNCl^-$ and Na^+. The anion of chloramine-T gets protonated in acidic medium and the following two equilibra were reported to exist.[7, 8]

$$TsNCl^- + H^+ \rightleftharpoons TsNHCl$$

$$2TsNHCl \rightleftharpoons TsNCl_2 + TsNH_2$$

where $TsNCl_2$ is dichloro *p*-toulene suphonamide (DCT). Thus in acidic media there are three possible reactive species of chloramine-T, viz. $TsNCl^-$, $TsNCl_2$, and TsNHCl. On assuming $TsNCl_2$ as reactive species, negative effect of PTS is required contrary to its zero effect on the rate, ruling out involvement of $TsNCl_2$ as reactive species in the reaction. First order dependence on H^+ is not explained when $TsNCl^-$ is taken as reactive species. Hence under the given conditions the only choice left is TsNHCl, which when taken as reactive species, clearly and convincingly explains the kinetic results. In the light of above statement and other kinetic results, the following mechanistic steps are suggested.

$$TsNCl^{-+} + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} TsNHCl \qquad (i)$$

$$TsNHCl + S \xrightarrow{k_2} X \text{ (Intermediate)} \qquad (ii)$$

$$X + TsNHCl \xrightarrow[\text{fast}]{k_3} \text{Products} \qquad (iii)$$

where S stands for *p*-hydroxy benzoic acid. On applying steady state treatment on [TsNHCl] and [X] and on assuming the inequality $k_{-1} \gg k_2$ [S], the following final rate law is obtained.

$$\frac{-d[CAT]}{dt} = K[CAT][S][H^+] \qquad (2)$$

where $K = k_1/k_{-1}$

The rate law (2) fully explains all the kinetic data.

REFERENCES

1. K. Weber and F. Valic, *Z. Phy. Chem.*, **238,** 353 (1968).
2. L. Pryde and F.B. Soper, *J. Chem. Soc.*, 1510 (1931).
3. H.M.K. Naidu and D.S. Mahadevappa, *Monatsch Chem.*, **109,** 269 (1978).
4. R. Filler, *Chem. Rev.*, **63,** 21 (1963).
5. P.S. Radhakrishnamurty and M.D.F. Rao, *Indian J. Chem.*, **16A,** 259 (1977).
6. F. Feigl, Spot Tests in Organic Analysis, Elsevier, New York (1966).
7. J.C. Morris, J.A. Salazar and N.A. Wineman, *J. Am. Chem. Soc.*, **70,** 2036 (1948).
8. S. Vivekanand, K. Venkatarao and N. Santappa, *Indian J. Chem.*, **17A,** 503 (1978).

(*Received*: 4 July 1994; *Accepted*: 20 January 1995) AJC-937

ERRATUM

Infrared spectra of N-2-pyridyl formamide, Vol. 6(4), 889–892 (1994). The correct structure of the N-2-pyridyl formamide is as below:

$C_6N_2H_6O$

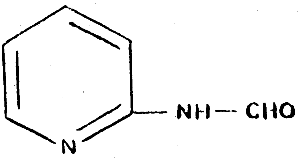

Fig. 1. 2-Pyridyl formamide (N-2-Pyridyl methanamide).