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# KINETICS AND MECHANISM OF OXIDATION OF FORMIC ACID WITH CHLORAMINE-T IN AQUEOUS ACIDIC MEDIUM

(Miss) Nidhi Sharma, S.K. Mishra and P.D. Sharma*

Department of Chemistry, University of Rajasthan,
Jaipur-302 004 (INDIA)

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The oxidation of formic acid with chloramine-T has been observed to occur via two paths, one dependent and other independent of hydrogen ion concentration. The rate of the reaction is also retarded by toluene-p-sulphonamide, one of the reaction products.

Oxidative decarboxylation of formic acid had been reported with various metal oxidants in acid media and the empirical rate law reported for most of these reactions consists of two terms - one independent and other inverse in hydrogen ion concentration[1-5]. The oxidants Cerium(IV)[2] and Cobalt(III)[6] subscribe to a different trend of reactivity with formic acid. However, oxidation studies with non-metal oxidants are scanty. The present paper concerns with the kinetics of the chloride ion catalyzed oxidation of formic acid with N-chlorotoluene-p-sulphonamide (Chloramine-T) in acid medium. This study appears interesting from two view points :

Firstly, the evidences available for the metal ion oxidations of formic acid suggest the formation of an intermediate complex between metal ion and the formate or formic acid. Such a proposition appears unlikely in the reference reaction in view of non-complexing nature of the oxidant.

Secondly, the mode of operation of chloride ion catalysis in chloramine-T oxidations is not, yet, well established. The catalysis whether it occurs through the catalyst redox cycle or via any other mode is an important aspect for probing the chemistry of chloramine-T.

## Experimental

All solutions were prepared from the reagent grade chemicals. Sodium formate (BDH, LR) was used as such and the solution was prepared by dissolving the required amount in a known volume of de-ionized water. Sodium salt of N-chlorotoluene-p-sulphonamide (E. Merck, GR) was employed for the solutions of chloramine-T and these were stored in brown coloured bottles to check the photolight decomposition. Chloramine-T solutions were always standardized iodometrically[7,8] before use.

Doubly distilled water was employed, second distillation being from alkaline permanganate solution in an all glass assembly.

Kinetics of the reaction were carried out by taking reagents in separate bottles thermostated at ± 0.1°C unless stated otherwise and these were mixed rapidly minimizing the error in measurements of initial time readings. Kinetic measurements were made by quenching aliquot samples (5 or 10 $cm^3$) in an excess of potassium iodide ( $\backsim$ 20%) in $H_2SO_4$ ($\backsim$ 1 mol $dm^{-3}$) medium and the liberated iodine was titrated against thiosulphate solution using starch as an indicator. A few experiments were also conducted in bottles blackened from the outside to check the effect of photolight on the rate of the reaction, however, rates remained unaffected. Reactions were studied in initial stages ( $\backsim$ 40%) to avoid the interference caused by p-toluenesulphonamide. Results were reproducible within an uncertainty of ± 6% .

## Results

The reaction of formic acid with chloramine-T (henceforth known as CAT) is immeasurably slow in acid medium. However, the reaction is appreciably catalyzed by chloride ions. The stoichiometry of the reaction determined with CAT in excess over formic acid in presence of chloride ions conforms to the eqn (1).

$$RNHCl + HCO_2H \xrightarrow{Cl^-} RNH_2 + CO_2 + H^+ + Cl^- \qquad (1)$$

$$\text{where } R = CH_3\text{-}C_6H_4SO_2$$

Attempts were unsuccessful in quantifying $CO_2$ owing to low amount of the gas formed in the reaction. This was limited experimentally as the higher concentrations of chloramine-T ($>$ 0.003 mol $dm^{-3}$) are precipitated in the hydrogen ion concentration employed in the reaction. Further, chloramine-T interferes in spectrophotometric analysis of p-toluenesulphonamide. These are the main reasons why the reaction products were not quantified. However, qualitative tests indicated presence of both the products in the reaction systems. Since the monomer methylmethacrylate is not polymerized in the reaction mixture and hence the possibility of a chain reaction is ruled out.

Chloramine-T and Formic Acid Dependence -

It was observed for pseudo-first order conditions that plots of $\log_{10}$ CAT $_t$ against time yielded straight lines with pseudo-first order rate constants being independent of the initial concentration of CAT. However, pseudo-first order rate constants were a linear formation of initial concentrations of formic acid confirming order with respect to the latter to be one. Thus, the first order dependence of the rate on the concentrations of CAT and formic acid each conforms to the experimental rate law (2) at constant hydrogen ion concentration.

$$-\frac{d[CAT]}{dt} = k'[CAT]_T[HCO_2H]_T \qquad (2)$$

$[CAT]_t$ and $[HCO_2H]_t$ represent the analytical concentrations of CAT and formic acid respectively. 'k′' is the observed second order rate constant. Initial rates[9] were also computed employing plane mirror method for few reactions. The second order rate constants derived from pseudo-first order rate constants and initial rates are mentioned in the last column of Table-1 and agree with each other within an error of ± 10% .

Hydrogen-Ion Dependence -

Hydrogen-ion concentration was varied in the range (0.01-0.25) mol $dm^{-3}$ at fixed concentrations of CAT, formic acid and I = 2.0 mol $dm^{-3}$ (adjusted with sodium nitrate). Hydrogen-ion concentrations $>$ 0.25 mol $dm^{-3}$ were not employed as the hydrolysis of CAT yielded white turbidity. The rate of the reaction decreases with increasing concentration of hydrogen-ions and finally tends towards a limiting value at higher concentrations of the latter. A plot of rate against $[H^+]^{-1}$ concentration from eqn (3) yielded a straight line with non-zero intercept.

$$-\frac{d[CAT]}{dt} = \left\{ a + \frac{b}{[H^+]} \right\} [HCO_2H]_t[CAT]_t \qquad (3)$$

where 'a' and 'b' are constants.

Effect of Chloride Ions -

The concentration of chloride ions was varied from 0.05 to 0.4 mol $dm^{-3}$ at I = 2.0 mol $dm^{-3}$ and also at three hydrogen ions fixing the concentrations of CAT and formic acid. The rate of the reaction initially increases with increasing concentration of chloride ions and finally tends towards a limiting value. Results are given in Table-2.

Effect of p-toluenesulphonamide -

The concentration of p-toluenesulphonamide was varied from $1.0\times10^{-3}$ to $4.0\times10^{-3}$ mol $dm^{-3}$ at fixed concentrations of $[CAT] = 1.8\times10^{-3}$ mol $dm^{-3}$; $[HCO_2H] = 0.05$ mol $dm^{-3}$ and I = 2.0 mol $dm^{-3}$. The rate is insignificantly affected at lower concentrations of the p-toluenesulphonamide ($<0.002$ mol $dm^{-3}$). However, higher concentrations of the amide bring pronounced retarding effect on the rate. This necessitated the selection of the experimental conditions in the reaction in such a way that the concentration of the amide may not affect the rate of the reaction.

Discussion -

Different forms of CAT are known to be present in acidic and alkaline solutions[10-14]. However, RNHCl had been considered to be the predominant and reactive species of CAT in view of the known equilibrium constants and equilibria[11] governing the CAT species in acid medium. The chloride ion catalysis observed in the reaction eliminated the possibility of $RNCl^-$ to be the reactive species of CAT only on the premise that $Cl^-$ ion catalysis was not observed in alkaline medium. $RNCl^-$ is reported to be the predominant and reactive species of CAT in alkaline medium[8]. Further, first order dependence with respect to CAT eliminates the reactivity of $RNCl_2$. Had the CAT species RNHCl disproportionated, the order with respect to the former would have been found to be two.

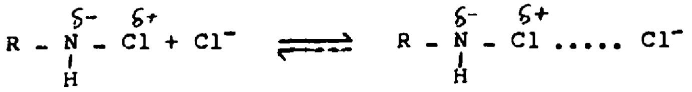
The hydrogen-ion concentration employed in the reaction indicates that CAT almost completely is in the form of RNHCl and as such hydrogen ion dependence does not appear to be related to CAT species. Thus, the term inverse in hydrogen-ion concentration in the rate law (3) in all probability comes from the pre-equilibrium (4).

$$HCO_2H \rightleftharpoons HCO_2^- + H^+ \qquad (4)$$

Moreover, the molecular form appears to be less reactive than formate ion in spite of the fact that the concentration of the formate anion is significantly less than that of the former in view of the hydrogen ion concentration employed in the reaction. However, such an observation does not appear unique in view of the kinetic observations reported for the oxidation of formic acid with permanganate ion[1] in acid medium. It had been reported in this referred reaction[1] that the molecular form, in spite of being present predominantly in solution, the contribution of the path involving the former is negligible to to that of the formate anion.

So far as $Cl^-$ ion catalysis is concerned, the probability of catalyst redox cycle $Cl_2/Cl^-$ does not appear feasible in view of the fact that the order with respect to each reactant is one. Further, the oxidation of formic acid[15,16] with $Cl_2$ to $CO_2$ in aqueous acidic solution is reported to be rapid. Since the rate of the reaction is not independent of formic acid and hence the possibility of the referred redox cycle of the catalyst is eliminated.

Thus the role of the $Cl^-$ ions as catalyst is to modify the reactive species of chloramine-T and this is achieved through the complexation of RNHCl and $Cl^-$ ions. The possibility of such a complex is strengthened due to the electrophilicity of $\rangle$N-Cl group of CAT and the formation constant of such a complex depends upon the electrophilic nature of this group. So far as the structure of such a complex is concerned, it can be depicted tentatively as in eqn (5).



$$R - \underset{\substack{| \\ H}}{\overset{\delta-}{N}} - \overset{\delta+}{Cl} + Cl^- \rightleftharpoons R - \underset{\substack{| \\ H}}{\overset{\delta-}{N}} - \overset{\delta+}{Cl} \,.....\, Cl^- \qquad (5)$$

This is not unique in the sense that such a complex has also been assumed in other reactions of chloramine-T[17-19]. The catalysis of $Cl^-$ ions is similar to that observed in the Orten rearrangement[20] of organic haloamides which consists of the migration of chlorine from the side chain and chloride ions. The complex formed in such a process could release elemental chlorine in a slow step or may directly react with the substrate.

Thus, the $RNHCl_2^-$, being the reactive species of CAT in presence of $Cl^-$ ions, reacts independently with molecular and ionic forms of formic acid bringing inverse hydrogen-ion term in the rate law. Considering all these facts and experimental observations, a probable reaction mechanism comprising steps (6) to (9) can be suggested as follows :

$$HCO_2H \overset{K}{\rightleftharpoons} HCO_2^- + H^+ \tag{6}$$

$$RNHCl + Cl^- \overset{K_1}{\rightleftharpoons} RNHCl_2^- \tag{7}$$

$$RNHCl_2^- + HCO_2H \xrightarrow{k_1} RNH_2 + CO_2 + H^+ + 2Cl^- \tag{8}$$

$$RNHCl_2^- + HCO_2^- \xrightarrow{k_2} RNH_2 + CO_2 + 2Cl^- \tag{9}$$

Rate law (10) or (11) obeys if eqns (8) and (9) are considered to be the rate determining steps.

$$-\frac{d[CAT]}{dt} = \left\{k_1 + \frac{k_2K}{[H^+]}\right\}\left\{\frac{K_1\,[Cl^-]}{1+K_1[Cl^-]}\right\}[CAT]_T[HCO_2H]_T \tag{10}$$

$$\text{or} \quad k' = \left\{k_1 + \frac{k_2K}{[H^+]}\right\}\left\{\frac{K_1[Cl^-]}{1+K_1[Cl^-]}\right\} \tag{11}$$

where k' is the observed second order rate constant,

A plot of $[k']^{-1}$ versus $[Cl^-]^{-1}$ from eqn (11) at constant hydrogen-ion concentration, was constructed and a straight line with non-zero intercept, was obtained. (Fig. 1). The value of '$K_1$' was calculated to be 3.1, 3.20 and 3.35 $dm^3 mol^{-1}$ at three $[H^+]$ ions viz. 0.05, 0.1 and 0.15 mol $dm^{-3}$ respectively at I = 2.0 mol $dm^{-3}$ and $60^\circ$. These values are almost of similar magnitude and also independent[17-19] of hydrogen-ion concentration. However, if temperature and ionic strength are taken into account the value of '$K_1$' obtained in the reference reaction appears to be closer to that reported[18] earlier. Further, it is also true that the ratio of $K_1$ ($CAT$-$Cl^-$)/$K_1$($CAB$-$Cl^-$), (CAB is chloramine T)[21] is less than one, if the Hammett reaction constant $\sigma$- values for 'H' and '$CH_3$' are any guide.

Further, the intercepts obtained from the figure (1), at different hydrogen ion concentrations according to rate law (11) can also be given by the relationship (12)

$$[\text{Intercept}]^{-1} = \left\{ k_1 + \frac{k_2K}{[H^+]} \right\} \qquad (12)$$

However, a plot of $[\text{intercept}]^{-1}$ versus $[H^+]^{-1}$ from equation (12) was further constructed and a straight line with non-zero intercept was obtained (Fig. 2). '$k_1$' and '$k_2K$' were calculated from the intercept and gradient of the Fig. 2 to be $2.7\times10^{-3}$ $dm^3mol^{-1}sec^{-1}$ and $3.7\times10^{-4}$ $dm^6$ $mol^{-2}sec^{-1}$ respectively at I = 2.0 mol $dm^{-3}$ and 60°. Thus on the basis of the magnitudes of '$k_1$' & '$k_2$' ($K^{22} = 5.4\times10^{-4}$ at 30°), one can argue that the path ($RNHCl_2^-$ + $HCO_2^-$) predominantly overtakes the path ($RNHCl_2^-$ + $HCO_2H$) in spite of the fact that such a conclusion appears against the electrostatic considerations. However, it is not a unique proposition in view of the fact that the similar pattern of reactivity had been reported in the reaction of $MnO_4^-$ and $HCO_2H$ where most of the reaction events are governed by the path involving $MnO_4^-$ & $HCO_2^-$ species. Further, the reaction[15,16] of formic acid with $Cl_2$ also subscribes the similar reactivity pattern with the formate ion being $\sim 10^4$ times more reactive than the molecular form of the acid.

The oxidation of formic acid with CAT in presence of $Cl^-$ ions probably takes place either via H-atom transfer or hydride ion transfer. However, it is difficult to distinguish between the two possibilities merely on the basis of kinetic results in spite of the observations that the oxidation of α-hydroxy-acids[23] and glucose[24] with CAT are reported to favour hydride ion transfer. There appears to be a remote possibility for hydride ion transfer in view of the absence of any driving force available with the complex ion to react with the substrate It is probably the slow reactivity of this complex through the release of elemental chlorine or it reacts with the substrate in a slow step yielding the end products of the reaction.

$$^-O - \overset{\overset{O}{\|}}{C} - H + RNHCl_2^- \longrightarrow RNH_2 + CO_2 + 2\,Cl^-$$

The relatively higher energy of σ- (C-H) for $HCO_2^-$ [25,26] is also, expected to promote the electronic interaction between σ-(C-H) and chloramine-T.

## Table 1

Pseudo-first order rate constants (k) and second order rate constants(k') for different concentrations of Chloramine-T and formic acid at $[H^+] = 0.1$ mol dm$^{-3}$, $[Cl^-] = 0.1$ mol dm$^{-3}$ and 60°C in the reaction of Chloramine-T and formic acid in solution.

| $10^2$[HCOONa] | $10^3$[CAT] | $10^8$(ir) | $10^5$k/ | $10^3$k'/dm$^3$mol$^{-1}$sec$^{-1}$ |
|---|---|---|---|---|
| mol dm$^{-3}$ | | dm$^3$mol$^{-1}$sec$^{-1}$ | sec$^{-1}$ | |
| 0.50 | 1.75 | 1.75 | - | (2.0) |
| 0.60 | 1.75 | 2.10 | - | (2.0) |
| 0.70 | 1.75 | 2.40 | - | (1.96) |
| 0.80 | 1.75 | 2.85 | - | (2.04) |
| 1.0 | 1.75 | 3.60 | - | (2.06) |
| 1.5 | 1.75 | 5.10 | - | (1.94) |
| 2.5 | 1.75 | 8.50 | 5.1 | 1.94(2.04)* |
| 3.0 | 1.75 | - | 5.65 | 1.88 |
| 3.5 | 1.75 | - | 6.65 | 1.90 |
| 4.0 | 1.75 | - | 7.70 | 1.93 |
| 4.5 | 1.75 | - | 8.45 | 1.88 |
| 3.0 | 2.25 | - | 5.40 | 1.80 |
| 3.5 | 2.25 | - | 6.25 | 1.79 |
| 4.0 | 2.25 | - | 7.16 | 1.79 |
| 4.5 | 2.25 | - | 8.15 | 1.80 |
| 5.0 | 2.25 | - | 8.75 | 1.75 |
| 6.0 | 2.25 | - | 10.50 | 1.75 |
| 2.0 | 1.35 | - | 3.83 | 1.92 |
| 2.5 | 1.35 | - | 4.79 | 1.92 |
| 3.0 | 1.35 | - | 5.75 | 1.92 |
| 3.5 | 1.35 | - | 6.71 | 1.92 |
| 4.0 | 1.35 | - | 7.20 | 1.80 |
| 4.5 | 1.35 | - | 8.10 | 1.80 |
| 5.0 | 1.35 | - | 8.75 | 1.75 |
| 6.0 | 1.35 | - | 10.80 | 1.80 |
| 5.0 | 0.85 | 8.1 | 9.0 | 1.80(1.91) |
| 5.0 | 1.27 | 12.0 | 9.0 | 1.80(1.89) |
| 5.0 | 1.70 | 15.5 | 9.0 | 1.80(1.82) |
| 5.0 | 2.12 | 18.5 | 9.0 | 1.80(1.75) |
| 5.0 | 2.50 | 22.0 | 9.0 | 1.80(1.76) |
| 5.0 | 2.90 | 25.50 | 9.0 | 1.80(1.76) |
| 2.0 | 1.30 | 5.26 | 3.83 | 1.92(2.02) |
| 2.0 | 1.70 | 7.0 | 3.83 | 1.92(2.05) |
| 2.0 | 2.50 | 8.98 | 3.83 | 1.92(1.80) |
| 2.0 | 2.90 | 11.5 | 3.83 | 1.92(1.98) |
| | | | | av. (1.87 ± 0.1) |

* Values given in parenthesis were derived from initial rates (ir).

Table 2

Second order rate constants for the variation of chloride ion.
$10^3$[CAT]= 1.75 mol dm$^{-3}$; $10^2$[HCOONa]= 5.0 mol dm$^{-3}$, 60°C.

| [$H^+$] mol dm$^{-3}$ | [$Cl^-$] mol dm$^{-3}$ | $10^3$k' dm$^3$mol$^{-1}$sec$^{-1}$ |
|---|---|---|
| 0.05 | 0.15 | 2.9 |
| | 0.20 | 3.5 |
| | 0.25 | 4.1 |
| | 0.30 | 4.4 |
| | 0.40 | 4.9 |
| 0.1 | 0.07 | 1.3 |
| | 0.09 | 1.5 |
| | 0.15 | 2.1 |
| | 0.20 | 2.5 |
| | 0.25 | 2.9 |
| | 0.30 | 3.2 |
| | 0.35 | 3.4 |
| | 0.40 | 3.8 |
| 0.15 | 0.07 | 1.1 |
| | 0.09 | 1.3 |
| | 0.15 | 1.7 |
| | 0.20 | 2.2 |
| | 0.30 | 2.7 |
| | 0.35 | 2.9 |
| | 0.40 | 3.3 |

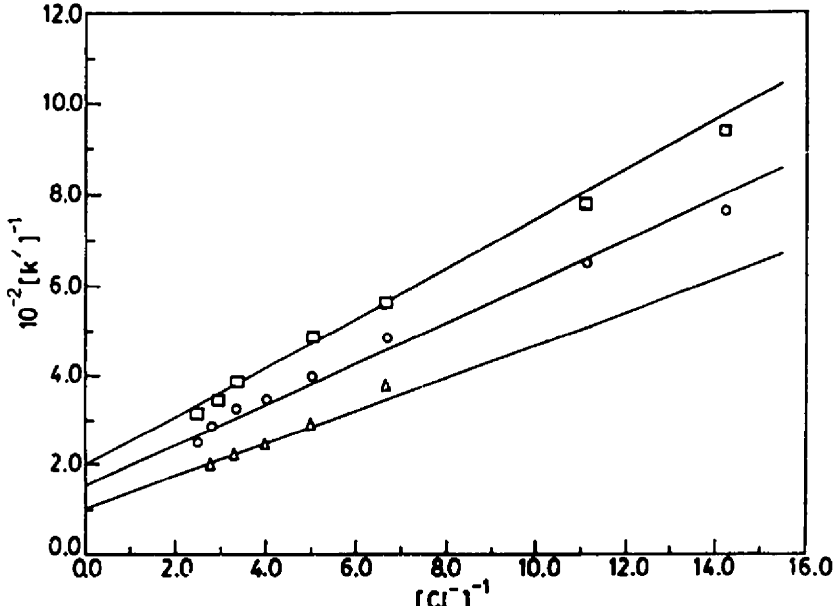


Fig.1. Plot of $(k\ )^{-1}$ vs $[Cl^-]^{-1}$ at different $[H^+]$ at 60 °C.
$[CAT] = 1.75 \times 10^{-3}$ mol $dm^{-3}$ and $[HCOONa] = 5.0 \times 10^{-2}$ mol $dm^{-3}$
$[H^+] = 0.05$ (▲), 0.10 (○) and 0.15 (□) mol $dm^{-3}$.

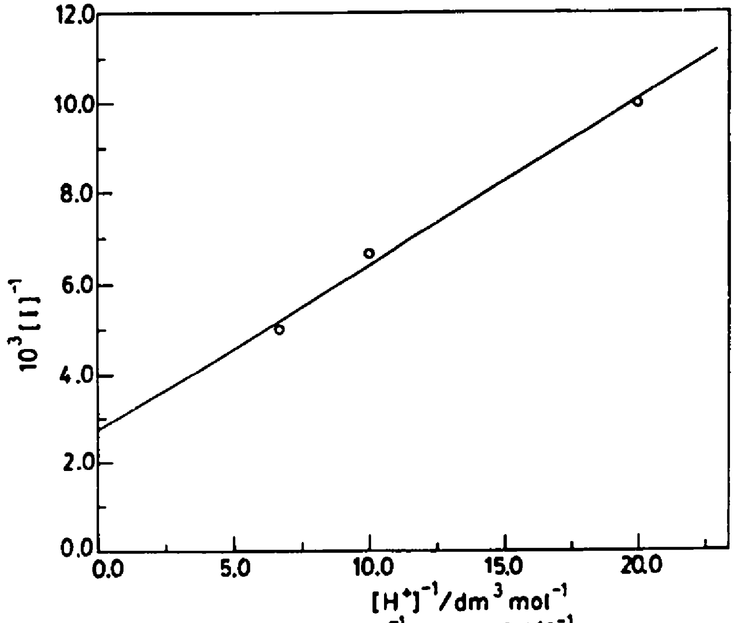


Fig. 2. Plot of $[\text{Intercept}]^{-1}$ versus $[H^+]^{-1}$
[From Fig - (1)]

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