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Research Article

KINETICS OF MECHANISM OF OXIDATION OF DIACETYL BY VARIETY OF N-HALO COMPOUNDS LIKE TRICHLORO ISOCYANURIC ACID (TCICA), DICHLORO DIMETHYL HYDANTOIN (DCDMH) AND CHLORAMINE-T(CAT) – A COMPARATIVE STUDY

LMV. Subba Rao Tanguturu[1]*, B. Syama Sundar[2] and PS. Radhakrishna Murti[3]

[1]Department of Chemistry, S & H, VVIT, Nambur,
Guntur, Andhra Pradesh, India.
[2]Yogi Vemana University, Acharya Ngarjuna University,
Guntur, Andhra Pradesh, India.
[3]Department of Chemistry, T.J.P.S College (P.G Courses),
Guntur, Andhra Pradesh, India.

ABSTRACT

Kinetics and oxidation of diacetyl have been studied in aqueous acetic acid, perchloric acid mixtures by a variety of N-halo compounds like Trichloro isocyanuric acid (TCICA), Dichloro dimethyl Hydantoin (DCDMH) and Chloramine-T (CAT). With a view to comparing their kinetic orders, relative oxidizing capacities and to throw light on the mechanistic pathways involved in these processes, the experiments were conducted under similar conditions. Reaction kinetics exhibits first order dependence in [TCICA] / [DCDMH], [Diacetyl] and [H^+]. The rate increases with decreasing dielectric constant of the medium. With chloramines-T the kinetic orders are first order in [CAT], first order in [Substrate] and first order in [H^+] at higher [H^+] and independent at lower [H^+]. The derived Arrhenius parameters at 313K are found to be of right order of magnitude for these reactions. In all these cases the product was found to be acetic acid exclusively. The order of oxidizing capacity is found to be TCICA > DCDMH > CAT. A suitable rate law and mechanism consistent with the kinetic data is proposed.

Keywords: Kinetics, oxidation, trichloro isocyanuric acid(TCICA) and Chloramine-T (CAT).

INTRODUCTION

Oxidation of α-diketones by a variety of oxidizing agents like periodate, Ce(IV), V(V), Mn(VII), H2O2 etc is well documented1-15. There is no systematic investigation to establish the kinetics of oxidation of diacetyl by N-halo compounds. Hence it was thought worthwhile to find out the differential effect between Trichloro isocyanuric acid (TCICA), Dichloro dimethyl Hydantoin (DCDMH) which have ring substituted chlorines and Chloramine-T (CAT) which has halogen attached to nitrogen outside the ring system.

EXPERIMENTAL

All the reagents were of analytical reagent grade.

KINETIC METHOD

Estimation of N-halo derivatives like TCICA, DCDMH and CAT

The solution of TCICA / DCDMH / CAT and aliquots from reaction mixture are well estimated iodometrically. 5.0ml of TCICA / DCDMH / CAT is dumped into an iodine flask containing 5.0ml of 4N sulphuric acid and 5.0ml of 4% potassium iodide solution and kept in dark for 3 minutes. Then the solution is titrated against standard thiosulphate taken in a burette. The end point is indicated by the disappearance of the starch – iodine blue colour.

RESULTS AND DISCUSSION

In the present investigation kinetics of oxidation of diacetyl by variety of N-halo derivatives like TCICA, DCDMH and CAT in aqueous acetic acid perchloric acid mixtures at 40^0C were reported here. The relevant kinetic data are given below

Kinetics of oxidation of diacetyl by TCICA, DCDMH and CAT

The kinetic orders were found to be similar in all these N-halo derivatives.

Effect of oxidant

The reaction has been found to be first order in TCICA, DCDMH and CAT. A plot of log(a-x) Vs time is linear. The first order nature is also confirmed by the constancy of the first order rate constants obtained at different concentrations of the oxidant.

Effect of Substrate

Variation of [substrate] indicted that the reaction is first order in substrate in all these three cases. A plot of log k Vs log[S] is linear with unit slope confirming first order dependence on substrate (Tables I & II).

Effect of varying [H^+] on reaction rate

The reaction has been found to be first order on [H^+] in the range between 0.058M – 0.464M. A plot of log k Vs log [H^+] has unit slope confirming the first order dependence on [H^+]. At high [H^+] (0.464M – 1.392M) the reaction is independent on [H^+] in case of TCICA and DCDMH. But in the case of CAT the reaction was found to be independent in lower [H^+] (0.116M – 0.696M) at higher [H^+] (1.16M – 2.0M) the reaction is first order on [H^+]. The relevant kinetic data are given in Tables I & II.

Effect of variation of solvent

Increase in the percentage of acetic acid resulted in the decrease of rate in all the cases TCICA, DCDMH and CAT. The plots of log k Vs 1/D is linear.

Effect of temperature

The reaction kinetics have been studied at various temperatures in the range of 30^0C to 60^0C under similar experimental conditions to evaluate the Arrhenius parameters. The first order rate constants were calculated and presented in Tables I & II. The reaction rate increase with increase of temperature and the plot of log k Vs 1/T is linear.

Oxidant	E_a kJmol^{-1}	$\Delta H^\#$ kJmol^{-1}	$\Delta S^\#$ JK^{-1}mol^{-1}	$\log_{10}$pz	$\Delta G^\#$ kJmol^{-1}
TCICA	64.03	61.26	111.82	7.43	98.50
DCDMH	71.71	68.61	98.40	8.35	100.12
CAT	85.05	82.28	61.19	10.08	102.66

In the present investigation it is fascinating to observe that the activation energy is lower for oxidation of diacetyl with TCICA followed by DCDMH and CAT with higher energies of activation. Similarly enthalpy of activation is lowest for TCICA. This makes it clear that faster reactions with TCICA has lower activation energy. Similar trends are observed for other thermodynamic parameters like entropy of activation and probability factor. These parameters are in consonance with the general principles of Arrhenius theory of activation. The derived Arrhenius parameters at + 313K are found to be right order of magnitude for these reactions.

CONCLUSION

Comparison of oxidizing capacities of TCICA, DCDMH and CAT in these reactions

[Diacetyl] = 0.01M	Temperature = 40^{0}C
[Oxidant] = 0.0005M	[Solvent] = AcOH : H_2O = 50% : 50%
[$HClO_4$] = 0.116M	

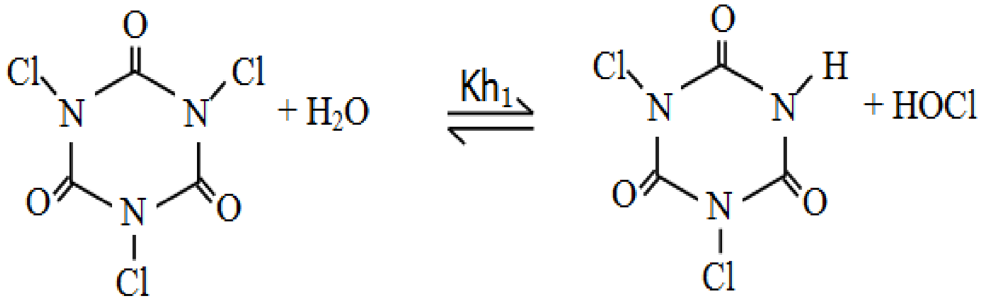
Oxidant	k x 10^4 sec^{-1}
TCICA	8.9918
DCDMH	1.1239
CAT	0.3719

Nature of oxidising species and order of reactivity

Data in above table indicates the order of reactivity of oxidant used in these reactions i.e., TCICA > DCDMH > CAT. The difference in these N-halo compounds is mainly due to difference in their first step hydrolysis. The higher reactivity of TCICA is mainly due to first step hydrolysis in these species very faster in comparison with DCDMH. The important steps connected with various reactant species in the present reaction are shown in the following scheme.

Nature of 1,3,5-trichloro-1,3,5-triazine-2,4,6-trione or Trichloro isocyanuric acid (TCICA)

The important steps connected with the various reactant species in the present reaction are shown in the following scheme.



TCICA DCICA ($Kh_1 = 3.0 \text{ x } 10^{-4}M$)

$$DCICA + H_2O \xrightleftharpoons{Kh_2} MCICA + HOCl \qquad (Kh_2 = 1.9 \text{ x } 10^{-4}M)$$

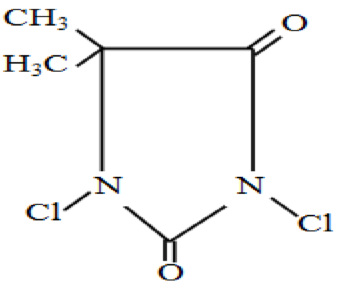
$$MCICA + H_2O \xrightleftharpoons{Kh_3} ICA + HOCl \qquad (Kh_3 = 73M)$$

$$HOCl + H^+ \rightleftharpoons H_2OCl^+$$

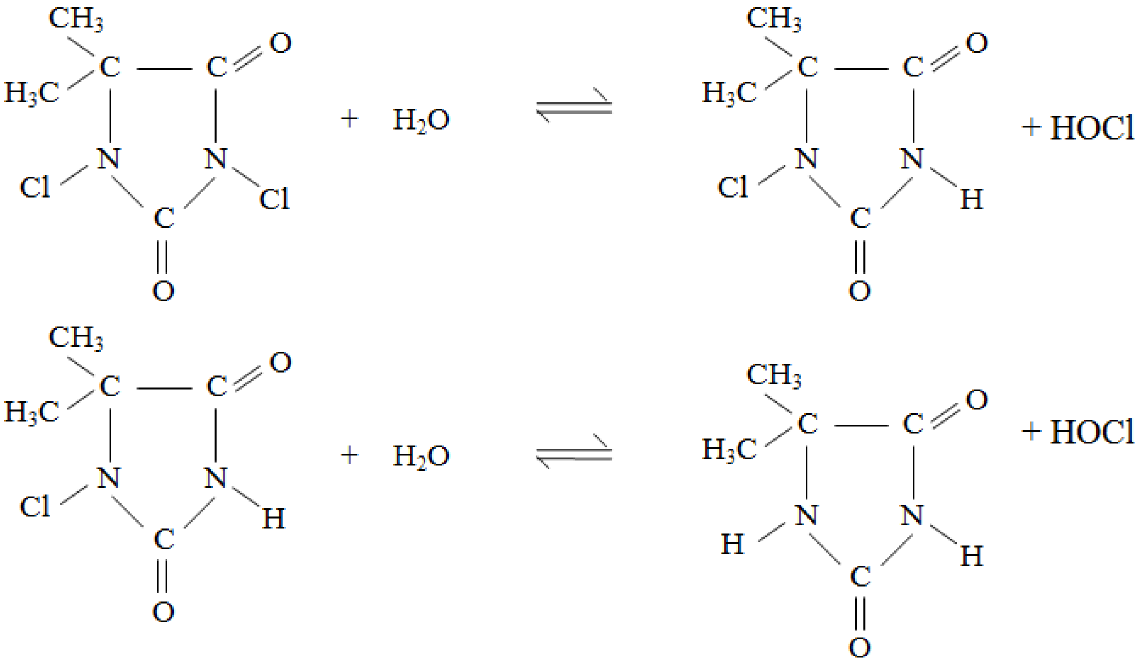
The magnitudes at 25^{0}C of relevant equilibria shown in the above scheme, suggest that the concentration of MCICA and ICA would be negligible in acid medium as (Kh_1, Kh_2, Kh_3) and (Kh_1,Kh_2) are negligible in comparison with Kh_3.

Nature of 1,3-dichloro-5,5-dimethyl hydantoin (DCDMH)

Dichloro dimethyl hydantoin has the following configuration. This is also referred to as 1,3-dichloro-5,5-dimethyl hydantoin (DCDMH).



On hydrolysis it yields the monochloro dimethyl hydantoin and finally dimethyl hydantoin. In aqueous solution the following equilibrium exists.



The extent of each of HOCl, Cl^+ would be negligible in predominantly in the employment of aqueous acid solutions. If it is assumed that the TCICA / DCDMH species itself has a negligible contribution towards the overall reaction rate as a first approximation, it is safe to conclude that the effective reactive species is H_2OCl^+.

Nature of chloramine-T (CAT)

$$R - N\,(Na)\,Cl \longrightarrow R - N^{-}\,Cl + Na^{+} \qquad R = H_3C - C_6H_4SO_2 -$$

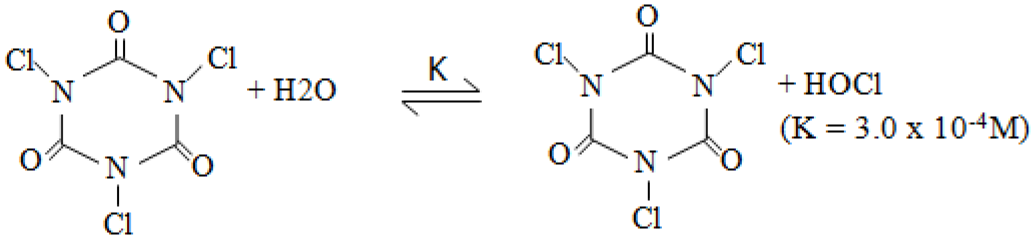
$$R - N^{-}Cl + H^{+} \overset{K}{\rightleftharpoons} RNHCl$$

The lower reactivity in chloramine-T is mainly due to the formation of very mild oxidant RNHCl.

Rate law and mechanism

The corresponding rate law and mechanism are discussed below

Kinetics of oxidation of diacetyl by TCTCA and DCDMH

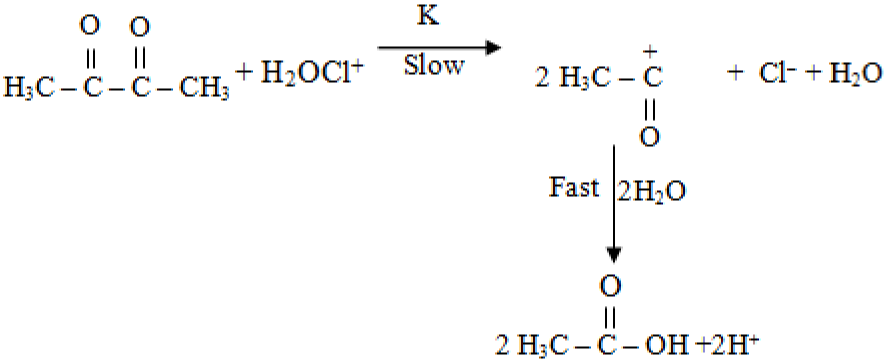


$$DCICA + H_2O \overset{K_1}{\rightleftharpoons} MCICA + HOCl \qquad (K_1 = 1.9 \times 10^{-4}M)$$

$$MCICA + H_2O \overset{K_2}{\rightleftharpoons} ICA + HOCl \qquad (K_2 = 73M)$$

$$HOCl + H^{+} \overset{K_3}{\rightleftharpoons} H_2OCl^{+}$$

Note: The reactive species in both the cases i.e., TCICA and DCDMH is H_2OCl^+



$$H_3C-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3 + H_2OCl^{+} \xrightarrow[\text{Slow}]{K} 2\,H_3C-\underset{\underset{O}{\|}}{\overset{+}{C}} + Cl^{-} + H_2O$$

$$2\,H_3C-\underset{\underset{O}{\|}}{\overset{+}{C}} \xrightarrow[\text{Fast}]{2H_2O} 2\,H_3C-\overset{\overset{O}{\|}}{C}-OH + 2H^{+}$$

The process is by C – C cleavage leading to two acylium ions which lead to the formation of two moles of acetic acid.

Rate law

Rate $= k\,[S]\,[H_2OCl^{+}]$

$= k\,K_3\,[HOCl]\,[S]\,[H^{+}]$

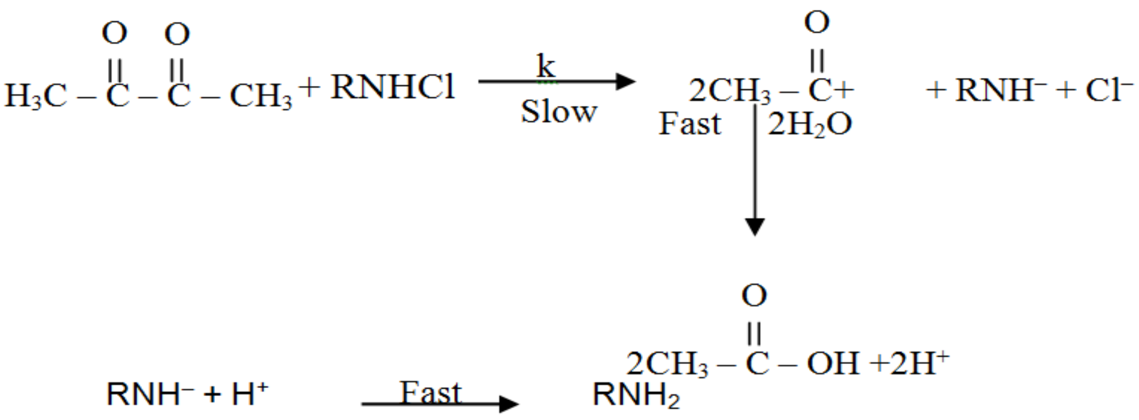
$= k\,K\,K_1\,K_2\,K_3\,[S]\,[TCICA]\,[H^{+}]$

The above rate equation explains all the experimental observations and as a result, supports the mechanism.

Kinetics of oxidation of diacetyl by CAT

$$R - N(Na)Cl \longrightarrow R - N^{-}Cl + Na^{+} \qquad R = H_3C - C_6H_4SO_2 -$$

$$R - N^{-}Cl + H^{+} \overset{K}{\rightleftharpoons} RNHCl$$



$$H_3C - \overset{O}{\overset{||}{C}} - \overset{O}{\overset{||}{C}} - CH_3 + RNHCl \xrightarrow[\text{Slow}]{k} 2CH_3 - \overset{O}{\overset{||}{C}}{}^{+} + RNH^{-} + Cl^{-}$$

$$2CH_3 - \overset{O}{\overset{||}{C}}{}^{+} \xrightarrow[\text{Fast}]{2H_2O} 2CH_3 - \overset{O}{\overset{||}{C}} - OH + 2H^{+}$$

$$RNH^{-} + H^{+} \xrightarrow{\text{Fast}} RNH_2$$

Rate law:

$$\text{Rate} = k\,[S]\,[RNHCl]$$
$$= k\,K\,[S]\,[CAT]\,[H^{+}]$$
$$= \frac{k\,K\,[S]\,[CAT]_T\,[H^{+}]}{1 + K[H^{+}]}$$

The rate law explains the observed kinetic orders - first order in oxidant, first order in substrate, independent in acidity at lower concentration of H^{+} and first order in H^{+} at higher concentration of H^{+}

Table 1: Kinetics of oxidation of diacetyl by TCICA and DCDMH

Variant	[Non variant] M	[Variant] M	TCICA k x 10^{4}sec^{-1}	DCDMH k x 10^{4}sec^{-1}
Oxidant	[Diacetyl] = 0.1 [$HClO_4$] = 0.116	0.0005 0.0010 0.0020	8.9918 8.8634 8.8491	1.1239 1.1125 1.0853
Diacetyl	[Oxidant] = 0.0005 [$HClO_4$] = 0.116	0.0025 0.0050 0.0100 0.0150	2.2754 4.5160 8.9918 13.6102	0.2809 0.5625 1.1239 1.6699
$HClO_4$	[Oxidant] = 0.0005 [Diacetyl] = 0.0025	0.058 0.116 0.232 0.464 0.696 1.392	1.1248 2.2754 4.3198 8.4184 8.3844 8.3721	0.1406 0.2809 0.5468 1.0378 1.0214 1.0203
Solvent	[Diacetyl] = 0.0025 [Oxidant] = 0.0005 [$HClO_4$] = 0.116	30% 50% 70%	4.2508 2.2754 1.0264	0.5303 0.2809 0.1257
Temperature	[Diacetyl] = 0.005 [Oxidant] = 0.0005 [$HClO_4$] = 0.116	30°C 40°C 50°C 60°C	2.3768 4.5160 9.9352 24.825	0.2964 0.5625 1.2737 3.1624

Solvent = AcOH : H_2O = 50% : 50% Temperature = 40°C

Table 2: Kinetics of oxidation of diacetyl by CAT

Variant	[Non variant] M	[Variant] M	CAT k x 10^4sec^{-1}
CAT	[Diacetyl] = 0.1 [$HClO_4$] = 0.116	0.00050 0.00075 0.00100	5.4545 5.3424 5.3109
Diacetyl	[CAT] = 0.0005 [$HClO_4$] = 1.16	0.010 0.025 0.050 0.100	0.6583 1.3966 2.6984 5.4545
Solvent	[CAT] = 0.0005 [Diacetyl] = 0.1 [$HClO_4$] = 1.16	30% 50% 70%	10.1478 5.4545 3.2058
Temperature	[Diacetyl] = 0.01 [CAT] = 0.0005 [$HClO_4$] = 1.16	30 40 50 60	0.2633 0.6583 1.8432 5.5178
$HClO_4$	[Diacetyl] = 0.01 [CAT] = 0.0005	0.116 0.232 0.464 0.696 1.160 1.500 2.000	0.3719 0.3924 0.3996 0.4132 0.6583 1.0516 1.4264

Solvent = AcOH : H_2O = 50% : 50% Temperature = 40^0C

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