© *Proc. Indian natn. Sci. Acad.*, **52**, A, No. 5, 1986, pp. 1205–1213.
Printed in India.

OXIDATION OF BENZHYDROL AND PARACHLOROBENZHYDROL BY N-BROMO ACETAMIDE AND TRICHLOROISOCYANURIC ACID IN ACID MEDIUM: A KINETIC STUDY

SUBAS C PATI, ASHOK KUMAR SAHU *and* Y SRIRAMULU

Department of Chemistry, Berhampur University, Berhampur 760 007, Orissa, India

(*Received 20 November 1984; After revision 28 April 1986*)

The kinetics of oxidation of benzhydrol and parachlorobenzhydrol has been studied in acetic acid-perchloric acid by trichloroisocyanuric acid (TCCA) and N-bromo acetamide (NBA). The reaction is found to be first order in substrate, zero order in oxidant and fractional order in [H^+] in the oxidation reactions with trichloroisocyanuric acid (TCCA). In the oxidation reactions with N-bromo acetamide the reaction is found to be first order in substrate, first order in oxidant and first order in [H^+]. The reaction rate is increased with increase in percentage of acetic acid in the case of NBA reactions whereas there is a marginal effect in TCCA reactions. The rate of oxidation is retarded by the addition of acetamide in the oxidation reactions by NBA. It is postulated that the reactive oxidising species is $[H_2OBr]^+$ in oxidation reactions by NBA. Suitable mechanisms are postulated taking all these observed data into consideration for both the oxidation reactions. The Arrhenius activation parameters have been evaluated for both the oxidation processes.

Key Words: Trichloroisocyanuric Acid; N-bromo Acetamide; Oxidation; Kinetics; Benzhydrol

INTRODUCTION

THE use of N-bromo acetamide (NBA) is very well established in synthetic organic chemistry as an oxidant. However, unlike N-bromo succinimide (NBS) and N-chloro succinimide (NCS) which have received much attention as important oxidants and halogenating agents,[1–3] N-bromo acetamide has not been used as an oxidant in many organic and inorganic reactions except a few reports appearing in literature regarding oxidation of hydroxy derivatives.[4]

A survey of literature reveals that no work has been reported on the kinetics of oxidation of organic substrates by trichloroisocyanuric acid (TCCA). To our knowledge this is the first kinetic report on the oxidation of organic molecules by TCCA. In this communication, we are reporting the kinetics of oxidation of benzhydrol and *p*-chlorobenzhydrol by TCCA in acid medium. For the purpose of comparison, the oxidation of benzhydrol and *p*-chlorobenzhydrol have been studied separately by NBA and TCCA to find the mechanistic pathways involved in the process.

Materials and Methods

Trichloroisocyanuric acid was of Fluka (AR) grade and the organic substrates used are of BDH (Analar) grade. Analar grade acetic acid was purified by standard methods and solutions were prepared in conductivity water.

The disappearance of NBA and TCCA has been estimated by the standard iodometric method and the estimations are reproducible within $\pm$ 2 per cent error. The oxidation of solvent is marginal and due corrections were applied while computing rate constants. The standard experiments have been conducted with acetic acid as solvent with 50 per cent composition in case of benzhydrol but due to difficulty in dissolution of parachlorobenzhydrol, 80 per cent of acetic acid has been used. The product in both the oxidations is corresponding benzophenone as identified by their 2 : 4-dinitrophenyl hydrazones.

Results and Discussion

The oxidation of benzhydrol and *p*-chlorobenzhydrol has been investigated by both NBA and TCCA in presence of perchloric acid in aqueous acetic acid medium.

Effect of Substrate Concentration

In the oxidation reactions of benzhydrol and parachlorobenzhydrol by NBA and TCCA, the effect of change of concentration of substrate on the reaction kinetics has been studied. It is found that dependence on substrate is unity in the concentration range studied in both the oxidation reactions; Table 1*a* 1*b*. Plots of log k_0 *vs* log [*S*] in case of TCCA reaction and log k_1*vs* log [*S*] in case of NBA reaction are linear with unit slope which confirms the first oder dependence on the substrate in both the cases.

Table I*a*

Substrate variation

[NBA] = 5.0×10^{-4}M, [H^+] = 1.0×10^{-2}M, Temp. = 35 °C.

Substrate	10^3[S] M	$10^3 \times k_1$ min^{-1}	% HOAc (V/V)
Benzhydrol	5.0	5.681	50
	10.0	10.317	50
	20.0	21.450	50
	40.0	46.310	50
Parachlorobenzhydrol	1.25	0.780	80
	2.50	1.561	80
	5.00	2.742	80
	10.0	6.136	80

TABLE Ib

Substrate variation

[TCCA] = 5.0×10^{-4}M, [H^+] = 1.0×10^{-2}M, Temp. = 35 °C.

Substrate	10^3[S] M	$10^6 \times k_0$ litre mole min^{-1}	% HOAc (*v/v*)
Benzhydrol	5.0	0.49	50
	10.0	1.00	50
	20.0	2.20	50
	40.0	4.40	50
Parachlorobenzhydrol	2.5	0.108	80
	5.0	0.214	80
	7.5	0.322	80
	10.0	0.430	80

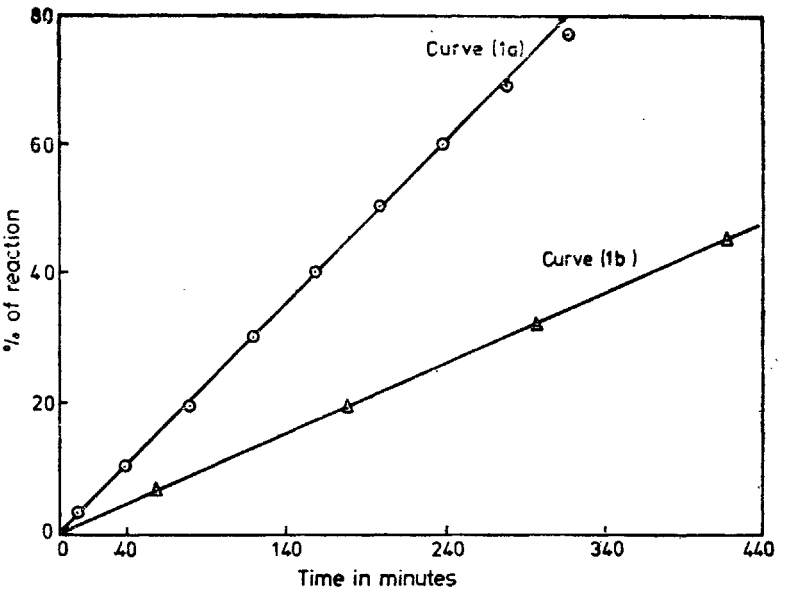

FIG 1. *a.* Benzhydrol *vs* TCCA
(% of reaction *vs* Time)
[s] =0.01 M, [O] =0.0005 M, [H^+] 0.01 M, HOAc =50% (v/v) and Temp. = 35 °C

b. p-Chlorobenzhydrol *vs* TCCA
(% of reaction *vs* Time)
[s] =0.01 M, [O] =0.0005 M, [H^+] =0.01 M, HOAc =80% (v/v) and Temp. = 35 °C

Effect of Varying Oxidant Concentration

The plots of concentration of TCCA consumed (x) versus time (t) are linear passes through origin, Fig. 1*a, b*. The ratio of x/t remains constant in a single

run (where x, the concentration of oxidant reacted after interval of time (t). In order to avoid the influence of oxidation products on the rate of the oxidation reaction, the rate constants have been computed from the initial part of the reaction. The rate constants k_0 at varying initial concentrations of TCCA are recorded in Table II*a*. The near constancy of k_0-values proves the zero order kinetics with respect to oxidant (TCCA).

In the oxidation reactions of NBA the first order rate constants are found to be fairly constant indicating the first order dependence with respect to oxidant. The first order rate constants are recorded in Table II*b*.

TABLE II*a*

Oxidant variation

[Substrate] = 10.0×10^{-3} M, Oxidant = TCCA
[H^+] = 1.0×10^{-2} M, Temp. = 35 °C

Substrate	10^4 [O] M	$10^6 \times k_0$ litre mole min^{-1}	% HOAc (*v*/*v*)
Benzhydrol	2.185	1.09	50
	4.393	1.00	50
	8.771	1.09	50
	18.510	1.20	50
Parachlorobenzhydrol	0.965	0.428	80
	1.957	0.418	80
	4.038	0.430	80
	8.070	0.445	80

TABLE II*b*

Oxidant variation

[Substrate] = 10×10^{-3}M Oxidant = NBA
[H^+] = 1.0×10^{-2}M, Temp. = 35 °C

Substrate	10^4[O] M	$10^2 \times k_1$ min^{-1}	% HOAc (*v*/*v*)
Benzhydrol	2.468	1.004	50
	5.000	1.031	50
	9.900	1.018	50
	19.62	0.976	50
Parachlorobenzhydrol	2.175	0.577	80
	4.800	0.713	80
	9.500	0.572	80
	19.600	0.601	80

Effect of Varying $HClO_4$ Concentration

In the oxidation reactions of NBA the rate of oxidation increases with increase in the concentration of H^+. The plot of log k_1 *vs* log [H^+] is linear with unit slope

indicating first order dependence with respect to $HClO_4$. This clearly indicates the reactive species in these oxidation reactions are protonated species of NBA. The first order rate constants are given in Table III*a*.

In the oxidation reactions of TCCA, the rate of oxidation is not increasing substantially with increase in the perchloric acid concentration. The plot of log k_0 *vs* log $[H^+]$ is linear with a slope less than unity indicating a fractional dependence with respect to $[H^+]$ (Table III*b*).

TABLE III*a*

Acid variation

[NBA] = 5.0 × 10^{-4}M, [Substrate] = 10.0 × 10^{-2}M, Temp. = 35 °C.

Substrate	10^2 [$HClO_4$] M	$10^3 \times k_1$ min^{-1}	% HOAc (*v*/*v*)
Benzhydrol	0.5	5.36	50
	1.0	10.31	50
	2.0	21.53	50
	4.0	39.15	50
Parachlorobenzhydrol	0.5	2.99	80
	1.0	6.13	80
	2.0	11.66	80
	4.0	23.04	80

TABLE III*b*

Acid variation

[TCCA] = 5.0 × 10^{-4}M, [Substrate] = 10.0 × 10^{-3}M, Temp. = 35 °C.

Substrate	10^2 [$HClO_4$]M	$10^6 \times k_0$ litre mole min^{-1}	% HOAc (*v*/*v*)
Benzhydrol	0.5	0.71	50
	1.0	1.00	50
	2.0	1.60	50
	4.0	2.42	50
	8.0	3.51	50
Parachlorobenzhydrol	1.0	0.43	80
	2.0	0.65	80
	4.0	1.16	80
	8.0	1.55	80

Effect of Solvent Composition

In order to determine the effect of solvent composition on the reaction rate, the reactions have been carried out at different compositions of aqueous acetic acid. The rate constants obtained are given in Table IV*a*, *b*. It is found that the increase in percentage of acetic acid, the rate of the reaction increases in the

oxidation reaction by NBA and in oxidation reactions by TCCA the effect of solvent is marginal and there is no substantial change in the rate of the reaction.

TABLE IV*a*

Effect of solvent composition

[Substrate] = 10.0×10^{-3}M [H$^+$] = 1.0×10^{-2}M
[NBA] = 5.0×10^{-4}M Temp. = 35 °C

Substrate	% HOAc (v/v)	$10^3 \times k_1$ min^{-1}
Benzhydrol	40	8.93
	50	10.31
	60	16.16
Parachlorobenzhydrol	80	6.11
	90	14.79

TABLE IV*b*

Effect of solvent composition

[Substrate] = 10.0×10^{-3}M [H$^+$] = 1.0×10^{-2}M
[TCCA] = 5.0×10^{-4}M Temp. = 35 °C

Substrate	% HOAc (v/v)	$10^6 \times k_0$ litre mole min^{-1}
Benzhydrol	50	1.00
	60	0.99
	80	0.84
Parachlorobenzhydro	80	0.43
	85	0.41
	90	0.38

Effect of Temperature on the Reaction Kinetics

The effect of temperature on the reaction rate has been studied at 35, 40 and 50 °C and respective rate constants are recorded in Table V*a*, *b*. The plots of log k_1 *vs* $1/T$ and log k_0 *vs* $1/T$ are linear. The various thermodynamic parameters calculated are given in Table VI*a* and *b*. The Arrhenius parameters indicate that both the enthalpy and entropy of activation are controlling the rate of the reaction.

Structural Effect

Parachlorobenzhydrol reacts slower than benzhydrol due to inherent overall electron withdrawing nature of the chloro substituent. This is also in consonance with the σ value of the parachloro substituent ($\sigma^+ = 0.226$).

TABLE V*a*

Effect of temperature

[NBA] = 5.0×10^{-4}M, [Substrate] = 10.0×10^{-3}M, [H$^+$] = 1.0×10^{-2}M

Substrate	Temp. °K	$10^3 \times k_1$ min^{-1}	% HOAc (v/v)
Benzhydrol	303	6.31	50
	308	10.31	50
	313	19.83	50
	318	36.79	50
Parachlorobenzhydrol	308	6.13	80
	313	11.79	80
	318	20.17	80
	323	33.92	80

TABLE V*b*

Effect of temperature

[TCCA] = 5.0×10^{-4}M, [Substrate] = 10.0×10^{-3}M, [H$^+$] = 1.0×10^{-2}M

Substrate	Temp. °K	$10^6 \times k_0$ litre mole min^{-1}	% HOAc (v/v)
Benzhydrol	308	1.00	50
	313	1.32	50
	318	2.05	50
	323	2.67	50
Parachlorobenzhydrol	308	0.43	80
	313	0.48	80
	318	0.64	80
	323	0.80	80

TABLE VI*a*

Arrhenius activation parameters

Substrate versus NBA	$\Delta E^{\neq}$ k.J/mole	$\Delta H^{\neq}$ k.J/mole	$\log_{10} A$	$\Delta S^{\neq}$ J.K^{-1} mole^{-1}
Benzhydrol	85.1	82.5	12.6	−11.0
Parachlorobenzhydrol	86.0	88.4	12.5	−12.3

TABLE VI*b*

Arrhenius activation parameters

Substrate versus TCCA	$\Delta E^{\neq}$ k.J/mole	$\Delta H^{\neq}$ k.J/mole	$\log_{10} A$	$\Delta S^{\neq}$ J.K^{-1}/mole^{-1}
Benzhydrol	57.4	54.8	3.9	−165.5
Parachlorobenzhydrol	54.7	52.1	3.1	−193.6

Mechanism

NBA Reactions—The retardation in the rate of the reaction with added acetamide from 6.136×10^{-3} min^{-1} to 2.55×10^{-3} min^{-1} with benzhydrol and from 1.03×10^{-2} min^{-1} to 2.905×10^{-3} min^{-1} with parachlorobenzhydrol in the oxidation reaction by NBA suggests that the pre-equilibrium step involves a process in which acetamide is one of the products.

The reaction has also been studied in presence and absence of mercuric acetate and there is no change in the rate of reaction.

The linear increase in the rate of the oxidation with acid indicates the protonation of HOBr to give H_2OBr^+ which is a stronger electrophile and oxidant. The plot of log k_1 versus $1/D$ is linear with the positive slope indicating an ion-dipole reaction according to Amis.[5] This is in accordance with the suggestion that $(H_2OBr)^+$ is the active oxidising species.

The mechanism of oxidation of benzhydrol and parachlorobenzhydrol by NBA has to be through the formation of an ester as the absence of primary kinetic isotopic effect rules out a rate determining C-H bond fission. Hence, the sequence is as follows:

$$CH_3CONHBr + H_2O \rightleftharpoons CH_3CONH_2 + HOBr$$

$$HOBr + H^+ \rightleftharpoons H_2OBr^+$$

$$R{-}\underset{\displaystyle OH}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}{-}R' + H_2OBr^+ \xrightarrow{\text{slow}} RR'CH{-}O{-}Br + H_3{}^+O$$

$$R{-}\underset{\displaystyle CBr}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}{-}R' \xrightarrow{\text{fast}} R{-}CO{-}R' + H^+ + Br^-$$

TCCA Reactions—The oxidation of benzhydrol by TCCA is similarly routed through the same pathway except that the formation and the decomposition of the ester take place in fast steps as there is no kinetic dependence on (TCCA). Hence, the sequences are as follows :

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!CHOH + H^+ \overset{\text{slow}}{\rightleftharpoons} \begin{matrix} R \\ R' \end{matrix}\!\!>\!CHOH_2^+$$

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!CHOH_2^+ + TCCA \xrightarrow{\text{fast}} \text{Products}$$

It may appear that the rate-determining conjugate acid formation of alcohols is a little farfetched at the outset but it is quite reasonable if we compare the pK_a values of conjugate acids of methanol and acetone which are of the order -2.2

and -1.58 respectively.[6,7] This indicates that protonation of a conjugated system like benzhydrol is quite likely like the enols.

Alternatively, to explain the zero order dependence on TCCA one could think of complexation between TCCA and alcohol in a equilibrium step followed by rate determining decomposition of complex into products. It is quite possible that observed zero order may be only a limiting case in the concentration range studied. This fact along with the rate law is also mentioned as an alternative possibility.

$$[\text{Substrate}]_{\text{Total}} = [\text{Substrate}] + \text{Complex}$$

$$[\text{Substrate}] + [\text{H}^+] + [\text{TCCA}] \rightleftharpoons \text{Complex}$$

$$[S] = \frac{[S]^T}{1 + K[\text{TCCA}][\text{H}^+]}$$

$$\text{Complex} \xrightarrow{\text{R.D.S.}} \text{Products}$$

$$\text{Rate} = k[\text{Complex}]$$

$$= kK[\text{TCCA}][S][\text{H}^+]$$

$$= \frac{kK[\text{TCCA}][S]_T[\text{H}^+]}{1 + K[\text{TCCA}][\text{H}^+]}$$

The above rate law reasonably explains the observed fractional order on H^+, first order on substrate and zero order on oxidant.

Acknowledgement

Thanks are due to Professor P S Radhakrishnamurti, Professor and Chairman, Department of Chemistry, Berhampur University, for his keen interest throughout the work. One of us (AKS) thanks the UGC, New Delhi for a fellowship.

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