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Effect of Transition Metal Ions on the Oxidation of Benzaldehyde by Bromine

A. DAYALAN* and S. MARTIN
Department of Chemistry, Autonomous Loyola College, Chennai-600 034, India
E-mail: dayalansgp@gmail.com

The kinetics of transition metal ion catalyzed oxidation of benzaldehyde by bromine in aqueous acetic acid was studied iodimetrically. The reactions were monitored at different conditions such as change in concentration of bromine, benzaldehyde, solvent composition (acetic acid-water), ionic strength and temperature. Kinetic parameters such as specific reaction rate, energy of activation, enthalpy of activation, entropy of activation and free energy of activation were evaluated. Typical values observed are: $k_{obs} = 1.16 \times 10^{-4}$ s^{-1}, $\Delta E^{\#} = 78.05$ $kJmol^{-1}$, $\Delta H^{\#} = 75.43$ kJ mol^{-1}, $\Delta S^{\#} = -71.14$ J K^{-1} mol^{-1} and lnA = 21.96 for the uncatalysed reaction. Transition metal ions were found to act as mild catalyst and the catalytic activity of the ions studied was found to be in the order: $Fe^{3+} > Co^{2+} > Mn^{2+} > Ni^{2+} > Zn^{2+}$.

Key Words: Transition metals, Benzaldehyde, Oxidation, Bromine.

INTRODUCMTION

Several aldehydes have been used as substrate for redox studies. Kinetics of oxidation of acetaldehyde by potassium permanganate in acid medium was found[1] to be first-order with respect to acetaldehyde as well as permanganate .The oxidation of acetaldehyde by chromic acid in perchloric acid medium was reported[2] to obey rate law : Rate = $k[CH_3CHO][HCrO_4^-][H^+]$. Kinetics of base catalyzed oxidation of benzaldehyde by aqueous $KMnO_4$ was observed[3] to be first-order each in substrate and the oxidant. Ruthenium(III) catalyzed oxidation of substituted benzaldehydes by sodium metaperiodate in alkaline medium showed first-order dependence each in RC_6H_4CHO [R=H, *p*-Cl, Me, *p*-Br, $-NO_2$, -OMe] and a zero-order dependence with respect to oxidant[4-6]. Similarly, the kinetics of osmium(VIII) catalyzed oxidation of aromatic aldehydes by sodium periodate showed[5] a zero-order dependence on $[IO_4^-]$ and first-order dependence on [substrate]. This report is a study of the oxidation of benzaldehyde by bromine in aqueous acetic acid and the effect of transition metal ions such as Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+} as catalyst.

EXPERIMENTAL

The acetic acid was refluxed with 5 % by weight of potassium dichromate for 1 h. The process was repeated till all the oxidizable impurities were completely oxidized as evidenced from the persistence of the red orange colour of solution during final refluxing. The final sample thus got was distilled after adding a small quantity of acetic anhydride. The head and tail fractions were discarded and the fraction distilling at 118-119ºC was collected[7]. Required volume of the bromine (Merck) was mixed with the distilled glacial acetic acid and standardized by titrating against standard sodium thiosulphate. Benzaldehyde (BDH) was washed with 10% aqueous sodium bicarbonate until no effervescence was noticed and dried over anhydrous sodium carbonate.

Kinetic studies: Required volumes of benzaldehyde in distilled glacial acetic acid, metal ion used as catalyst and potassium nitrate to maintain ionic strength, were mixed and thermostated at the required temperature along with bromine in distilled acetic acid in a separate bottle. The reaction was initiated by adding the required volume the bromine solution to the thermostated reaction mixture containing benzaldehyde. At required time intervals, 10 mL aliquots were withdrawn and titrated against sodium thiosulphate iodometrically. The reactions were studied at different conditions such as change in concentration of bromine, benzaldehyde, solvent composition (acetic acid-water), ionic strength and temperature.

Stoichiometry: The stoichiometry of the reaction was determined by mixing a known amount benzaldehyde with a known excess of bromine solution. The amount of unreacted bromine was determined iodometrically.

Product analysis: Benzaldehyde and bromine in 1:5 molar ratio was mixed in acetic acid and allowed to react for a day to ensure completion of reaction. The reaction mixture was diluted with water and cooled to give a white precipitate. The precipitate was recrystallized from hot water. The melting point of the recrystallized sample was found to be 121ºC, which corresponds to the melting point of benzoic acid. A portion of the product was dissolved in 10 mL of 10% NaOH and 10 mL of 1 g of s-benzyl isothiuronium chloride in NaOH was added. The white precipitate obtained was filtered and recrystalized from alcohol. The melting point of the recrystalised sample was found to be 171ºC which is the melting point of the s-benzyl isothiouranium derivative of benzoic acid.

RESULTS AND DISCUSSION

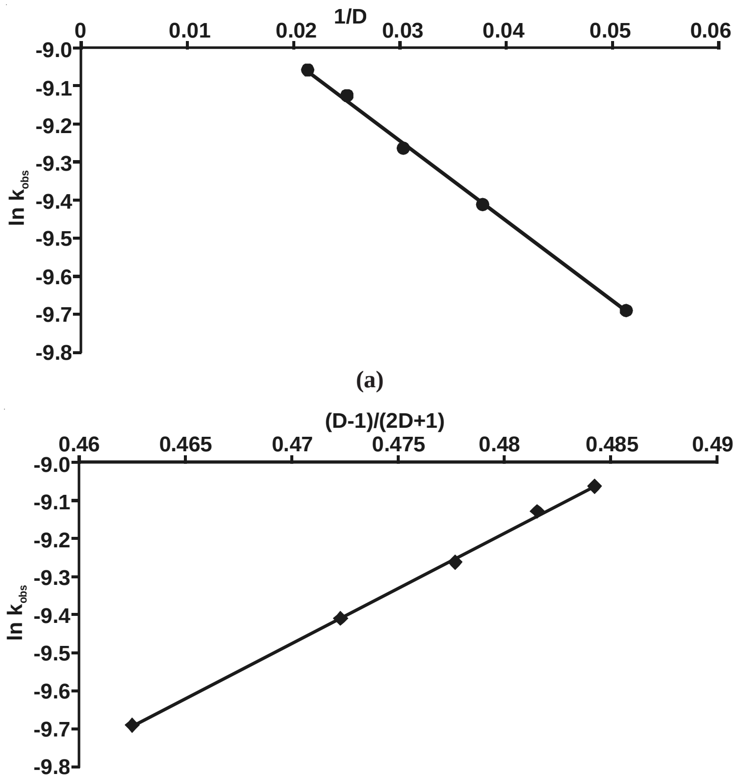
Effect of solvent composition and concentration of benzaldehyde and bromine

The concentration of bromine was varied from 0.02 to 0.08 M and that of benzaldehyde from 0.2 to 0.8 M keeping all the other conditions same. The pseudo-first order rate constants, k_{obs} with respect to bromine were found to increase with increasing their concentrations. Plots of log Rate *vs.* log $[C_6H_5CHO]_o$ or log $[Br_2]_o$ and k_{obs} *vs.* $[C_6H_5CHO]_o$ or $[Br_2]_o$ were found to be linear with slope nearly one indicating first order dependence with respect to benzaldehyde and bromine (Table-1).

TABLE-1
OXIDATION OF BENZALDEHYDE BY BROMINE IN AQUEOUS ACETIC ACID- EFFECT OF VARIATION OF CONCENTRATIONS, SOLVENT COMPOSITION, IONIC STRENGTH (μ) AND TEMPERATURE (T)

$[C_6H_5CHO]$ (M)	$[Br_2]$ (M)	CH_3COOH (%)	μ (M) (KNO_3)	Temperature (K)	$k_{obs} \times 10^4$ (s^{-1})
0.2	0.02	40	0.04	303	1.16
0.4	0.02	40	0.04	303	2.29
0.5	0.02	40	0.04	303	2.89
0.6	0.02	40	0.04	303	3.51
0.8	0.02	40	0.04	303	4.58
0.2	0.04	40	0.04	303	2.26
0.2	0.05	40	0.04	303	2.85
0.2	0.06	40	0.04	303	3.41
0.2	0.08	40	0.04	303	4.61
0.2	0.02	50	0.04	303	1.09
0.2	0.02	60	0.04	303	0.95
0.2	0.02	70	0.04	303	0.82
0.2	0.02	80	0.04	303	0.62
0.2	0.02	40	0.05	303	1.04
0.2	0.02	40	0.06	303	0.96
0.2	0.02	40	0.08	303	0.82
0.2	0.02	40	0.10	303	0.72
0.2	0.02	40	0.04	308	2.08
0.2	0.02	40	0.04	318	5.29
0.2	0.02	40	0.04	323	7.85
0.2	0.02	40	0.04	328	12.91

The percentage, by volume, of acetic acid in the system was changed over a range from 40 to 80, keeping all the other conditions like $[C_6H_5CHO]_o$ $[Br_2]_o$ and temperature same. An increase in the dielectric constant of the medium (increase in the percentage of water) increases the rate of the reaction. The plots of ln k_{obs} *vs.* D^{-1} and ln k_{obs} *vs.* $(D-1)(2D+1)^{-1}$ (Fig. 1) were found to linear with negative and positive slopes, respectively as in the case of reaction between non-ionic $(C_2H_5)_3N$ and C_2H_5I which shows an increase in rate constant with an increase in dielectric constant of the medium[8]. The results can be interpreted to mean that in the transition state partial charges are created from neutral molecules. It is also known that bromine is more powerful oxidizing agent in the form of molecular species, rather than as hypobromite ion. Hence, the oxidizing species in the reaction is likely to be neutral bromine rather than any other bromine species that may be generated by the interaction of bromine with solvent system.



(a)

(b)

Fig. 1. Oxidation of C_6H_5CHO by Br_2 in aqueous CH_3COOH
Effect of the dielectric constant (D) of the medium
$[C_6H_2CHO]_o = 0.2$ M, $[Br_2]_o = 0.02$ M, $\mu = 0.04$ M (KNO_3), T = 303 K

Effect of temperature: The reaction was studied at various temperatures in the range of 303 to 323 K at 40% aq. acetic acid medium. The plots of ln k_{obs} *vs.* 1/T and ln (k_{obs}/T) *vs.* 1/T were found to be linear, with correlation coefficient nearly unity, with negative slopes and positive intercepts (Fig. 2). The various activation parameters have been calculated as $\Delta E^\# =$ 78.05 kJ mol^{-1}; $\Delta H^\# =$ 75.43 kJ mol^{-1}, $\Delta S^\# = -71.14$ Jmol^{-1}K^{-1} and ln A =

21.96. The negative value of entropy of activation probably due to loss of translational and rotational degrees of freedom of bound solvent molecules when the transition state is strongly solvated.

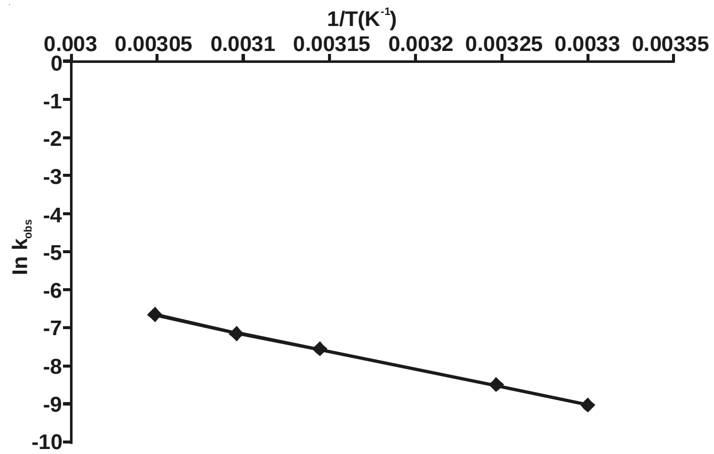


Fig. 2a. Oxidation of benzaldehyde by Br_2 in 40 % aqueous CH_3COOH
Determination of energy of activation
$[C_6H_2CHO]_o$ = 0.2 M, $[Br_2]_o$ = 0.02 M, μ = 0.04 M (KNO_3), T = 303 K

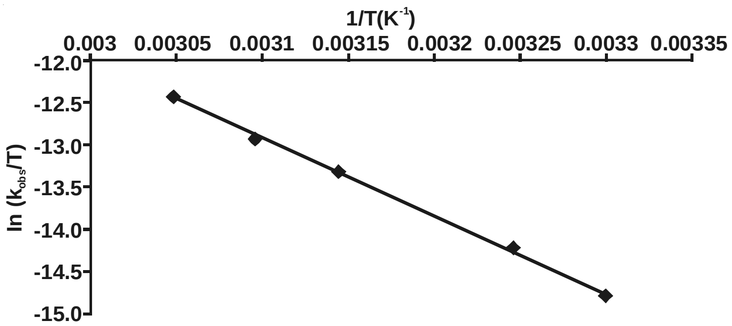


Fig. 2b. Oxidation of benzaldehyde by Br_2 in 40 % aqueous CH_3COOH
Determination of thermodynamic parameters
$[C_6H_2CHO]_o$ = 0.2 M, $[Br_2]_o$ = 0.02 M, μ = 0.04 M (KNO_3), T = 303 K

Effect of ionic strength: The ionic strength of the reaction medium was changed over a range of 0.03 to 0.12 M using KNO_3, keeping all other conditions unchanged. The results show that the rate decreases with increase in ionic strength of the medium. The small effect of ionic strength on the rate of the reaction could be attributed[8] to reaction between neutral molecule (C_6H_5CHO) and molecule (Br_2) giving one of a polar product (HBr) (Fig. 3).

Effect of catalyst: The reaction followed first order kinetics in the presence of all the metal ions used. The pseudo-first rate constant with respect to bromine in the presence of 0.02 M each of the metal ions Fe^{3+},

Co^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+} were found to be 3.02×10^{-4} , 2.74×10^{-4} , 2.34×10^{-4}, 1.98×10^{-4} and 1.23×10^{-4} s^{-1}, respectively (Fig. 4), compared to the rate constant for the uncatalysed reaction *viz.*, 1.16×10^{-4} s^{-1} under identical conditions suggesting that the metal ions act as mild catalyst with Fe^{2+} and Co^{2+} being more effective among the ions used.

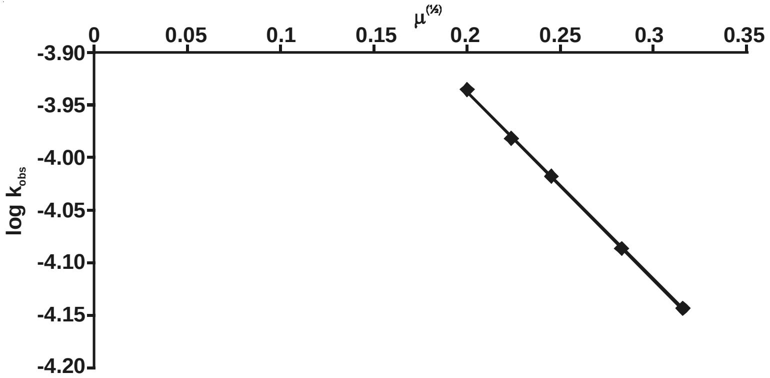


Fig. 3. Oxidation of C_6H_5CHO by Br_2 in 40 % aqueous CH_3COOH
Effect of ionic strength $[C_6H_5CHO]_o = 0.2$ M, $[Br_2]_o = 0.02$ M, T = 303 K

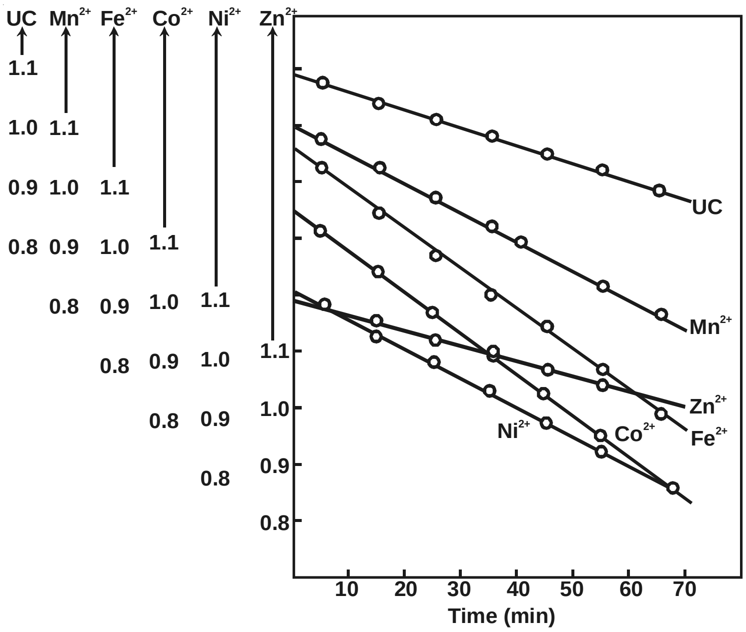
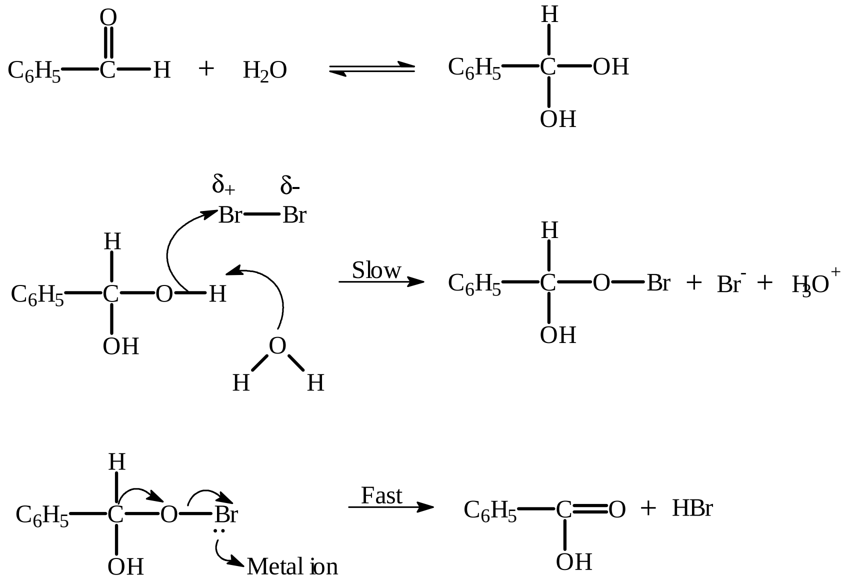


Fig. 4. Kinetics of oxidation of C_6H_5CHO by Br_2 in 40 % aqueous CH_3COOH
Effect of metal ions $[C_6H_2CHO]_o = 0.2$ M, $[Br_2]_o = 0.02$ M, μ = 0.04 M (KNO_3), T = 303 K, UC = Uncatalyzed reaction

Stoichiometry

The stoichiometry of the reaction (benzaldehyde: bromine) was found to be 1:1. The order of reaction with respect to both benzaldehyde and bromine has been found to be one and hence the reaction between benzaldehyde and bromine obey the empirical rate law: Rate = k_2 [Br_2][C_6H_5CHO].

The increase in ionic strength of medium decreases rate of reaction. The fact that the reaction does not involve the formation of free radicals was proved by the non-appearance of precipitate when the reaction was carried out in the presence of acrylo nitrile which is a free radical trapper. On the basis of the above evidences, the following mechanism may be proposed for the oxidation of benzaldehyde by bromine.



The increase in the percentage of water increases the reaction rate which may be due to increase in the extent of hydration of benzaldehye with increase in water content. It also further indicates that the transition state is more polar than the reactants.

The catalytic activity of the metal ions was found to be in the order: $Fe^{3+} > Co^{2+} > Mn^{2+} > Ni^{2+} > Zn^{2+}$. The metal ion may involve in the fast step involving the removal of Br^- by coordinating with it in the intermediate. The greater catalytic activity of Fe^{3+} and Co^{2+} could be attributed to their ability to act as better electron accepter.

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