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Kinetics and Thermodynamics of Oxidation of 3,4,5-trimethoxy Aniline by Tetrabutylammonium Bromochromate in Acetic Acid-water Medium

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ABSTRACT

Anilines are widely used in the manufacture of dyes, medicinal, plastics and perfumes. Anilines are readily oxidized to give products depending on reaction conditions. Conversion of anilines to azobenzene is important in organic synthesis. The kinetics of oxidation of 3,4,5-trimethoxy aniline (3,4,5-TMA) by Tetrabutyl Ammonium Bromochromate (TBABC) in the presence of perchloric acid in aqueous acetic acid medium has been described. The reaction is first order with respect to [TBABC], [3,4,5-TMA] and [H^+]. The reaction rate has been determined at different temperatures and activation parameters calculated.

Keywords: Tetrabutylammonium bromochromate, 3,4,5-trimethoxy aniline, Thermodynamic parameters, Kinetics

INTRODUCTION

Aniline is used to make a wide variety of products such as polyurethane foam, agricultural chemicals, synthetic dyes, and antioxidants, stabilizers for the rubber industry, herbicides, varnishes and explosives. It is a metabolite of the xylidine group of anaesthetics including lidocaine, and is produced by the reduction of certain azo dyes by intestinal microflora. It may also enter the environment through degradation of certain pesticides.

Aniline can be toxic if ingested, inhaled, or by skin contact. Aniline damages hemoglobin, a protein that normally transports oxygen in the blood. The damaged hemoglobin cannot carry oxygen. This condition is known as methemoglobinemia and its severity depends on how much you are exposed to and for how long. Methemoglobinemia is the most prominent symptom of aniline poisoning in humans, resulting in cyanosis (a purplish blue skin color) following acute high exposure to aniline. Direct contact with aniline can also produce skin and eye irritation. Long-term exposure to lower levels of aniline may cause symptoms similar to those experienced in acute high-level exposure. There is no reliable information on whether aniline has adverse reproductive effects in humans. Studies in animals have not demonstrated reproductive toxicity for aniline. Recently a simple, sensitive and environmentally benign method for the direct determination of aniline and its derivatives in environmental water samples by Capillary Zone Electrophoresis (CZE) with field-enhanced sample injection has been described [1].

Oxidation is an essential reaction for different organic synthesis. Chromium compounds have been used a versatile oxidant for many types of substrates varying from metal ions to naturally occurring organic compounds. Cr(VI) as chromate or dichromate is highly soluble in water, and is reported to be highly toxic [2]. Hence, there is continued interest in the development of new Cr(VI) reagents for the effective and selective oxidation of organic substrates, in particular alcohols, under mild conditions. Therefore, the search for new oxidizing agents is of interest to synthetic organic chemists.

Some new Cr(VI) based reagents like 4-(dimethylamino)pyridinium chlorochromate [3], benzimidazolium fluorochromate [4], tetraethylammonium chlorochromate [5], tripropylammonium fluorochromate [6], tetrahexylammonium fluorochromate [7], quinoxalinium dichromate [8] and tetrabutylammonium bromochromate [9] have been used to study the oxidation of various organic compounds.

Tetrabutylammonium bromochromate is developed recently. It is a more efficient and stronger oxidizing agent. This new compound is more efficient for quantitative oxidation of several organic substrates and has certain advantages over similar oxidizing agents in terms of the amount of oxidant and solvent required, short reaction times and high yields.

Literature survey reveals that various oxidizing agents have been extensively used for the mechanism of oxidation of anilines [10-14]. Aniline is a synthetic compound widely used in industrial and pesticide production, which can lead to environmental pollution. Its high concentration in rivers and lakes is hazardous to aquatic species. The mechanism of aniline toxicity has been studied extensively in animals and algae. Aniline genotoxicity in plants provide evidence that aniline is a serious environmental pollutant causing deleterious genotoxic effects on wheat root tip cells and growth toxic effects on wheat seedlings [15]. Keeping this in view, we report the kinetics of oxidation of 3,4,5-trimethoxy aniline by TBABC and evaluated various thermodynamic parameters.

EXPERIMENTAL

Materials and reagents

All the employed chemicals and solvents were of analytical grade. Tetrabutylammonium bromochromate (TBABC) was prepared by a reported method [9] and its purity was checked by the iodometric method. Doubly distilled water was used for all purposes. Acetic acid was purified by standard method and the fraction distilling at 118ºC was collected.

Kinetic measurements

The pseudo-first-order conditions were attained by maintaining a large excess (×15 or more) of 3,4,5-trimethoxy aniline over TBABC. The solvent was 50% acetic acid –50% water (*v/v*), unless specified otherwise. The reactions were followed, at constant temperatures (±0.01 K), by monitoring the decrease in [TBABC] spectrophotometrically at 362 nm using UV-Vis spectrophotometer, Shimadzu UV-1800 model.

Data analysis

Correlation analysis was carried out using Microcal Origin (Version 6.1) computer software. The goodness of the fit is discussed using the correlation coefficients and standard deviations.

Stoichiometry and product analysis

The stoichiomety of the reaction was determined by carrying out several sets of experiments with varying amounts of TBABC largely in excess over anisidines. The estimation of unreacted TBABC showed that 1 mol of TBABC reacts with 1 mol of 3,4,5-trimethoxy aniline. The oxidative products of 3,4,5-trimethoxy aniline were analysed using preparative TLC on silica gel, which yields the methoxy azobenzene.

RESULTS AND DISCUSSION

The oxidation of 3,4,5-trimethoxy aniline by TBABC has been conducted in 50% acetic acid and 50% water medium at 303 K, under pseudo first order conditions and the result obtained were discussed in the following paragraphs.

Order of the reaction

The values of k_1 were independent of the initial concentration of TBABC (Table 1) suggesting the reactions were of first order with respect to TBABC. The reaction was catalysed by hydrogen ions and the order with respect to $[H^+]$ was one. Linear plots of log k_1 versus log [3,4,5-TMA] with unit slope demonstrate the first-order dependence of the rate on [3,4,5-TMA] (Figure 1). Under pseudo-first-order conditions, the plot of k_1 *versus* [3,4,5-TMA] is linear passing through origin (Figure 2). These results confirm the first-order nature of the reaction with respect to 3,4,5-trimethoxy aniline.

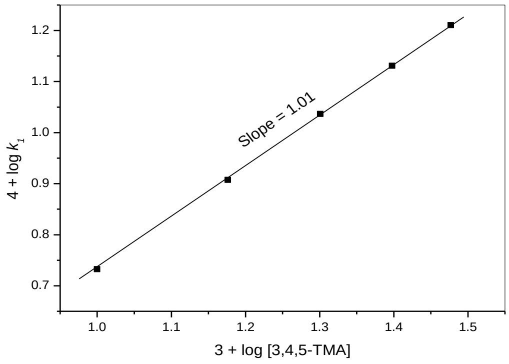


Figure 1: Showing the order plot of 3,4,5-trimethoxy aniline

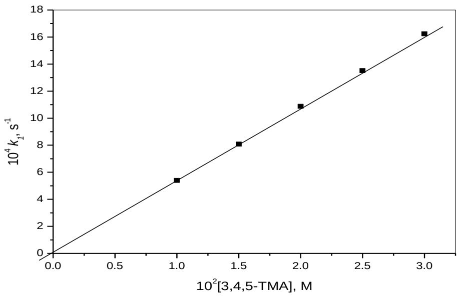
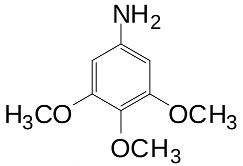


Figure 2: Showing direct plot for of 3,4,5-trimethoxy aniline

Effect of acrylonitrile and $MnSO_4$

The oxidation of 3,4,5-trimethoxy aniline in a nitrogen atmosphere failed to induce the polymerization of acrylonitrile. Furthermore, the rate of oxidation decreased with the addition of Mn(II), indicating the involvement of a two-electron reduction of Cr(VI) to Cr(IV) (Table 1). Therefore, a one-electron oxidation, giving rise to free radicals, is unlikely.

Table 1: Rate constants for the oxidation of 3,4,5-trimethoxy aniline by TBABC in aqueous acetic acid medium at 303 K[a,b]

10^3[TBABC] (mol dm^{-3})	 **10^2[3,4,5-TMA] (mol dm^{-3})**	**[H^+] (mol dm^{-3})**	**10^4 k_1 (s^{-1})**
0.6	2	0.16	10.8
1	2	0.16	10.88
1.6	2	0.16	10.94
2	2	0.16	10.86
2.6	2	0.16	10.82
1	1	0.16	5.4
1	1.5	0.16	8.08
1	2.5	0.16	13.52
1	3	0.16	16.24
1	2	0.1	6.82
1	2	0.2	13.56
1	2	0.26	17.58
1	2	0.3	20.32
1	2	0.16	10.74[c]
1	2	0.16	8.66[d]

[a]As determined by a spectrophotometric technique following the disappearance of oxidant 10^2[3,4,5-TMA]=2.0 mol dm^{-3}; 10^3[TBABC]=1.0 mol dm^{-3}; [H^+]=0.16 mol dm^{-3} Solvent composition: 50% Acetic acid –50% Water (v/v); [b]Estimated from pseudo-first order plots over 80% reaction; [c]Contained 0.001 mol dm^{-3} acrylonitrile; [d]In the presence of 0.003 mol dm^{-3} Mn(II).

Effect of solvent polarity on reaction rate

The effect from solvent composition on the reaction rate was studied by varying the concentration of acetic acid from 30% to 70%. The pseudo-first-order rate constants were estimated for the oxidation of 3,4,5-trimethoxy aniline with TBABC in the presence of perchloric acid at a constant ionic strength. The reaction rate is increases markedly with the increase in the proportion of acetic acid in the medium (Table 2). The plot of log k_1 versus 1/D (dielectric constant) is linear with positive slope suggesting the presence of either dipole–dipole or ion–dipole type of interaction between the oxidant and the substrate (Figure 3). Positive slope of log k_1 versus 1/D plot indicates that the reaction involves a cation-dipole type of interaction in the rate determining step.

Table 2: Pseudo-first order rate constants for the oxidation of 3,4,5-trimethoxy aniline by TBABC at various percentage of acetic acid-water at various temperatures

%AcOH - H_2O (*v/v*)	**Dielectric constant**	**10^4 k_1 (s^{-1})**			
		298 K	**303 K**	**308 K**	**313 K**
30-70	72	6.18	8.7	12.22	17.04
40-60	63.3	6.9	9.66	13.5	18.96
50-50	56	7.78	10.88	15.24	21.32
60-40	45.5	9.18	12.9	18.06	25.46
70-30	38.5	11.28	15.72	22.02	30.88

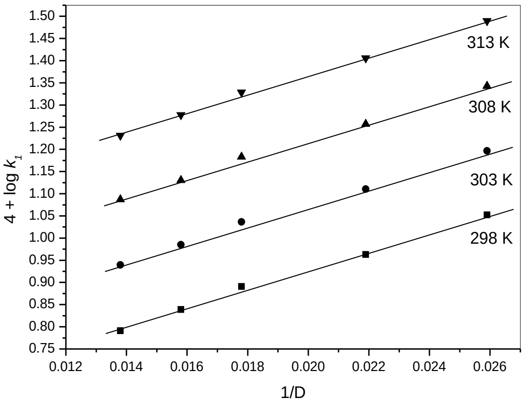


Figure 3: Plot of 1/D against log k_1 showing effect of solvent polarity

Amis (1967) holds the view that in an ion-dipole reaction involving a positive ionic reactant, the rate would decrease with increasing dielectric constant of the medium and if the reactant were to be a negatively charged ion, the rate would increase with the increasing dielectric constant. In this case there is a possibility of a positive ionic reactant, as the rate decreases with the increasing dielectric constant of the medium [16]. Due to the polar nature of the solvent, transition state is stabilized, i.e., the polar solvent molecules surround the transition state and result in less disproportion.

Thermodynamic parameters

The kinetics of oxidation of 3,4,5-trimethoxy aniline was studied at four different temperatures *viz*., 298, 303, 308 and 313 K. The second order rate constants were calculated (Table 3). The Arrhenius plot of log k_2 versus 1/T is found to be linear. The enthalpy of activation, entropy of activation and free energy of activation were calculated from k_2 at 298, 303, 308 and 313 K using the Eyring relationship by the method of least square and presented in Table 3. The entropy of activation is negative for 3,4,5-trimethoxy aniline.

Table 3: Second order rate constants and activation parameters for the oxidation of 3,4,5-trimethoxy aniline by TBABC in acetic acid-water medium

%AcOH - H_2O (*v/v*)	**10^2k_2 (dm^3 mol^{-1} s^{-1})**				**E_a**	**$-\Delta S^\#$**	**$\Delta H^\#$**	**$\Delta G^\#$**
	298 K	**303 K**	**308 K**	**313 K**				
30-70	3.09	4.35	6.11	8.52	53.22	105.67	49.97	81.98
40-60	3.45	4.83	6.75	9.48	51.69	105.1	49.2	81.04
50-50	3.89	5.44	7.62	10.66	52.26	104.9	49.78	81.56
60-40	4.59	6.45	9.03	12.73	52.46	102.6	50.16	81.24
70-30	5.64	7.86	11.01	15.44	53.42	101.45	49.04	79.78

10^2[3,4,5-TMA]=2.0 mol dm^{-3} ; 10^3[TBABC]=1.0 mol dm^{-3}; [H^+]=0.16 mol dm^{-3}; E_a (kJ mol^{-1}); $-\Delta S^\#$ (J K^{-1} mol^{-1}); $\Delta H^\#$ (kJ mol^{-1}); $\Delta G^\#$ (kJ mol^{-1}) (at 303 K)

Mechanism of oxidation

The product of the oxidation of 3,4,5-trimethoxy aniline is methoxy azobenzene. The oxidation of 3,4,5-trimethoxy aniline by TBABC in acetic acid water medium is remarkably slow, but is catalyzed in the presence of perchloric acid, and the reaction proceeds at a comfortable rate. Catalysis by perchloric acid suggests protonation of TBABC species rather than the 3,4,5-trimethoxy aniline molecule, which would have resulted in retardation. The reaction did not promote polymerization of acrylonitrile indicating absence of free radicals. However, the addition of Mn (II), in the form of $MnSO_4$, retards the rate of oxidation. This indicates the involvement of Cr(IV) intermediate in the oxidation of 3,4,5-trimethoxy aniline by Cr(VI) reagent. Positive slope of log k_1 versus 1/D plot indicates that the reaction involves a cation-dipole type of interaction in the rate determining step. The product formation is in accordance with the literature report [17]. The sequence of the oxidation is similar to that reported in the literature [18]. The negative entropy of activation in conjunction with other kinetic observations supports the mechanism.

CONCLUSION

The kinetics of oxidation of 3,4,5-trimethoxy aniline have been investigated in aqueous acetic acid medium in the presence of perchloric acid by spectrophotometrically at 303 K. The oxidation of 3,4,5-trimethoxy aniline by TBABC is first order each with respect to 3,4,5-trimethoxy aniline, TBABC and hydrogen ion. The oxidation is catalysed by perchloric acid. The lowering of dielectric constant of reaction medium increases the reaction rate significantly. The reaction does not show the polymerization, which indicates the absence of free radical intermediate in the oxidation. The reaction rate has been determined at different temperatures and activation parameters calculated.

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