

Kinetics of oxidation of ethylenediamine tetraacetic acid by aromatic N-bromamines in buffer medium

K MOHAN, S ANANDA and D S MAHADEVAPPA*

Department of Chemistry, University of Mysore, Manasagangothri, Mysore 570 006, India

MS received 11 March 1986; revised 29 December 1986

Abstract. Kinetics of oxidation of disodium ethylene-diamine-tetraacetic acid (EDTA) by bromamine-B (BAB) and bromamine-T (BAT) was investigated at 30°C in acetate buffer of pH 5. The oxidation behaviour is similar, with a first-order dependence of rate on [oxidant] and fractional orders in [EDTA] and [H⁺]. The influence of the reaction products, halide ions, ionic strength and dielectric constant of medium on the rate has been studied. A possible mechanism is suggested.

Keywords. Bromamine-T; bromamine-B; kinetics; EDTA; acetate buffer.

1. Introduction

The disodium salt of ethylenediaminetetraacetic acid (Na₂H₂Y or EDTA) is well-known as a chelating agent in complexometry and is employed for identification and differential estimation of a number of metal ions. Although this aspect of EDTA chemistry is described in great detail in literature, very little is known about the behaviour of oxidants towards this compound. Hanna *et al* (1969) have shown that HCHO and CO₂ are formed in the oxidation of EDTA by Ce(IV). Similar results were obtained by Rao (1970). Sanehi *et al* (1973) have carried out a systematic investigation of the oxidation of EDTA with chloramine-T (CAT) in acetate buffer medium, but the products have not been identified. The iron(III) catalysed oxidation of EDTA in aqueous solution at elevated temperatures (100-170°C) has shown the formation of ethylene triacetic acid (Motekaitis *et al* 1980). Formation of HCHO, CO₂ and N-hydroxy methylethylene diamine was observed during the oxidation of EDTA with a suspension of PbO₂ in H₂SO₄ (Ito *et al* 1980).

The chemistry of N-halo-N-sodiosulphonamides in aqueous solution has received considerable attention and the existing literature on the prominent member of this class, namely chloramine-T has been reviewed (Campbell and Johnson 1978). Reports on the bromine analogues, bromamine-B or BAB and bromamine-T or BAT (RNBr Na where R = C₆H₅SO₂ for BAB, and *p*-CH₃C₆H₄SO₂ for BAT), however, are scanty. As part of our broad programme (Mahadevappa *et al* 1984, 1985) on the mechanistic studies of aromatic bromamines, we now report the mechanistic aspects of oxidation of EDTA by BAB and BAT in acetate buffer of pH 5 at 30°C.

* To whom all correspondence should be addressed.

2. Experimental

Preparation of BAB and BAT, and its purification have been reported in previous communications (Ahmed and Mahadevappa 1980; Nair and Indrasenan 1976). Aqueous solutions of the oxidants were standardized iodometrically and preserved in brown bottles. All other chemicals were of analytical grade. Triply distilled water was used throughout.

The reaction was carried out in glass-stoppered pyrex boiling tubes whose outer surface was coated black to eliminate photo-chemical effects. Requisite amounts of EDTA, sodium perchlorate and buffer (to keep the total volume constant for all runs) were taken in the tube and thermostated at 30°C for thermal equilibrium. A measured amount of oxidant solution was also thermostated at the same temperature and rapidly added to the mixture in the boiling tube. The progress of the reaction was monitored by iodometric determination of unreacted oxidant in a measured aliquot of the reaction mixture at different intervals of time. The course of the reaction was studied for two half-lives. The pseudo first-order rate constants (k') calculated were reproducible to $\pm 3\%$. Regression analysis of experimental data was carried out on a EC-75 statistical calculator.

Stoichiometry

Reaction mixtures under conditions, $[\text{EDTA}] \gg [\text{oxidant}]$, were equilibrated at 30°C in the presence of acetate buffer of pH 5 for 48 hours. Spot tests (Feigl 1956) indicated the presence of ethylene diamine (en) in the reaction mixture. The amine was transferred to the organic layer by solvent extraction with ether, which was then evaporated, and a concentrated aqueous solution of en was prepared. It was then estimated gravimetrically (Vogel 1961) as the complex $[\text{Cu en}_2][\text{HgI}_4]$. Quantitative estimation of amine was also carried out in a similar manner under conditions, $[\text{oxidant}] \gg [\text{EDTA}]$, after removing the excess oxidant with KI and thiosulphate. The results are shown below:

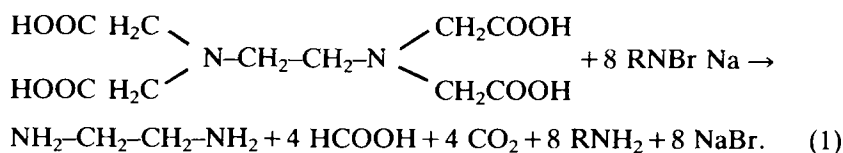
<i>EDTA taken</i> (m moles)	<i>BAT taken</i> (m moles)	<i>en theoretical</i> (m moles)	<i>en found</i> (m moles)
2.0	0.30	0.038	0.031
2.0	0.80	0.100	0.980
0.5	20.00	0.500	0.440
1.0	20.00	1.000	0.960
2.0	20.00	2.000	1.930
1.0	20.00	1.000	0.980
	(with BAB)		

The stoichiometry of the reaction (1) was established under conditions by equilibrating reaction mixtures containing excess oxidant and then estimating the unreacted oxidant. The results are as follows:

EDTA taken = 5×10^{-4} mole

Time (hours)	Oxidant consumed (meq)		Number of eq. per mole of EDTA
	BAB	BAT	
20	7.50	7.50	15.0
25	7.70	7.74	15.4
30	7.95	7.91	15.9
40	8.02	8.00	16.0
48	8.07	8.01	16.1

The stoichiometry of the oxidation of EDTA with the bromamines can be represented as follows:



Benzene sulphonamide was detected by TLC. Formic acid was detected by the chromatographic acid procedure (Feigl 1956) after reducing with Mg and HCl, while CO_2 was identified by the conventional limewater test.

3. Results

The kinetics of oxidation of EDTA by BAB and BAT was investigated at several initial concentrations of the reactants in buffer medium at pH 5. Results obtained with BAT are shown in parentheses along with those obtained for BAB.

At constant pH, $[\text{EDTA}]_0$, plots of $\log [\text{oxidant}]$ versus time are linear ($r > 0.9980$) indicating a first-order dependence of rate on $[\text{oxidant}]_0$. The pseudo first-order rate constants k' are given in table 1. The rate increases with $[\text{EDTA}]$ (table 2) and a plot of $\log k'$ versus $\log [\text{EDTA}]_0$ is linear ($r > 0.9980$) with a slope of 0.64 (0.63). The rate of reaction decreases with increase in pH from 5.0 to 6.2 (table 3). A plot of $\log k'$ against pH is linear ($r > 0.9601$) with a slope of 0.45 (0.37). The effect of adding reaction product, benzene sulphonamide or toluene sulphonamide (RNH_2) to the reaction mixture had negligible influence on the rate. The ionic strength of the medium was varied by adding sodium perchlorate, but this had no effect on the rate of reaction. The dielectric constant (D) of the medium was varied by adding different proportions of methanol to the reaction mixture. Plots of $\log k'$ versus $1/D$ were linear ($r > 0.9937$) with a positive slope indicating charge dispersal in the transition state. Blank experiments showed that methanol is not oxidized by BAB or BAT under the experimental conditions.

The reaction rates were studied at different temperature (303–313 K). Plots of $\log k'$ versus $1/T$ were linear ($r > 0.9921$) from which the energy of activation E_a and other kinetic and thermodynamic parameters were calculated (table 4).

Addition of reaction mixture to acrylamide did not initiate polymerization showing the absence of free radicals.

Table 1. Effect of varying concentrations of oxidant on the rate of reaction in pH 5 buffer medium.

$[\text{EDTA}]_0 = 0.02 \text{ mol dm}^{-3}$; $\mu = 0.5 \text{ mol dm}^{-3}$;
temperature = 30°C

$10^3[\text{oxidant}]_0$ mol dm^{-3}	$k' \times 10^4 \text{ s}^{-1}$	
	BAB	BAT
1.0	9.68	8.89
2.0	9.72	8.70
3.0	9.70	8.84
4.0	9.73	8.62
5.0	9.74	8.67
6.0	9.70	8.52

Table 2. Effect of varying concentrations of EDTA on the rate of reaction in pH 5 buffer medium.

$[\text{BAB}][\text{BAT}] = 0.003 \text{ mol dm}^{-3}$; $\mu = 0.5 \text{ mol dm}^{-3}$;
temperature = 30°C

$10^2[\text{EDTA}]$ mol dm^{-3}	$k' \times 10^4 \text{ s}^{-1}$	
	BAB	BAT
1.0	6.14	5.56
1.5	8.13	7.62
2.0	9.70	8.84
2.5	11.3	10.0
3.0	13.2	11.6
4.0	15.0	13.7
5.0	17.0	15.4

Table 3. Effect of varying pH on the rate of oxidation of EDTA by BAB (BAT) in pH 5 medium.

$[\text{BAB}][\text{BAT}] = 0.003 \text{ mol dm}^{-3}$; $[\text{EDTA}] = 0.02 \text{ mol dm}^{-3}$;
temperature = 30°C $\mu = 0.5 \text{ mol dm}^{-3}$

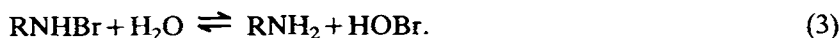
pH	$k' \times 10^4 \text{ s}^{-1}$	
	BAB	BAT
5.0	9.70	8.84
5.5	7.42	7.20
5.7	5.83	6.11
6.0	4.17	4.27
6.2	2.70	3.13

Table 4. Kinetic and thermodynamic parameters for the oxidation of EDTA by BAB and BAT in acetate buffer of pH 5.

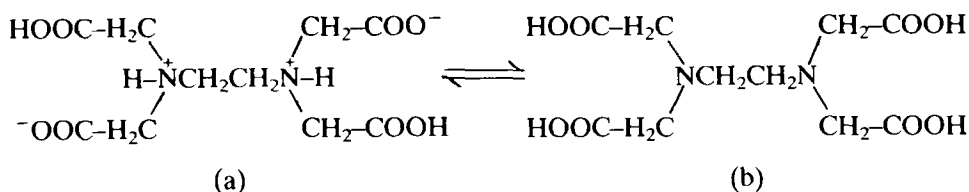
	E_a kJ mol ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger JK mol ⁻¹	ΔG^\ddagger kJ mol ⁻¹	log <i>A</i>
BAB	79.5	76.9	-48.8	92.0	12.0
BAT	90.2	87.7	-14.5	92.1	13.0

4. Discussion

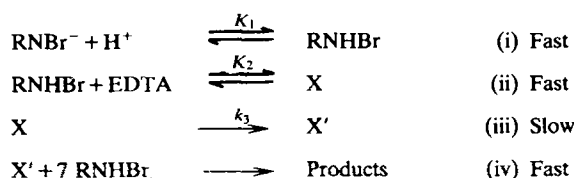
Investigations of Pryde and Soper (1926, 1931), Morris *et al* (1948) and Bishop and Jennings (1958) have established the nature of equilibria present in acidified chloramine-T solutions. The bromamine (BAB or BAT) is analogous to chloramine-T in its properties and in acid solutions the probable oxidizing species are the free acid RNHBr, dibromamine (RNBr₂) and HOBr. At pH > 4, the dibromamine does not exist in appreciable quantities. If HOBr is the active species, then a first order retardation by the added sulphonamide should have been observed (3).



Absence of a retardation effect by the sulphonamide rules out the involvement of HOBr in the reaction sequence. Bishop and Jennings (1958) have shown in their studies on aqueous solutions of CAT, that at pH > 3, the concentration of anion RNCl⁻ is greater than that of the free acid. Hence a protonation equilibrium (2) involving the anion can be assumed in aqueous solutions of RNBr Na in acetate buffer. EDTA can exist (Vogel 1978) in the form of a zwitterion (a) or as a neutral molecule (b).



Assuming that the substrate is in the neutral form, scheme 1 can be proposed for the oxidation of EDTA with BAB or BAT.



Scheme 1

If [RNBr Na] represents the total concentration of oxidant, then



for which rate law (4) can be derived.

$$-\frac{d[\text{RNBr Na}]}{dt} = \frac{k_3 K_1 K_2 [\text{RNBr Na}]_t [\text{EDTA}][\text{H}^+]}{1 + K_1[\text{H}^+] + K_1 K_2 [\text{EDTA}][\text{H}^+]} \quad (4)$$

Rate law (4) is in agreement with experimental results, where a first-order dependence on [RNBr Na] and fractional orders in [substrate] and $[\text{H}^+]$ were observed. Equation (4) can be transformed into (5) and (6).

$$\frac{1}{k'} = \frac{1}{k_3 K_2 [\text{EDTA}]} \left\{ 1 + \frac{1}{K_1 [\text{H}^+]} \right\} + \frac{1}{k_3}, \quad (5)$$

$$\frac{1}{k'} = \frac{1}{[\text{H}^+]} \left\{ \frac{1}{k_3 K_1 K_2 [\text{EDTA}]} \right\} + \left\{ \frac{1}{k_3 K_2 [\text{EDTA}]} + \frac{1}{k_3} \right\}. \quad (6)$$

From the linear double reciprocal plots of $1/k'$ versus $1/[\text{EDTA}]$ ($r > 0.9978$) and $1/k'$ versus $1/[\text{H}^+]$ ($r > 0.9957$) values of decomposition constant k_3 , formation constant K_2 and protonation constant K_1 can be calculated. It may be noted that values of K_1 can be calculated both from (5) and (6). The results are shown in table 5. The value of K_1 obtained for BAB compares favourably with the value of 0.7×10^5 at 25°C found by Hardy and Johnston (1973). The formation constants of EDTA-oxidant complex are around 40, while the decomposition constants are $2.72 \pm 0.17 \times 10^{-3} \text{ s}^{-1}$.

The positive dielectric effect indicates charge dispersal in the transition state (scheme 1). The moderate ΔH^* and the large negative ΔS^* values support a rigid transition state. The mechanism of oxidation of EDTA by BAB and BAT envisages an electrophilic attack by the positive halogen of oxidant at the neutral nitrogen which subsequently leads to disruption of the substrate molecule, as explained in scheme 2.

Table 5. Values of protonation, decomposition and formation constants of EDTA-BAB or BAT complexes at 30°C , determined from double reciprocal plots.

	$10^5 K_1$ ($\text{dm}^3 \text{ mol}^{-1}$)		K_2 ($\text{dm}^3 \text{ mol}^{-1}$)	$10^3 k_3$ (s^{-1})
	a	b		
BAB	2.36	2.59	37.9	2.89
BAT	4.32	4.10	34.5	2.55

^a Values of K_1 calculated from (5); ^b Values of K_1 calculated from (6).

Acknowledgement

One of the authors (KM) is grateful to the Management, A.V.K. College for Women, Hassan, for encouragement.

References

- Ahmed M S and Mahadevappa D S 1980 *Talanta* **27** 669
Bishop E and Jennings V J 1958 *Talanta* **1** 197
Campbell M M and Johnson G 1978 *Chem. Rev.* **78** 65
Feigl F 1956 *Spot tests in organic analysis* (Amsterdam: Elsevier) pp. 282, 340, 396
Hanna S B, Al-Hashimi S, Webb W H and Carroll W R 1969 *Z. Anal. Chem.* **246** 231
Hardy F F and Johnston J P 1973 *J. Chem. Soc. Perkin II* 742
Ito S, Matsuda T and Nagai T 1980 *Talanta* **27** 25
Mahadevappa D S, Ananda S, Murthy A S A and Rangappa K S 1984 *Tetrahedron* **40** 1673
Mahadevappa D S, Ananda S, Murthy A S A and Rangappa K S 1985 *J. Chem. Soc. Perkin II* 39, and references therein.
Morris J C, Salazar J R and Winemann M A 1948 *J. Am. Soc.* **70** 2036
Motekaitis R J, Martell A E and Hayes D 1980 *Can. J. Chem.* **58** 1999
Nair C G R and Indrasenan P 1976 *Talanta* **23** 239
Pryde B G and Soper F G 1926 *J. Chem. Soc.* 1582
Pryde B G and Soper F G 1931 *J. Chem. Soc.* 1514
Rao G N 1970 *Indian J. Chem.* **8** 328
Sanehi R, Mehrotra R M and Mushran S P 1973 *Z. Naturforsch.* **B28** 483
Vogel A I 1961 *Text-book of quantitative inorganic analysis* (London: Longmans) p. 499
Vogel A I 1978 *Text-book of quantitative inorganic analysis* 4th edn, (London: ELBS) p. 261