

## Mechanistic investigation of oxidation of a diketone by bromamine-B in acid medium

T ASHA IYENGAR, D S MAHADEVAPPA\* and PUTTASWAMY†

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

†Department of Chemistry, Bangalore Institute of Technology, V V Puram, Bangalore 560 004, India

MS received 18 March 1992; revised 22 June 1992

**Abstract.** Oxidation of acetylacetone (AA) by bromamine-B (BAB) in HCl medium (0.1 to 0.6 mol dm<sup>-3</sup>) at constant ionic strength has been investigated at 40°C. The rate is first order in [BAB]<sub>0</sub> and fractional order each in [AA]<sub>0</sub> and [H<sup>+</sup>]. The reaction is also catalysed by chloride ion. Michaelis–Menten type of kinetics is observed. Decrease in dielectric constant of medium increases the rate. A solvent isotope effect  $k^{\text{H}_2\text{O}}/k^{\text{D}_2\text{O}} = 0.96$  has been noted. Activation parameters for the rate limiting step have been computed. The mechanism involves the enol form of the diketone.

**Keywords.** Bromamine-B; acetylacetone; HCl medium; oxidation kinetics.

### 1. Introduction

Organic haloamines contain halogen in the +1 state and they have versatile properties, both as oxidants and halogenating agents. Oxidative behaviour of aliphatic ketones with haloamines has been extensively studied. Mahadevappa *et al* (1986, 1988) have investigated the oxidation of aliphatic ketones in acidic and basic media. Diketones (Mahadevappa and Puttaswamy 1988) are reported to be the products of oxidation. There are not many reports in literature on the consecutive oxidation of diketones. It was therefore of interest to investigate this possibility with haloamines under experimental conditions employing chloride assisted catalysis. This paper reports studies on the kinetics and mechanism of oxidation of a typical diketone, acetylacetone (AA) – a  $\beta$ -diketone, by BAB in presence of HCl at 40°C.

### 2. Experimental

Bromamine-B was prepared as reported in literature (Ahmed and Mahadevappa 1980). Its purity was checked by iodometry and by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. An aqueous solution of BAB was standardized iodometrically and stored in brown bottles to arrest photochemical deterioration. Analar grade acetylacetone (IDPL India) was distilled before use and an aqueous solution of the desired strength was prepared

---

\*For correspondence

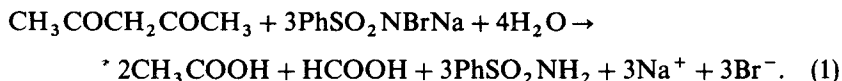
freshly each time. All other chemicals were of analytical grade. Triple-distilled water was used throughout. Constant ionic strength of the medium was maintained by using a concentrated solution of  $\text{NaClO}_4$ . Heavy water ( $\text{D}_2\text{O}$ , 99.2%) was supplied by the Bhabha Atomic Research Centre, Trombay.

The reaction was carried out in glass-stoppered pyrex boiling tubes whose outer surface was black-coated to eliminate photochemical effects. Solutions containing appropriate amounts of substrate,  $\text{HCl}$ ,  $\text{NaClO}_4$  and water (for constant volume) were taken in the tube and thermostatted at  $40^\circ\text{C}$  for thermal equilibrium. A measured amount of BAB, also thermostatted at the same temperature, was rapidly added to the mixture. The progress of reaction was monitored upto two half-lives by iodometric determination of unreacted BAB in a measured aliquot of the reaction mixture at different intervals of time. The pseudo first-order rate constants,  $k'$ , calculated were reproducible to  $\pm 3\%$ .

Regression analysis of experimental data (to obtain regression coefficient ' $r$ ' and standard deviation ' $s$ ' of points from the regression line) was carried out on an EC-72 statistical calculator.

### 2.1 Stoichiometry

Varying ratios of oxidant to substrate (substrate  $\gg$  oxidant) in the presence of  $0.2 \text{ mol dm}^{-3}$  were equilibrated at  $40^\circ\text{C}$  for 24 h after which the following stoichiometry was observed for the oxidation reaction:



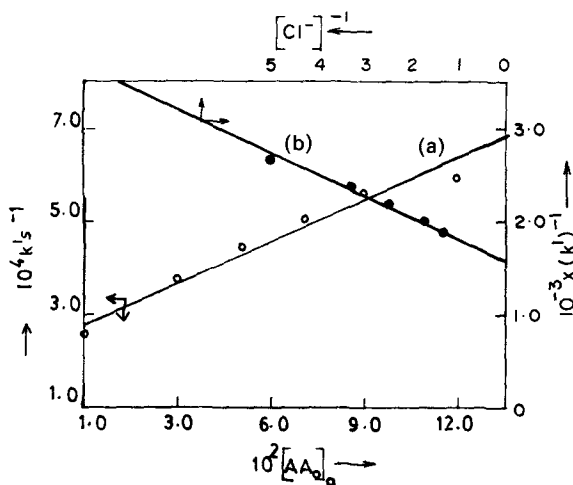
Benzenesulphonamide was detected by TLC using petroleum ether- $\text{CHCl}_3$ -1-butanol (2:2:1, v/v) as the solvent and iodine as spray reagent ( $R_f = 0.88$ ). Formic acid was detected by the chromotropic acid test after reducing it with  $\text{Mg}$  and  $\text{HCl}$  and acetic acid was identified by spot tests (Feigl 1956).

### 3. Results

The kinetics of oxidation of acetylacetone by BAB was investigated at several initial concentrations of the reactants in  $\text{HCl}$  medium.

At constant  $[\text{HCl}]$  and  $[\text{AA}]_0$  ( $[\text{AA}]_0 \gg [\text{BAB}]_0$ ), plots of  $\log [\text{BAB}]$  vs. time were linear indicating a first order dependence of rate on  $[\text{BAB}]_0$ . The rate constant  $k'$  was not affected by a change in  $[\text{BAB}]_0$ . (Average  $10^4 k' = 3.62 \pm 0.10 \text{ s}^{-1}$ ). Values of  $k'$  increased with increase in  $[\text{AA}]_0$ . A plot of  $k'$  vs.  $[\text{AA}]_0$  was linear, with a slope of 0.4 (figure 1) and an intercept on the Y-axis. The rate of reaction increased with increase in  $[\text{HCl}]$  (table 1) and a plot of  $\log k'$  vs  $\log [\text{HCl}]$  was linear ( $r = 0.9998$ ,  $s = 0.001$ ) with a slope of 0.66.

Keeping the total chloride ion concentration in the reaction mixture constant at  $0.6 \text{ mol dm}^{-3}$  with  $\text{NaCl}$ ,  $[\text{H}^+]$  was varied using  $\text{HCl}$ . The rate increased (table 1) with increase in  $[\text{H}^+]$ . A plot of  $\log k'$  vs  $\log [\text{H}^+]$  was a straight line ( $r = 0.9981$ ,  $s = 0.008$ ) with a fractional slope (0.40). At constant  $[\text{H}^+] = 0.2 \text{ mol dm}^{-3}$ , maintained with  $\text{HCl}$ , the rate increased with the addition of  $\text{NaCl}$  (table 1). A plot of  $\log k'$  vs  $\log [\text{Cl}^-]$  was



**Figure 1.** Plot of: (a)  $k'$  vs  $[AA]_0$ , (b)  $1/k'$  vs  $1/[Cl^-]$ .  $[BAB]_0 = 0.001 \text{ mol dm}^{-3}$ ;  $\mu = 0.5 \text{ mol dm}^{-1}$ ; temperature =  $40^\circ\text{C}$ , and, (a)  $[HCl] = 0.2 \text{ mol dm}^{-3}$ ; (b)  $[AA]_0 = 0.03 \text{ mol dm}^{-3}$  and  $[H^+] = 0.2 \text{ mol dm}^{-3}$

**Table 1.** Effect of varying  $[HCl]$ ,  $[H^+]$  and  $[Cl^{-1}]$  on the rate.

$[BAB]_0 = 0.001 \text{ mol dm}^{-3}$ ,  $[AA]_0 = 0.03 \text{ mol dm}^{-3}$ ,  $\mu = 0.5 \text{ mol dm}^{-3}$ , temperature =  $40^\circ\text{C}$ .

$[HCl]$ ( $\text{mol dm}^{-3}$ )	$10^4 k'$ ( $\text{s}^{-1}$ )	$[H^+]$ <sup>a</sup> ( $\text{mol dm}^{-3}$ )	$10^4 k'$ ( $\text{s}^{-1}$ )	$[Cl^-]$ <sup>b</sup> ( $\text{mol dm}^{-3}$ )	$10^4 k'$ ( $\text{s}^{-1}$ )
0.1	2.30	0.1	3.72	0.2	3.68
0.2	3.68	0.2	4.70	0.3	4.20
0.3	4.82	0.3	5.58	0.4	4.65
0.4	5.68	0.4	6.43	0.6	4.98
0.5	6.70	0.5	6.95	0.8	5.30
0.6	7.56	0.6	7.4	—	—

<sup>a</sup> $[Cl^-] = 0.6 \text{ mol dm}^{-3}$  (constant); <sup>b</sup> $[H^+] = 0.2 \text{ mol dm}^{-3}$  (constant).

linear ( $r = 0.9889$ ,  $s = 0.01$ ) with a slope of 0.26. Also, a plot of  $1/k'$  vs  $1/[Cl^-]$  (figure 1), was linear with a  $y$ -intercept ( $r = 0.9981$ ,  $s = 0.002$ ), indicating simultaneous catalysis by  $Cl^-$  ion.

Addition of reaction product, benzenesulphonamide, had no effect on the rate suggesting that it is not involved in pre-equilibrium with the oxidant. Variation of ionic strength of the medium by adding  $NaClO_4$  did not affect the rate. Similarly, addition of  $Br^-$  ions in the form of  $NaBr$  did not influence the rate. The dielectric constant ( $D$ ) of the medium was varied by adding 0–40% of methanol to the reaction mixture. The rate increased slightly (table 2) with increase in methanol content and a plot of  $\log k'$  vs  $1/D$  where  $D$  is the dielectric constant of medium was a straight line ( $r = 0.9982$ ,  $s = 0.008$ ) with a positive slope. Blank experiments indicated that methanol was very slightly oxidized (< 2%) by BAB under the experimental conditions. This was taken into account in the calculation of net reaction rate constant for the oxidation of AA each time.

**Table 2.** Effect of varying dielectric constant of medium on the rate.

[BAB]<sub>0</sub> = 0.001 mol dm<sup>-3</sup>; [AA]<sub>0</sub> = 0.03 mol dm<sup>-3</sup>;  
[HCl] = 0.2 mol dm<sup>-3</sup>; μ = 0.5 mol dm<sup>-3</sup>; temperature = 40°C.

Methanol % (v/v)	10 <sup>2</sup> /D	10 <sup>4</sup> k'(s <sup>-1</sup> )
0	1.30	3.68
10	1.38	4.20
20	1.48	4.96
30	1.60	5.85
40	1.72	7.45

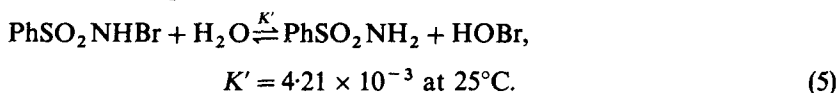
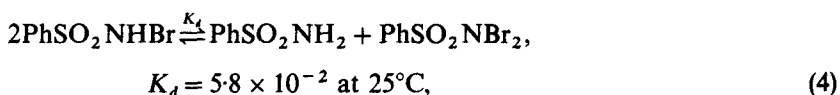
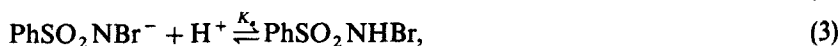
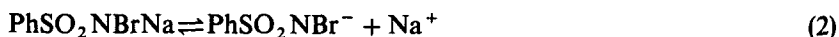
**Table 3.** Kinetic and thermodynamic parameters for the oxidation of acetylacetone by BAB in HCl medium.

Thermodynamic parameters	E <sub>a</sub> (kJ mol <sup>-1</sup> )	ΔH <sup>‡</sup> (kJ mol <sup>-1</sup> )	ΔG <sup>‡</sup> (kJ mol <sup>-1</sup> )	ΔS <sup>‡</sup> (JK <sup>-1</sup> mol <sup>-1</sup> )	log A
Composite reaction	68.4	65.8 ± 0.01	97.7 ± 0.1	-101.3 ± 0.1	7.5
Rate-limiting step	71.7	69.0 ± 0.01	95.9 ± 0.1	-85.1 ± 0.1	8.4

The reaction was studied at different temperatures (303–323 K) and from the linear plots of log k' vs. 1/T (r = 0.9995, s = 0.07), values of activation parameters for the overall reaction were computed (table 3). Study of rate in D<sub>2</sub>O medium showed that k'<sub>D<sub>2</sub>O</sub> was 3.84 × 10<sup>-4</sup> s<sup>-1</sup> while k'<sub>H<sub>2</sub>O</sub> = 3.68 × 10<sup>-4</sup> s<sup>-1</sup> leading to solvent isotope effect of k'<sub>H<sub>2</sub>O</sub>/k'<sub>D<sub>2</sub>O</sub> = 0.96. Addition of acrylamide solution to the reaction mixture in an inert atmosphere did not initiate polymerization of the latter indicating the absence of free radical formation in the reaction sequence.

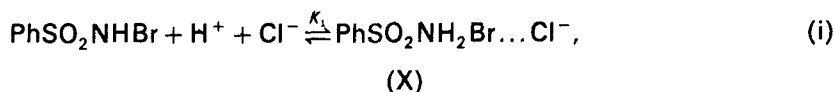
#### 4. Discussion

Bromamine-B (BAB) is analogous to chloramine-T in its properties. In aqueous solutions BAB ionizes and the anion is protonated in acid solutions (Hardy and Johnston 1973). The free acid formed can undergo disproportionation and/or hydrolysis. Therefore, in acid solutions, the prominent oxidant species are the free acid (PhSO<sub>2</sub>NHBr), dibromamine (PhSO<sub>2</sub>NBr<sub>2</sub>) and HOBr.



If  $\text{PhSO}_2\text{NBr}_2$  were to be the reactive species, then the rate law predicts a second-order dependence of rate on  $[\text{BAB}]_0$ , (4), and a retardation of rate by the added sulphonamide (BSA). Similarly, if  $\text{HOBr}$  is the reactive species, a first-order retardation by BSA, (5), is expected. Since these were not experimentally observed, the likely oxidizing species of the diketone is the free acid  $\text{PhSO}_2\text{NHBr}$ . Calculations of Hardy and Johnston (1973) on aqueous BAB and observations of Bishop and Jennings (1958) and Morris *et al* (1948) on aqueous CAT solutions have clearly shown that the conjugate acid is a predominant species in acid solutions of haloamines.

The oxidation of acetylacetone by BAB shows first-order dependence of rate on  $[\text{BAB}]_0$  and fractional orders in  $[\text{AA}]_0$ ,  $[\text{H}^+]$  and  $[\text{Cl}^-]$ . There is no involvement of benzenesulphonamide in pre-equilibrium with the oxidant and the absence of any ionic strength effect suggests that neutral species are taking part in the rate-limiting step. Based on the above observations, the mechanism of reaction is best explained by scheme 1 which predicts simultaneous catalysis by  $\text{H}^+$  and  $\text{Cl}^-$  ions (Bell 1941). Acetylacetone reacts in the enol form (Gould 1959) which is present upto 76% in an equilibrium solution:



Scheme 1.

Step (iii) determines the overall rate,

$$\text{rate} = \frac{-d[\text{BAB}]}{dt} = k_3[\text{X}']. \quad (6)$$

If  $[\text{BAB}]_t$  represents the total concentration of the oxidant, then

$$[\text{BAB}]_t = [\text{PhSO}_2\text{NHBr}] + [\text{X}] + [\text{X}'],$$

from which, solving for  $[\text{X}']$  and substituting its value in (6), rate law (7) can be derived:

$$\text{rate} = \frac{-d[\text{BAB}]}{dt} = \frac{k_3 K_1 K_2 [\text{BAB}]_t [\text{AA}]_0 [\text{H}^+] [\text{Cl}^-]}{1 + K_1 [\text{H}^+] [\text{Cl}^-] + K_1 K_2 [\text{AA}]_0 [\text{H}^+] [\text{Cl}^-]}. \quad (7)$$

Rate law (7) is in agreement with experimental results. Equation (7) can be transformed as,

$$\frac{1}{k'} = \frac{1}{k_3 K_2 [\text{AA}]} \left\{ \frac{1}{K_1 [\text{H}^+] [\text{Cl}^-]} + 1 \right\} + \frac{1}{k_3}. \quad (8)$$

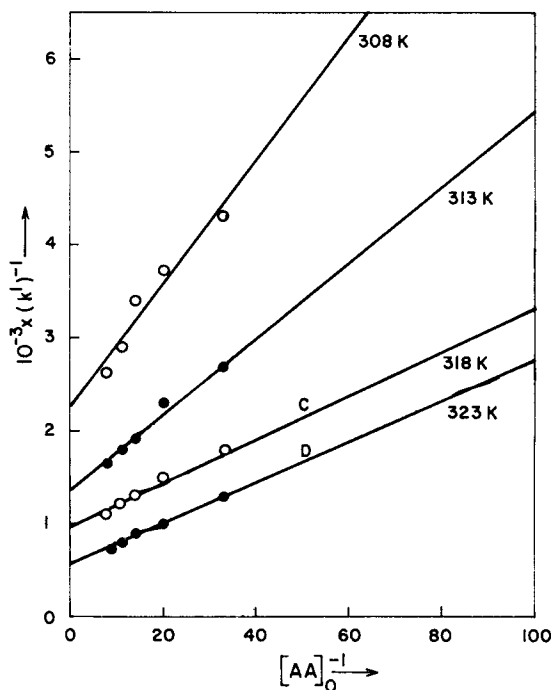


Figure 2. Double reciprocal plots of  $1/k'$  vs  $1/[AA]_0$  at (a) 308, (b) 313, (c) 318 and (d) 323 K.  $[BAB]_0 = 0.001 \text{ mol dm}^{-3}$ ;  $[HCl] = 0.2 \text{ mol dm}^{-3}$  and  $\mu = 0.5 \text{ mol dm}^{-3}$ .

From the intercepts of the linear double reciprocal plots of  $1/k'$  vs  $1/[AA]_0$  at fixed  $[HCl]$ ,  $1/k'$  vs  $1/[H^+]$  and  $1/k'$  vs  $1/[Cl^-]$ , values of decomposition constant  $k_3$  found were,  $7.41 \times 10^{-4}$ ,  $10.27 \times 10^{-4}$  and  $6.16 \times 10^{-4} \text{ s}^{-1}$ , respectively, and were therefore comparable.

Since the rate was fractional in  $[AA]_0$ , Michaelis–Menten kinetics (Laidler 1965) were adopted to study the effect of  $[AA]_0$  on rate at different temperatures (figure 2) by plotting  $1/k'$  vs  $1/[AA]_0$ . Values of  $k_3$  obtained were ( $\times 10^4 \text{ s}^{-1}$ ): 4.49 (308 K), 7.41 (313 K), 10.85 (318 K) and 17.72 (323 K). Activation parameters (table 3) for the rate-limiting step were computed from the Arrhenius plot of  $\log k_3$  vs  $1/T$  ( $r = 0.9978$ ,  $s = 0.02$ ).

The increase in rate with decrease in permittivity of the medium suggests a charge dispersal in the transition state and the rate increases only slightly in  $D_2O$  medium, contrary to expectations (Collins and Bowman 1970) for pre-equilibrium proton transfer reactions. This could be due to the hydrolysis step (scheme 1) wherein the normal kinetic isotope effect [ $k'_H/k'_D > 1$ ] counterbalances the solvent isotope effect [ $k'_{H_2O}/k'_{D_2O} < 1$ ] resulting in a net effect,  $k'_H/k'_D \geq 1$ . The high negative  $\Delta S^\ddagger$  value suggests that the transition state is fairly rigid with few degrees of freedom.

A detailed mode of oxidation of acetyl acetone by BAB is given in scheme 2. The interhalogen intermediate species formed from  $PhSO_2NHBr$  and  $H^+$  and  $Cl^-$  reacts with the substrate which is present in enol form, in an equilibrium step to form the substrate–BAB complex ( $X'$ ). This decomposes in a rate-limiting step to the products. A total of three moles of the oxidant is consumed to yield the ultimate products.



- Gould E S 1959 *Mechanism and structure in organic chemistry* (New York: Holt, Rinehart and Winston) p. 376
- Hardy F E and Johnston J P 1973 *J. Chem. Soc., Perkin Trans. II* 742
- Laidler K J 1965 *Chemical kinetics* (Bombay: Tata-McGraw Hill) p. 474
- Mahadevappa D S, Mohan K and Ananda S 1986 *Tetrahedron* **42** 4857
- Mahadevappa D S, Mohan K and Ananda S 1988 *Indian J. Chem.* **A27** 702
- Mahadevappa D S and Puttaswamy 1988a *Bull. Chem. Soc. Japan* **61** 543
- Mahadevappa D S and Puttaswamy 1988b *Cienc. Cult. (Sao Paulo)* **40** 601
- Morris J C, Salazar J A and Wineman M A 1948 *J. Am. Chem. Soc.* **70** 2036