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KINETICS AND MECHANISM OF BROMAMINE-T OXIDATION OF SOME CYCLIC KETONES IN ACIDIC MEDIA

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Abstract Kinetics of the oxidation of cyclopentanone and cyclohexanone by bromamine-T (BAT) have been reported in perchloric acid media. A zero order dependence to BAT and first order dependence on both ketones and hydrogen ion concentrations have been observed. Observed stoichiometry, zero effects of ionic strength of the medium and *p*-toluenesulphonamide (TSA) and a negative dielectric effect point to a mechanism involving acid catalysed enolisation of ketones in the slow and rate determining step, followed by its subsequent fast interaction with BAT giving corresponding 1,2-diketones as final products. A solvent isotope effect (kD_2O/kH_2O = 2.0–2.2 (35°), 2.1–2.3 (40°) and 2.2–2.4 (35°), 2.3–2.5 (40°) for cyclopentanone and cyclohexanone, respectively) has been observed. Various thermodynamic parameters have been computed.

Kinetic investigations involving aliphatic, cyclic, aromatic ketones and various oxidising agents have been earlier reported by many workers.[1-7] Bromamine-T is a potent oxidising agent and has been used in the estimation of several organic compounds.[8] Some investigations involving BAT oxidation of alcohols[9-11] in the presence of Ru(III) as catalyst in perchloric acid are reported but its mode of oxidation is quite unknown for uncatalysed reactions. The present work constitutes an investigation on the kinetics and mechanism of the oxidation of cyclopentanone and cyclohexanone by bromamine-T in acidic media.

EXPERIMENTAL

BAT soln was prepared and standardised by the method reported.[9] Both ketones were commercial (E. Merck) products. Chloramine-T (E. Merck p.a.), TSA (Koch-light, England) and perchloric acid (E. Merck) samples were used. All other chemicals were of analytical grade. Bidistilled water was used throughout the course of investigation. D_2O (purity 99%) was supplied by BARC, Bombay (India).

The kinetic procedure employed was the same as reported.[9] The kinetics were followed by determining unreacted [BAT] iodometrically at different time intervals. The reactions were followed up to two half lives and duplicate kinetic runs showed reproducible results within ± 2.08%.

Stoichiometry and product analysis. The stoichiometry of the reaction was ascertained by carrying out several sets of experiments with varying amounts of BAT concentration largely in excess over cyclic ketones concentration. The estimation of unreacted [BAT] showed that one mol of each cyclic ketone consumes two mols of BAT. Accordingly, the following stoichiometric Eq. (1) can be formulated where n = 1 in cyclopentanone and 2 in cyclohexanone.

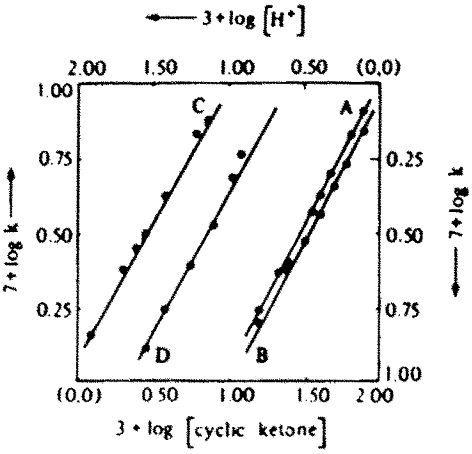
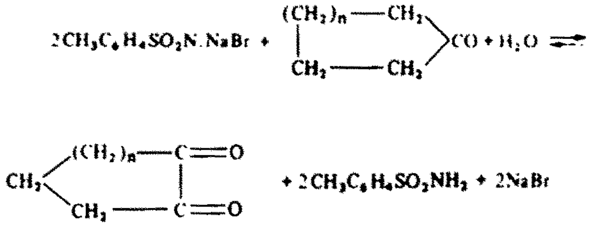


Fig. 1. Plot of log k vs log [cyclic ketone]. [BAT] = 1.04×10^{-3} M, temp 35°. A, [$HClO_4$] = 2.00×10^{-2} M (cyclopentanone); B, [$HClO_4$] = 8.33×10^{-3} M (cyclohexanone). Plot of log k vs log [H^+]. [BAT] = 1.20×10^{-3} M, temp 35°. C, [cyclopentanone] = 2.50×10^{-2} M; D, [cyclohexanone] = 2.00×10^{-2} M.

The end products, corresponding 1,2-diketones, were identified by adopting TLC followed by conventional spot test analysis[12] and also through dinitrophenyl hydrazine (DNP) derivative.[13]



(1)

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Table 1. Effect of [BAT], [H$^+$], ionic strength and [TSA] variation on reaction rate

[BAT] 10^3 M	[Ketone] 10^2 M	[HClO$_4$] 10^2 M	k × 10^7 mol l^{-1} sec^{-1} Cyclopentanone 35°	Cyclopentanone 40°	Cyclohexanone 35°	Cyclohexanone 40°
0.80	2.00	5.00	3.76	6.30	11.90	17.56
1.04	2.00	5.00	3.90	6.38	11.90	17.48
1.20	2.00	5.00	3.86	6.10	12.33	17.80
2.00	2.00	5.00	4.08	6.18	11.00	17.64
2.56	2.00	5.00	4.02	6.25	12.00	17.70
4.00	2.00	5.00	3.96	6.30	12.16	17.62
4.00^a	2.00	5.00	3.98	6.30	12.18	17.60
4.00^b	2.00	5.00	3.97	6.28	12.16	17.63
4.00^c	2.00	5.00	3.99	6.31	12.15	17.61
4.00^d	2.00	5.00	3.98	6.29	12.16	17.62
2.00^e	2.00	5.00	4.06	6.16	11.04	17.62
2.00^f	2.00	5.00	4.08	6.15	11.10	17.65
2.00^g	2.00	5.00	4.07	6.17	11.06	17.63
2.00^h	2.00	5.00	4.06	6.16	11.08	17.61

[TSA] = 2.00 (a), 2.50 (b), 4.00 (c) and 6.00 (d) × 10^{-3} M.
Ionic strength (μ) = 0.06 (e), 0.09 (f), 0.15 (g) and 0.24 (h) M.

RESULTS AND DISCUSSION

The zero order dependence on BAT was established by effecting five-fold variation in [BAT] at 35° (Table 1). The reaction follows first order kinetics with respect to each cyclic ketone and H$^+$ ions which was obvious from slope values (nearly one) of the straight lines obtained from log k *vs* log [cyclic ketone] plots (Figs 1A and B) and log k *vs* log [H$^+$] plots (Figs 1C and D). Insignificant effect of ionic strength (affected by addition of different amounts of NaClO$_4$) and [TSA] variation was observed and recorded in Table 1. Table 2 records the kinetic data obtained at 30, 35, 40 and 45°. The values of energy of activation (ΔE) and entropy of activation (ΔS) are 18.26 Kcal/mol and −15.63 e.u., respectively for cyclopentanone and 16.30 Kcal/mol and −19.84 e.u., respectively for cyclohexanone oxidations. The effect of solvent composition (MeOH–H$_2$O in different ratios) and solvent isotope (D$_2$O- H$_2$O in different ratios) was studied and the results are recorded in Table 2.

The overall second order rate constants were found to be 3.76, 6.30, 11.90, 17.56 × 10^{-4} mol^{-1} l sec^{-1} at 35° and 40° for cyclopentanone and cyclohexanone, respectively.

The reaction is not affected by added radical scavengers like allyl acetate as allyl acetate, up to 0.02 M did not affect the oxidation rate.

The following equilibria[9] are reported to exist in acidified BAT solution (where $T_s = CH_3C_6H_4SO_2$)

$$T_sNBr + H_3O^+ \rightleftharpoons T_sNHBr + H_2O \tag{2}$$

$$2T_sNHBr \rightleftharpoons T_sNBr_2 + T_sNH_2 \tag{3}$$

$$T_sNHBr + H_2O \rightleftharpoons T_sNH_2 + HOBr \tag{4}$$

$$T_sNBr_2 + 2H_2O \rightleftharpoons T_sNH_2 + HOBr. \tag{5}$$

Thus T$_s$NHBr, T$_s$NBr$_2$ and HOBr seem to be probable oxidising species of bromamine-T. Soper[14] has reported that [HOCl] is very small in acidified chloramine-T solution and is independent of chloramine-T. Similar conclusions can also be drawn for [HOBr] in acidified BAT solution and thus any role of HOBr as an oxidant is unlikely. The remaining

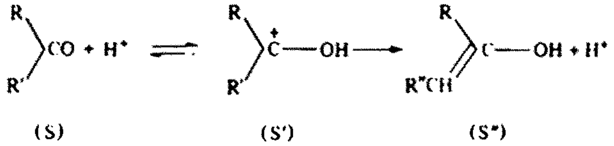
Table 2. Effect of solvent isotope, solvent composition and temperature on reaction rate [BAT] = 2.00 × 10^{-3} M

Temp. °C	Methanol–water V/V (%)	D$_2$O H$_2$O V/V (%)	k × 10^7 mol l^{-1} sec^{-1} Cyclopentanone†		Cyclohexanone‡	
30	0-100	0 100	1.82		1.83	
35	0–100	0–100	3.25		3.13	
40	0 100	0–100	5.32		4.88	
45	0–100	0–100	7.10		7.03	
35	10–90	0- 100	3.75		3.62	
35	20–80	0–100	4.02		3.98	
35	30–70	0–100	4.60		4.52	
35	40–60	0–100	5.22		5.18	
35	0–100	30–70	6.50	11.17*	6.89	7.20*
35	0–100	50–50	6.89	11.72*	7.26	7.58*
35	0 100	70 30	7.15	12.24*	7.51	7.83*

† → [Cyclopentanone] = 2.50 × 10^{-2} M and [HClO$_4$] = 3.34 × 10^{-2} M.
‡ → [Cyclohexanone] = 3.29 × 10^{-2} M and [HClO$_4$] = 8.34 × 10^{-3} M.
* → at 40°.

species, i.e. either T_sNHBr or T_sNBr_2 seems to be the real oxidising species of BAT. It is not possible to establish the predominance of one species over the other with the present kinetic data. Therefore, BAT as such has been used in the mechanism (steps III & IV) for oxidising species. Strict zero order dependence on BAT does not help in distinguishing either of the two species as real oxidising species of BAT. Zero effect of TSA suggests the formation of TSA after slow and rate determining step (II). Zero order dependence of the reaction on BAT suggests involvement of BAT in a fast step preceded by slow and rate determining enolisation step. Such contention is also supported by Littler and Waters.[15]

Ketones are known to enolise in acidic media as follows:



(6)

where S represents the ketone, S' the conjugate acid and S" its enolic form.

The following mechanism is suggested for the acid catalysed oxidation of both cyclic ketones (S) by BAT.

$$S + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S' \quad \text{fast} \qquad \text{(I)}$$

$$S' \xrightarrow{k_2} S'' + H^+ \qquad \text{(II)}$$

Slow and rate determining step

$$S'' + BAT \xrightarrow{k_3} X + T_sNH_2 \quad \text{fast} \qquad \text{(III)}$$

(Intermediate species)

$$X + BAT \xrightarrow{k_4} \text{Final product} + T_sNH_2 \quad \text{fast} \quad \text{(IV)}$$

Application of steady state treatment to S' gives the rate law as:

$$-\frac{d[BAT]}{dt} = \frac{2k_1k_2}{k_{-1}+k_2}[S][H^+]. \qquad (7)$$

The rate law (7) accords well with observed stoichiometry and kinetic orders. The proposed mechanism is thus supported by negative dielectric effect and solvent isotope effect. Substantial deuterium isotope effect is in excellent agreement with carbonium ion character in the transition state (Eq. 6) and indicates a pre-equilibrium fast proton transfer with specified acid catalysed reaction,[16,17] which establishes involvement of enol form and not the keto form of the cyclic ketone.

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