

Oxidation of phenylmethylcarbinols by bromamine-*T*

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Abstract. The kinetics of oxidation of phenylmethylcarbinol and substituted phenylmethylcarbinols by bromamine-*T* have been studied in aqueous acetic acid medium in the presence of sulphuric acid. The effects of added toluene-*p*-sulphonamide and sodium bromide have been investigated. The solvent effect and temperatures effect on these reactions have also been studied. The Hammett correlation gives a ρ value of -2.5 . A suitable mechanism consistent with the experimental observations has been suggested.

Keywords. Bromamine-*T*; phenylmethylcarbinols; oxidation; Hammett plot; activation parameters.

1. Introduction

A useful class of halogen containing oxidants is the group referred to as N-halo compounds which are potential sources of a positive halonium ion or a derivative thereof, which have good oxidising capabilities (Stewart 1964; Waters 1964; Wiberg 1965; Filler 1963; Barker 1964; Carr and England 1958; Campbell and Johnson 1978). Bromamine-*T* (BAT) is one such compound increasingly used in organic chemistry (Kremlev *et al* 1969). The present work reports the kinetic and mechanistic aspects of the oxidation of several substituted phenylmethylcarbinols by BAT with phenylmethylcarbinol (PMC) as the reference compound.

2. Experimental

Bromamine-*T* was prepared by the bromination of chloramine-*T* (CAT) in alkaline medium. The various substituted phenylmethylcarbinols used were of extra pure variety and were used without further purification.

The rate of reaction was followed by titrimetric methods, the disappearance of BAT being monitored iodometrically. The reactions were carried out in binary solvent mixtures of acetic acid and water to over 75% conversion. The rate constants were evaluated by using the respective integrated rate expression. Further oxidation or bromination of the product, acetophenone, was independently checked to be negligible under the conditions employed.

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3. Results and discussion

The rates of the reactions of PMC with BAT have been determined under a variety of conditions of concentrations of BAT, alcohol, mineral acids, added sulphonamide and NaClO₄. The effect of changes in solvent polarity, temperature and structural modifications in the alcohol moiety has also been investigated (tables 1 to 6)

Table 1. Order dependence on [BAT] and [PMC]
[H₂SO₄] = 0.1M. 30° C. 50% HOAc-50% H₂O (V/V)

10^3 [BAT] M	10^2 [PMC] M	$10^4 k_{obs} \text{ sec}^{-1}$	$10^3 k_2$ lit mole ⁻¹ sec ⁻¹
1.26	4.26	4.14	—
1.69	4.26	4.19	—
2.42	4.26	4.16	—
3.38	4.26	4.17	—
4.45	4.26	4.12	—
1.69	2.13	2.10	9.86
1.69	6.39	6.29	9.84
1.69	8.52	8.39	9.85
1.69	10.70	10.50	9.86

Table 2. Effect of acidity
[PMC] = 1.95×10^{-2} M. [BAT] = 1.84×10^{-3} M. 30° C
50% HOAc - 50% H₂O (V/V)

[H ₂ SO ₄] M	$10^4 k_{obs} \text{ sec}^{-1}$	[HClO ₄]	$10^4 k_{obs} \text{ sec}^{-1}$
0.0	0.237	0.0	0.142
0.1	2.24	0.1	4.14
0.2	3.77	0.2	7.15
0.3	5.48	0.3	9.80
0.4	6.76	0.4	12.00
0.8	12.00	0.8	20.90
1.0	20.20	1.0	34.60

Table 3. Effect of added TSA and NaBr
[PMC] = 2.23×10^{-2} M. [BAT] = 1.84×10^{-3} M
[H₂SO₄] = 0.2 M. 30° C. 50%
HOAc-50%·H₂O (V/V)

10^4 [TSA] M	$10^4 k_{obs} \text{ sec}^{-1}$	10^2 [NaBr] M	$10^4 k_{obs} \text{ sec}^{-1}$
0.00	4.01	0.0	4.01
2.12	2.98	1.0	5.37
6.40	2.21	2.0	5.12
8.26	2.02	4.0	4.68
12.4	1.84	8.0	3.47
24.1	1.02	10.0	2.69

Table 4. Effect of solvent polarity
 [PMC] = 2.06×10^{-2} M. [BAT] = 1.85×10^{-3} M
 [H₂SO₄] = 0.3 M. 30° C

Solvent composition % HOAc-% H ₂ O (V/V)	$10^4 k_{\text{obs}} \text{ sec}^{-1}$
20-80	7.03
30-70	5.89
40-60	5.26
50-50	5.07
60-40	4.18
70-30	3.73
80-20	2.44

Table 5. Effect of structural modification
 [BAT] = 1.87×10^{-3} . [H₂SO₄] = 0.16 M.
 50% HOAc-50% H₂O (V/V). 30° C.

RC ₆ H ₄ CH(OH)CH ₃	10^2 [substrate] M	$10^5 k_{\text{obs}} \text{ sec}^{-1}$	$10^3 k_2$ lit mole ⁻¹ sec ⁻¹
H	1.99	26.50	13.30
	3.98	52.10	13.10
4-ph	2.01	121.00	60.40
	4.22	256.00	60.60
4-Me	1.89	198.00	105.00
	4.02	414.00	103.00
4-Cl	1.97	9.97	5.06
	4.11	20.90	5.09
4-Br	2.12	10.70	5.07
	3.86	19.60	5.08
3-Cl	2.01	2.85	1.42
	3.97	5.72	1.44
3-Br	2.14	3.01	1.40
	3.56	4.91	1.38

Table 6. Activation parameters.

RC ₆ H ₄ CH(OH)CH ₃ R =	E _a kcal/mole	ΔH^\ddagger kcal/mole	ΔS^\ddagger e.u.	ΔG^\ddagger kcal/mole
H	14.2	13.6	22.4	20.4
4-Ph	9.93	9.32	33.3	19.4
4-Me	9.13	8.52	34.9	19.1
4-Cl	13.5	12.9	26.4	20.9
4-Br	13.5	12.9	26.5	20.9
3-Cl	15.5	14.9	22.6	21.7
3-Br	15.8	15.2	21.6	21.7

The oxidation of phenylmethylcarbinols under investigation obeys the following rate-law:

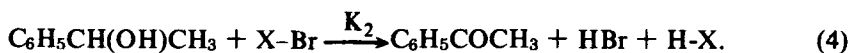
$$\frac{-d[\text{BAT}]}{dt} = k [\text{alcohol}] [\text{BAT}] [\text{H}^+]^x \quad (1)$$

where $1 < x > 0$. The first order dependence both on [BAT] and [PMC] indicates that the slow step of the reaction involves an interaction between one molecule of substrate and one molecule of oxidant.

The following scheme is in keeping with the rate-law and other observations.



(where X = OH or OAc)



Basically, the mechanism assumes one or more pre-equilibria for the formation of active oxidant species followed by a slow rate-determining interaction with the alcohol moiety to give the products. Applying equilibrium conditions for the formation of the oxidant species X-Br, one can arrive at the following rate expression (5)

$$\frac{-d[\text{BAT}]}{dt} = k_{\text{obs}} [\text{BAT}] = \frac{k_2 K_1 K_2 [\text{PMC}] [\text{BAT}^-]_i [\text{H}_3\text{O}^+]}{[\text{TSA}] \{1 + K_1 [\text{H}_3\text{O}^+]\}} \quad (5)$$

where $[\text{BAT}^-]_i$ = initial concentration of BAT.

The rate expression (5) is identical with the experimental rate-law and it also explains the fractional order dependence on $[\text{H}^+]$. The above expression would demand a linear relationship between $[\text{substrate}]/k_{\text{obs}}$ versus $1/[\text{H}^+]$ with a finite intercept as has been realised.

An alternative way in which the fractional order dependence of the rate on the concentration of acid can be explained is to assume that two pathways are available for the oxidation of the alcohol—that is acid-dependent pathway and an acid independent one.

$$\frac{-d[\text{BAT}]}{dt} = k_{\text{obs}} [\text{BAT}] = k_2' [\text{BAT}] [\text{PMC}] + k_3'' [\text{BAT}] [\text{PMC}] [\text{H}^+] \quad (6)$$

wherefrom it can be seen that

$$\frac{k_{\text{obs}}}{[\text{PMC}]} = k_2' + k_3'' [\text{H}^+] \quad (7)$$

a relationship which would require a linear correlation in a plot of $k_{\text{obs}}/[\text{PMC}]$ versus $[\text{H}^+]$ with a finite intercept on the Y-axis. Such plot is brought out in figure 1

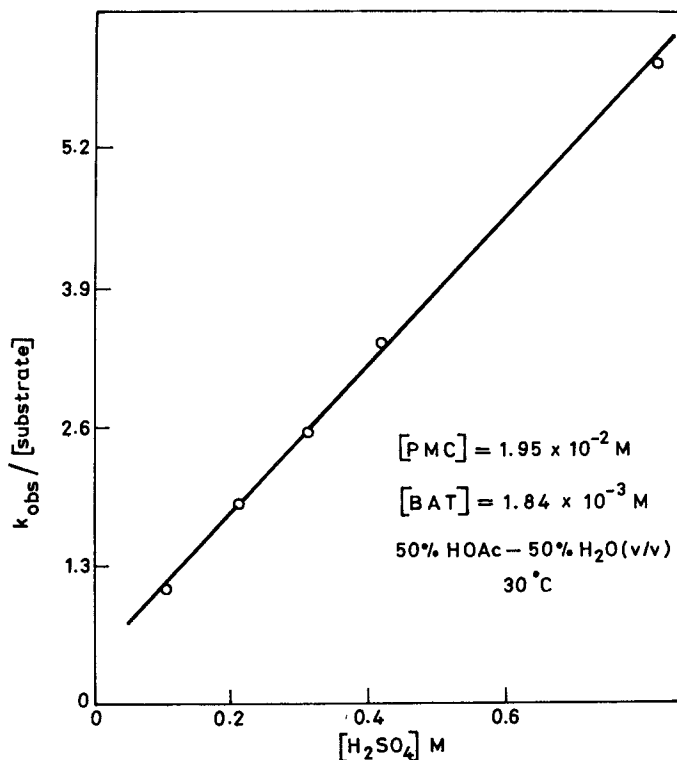


Figure 1. Plot of $k_{\text{obs}}/(\text{substrate})$ vs (acid).

confirming the operation of two such pathways. This formalism is probably on the right lines as could be seen from the fact that the acid-independent pathway for the oxidation of PMC has a k_2' value which is greater than that for the oxidation of the less reactive alcohol, benzyl alcohol by BAT (Gunasekaran and Venkatasubramanian 1980) ($k_2' = 5.01 \times 10^{-3}$ lit mole⁻¹ sec⁻¹ for PMC-BAT system and $k_2 = 9.78 \times 10^{-4}$ lit mole⁻¹ sec⁻¹ for benzylalcohol-BAT system under identical conditions). The finer details of the slow step could be pictured as



The slow step in the oxidation of PMC by BAT should proceed by an abstraction of the hydrogen on the α -carbon atom as a hydride ion, for the generation of a carbocationic centre in the transition state could be expected to be stabilized by electron-releasing substituents in the phenyl group of PMC and an opposite effect for electron-withdrawing substituents. A Hammett analysis of the rate-data of this reaction yields a ρ value of -2.5 substantiating the above proposal. It may be recalled here that the Hammett ρ obtained for the oxidation of PMC by the related oxidant NBS is

-2.4 further underscoring the mechanistic similarities (Thiagarajan and Venkatasubramanian 1967). The faster oxidation of PMC than of benzyl alcohol is also in keeping with this picture for the additional $-\text{CH}_3$ on the α -carbon atom would not only facilitate the loss of the hydride ion but would also stabilise the developing carbonyl double bond in the transition state by hyperconjugation. The foregoing discussion is also in accord with the formalism that the reaction is essentially between two dipolar molecules. Such a reaction, according to Laidler and Eyring (1940), would proceed with a faster rate when the solvent is changed to a more polar one.

The observed acceleration in rate in the presence of initially added bromide ions is also consistent with the proposed mechanism, for, the added Br^- ions would react with BATH and generate molecular bromine which would be a better oxidising agent than HOBr or CH_3COOBr . However, further additions of the Br would tend to convert the active Br_2 into the inactive Br_3 leading to rate retardations.

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