

Substituent effects on oxidation of phenacyl bromides by manganese(III) sulphate in sulphuric acid and acetic acid media

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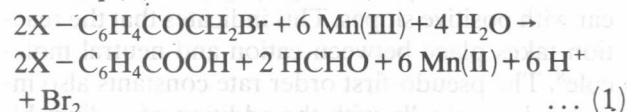
The oxidation of phenacyl bromides by manganese(III) sulphate in acetic acid-sulphuric acid medium is first order each in [phenacyl bromide] and $[\text{Mn}(\text{HSO}_4)^{2+}]$. The reactions are acid-catalysed and participation of water in the reaction is confirmed on the basis of the Hammett's acidity and Bunnett's criteria. The effects of ionic strength and dielectric constant of the medium reveal that the reaction is between a positive ion and dipole. No substituent effect is noticed and isokinetic temperature is evaluated as 297 K which is close to the reaction temperature. A free radical mechanism consistent with the experimental observations is proposed and the activation parameters are reported.

In earlier investigations from our laboratory it was shown that α -haloketones such as phenacyl bromides undergo oxidation by $\text{V(V)}^{1,2}$ and Ce(IV)^3 in sulphuric-acetic acid medium through direct attack of the oxidant on the substrate via a free radical pathway. The title investigation is in continuation of these studies.

Experimental

The reagents and methods employed to follow the reaction were the same as described earlier^{1,3}.

Stoichiometry, determined under the condition: $[\text{Mn(III)}] \gg [\text{substrate}]$ was found to be 3:1 in accord with Eq. (1)



The products were identified to be the corresponding benzoic acids and formaldehyde.

Results and discussion

Under the experimental conditions acetic acid did not react with the oxidant and the phenacyl bromides did not undergo hydrolysis. Oxidation of various phenacyl bromides exhibited a first order dependence on $[\text{Mn(III)}]$. Even though the pseudo-first order plots ($\log c$ versus time) were linear at all $[\text{Mn(III)}]$, the rate constants (k_1) decreased with increase in $[\text{Mn(III)}]$ (Table 1). A similar decrease in k_1 with increase in $[\text{Mn(III)}]$ was also observed in the oxidation of formaldehyde⁴ by manganese(III) pyrophosphate, of maleic acid⁵ by manganese(III) sulphate and of citric acid⁶ by manganese(III) acetate. The decrease is probably either due to the presence of several species of Mn(III) in solution, of which only one may be reactive and its concentration may be dependent on the conditions used or the reactive Mn(III) species may not increase in the same proportion as total $[\text{Mn(III)}]$, or it may be due to a double salt formation⁷ resulting in the decreased concentration of the active species.

The plot of $\log k_1$ against $\log [\text{substrate}]$ was linear with a slope of unity and a plot of k_1 against [substrate] was also linear passing through the origin for all the substrates showing that the order in [substrate]

Table 1—Dependence of rate on [substrate] and $[\text{Mn(III)}]$ in manganese(III)-phenacyl bromide reactions
 $[\text{H}_2\text{SO}_4] = 3.0 \text{ mol dm}^{-3}$; $\text{CH}_3\text{COOH} = 60\% (\text{v/v})$; temp. = 318 K

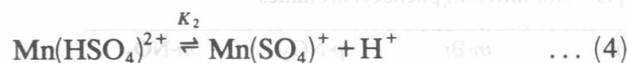
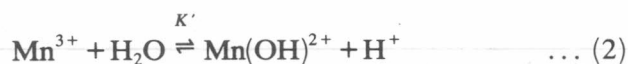
[Substrate] mol dm^{-3}	[Mn(III)] mol dm^{-3}	$10^4 k_1 (\text{s}^{-1})$ for different phenacyl bromides				
		H	<i>p</i> -Br	<i>m</i> -Br	<i>p</i> -NO ₂	<i>m</i> -NO ₂
0.008	0.004	4.10	4.03	4.24	4.42	3.84
0.010	0.004	4.96	5.02	5.37	5.76	4.62
0.015	0.004	7.50	7.35	8.43	8.54	6.63
0.020	0.004	9.60	9.66	10.38	10.66	8.74
0.030	0.004	14.10	14.84	16.26	15.30	14.04
0.020	0.003	12.20	13.30	14.40	14.70	13.52
0.020	0.006	7.68	7.80	8.06	8.90	7.40
0.020	0.008	6.29	6.70	7.04	8.00	6.85

was unity and the reaction is of second order (Table 1).

The rates of oxidation of phenacyl bromides increased with increasing proportion (40 to 65% v/v) of acetic acid (Table 2). The reaction rate increased with decrease in the dielectric constant (D) of the medium and the plots of $\log k_1$ against $1/D$ were linear with positive slopes. This indicates that the reaction takes place between cation and neutral molecule⁸. The pseudo-first order rate constants also increased marginally with the addition of sodium bisulphate. The plots of $\log k_1$ against ionic strength (μ) were fairly linear with positive slopes confirming the reaction to be of cation-dipole type⁹.

The oxidation of phenacyl bromides by Mn(III) is an acid-catalysed reaction. The k_1 values increased with increase in $[H_2SO_4]$. The plots of $\log k_1$ against $\log [\text{acid}]$ failed to give any meaningful results. The plots of $\log k_1$ against $-H_0$ were linear for all the substrates with slopes in the range of 0.45 to 0.79. According to Hammett's hypothesis the involvement of water in the rate-limiting step may be assumed, because the slope values are less than unity. These conclusions are also confirmed by Bunnett's hypothesis¹⁰. The plots of $\log k_1 + H_0$ against $-\log a_{H_2O}$ for all the substrates yielded curves with positive slopes which did not exceed 2.6. This indicates the probability of involvement of water as a nucleophile in the rate-determining step.

There are several reactive species of manganese(III) in sulphuric acid, viz. $MnOH^{2+}$, $Mn(HSO_4)^{2+}$, $Mn(HSO_4)_2^+$, $Mn(SO_4)^+$, $Mn(SO_4)_2^-$ and $Mn(OH)_3(HSO_4)_3^{3-}$ and their presence depends on the experimental conditions. Yatsimiskii *et al.*¹¹ have concluded from their spectrophotometric data that complex formation between Mn(III) and HSO_4^- ions is favoured in the range of 2 to 10 mol dm^{-3} sulphuric acid. The equilibria (2-5) were assumed to exist in sulphuric acid solution:



According to equilibria (3) and (5) increase in $[H_2SO_4]$ and $[HSO_4^-]$ should increase the rate and it has been found to be so. The dependence of rate on $[\text{bisulphate}]$ can be explained by assuming either $Mn(HSO_4)^{2+}$ or $Mn(SO_4)_2^-$ as reactive species. The negative species $Mn(SO_4)_2^-$ may be discarded on the

Table 2—Effect of acetic acid on k_1 in manganese(III)-phenacyl bromide reactions

$[Manganese(III)] = 0.004 \text{ mol dm}^{-3}$; $[\text{substrate}] = 0.01 \text{ mol dm}^{-3}$; $[H_2SO_4] = 3.0 \text{ mol dm}^{-3}$; temp. = 318 K

Phenacyl bromide	$k_1 \times 10^4 \text{ (s}^{-1}\text{) at acetic acid \% (v/v)}$			
	40 (45.73)	50 (39.17)	60 (32.60)	65 (29.33)
H	3.16	4.00	4.96	7.90
<i>p</i> -Br	3.07	3.84	5.02	5.94
<i>m</i> -Br	3.76	4.22	5.37	6.14
<i>p</i> -NO ₂	4.26	4.73	5.76	6.91
<i>m</i> -NO ₂	3.46	4.02	4.62	5.44

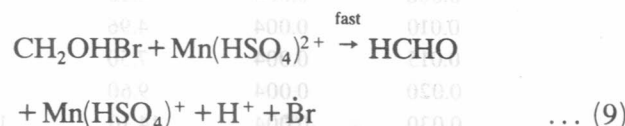
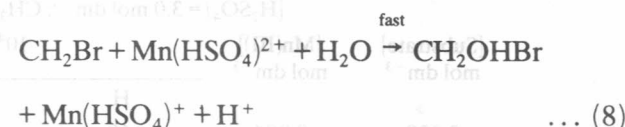
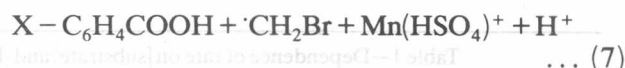
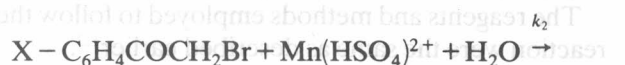
Values in parentheses are dielectric constant (D) of the media

basis of dielectric constant and ionic strength effects on the rate.

According to Chem and Irish¹² dissociation of sulphuric acid, viz. $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$ is predominant above 2.0 mol dm^{-3} H_2SO_4 while the dissociation of HSO_4^- ($HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$) is considered negligible. Hence the formation of $Mn(SO_4)^+$ complex may be ruled out under the experimental conditions. These observations confirm $Mn(HSO_4)^{2+}$ species to be the most likely reactive species present in the reaction medium. Added Mn(II) had no effect on the rate of oxidation suggesting that manganese(III) was the only active oxidising species present in the reaction^{13,14}. The presence of free radicals was confirmed by the polymerization of acrylonitrile in the present system.

Mechanism

Considering all the experimental observations a possible mechanism given in Scheme 1 is proposed.



Scheme 1

Table 3—Activation parameters in manganese(III)-phenacyl bromide reactions in sulphuric acid medium

[Manganese(III)]⁺ = 0.004 mol dm⁻³; [substrate] = 0.02 mol dm⁻³; [H₂SO₄] = 3.0 mol dm⁻³; CH₃COOH = 60% (v/v); temp. = 318K

Phenacyl bromide	$k_2 \times 10^2$ (dm ³ mol ⁻¹ s ⁻¹) at temp (K)					E_a (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)	$\Delta G^\ddagger$ (kJ mol ⁻¹)
	308	313	318	323	328				
H	1.78	2.95	4.80	8.30	13.50	85.43	83.43	-3	84.35
<i>p</i> -Br	1.77	2.90	4.83	7.70	12.67	83.30	80.67	-9	83.47
<i>m</i> -Br	1.65	3.16	5.19	9.12	12.45	92.09	89.46	19	85.94
<i>p</i> -NO ₂	1.54	2.69	5.33	8.32	13.59	91.01	88.37	16	85.86
<i>m</i> -NO ₂	1.45	2.57	4.37	7.59	11.75	87.16	84.52	2	86.40

The rate law from Scheme 1 is given by Eq. (11)

$$\frac{d[\text{Mn(III)}_t]}{dt} = \frac{k_2 K_1 [\text{Mn(III)}_t] [\text{Phenacyl bromide}] [\text{HSO}_4^-]}{1 + K_1 [\text{HSO}_4^-]} \dots (11)$$

This equation explains the first order dependence of rate on [Mn(III)_t], [Substrate] and variation of rate with [HSO₄⁻]. On rearrangement Eq. (11) leads to Eq. (12).

$$1/k_1 = \frac{1}{K_1 k_2 [\text{Phenacyl bromide}] [\text{HSO}_4^-]} + \frac{1}{k_2 [\text{phenacyl bromide}]} \dots (12)$$

Plots of 1/*k*₁ against 1/[HSO₄⁻] are fairly linear for all the phenacyl bromides studied. From the values of intercept and slope, the equilibrium constant *K*₁ is found to be 8.5 × 10⁻² dm³ mol⁻¹.

The rate measurements were also made at temperatures ranging from 308 K to 328 K and related thermodynamic parameters *E*_a, $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta G^\ddagger$ were evaluated (Table 3). The thermodynamic parameters are in close comparison with each other, and the $\Delta G^\ddagger$ values for all the reactions are fairly constant. This shows the applicability of isokinetic relationship for the series of compounds with slightly different structures undergoing a reaction by the same mechanism.

The isokinetic temperature (β) is evaluated from the linear plot of $\Delta H^\ddagger$ against $\Delta S^\ddagger$ to be 297K which is close to the experimental range of temperature. Poor correlation was obtained when log *k*'₂ was plotted against log *k*₂[°] and this is because all the *k*₂ values fall within the range of about 10% difference.

A glance at the results given in Table 3 shows that the reactivity of all the substituents studied is nearly the same (with about 10% difference). This suggests that the structural effect on the rate of reaction is negligible. This may be attributed to several reasons: (a) participation of substrate in a fast step after the

rate-determining step¹⁵, (b) the presence of an equilibrium step preceding the rate-determining step where both pre-equilibrium as well as the rate-controlling steps are sensitive to the substituents to the same extent but in a reverse manner¹⁶ and (c) an isokinetic temperature which is nearer to the experimental temperature, could make the reaction rate completely insensitive to structural effects^{17,18}. Of these three possibilities, the first two can be ruled out, since the kinetic data show that the reaction is strictly first order in [substrate], suggesting its participation in the slow step, and the mechanism proposed involves only a single step that is susceptible to structural effects. Therefore the insensitiveness of reaction rate could be attributed to the reason (c) given above.

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