Rate Data for Oxidation of p-Methylphenylhydrazine with Thallium (III) in Acid Chloride Solutions

U S BANTHIYA, B C JOSHI & Y K GUPTA*

Department of Chemistry, University of Rajasthan, Jaipur

The oxidation of p-methylphenylhydrazine (PMP) with Tl(III) in acid chloride solutions shows a first order dependence each on [Tl(III)], and [PMP] and an inverse dependence on [H⁺] and [Cl⁻]. Its reactivity is guided by the complex formation between Tl(III) and PMP.

A recent paper[1] from our laboratory described the oxidations of phenylhydrazine(P), p-nitrophenyl-hydrazine(PNP), o-nitrophenylhydrazine (ONP) and 2,4-dinitrophenylhydrazine (DNP) with thallium(III) in acid chloride solutions. p-Methylphenylhydrazine (PMP) is a similar compound and its oxidation has now been studied in [Cl⁻] range of 0.6 to 2.5 mol dm⁻³.

Experimental procedure and the reagents employed were the same as described earlier[1]. PMP. HCl was kindly provided by Prof. H A Itano, University of California, USA and its solution was prepared in perchloric acid of known concentration and standardized iodometrically. In the [Cl⁻] range of 0.6-2.5 mol dm⁻³ the predominant chlorocomplexes of thallium(III) would be $TlCl_4^-$. The range of [H⁺] investigated was 0.6 to 1.5 mol dm⁻³ and in this range the predominant species of PMP would be monoprotonated PMP. Stoichiometric investigations showed that the reaction occurred according to Eq. (1),
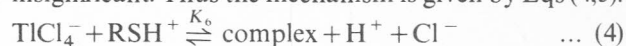
$$CH_3.C_6H_4.NH.NH_2 + 2Tl(III) + H_2O \rightarrow$$
$$CH_3.C_6H_4OH + Tl(I) + N_2 + 4H^+ \qquad ... (1)$$
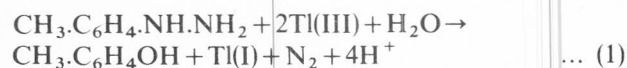
The final product phenol was identified by tlc. The presence of intermediate diazonium salt was confirmed by reaction with alkaline β-naphthol at 0-5° and the formation of an azo dye. The diazonium salt decomposes[2,3] to the corresponding phenol and nitrogen as shown in Eq. (2)

$$CH_3.C_6H_4.N^+ \equiv N + H_2O \rightarrow CH_3.C_6H_4OH$$
$$+ N_2 + H^+ \qquad ... (2)$$
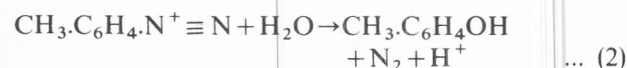
If the diazonium salt is isolated at low temperature and reacted with H_3PO_2, corresponding hydrocarbon is obtained (Eq. 3).

$$CH_3.C_6H_4.N_2^+ + H_3PO_2 + H_2O \rightarrow$$
$$CH_3.C_6H_5 + N_2 + H_3PO_3 + H^+ \qquad ... (3)$$
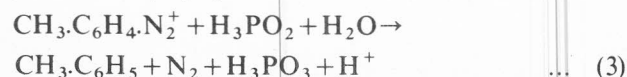
The first and second protonation constants[3] of PMP have been determined and found to be 2.5×10^5 and 0.08 dm³ mol⁻¹ respectively. Hence the concentration of unprotonated and diprotonated species would be insignificant. Thus the mechanism is given by Eqs (4,5).

$$TlCl_4^- + RSH^+ \overset{K_6}{\rightleftharpoons} complex + H^+ + Cl^- \qquad ... (4)$$

$$complex \overset{k}{\rightarrow} products \qquad ... (5)$$

where K_6 is the complex formation constant between chlorocomplexes of Tl(III) and PMP.
The rate law is given by Eq. (6),

$$-d[Tl(III)]/dt =$$
$$kK_6[Tl(III)] [PMP]/[H^+][Cl^-] \qquad ... (6)$$

In the oxidation of PMP the concentration of Tl(III) was varied in the range $(0.86-10.6) \times 10^{-3}$ mol dm⁻³ and that of PMP in the range $(1-16) \times 10^{-3}$ mol dm⁻³. A plot of initial rate[4] versus [Tl(III)] or [PMP] was linear passing through the origin showing first order dependence. Second-order rate constants $(kK_6 = k_2)$ were calculated from the initial rates as well as from pseudo-first order rate constants. There was good agreement in the two sets of values (Table 1). Similarly plots of initial rate or k_2 versus $[H^+]^{-1}$ and $[Cl^-]^{-1}$ were linear passing through the origin, thereby providing support to the rate law (6). Second order rate constants were obtained under the conditions $[H^+]$ = 0.5 mol dm⁻³, $[Cl^-]$ = 2.0 mol dm⁻³ and I = 3.75 mol dm⁻³ at different temperatures. The values of k_2(dm³mol⁻¹s⁻¹) were 0.085 ± 0.005, 0.15 ± 0.01 and 0.24 ± 0.01 at 25°, 30° and 35° respectively. The same values were obtained after multiplying them with $[Cl^-]$ and $[H^+]$ and thus they represent kK_6. The energy and entropy of activation were found to be 75 ± 0.4 kJ and mol⁻¹ and -22 ± 2 J K⁻¹mol⁻¹ respectively.

A comparison of the present results with those of Table 4 of the earlier paper[1] shows that the rate constants of this study are intermediate between those of P and PNP on one hand, and ONP and DNP on the other

Table 1—Values of $k_2 = kK_6$ for the Oxidation of PMP with Thallic Perchlorate from Various Rate Dependences at 30°

Type of dependence	Conc. range (mol dm⁻³)	k_2 (dm³mol⁻¹s⁻¹)	I (mol dm⁻³)
Tl(III)	$(0.86-10.6) \times 10^{-3}$	0.42 ± 0.02	2.4
PMP	$(1-16) \times 10^{-3}$	0.36 ± 0.04	2.5
H⁺	0.6 − 1.5	0.21 ± 0.02	3.5
Cl⁻	0.6 − 2.5	0.19 ± 0.02	3.5

hand, i.e., the second order rate constants follow the order:DNP> ONP > PMP > P> PNP. This behaviour of PMP can be rationalised as follows. Methyl group being an electron donating group, increases the electron density at the nitrogen thereby facilitating complex formation between Tl(III) and PMP. Though there is no kinetic evidence for complex formation, spectrophotometric results do provide marginal evidence. Further inhibition of the reaction by chloride ions is an indirect evidence for the complex formation.

References

1 Banthiya U S, Joshi B C & Gupta Y K, *Indian J Chem*, **20A** (1981) 43.
2 Bunnett J F & Zahler R E, *Chem Rev*, **49** (1951) 273.
3 Miller C O & Furman N H, *J Am chem Soc*, **59** (1937) 161.
4 Gupta A K, Ph.D. Thesis, Rajasthan University (1981).
5 Latshaw M, *J Am chem Soc*, **47** (1925) 793.