Oxidation of Hydrazine, Phenylhydrazine & Substituted Phenyl-hydrazines by Thallium(III) — Substituent Effects & Mechanism

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The kinetics of Tl(III) oxidation of hydrazine have been studied at different [substrate], [oxidant], acidity, ionic strength and temperatures in the presence of sodium chloride. The reaction exhibits a first order dependence on [Tl(III)] and [Hydrazine] and an inverse first order dependence on [Cl⁻] and [H⁺]. $Tl(OH)^{2+}$ is shown to be the active species under these conditions. Also the substituent effects in the Tl(III) oxidation of phenylhydrazine are reported. Hammett plot shows considerable scatter. Both bond formation and bond breaking are shown to be significant in this reaction. A suitable mechanism is proposed for the Tl(III) oxidation of phenyl-hydrazine.

ALTHOUGH the oxidation of hydrazine with thallium(III) has been investigated[1,2] the kinetic aspects of this reaction have not been studied fully. We have, therefore, investigated this reaction at different [substrate], [oxidant], acidity, ionic strength and temperature. Also, the kinetics and mechanism of oxidation of phenylhydrazine and substituted phenylhydrazines by thallium(III) do not seem to have been investigated so far. It is, however, known that this reaction proceeds elegantly to give the corresponding hydrocarbons. In view of the fact that Tl(III) behaves as a two-electron oxidant in its reaction with hydrazine[3], it was of interest to study the reaction between Tl(III) and phenylhydrazine from the kinetic point of view.

Materials and Methods

Hydrazine sulphate and thallium(III) oxide (BDH, 99% pure) were used as such. Phenylhydrazine and substituted phenylhydrazines (Koch-Light/Fluka AG) were of extra pure variety which were used either after a redistillation or recrystallization from suitable solvents. The reaction was monitored by estimating the unreacted [Tl(III)] by an iodometric procedure to a starch end-point[4]. As the reactions between Tl(III) and the substrates were generally very fast, the reaction rate was controlled by the initial addition of NaCl. The reactions were followed for over 3 half-lives and the data reported are the average of at least two runs in each case. The second order constants reported have been calculated from integrated second rate equations.

Results and Discussion

Dependence on thallium(III), hydrazine sulphate and phenylhydrazine — The oxidation of hydrazine sulphate by Tl(III) was studied in $2M$ sulphuric acid in the presence of $0.2M$ Na_2SO_4 and $0.005M$ NaCl, between 25° and 40°. The second order rate constants at different [hydrazine sulphate] in $2M$ sulphuric acid in the absence of chloride ion (at a conveniently low temperature) and also in the presence of $0.005M$ NaCl are summarized in Table 1.

These data show that the oxidation of hydrazine sulphate by Tl(III) is governed by the rate expression

$$-\frac{d[Tl(III)]}{dt} = k_2 [Tl(III)] [\text{hydrazine sulphate}]$$

The reaction exhibits total second order dependence — first order in [Tl(III)] and first in [phenyl hydrazine] as shown by log $(a-x/b-x)$ versus time plot (Fig. 1). The rate law for the oxidation of phenylhydrazines in $2M$ H_2SO_4 in the presence of $0.25M$ NaCl is also of the form

$$-\frac{d[Tl(III)]}{dt} = k_2 [Tl(III)] [\text{phenylhydrazine}]$$

Effect of acidity on the reaction rate — The effect of varying sulphuric acid on the rate was studied

TABLE 1 — RATE DEPENDENCE ON [Tl(III)] AND [HYDRAZINE SULPHATE] IN THE ABSENCE AND PRESENCE OF NaCl

{$[H_2SO_4]=2.0M$; $[Na_2SO_4]=0.2M$; temp.$=30°$}

[Reactant] M	$k \times 10$ litre mole⁻¹ sec⁻¹
(A) VARYING [Tl(III)] (A)	
0.001398	2.40
0.002070	2.20
0.002705	2.07
(B) VARYING [HYDRAZINE SULPHATE] (B)	
0.003056	74.0
0.003820	78.4
(C)	
0.002270	2.20
0.002406	2.06
0.004675	2.02
0.005792	2.09
0.006951	2.36
(D)	
0.00250	5.18
0.005640	5.05

(A) [Tl(III)]/[NaCl]=1 : 2.5.
(B) In the absence of NaCl.
(C) In the presence of $0.005M$ NaCl at $2.0M$ H_2SO_4.
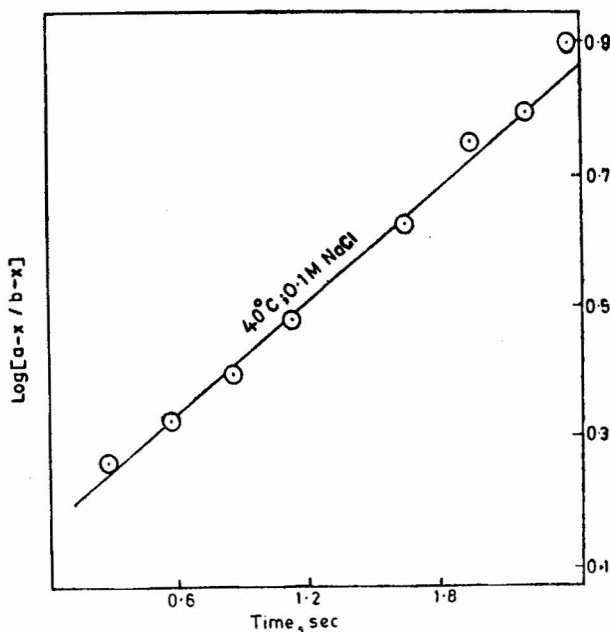(D) In the presence of $0.005M$ NaCl at $1.0M$ H_2SO_4.

Fig. 1 — Second order plot for the oxidation of 2,4-dinitro-phenylhydrazine by Tl(III); [NaCl]$=0.1M$; and temp.$=40°$

at different [H$^+$] in the range 0·5 to 5·0M. The reaction rate drops with increasing acidity up to 2·0M. Beyond this acidity, there is only small increase in the rate (Table 2). It is observed that a plot of log [H$^+$] against log k_2 is linear with a slope equal to —1 up to 2M.

Effect of added chloride ion on reaction rate — Added chloride ion reduces the reaction rate considerably (Table 3). A plot of log k_2 versus log [Cl$^-$] is linear with a slope equal to —1.

Dependence on ionic strength — The effect of added Na$_2$SO$_4$ and KHSO$_4$ in the range 0·2 to 2·0M on the oxidation rate shows that the reaction rate increases with an increase in Na$_2$SO$_4$ concentration; the rate is unaffected by changes in added KHSO$_4$ (Table 4).

Substituent effect — The effect of suitably positioned substituents in the phenyl ring of phenylhydrazine has been studied for the following compounds, viz. 4-bromo, 4-chloro, 4-nitro, 2-,nitro and 2,4-dinitro between 25° and 40°. Table 5 gives a comparative picture of the effect of substituents on the reactivity. It is evident from the magnitude of these changes in the rate constants that the reaction is susceptible to polar effects. The rate data (Table 5) have been cast into a Hammett plot in Fig. 2. The points are considerably scattered. All substituents except the 2,4-dinitro groups increase the rate. This type of scatter in Hammett plots is not quite uncommon and is encountered with reactions in which either a change of mechanism occurs or when both bond formation and bond breaking are significant.

Mechanism of oxidation of hydrazine and phenyl-hydrazine — From the experimentally observed inverse dependence on the rate of the reaction on [H$^+$] and [Cl$^-$], certain conclusions can be drawn on the nature of the active species in this reaction. In the presence of added chloride ion, it can be

assumed that the whole of the Tl(III) species is initially present as unreactive TlCl^{2+}. However, a partial hydrolysis of this will give the more reactive species Tl(OH)$^{2+}$ (Eq. 1). The rate of hydrolysis

TABLE 2 — EFFECT OF ACIDITY ON Tl(III) OXIDATION OF HYDRAZINE SULPHATE

{[Hydrazine sulphate]$=0.002M$; [NaCl]$=0.005M$; [Tl(III)] $=0.002M$; [Na$_2$SO$_4$]$=0.2M$; temp.$=30°$}

[H$_2$SO$_4$] M	$k_2 \times 10$ (litre mole^{-1} sec^{-1})
0·5	8·11
1·0	5·18
1·5	3·57
2·0	2·20
3·0	3·00
4·0	2·72
5·0	3·32

TABLE 3 — EFFECT OF ADDED CHLORIDE ION ON REACTION RATE

{[Hydrazine sulphate]$=0.002M$; [Tl(III)]$=0.002M$; [H$_2$SO$_4$] $=2M$; [Na$_2$SO$_4$]$=0.2M$; temp.$=30°$}

[NaCl] M	$k_2 \times 10^3$ (litre mole^{-1} sec^{-1})
0·005	220
0·0075	145
0·01	100
0·025	38·6
0·05	10·0
0·1	6·82

TABLE 4 — RATE DEPENDENCE ON ION STRENGTH

{[Hydrazine sulphate]$=0.002M$; [H$_2$SO$_4$]$=2M$; [Tl(III)] $=0.002M$; [NaCl$^-$]$=0.005M$; temp.$=30°$}

[Na$_2$SO$_4$] M	[KHSO$_4$] M	$k_2 \times 10$ (litre mole^{-1} sec^{-1})
—	—	—
0·2	—	2·20
0·4	—	3·15
1·0	—	5·79
1·5	—	5·57
2·0	—	8·16
—	0·2	2·62
—	0·4	2·64
—	0·8	2·83
—	1·0	2·37
—	1·5	2·78

TABLE 5 — SUBSTITUENT EFFECT IN Tl(III) OXIDATIONS OF SUBSTITUTED PHENYLHYDRAZINES (RC$_6$H$_4$—NH=NH$_2$)

{[Tl(III)]$=0.002M$; [Na$_2$SO$_4$]$=0.2M$; [H$_2$SO$_4$]$=2.0M$; [NaCl] $=0.25M$; temp.$=30°$}

R	k_2 (litre mole^{-1} sec^{-1})
H	1·51
4-Br	3·46
4-Cl	5·60
4-NO$_2$	1·71
2-NO$_2$	2·80
2,4-Dinitro	0·33

will be given by Eq. (2)

$$H_2O + TlCl^{2+} \rightleftharpoons Tl(OH)^{2+} + H^+ + Cl^- \qquad ...(1)$$
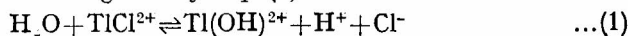
$$K_h = \frac{[Tl(OH)^{2+}][H^+][Cl^-]}{[TlCl^{2+}]} \qquad ...(2)$$

Eq. (2) can be rewritten as

$$[Tl(OH)^{2+}] = \frac{K_h[TlCl^{2+}]}{[H^+][Cl^-]} \qquad ...(3)$$

From the rate expression,

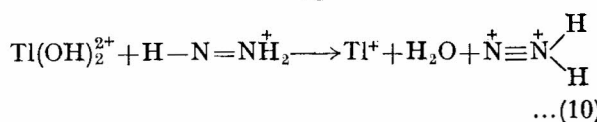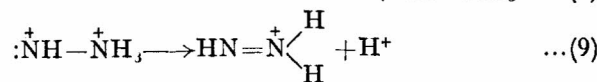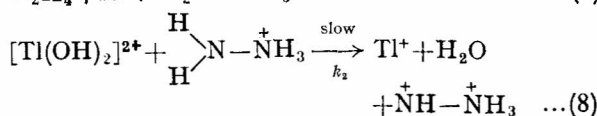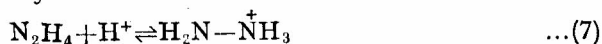$$\frac{-d[Tl(III)]}{dt} = k_{obs}[Tl(III)] \text{ [hydrazine sulphate]} \qquad ...(4)$$

$$= \frac{k_2 K_h[TlCl^{2+}]}{[H^+][Cl^-]} \text{ [hydrazine sulphate]} \qquad ...(5)$$

Therefore, $k_{obs} = k_2 K_h/[H^+][Cl^-]$ ...(6)

K_h value calculated from our experimental results on the basis of k_{obs} versus $1/[H^+]$ and k_{obs} versus $1/[Cl^-]$ plots comes to 2.63×10^{-5} (ref. 6). On the basis of the foregoing data the mechanism shown in Scheme 1 can be formulated for the oxidation of hydrazine.

$$N_2H_4 + H^+ \rightleftharpoons H_2N - \overset{+}{N}H_3 \qquad ...(7)$$

$$[Tl(OH)_2]^{2+} + \overset{H}{\underset{H}{>}}N - \overset{+}{N}H_3 \xrightarrow[k_2]{slow} Tl^+ + H_2O + \overset{+}{N}H - \overset{+}{N}H_3 \quad ...(8)$$

$$:\overset{+}{N}H - \overset{+}{N}H_3 \longrightarrow HN = \overset{+}{N}\overset{H}{\underset{H}{<}} + H^+ \qquad ...(9)$$

$$Tl(OH)_2^{2+} + H - N = N\overset{+}{H}_2 \longrightarrow Tl^+ + H_2O + \overset{+}{N} \equiv \overset{+}{N}\overset{H}{\underset{H}{<}} \qquad ...(10)$$

$$\overset{+}{N} = \overset{+}{N}\overset{H}{\underset{H}{<}} \longrightarrow N \equiv N + 2H^+$$
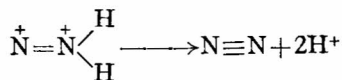
Scheme 1

The mechanism shown in Scheme 2 may be proposed for the oxidation of phenylhydrazines by Tl(III).

This mechanism is consistent with the substituent effects observed with ring substituted phenylhydrazines. First the introduction of a phenyl ring boosts the rate of oxidation by a factor of 1000. This is
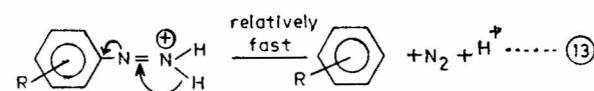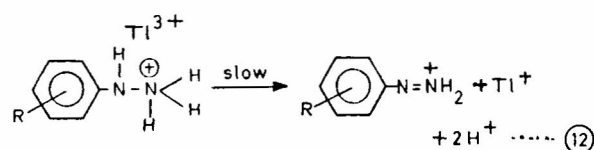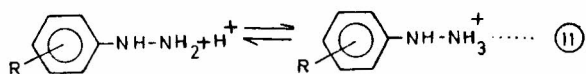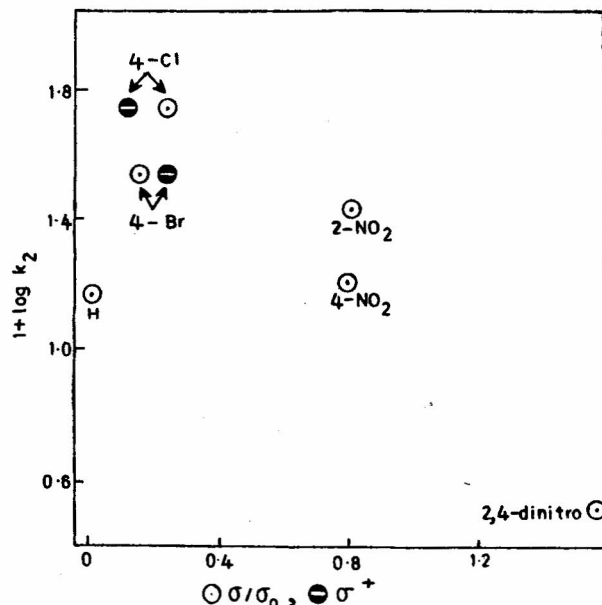
Scheme 2

Fig. 2 — Hammett plot for substituted phenylhydrazines; $[H_2SO_4] = 2M$; $[Na_2SO_4] = 0.2M$; $[NaCl] = 0.25M$; and temp. $= 30°$

consistent with the stabilization that the developing double bond in the slow step (Eq. 12) will get from the phenyl ring. Further the scatter in Hammett plot stresses that both bond formation and bond breakage are important (Fig. 2). A 4-bromo or a 4-chloro substituent will not stabilize the developing double bond in the slow step but will also aid the cleavage of $-N-H$ bond. The fact that a 4-NO$_2$ function also increases the rate is strongly indicative of the fact that the breaking of the C$-$N bond in step (13) is also relatively important. This duality of slow steps would account for the observed structure-activity relationship. The increased rate for 2-nitrophenylhydrazine can be traced to a field effect of the type (I) which would stabilize the

I
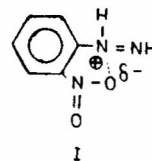
product of reaction (12). With two strongly electron withdrawing nitro groups, however, the removal of hydrogen as hydride anion in step (12) is strongly retarded, leading to a lowered rate.

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