

Kinetics & Mechanism of Oxidation of Phenylhydrazine, *p*-Nitrophenylhydrazine, *o*-Nitrophenylhydrazine & 2,4-Dinitrophenylhydrazine with Thallium(III) in Acid Chloride Medium

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Kinetics of Tl(III) oxidation of the title substrates in acid chloride medium have been investigated iodometrically. The reaction in the absence of chloride ions is very fast. The mechanism involves complex formation between Tl(III) and the phenylhydrazine before the redox reaction occurs. The order of reactivity is 2,4-dinitrophenylhydrazine > *o*-nitrophenylhydrazine > phenylhydrazine \approx *p*-nitrophenylhydrazine. Nitro group at *para*-position has the usual electron withdrawing effect, but substitution at *ortho*-position helps in the formation of a chelate with Tl(III) resulting in larger rate in the case of *o*-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine.

THE kinetic studies on the oxidation of hydrazine with thallium(III) in aqueous perchloric acid¹, aqueous acetic acid² and chloride media, carried out in the authors' laboratory indicate that the redox reaction is preceded by complex formation between thallium(III) and hydrazine. The formation constant, though small in magnitude, appears to play a significant role in controlling the overall reaction rate. It is, therefore, considered of interest to investigate the oxidation of phenylhydrazine (P), *p*-nitrophenylhydrazine (PNP), *o*-nitrophenylhydrazine (ONP) and 2,4-dinitrophenylhydrazine (DNP) from the viewpoint of complex formation and reactivity of the complexes.

The kinetics of oxidation of P and DNP by Tl(III) have been studied by Srinivasan and Venkatasubramanian⁴ in a medium of sulphate and chloride. Since Tl(III) forms complexes with both sulphate⁵ and chloride⁶, the reactive species of Tl(III) is less-defined in such systems. Similarly hydrogen ion dependence needs to be re-investigated employing only aqueous perchloric acid solutions. Since the reactions in aqueous perchloric acid are immeasurably fast, they have been carried out in suitable chloride medium to permit conventional methods of analysis.

Materials and Methods

Thallic perchlorate was prepared by dissolving thallic oxide (BDH) in 70% perchloric acid (E. Merck) and standardized iodometrically^{7,8}. Fresh solutions of P, prepared by dissolving the required quantity of the reagent (Riedel) in distilled water, were always used. Solutions of DNP (BDH, AR) were prepared by dissolving the required quantity of the compound in perchloric acid and standardized iodometrically⁹. PNP and ONP were prepared by the known methods¹⁰ and their solutions were prepared as in the case of DNP.

Lithium perchlorate was prepared by dissolving lithium carbonate (BDH) in 70% HClO₄, heating to expel CO₂ and adjusting the pH of the cooled solution to 6.7-7.0. Solutions of sodium perchlorate were prepared in the usual way by direct weighing. Doubly distilled water, second distillation being from the permanganate, was employed for preparing all solutions.

Kinetic procedure — Reactions were carried out at 30° ± 0.1°C, unless otherwise mentioned. The total volume of the reaction mixture was 50 ml. The kinetics were followed by removing 5ml aliquots of the reaction mixture at regular intervals and estimating Tl(III) iodometrically^{7,8}. The duplicate rate measurements were reproducible within ± 5%. The rate constants were calculated from the pseudo-first order plots (excess reducing substance) and also from the initial rates determined by the plane mirror method¹¹. In general, the results obtained from initial rates were similar to those obtained from the first order plots.

Spectrophotometry — Absorptions of mixtures of Tl(III) and the phenylhydrazines in the presence of chloride ions were measured in the following way since Tl(III) and the phenylhydrazines would react during the time of measurement. At each wavelength the two reactants were mixed and absorptions were noted at intervals of one, two and three minutes, and extrapolated to zero time to obtain the absorption of unreacted mixture. This procedure though not very accurate, was the only way to know the absorption patterns of mixtures of Tl(III) and different phenylhydrazines.

Stoichiometry — The results of stoichiometric runs indicated that each mol of any phenylhydrazine required (2 ± 0.1) mol of Tl(III) and the product was phenol or substituted phenol and nitrogen (Eq. 1).



Phenol, *p*-nitrophenol, *o*-nitrophenol and 2,4-dinitrophenol respectively were obtained from P, PNP, ONP and DNP by ether extraction and characterised (m.m.p.).

Results

Thallium(III) dependence — The concentration of Ti(III) was varied in the range 6×10^{-4} to 2×10^{-2} M at fixed $[\text{H}^+]$ and $[\text{Cl}^-]$. The results for all the reducing substances are given in Table 1. The plot of initial rate versus Ti(III) was linear passing through the origin in each case. The order in Ti(III) is thus one. In case of runs with excess reducing substance, first order plots were also drawn. Apparent second order rate constants (k_2) obtained from the initial rates (i.r.) and from the pseudo-first-order rate constants (k_1) were similar.

Reducing substance dependence — The concentration of the reducing substance was varied in the range 5×10^{-4} to 2×10^{-2} M at fixed concentrations of other reactants. The plot of initial rate versus concentration of reducing substance was linear passing through the origin. Under condition of excess reducing substance, first order plots were

TABLE 1 — EFFECT OF VARYING [Ti(III)] ON THE REACTION RATES IN THE OXIDATION OF VARIOUS PHENYLHYDRAZINES

[RS = reducing substance]				
$10^3[\text{Ti(III)}], M$	$10^6(\text{i.r.}), \text{mol sec}^{-1}$	$(\text{i.r.})/[\text{Ti(III)}][\text{RS}], M^{-1}\text{S}^{-1}$	$10^3k_1, \text{sec}^{-1}$	$k_1/[\text{RS}], M^{-1}\text{sec}^{-1}$
$10^3[\text{P}] = 0.825M; [\text{Cl}^-] = 2.0M; [\text{H}^+] = 0.5M; I = 2.5M$				
1.055	1.47	0.17	1.37	0.17
2.11	3.26	0.18	1.34	0.16
3.165	4.72	0.18	1.36	0.16
4.22	6.11	0.175		
5.275	8.0	0.18		
6.33	9.5	0.18		
$10^3[\text{PNP}] = 4.0M; [\text{Cl}^-] = 1.6M; [\text{H}^+] = 0.8M; I = 2.4M$				
1.35	5.8	0.11	3.76	0.094
2.70	11.8	0.11	3.26	0.082
4.05	17.3	0.11	3.26	0.082
5.40	22.0	0.10	3.3	0.083
6.75	29.1	0.11	3.68	0.092
8.10	36.6	0.11		
9.45	39.1	0.10		
10.8	46.2	0.11		
$10^3[\text{ONP}] = 6.0M; [\text{Cl}^-] = 1.2M; [\text{H}^+] = 0.8; I = 2.0M$				
0.625	1.40	0.37		
1.40	4.0	0.47		
2.70	8.1	0.50		
4.00	12.0	0.50		
$10^3[\text{DNP}] = 2.4M; [\text{Cl}^-] = 1.2M; [\text{H}^+] = 0.84M; I = 2.04M$				
0.6	3.80	0.26	7.0	0.29
1.075	8.0	0.31	7.6	0.32
2.375	16.2	0.29	7.5	0.31
3.41	22.5	0.28	7.8	0.32
4.67	29.8	0.27	7.4	0.31

also drawn. These data are given in Table 2 and the results in the two cases are similar.

Hydrogen ion dependence — Hydrogen ion concentration was varied from 0.2 to 1.5 M employing perchloric acid at constant ionic strength of 3.2 or 3.5 M adjusted with lithium perchlorate. The rate decreased with the increase in $[\text{H}^+]$. In the case of P and PNP, the plots of k_1 versus $[\text{H}^+]^{-1}$ were linear passing through the origin as shown in Fig. 1. In the other two cases the plots of $(k_1[\text{H}^+])^{-1}$ versus $[\text{H}^+]$ were linear with an intercept.

Chloride ion dependence — Since Ti(III) is known to form a number of complexes¹² with chloride ion, it was necessary to know the reactive chloro-species in the system and hence the $[\text{Cl}^-]$ was varied from 0.6 to 2.5 M at constant ionic strength of 3.0 M or

TABLE 2 — EFFECT OF VARYING THE CONCENTRATION OF REDUCING SUBSTANCE (RS) ON THE REACTION RATES IN THE OXIDATION OF VARIOUS PHENYLHYDRAZINES

$10^3[\text{RS}], M$	$10^6(\text{i.r.}), M \text{ sec}^{-1}$	$(\text{i.r.})/[\text{Ti(III)}][\text{RS}], M^{-1} \text{ sec}^{-1}$	k_1, sec^{-1}	$k_1/[\text{RS}], M^{-1} \text{ sec}^{-1}$
$10^{-3}[\text{Ti(III)}] = 1.07M; [\text{Cl}^-] = 2.0M; [\text{H}^+] = 0.30M; I = 2.3M; \text{RS} = \text{P}$				
1.98	0.48	0.22		
3.20	0.845	0.24		
4.80	1.12	0.23		
6.40	1.79	0.26	1.50	0.24
8.00	2.19	0.25	1.80	0.23
9.60	3.11	0.30	2.20	0.22
12.80	4.06	0.29	3.30	0.26
16.8	4.5	0.25	4.40	0.26
19.2	5.66	0.27	5.0	0.30
$10^3[\text{Ti(III)}] = 2.75M; [\text{Cl}^-] = 1.6M; [\text{H}^+] = 0.8; I = 2.4M; \text{RS} = \text{PNP}$				
1.0	0.35	0.12		
3.0	0.90	0.12		
5.0	1.50	0.11		
6.0	1.75	0.11	0.76	0.12
7.0	2.0	0.10	0.875	0.12
8.0	2.4	0.11	0.997	0.12
9.0	2.7	0.11	1.07	0.12
10.00	3.0	0.11	1.15	0.11
20.0	6.0	0.11	2.05	0.10
$10^3[\text{Ti(III)}] = 1.40M; [\text{Cl}^-] = 1.2M; [\text{H}^+] = 0.8M; I = 2.0M; \text{RS} = \text{ONP}$				
0.50	0.30	0.43		
1.0	0.50	0.36		
2.0	1.40	0.50		
4.0	3.0	0.54	1.70	0.42
6.0	4.0	0.48	2.50	0.42
8.0	5.9	0.53	3.50	0.43
$10^3[\text{Ti(III)}] = 2.37M; [\text{Cl}^-] = 1.2M; [\text{H}^+] = 0.84M; I = 2.04M; \text{RS} = \text{DNP}$				
0.553	0.50	0.38		
0.885	0.70	0.33		
1.105	1.00	0.37		
2.21	1.70	0.33		
6.64	5.60	0.35		
8.85	6.80	0.32	2.97	0.33
11.05	8.60	0.33	4.03	0.37
18.2	14.0	0.33	4.86	0.27
24.0	18.4	0.32	8.83	0.37

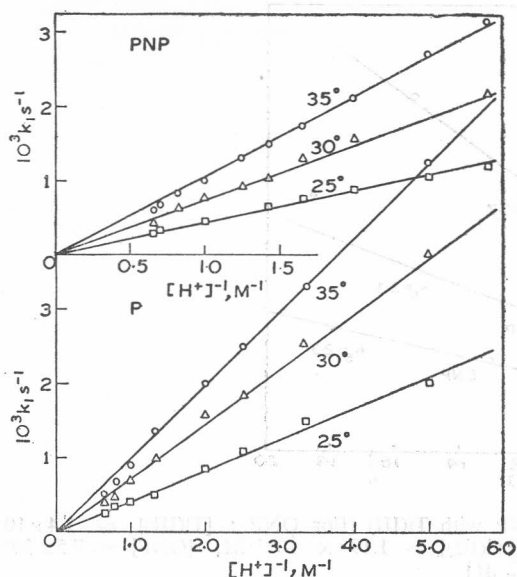


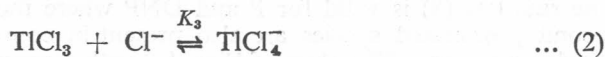
Fig. 1 — Hydrogen-ion dependence in the oxidation of phenylhydrazine (P) and *p*-nitrophenylhydrazine (PNP) by Tl(III) {For P : [Tl(III)] = $2.10 \times 10^{-3} M$; [P] = $1.8 \times 10^{-2} M$; [Cl⁻] = $2.0 M$; $I = 3.5 M$; for PNP : [Tl(III)] = $2.22 \times 10^{-3} M$; [PNP] = $2.0 \times 10^{-2} M$; [H⁺] = $0.7 M$; $I = 3.2 M$; for ONP : [Tl(III)] = $1.4 \times 10^{-3} M$; [ONP] = $6.0 \times 10^{-3} M$; [H⁺] = $0.8 M$; $I = 3.2 M$; and for DNP; [Tl(III)] = $1.375 \times 10^{-3} M$; [DNP] = $9.5 \times 10^{-3} M$; [H⁺] = $0.73 M$; $I = 3.2 M$ }

3.2 *M* adjusted with sodium perchlorate. Concentrations lower than 0.6 *M* could not be employed because the reaction was too fast and could not be studied by conventional methods. In all the cases the plots of k_1 versus [Cl⁻]⁻¹ were linear passing through the origin (Fig. 2), indicating that only one chloro complex is significantly reactive in such chloride systems.

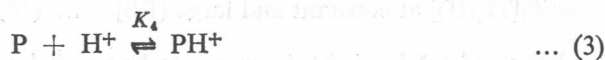
Effect of varying ionic strength—The pseudo-first-order rate constants considerably decreased with the increase in ionic strength (Table 3).

Discussion

Thallium (III) forms strong complexes¹³⁻¹⁵ with chloride, and formation constants for TlCl²⁺, TlCl₂⁺, TlCl₃ and TlCl₄⁻ have been reported¹⁴ to be 5.22×10^6 , 1.25×10^5 , 482 and 65.3 respectively at $I = 0.5 M$ and 25°. It is, therefore, obvious that in chloride systems employed, TlCl₄⁻ would predominantly be present in equilibrium with TlCl₃.



Since the hydrolysis constant of Tl³⁺ is very small¹⁶ as compared to the formation constants of chloro complexes, in all probability the hydrogen ion dependence is associated with the protonation of the phenylhydrazines through the following two equilibria (say for P).



First protonation constant for P and PNP are reported^{17,18} to be 1.86×10^5 and 2×10^4 res-

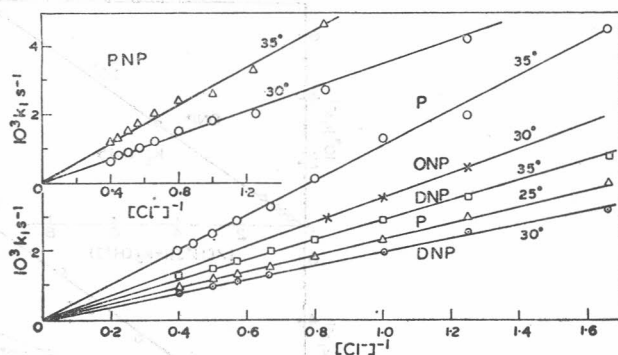
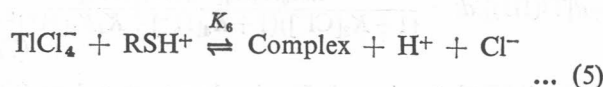


Fig. 2 — Chloride ion dependence in the oxidation of P, PNP, ONP and DNP with Tl(III) {For P : [Tl(III)] = $2.7 \times 10^{-3} M$; [P] = $1.8 \times 10^{-2} M$; [H⁺] = $0.5 M$; $I = 3.0 M$; for PNP : [Tl(III)] = $2.22 \times 10^{-3} M$; [PNP] = $2.0 \times 10^{-2} M$; [H⁺] = $0.7 M$; $I = 3.2 M$; for ONP : [Tl(III)] = $1.4 \times 10^{-3} M$; [ONP] = $6.0 \times 10^{-3} M$; [H⁺] = $0.8 M$; $I = 3.2 M$; and for DNP; [Tl(III)] = $1.375 \times 10^{-3} M$; [DNP] = $9.5 \times 10^{-3} M$; [H⁺] = $0.73 M$; $I = 3.2 M$ }

pectively. The protonation constants ONP and DNP are also likely to be large and hence all the phenylhydrazines would be largely protonated, but the unprotonated species appears to be the reactive species. However, in the case of P and DNP the results show that further protonation is also significant and hence both the protonated species would exist in the system. The second protonation constant could be estimated kinetically by a plot of $(k[\text{H}^+])^{-1}$ versus [H⁺]. The values of K_5 were thus estimated to be 3.3 and $0.45 M^{-1}$ at 30° respectively. The values for P at 25° and 35° were found to be 2.3 and $5.7 M^{-1}$ respectively. The plots of k_1 versus reciprocal of [H⁺] ($1 + K_5[\text{H}^+]$) were linear passing through the origin (Fig. 3).

Another fact of mechanistic importance is the complex formation between chloro-complexes of Tl(III) and the phenylhydrazines. There is no kinetic evidence, but the spectrophotometric results show this (Fig. 4). Further there is red shift in the absorption pattern with the introduction of nitro group in the benzene ring and the shift becomes larger with the introduction of two nitro groups. This is in line with the electron withdrawing character of the nitro group. Also the fact the chloride ions decelerate the rate, is an indirect evidence¹⁹ for the complex formation since in the presence of chloride ions, the coordination sites on Tl(III) are blocked and the complex formation between Tl(III) and phenylhydrazine which precedes the redox process, is inhibited. If the predominant species TlCl₄⁻ and RSH⁺ (where RS is the reducing substance) are considered to be reactive, the mechanism is given by Eqs (5) and (6).



Considering the various equilibria and the above

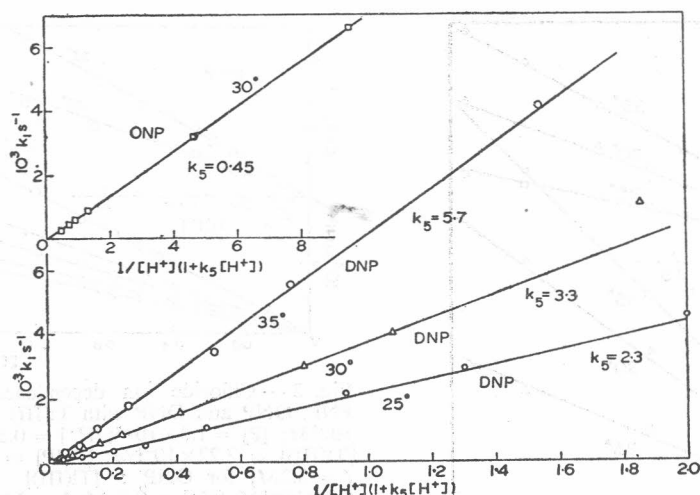


Fig. 3 — Hydrogen ion dependence in the oxidation of ONP and DNP with Ti(III) {For ONP : $[Ti(III)] = 1.4 \times 10^{-3} M$, $[ONP] = 6.0 \times 10^{-3} M$; $[Cl^-] = 1.2 M$; $I = 3.2 M$; and for DNP : $[Ti(III)] = 1.19 \times 10^{-3} M$; $[ONP] = 7.5 \times 10^{-3} M$; $[Cl^-] = 1.2 M$; $I = 3.2 M$ }

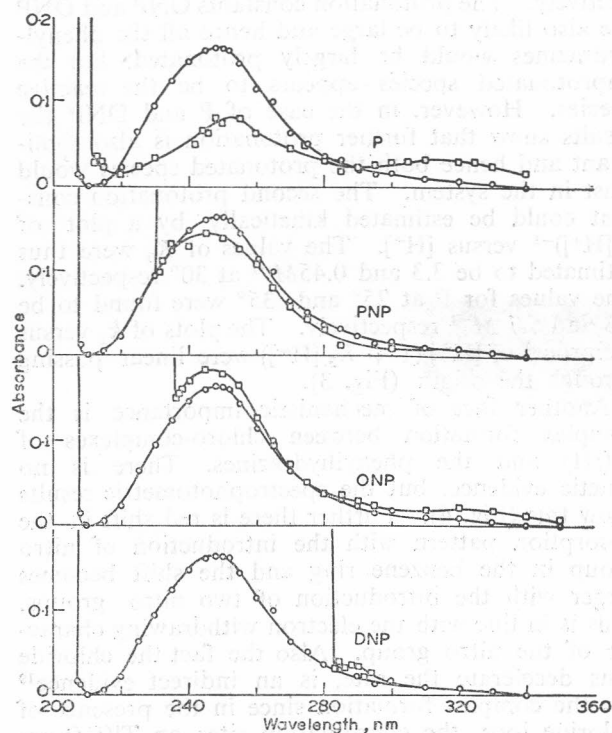


Fig. 4 — Absorbance of thallium(III) and mixtures of Ti(III) and P, PNP, ONP or DNP in chloride medium ($[H^+] = 0.5 M$; $[Cl^-] = 2.0 M$; $[Ti(III)] = 1 \times 10^{-5} M$ (O); [P], [PNP], [ONP] or [DNP] = $4 \times 10^{-4} M$; (O))

two steps, the following rate law may be deduced :

$$-d[Ti(III)]/dt = \frac{kK_6K_3K_4[Ti(III)][RS]}{(1+K_3[Cl^-])(1+K_4[H^+]+K_4K_5[H^+]^2)} \quad \dots (7)$$

Since $K_3[Cl^-] \gg 1$ and K_4 is large, rate law (7) reduces to Eq. (8)

$$d[Ti(III)]/dt = \frac{kK_6[Ti(III)][RS]}{[Cl^-][H^+](1+K_5[H^+])} \quad \dots (8)$$

TABLE 3 — EFFECT OF VARYING IONIC STRENGTH IN THE OXIDATION OF PHENYLHYDRAZINES WITH Ti(III) IN CHLORIDE MEDIUM AT 30°

Conditions	$[NaClO_4]$ (M)	I (M)	$10^3 k_1$ (sec ⁻¹)
OXIDATION OF DNP			
$[Ti(III)] = 1.375 \times 10^{-3} M$	0	1.93	3.50
$[DNP] = 9.5 \times 10^{-3} M$	0.32	2.25	3.22
$[Cl^-] = 1.2 M$	0.96	2.89	1.68
$[H^+] = 0.73 M$	1.52	3.45	1.00
OXIDATION OF PNP			
$[Ti(III)] = 2.22 \times 10^{-3} M$	0	2.22	1.97
$[PNP] = 1.25 \times 10^{-3} M$	0.26	2.48	1.64
$[Cl^-] = 1.6 M$	0.80	3.02	0.80
$[H^+] = 0.6 M$	1.33	3.53	0.50
OXIDATION OF P			
$[Ti(III)] = 2.11 \times 10^{-3} M$	0.1	2.6	3.95
$[P] = 1.875 \times 10^{-2} M$	0.2	2.7	3.55
$[Cl^-] = 2.0 M$	0.5	3.0	2.65
$[H^+] = 0.5 M$			

The rate law (8) is valid for P and DNP where the second protonated species are also present in comparable amounts. The plots of Figs. 1-3 with respect to hydrogenion and Chlorideion dependences are obvious from Eq. (8). At constant $[H^+]$ and $[Cl^-]$, the rate law further reduces to Eq. (9).

$$-d[Ti(III)]/dt = k_2[Ti(III)][RS] \quad \dots (9)$$

or

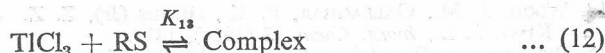
$$= k_1[Ti(III)] \text{ at constant and large } (RS) \quad \dots (10)$$

For PNP and ONP, $K_5 [H^+]$ appears to be much less than 1 and hence the rate law (8) reduces to Eq. (11)

$$-d[Ti(III)]/dt = \frac{kK_6[Ti(III)][RS]}{[Cl^-][H^+]} \quad \dots (11)$$

The values of k_2 which are equal to (kK_6) are given in Table 4. Since K_6 is not known, the value of k cannot be calculated.

An alternative mechanism leading to the similar rate laws (8) and (11) with $TlCl_3$ and RS as the reactive species, can also be given.



The rate law (13) can be easily deduced from (2), (3) and (4), and knowing that $K_3[Cl^-] \gg 1$ and $K_4[H^+] \gg 1$.

$$-d[Tl(III)]/dt = \frac{kK_{13}[Tl(III)][RS]}{K_3K_4[Cl^-][H^+](1+K_5[H^+])} \quad \dots (14)$$

In this case k_2 would be equal to kK_{13}/K_3K_4 . K_3 and K_4 are known, but K_{13} is again not known and hence k cannot be calculated. However, it should be

TABLE 4 — RATE CONSTANT (kK_6) FOR DIFFERENT PHENYLHYDRAZINES FROM VARIOUS CONCENTRATION DEPENDENCES

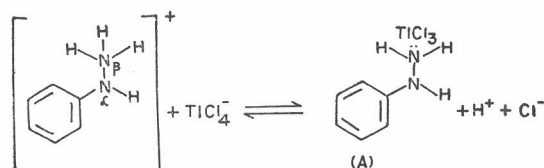
Type of conc. dependence	kK_6 M sec ⁻¹ at			I (M)
	25°	30°	35°	
PHENYLHYDRAZINE				
Tl(III)	—	(0.175 ± 0.01)* (0.165 ± 0.01)†		2.5
P	—	(0.156 ± 0.02)* (0.150 ± 0.012)†		2.3
H ⁺	(0.047 ± 0.003)†	(0.083 ± 0.002)†	(0.107 ± 0.006)†	3.5
Cl ⁻	(0.064 ± 0.0015)†		(0.139 ± 0.001)†	3.0
<i>p</i> -NITROPHENYLHYDRAZINE				
Tl(III)		(0.133 ± 0.006)* (0.110 ± 0.01)†		2.4
PNP		(0.140 ± 0.0025)* (0.147 ± 0.0013)†		2.4
H ⁺	(0.035 ± 0.0015)†	(0.060 ± 0.0015)†	(0.083 ± 0.002)†	3.2
Cl ⁻		(0.060 ± 0.0025)†	(0.098 ± 0.006)†	3.2
<i>o</i> -NITROPHENYLHYDRAZINE				
Tl(III)		(0.60 ± 0.05)* (0.61 ± 0.06)*		2.0
ONP		(0.55 ± 0.013)†		2.0
H ⁺		(0.138 ± 0.002)†		3.2
Cl ⁻		(0.130 ± 0.003)†		3.2
2,4-DINITROPHENYLHYDRAZINE				
Tl(III)		(1.06 ± 0.04)* (1.18 ± 0.04)†		2.0
DNP		(1.29 ± 0.08)* (1.27 ± 0.13)†		2.0
H ⁺	(0.25 ± 0.03)†	(0.60 ± 0.04)†	(1.13 ± 0.06)†	3.2
Cl ⁻		(0.53 ± 0.05)†	(1.15 ± 0.06)†	3.2

*From initial rates

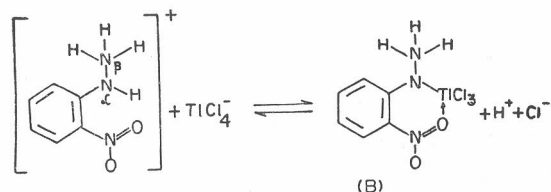
†From pseudo-first order plots.

emphasized that the two alternative mechanisms cannot be distinguished kinetically.

From Table 4 it is obvious that the rate constants for the four reactions are in the order DNP > ONP > P > PNP. These rate constants would depend primarily on the extent of complex formation between Tl(III) and the phenylhydrazines. The complexing tendency, in general, would depend on the availability of the lone pair of electrons on the nitrogen of the phenylhydrazines or the basicity of the phenylhydrazines. If we consider the pK_a values determined in mixtures of water and dioxan (50-50), the values for P, PNP, ONP and DNP are 4.66, 3.87, 3.72 and 3.57 respectively. This, therefore, is the order of decreasing basicity of the bases. It is obvious that the basic character alone of the base cannot explain the order of reactivity observed. Complex formation between Tl(III) and P or PNP can be explained by invoking coordination of $TlCl_4^-$ at the protonated P or PNP as shown in structure (A).



Introduction of nitro group at the *para*-position may slightly decrease the electron density at N(β), but the effect would not be much and hence the rates are not very different for PNP. In the case of ONP, the nitro group introduced at *ortho*-position is near N(α) and a chelate may be formed with Tl(III) (see structure B).



Although Tl(III) is known²⁰ to form complexes with oxygen donor, the complexing in general, is weak except in the case of carboxylates and particularly acetates²¹. In *para*-compound the complexation is more likely at nitrogen than at oxygen, but when both the sites are in proximity, a situation for chelation exists and it would take place readily. Thus the rate is larger in case of ONP than in P. With the introduction of one more nitro group, the electron density at N(α) of the phenylhydrazine decreases and the proton is less firmly held. Thus complexing tendency of DNP would increase and the rate would be larger than in case of ONP. It, therefore, appears that the basic reason for the difference in the rates of P and PNP on one hand, and ONP and DNP on the other, is the difference in the sites of complex formation.

