

# Oxidation of Nicotinic Acid Hydrazide (NH) And Iso-Nicotinic Acid Hydrazide (INH) by Iron(III) in Presence of Triazines (PDTS & PPDTS): A Mechanistic Study

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## ABSTRACT

Oxidation of nicotinic acid hydrazide (NH) and iso-nicotinic acid hydrazide (INH) by iron(III) in presence of triazines (i.e. 3-((2-pyridyl)-5,6-bis(4-phenyl sulphonic acid)-1,2,4 triazine (PDTS), 3-(4-(4-phenyl sulphonic)-2-pyridyl)-5,6-bis(4-phenylsulphonic acid)-1,2,4-triazine (PPDTS)) has been studied. These reactions enhanced in presence of triazines due to increase redox potential of Fe(III)/Fe(II) couple and also iron(III) acts as better oxidizing agent in presence of triazines. The oxidation of nicotinic acid hydrazide/ iso nicotinic hydrazide by iron(III) in the presence of PDTS is first order with respect to Fe(III). The reactions are accelerated by PDTS and plots of  $1/k_{obs}$  versus  $1/[PDTS]^2$  are straight lines with positive slopes and positive intercepts on the ordinate indicating the formation of a 1:2 complex between Fe(III) and PDTS. It has also been observed that these reactions are decelerated by  $H^+$  ion. Iron(III) exists mainly as hexa aquoiron(III) under the present experimental conditions. Activation parameters have been computed. Specific rate constants ( $k$ ) and equilibrium constants ( $K_1$  and  $K_2$ ) for iron(III)-PDTS-NH and iron(III)-PDTS-INH are nearly equal. This indicates that these two isomers show similar activity towards oxidation by iron(III). A similar trend is also noticed in the oxidation of NH/INH by iron(III) in the presence of PPDTS. The PDTS systems exhibit higher  $\Delta H^\ddagger$  values than the PPDTS systems. The entropies of activation,  $\Delta S^\ddagger$  for these reactions also fall in line with this analysis.  $\Delta S^\ddagger$  values are the lowest in the PPDTS systems which indicates that the transition states are highly ordered compared to those in the presence of PDTS.

**Keywords:** Oxidation, Fe(III), PDTS, PPDTS, Hydrazides And Kinetics

## I. INTRODUCTION

Ferriin chromogen is the most widely used colorimetric reagent for the determination of iron. Several compounds containing ferriin chromogen have been prepared and characterized [1-4]. The widest use of ferrozine (PDTS) in automated analyzers [5, 6], determination of iron in potable water [7] and in high purity reagent solutions [8]. The compound 3-(4-phenyl-2-pyridyl)-5,6-diphenyl-1,2,4-

triazine, PPDTS used for the determination of iron in sea water [9].

Redox reactions find analytical applications when the redox potential of the half-cell reactions differs by at least 0.2 V. In situations where this condition is not satisfied, it is often possible to alter the potential of the couple through a change in the activity of the oxidized or reduced form or of both, of a redox couple. In the presence of bipyridine and phenanthroline there is an increase in the redox potential [10] of

Fe(III)/Fe(II) couple:  $(\text{Fe}(\text{bpy})_3^{3+}/\text{Fe}(\text{bpy})_3^{2+}$ ,  $E^0 = 0.97$  V,  $\text{Fe}(\text{phen})_3^{2+}/\text{Fe}(\text{phen})_3^{3+}$ ,  $E^0 = 1.06$  V). Thus iron(III) acts as a better oxidizing agent in the presence of bipyridien and phenanthroline. Ratnam and Anipindi [11] studied the oxidation of hydroxylamine, semicarbazide and thiosemicarbazide by iron(III) in the presence of PDTS, PPDTS by conventional spectrophotometry.

Iso-nicotinic acid hydrazide, INH is affront-line drug which forms part of the core treatment of tuberculosis. The kinetic and mechanistic study of the oxidation of INH and its meta-isomer has drawn the attention of several investigators [12-14].

## II. MATERIALS AND METHODS

Nicotinic acid hydrazide (NH), isonicotinic acid hydrazide (INH) obtained from Fluka AG & PDTS and PPDTS obtained from GFS Chemicals Inc. Columbus, USA were used as such without any further purification. All the chemicals employed were of analytical reagent grade. Millipore water was used for the preparation of all the solutions.

### 2.1 Equipment

The absorption spectra were recorded using a Shimadzu 1800 UV-visible recording spectrophotometer. The kinetic runs were also performed in this instrument by attaching a cell positioned CPS 240A having a six cell holder in which the temperature can be controlled to  $\pm 0.1$  °C by Peltier effect. The reactants were thermally equilibrated to the experimental temperature using a Shimadzu TB-85 thermobath.

### 2.2 Product analysis

The visible absorption spectra of the products show a single absorption maximum at 562 nm. The molar extinction coefficient values of the products,  $28000 \pm 200$  agree well with that of  $\text{Fe}(\text{PDTS})_3^{4+}$  indicating that iron(III) is quantitatively reduced to iron(II) and forms  $\text{Fe}(\text{PDTS})_3^{4+}$ , similarly the visible absorption spectra of the products obtained in the presence of

PPDTS show  $\lambda_{\text{max}}$  at 563 nm with molar extinction coefficient values  $30700 \pm 200$  confirming  $\text{Fe}(\text{PPDTS})_3^{7-}$  as the final product.

### 2.3 Stoichiometry

A known excess of iron(III) was added to a solution containing known amounts of hydrazide (NH/INH), triazine (PDTS/PPDTS). The reaction was allowed to completion, which is indicated by the constancy of absorbance of the reaction mixture. The amount of iron(II) formed was computed from the absorbance at 562 nm and using the molar extinction coefficient value of 27900 for  $\text{Fe}(\text{PDTS})_3^{4+}$  in presence of PDTS, while in presence of PPDTS, the amount of iron(II) was computed from the absorbance at 563 nm and using the molar extinction coefficient value of 30700 for  $\text{Fe}(\text{PPDTS})_3^{7-}$ . Iron(II) formed was calculated and from this amount of iron(III) reacted was calculated. From these values the ratio of the amount of iron(III) and NH/INH reacted has been computed. The results are presented in Table 1. The results suggest that the stoichiometric ratio,  $[\text{Fe(III)}] : [\text{Sub}]$  is 4:1 for both oxidations of NH/INH in presence of PDTS and PPDTS.

### 2.4 Free radical test

The free radical intermediates formation was tested by using acrylonitrile. These tests were performed by taking requisite quantities of the substrate (NH/INH), triazine (PDTS/PPDTS),  $\text{HNO}_3$  and acrylonitrile. Precipitate or turbidity was not noticed in the reaction mixture indicating the absence of free radical intermediates.

### 2.5 Kinetic procedure

The kinetics of these reactions was followed at 562 nm and 563 nm in the presence of PDTS and PPDTS respectively. Absorbance values at different time intervals,  $A_t$  were recorded against water as blank and the absorbance values at infinite time  $A_\infty$  were obtained by allowing the reaction mixtures to stand sufficient time so that reactions go to completion. The pseudo-first order rate constants,  $k_{\text{obs}}$  were evaluated from the slopes of the plots of time,  $t$  versus  $\log(A_\infty -$

A<sub>t</sub>). About 50 % of the kinetic runs were performed in duplicate.

### III. RESULTS AND DISCUSSION

#### 3.1 Effect of iron(III)

The kinetics of these reactions was followed under pseudo-first order conditions isolating the oxidant i.e., [NH]/[INH], [triazine]  $\gg$  [Fe(III)]. Kinetic runs were carried out varying the concentrations of iron(III) and keeping the concentrations of NH/INH, PDTS/PPDTS, HNO<sub>3</sub> and ionic strength are constant.  $k_{obs}$  values are independent of the initial concentrations of Fe(III) are confirming that these are first-order in iron(III) (Table 2).

#### 3.2 Effect of substrate

Kinetics were studying the concentrations of NH/INH and keeping the concentrations of Fe(III), PDTS/PPDTS, hydrogen ion and ionic strength are constants. It has been observed that the rate of the reaction increases with increase in the concentration of substrate. The rates are tabulated in Table 2. Plots of  $1/k_{obs}$  versus  $1/[substrate]$  are perfect straight lines with positive slopes and positive intercepts on the ordinate indicating a Michaelis-Menten type of behavior suggesting the formation of 1:1 complex between iron(III) and substrate (Figure 1).

#### 3.3 Effect of triazine

Kinetic runs were carried out at various [PDTS]/[PPDTS], keeping [oxidant], [substrate], [H<sup>+</sup>] and ionic strength constant. The rate data (Table 2) indicates that the  $k_{obs}$  values increase with increases in [triazine]/ Plots of  $1/k_{obs}$  versus  $1/[triazine]^2$  are linear with positive slopes and positive intercepts on the ordinate, indicating Michaelis-Menten behavior (Figure 2) which confirms the formation of 1:2 complex between Fe(II) and triazine.

#### 3.4 Effect of hydrogen ion

Kinetic runs were also performed at different [H<sup>+</sup>], keeping the concentrations of Fe(III), triazine and NH/INH constant and the pseudo-first order

constants were evaluated and presented In Table 2. The data suggest that these reactions are decelerated by hydrogen ion.

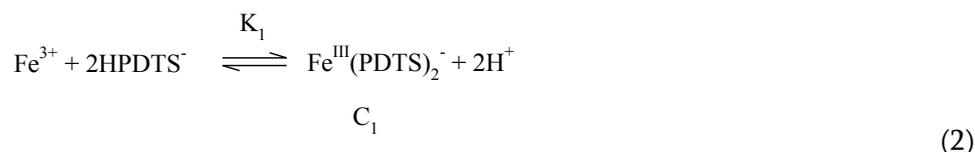
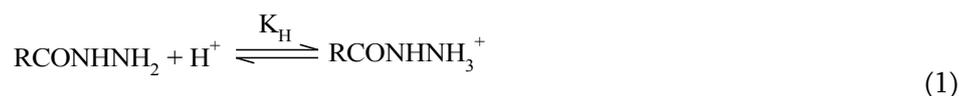
#### 3.5 Effect of ionic strength

The  $k_{obs}$  values were also evaluated at different  $\mu$  values, keeping the concentrations of all other reactants constant. The data shows that the rate of reaction is independent of ionic strength (Table 2). This shows that the rate-determining step involves an ion and a neutral molecule or two neutral species.

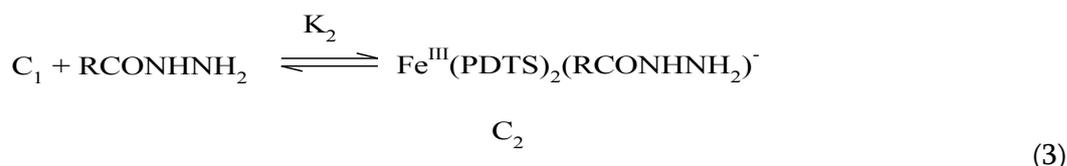
#### 3.6 Mechanism for Fe(III)-NH/INH-PDTS system

The oxidation of nicotinic acid hydrazide/ iso nicotinic hydrazide by iron(III) in the presence of PDTS is first order with respect to Fe(III). The reactions are accelerated by PDTS and plots of  $1/k_{obs}$  versus  $1/[PDTS]^2$  are straight lines with positive slopes and positive intercepts on the ordinate indicating the formation of a 1:2 complex between Fe(III) and PDTS. It has also been observed that these reactions are decelerated by H<sup>+</sup> ion.

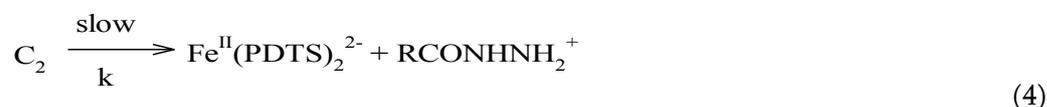
Iron(III) exists mainly as hexa aquoiron(III) under the present experimental conditions ( $[Fe(III)] \approx 10^{-5}$  mol dm<sup>-3</sup>, pH < 2.0)[17, 18, 19]. The protonation constants of PDTS at 25°C are 3.032 [20]. Hence under experimental conditions PDTS exist mostly in monoprotonated forms. The protonation constants of NH and INH are very high [21] (  $-\log K_H$  values of NH and INH are 2.26 and 2.13 respectively). Hence under the present conditions these two hydrazides also exist as monoprotonated species to a very large extent. However, the unprotonated forms of NH and INH are considered as the active species in view of their greater nucleophilicity over the monoprotonated forms. For convenience NH/INH represented as RCONHNH<sub>2</sub> in mechanism



$C_1$  then reacts with  $\text{RCONHNH}_2$  in an equilibrium step to give  $\text{Fe}^{\text{III}}(\text{PDTS})_2(\text{RCONHNH}_2)^-$



The dissociation of intermediate  $C_2$  to give  $\text{Fe}^{\text{II}}(\text{PDTS})_2^{2-}$  and  $\text{RCONHNH}_2^+$  is considered as the rate-determining step.



The  $\text{Fe}(\text{II})$  species,  $\text{Fe}^{\text{II}}(\text{PDTS})_2^{2-}$  reacts with another mole of  $\text{HPDTS}^-$  to give  $\text{Fe}^{\text{II}}(\text{PDTS})_3^{4-}$  in a series of fast steps. The oxidized form of substrate further rearranges giving the final products.



The rate of the reactions is given by

$$\text{Rate} = k [C_2]_e \quad (6)$$

$$\text{From equation (2), } K_1 = \frac{[C_1]_e [\text{H}^+]_e^2}{[\text{HPDTS}^-]_e^2 [\text{Fe}^{3+}]_e} \quad (7)$$

$$\text{Therefore } [\text{Fe}^{3+}]_e = \frac{[C_1]_e [\text{H}^+]_e^2}{K_1 [\text{HPDTS}^-]_e^2} \quad (8)$$

$$\text{Similarly from equation (3), } K_2 = \frac{[C_2]_e}{[C_1]_e [\text{RCONHNH}_2]_e} \quad (9)$$

$$\text{Or } [C_1]_e = \frac{[C_2]_e}{K_2 [\text{RCONHNH}_2]_e} \quad (10)$$

Applying equilibrium treatment the rate law can be derived as follows:

$$[\text{Fe}(\text{III})]_t = [\text{Fe}^{3+}]_e + [C_1]_e + [C_2]_e \quad (11)$$

$$= \frac{[C_1]_e [\text{H}^+]_e^2}{K_1 [\text{HPDTS}]_e^2} + [C_1]_e + [C_2]_e \quad (12)$$

$$= \frac{[C_2]_e [\text{H}^+]_e^2}{K_1 K_2 [\text{HPDTS}^-]_e^2 [\text{RCONHNH}_2]_e} + \frac{[C_2]_e}{K_2 [\text{RCONHNH}_2]_e} + [C_2]_e \quad (13)$$

$$= [C_2]_e \left\{ \frac{[H^+]_e^2 + K_1[HPDTS^-]_e^2 + K_1K_2[HPDTS^-]_e^2[RCONHNH_2]_e}{K_1K_2[HPDTS^-]_e^2[RCONHNH_2]_e} \right\} \quad (14)$$

$$[C_2]_e = \frac{K_1K_2[Fe(III)]_t[HPDTS^-]_e^2[RCONHNH_2]_e}{[H^+]_e^2 + K_1[HPDTS^-]_e^2 + K_1K_2[HPDTS^-]_e^2[RCONHNH_2]_e} \quad (15)$$

Replacing  $[HPDTS^-]_e$  with  $[PDTS]$  and  $[H^+]_e$  with  $[H^+]$  (where  $[PDTS]$  and  $[H^+]$  are initial constants of PDTS and  $H^+$  respectively)

$$[C_2]_e = \frac{K_1K_2[Fe(III)]_t[HPDTS^-]_e^2[RCONHNH_2]_e}{[H^+]_e^2 + K_1[HPDTS^-]_e^2 + K_1K_2[HPDTS^-]_e^2[RCONHNH_2]_e} \quad (16)$$

$$[RCONHNH_2]_t = [RCONHNH_2]_e + [RCONHNH_3^+]_e \quad (17)$$

$$[RCONHNH_2]_t = [RCONHNH_2]_e + K_H[H^+] [RCONHNH_3^+]_e \quad (18)$$

$$= [RCONHNH_2]_e \{1 + K_H[H^+]_e\} \quad (19)$$

Since the protonation constant of substrates are very high,  $K_H[H^+] \gg 1$ . Hence the above equation can be written as

$$[RCONHNH_2] = [RCONHNH_2]_t / K_H[H^+]_e \quad (20)$$

$$\text{Rate} = k[C_2]_e = \frac{kK_1K_2[Fe(III)]_t[HPDTS^-]_e^2[RCONHNH_2]_e}{[H^+]_e^2 + K_1[HPDTS^-]_e^2 + K_1K_2[HPDTS^-]_e^2[RCONHNH_2]_e} \quad (21)$$

Substituting the value of  $[RCONHNH_2]_e$  in the equation (21)

$$\text{Rate} = k[C_2]_e = \frac{kK_1K_2[Fe(III)]_t[HPDTS^-]_e^2 \{ [RCONHNH_2]_t / K_H[H^+]_e \}}{[H^+]_e^2 + K_1[HPDTS^-]_e^2 + K_1K_2[HPDTS^-]_e^2 \{ [RCONHNH_2]_t / K_H[H^+]_e \}} \quad (22)$$

On replacing  $[H^+]_e$  by  $[H^+]$  equation (22) transforms to

$$\text{Rate} = \frac{kK_1K_2[Fe(III)]_t[PDTS]^2[RCONHNH_2]_t}{K_H[H^+]^3 + K_HK_1[H^+][PDTS]^2 + K_1K_2[PDTS]^2[RCONHNH_2]_t} \quad (23)$$

Since  $[RCONHNH_2]_t$  is the initial concentration of substrate this can be written as  $[RCONHNH_2]$

$$\text{Rate} = \frac{kK_1K_2[Fe(III)]_t[PDTS]^2[RCONHNH_2]}{K_H[H^+]^3 + K_HK_1[H^+][PDTS]^2 + K_1K_2[PDTS]^2[RCONHNH_2]} \quad (24)$$

This rate law satisfies all the experimental observations. Then the pseudo-first order rate constant  $k_{obs}$  is given by

$$k_{obs} = \frac{kK_1K_2[Fe(III)]_t[PDTS]^2[RCONHNH_2]}{K_H[H^+]^3 + K_HK_1[H^+][PDTS]^2 + K_1K_2[PDTS]^2[RCONHNH_2]} \quad (25)$$

Equation (25) can be rearranged as,

$$\frac{1}{k_{obs}} = \frac{K_H[H^+]^3}{kK_1K_2[PDTS]^2[RCONHNH_2]} + \frac{K_H[H^+]}{kK_2[RCONHNH_2]} + \frac{1}{k} \quad (26)$$

According to the equation (26), plots of  $1/k_{\text{obs}}$  versus  $1/[\text{PDTS}]^2$  should be linear with positive slopes and positive intercepts on the ordinate. However, the dependence of rate on hydrogen ion concentration is not simple. On rearrangement the above equation transforms to

$$(1/k_{\text{obs}} - 1/k) \frac{1}{[\text{H}^+]} = \frac{K_{\text{H}}[\text{H}^+]^2}{kK_1K_2[\text{PDTS}]^2[\text{RCONHNH}_2]} + \frac{K_{\text{H}}}{kK_2[\text{RCONHNH}_2]} \quad (27)$$

According to the above equation, a plot of  $(1/k_{\text{obs}} - 1/k)[\text{H}^+]$  versus  $[\text{H}^+]^2$  should be linear with positive slope and intercept. Such plots are obtained in the case of oxidation of both NH and INH also (Figure 3). The intercepts of the plots of  $1/k_{\text{obs}}$  versus  $1/[\text{RCONHNH}_2]$  is  $1/k$  and hence the reciprocal of the intercept gives  $k$  value. From the slope and intercept values of the plots of  $(1/k_{\text{obs}} - 1/k)/[\text{H}^+]$ , the values of  $K_1$  and  $K_2$  have been evaluated using the literature value of  $K_{\text{H}}$  of these nicotinic acid hydrazides. The values are presented in the Table 3.

The values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are computed for iron(III)-PDTS-NH system using the specific rate constants,  $k$  and these values are  $130 \text{ KJ mol}^{-1}$  and  $70 \text{ J mol}^{-1} \text{ K}^{-1}$  respectively. Similarly  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values iron(III)-PDTS-INH system are  $124 \text{ KJ mol}^{-1}$  and  $49 \text{ Jmol}^{-1} \text{ K}^{-1}$  respectively.

The given reaction involves electrophilic substitution on the hydrazide nitrogen with the formation of N-Fe bond. This intermediate reacts with another  $\text{Fe}^{\text{III}}(\text{PDTS})_2$ . The resultant intermediate subsequently decomposes with direct two-electron transfer from hydrazide to two iron(III) centre to give another intermediate. The intermediate in a series of fast steps give the final products (Scheme 1).

### 3.7 Mechanism for Fe(III)-NH/INH-PPDTS system

In the oxidation of nicotinic acid *iso*-nicotinic acid hydrazides by iron(III) in the presence of PPDTS follows a similar trend as that noticed in the presence of PDTS. This suggests that oxidation of these two hydrazides also occurs by the mechanism proposed for iron(III)-PDTS-NH/INH systems. The values of specific rate constant ( $k$ ) and equilibrium constants

( $K_1$  and  $K_2$ ) are evaluated by a similar procedure used in the iron(III)-PDTS-NH/INH system and these values are presented in Table 3.

The values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are computed for iron(III)-PPDTS-NH system using the specific rate constants and these values are  $54 \text{ KJ mol}^{-1}$  and  $-194 \text{ Jmol}^{-1} \text{ K}^{-1}$  respectively and those for iron(III)-PPDTS-INH system are  $61 \text{ K J mol}^{-1}$  and  $-170 \text{ J mol}^{-1} \text{ K}^{-1}$  respectively. The mechanism represented in scheme 2.

### 3.8 Discussion

The data in Table 3 suggests that the specific rate constants ( $k$ ) and equilibrium constants ( $K_1$  and  $K_2$ ) for iron(III)-PDTS-NH and iron(III)-PDTS-INH are nearly equal. This indicates that these two isomers show similar activity towards oxidation by iron(III). A similar trend is also noticed in the oxidation of NH/INH by iron(III) in the presence of PPDTS.

A further examination of the data suggests that the specific rate constants for the oxidation of these isomers by iron(III) in the presence of PPDTS are lower than those in presence of PDTS. This can be attributed to higher stability of the ternary complexes,  $\text{Fe}^{\text{III}}(\text{PDTS})_2(\text{NH/INH})^3$  than  $\text{Fe}^{\text{III}}(\text{PDTS})_2(\text{NH/INH})$ . PPDTS is expected to form more stable complexes with iron(III) than PDTS, due to its greater  $\pi$ -electron delocalization.

The  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values are also in consonance with the above conclusion. The PDTS systems exhibit higher  $\Delta H^\ddagger$  values than the PPDTS systems. The entropies of activation,  $\Delta S^\ddagger$  for these reactions also fall in line with this analysis.  $\Delta S^\ddagger$  values are the lowest in the PPDTS systems which indicates that the

transition states are highly ordered compared to those in the presence of PDTS.

#### IV. CONCLUSIONS

Oxidation of either hydrazide, the reactions are first order in iron(III) and decelerated by hydrogen ion. Plots of  $1/k_{obs}$  versus  $1/[substrate]$  and  $1/k_{obs}$  versus  $[triazine]^2$  are linear with positive intercepts on the ordinate indicating Michaelis-menten type of behavior suggesting the formation of 1: complex between iron(III) and substrate and 1:2 complex between iron(III) and triazine. Specific rate constants ( $k$ ) and equilibrium constants ( $K_1$  and  $K_2$ ) for iron(III)-PDTS-NH and iron(III)-PDTS-INH are nearly equal. This indicates that these two isomers show similar activity towards oxidation by iron(III). A similar trend is also noticed in the oxidation of NH/INH by iron(III) in the presence of PPPTS. The PDTS systems exhibit higher  $\Delta H^\ddagger$  values than the PPPTS systems. The entropies of activation,  $\Delta S^\ddagger$  for these reactions also fall in line with this analysis.  $\Delta S^\ddagger$  values are the lowest in the PPPTS systems which indicates that the transition states are highly ordered compared to those in the presence of PDTS.

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**Table 1.** Stoichiometry for the oxidation of nicotinic and *iso*-nicotinic acid hydrazide by iron(III) in the presence of PDTS

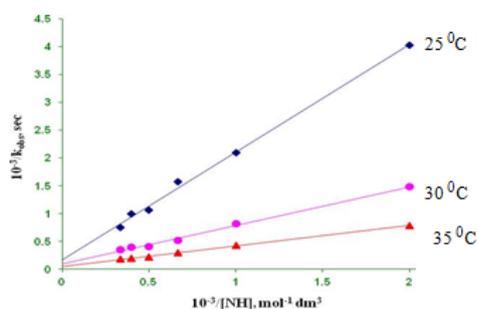
Substrate	[Sub] x 10 <sup>5</sup> mol dm <sup>-3</sup>	[Fe(III)] <sub>t</sub> x 10 <sup>4</sup> mol dm <sup>-3</sup>	[Fe(III)] <sub>r</sub> x 10 <sup>5</sup> mol dm <sup>-3</sup>	$\frac{[\text{Fe(III)}]_r}{[\text{Sub}]}$
In the presence of PDTS				
NH	1.0	1.0	4.05	4.05
	1.0	2.0	3.95	3.95
	2.0	3.0	7.86	3.93
INH	1.0	1.0	3.94	3.94
	1.0	2.0	4.01	4.01
	2.0	3.0	8.09	4.05
In the presence of PPDS				
NH	1.0	1.0	4.02	4.02
	1.0	2.0	4.10	4.10
	2.0	3.0	8.03	4.02
INH	1.0	1.0	3.99	3.99
	1.0	2.0	4.03	4.03
	2.0	3.0	7.90	3.95

[Sub] = [NH] / [INH], t = total, r = reacted

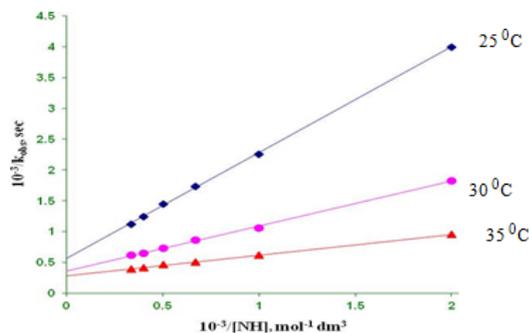
**Table 2.** Effects of substrates on rate of oxidation of NH/INH by Fe(III) in presence of PDTS/PPDTS

[Substrate] x 10 <sup>3</sup> mol dm <sup>-3</sup>	k <sub>obs</sub> x 10 <sup>3</sup> , sec <sup>-1</sup>											
	PDTS						PPDTS					
	NH			INH			NH			INH		
	25 <sup>0</sup> C	30 <sup>0</sup> C	35 <sup>0</sup> C	25 <sup>0</sup> C	30 <sup>0</sup> C	35 <sup>0</sup> C	25 <sup>0</sup> C	30 <sup>0</sup> C	35 <sup>0</sup> C	25 <sup>0</sup> C	30 <sup>0</sup> C	35 <sup>0</sup> C
0.5	0.25	0.68	1.27	0.23	0.58	1.68	0.23	0.55	1.05	0.17	0.63	1.11
1.0	0.48	1.22	2.30	0.42	1.09	3.02	0.40	0.94	1.62	0.32	1.04	1.73
1.5	0.63	1.93	3.43	0.65	1.59	4.10	0.58	1.17	1.98	0.43	1.31	2.16
2.0	0.94	2.48	4.69	0.79	2.03	6.17	0.69	1.36	2.15	0.53	1.51	2.41
2.5	1.00	2.55	5.19	0.97	2.48	6.49	0.81	1.54	2.41	0.62	1.66	2.65
3.0	1.18	2.86	5.54	1.18	2.82	8.74	0.90	1.61	2.56	0.69	1.80	2.84

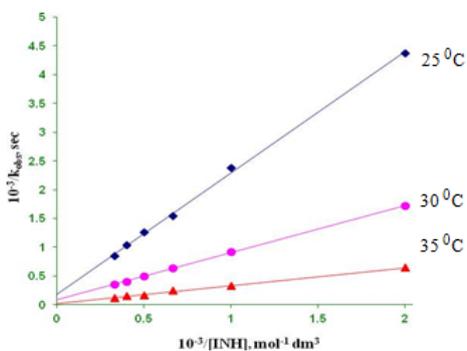
**Figure 2.** Effect of Substrate on rate



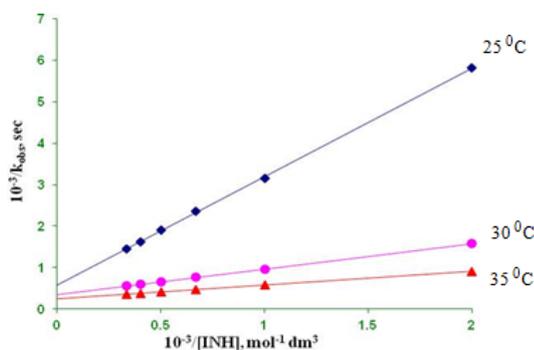
[Fe(III)] = 2.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>, [PDTS] = 1.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 4.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>



[Fe(III)] = 2.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>, [PPDTS] = 1.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 4.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>

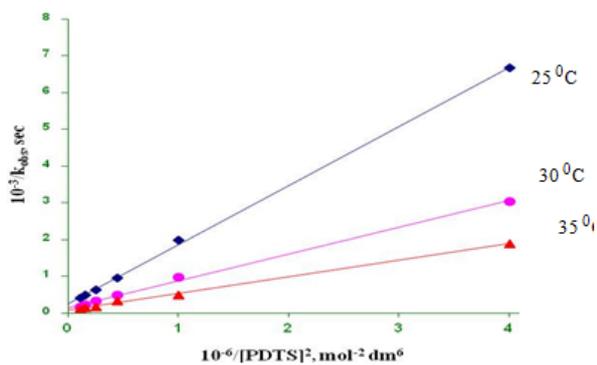


[Fe(III)] = 2.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>, [PDTS] = 1.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 4.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>, μ = 0.1

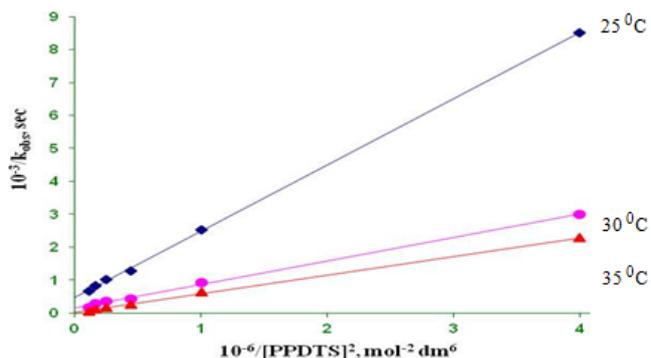


[Fe(III)] = 2.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>, [PPDTS] = 1.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 4.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>, μ = 0.1

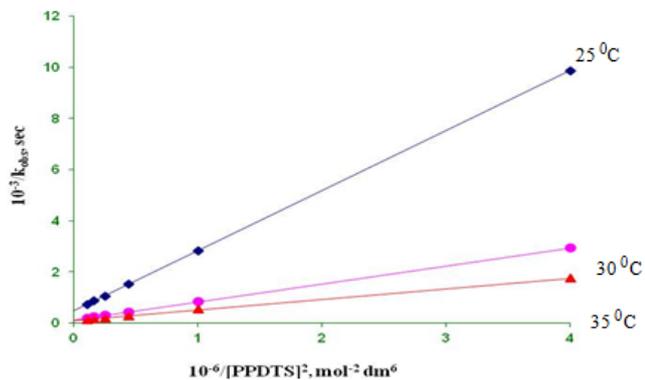
**Figure 2.** Effect of triazine on rate



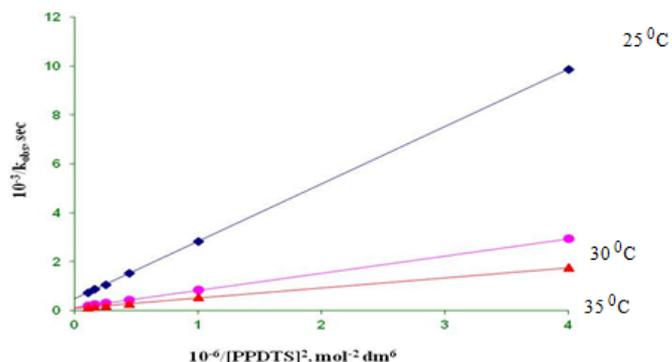
$[E_a(III)] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$   $[INH] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$   $[H^+] = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$   $\mu = 0.1$



$[E_a(III)] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$   $[INH] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$   $[H^+] = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$   $\mu = 0.1$



$[E_a(III)] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$   $[INH] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$   $[H^+] = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$   $\mu = 0.1$



$[E_a(III)] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$   $[INH] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$   $[H^+] = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$   $\mu = 0.1$