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Research Article

Kinetic Study of SN^2 Reaction between Paranitrophenyl Benzoate and Hydrazine in the Presence of CTAB Reverse Micelles

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Abstract

Kinetic study of the reaction between p-Nitrophenyl benzoate (PNPB) by hydrazine (HYN) in the presence of Cetyltrimethylammonium bromide (CTAB)/Chloroform/Hexane reverse micellar medium shows that the reaction obeys first order kinetics with respect to each of the reactants. The rate of the reaction is much slower in reverse micellar medium compared to aqueous medium under identical conditions ($k'_{Aq} = 2.84\times10^{-3}$ sec^{-1}, $k_{rm} = 1.34\times10^{-4}$ sec^{-1}). The rate constants for the reaction in the reverse micellar medium have been determined at different values of W {W=[H_2O]/[CTAB]} and at different concentrations of CTAB. It was found that the observed rate constant decreases with W. This kinetic behaviour was interpreted by using modified Berezin pseudo phase model, taking into consideration the distribution of the reactants, PNPB and hydrazine between the three pseudo phases, *i.e.*, water pool, interface an organic phase.

Keywords: CTAB reverse micelles; Hydrazine; Kinetics; p-Nitrophenyl benzoate; Water pools

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1.Introduction

The surfactant aggregates formed spontaneously in organic solvents are called reverse micelles and water is readily solubilized in the polar core of reverse micelle forming a water pool, characterized by a parameter W {W=[H_2O]/[CTAB]} [1–3]. This solubilized water exhibits special properties like lower dielectric constant, higher ionic strength (in the case of reverse micelles made of ionic surfactants) and altered nucleophilicity compared to bulk water [4–8]. Since the water pool has different properties compared to ordinary water, the rates of reactions and mechanisms can be expected to be different.

Reverse micelles are known to solubilise both polar and non-polar solutes [9–12] and because of these unique properties they are widely used as reaction media to design variety of reactions and synthesize novel materials [13–15]. This media is also very useful for the synthesis of nanoparticles with desired shape and size [16–20]. Three reactions, kinetics of dissociation of $[Fe(tptz)_2]^{2+}$, oxidation of $[Fe(phen)_3]^{2+}$, indigo carmine and toluidine blue by periodate in the presence of CTAB reverse micelles have been earlier reported from this laboratory [21–23]. In the kinetics of dissociation of $[Fe(tptz)_2]^{2+}$, low

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dielectric constant of the water pool facilitates the formation of ion pair between complex and Br^- ion of CTAB and leads to increase in rate of reaction. In the study of kinetics of oxidation of $[Fe(phen)_3]^{2+}$ in CTAB reverse micelles, kinetic results have been quantitatively explained based on ionic strength of the water pool using Guggenheim equation. In the study of kinetics of oxidation of Indigo Carmine by periodate in CTAB reverse micelles, it was found that water molecule exists in the rate determining step of the reaction mechanism and the observed kinetic results have been quantitatively explained using Berezin pseudo phase model. In order to further explore the applications of reverse micelles and to develop kinetic models for a variety of reactions, an organic reaction (SN^2 reaction) between Paranitrophenyl benzoate and hydrazine in CTAB reverse micellar medium, was chosen for study. The results of the kinetic study of this reaction along with the kinetic model are presented in this paper.

2. Materials and Methods

2.1 Materials

Stock solutions of PNPB (99% pure, Merck, India) and hydrazine (99% pure, Merck, India) were prepared in double distilled water. Chloroform and hexane were used after distillation. Stock solutions of CTAB (Cetyl tri methyl ammonium bromide, 98% pure, Sigma, India) were prepared in 3:2 (v/v) chloroform-hexane mixtures.

2.2 Preparation of Reverse Micellar Medium and Initiation of the Reaction

An amount of 0.04 mL of hydrazine solution of concentration 2.5 $mol.dm^{-3}$ was added into 10 mL of 0.1 $mol.dm^{-3}$ CTAB solution using a micro pipette. 0.02 mL of PNPB solution of concentration 0.02 $mol.dm^{-3}$ was then added to initiate the reaction. The reaction mixtures were shaken sufficiently to obtain a homogenous reverse micellar medium. The reaction was studied by changing the value of W in the range 3.33 to 20.0 by varying the molar ratio of [Water] to [CTAB].

2.3 Experimental Method of Following the Reaction

The reaction was monitored by measuring the increase in absorbance of the product p-Nitro phenol where it has maximum absorbance at a wave length of 400 nm, using a SHIMADZU UV-1800 double beam spectrophotometer. The reaction was carried out under pseudo first order conditions, [HYD] >> [PNPB] and the pseudo first order rate constants k' were obtained from plots of $\log(A_\infty - A_t)$ versus time. The second order rate constants, k_2, were obtained by dividing the pseudo first order rate constants, by the overall concentration of hydrazine. The kinetic data obtained are the averages from triplicate runs with reproducibility less than ±4%.

3. Results and Discussion

The kinetic investigations of the reaction have been carried out under the conditions, {[HYD]>>[PNPB]}, and plots of $\log(A_\infty - A_t)$ versus time were found to be good straight lines showing first order dependence with respect to PNPB (Figure 1). The pseudo first order rate constant k', was found to be directly proportional to concentration of hydrazine showing first order kinetics with respect to hydrazine (Figure 2). The reaction has also been carried out in aqueous medium under identical condi-

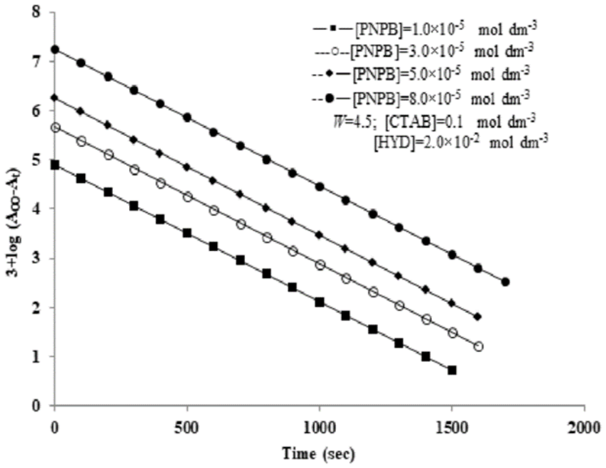


Figure 1. Plots of log ($A_\infty - A_t$) versus time.

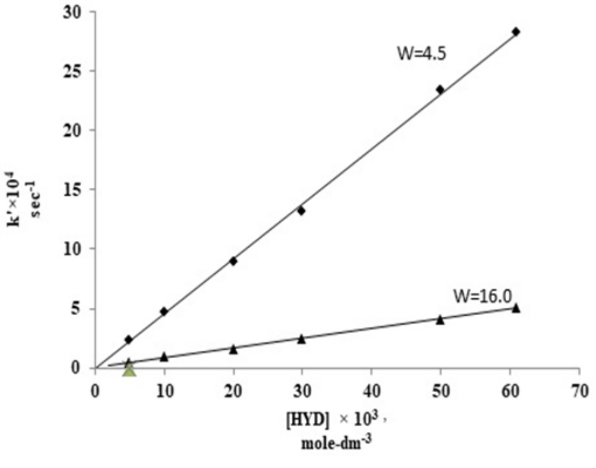


Figure 2. Plots of k' versus $[HYD]_o$.

tions and similar kinetic features were observed. The reaction is much faster in the presence of aqueous medium (approximately twenty five times) compared to CTAB reverse micellar medium (Table 1).

The slow rate of reaction in the presence of reverse micelles can be explained as follows: the reaction follows an SN^2 mechanism and the transition state develops a partial negative charge compared to the reactants which are neutral (Scheme 1). Since high dielectric constant conditions favours such a transition state, the reaction is much faster in aqueous medium compared to CTAB reverse micelles.

3.1 Effect of *W* on Rate of Reaction

Three different sets of experiments were conducted at three different concentrations of CTAB. At each fixed concentration of CTAB, a series of experiments were carried out at different values of *W* (Table 2). It can be observed from the table that the pseudo first order rate constants k', decrease with increase in *W*. Hydrazine is highly hydrophilic species and therefore can exist in the aqueous water pool and interface. Since PNPB is an organic compound, found to be distributed between the three pseudo phases. K_{HY} and K_{PNPB} represent distribution constants between the water pool and the interface and Q_{PNPB} is the distribution constant between the water pool and the oil phase and are given by the equations;

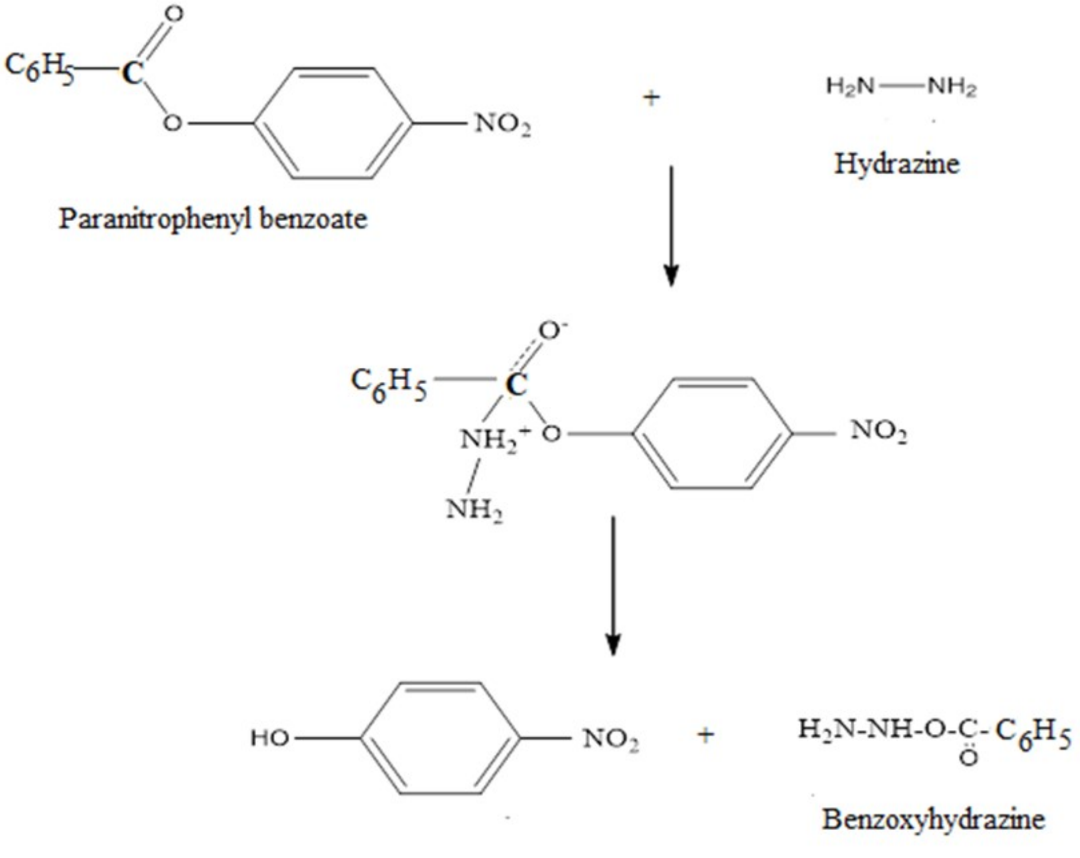
$$K_{HYD} = \frac{[HYD]_s}{[HYD]_w}; K_{PNPB} = \frac{[PNPB]_s}{[PNPB]_w}; G_{PNPB} = \frac{[PNPB]_o}{[PNPB]_w} \quad (1)$$

Accordingly, the mechanism shown in Scheme 2 is considered to explain the kinetic behaviour [25,26].

In the reaction Scheme 2, the overall concentrations of hydrazine and PNPB are related to the corresponding local concentrations in

Table 1. Comparison of rate constants in the aqueous medium and in the presence of reverse micelles (0.1 mol.dm^{-3} CTAB) at same ionic strength (μ), [HYD] = 2.0×10^{-2} mol.dm^{-3}; [PNPB] = 5.0×10^{-5} mol.dm^{-3}; T = 304±0.1 K.

μ (mol.dm^{-3})	$k'_{aq.med}\times10^3$ (sec^{-1})	$k'_{(rev\ mic)}\times10^4$ (sec^{-1})
3.46	2.84	1.34
4.16	2.84	1.91

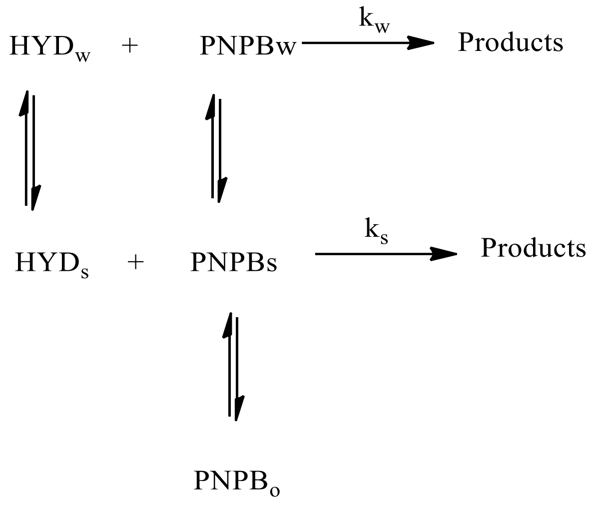


Scheme 1. Reaction mechanism

each region by the mass balance Equations (2) and (3).

$$[HYD]_{OVR} = [HYD]_w \phi_w + [HYD]_s \phi_s \quad (2)$$

$$[PNPB]_{OVR} = [PNPB]_w \phi_w + [PNPB]_s \phi_s + [PNPB]_o \phi_o \quad (3)$$



Scheme 2. Distribution of reactants

where,

$$\phi_w = 0.018[CTAB]_o W \quad (4)$$

$$\phi_s = 0.323[CTAB]_o \quad (5)$$

$$\phi_0 = 1 - (\phi_w + \phi_s) \quad (6)$$

where, ϕ_w, ϕ_s and ϕ_o represent the volume fractions of the aqueous droplets, the interface and the oil phase, respectively. The overall second order rate constant, k_2 is given by Equation (7).

$$k_2 = \frac{k'}{[HYD]_{OVR}} = \frac{k_w\phi_w + k_s\phi_s K_{HYD} K_{PNPB}}{(\phi_w + K_{HYD}\phi_s)(k_w\phi_w + k_s\phi_s K_{HYD} K_{PNPB})} \quad (7)$$

Equation (7) can be simplified by assuming that the hydrophobic PNPB reside preferentially in the oil phase compared to aqueous pools and that ϕ_0 is larger than either ϕ_w and ϕ_s. As a consequence, Equation (7) is reduced, after an appropriate rearrangement and by the use of Equation (4) to Equation (6). In this equation, the denominator involved the parameter W

Table 2. Effect of W and [CTAB] on observed first order rate constant (k'): [PNPB] = 5.0×10⁻⁵ mol.dm⁻³; [HYD] = 2.0×10⁻² mol.dm⁻³; T = 302 K.

CTAB (mol.dm⁻³)	$[Br^-]_e$	W	$k'\times10^4$ (sec⁻¹)	$k_2\times10^2$ (= $k'/[HYD]_o$)
0.1	22.2	2.5	20.0	10.0
	15.6	3.5	13.6	6.80
	12.1	4.5	8.92	4.46
	8.47	6.5	5.81	2.90
	6.53	8.5	4.10	2.05
	4.16	13.0	1.91	0.95
	3.46	16.0	1.34	0.67
	2.77	20.0	0.92	0.46
0.2	22.2	2.5	19.2	9.6
	15.6	3.5	13.4	6.7
	12.1	4.5	8.80	4.4
	8.47	6.5	5.43	2.71
	6.53	8.5	3.80	1.9
	4.16	13.0	1.78	0.89
	3.46	16.0	1.28	0.64
	2.77	20.0	0.86	0.43
0.3	22.2	2.5	20.0	10.0
	15.6	3.5	13.2	6.60
	12.1	4.5	8.64	4.32
	8.47	6.5	5.63	2.81
	6.53	8.5	3.0	1.5
	4.16	13.0	1.82	0.91
	3.46	16.0	1.32	0.66
	2.77	20.0	1.04	0.52

which is important in determining the observed decreasing trend of k_2 with increasing molar ratio W.

$$k_2\phi_o = \frac{1.80\times10^{-3}k_w W + k_s\phi_s K_{HYD}K_{PNPB}}{Q_{PNPB}\left(1.80\times10^{-3}W + K_{HYD}\phi_s\right)} \qquad (8)$$

The partition coefficient of hydrazine can be assumed to be much less than 1 since there is no exchange between hydrazine with the counter ions Br^- of CTAB. Since the values of ϕ_s lie in the range 0.89–0.95 the term $K_{HYD}\phi_s$ can be neglected and Equation (8) now becomes,

$$k_2\phi_o = \frac{\left(\frac{1.80\times10^{-3}k_w}{Q_{PNPB}}\right)W + \frac{k_s\phi_s K_{HYD}K_{PNPB}}{Q_{PNPB}}}{\left(1.80\times10^{-3}W\right)} \qquad (9)$$

$$k_2\phi_o = \frac{k_w}{Q_{PNPB}} + \frac{k_s\phi_s K_{HYD}K_{PNPB}/Q_{PNPB}}{\left(1.80\times10^{-3}W\right)} \qquad (10)$$

According to Equation (10), a plot of $k_2\phi_o$ versus $1/W$ should be linear. Such a plot was obtained and Figure 3 shows that the plots of $k_2\phi_o$ versus $1/W$ are good straight lines for 0.1 mol dm^{-3} of CTAB and is true for all concentrations of CTAB. At low values of W (3.33–4.44) small deviation from linearity was observed. This linear trend implies the absence of special properties of the water pool and their effect on the reaction rate. Since the properties exist at $W < 4$, there is a deviation from linear trend at low W values.

4. Conclusions

The SN^2 reaction of the PNPB by hydrazine obeys first order kinetics with respect to each of the reactants in aqueous as well as CTAB/Hexane/Chloroform reverse micellar medium. The reaction has been found to be inhibited around twenty times in the presence of CTAB reverse micelles compared to aqueous medium which can be attributed to low dielectric constant of water pool. The second order rate constant decreases with W and is independent of CTAB concentration. The kinetic results are interpreted by applying Berezin pseudo phase model and accordingly the plots of $k_2\phi_o$ versus $1/W$ are good straight lines for all concentrations of CTAB.

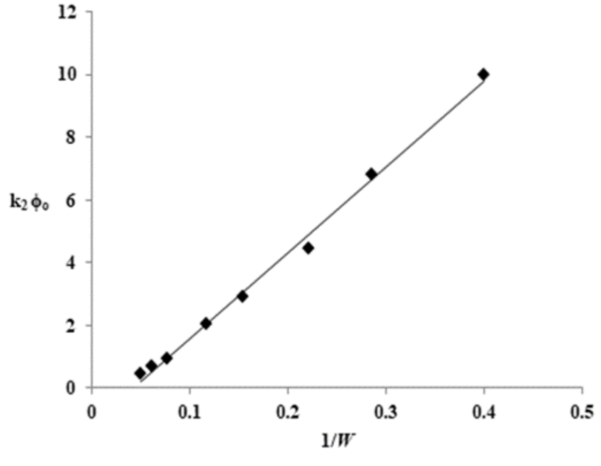


Figure 3. Plots of $k_2\phi_o$ vs $1/W$.

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APPENDICES

A. Expression for Rate and Rate Constant

$$Rate = k\left[HYD\right]_{OVR}\left[PNPB\right]_{OVR}$$

$$Rate = k'\left[PNPB\right]_{OVR} \qquad where\ k' = k\left[HYD\right]_{OVR} \qquad \left(PNPB\ is\ isolated\right)$$

$$k' = {}^{Rate}\!\big/_{\left[PNPB\right]_{OVR}}$$

$$Rate = k_w\phi_w\left[HYD\right]_w\left[PNPB\right]_w + k_s\phi_s\left[PNPB\right]_s\left[HYD\right]_s$$

$$k' = \frac{k_w\phi_w\left[HYD\right]_w\left[PNPB\right]_w + k_s\phi_s\left[PNPB\right]_s\left[HYD\right]_s}{\left[PNPB\right]_{OVR}}$$

$$k' = \frac{k_w\phi_w\left[HYD\right]_w\left[PNPB\right]_w + k_s\phi_s\left[PNPB\right]_s\left[HYD\right]_s}{\left[PNPB\right]_w\phi_w + \left[PNPB\right]_s\phi_s + \left[PNPB\right]_o\phi_o}$$

$$k_2 = \frac{k'}{\left[HYD\right]_{OVR}} = \frac{k_w\phi_w\left[HYD\right]_w\left[PNPB\right]_w + k_s\phi_s\left[PNPB\right]_s\left[HYD\right]_s}{\left\{\left[HYD\right]_w\phi_w + \left[HYD\right]_s\phi_s\right\}\left\{\left[PNPB\right]_w\phi_w + \left[PNPB\right]_s\phi_s + \left[PNPB\right]_o\phi_o\right\}}$$

Dividing with $[HYD]_w[PNPB]_w$ both numerator and denominator and replacing

$$K_{HYD} = \frac{\left[HYD\right]_s}{\left[HYD\right]_w};\ K_{PNPB} = \frac{\left[PNPB\right]_s}{\left[PNPB\right]_w};\ Q_{PNPB} = \frac{\left[PNPB\right]_o}{\left[PNPB\right]_w}$$

We get

$$k_2 = \frac{k_w\phi_w + k_s\phi_s K_{HYD}K_{PNPB}}{\left(\phi_w + K_{HYD}\phi_s\right)\left(\phi_w + K_{PNPB}\phi_s + Q_{PNPB}\phi_o\right)}$$

B. Product of Reaction between Para Nitro Phenyl Benzoate and Hydrazine

The product analysis was carried out by reacting 4.0×10^{-5} mol.dm^{-3} para nitrophenyl benzoate with equivalent amount of hydrazine in aqueous and CTAB reverse micellar medium. After completion of the reaction, the yellow coloured product obtained was subjected to column chromatography to separate the two products and then NMR and mass spectrum of the product was obtained (Figure S1 & Figure S2). The spectra were found to be exactly identical with the spectra of para nitro phenol.

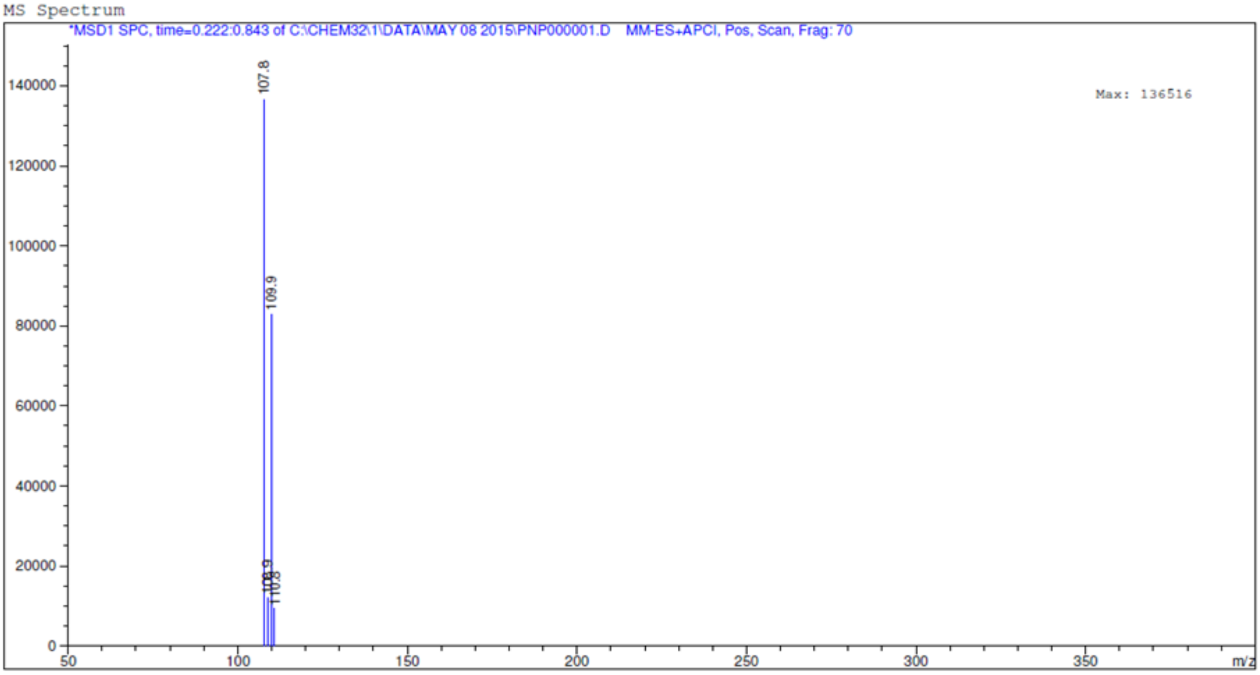

Figure S1. Product chromatogram

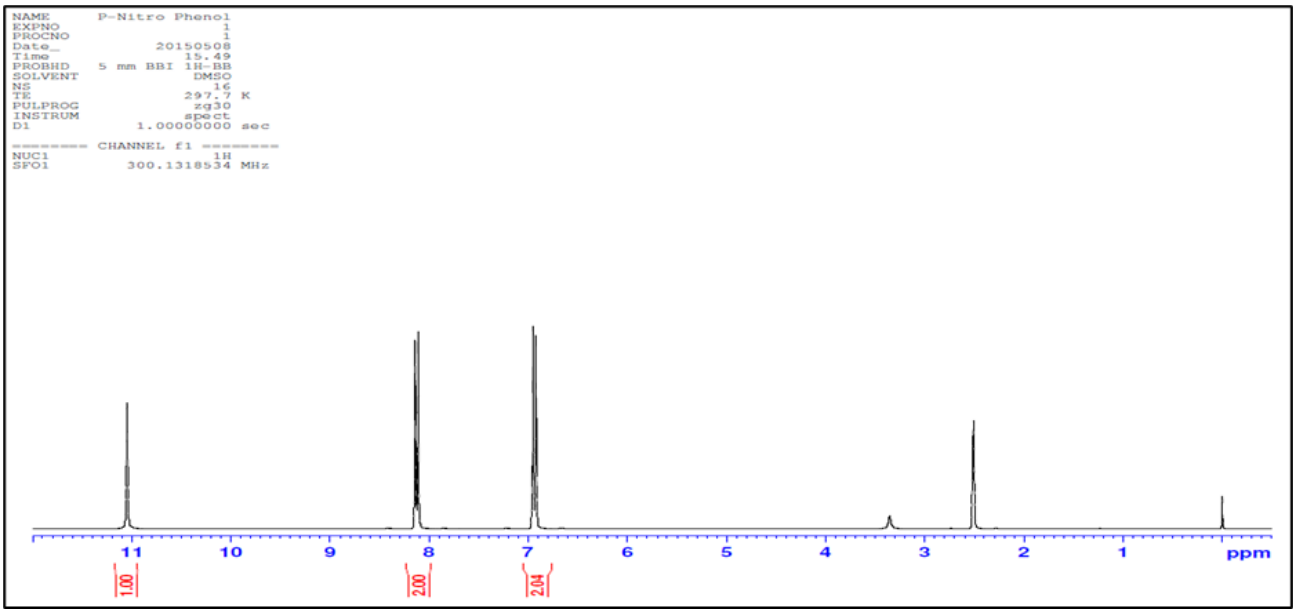

Figure S2. NMR mass spectrum of the product