

ESTERIFICATION OF PHTHALIC ANHYDRIDE WITH 2-ETHYLHEXANOL

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ABSTRACT:

The kinetics of esterification of phthalic anhydride (PAN) with 2-ethylhexanol (2EH) has been studied using methane sulphonic acid (MSA) and para- toluene sulphonic acid (p-TSA) as a catalyst. In each case, the kinetic parameters (rate constant, order with respect to reactants and catalyst, activation energy, and collision frequency) have been determined. It has been found that the reaction follows an overall second order kinetics, first order with respect to each reactant. The order with respect to both the catalysts has also been determined and it has been found that the reaction shows first order dependence on catalyst concentration. Furthermore, the literature pertaining to the synthesis of di-octyl phthalate (DOP) has been critically analysed and reported in the present work.

Key words: Di-2-ethylhexyl phthalate, Phthalic anhydride, 2- Ethyl hexanol, Esterification, Kinetics

1. INTRODUCTION

DOP, synthesized by esterification of PAN with 2EH, is the most widely used plasticizer. Normally sulphuric acid and p-TSA are used as a catalyst. Sulphuric acid and p-TSA, however, suffer from the disadvantage of by-product formation and colouration of the product due to various side reactions with increasing temperatures, in particular. In comparison with sulphuric acid and p-TSA, the non-acidic alkyl titanates have the advantage of very low by-product formation.^{1, 2} Their activity, however, is much lower than that of the Bronsted acids, necessitating reaction temperature of more than 200°C. Further, the titanates also suffer from the disadvantages of higher cost and difficult separation from the products. The solid acid catalysts overcome the disadvantages of Bronsted acids and titanates.³ Nevertheless, they suffer from disadvantages of easily deactivation, operation loss, and high mass transfer resistance.

The heteropolyacids (HPAs) have also been used to catalyze the esterification reaction in the presence of low boiling carrier liquid like benzene, toluene, xylene, and dichloromethane to remove the water azeotropically.⁴ The use of low boiling carrier, however, tends to reduce the rate of esterification reaction. In addition, the HPAs catalyze both, the esterification and hydrolysis reactions which result into lower yield of DOP at a given temperature. Further, their activity reduces drastically with a reuse. Recently, functionalized ionic liquids have also been exercised to catalyse the esterification reaction.⁵ The pertinent dispersion of ionic liquid in the reaction phase is, however, necessary during the course of reaction to obtain high yield of DOP. In addition, some ionic liquid gradually decomposes under a given reaction conditions which results into dissolution of ionic liquid in the reaction mixture, giving poor yield of DOP. The ionic liquids also associated with the disadvantages like reduction of catalytic activity with reuse and colorization of the product.

Table 1. Summary of the previous work

Sr. No.	Catalyst	Parameters studied and their range			Kinetics		Concluding Remark
		T, °C	[Catalyst]	MR	E kcal.mol ⁻¹	A	
1	p-TSA ¹ TBT ¹ TBZ ¹	135-200	0.5% (mol% based on phthalic anhydride)	1:1.1-1:1.2	15.50 25.06 12.30	6.7×10 ⁷ , L ² .mol ⁻² .min ⁻¹ 1.26×10 ¹⁰ , L.mol ⁻¹ .min ⁻¹ 4.4×10 ⁴ , L.mol ⁻¹ .min ⁻¹	The reaction was found to be first order in the MOP and 2EH. The kinetics has been explained using bimolecular acyl oxygen fission.
2	Superacidic heterogenous catalysts ³	160-200	0.48-1.20%, (w/w)	1:1- 1:5	11.05	0.12-0.43 (cm ³ .mol ⁻¹ s ⁻¹).(cm ² .cm ⁻³)	The reaction was found to be a surface reaction controlled under the range of conditions with overall second order kinetics.
3	Sulphuric acid ⁷	115-160	0.0078 mol.L ⁻¹ -0.0313,	1:1- 1:11	11.30	1.66×10 ⁶ , L.mol ⁻¹ .min ⁻¹	The reaction was appeared to be independent of the concentration of 2EH and first order dependence was observed with respect to MOP.
4	p-TSA ⁸	120-160	0.005-.017, mol.L ⁻¹	1:1- 1:11	15.30	1.83×10 ¹⁰ , L.mol ⁻¹ .min ⁻¹	The reaction appears to be first order with respect to MOP and the reaction rate does not depend on the concentration of 2EH.
5	TBT ²	150-185	0.0032-.0096, mol.L ⁻¹	1:1- 1:11	17.00	5.83×10 ⁸ , L ² .mol ⁻² .min ⁻¹	The reaction shows first order dependence with respect to MOP and 2EH
6	Zeolites ⁸	200	-	-	-	-	Zeolite catalysts are recommended since lighter colour DOP was obtained.
7	Non-catalytic ⁹	140-175	-	1:1- 1:6	18.6	1.17×10 ⁷ , L ² .mol ⁻² .min ⁻¹	The reaction appears to be second order with respect only to MOP and the reaction rate does not depend on the concentration of 2EH.
8	HPA ⁴	110	0.06% (mol% based on PAN)	1:1	-	-	The use of molybdenum substituted heteropolyacids has been suggested for the synthesis of DOP
10	Functionalized ⁵	115-125	15% (w of the	1:1.5	-	-	The use 1-methyl-3-(3-sulfopropyl)-

	ionic liquids		raw materials)				imidazolium hydrogen sulphate as catalyst has been recommended for synthesis of DOP.
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Table 2. Summary of the present work

Sr. No.	Catalyst	Parameter studied and their range			Kinetics		Colour ^a	Finding
		T, °C	[catalyst], mol.L ⁻¹	MR	E kcal.mol ⁻¹	A L ² .mol ⁻² .min ⁻¹		
1	MSA	140-160	0.024-0.090	1:1- 1:1.8	11.94	1.20×10^{12}	2-3	The kinetics of the reaction shows first order dependence in MOP, 2EH, and a catalyst
2	p-TSA	140-160	0.026-0.074	1:1.11- 1:1.8	13.80	5.99×10^{13}	5-6	

MR: molar ratio of the reactants

a : colour of the crude product on the Gardner scale

Table 1 shows the summary of previous work. It can be seen from Table 1 that there is a discrepancy in the published literature with respect to the kinetics using p-TSA. Butada and Pangarkar¹ have reported that the esterification of mono-2-ethylhexyl phthalate (MOP), monoester (MOP), and 2EH shows first order dependence with respect to both the reactants while Skrzypek et al.,⁶ have reported that the reaction appears to be first order with respect to MOP and it is independent of concentration of 2EH. Further, it has also been reported in the literature that MSA is advantageous over p-TSA due to its non-oxidizing characteristics.^{7,8,9} However, systematic investigation of esterification of PAN with 2EH using MSA has not studied pertinently to validate the supremacy of MSA over p-TSA. Therefore, the objectives of present investigation are: (i) to study the kinetics of esterification using p-TSA to overcome the discrepancy existing in the literature, and (ii) to study the possible advantages of MSA over p-TSA which mainly includes kinetics of the reaction, and product decolorization.

2. Experimental

2.1. Chemicals

PAN, 2EH, p-TSA, and MSA were purchased from S.D. Fine Chemicals Ltd, Mumbai, India and were used without further purification.

2.2. Experimental set-up

Experiments were conducted in a glass reactor of 500 ml capacity having a torishperical bottom. The glass reactor was provided with a six blade agitator, four glass baffles, and a thermometer pocket. The reaction temperature was maintained constant ($\pm 1^\circ\text{C}$) with the help of a relay heating circuit in an oil bath. The reactor was connected to a Dean and Stark apparatus for separating the water-2EH mixture and for refluxing 2EH back to the reactor.

2.3. Procedure

In a typical run, equimolar quantities of PAN and 2EH were first reacted at 145-150°C for 10-15 min to give MOP. The complete formation of MOP was confirmed by volumetric titration. The PAN gets completely converted to the MOP, so that the MOP concentration at this stage can be taken as the initial concentration. Further, the DOP formation starts only after the addition of a second mole of the 2EH and a catalyst at a predetermined temperature and therefore the MOP concentration goes on decreasing. The reaction could, therefore, be monitored on the basis of the number of acid groups esterified by titrating the reaction mixture against alcoholic KOH solution with phenolphthalein as indicator. Alcoholic KOH was used in order to avoid phase separation during analysis.

2.4 Analysis

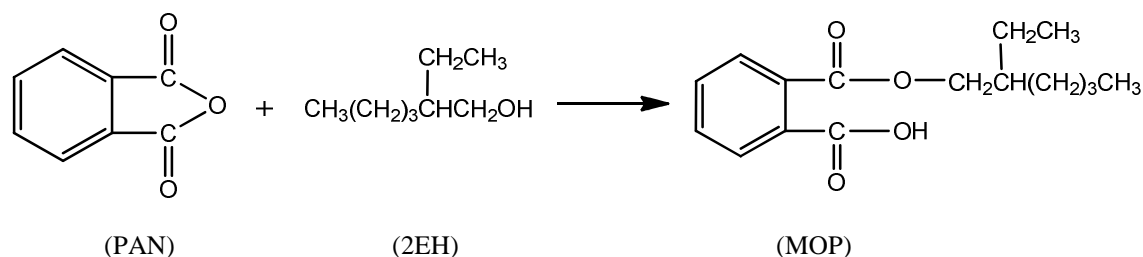
The reaction was monitored by chemical as well as instrumental analysis. In chemical analysis the reaction samples were titrated against alcoholic KOH solution, that is, the number of acid groups titrated against a base, which is a simple acid-base titration, whereas for gas chromatography (GC) analysis the samples were diluted and neutralised by an alkali solution and then injected into a gas chromatograph (model Chemito), using a flame ionization detector and an Oracle integrator, with a S.S. column packed with 5% OV-17 on Chromosorb WHP (length 2 m, I.D. 1/8 inches). Chemical analysis was used to get information on the reacted acid groups and GC on the unreacted alcohol remaining in the reaction mixture.

3. Result and discussion

3.1 Reaction pathway

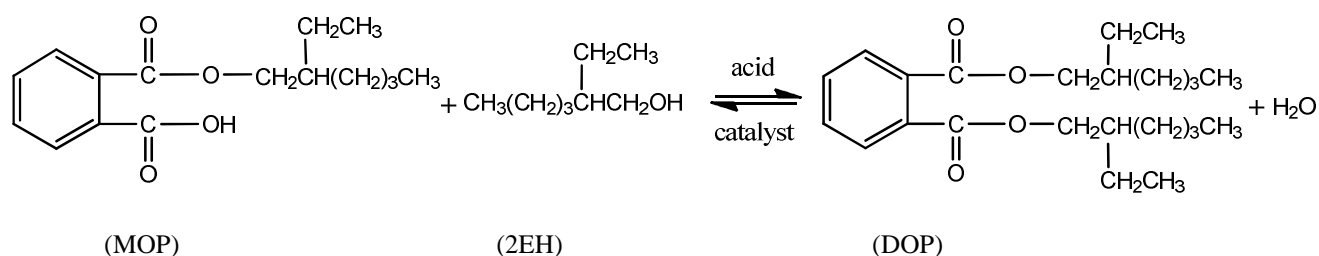
The esterification of PAN with 2EH proceeds in the two steps as shown by following chemical reactions:

Step 1: Formation of MOP



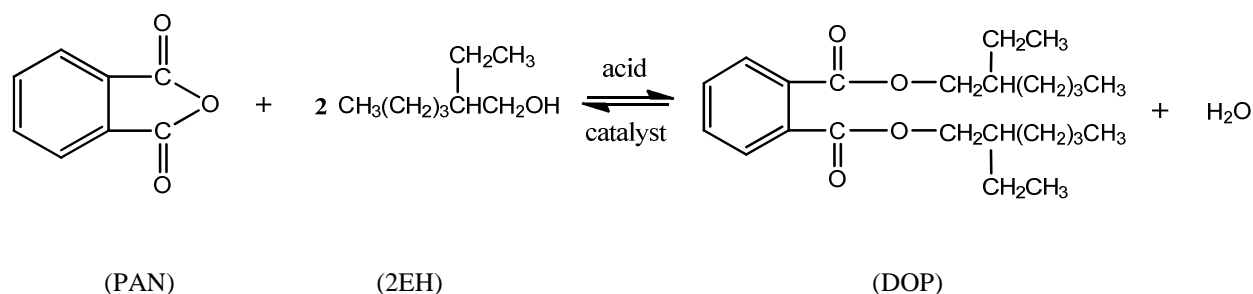
Scheme 1. Formation of MOP

Step 2: Formation of DOP



Scheme 2. Formation of DOP

Overall reaction



Scheme 3. Overall reaction for formation of DOP

The first reaction giving MOP is very fast and is completed in a short time without any catalyst as shown in scheme 1 and thus the kinetics of the overall reaction is normally studied by looking at the DOP formation in the second stage of the reaction between the MOP and 2EH as shown in scheme 2, wherein the catalyst can have a real influence. Since this is an equilibrium reaction, it is essential to remove the water formed during the course of the reaction continuously to drive the reaction towards the product (DOP) side. Otherwise the reaction attains equilibrium at 70% conversion to DOP with the remaining part present as MOP. Water forms an azeotrope with 2EH in 80:20% weight ratio which can be distilled off.

3.2 Kinetic studies

3.2.1. Effect of speed of agitation

Experiments were conducted at various speeds viz. 800 rpm, 1000 rpm and 1200 rpm using MSA and p-TSA as a catalyst. The MSA and p-TSA concentrations were kept equal to 0.45% (w/w) and 1.25% (w/w),

respectively while molar ratio of reactants and temperature were maintained at 1:1.11 and 150°C, respectively. The change in concentration with respect to time shows similar trend for MSA and p-TSA. Figure 1 shows the effect of speed of agitation on the conversion of MOP using MSA as a catalyst. It has been seen that there is no appreciable change in conversion at various speeds (800rpm- 1200rpm) of agitation, indicating mass transfer resistances were absent. All further experiments were, therefore, carried out at a constant speed of agitation of 1000 rpm.

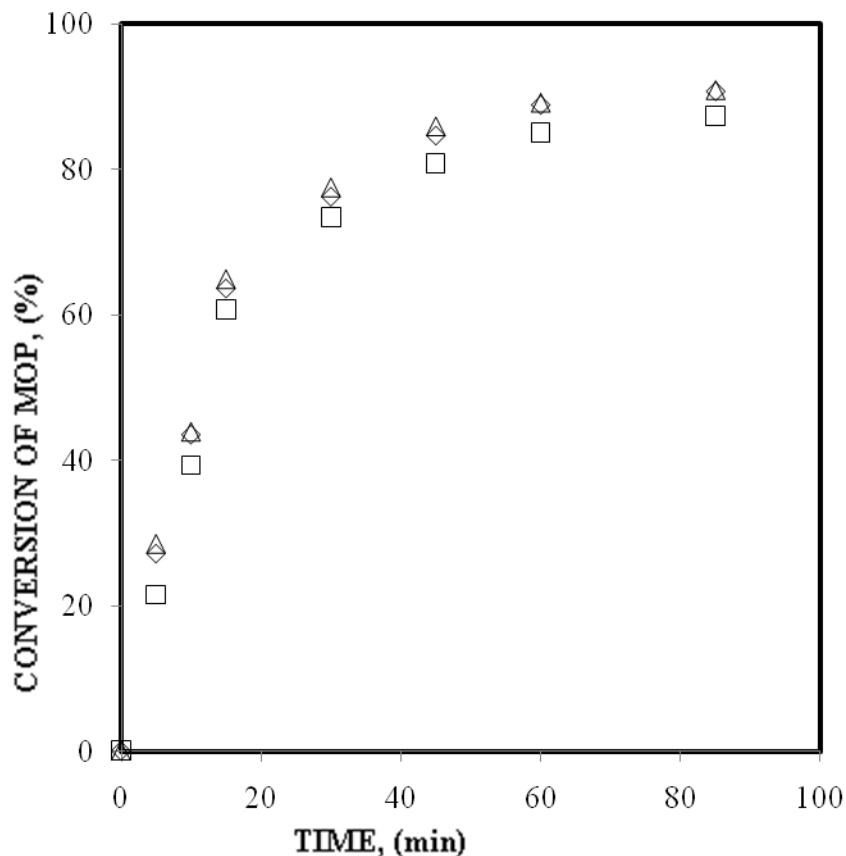
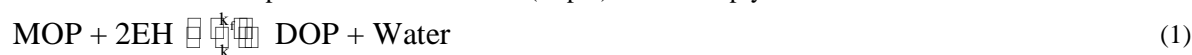


Figure 1. Effect of speed of agitation on the conversion of MOP

□, 800 rpm ; ◇, 1000 rpm; △, 1200 rpm

3.2.2. Kinetics

The reaction represented in Section 3.1 (step 2) can be simply written as follows:



k_f is a forward reaction rate constant and k_r is a reverse reaction (hydrolysis) rate constant. Since during the course of reaction, water formed is continuously removed, the reversible reaction becomes irrelevant. Therefore, the rate expression can be written as follows:

$$-\frac{d[\text{MOP}]}{dt} = -\frac{d[2\text{EH}]}{dt} = k[\text{MOP}]^x [\text{2EH}]^y \quad (2)$$

where x is the order in MOP and y is the order in 2EH, and $[]$ indicate concentration of a given species. The specific rate constant k could be considered as a function of the catalyst concentration as follows:

$$k = k' [\text{catalyst}]^z \quad (3)$$

where z is the order in the catalyst.

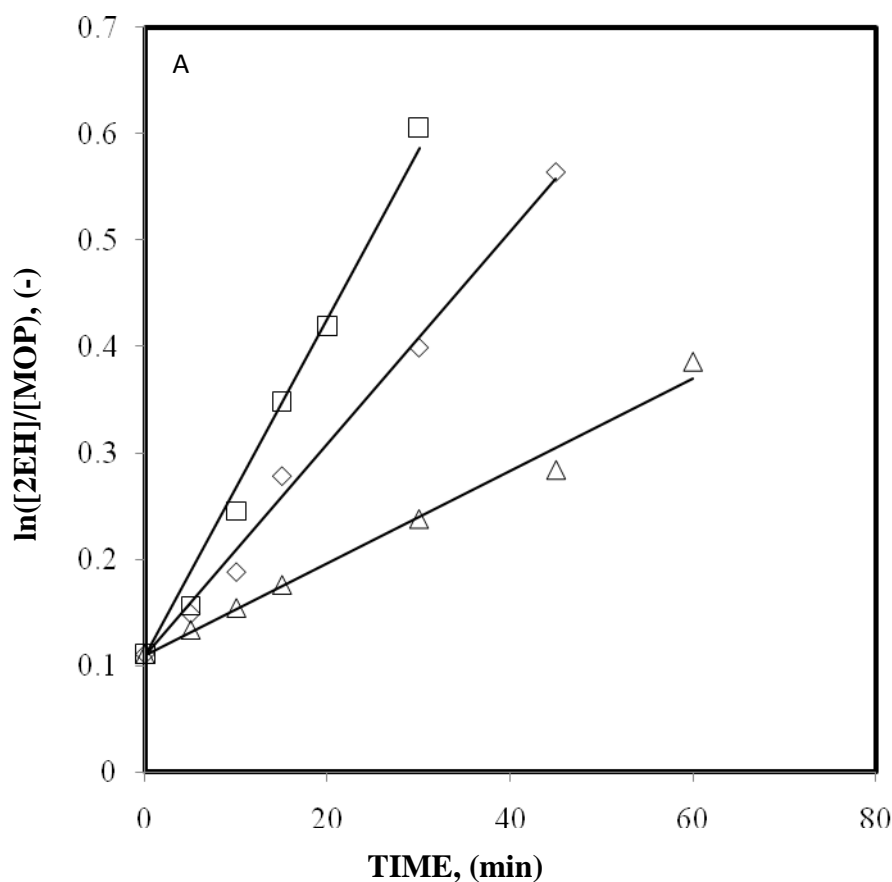
An integral method of analysis can be approximated for estimating rate constant and the order of the reaction wherein we guess the order with respect to the reactants. In the present case, the order with respect to the reactants has been assumed to be one. Thus integrating Eq. 2 between the limits $[MOP]^0$ (initial concentration of MOP) to $[MOP]$ as time goes from 0 to t, we get following rate expression:

$$\ln\left(\frac{[2EH]}{[MOP]}\right) = k\left([2EH]^0 - [MOP]^0\right)t + \ln\left(\frac{[MOP]^0}{[2EH]^0}\right) \quad (4)$$

where $[2EH]^0$ is an initial concentration of 2EH. A plot of $\ln([2EH]/[MOP])$ vs time, therefore, should give a straight line showing first order dependence on the concentration of both the reactants with a slope as $k([2EH]^0 - [MOP]^0)$.

3.2.2.1. Effect of temperature

Experiments were carried out using p-TSA and MSA as a catalyst at three different temperatures (140, 150, and 160°C). The molar ratio of reactants was kept constant at 1:1.11 while MSA and p-TSA concentrations were maintained at 0.45% (w/w) and 1.25% (w/w), respectively. Figure 2A and Figure 2B show the variation of $\ln[2EH]/[MOP]$ vs time for MSA and p-TSA, respectively. The specific value of k (rate constant) was determined by the slope of the lines at different temperatures. The straight lines obtained in each case indicate the reaction to be of first order with respect to both, MOP and 2EH.



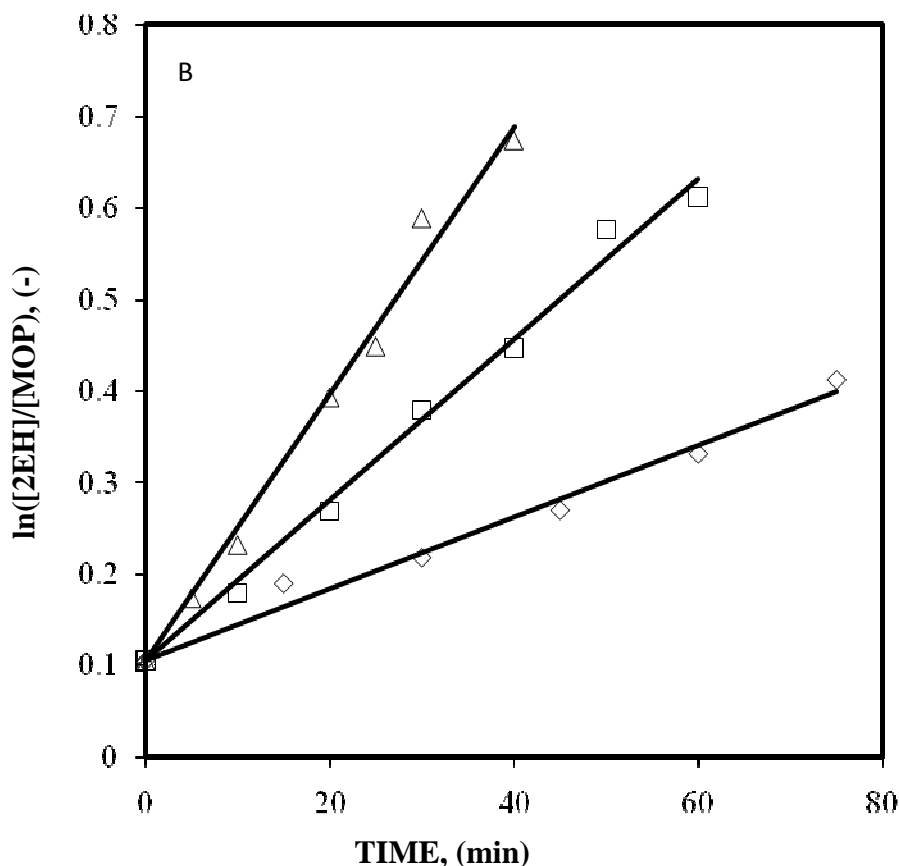


Figure 2. Second order kinetic plot

(A): Δ , 140°C; \diamond , 150°C; \square , 160°C (B): \diamond , 140°C; \square , 150°C; Δ , 160°C

3.2.2.2. Effect of catalyst loading

The concentration of the catalyst remains constant throughout the reaction since it is used up to accelerate the rate of reaction and regenerated during the course of the reaction. Therefore, in Eq. 2, k may be assumed to be equal to $k'[\text{catalyst}]$. In order to find the effect of catalyst loading, Eq. 2 can be written as follows:

$$r_{\text{MOP}} = -\frac{d[\text{MOP}]}{dt} = -\frac{d[2\text{EH}]}{dt} = k'[\text{Catalyst}]^z [\text{MOP}]^x [2\text{EH}]^y \quad (5)$$

$$\ln(r_{\text{MOP}}) = \ln k' + z \ln[\text{Catalyst}] + x \ln[\text{MOP}] + y \ln[2\text{EH}] \quad (6)$$

where r_{MOP} is the rate of reaction. If we find the rate of reaction at constant $[\text{MOP}]$ and $[2\text{EH}]$ at a given temperature and various catalyst concentrations, then a plot of $\ln(r_{\text{MOP}})$ against $\ln[\text{catalyst}]$ would give a straight line, the slope of which would be the order with respect to the catalyst. The rate at a given MOP concentration can be found from the slope of $[\text{MOP}]$ vs time curve or by differentiating the polynomial equation for $[\text{MOP}]$ vs time.

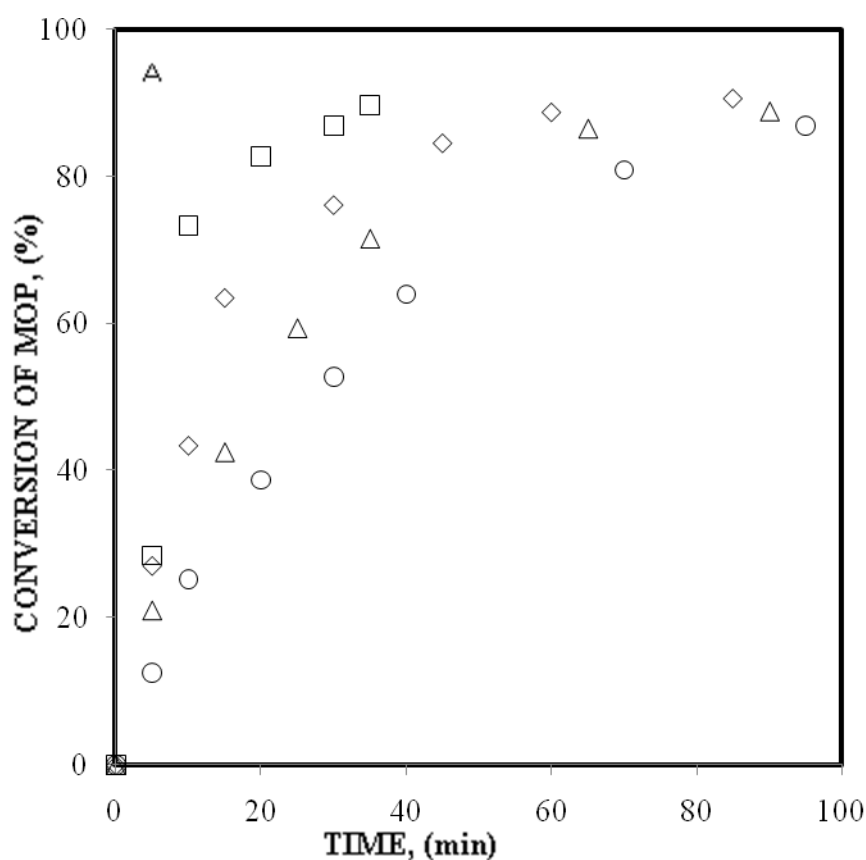
Figure 3A and 3B show the effect of catalyst loading on the conversion of MOP at 150°C and 1:1.11 molar ratio of the reactants for MSA and p-TSA, respectively. The rate of the reaction was calculated by plotting $[\text{monoester}]$ vs time and finding out the slope at $[\text{monoester}]$ equal to 1.6 mol.L⁻¹. Figure 4 shows that the order with respect to the catalysts is close to unity for both the catalysts. Thus the reaction of MOP with 2EH using MSA and p-TSA as a catalyst shows a first order dependence with respect to both the reactants as well as with respect to the catalyst, in the range of parameters studied. The Arrhenius equation parameters, E

(activation energy, cal mol^{-1}) and A (frequency factor, $\text{L}^2.\text{mol}^{-2}.\text{K}^{-1}$) were also determined for both the catalysts from the data for reaction carried out at three different temperatures and different catalyst concentrations. The data of k against temperature were fitted by linear regression, and E and A were determined. The rate expressions obtained for MSA and p-TSA, respectively are as follows:

$$-r_{\text{MOP}} = 1.20 \times 10^{12} \exp\left(\frac{-11940}{T}\right) [\text{Calatyst}] [\text{MOP}] [2\text{EH}] \quad (7)$$

$$-r_{\text{MOP}} = 5.99 \times 10^{13} \exp\left(\frac{-13800}{T}\right) [\text{Calatyst}] [\text{MOP}] [2\text{EH}] \quad (8)$$

The kinetic parameters of the reaction are reported in Table 2 in detail. Table 2 also shows the colour of the final reaction mixture measured on the Gardner scale. The MSA catalyst gives a very low colour index 2-3 on the Gardner scale as compared with a colour index of 5-6 obtained from p-TSA catalyst. Moreover, action rate with MSA catalyst was considerably higher as compared to the rate with p-TSA.



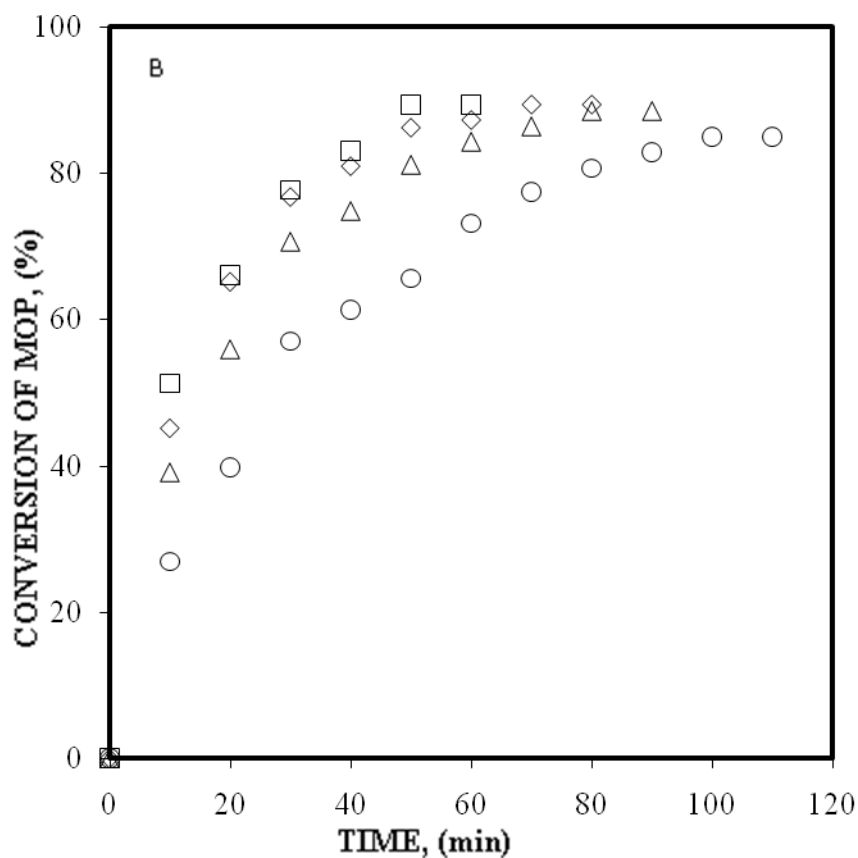


Figure 3. Effect of catalyst concentration on the conversion of MOP

(A): ○, 0.25% (w/w); △, 0.35% (w/w); ◇, 0.45% (w/w); □, 0.95% (w/w)

(B): ○, 0.5% (w/w); △, 1% (w/w); ◇, 1.25% (w/w); □, 1.4% (w/w)

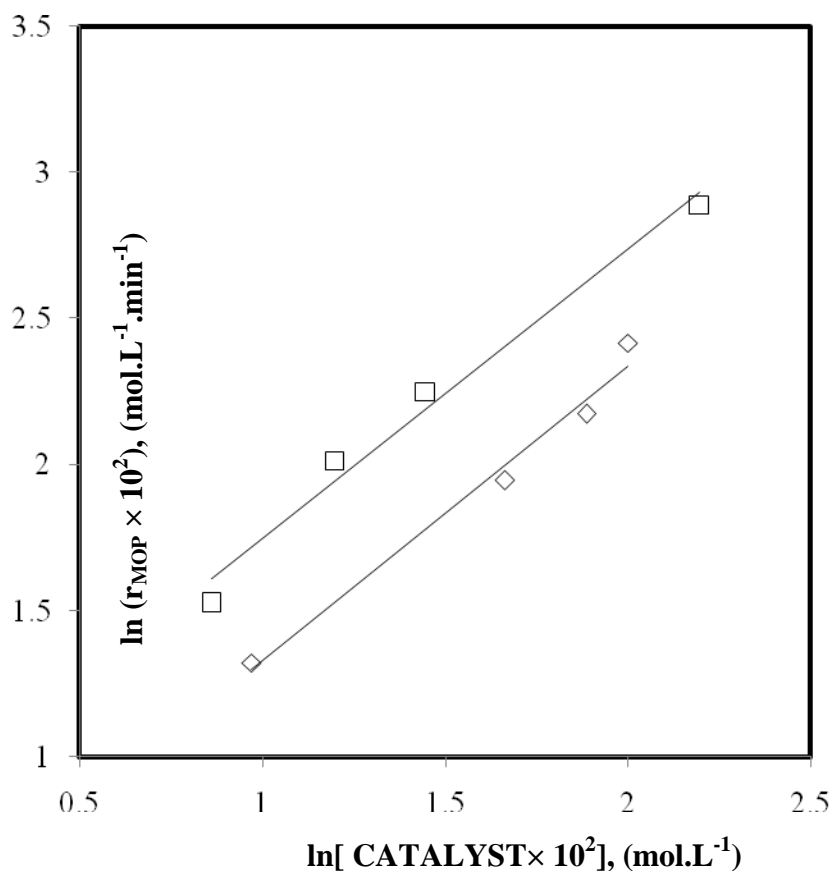
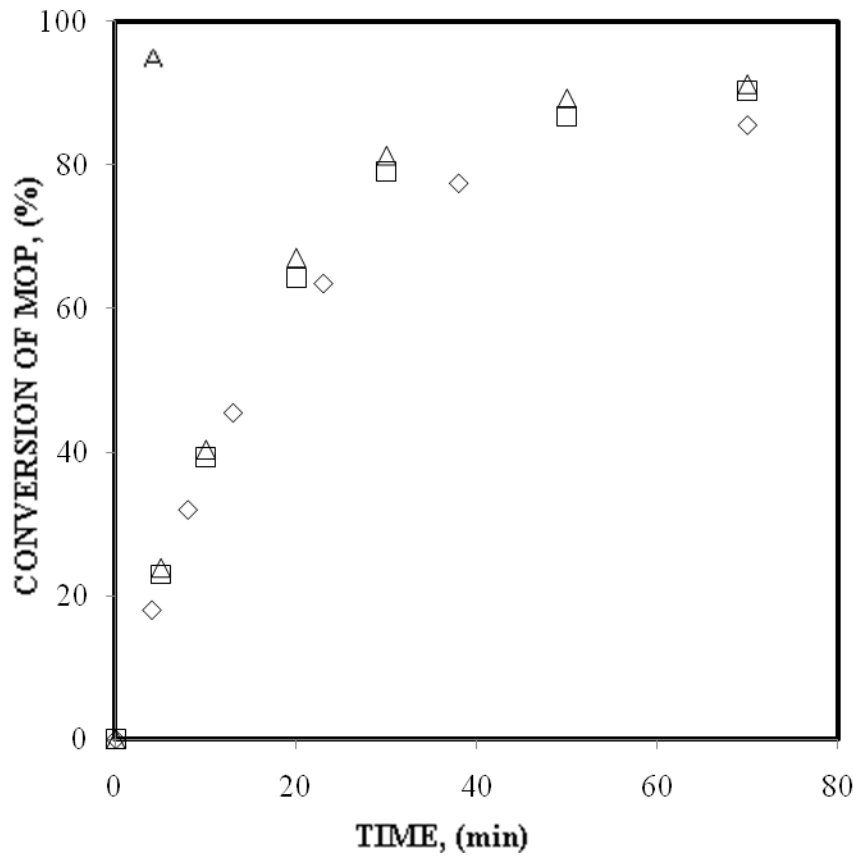


Figure 4. Effect of catalyst concentration on the rate of reaction

□, MSA; ◇, p-TSA

3.2.2.3. Effect of molar ratio of reactants

Experiments were conducted at three different molar ratios of monoester to 2EH (1:1.1, 1:1.4, and 1:1.8) at 150^oC using MSA and p-TSA as a catalyst. The MSA and p-TSA concentrations were kept constant at 0.45% (w/w) and 1.25% (w/w), respectively. Figure 5A and 5B show the effect of variation of the molar ratio of MOP to 2EH on the conversion of MOP for MSA and p-TSA, respectively. It has been seen that the conversion of MOP increases with an increase in the molar ratio. However, an increase in molar ratio shows no effect on the conversion of MOP for an initial period of 20 min.



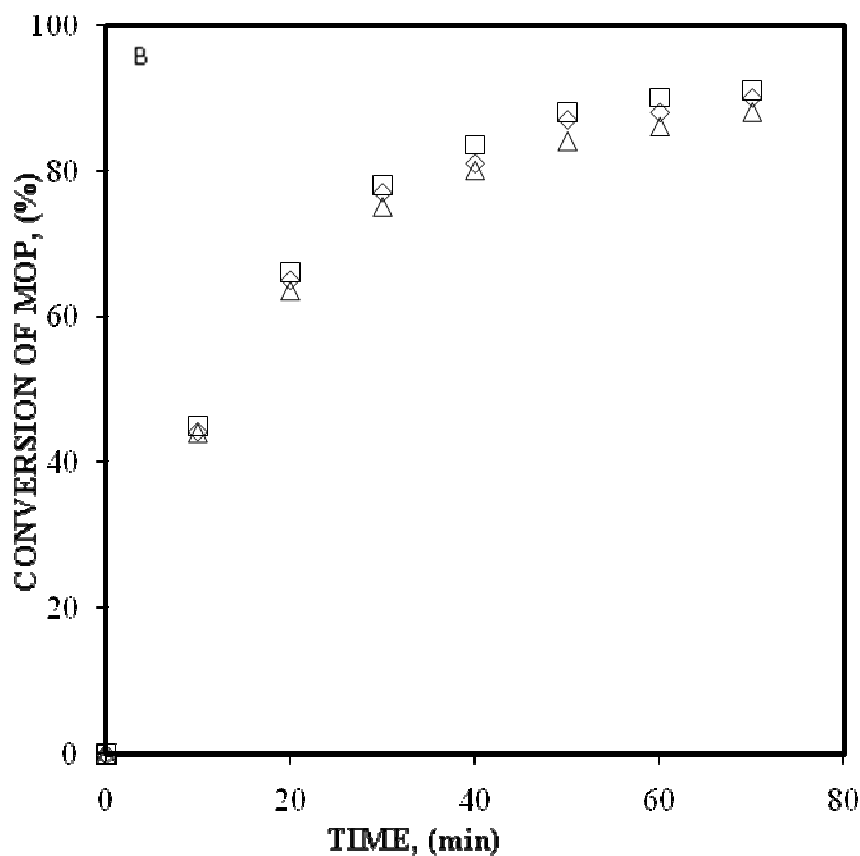


Figure 5. Effect of molar ratio on the conversion of MOP

(A): \diamond , 1:1.1; \square , 1:1.4; Δ , 1:1.8 (B): Δ , 1:1.11; \diamond 1:1.4; \square 1:1.8

4. Conclusions

The following conclusions can be drawn from the present study:

1. The kinetics of the reaction between PAN and 2EH using MSA and p-TSA essentially follows an overall second order kinetics, first with respect to each reactant in the range of variable studied. Further, first order dependence has been found with respect to the concentration of both the catalysts.

2. Under identical conditions, the rate of reaction using MSA has been found higher (~1.6 times) as compared to the rate with p-TSA. Moreover, the colour indexes for final reaction mixture on the Gardner scale were found to be 2-3 and 5-6 for MSA and p-TSA, respectively.

Nomenclature

[2EH] = concentration of 2EH, mol.L^{-1}

[Catalyst] = concentration of catalyst, mol.L^{-1}

[MOP] = concentration of monoester, mol.L^{-1}

A = frequency factor, $\text{L}^2.\text{mol}^{-2}.\text{min}^{-1}$

E = activation energy of a reaction, cal.mol^{-1}

k	= second order rate constant, $L \cdot mol^{-1} \cdot min^{-1}$
k'	= third order rate constant, $L^2 \cdot mol^{-2} \cdot min^{-1}$
r_{MOP}	= rate of reaction with respect to MOP, $mol \cdot L^{-1} \cdot min^{-1}$
t	= reaction time, min
T	= temperature, K
x	= order with respect MOP concentration, -
y	= order with respect to 2EH concentration, -
z	= order with respect to catalyst concentration, -

Subscripts

f	= forward reaction
r	= reverse reaction

Superscript

O	= initial condition
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Abbreviations

2EH	= 2-ethyl hexanol
DOP	= di-octyl phthalate
HPA	= heteropolyacid
MOP	= monoester (mono-2-ethyl hexyl phthalate)
MSA	= methane sulphonic acid
p-TSA	= para- toluene sulphonic acid
TBT	= tetrabutyl titanate
TBZ	= tetrabutyl zirconate

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