

# A green route for the acylation of resorcinol with acetic acid

G.D. Yadav, A.V. Joshi

**Abstract** 2',4'-Dihydroxyacetophenone, also known as resoacetophenone, is a commercially important intermediate which is generally prepared by the acylation of resorcinol with acetic acid in the presence of a molar excess of zinc chloride, which leads to waste disposal problems. The most frequently used acylating agents such as acetic anhydride and acetyl chloride have several disadvantages and need to be replaced by cheap and benign agents. In this connection, acetic acid is a better choice but with a non-polluting and reusable catalyst. The synthesis of 2',4'-dihydroxyacetophenone from resorcinol and acetic acid was carried out in the presence of a variety of solid acid catalysts such as montmorillonite clay (K-10), dodecatungstophosphoric acid (DTP) supported on K-10, sulfated zirconia and ion exchange resins. Amongst these catalysts, Amberlyst-36, an ion exchange resin, was found to be the most effective. The effects of various parameters on the rate of reaction and selectivity were investigated to establish the intrinsic kinetics of the reaction. It was possible to deduce the adsorption equilibrium constant and rate constant simultaneously for the reaction including the corresponding energies of activation. The catalyst is reusable. The process is in consonance with the principles of green chemistry.

## Introduction

Acylation of resorcinol is a very important reaction leading to the formation of 2',4'-dihydroxy acetophenone known as resoacetophenone. Resoacetophenone finds wide

applications as an intermediate in the manufacture of pharmaceuticals, perfumes (Kanachika et al. 1990), fine chemicals (Tanaka and Goto 1986), cosmetics (Satoh et al. 1992) and leukotriene antagonists (Marshall et al. 1988). Resoacetophenone is used in spectrophotometric determination of iron (Chowdary and Appalaraju 1975) and its application in sunscreen composition has also been reported (Bognar et al. 1971). It is employed as an intermediate for the preparation of allergy therapeutic agents (Fukumoto et al. 1995, 1996), UV-screening cosmetics (Satoh et al. 1992), food preservatives (Nishina and Sakurai 1994) and as a honey bee repellent (Gupta 1988).

The Friedel–Crafts acylation of aromatics is the method of choice in today's organic chemistry for synthesizing aromatic ketones as reactive intermediates for the production of fine chemicals. The conventional method of preparation of these aromatic ketones is the homogeneous Friedel–Crafts acylation of the corresponding hydrocarbons with carboxylic acid derivatives such as anhydrides or chlorides by using Lewis acids ( $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{BF}_3$ ,  $\text{ZnCl}_2$ ,  $\text{TiCl}_4$ ,  $\text{ZrCl}_4$ ) or Bronsted acids (polyphosphoric acid, HF). For this purpose, the catalyst has to be employed in quantities over stoichiometric proportion of the reagent (Olah 1963).

On the industrial scale, the use of metal halide types of acids, which are preferred catalysts, creates work-up and effluent problems. Indeed, during the workup of acylation mixtures, catalysts are destroyed which produce relatively large amounts of hydrochloric acid in the off-gas or in the effluent. This hydrochloric acid, which has to be disposed of, originates both from the catalyst and from acyl chloride employed for the acylation. In addition, the corrosion problem due to hydrochloric acid must be solved.

Pressure from legislative and environmental bodies together with a growing awareness within the chemical industry has led to a search for new eco-friendly processes to replace unacceptable outdated reactions. Therefore, a process that could be environmentally friendly and also inexpensive, with respect to the disadvantage indicated, is most desirable. Solid acids that give the desired level of activity but which can be easily removed from the reaction mixture with no residual inorganic contamination of the organic products offer obvious advantages over existing methods. Among several other researchers all over the world, considerable progress has been made in achieving these goals through recent developments in solid acid catalysis in our laboratory (Kumbhar and Yadav 1989; Yadav and Kirthivasan 1995; Yadav and Thorat 1996a, 1996b; Yadav and Krishnan 1998, 1999; Yadav and Nair

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1998, 1999; Yadav and Pujari 1999; Yadav and Goel 2000; Yadav et al. 2000, 2001a, 2001b; Yadav and Doshi 2002; Yadav and Sengupta 2002).

In Friedel–Crafts acylation, typically acetyl chloride, acetic anhydride and acetic acid are used as acylating reagents with homogeneous catalysts. The majority of the work is reported with acetic anhydride using Friedel–Crafts homogeneous catalysts. However, acetic acid has been used in a very few reactions mostly in the vapour phase. The mechanism is again dehydration of the acid to anhydride, which combines with the catalytic site. The use of a carboxylic acid is a greener process, since the anhydrides are always commercially produced from the acids by dehydration. In the case of acetic anhydride, it is a narcotic and is not freely available even for laboratory purposes and one has to give account of every millilitre of the liquid to authorities. The industry has to make special provisions. Besides, it costs more. The atom economy is poor because the co-product of the acylation is acetic acid, which has to be recovered. Acetyl chloride produces HCl, which is corrosive and has to be neutralized. So from a green chemistry viewpoint, the carboxylic acid is the best choice. Water is the co-product, which is benign.

Resoacetophenone is synthesized by Friedel–Crafts acylation of resorcinol. As mentioned earlier the acylating agents such as acetic anhydride and acetyl chloride have several disadvantages. Acetic anhydride gives acetic acid as a co-product whereas acetyl chloride leads to HCl generation. Acetic anhydride is a restricted chemical due to its potential use in narcotics and not readily available in many countries. It would be attractive from a green chemistry viewpoint to use acetic acid as the acylating agent with a solid acid. The preparation of resoacetophenone by Fries rearrangement of phenolic esters (Sharghi and Kaboudin 1998), and acylation with carboxylic acid has been studied with such catalysts as Amberlyst-15 (Fukumoto et al. 1996), zeolites (Van Bekkum et al. 1994), zinc chloride and HCl (Wang et al. 1993), BF<sub>3</sub> etherate (Panasencko et al. 1994), BF<sub>3</sub> complex (Mani et al. 1991), HBr (Marshall et al. 1988), HClO<sub>4</sub> (Mezheritskii and Dorofeenko 1969) and neat acid (Brown et al. 2000). The use of acetic anhydride as acylating agent has been made with ZnCl<sub>2</sub> and acetic acid (Kanechika et al. 1990), acetic acid (Tanaka and Goto 1986) and sodium acetate (Sato and Niwano 1993). Acyl chlorides are also used in acylating resorcinol (Farkas et al. 2000). The mono and diesters of resorcinol are also isomerized to get resoacetophenone. The foregoing shows that a lot of work has been reported with hazardous and polluting acids as catalysts for the acylation of resorcinol and also no kinetic information is available for solid acid catalysis. The current paper reports the acylation of resorcinol with acetic acid over different non-zeolitic solid acids in the presence of a variety of solid acid catalysts such as montmorillonite clay (K-10), dodecatungstophosphoric acid (DTP) supported on K-10, sulfated zirconia and ion exchange resins, including kinetic modeling. The results are novel and in consonance with the practice of green chemistry.

## Experimental

### Chemicals

Resorcinol, acetic acid, zirconium oxychloride, dodecatungstophosphoric acid and zinc chloride were obtained from M/s s.d. Fine Chemicals Pvt. Ltd., Mumbai, India, Filtrol-24 from Fluka, Germany, Amberlyst-36 from Rohm and Hass, USA, Indion-130 from Ion Exchange (I) Ltd., Mumbai, India and K-10 clay from Aldrich, Germany. All chemicals were analytical grade reagents and used without further purification.

### Catalysts

Dodecatungstophosphoric acid (DTP)/K-10 was prepared by a well-established procedure in our laboratory (Yadav and Kirthivasan 1995). Sulfated zirconia was also prepared by an established procedure (Kumbhar and Yadav 1989). The catalysts used for the reaction were dried at 110 °C for 2 h before use.

### Reaction procedure

The reaction was carried out in a flat bottom cylindrical glass vessel of 100 cm<sup>3</sup> capacity equipped with four baffles, a turbine stirrer and a condenser. The assembly was kept in an isothermal oil bath at a desired temperature and mechanically agitated with an electric motor.

All control experiments were preformed with 0.05 mol resorcinol, 0.5 mol acetic acid and 0.0515 g catalyst per cm<sup>3</sup> liquid phase, at 120 °C with a speed of 800 rpm. Typically the reaction mixture was allowed to reach the desired temperature, the catalyst added and the initial/zero time sample collected immediately after addition of catalyst. Agitation was then commenced at a particular speed. Samples were withdrawn periodically for analysis.

### Analysis

Analysis of the reaction mixture was done by HPLC (Tosoh), using the following conditions:

- Column=C-18 (reverse phase)
- Mobile phase=methanol:water (50:50)
- Detector wavelength=278 nm
- Flow rate of mobile phase=1 ml/min

Identification of the products was done by matching the retention time of reaction products with the authentic compounds. Typically the acylation led to the formation of 2',4'-dihydroxyacetophenone and the monoester of resorcinol. When the reaction time was prolonged beyond 3 h, then trace quantities of resoacetophenone monoacetate were obtained.

### Reaction scheme

In the presence of an acid catalyst, acetic acid forms a carbocation, which attacks resorcinol to form the monoester of resorcinol, which further undergoes Fries rearrangement to form resoacetophenone. The reaction scheme is as shown in Fig. 1.

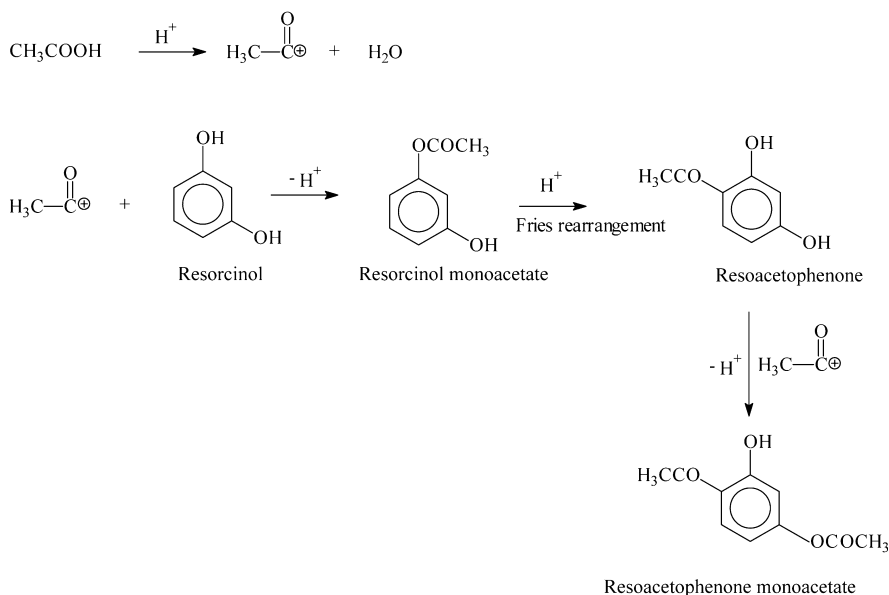


Fig. 1. Reaction scheme for acylation of resorcinol with acetic acid

## Results and discussion

### Efficacies of various catalysts

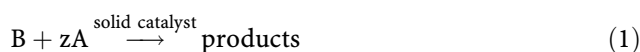
The different solid acid catalysts employed were K-10 montmorillonite, 20% DTP/K-10, sulfated zirconia, Filtrol-24, Indion-130 and Amberlyst-36, with a loading of  $0.0515 \text{ g/cm}^3$  based on the liquid volume of the reaction mixture at  $120^\circ\text{C}$ . The mole ratio of resorcinol to acetic acid was kept at 1:10, with a speed of agitation of 800 rpm (Table 1). Amberlyst-36 led to the maximum conversion of resorcinol and selectivity to resoacetophenone compared to other catalysts. Amberlyst-36 has a higher ion exchange capacity ( $5.45 \text{ meq/g}$ ) than Indion-130 ( $4.8 \text{ meq/g}$ ). These are Bronsted acids and so give more conversion.

### Effect of speed of agitation

This is a typical solid-liquid slurry reaction involving the transfer of resorcinol, the limiting reactant (B) and acetic acid (A) from the bulk liquid phase to the catalyst wherein external mass transfer of reactants to the surface of the catalyst particle, followed by intra-particle diffusion, adsorption, surface reaction and desorption, take place. Details of this theory for general slurry reactions are given elsewhere (Yadav and Krishnan 1999). The influence of external solid-liquid mass transfer resistance must be ascertained before a true kinetic model can be developed.

Table 1. Efficacies of various catalysts on conversion of resorcinol (resorcinol: acetic acid=1:10, catalyst loading= $0.0515 \text{ g/cm}^3$ , temperature= $120^\circ\text{C}$ , speed of agitation=800 rpm, time=5 h)

Catalyst	% Conversion	% Selectivity of resoacetophenone
Indion-130	56.7	98.0
Amberlyst-36	63.0	98.7
S-ZrO <sub>2</sub>	6.1	42.6
Filtrol-24	7.4	64.8
K-10	3.8	41.5
DTP/ K-10	12.3	71.8



At steady state, the rate of mass transfer per unit volume of the liquid phase ( $\text{mol cm}^{-3} \text{ s}^{-1}$ ) is given by:

$$R_B = k_{\text{SL-B}} a_p \{ [B_0] - [B_s] \} \quad (2)$$

(rate of transfer of B from bulk liquid to external surface of the catalyst particle)

$$= z k_{\text{SL-A}} a_p \{ [A_0] - [A_s] \} \quad (3)$$

(rate of transfer of A from the bulk liquid phase to the external surface of the catalyst particle;  $z=1$  in this case)

$$= r_{\text{obs}} \quad (4)$$

(observed rate of reaction within the catalyst particle).

Here the subscripts "0" and "s" denote the concentrations in bulk liquid phase and external surface of catalyst, respectively.

Depending on the relative magnitudes of external resistance to mass transfer and reaction rates, different controlling mechanisms have been put forward (Kumbhar and Yadav 1989). When the external mass transfer resistance is small, then the following inequality holds:

$$1/r_{\text{obs}} \gg \frac{1}{k_{\text{SL-A}} a_p [A_0]} \text{ and } \frac{1}{k_{\text{SL-B}} a_p [B_0]} \quad (5)$$

The observed rate  $r_{\text{obs}}$  could be given by three types of models wherein the contribution of intra-particle diffusional resistance could be accounted for by incorporating the effectiveness factor  $\eta$ . These models are:

1. The Power Law model if there is very weak adsorption of reactant species
2. The Langmuir-Hinselwood-Hougen-Watson model
3. The Eley-Rideal model

It was therefore necessary to study the effects of speed of agitation and catalyst loading to ascertain the absence of external and intra-particle resistance so that a true intrinsic kinetic equation could be used. The conversion was practically the same in the range of 800–1200 rpm, which indicated the absence of external solid–liquid mass transfer resistance (Fig. 2). Theoretical analysis was also done, as delineated below, to ensure that the external mass transfer resistance was indeed absent as delineated below.

According to Eq. (5), it is necessary to calculate the rates of external mass transfer of resorcinol (B) and acetic acid (A) and compare them with the rate of reaction.

For a typical spherical particle, the particle surface area per unit liquid volume is given by

$$a_p = \frac{6w}{\rho_p d_p} \quad (6)$$

where  $w$ =catalyst loading ( $\text{g}/\text{cm}^3$ ) of liquid phase,  $\rho_p$ =density of particle ( $\text{g}/\text{cm}^3$ ) and  $d_p$ =particle diameter (cm).

In resorcinol acylation, for a catalyst loading of  $0.0515 \text{ g}/\text{cm}^3$  with an average particle size ( $d_p$ ) of 0.03 cm, the value of  $a_p=10.84 \text{ cm}^2/\text{cm}^3$  of the liquid phase, the liquid phase diffusivity values of the reactants B (resorcinol) and A (acetic acid), denoted by  $D_{AB}$  and  $D_{BA}$ , were calculated using the Wilke–Chang equation (Reid et al. 1977) at  $120^\circ\text{C}$  as  $2.41 \times 10^{-5}$  and  $1.17 \times 10^{-5} \text{ cm}^2/\text{s}$ , respectively. The solid–liquid mass transfer coefficients for both A and B were calculated from the limiting value of the Sherwood number (e.g.  $Sh_{-B}=k_{SL-B}d_p/D_{BA}$ ) of 2. The actual Sherwood numbers are typically higher by an order of magnitude in well-agitated systems but for conservative estimations a value of 2 is taken (Yadav and Thorat 1996a; Yadav and Krishnan 1998). The solid–liquid mass transfer coefficients  $k_{SL-A}$  and  $k_{SL-B}$  values were obtained as  $1.61 \times 10^{-3}$  and  $7.8 \times 10^{-4} \text{ cm}/\text{s}$ , respec-

tively. The initial rate of reaction was calculated from the conversion profiles. A typical calculation shows that for a standard reaction, the initial rate was calculated as  $2.35 \times 10^{-7} \text{ mol}/\text{cm}^3 \text{ s}$ . Therefore, putting the appropriate values in Eq. (5):

$$1/r_{\text{obs}} \gg \frac{1}{k_{SL-A}a_p[A_0]} \text{ and } \frac{1}{k_{SL-B}a_p[B_0]} \quad (7)$$

i.e.  $4.25 \times 10^6 \gg 3.91 \times 10^3$  and  $8.05 \times 10^4$

The above inequality demonstrates that there is an absence of resistance due to the solid–liquid external mass transfer for both the species A and B and the rate may be either surface reaction controlled or intra-particle diffusion controlled. Therefore, the effects of catalyst loading at a fixed particle size and temperature were studied to evaluate the influence of intra-particle resistance. All further experiments were done at 800 rpm.

### Effect of catalyst loading

In the absence of external mass transfer resistance, the rate of reaction is directly proportional to catalyst loading based on the entire liquid phase volume. The catalyst loading was varied over a range of  $0.013$ – $0.068 \text{ g}/\text{cm}^3$  on the basis of total volume of the reaction mixture for resorcinol and acetic acid. Figure 3 shows the effect of catalyst loading on the conversion of resorcinol. The conversion increases with increasing catalyst loading, which is obviously due to the proportional increase in the number of active sites. The selectivity is greater than 95% for resoacetophenone in all the cases. All further experiments were carried out at  $0.0515 \text{ g}/\text{cm}^3$  of catalyst loading.

As shown by Eqs. (1) and (2), at steady state, the rate of external mass transfer (i.e. from the bulk liquid phase in which A and B are located with concentration  $[A_0]$  and  $[B_0]$ , respectively) to the exterior surface of the catalyst is proportional to  $a_p$ , the exterior surface area of the catalyst where the concentrations of A and B are  $[A_S]$  and  $[B_S]$ , respectively. For a spherical particle,  $a_p$  is also propor-

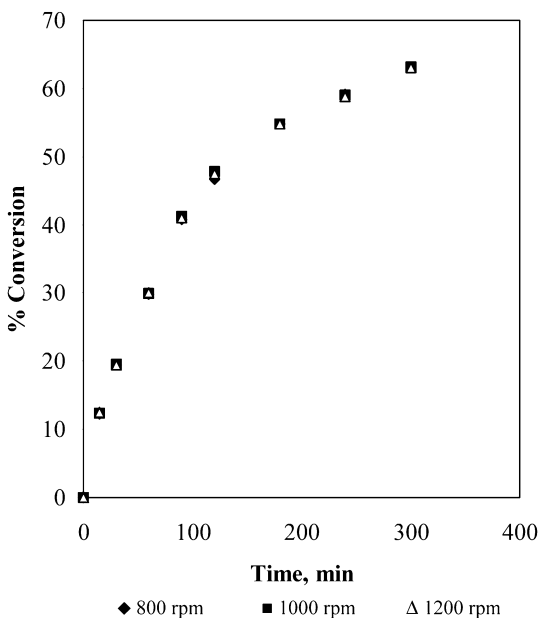


Fig. 2. Effect of speed of agitation on conversion of resorcinol. Resorcinol:acetic acid: 1:10; catalyst loading:  $0.0515 \text{ g}/\text{cm}^3$ ; temperature:  $120^\circ\text{C}$ ; time: 5 h; catalyst: Amberlyst-36

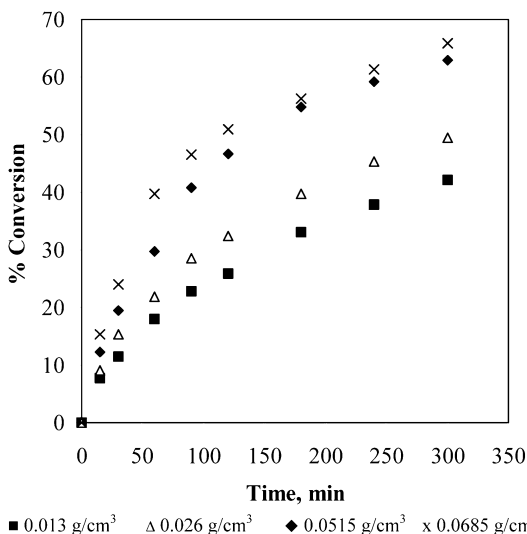


Fig. 3. Effect of Catalyst loading on conversion of resorcinol. Resorcinol: acetic acid: 1:10; catalyst: Amberlyst-36; time: 5 h; temperature:  $120^\circ\text{C}$ ; speed of agitation: 800 rpm

tional to  $w$ , the catalyst loading per unit liquid volume as shown by Eq. (6). It is possible to calculate the values of  $[A_S]$  and  $[B_S]$ . For instance,

$$k_{SL-A} a_p \{ [B_0] - [B_S] \} = r_{obs} \text{ at steady state} = 2.35 \times 10^{-7} \text{ mol cm}^{-3} \text{ s}^{-1} \quad (8)$$

Thus putting the appropriate values, it is seen that  $[B_S] \approx [B_0]$ , and similarly  $[A_S] \approx [A_0]$ . Thus, any further addition of catalyst is not going to be of any consequence for external mass transfer.

### Proof of absence of intra-particle resistance

The average particle diameter of the catalyst used in the reactions was 0.03 cm and thus a theoretical calculation was done based on the Wiesz-Prater criterion to assess the influence of intra-particle diffusional resistance (Fogler 1995).

According to the Wietz-Prater criterion, the dimensionless parameter  $C_{wp}$  which represents the ratio of the intrinsic reaction rate to the intra-particle diffusion rate, can be evaluated from the observed rate of reaction, the particle radius ( $R_p$ ), effective diffusivity of the limiting reactant ( $D_e$ ) and concentration of the reactant at the external surface of the particle.

- If  $C_{wp} = -r_{obs} \rho_p R_p^2 / D_e (B_s) \gg 1$ ,
  - then the reaction is limited by severe internal diffusional resistance.
- If  $C_{wp} \ll 1$ ,
  - then the reaction is intrinsically kinetically controlled.

The effective diffusivity of resorcinol ( $D_{e-B}$ ) inside the pores of the catalyst was obtained from the bulk diffusivity ( $D_{BA}$ ), porosity ( $\epsilon$ ) and tortuosity ( $\tau$ ), where  $D_{e-B} = D_{BA} \epsilon / \tau$ . In the present case, the value of  $C_{wp}$  was calculated as 0.023 for the initial observed rate, which is much less than 1, and therefore the reaction is intrinsically kinetically controlled. A further proof of the absence of the intra-particle diffusion resistance was obtained through the study of the effect of temperature.

### Effect of mole ratio

The mole ratio of resorcinol to acetic acid was varied from 1:1 to 1:10 mole for which the standard catalyst loading of 0.0515 g/cm<sup>3</sup> was used. The conversion of resorcinol was found to be only 27.6%, when the resorcinol to acetic acid mole ratio was 1:1 (Fig. 4). With an increase in mole ratio to 1:10, the conversion of resorcinol increased to 63%. This is because with an increase in mole ratio the dilution of water in acetic acid increases, whereas the selectivity towards resoacetophenone remains almost the same. All further experiments were carried out at resorcinol to acetic acid mole ratio of 1:10.

### Effect of temperature

The effect of temperature on conversion under otherwise similar conditions was studied in the temperature range of

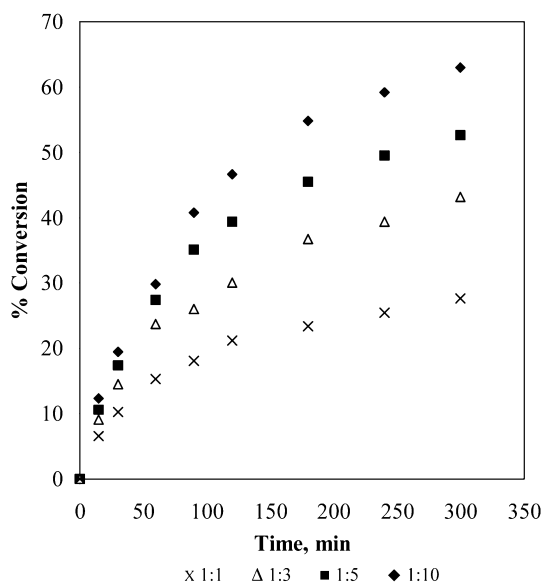


Fig. 4. Effect of mole ratio on conversion of resorcinol. Catalyst: Amberlyst-36; temperature: 120 °C; speed of agitation: 800 rpm; time: 5 h; catalyst loading: 0.0515 g/cm<sup>3</sup>

90–120 °C (Fig. 5). The conversion was found to increase substantially from 7.8 to 63% and selectivity towards resoacetophenone also increased from 83 to 98.7% with increase in temperature from 90 to 120 °C. With an increase in temperature, formation of carbocation, due to dehydration of acetic acid, increases and hence more conversion is obtained. All standard experiments were carried out at 120 °C.

### Effect of addition of water

A known quantity of water, in the range of 0.0167–0.1 mol, was added to the reaction mixture and the catalyst loading was kept constant, under otherwise similar

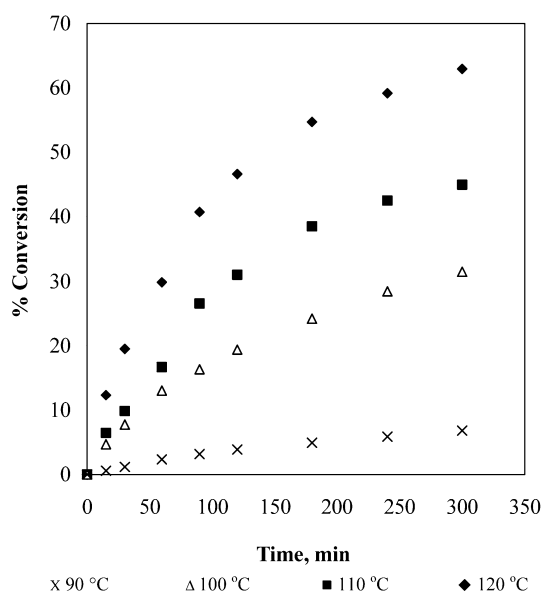


Fig. 5. Effect of temperature on conversion of resorcinol. Resorcinol:acetic acid: 1:10; catalyst: Amberlyst-36; time: 5 h; speed of agitation: 800 rpm; catalyst loading: 0.0515 g/cm<sup>3</sup>

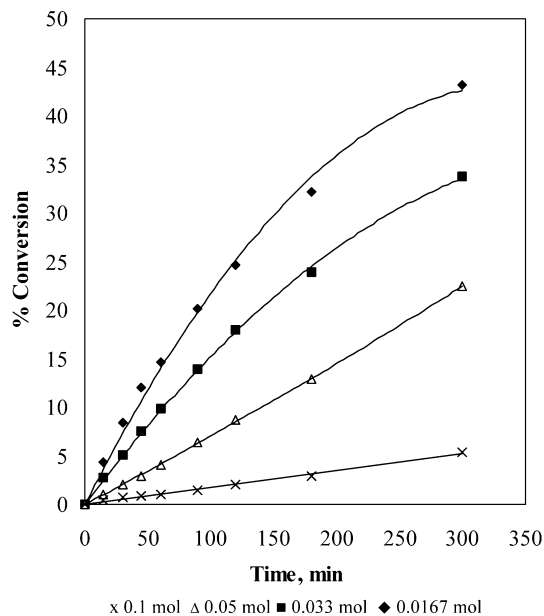


Fig. 6. Effect of water on conversion of resorcinol. Resorcinol:acetic acid: 1:10; catalyst: Amberlyst-36; time: 5 h; temperature: 120 °C; speed of agitation: 800 rpm; catalyst loading: 0.0515 g/cm<sup>3</sup>

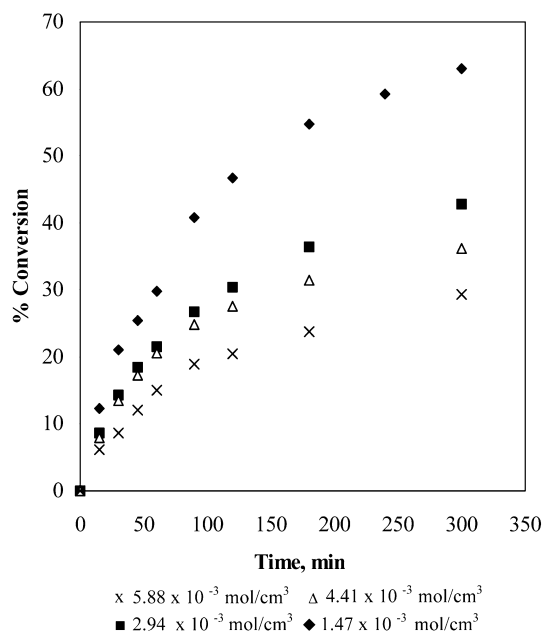


Fig. 7. Effect of concentration of resorcinol. Resorcinol:acetic acid; catalyst: Amberlyst-36; time: 5 h; temperature: 120 °C; speed of agitation: 800 rpm; catalyst loading: 0.0515 g/cm<sup>3</sup>

reaction conditions (Fig. 6). It was observed that the presence of water had a pronounced effect on the conversion of resorcinol, which decreased from 43.2% to 5.43% when the quantity of water added to reaction mixture was increased from 0.0167 to 0.1 mol. In the presence of water, dehydration of acetic acid leading to generation of carbocation is suppressed resulting in lower conversion.

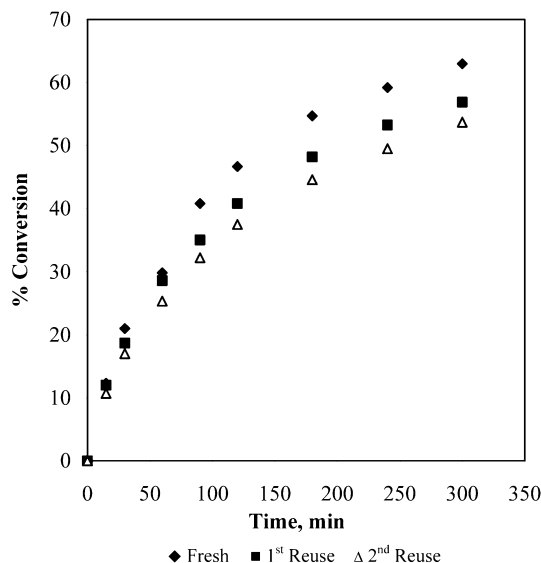


Fig. 8. Effect of reusability of catalyst. Resorcinol:acetic acid: 1:10; catalyst: Amberlyst-36; time: 5 h; temperature: 120 °C; speed of agitation: 800 rpm; catalyst loading: 0.0515 g/cm<sup>3</sup>

**Effect of concentration of resorcinol**

The effect of concentration of resorcinol was studied in the range of 1.47–5.88×10<sup>-3</sup> mol/cm<sup>3</sup> (Fig. 7) by keeping the total volume of the reaction mixture the same. It was observed that conversion decreased with increasing concentration of resorcinol. Conversion decreased from 63% to 29.3% when the concentration of resorcinol was increased from 1.47×10<sup>-3</sup> to 5.88×10<sup>-3</sup> mol/cm<sup>3</sup>, which is due to a decrease in the formation of carbocation with an increase in the concentration of resorcinol.

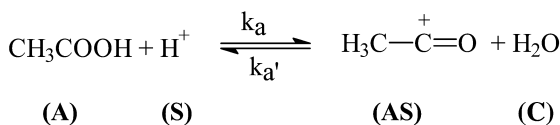
**Catalyst reusability**

The reusability of Amberlyst-36 was tested three times (Fig. 8). The catalyst was filtered, washed with methanol, dried in an oven at 120 °C for 2 h and weighed after each run. In the presence of the fresh catalyst, the conversion of resorcinol was 63%. During the third run, the conversion had decreased to 53.7% without any significant change in the selectivity of resoacetophenone. There is some loss of catalyst during filtration due to attrition. Thus the catalyst was satisfactorily reusable.

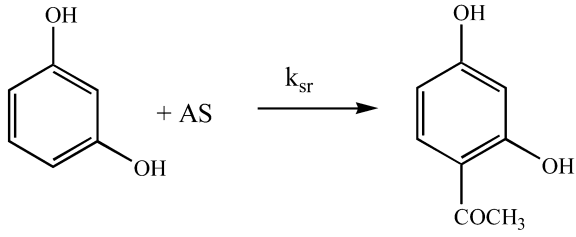
**Mechanism and reaction kinetics**

In the absence of mass transfer effects, the following mechanism is proposed based on the earlier work emanating from this laboratory. This model has already been discussed in detail for the acylation of 2-methoxy naphthalene (Yadav and Krishnan 1999).

The first step involves formation of carbocation by the adsorption of acetic acid on a catalytic site:



Now the reaction between the adsorbed A as AS and the liquid phase reactant B takes place as follows:



where  $k_{sr}$ =reaction rate constant.

The rate of reaction of resorcinol per unit liquid volume is given by

$$\frac{-dC_B}{dt} = k_{sr}C_B C_{AS} \tag{9}$$

After substituting for  $C_{AS}$

$$\frac{-dC_B}{dt} = k_{sr}C_B \frac{K_a C_A C_S}{C_C} = (k_{sr}K_a) \frac{C_A C_B C_S}{C_C} \tag{10}$$

The total site balance is as follows:

$$C_{total} = w = C_{AS} + C_S \tag{11}$$

where  $w$  is the catalyst loading

$$\frac{-dC_B}{dt} = \frac{k_{sr}K_a w C_A C_B}{C_C + K_a C_A} \tag{11a}$$

$$C_B = C_{Bo}(1 - X_B) \tag{12}$$

$$C_A = C_{Ao} - C_{Bo}X_B = C_{Bo}(M - X_B) \tag{13}$$

$$C_C = C_{Bo}X_B \tag{14}$$

where  $C_{Ao}/C_{Bo} = M$  is the initial mole ratio of acetic acid to resorcinol. Substituting for all terms of  $X_B$ , we get, for  $M=1$

$$K_a X_B + \ln(1 - X_B) + \left(\frac{X_B}{1 - X_B}\right) = k_{sr}K_a w t \tag{15}$$

For small values of  $K_a$ , the first term is negligible. For  $M \neq 1$  the following equation holds true:

$$-\ln(1 - X_B) + M \ln\left(\frac{M - X_B}{M}\right) = k_{sr}K_a(M - 1)w t \tag{16}$$

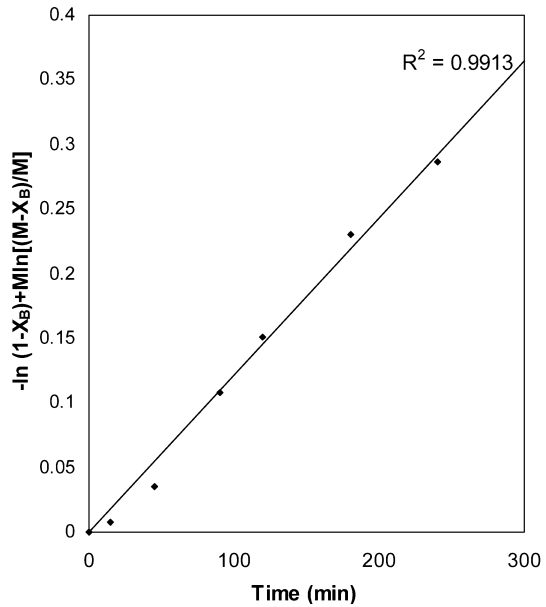


Fig. 10. Plot of  $-\ln(1-X_B) + M \ln [(M-X_B)/M]$  versus time for  $M \neq 1$

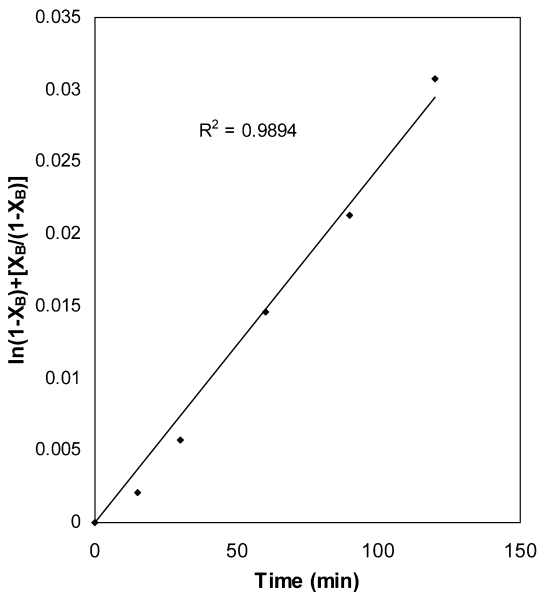


Fig. 9. Plot of  $\ln(1-X_B) + [X_B/(1-X_B)]$  versus time for  $M=1$

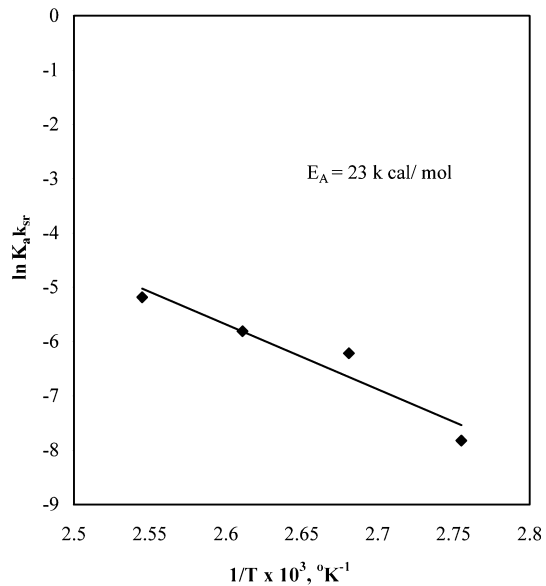


Fig. 11. Arrhenius plot

where  $k_{sr}$ =reaction rate constant,  $X_B$ =fractional conversion of resorcinol  $K_a=k_a/k_a'$ , and adsorption equilibrium constant.

From the concentration–time profile, the above rate equation was applied for the rates after 5 min when the acetic acid concentration had built up.

The various equations were validated against the experimental data to find that Eq. (15) for  $M=1$  (Fig. 9) and Eq. (16) for  $M \neq 1$  (Fig. 10), wherein  $K_a \ll 1$ , fit very well. The energy of activation was calculated from the Arrhenius plot (Fig. 11) and found to be 23 kcal/mol.

## Conclusions

This paper dealt with the acylation of resorcinol with acetic acid by employing different solid acid catalysts. Amberlyst-36 was found to be the best catalyst. The effects of various parameters on the rates of reaction were studied systematically. The reaction was found to be kinetically controlled. The Eley–Rideal type of mechanism was found to hold, by which acetic acid gets adsorbed on the acid site and a carbocation is generated which reacts with resorcinol from the liquid phase in the pore space. It was also possible to determine simultaneously the rate constant and the adsorption equilibrium constant for acetic acid. The process is greener because (a) it produces no waste, (b) it does not require any post treatment of effluent, (c) it is cheaper, (d) it uses less energy, (e) it does not use any hazardous substance and (f) water is the benign co-product. There are no restrictions whatsoever in any country on the use of acetic acid but there are for acetic anhydride. Only the mono-acylated product is formed by using appropriate conditions. The rates are faster and hence reactor volumes will be lower for continuous processes and less processing time will be required for batch processes.

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