

Kinetics of Alkylation of p-Cresol with Isobutylene Catalyzed by Sulfated Zirconia

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Absorption of isobutylene in p-cresol to prepare butylated hydroxytoluene (BHT), an important antioxidant, has been studied by using solid sulfated zirconia. Absorption is accompanied by complex chemical reactions. Detailed theoretical and experimental analysis of this system is reported here, and kinetic parameters have been established. Effects of various parameters such as partial pressure of isobutylene, catalyst loading, particle size, and temperature on the rates of reaction have been analyzed.

Introduction

Alkylphenols are commercially very important due to their diverse applications. 2,6-Di-*tert*-butyl-*p*-cresol or butylated hydroxytoluene (BHT) is an industrially important antioxidant used to inhibit gum formation in leaded gasoline. Its condensation product with formaldehyde is a particularly useful antioxidant for polymers, oils, waxes, etc. 3-Methyl-6-*tert*-butylphenol is used as an intermediate in the manufacture of musk ambrette. 4-Methyl-2,6-di-*tert*-butylphenol is widely used in motor and aviation gasolines, insulating oils, natural and synthetic rubbers, etc. 6-Isopropyl-3-methylphenol (thymol) is used in perfumes and also as disinfectant.

Alkylphenols are generally manufactured by addition of an alkyl group to the corresponding phenols. The source of alkyl group may be an aliphatic alcohol, a chloride, or an olefin. Olefins are preferred commercially due to their lower cost and ease of handling. The alkylation is usually carried out in the presence of Bronsted acid or Lewis acid catalysts. In the presence of acidic catalysts, substitution occurs at ortho and para positions. The ortho/para distribution depends on the reaction temperature, nature of the catalyst and catalyst concentration, and structure of the olefin employed. It is also dependent to a large extent on the positions already occupied by the substituent groups. In the case of *tert*-alkylphenols it rearranges and dealkylates in the presence of acidic catalyst at higher temperature. The reversibility of the alkylation reaction helps in the separation of certain close boiling compounds such as *m*- and *p*-cresol.

Various olefins such as propylene and butenes have been studied as alkylating agents in the presence of catalysts like $\text{SiO}_2\text{-Al}_2\text{O}_3$, γ -alumina, zeolites, H_2SO_4 , and ion exchange resins (Ullmann, 1985). Homogeneous acidic media have also been widely used (AlCl_3 , TiCl_4 , FeCl_3 , etc.) for alkylation reactions in liquid phase. The advantages of solid catalysts over liquid phase homogeneous catalysts are well-known.

The alkylation of cresols with isobutylene in presence of homogeneous acidic catalysts and solid catalysts such as cation exchange resins in the liquid phase has been reported in the literature (Weinrich, 1943; Gehlawat and Sharma, 1970; Kirk and Othmer, 1978; Rubinshtein *et al.*, 1980; Unni and Bhatia, 1982; Santacessaria *et al.*, 1988; Patwardhan, 1989). Malinowski (1975) has prepared 4-methyl-2-*tert*-butyl and 4-methyl-2,6-di-*tert*-

butylphenol in the presence of Lewatit SPC 120 and Amberlyst-15. Santacessaria *et al.* (1988) have reported a detailed kinetic study with the influence of heat and mass transfer on the alkylation of p-cresol with isobutylene catalyzed by cation exchange resins, particularly Amberlyst-15.

Alkylation of p-cresol with isobutylene is a combination of series and parallel steps proceeding via an intermediate. The reaction products are the monoalkylated and dialkylated *p*-cresols and the oligomerized isobutylene leading to dimer, trimer, and tetramer. BHT, a dialkylated product, is an important antioxidant.

Sulfated zirconia has been prepared and characterized in this laboratory and used for a variety of reactions. It was therefore thought desirable to test the efficacy of the sulfated zirconia as a superacid in the alkylation reaction of p-cresol with isobutylene in order to compare its performance with the cation-exchanged resins, particularly Amberlyst-15. One of the important aspects of this reaction is the complex kinetics which could be greatly influenced by the proper choice of a solid catalyst.

This paper deals with the modeling and experimental investigations of the absorption of isobutylene in *p*-cresol catalyzed by sulfated zirconia.

Experimental Section

Chemicals. p-Cresol, with a purity of >99%, was obtained from Fluka. Pure isobutylene gas from British Oxygen Company was used without any purification. Zirconium oxychloride and BHT were obtained from Loba Chemie.

Catalysts. Sulfated zirconia (S-ZrO_2) catalyst was prepared by the method described by Yadav and co-workers from this laboratory (Kumbhar *et al.*, 1988, 1990; Thorat, 1994). $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was dissolved in deionized water followed by precipitation to zirconium hydroxide by using aqueous ammonia solution. The precipitated zirconium hydroxide was made neutral (chloride and ammonia free) by washing with deionized water and subsequently dried at 110 °C for 24 h. It was then crushed to obtain the desired average particle size (100 μm).

The impregnation was performed by immersing the dried hydroxide in 0.5M H_2SO_4 in the ratio of 1 g of zirconium hydroxide to 15 cm^3 of H_2SO_4 followed by drying for 1.5 h and calcination at the desired temperature of 650 °C in a Pyrex tube for 3 h.

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Table 1. Textural and Structural Characteristics of Pure and Sulfated Zirconia Catalysts

sample	nature of phases	particle/crystallite size (Å)	surface area (m ² /g)	max pore radius (Å)	pore volume (mL/g)
pure ZrO ₂	monoclinic	204.8	19.20	29	0.52
S-ZrO ₂	tetragonal	164.67	91.14	20	0.93

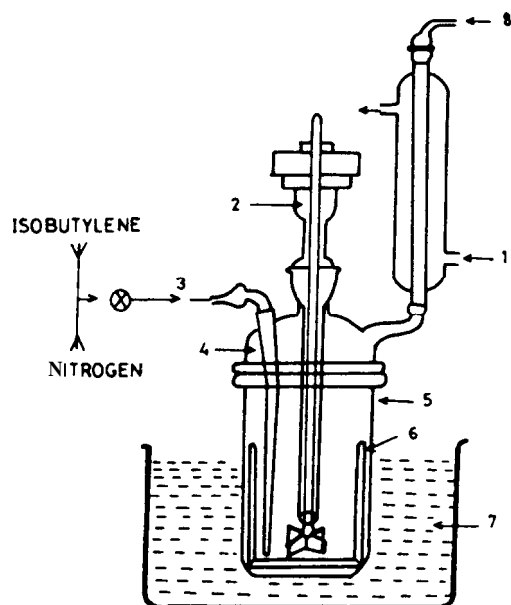


Figure 1. Experimental setup: 1, water inlet to condenser; 2, stirrer pulley; 3, gas inlet; 4, reactor cover; 5, reactor; 6, baffles; 7, thermostatic bath; 8, gas outlet.

Experimental Setup. All the experiments were carried out in a fully baffled four-necked glass reactor, 5 cm internal diameter, of 150 cm³ capacity (Figure 1). A six-bladed pitched impeller at a distance of 2–5 mm from the bottom of the reactor was placed for effective agitation. Isobutylene gas from a cylinder with a controlled flow rate was bubbled in the system with the help of a gas sparger. The outgoing (unreacted) gas was absorbed in aqueous acid solution or vented safely to atmosphere.

Reaction Procedure. The desired amount of *p*-cresol (0.3825 g-mol) was first fed to the reactor which was kept in a constant temperature oil bath, and the temperature was raised to 75 °C. Then a weighed quantity (1.24 g) of the catalyst 3% (w/w) based on *p*-cresol, which was dried at 110 °C for 1 h prior to use, was added to the reaction mixture. Isobutylene was introduced into the system. The flow of the gas was maintained in such a way as to have a positive flow at the reactor outlet and to maintain liquid phase saturated with the solute gas. The stirrer speed was kept at 1000 rpm for all the runs to eliminate the resistance to external mass transfer except where the effect of speed of agitation was studied. Samples (0.5 cm³) were withdrawn periodically, cooled, filtered, and analyzed by gas chromatography (GC).

Analysis. Analysis of the samples was done on a Netal gas chromatograph (Omega model) by using a flame ionization detector and a Perkin Elmer integrator. A stainless steel column (2 m x 3 mm) packed with 10% OV-17 liquid phase supported on a stationary phase of Chromosorb WHP was employed. Synthetic mixtures of authentic samples were used for standardization and quantification of the reaction mixtures.

Results and Discussion

Catalyst. Sulfated zirconia is a solid superacid with an acid strength of $H_0 = -16.04$. Structural and

textural studies including acidity measurements of superacidic S-ZrO₂ catalyst have been carried out by number of researchers (Hino and Arata, 1979; Tanabe et al., 1986, 1987; Scurell, 1987; Bensitel et al., 1987; Kumbhar et al., 1990; Kustov et al., 1994; Thorat, 1994) using various techniques such as XRD, XPS, BET, DTA-TGA, FTIR, and mercury porosimetry.

Recently, it has been reported that the superacidity of S-ZrO₂ is due to the presence of both Bronsted and Lewis acid sites (Kustov et al., 1994).

Table 1 lists our results of the structural and textural characteristics of pure and sulfated zirconia catalysts (for detailed characterization see Kumbhar (1988), Kumbhar et al. (1990), Kustov et al. (1994), and Thorat (1994)).

The alkylation reactions follow C-alkylations at temperatures above 30 °C and O-alkylation below 30 °C. Hence alkylation of *p*-cresol with isobutylene was studied at temperatures between 40 and 75 °C.

Reaction Pathway and Product Distribution. The absorption of isobutylene (A) in the liquid phase containing the reactant, *p*-cresol (B), catalyzed by the solid acid (C) leads to several products depending on the reaction conditions as follows:

Main Products: Alkylated *p*-Cresol.

monoalkylation of *p*-cresol



dialkylation of *p*-cresol



Byproducts: Oligomers of Isobutylene.

dimerization of isobutylene



trimerization of isobutylene



tetramerization (or quaternization) of isobutylene



where D = 2-*tert*-butyl-*p*-cresol, E = 2,6-di-*tert*-butyl-*p*-cresol (BHT), F = diisobutylene, G = triisobutylene, and H = tetraisobutylene.

As regards the current work, with sulfated zirconia as catalyst, the formation of higher oligomers was not noticed in the reaction mixture. Alkylated products of *p*-cresol containing diisobutylene (Cs) or triisobutylene (C₁₂) moieties, although possible, were also not detected. Trans-alkylation of dibutylated hydroxytoluene (BHT) was not observed. Thus, the above five reactions were considered in the development of a suitable model.

Model Development. There are several steps in this complex reaction scheme. A schematic representation is shown in Figure 2.

The rate of mass transfer of A from the gas-liquid interface to the exterior surface or the solid catalyst involves three steps in series which are as follows.

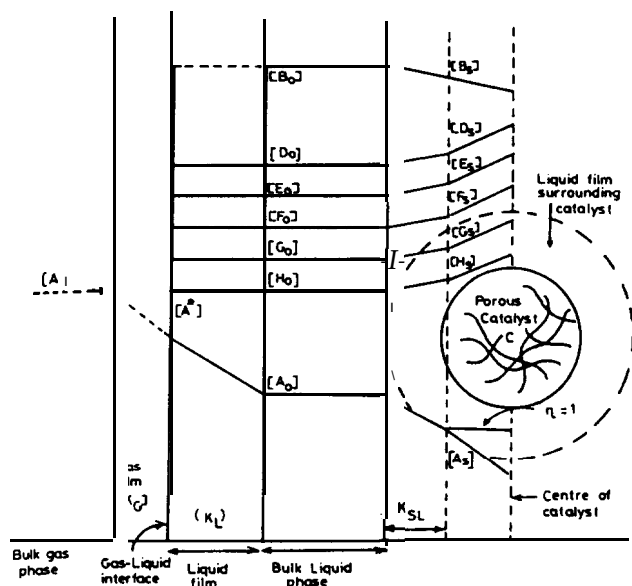


Figure 2. Typical concentration profiles for the alkylation of p-cresol with isobutylene. A = isobutylene; B = p-cresol; C = solid catalyst; D = 2-*tert*-butyl-p-cresol; E = 2,6-di-*tert*-butyl-p-cresol; F = diisobutylene; G = triisobutylene; H = tetraisobutylene.

(a) The first step is transport of gas phase reactant A from bulk gas phase to the gas-liquid interface. The rate of mass transfer based on liquid volume in g-mol/(cm³·s) is given by

$$R_A = k_{GA}[P_G - P_i] = k_{GA}[A_G - A_i]/H_A \quad (6)$$

(b) The second step is transport of dissolved gas at the interface to the bulk liquid phase:

$$R_A = k_{LA}[A^* - A_0] \quad (7)$$

(c) The third step is transport of A from bulk liquid phase to the catalyst surface:

$$R_A = k_{SL}a_p[A_0 - A_s] \quad (8)$$

It is possible to combine these three equations because these steps are in series, as

$$R_A = M_A[A_G - A_s] \quad (9)$$

where

$$\frac{1}{M_A} = \frac{H_A}{k_{GA}} + \frac{1}{k_{LA}} + \frac{1}{k_{SL}a_p} = \frac{1}{K_{LA}} + \frac{1}{k_{SL}a_p}$$

= overall resistance to external mass transfer from gas phase to the catalyst surface (10)

Many times the gas to bulk liquid transport is combined to yield the overall gas to liquid mass transfer coefficient, \bar{K}_{LA} , and then eq 9 can be written as

$$R_A = M_A[A^* - A_s] \quad (9a)$$

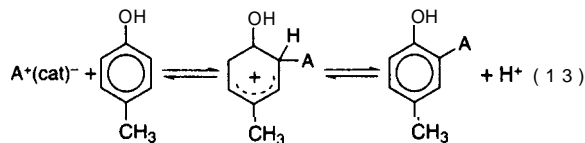
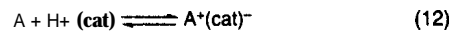
From the liquid phase, transport of the reactant B also takes place

$$R_B = k_{SL-B}a_p[B_0 - B_s] \quad (11)$$

The species A and B diffuse inside the pores and the reaction takes place on the catalyst surface.

As said earlier, there were several parallel and series reactions occurring on the catalyst surface. No homo-

geneous phase reactions were found to take place. The role of adsorption of the different species on the catalyst surface and the formation of surface complexes needs to be clarified. Gehlawat and Sharma (1970), Unni and Bhatia (1982) and Santacessaria et al. (1988) have assumed a second order kinetics and the reaction mechanism is



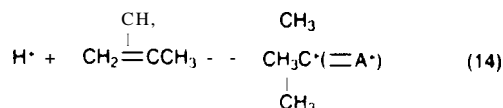
In this case, the chemisorption of p-cresol and the reactant products on the catalyst surface is assumed to be negligible. The reaction is between the chemisorbed isobutylene and the reactant in the pore space. The work carried out in this laboratory has demonstrated that adsorption of reactive species can be quite significant leading to inversion in reactivity in parallel reactions in a single pot, catalyzed by solid acid catalysts such as sulfated zirconia, Filtrol 24, and Amberlyst-15 (Yadav et al., 1993). Therefore, it was thought desirable to check whether simple second order kinetics would be valid for formation of monoalkylated and dialkylated products. As mentioned earlier, the oligomerization of isobutylene up to tetramers is also significant in the current work. Indeed Santacessaria et al. (1988) have assumed that only isobutylene covers the surface of the catalyst.

The intermediates formed in the pore space diffuse out to the bulk liquid phase as well as further react with isobutylene, thereby complicating the analysis of rate data.

Langmuir-Hinshelwood versus Eley-Rideal Mechanism. In the case of alkylation of p-cresol, several possibilities exist as regards the chemisorption of the reactive species followed by reaction on the catalyst surface. In acid catalysis, the most important step is the formation of the carbonium or carbenium ion on the catalyst surface as a result of acidic or superacidic centers formed from the combination of Lewis and Brønsted acids. Aromatic compounds are protonated by strong acids, but olefins are better proton acceptors. Strong acids are capable of protonating olefins and aromatic compounds, but since the identity of the proton donor species is often not known, it is represented by a general symbol H⁺. The metal ions (a Lewis acid) M⁺ act as catalysts by bonding to organic reactants, introducing charge into them and often polarizing them and inducing formation of carbenium ions.

Thus, whatever may be the nature of the acid center, the formation of carbenium ions is the first step and thus which species is most likely to get transferred to the carbenium form should be understood to throw light on product distribution.

Among the various species adsorbed on the catalyst surface, the formation of carbenium ion will result preferentially from the relatively strong base. On the basis of the pK_a values, isobutylene is a stronger base in comparison with p-cresol and hence the carbenium ion formation is typically shown as



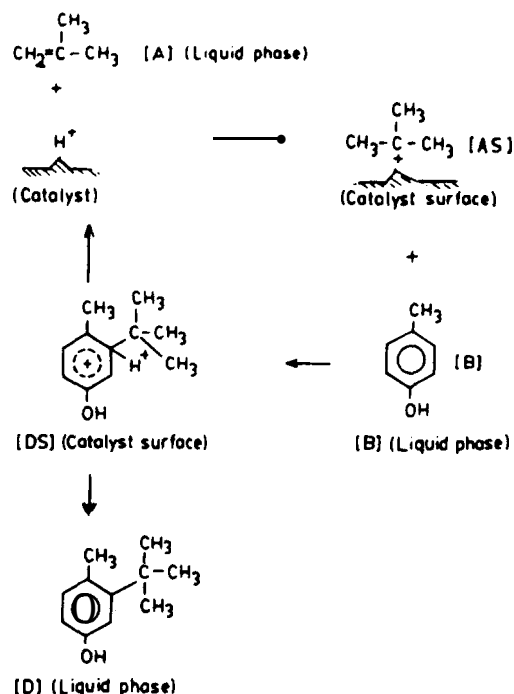


Figure 3. Catalytic cycle for monoalkylation of p-cresol with isobutylene.

This is also evident from the fact that oligomerization products are also present in the reaction mixture. When present alone, p-cresol can form a carbenium ion with the active center as the benzene ring is activated. Therefore, the rate data should be analyzed carefully. On one hand, all components present in the reaction mixture could be assumed to occupy the catalyst surface with the reaction proceeding via the carbenium ion of isobutylene (Langmuir-Hinshelwood mechanism), and on the other hand, it is only the carbocation of isobutylene on the catalyst surface that is assumed to react with the reactants in the liquid phase inside the pores but adjacent to the catalyst surface (Eley-Rideal mechanism).

Both these models were used in the analysis of the data presented here. The Eley-Rideal mechanism was found to be satisfactory and is hence presented in what follows.

Eley-Rideal Mechanism. If S is the vacant acidic center, then the dissolved isobutylene from the liquid phase next to the catalyst surface gets chemisorbed according to



where AS is the carbenium ion on the surface of the catalyst which reacts with p-cresol (B) in the liquid phase adjacent to the surface complex:



The surface complex of monoalkylated product DS desorbs to



This sequence represents the formation of 2-tert-butyl-p-cresol (D), the monoalkylated product as given in Figure 3.

Other catalytic cycles for the dialkylation and oligomeric reactions can be similarly written. There were no reaction products arising out of the carbenium ions of p-cresol or diisobutylene, and hence the Eley-Rideal mechanism was found to have an experimental support.

The rate of chemisorption of isobutylene is given by

$$r_1 = k_1(C_A C_v - C_{AS}/K_1) \quad (18)$$

where C_v is the concentration of the vacant sites, k_1 and k_1' are the adsorption and desorption constants, and K_1 is the equilibrium constant. The chemisorbed species AS in the carbenium ion form undergoes five significant reactions as follows

monoalkylation



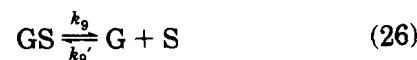
dialkylation



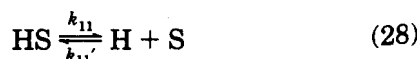
dimerization



trimerization



tetramerization



Material balance on the total number of sites C_t gives the following equation:

$$C_t = C_A + C_{DS} + C_{ES} + C_{FS} + C_{GS} + C_{HS} + C_v \quad (29)$$

If it is assumed that the surface reactions are rate determining, have very large forward rate constants, and are irreversible, then it is possible to find the concentration of vacant sites as follows:

$$C_v = \frac{C_t}{1 + K_1 C_A + K_3 C_D + K_5 C_E + K_7 C_F + K_9 C_G + K_{11} C_H} \quad (30)$$

if $K_3, K_5, K_7, K_9, K_{11} \ll K_1$

$$C_v = \frac{C_t}{1 + K_1 C_A} \quad (31)$$

which shows that only chemisorption of isobutylene is significant.

Using eq 30, the following expression for the rate of monoalkylation of B is obtained:

$$r_2 = k_2 \left[\frac{K_1 C_A C_B - K_3 C_D / K_2}{1 + \sum K_i C_i} \right] \quad (32)$$

The rate of dialkylation is

$$r_4 = k_4 \left[\frac{K_1 C_A C_D - K_5 C_E / K_4}{1 + \sum K_i C_i} \right] \quad (33)$$

The rate of dimerization is

$$r_6 = k_6 \left[\frac{K_1 C_A^2 - K_7 C_F / K_6}{1 + \sum K_i C_i} \right] \quad (34)$$

The rate of trimerization is

$$r_8 = k_8 \left[\frac{K_1 C_A C_F - K_9 C_G / K_8}{1 + \sum K_i C_i} \right] \quad (35)$$

The rate of tetramerization is

$$r_{10} = k_{10} \left[\frac{K_1 C_A C_G - K_{11} C_H / K_{10}}{1 + \sum K_i C_i} \right] \quad (36)$$

The above equations can be written in terms of catalyst loading W and in the presence of internal effectiveness factor η , wherein corresponding terms will be multiplied by ηW .

A material balance on isobutylene shows that the net rate of isobutylene consumption is

$$-r_{\text{isob}} = r_2 + r_4 + 2r_6 + 3r_8 + 4r_{10} = -dC_A/dt \quad (37)$$

The net rate of *o*-cresol consumption is

$$-r_{p\text{-cresol}} = -r_B = r_2 = -dC_B/dt \quad (38)$$

The net rate of formation of monoalkylated product is

$$F_{\text{mono}} = r_2 - r_4 = dC_D/dt \quad (39)$$

The net rate of formation of dialkylated product is

$$r_{\text{dialk}} = r_4 = dC_E/dt \quad (40)$$

The net rate of dimerization is

$$r_{\text{dimer}} = r_6 - r_8 = dC_F/dt \quad (41)$$

The net rate of trimerization is

$$r_{\text{trimer}} = r_8 - r_{10} = dC_G/dt \quad (42)$$

The net rate of tetramerization is

$$r_{\text{tetramer}} = r_{10} = dC_H/dt \quad (43)$$

(assuming no higher oligomers are formed).

If it is assumed that the above reactions are irreversible, then the individual rates are

$$-dC_A/dt = k_2 C_A C_B + k_4 C_A C_D + 2k_6 C_A^2 + 3k_8 C_A C_F + 4k_{10} C_A C_G \quad (44)$$

$$-dC_B/dt = k_2 C_A C_B \quad (45)$$

$$dC_D/dt = k_2 C_A C_B - k_4 C_A C_D \quad (46)$$

$$dC_E/dt = k_4 C_A C_D \quad (47)$$

$$dC_F/dt = k_6 C_A^2 - k_8 C_A C_F \quad (48)$$

$$dC_G/dt = k_8 C_A C_F - k_{10} C_A C_G \quad (49)$$

$$dC_H/dt = k_{10} C_A C_G \quad (50)$$

The material balance on species B gives

$$dC_B/dt + dC_D/dt + dC_E/dt = 0 \quad (51)$$

and for species A gives

$$dC_A/dt + dC_D/dt + 2dC_E/dt + 2dC_F/dt + 3dC_G/dt + 4dC_H/dt = 0 \quad (52)$$

Thus, the difference equations can be written as

$$\Delta C_B + \Delta C_D + \Delta C_E = 0 \quad (53)$$

and

$$\Delta C_A + \Delta C_D + 2\Delta C_E + 2\Delta C_F + 3\Delta C_G + 4\Delta C_H = 0 \quad (54)$$

If, at time $t = 0$,

$$C_A = C_{A0}, C_B = C_{B0} \quad (55)$$

and all other species are absent, then,

$$C_{B0} = C_B + C_D + C_E = \text{constant at all times} \quad (56)$$

The total amount of gas reacted at a given time will be equal to the amount of the various species formed.

If the reaction mixture is saturated with A at $t = 0$ and the reaction conducted in a batch mode, then at any time t ,

$$C_{A0} - C_A = C_D + 2C_E + 2C_F + 3C_G + 4C_H \quad (57)$$

For a semibatch operation the right-hand side of eq 57 gives the total amount of gas reacted at any time t . Indeed the material balance done on B matches within 5–10% in most of the cases, which is reasonable because some vapors of *o*-cresol are lost along with the outgoing

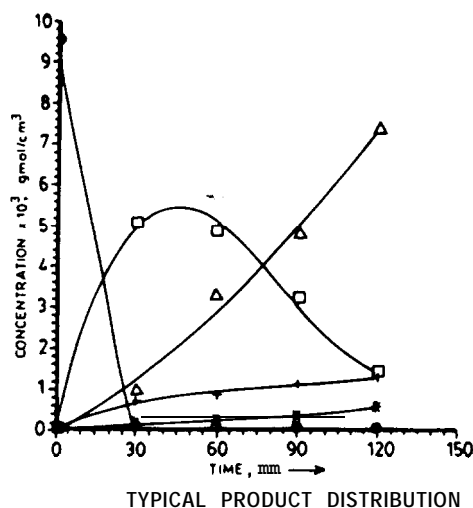


Figure 4. Typical product distribution: (+) triisobutylene; (x) tetraisobutylene; (O) p-cresol; (□) 2-tert-butyl-p-cresol; (Δ) BHT; (*) diisobutylene. Conditions: catalyst S-ZrO₂; loading 3% (w/w); temperature 75 °C; stirrer speed 1000 rpm.

gas, because of its finite vapor pressure at the operating temperature.

Interpretation of Preliminary Data

The initial experiments were done with pure isobutylene gas and pure p-cresol without any solvent at a catalyst loading of 3% (w/w) of the liquid and solid at 75 °C. The solubility of isobutylene at this temperature was taken from Gehlawat and Sharma (1970) as 3.5×10^{-4} g-mol/(cm³·atm). The speed of agitation was maintained at 1000 rpm. Figure 4 presents the typical product distribution up to 2 h of reaction time. It was necessary to ascertain that positive flow of the gas was maintained at all times and the influence of external mass transfer resistance was properly assessed.

It is interesting to recall the work of Santacessaria *et al.* (1988) in this regard, who have used a much higher loading of catalyst but have found similar concentration profiles. Further, their experimental results and theoretical predictions do not match. It was therefore decided to analyze the influence of both external and internal mass transfer resistances. The net initial rates of reactions of isobutylene and p-cresol and those of formation of alkylated and dialkylated p-cresol and the various oligomers of isobutylene were calculated from the experimental data.

The rates were calculated as g-mol/(cm³ of liquid-s) and then converted on the unit catalyst weight as g-mol/(g of catalyst-s). Before the exact form of the rate equations was ascertained with regard to the contribution of the various transport and kinetic terms, a systematic study was conducted to evaluate these resistances under the operating conditions.

Effect of External Mass Transfer Resistance. (i) Gas Side Mass Transfer Coefficient (k_{GA}). The effect of external mass transfer resistance as reflected in ($1/M_A$) was studied at three different speeds of agitation. It was found that the same product distribution was obtained and hence there was no resistance due to external mass transfer.

Since pure gas was used, there was no resistance to gas transfer from the gas phase to the gas-liquid interface. For such experiments wherein isobutylene

diluted with nitrogen was used, the gas side resistance at the operating conditions was negligible. The value of gas phase diffusivity of isobutylene into nitrogen, D_G , was calculated from the Wilke-Chang equation and the gas side true mass transfer coefficient, kc , was obtained from published information for mechanically agitated contactor wherein the correction for diffusivity was made on the basis that kc varies as the square root of diffusivity (Yadav and Sharma, 1979). A typical value of gas-liquid interfacial area a for the contactor was obtained from Ramchandran and Chaudhari (1983). The value of $k_{GA}[A^*] \gg R_A$, the volumetric rate of absorption of isobutylene in the organic phase, was expressed as g-mol/(cm³ of liquid-s) in all cases.

(ii) Gas-Liquid Mass Transfer Coefficient (k_{LA}). Bern *et al.* (1976) have proposed a correlation for k_{LA} for agitated slurry reactors for gas-organic liquid phase-solid systems which was used to find the value of k_{LA} , the volumetric coefficient at the operating speed. For instance, at a speed of 750 rpm, the minimum speed, the value of k_{LA} was obtained as 0.09 s^{-1} after correction for diffusivity based on the penetration model that the true liquid side mass transfer coefficient varies as the square root of diffusivity.

(iii) Solid-Liquid Mass Transfer Coefficient ($k_{SL}a_p$). Several correlations for solid-liquid mass transfer coefficient, k_{SL} , in slurry reactors have been compared by Ramchandran and Chaudhari (1983) for various particle sizes, and the correlation of Sano *et al.* (1974) was used to find the k_{SL} value at 750 rpm as 0.022 cm/s . The particle surface area was found from

$$a_p = 6W/\rho_p d_p \quad (58)$$

where W is the solid loading in g/cm³ of liquid and ρ_p and d_p are the particle density and average particle diameter, respectively. For 0.03102 g/cm^3 solid loading the surface area per unit liquid volume for $300 \mu\text{m}$ average particle comes out as 3.492 cm^{-1} . Thus, the k_{SL} for isobutylene is 0.0768 s^{-1} and for p-cresol it is 0.18 s^{-1} . M_A is then calculated as 0.0414 s^{-1} . The following inequality will ascertain that the external mass transfer resistance is absent, if

$$\frac{1}{M_A[A^*]} \ll \frac{1}{r_{\text{observed}}} \quad (59)$$

A typical value of the parameter $M_A[A^*]$ for isobutylene at a partial pressure of 0.16 atm, the least used, is $2.30 \times 10^{-6} \text{ g-mol/(cm}^3\cdot\text{s)}$ where $[A^*] = H_A P_A = 3.5 \times 10^{-4} \times 0.16 = 5.6 \times 10^{-5} \text{ g-mol/(cm}^3\cdot\text{s)}$. In terms of catalyst loading of 0.03102 g/cm^3 liquid phase, the external mass transfer rate is $7.38 \times 10^{-5} \text{ g-mol/(g of catalyst-s)}$, whereas the observed initial rate is $5.338 \times 10^{-8} \text{ g-mol/(g of catalyst-s)}$, which is much less than the mass transfer rate.

The above theoretical estimates also confirm the experimental observation that the rate was independent of the speed of agitation.

It was then decided to study the influence of internal diffusion and surface reaction on the rate of absorption. The concentration of A was the same up to the external surface of the catalyst, equal to A^* , the saturation concentration at the prevailing pressure.

The effect of other parameters was found under identical conditions on the rate of absorption of isobutylene, expressed as g-mol/g of catalyst-s. The individual rates of formation of each species were calculated,

Table 2. Solubility of Isobutylene (at 760 mmHg)

solvent	solubility (g-mol/mL $\times 10^4$)		
	60 °C	80 °C	102 °C
<i>p</i> -cresol	4.50	3.10	2.00
2- <i>tert</i> -butyl- <i>p</i> -cresol	5.40	3.70	
2,6-di- <i>tert</i> -butyl- <i>p</i> -cresol		3.90	2.75

and the overall rate of absorption was obtained from the knowledge of these rates.

(iv) **Solubility and Diffusivity.** The solubility values of isobutylene in *p*-cresol, 2-*tert*-butyl-*p*-cresol, and 2,6-di-*tert*-butyl-*p*-cresol have been reported by Gehlawat and Sharma (1970) at various temperatures as given in Table 2. It can be seen that the solubility of isobutylene in a mixture of *p*-cresol and alkylated product is somewhat higher than that in *p*-cresol. However, since initial rate data were used in calculations, the values of solubility in the pure *p*-cresol solution were taken as representative.

The values of diffusivity of isobutylene in *p*-cresol at various temperatures were estimated from the Wilke-Chang equation as reported by Reid et al. (1977). The viscosity of molten *p*-cresol was in the range of 2-3.5 cP as reported by Gehlawat and Sharma (1970). The diffusivity of dissolved isobutylene in *p*-cresol, D_A , was found to be $0.8 \times 10^{-5} \text{ cm}^2/\text{s}$ at 65 °C, and was corrected for temperature according to the Stokes-Einstein equation $D_A\mu/T = \text{constant}$, where μ is the viscosity and T is the absolute temperature. The self-diffusivity of *p*-cresol was obtained from the Wilke-Chang equation. The effective diffusion coefficient D_e for isobutylene in sulfated zirconia was obtained from the following correction:

$$D_e = D_A\epsilon/\tau = 8.3 \times 10^{-6} \text{ cm}^2/\text{s} \quad (60)$$

where ϵ is the fractional porosity of the catalyst (0.5) and τ is the tortuosity of the catalyst taken as 3.

Analysis of Internal Diffusion Effects and Surface Kinetic Parameters. Since there were no external limitations to mass transfer, it was important to establish the effect of internal diffusion and surface reaction which are parallel processes. Santacessaria et al. (1988) have reported that the reaction is overall second order in all cases, which is based on the observation of Gehlawat and Sharma (1970) for homogeneous catalysis.

The validity of either the Eley-Rideal mechanism or the Langmuir-Hinshelwood mechanism can be verified by studying the effect of partial pressure of isobutylene on the rate of absorption.

The effect of partial pressure of isobutylene was studied by diluting the solute gas isobutylene with nitrogen. Under an otherwise similar set of conditions isobutylene was absorbed in the slurry containing 0.03102 g/cm^3 catalyst at 75 °C at 1000 rpm (Figure 5). The initial rates of absorption were calculated for three different partial pressures, namely, 0.165, 0.2838, and 0.3725 atm, and are plotted against partial pressure on a log-log scale (Figure 6). The slope of the graph is 0.386, suggesting that the rate of absorption is of a fractional order in partial pressure. The physical explanation is that chemisorption of isobutylene plays a role and that all sites are occupied by isobutylene.

The product distribution under various conditions show that sulfated zirconia leads to five parallel reactions of isobutylene and two series reactions of *p*-cresol,

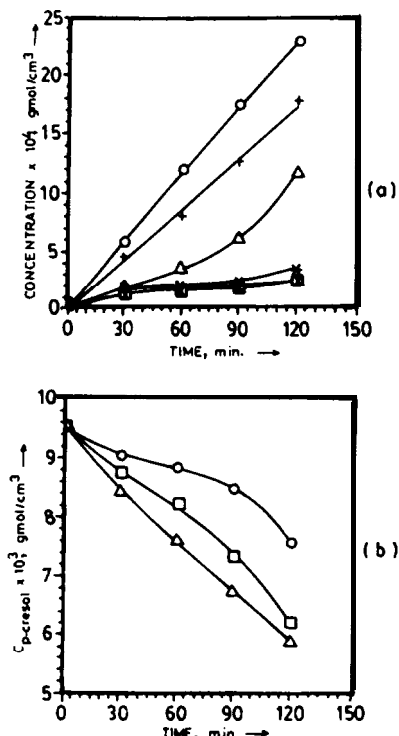


Figure 5. Effect of partial pressure: (a) product distribution; (b) *p*-cresol concentration. (a) Partial pressure 0.165 atm: (Δ) 2-*tert*-butyl-*p*-cresol; (*) diisobutylene. Partial pressure 0.284 atm: (+) 2-*tert*-butyl-*p*-cresol; (\times) diisobutylene. Partial pressure 0.373 atm: (O) 2-*tert*-butyl-*p*-cresol; (\square) diisobutylene. (b) Partial pressure (O) 0.165, (\square) 0.284, and (Δ) 0.373 atm. Conditions: catalyst S-ZrO₂; loading 3% (w/w); temperature 75 °C; stirrer speed 1000 rpm.

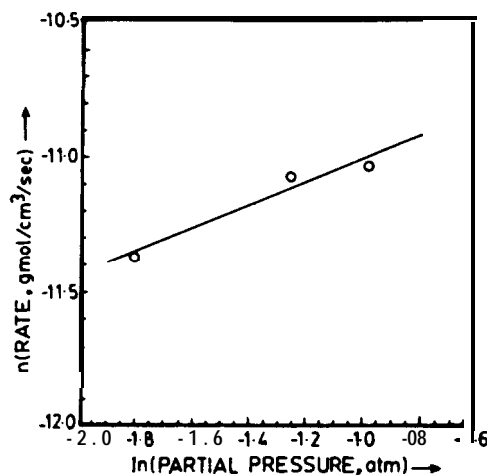


Figure 6. Effect of partial pressure on the initial rates of isobutylene. Conditions: catalyst S-ZrO₂; loading 3% (w/w); temperature 75 °C; stirrer speed 1000 rpm.

thereby involving a complex reaction pathway. Since *p*-cresol was used in pure form, its concentration throughout the pore space at the speed of agitation is uniform. The rate of transport of *p*-cresol from bulk liquid phase to the exterior surface in the reaction mixture is given by eq 11. Indeed all reactions under the conditions employed in this work were found to be irreversible.

Since the effect of partial pressure on the rate of reaction showed nonlinearity, the Eley-Rideal mechanism was taken as approximate in contrast to the Langmuir-Hinshelwood mechanism and further simplification was done. In the presence of internal diffusion, the rates of reaction of isobutylene and of *p*-cresol and those of formation of the products can be written

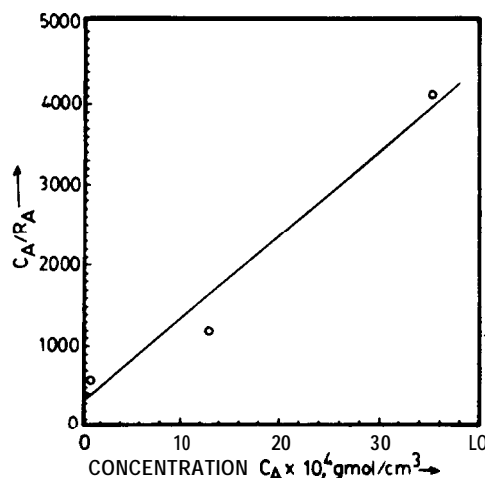


Figure 7. Plot of C_A/R_A against C_A . Conditions: catalyst S-ZrO₂; loading 3% (w/w); temperature 75 °C; stirrer speed 1000 rpm.

in a general form as

$$r_i = \eta_i W k_i \theta_A C_j \quad (61)$$

where C_j is the appropriate concentration depending on the rate of formation or reaction. η_i is the effectiveness factor and k_i is rate constant. θ_A is the fractional coverage of the catalyst by isobutylene, given as

$$\theta_A = \frac{K_A C_A}{1 + K_A C_A} = \frac{K_A H_A P_A}{1 + K_A H_A P_A} \quad (62)$$

If $K_A C_A \gg 1$, then the rate of reaction of isobutylene will be zero order in isobutylene because the entire surface will be covered by isobutylene. If, on the contrary, $K_A C_A \ll 1$, then the rate of reaction will be first order in A as has been claimed by Santacessaria et al. (1988) for ion exchange resin catalysts.

In eq 62 the value of θ_A is substituted and the resulting equation is inverted to get

$$\frac{1}{r_i} = \frac{1 + K_A C_A}{\eta_i W k_i K_A C_A C_j} \quad (63)$$

The rate constant $k_i K_A$ can be combined as k_i' and eq 63 can be transformed to

$$\frac{C_A}{r_i} = \frac{1}{\eta_i W k_i' C_j} + \frac{K_A C_A}{\eta_i W k_i' C_j} \quad (64)$$

As shown in Figure 7, a plot of C_A/rate versus C_A is straight line, since the concentration of A at the surface of catalyst is the saturation solubility. The slope is $K_A/\eta_i W k_i' C_j$ and the intercept is equal to $1/\eta_i W k_i' C_j$.

The division of slope by intercept gives the equilibrium constant K_A . Similar plots were made for other reactions to get the values of $\eta_i k_i$. It is important to isolate the effectiveness factor and rate constant. This was done by studying the effect of particle size on the rate of isobutylene absorption as shown typically (Figure 8). It was observed that there was no effect of reducing the particle size from 300 to 100 μm , thereby indicating the absence of intraparticle diffusional resistance.

Since at low partial pressure the formation of BHT and triisobutylene and tetraisobutylene were insignificant, the following method was used to calculate the other rate constants. The K_A value was known as given by Figure 7, and it was used for the experiments done at 1 atm pressure of isobutylene, wherein these products

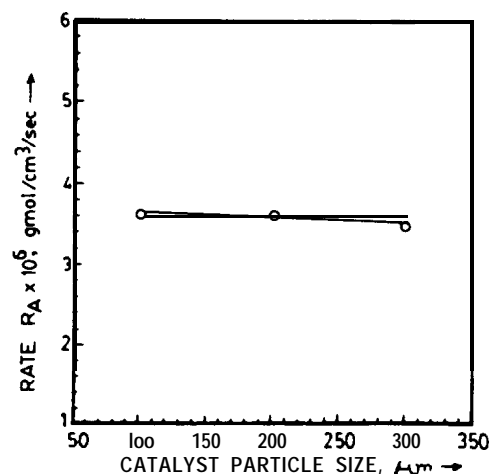


Figure 8. Effect of catalyst particle size on initial rate of isobutylene. Conditions: catalyst S-ZrO₂; loading 3% (w/w); temperature 75 °C; stirrer speed 1000 rpm.

were formed.

$$r_i = \frac{\eta_i W k_i K_A C_A C_j}{1 + K_A C_A} \quad (65)$$

Since the initial rates of formation were known, the constant $\eta_i k_i$ could be calculated from the following equations:

$$r_2 = -dC_B/dt = \eta_2 W k_2 \theta_A C_B \quad (66)$$

$$r_4 = dC_E/dt = \eta_4 W k_4 \theta_A C_D \quad (67)$$

$$r_{10} = dC_H/dt = \eta_{10} W k_{10} \theta_A C_G \quad (68)$$

$$r_8 = dC_G/dt + dC_H/dt = \eta_8 W k_8 \theta_A C_F \quad (69)$$

$$r_6 = dC_G/dt + dC_H/dt + dC_F/dt = \eta_6 W k_6 \theta_A C_A \quad (70)$$

Effect of Temperature. The effect of temperature on the rates was studied at 45, 60, and 75 °C under otherwise similar conditions. The adsorption equilibrium constant K_A decreases with an increase in temperature, since pure isobutylene was used, the coverage $\theta_A \rightarrow 1$, i.e.,

$$K_A C_A \gg 1 \quad (71)$$

and hence the rate of reaction or formation of products is independent of partial pressure, at low temperature. Therefore,

$$r_i = \eta_i k_i W C_j \quad (72)$$

Hence the $\eta_i k_i$ values were obtained from initial rates. The reactions were conducted under otherwise similar conditions to get the activation energy values. Table 3 gives the activation energy data.

Calculation of Thiele Modulus. Since the reaction here follows the Eley-Rideal mechanism,

$$r_i = \frac{\eta_i W k_i C_A}{1 + K_A C_A} \quad (73)$$

Table 3. Kinetic Parameters^a

compound	preexponential factor (A) (cm ³ /g·mol·s)(cm ³ /g)	activation energy (E _{ACT}) (kcal/g·mol)	rate constant (k) (cm ³ /g·mol·s)(cm ³ /g)
p-cresol	4.4096 × 10 ¹⁴	22.879	1.675
BHT	1.2158 × 10 ⁸	17.532	1.083
diisobutylene	10.746	3.558	0.0578
triisobutylene	300.076	5.565	0.0886
tetraisobutylene	9.87 × 10 ⁻⁵	1.02	2.31 × 10 ⁻⁵

^a Catalyst S-ZrO₂; loading 3% w/w; temperature range 45-75 °C; stirrer speed 1000 rpm.

The effectiveness factor is given by $\eta_i = (1/\phi_i)(\coth 3\phi_i - (1/3)\phi_i)$, where ϕ_i = Thiele modulus.

$$\phi_i = \frac{R}{3}(\rho_p k_i C_i / D_e)^{1/2} \times \frac{K_A C_A}{(1 + K_A C_A)[2(K_A C_A - \ln(1 + K_A C_A))]^{1/2}} \quad (74)$$

This modulus is defined by Bischoff (1965) as an approximation (see Ramchandran and Chaudhari, 1983). The experimental Thiele modulus is obtained from the following equation:

$$\phi_{\text{exp}} = \frac{R}{3}(\rho_p R_A / D_e W A_s B_s)^{1/2} \text{ when } B_0 = \text{constant} \quad (75)$$

where $A_s = A^*$ and the rate R_A is in g·mol/(cm³·s).

The Thiele modulus value is decreased for the Eley-Rideal mechanism in comparison with a power law model, and hence it would lead to a higher effectiveness factor.

$$\text{for } \phi_{\text{exp}} \ll 1: \quad \eta = 1/\phi_{\text{exp}} \quad (76)$$

Measurement of Kinetic Parameters. According to the procedure delineated before, the measurement of kinetic rate constant and activation energies for all five significant reactions of isobutylene was possible.

The effect of temperature and particle size on the rate of reaction for the individual reactions was studied to determine whether intraparticle diffusion had any role to play.

Assuming the measured rate constant, k_m , as a product of the true or intrinsic rate constant, k , and the effectiveness factor, η , the Arrhenius plots were made as $\ln k_m$ versus $1/T$ for all five reactions whose rates are given by r_2, r_4, r_6, r_8 , and r_{10} given by eq 66, 67, 70, 69, and 68, respectively. Table 3 gives the values of activation energies and preexponential factors for these reactions. These activation energy values suggest that the mono- and dialkylation reactions are kinetically controlled. In fact the experimental values of Thiele modulus given by eq 74 show that $\phi_{\text{exp}} \ll 1$ and hence $\eta \rightarrow 1$.

The contribution of oligomerization reactions was small in comparison with that of alkylation reactions during the initial period.

Effect of Particle Size. The effect of particle size on rate of absorption of isobutylene shows that the rate is independent of the particle size when the particle size was reduced from 300 to 100 μm (Figure 8). This result should be interpreted correctly because the first two reactions of isobutylene consume more of it than the oligomerization and there were consecutive reactions of p-cresol (B) and parallel reactions of isobutylene. Thus

inside the pores. The activation energy values must therefore be inspected.

The values of activation energy for the alkylation and dialkylation reaction E_2 and E_4 are 22 and 17.5 kcal/g·mol, showing that these reactions respectively are surface reaction controlled and there is no internal diffusional resistance. Thus, rate constants k_2 and k_4 are intrinsic or true rate constants.

In the case of oligomerization reactions of isobutylene, the calculated activation energy values E_6, E_8 , and E_{10} for dimerization, trimerization, and tetramerization are 3.6, 5.6, and 1.0 kcal/g·mol, respectively. Such low values normally are indicative of either solid-liquid mass transfer limitation or intraparticle diffusion limitation. Therefore, a proper interpretation of the data is called for.

We have already shown that there was no solid-liquid mass transfer resistance by employing proper speeds of agitation. The studies on the effect of particle diameter on the rates and product distribution, as discussed earlier, showed that intraparticle diffusion limitation was absent. The mechanism clearly shows that isobutylene is the chemisorbed species (AS) on the catalyst surface, and according to the Eley-Rideal mechanism, it reacts with other reactive species from the liquid phase inside the pore space.

The oligomerization reactions take place *in situ* among the species generated over there as could be seen from eqs 23-28, and all these reactions are sequential. Thus, there is no question of any intraparticle diffusion limitation for any of the oligomerization reactions.

The dimerization reaction could theoretically have intraparticle diffusion limitation because isobutylene diffuses into the pore space. However, this possibility is discounted as shown for the alkylation reaction when isobutylene is a reactant itself. Therefore, none of the oligomerization reactions are controlled by intraparticle diffusion.

It is known from the published literature that low activation energy values, for kinetically controlled reactions, result from favorable thermodynamic interactions between the reactant and solution phase (Rajadhyaksha and Karwa, 1986). For instance, in the dimerization of α -methylstyrene in p-cresol solvent in the presence of ion exchange resin catalyst the activation energy values are low (Chaudhary and Sharma, 1989) although the reaction is kinetically controlled. In the current investigation, p-cresol is a solvent as well as reactant and the oligomerization reactions occur on the surface of the catalyst with chemisorbed isobutylene and oligomerizing species from the solution phase.

Thus, it is concluded that the oligomerization reactions are kinetically controlled with low values of activation energy.

Further, such a low value of E_{10} should be viewed in proper perspective because the measurement of very low

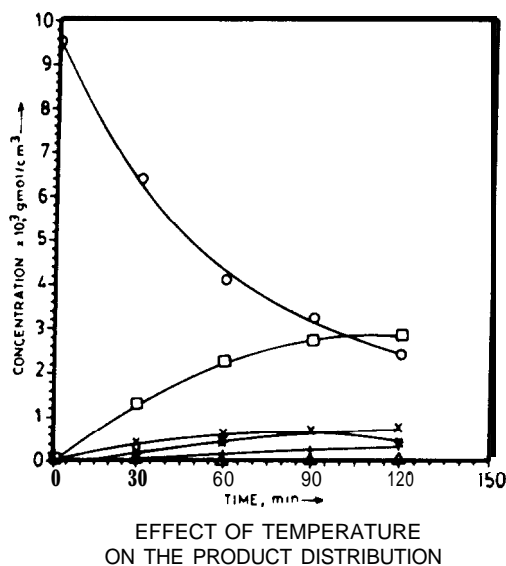


Figure 9. Effect of temperature on the product distribution: (+) triisobutylene; (x) tetraisobutylene; (O) p-cresol; (□) 2-tert-butyl-p-cresol; (Δ) BHT; (*) diisobutylene. Conditions: catalyst S-ZrO₂; loading 3% (w/w); temperature 45 °C; stirrer speed 1000 rpm.

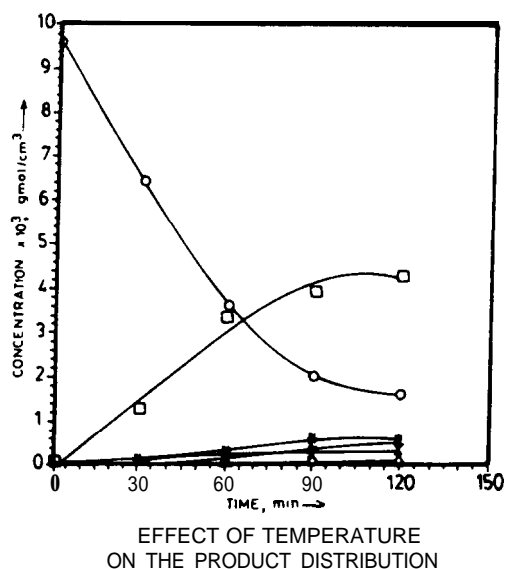


Figure 10. Effect of temperature on the product distribution: (+) triisobutylene; (x) tetraisobutylene; (O) p-cresol; (□) 2-tert-butyl-p-cresol; (Δ) BHT; (*) diisobutylene. Conditions: catalyst S-ZrO₂; loading 3% (w/w); temperature 60 °C; stirrer speed 1000 rpm.

so accurate and the various assumptions made may not be valid. The kinetic parameters are listed in Table 3.

Effect of Temperature on Product Distribution.

As expected from the kinetics, the increase in temperature favors the formation of monoalkylation and dialkylation of p-cresol in comparison with the oligomers (Figures 4, 9, and 10). Due to low activation energies, the formation of diisobutylene, triisobutylene, and tetraisobutylene decreases with an increase in temperature. The formation of tetramer decreases considerably whereas that of trimer increases. The concentration of trimer is higher than that of dimer as evident from eqs 46 and 67, because, k_8 increases more rapidly than k_6 ($k_8 > k_6 > k_{10}$).

Effect of Catalyst Loading. Figures 11 and 12 show the effect of catalyst loading on the product distribution at 75 °C at a stirrer speed of 1000 rpm. It is seen that with an increase in the catalyst loading the conversion of p-cresol and the formation of products goes on increasing linearly. This is because of the increase

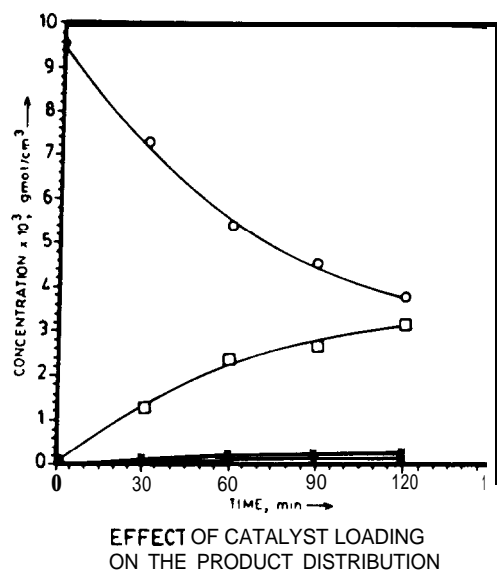


Figure 11. Effect of catalyst loading on the product distribution: (+) triisobutylene; (x) tetraisobutylene; (O) p-cresol; (□) 2-tert-butyl-p-cresol; (Δ) BHT; (*) diisobutylene. Conditions: catalyst S-ZrO₂; loading 1% (w/w); temperature 75 °C; stirrer speed 1000 rpm.

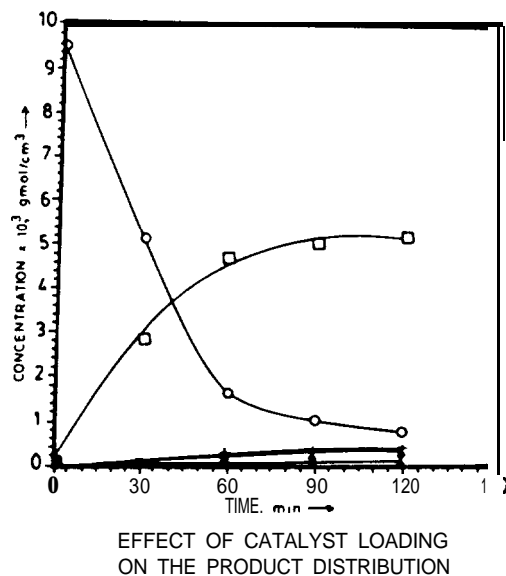


Figure 12. Effect of catalyst loading on the product distribution: (+) triisobutylene; (x) tetraisobutylene; (O) p-cresol; (□) 2-tert-butyl-p-cresol; (Δ) BHT; (*) diisobutylene. Conditions: catalyst S-ZrO₂; loading 2% (w/w); temperature 75 °C; stirrer speed 1000 rpm.

in the total number of acid sites available. This further indicated that the reaction is surface kinetically controlled.

Catalyst Activity Comparison

Sulfated Zirconia versus Ion Exchange Resin Catalyst (Amberlyst-15). The work of Santacessaria *et al.* (1988) using ion exchange resin catalyst could now be compared with the current work using sulfated zirconia. Sulfated zirconia offers more surface area than Amberlyst-15 catalyst and is more selective toward alkylated products than Amberlyst-15. However, there is significant formation of trimer in the case of Amberlyst-15. When the rate constants are compared on the basis of unit catalyst weight, ($\text{cm}^3/(\text{g}\cdot\text{mol}\cdot\text{s})$)(cm^3/g), sulfated zirconia is more active than Amberlyst-15. It could be seen that higher loading of Amberlyst-15 as

compared to sulfated zirconia is required, which is too high for industrial purposes.

Conclusions

The absorption of isobutylene in *p*-cresol catalyzed by sulfated zirconia is a very interesting system which could be analyzed on the basis of the Eley-Rideal mechanism.

All the reactions are kinetically controlled but the oligomerizations have low activation energies.

The developed model and the observed product distribution agree reasonably well.

Sulfated zirconia is a better catalyst than ion exchange resin for this reaction.

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Nomenclature

a = interfacial area, cm^2/cm^3
 A_0 = concentration of A in bulk liquid phase, $\text{g-mol}/\text{cm}^3$
 A_G = concentration of A in bulk gas phase, $\text{g-mol}/\text{cm}^3$
 A_i = initial concentration of A at gas-liquid interphase, $\text{g-mol}/\text{cm}^3$
 a_p = solid-liquid interfacial area, cm^2/cm^3
 A_s = concentration of A at the catalyst surface, $\text{g-mol}/\text{cm}^3$
 A^* = solubility of A, $\text{g-mol}/\text{cm}^3$
 B_0 = concentration of B in bulk liquid phase, $\text{g-mol}/\text{cm}^3$
 B_i = initial concentration of B in bulk liquid phase, $\text{g-mol}/\text{cm}^3$
 B_s = concentration of B at the catalyst surface, $\text{g-mol}/\text{cm}^3$
 C_i = concentration of species i , $\text{g-mol}/\text{cm}^3$
 D_e = effective diffusivity, cm^2/s
 d_p = particle diameter, cm
 H_A = Henry's constant, $\text{g-mol}/(\text{cm}^3 \cdot \text{atm})$
 K_i = equilibrium constant for species i
 k_G = true gas side mass transfer coefficient, cm/s
 k_L = true liquid side mass transfer coefficient, cm/s
 k_{SL} = solid-liquid mass transfer coefficient, cm/s
 k_1-k_9 = adsorption constants
 $k'_1-k'_9$ = desorption constants
 P_G = partial pressure of A in bulk, atm
 P_i = partial pressure of A at gas-liquid interface, atm
 R_A = rate of reaction for A
 r_2 = rate of reaction for D
 r_4 = rate of reaction for E
 r_6 = rate of reaction for F
 r_8 = rate of reaction for G
 r_{10} = rate of reaction for H
 W = catalyst loading, g/cm^3

Greek Symbols

ϵ = fractional porosity of catalyst
 η = effectiveness factor
 θ_i = fraction of total sites occupied by species i
 ρ_p = particle density, g/cm^3
 τ = tortuosity
 ϕ = Thiele modulus

Subscripts

A = isobutylene
 B = *p*-cresol

D = 2-*tert*-butyl-*p*-cresol
 E = 2,6-di-*tert*-butyl-*p*-cresol
 F = diisobutylene
 G = triisobutylene
 H = tetraisobutylene

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