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KINETICS OF REACTIONS OF ACETIC ACID AND 2-PROPANOL CATALYSED BY ZINC CHROMIUM FERRITE SPINEL

By

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Abstract

2-Propanol undergoes selective dehydrogenation on zinc chromium ferrite. The orders of the dehydrogenation reaction of 2-propanol and the esterification of acetic acid are determined using the technique of competitive reactions. The dehydrogenation follows a first order kinetics. The esterification follows the Langmuir-Hinshelwood mechanism. The value of the relative adsorption coefficient of 2-propanol and acetic acid is 4 and 1.5 at 405 and 430°C, respectively.

Introduction

Surface catalysed chemical reactions involving the interaction of two molecules of the same reactant or two different reactants may proceed either through the Langmuir-Hinshelwood mechanism or Rideal-Eley mechanism. Most of the bimolecular catalytic reactions follow the Langmuir-Hinshelwood mechanism,¹ while reactions such as the hydrogenation of olefins and the conversion of para and ortho hydrogens are known to follow a Rideal-Eley mechanism.^{2,3} The dehydrogenation of 2-propanol involves a single molecule and would be expected to follow first order kinetics. The usual methods of analysis, however, do not permit the unambiguous determination of the kinetic order. The present investigation is an attempt to determine the order of this reaction and to identify the mechanistic models that are valid for the dehydrogenation of 2-propanol and the esterification of acetic acid on zinc chromium ferrite.

Experimental

Acetic acid (BDH AR) used in this investigation was purified by distillation according to the method suggested by Orton and Bradfield⁴ and its

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purity checked by the freezing point (16.6°C). 2-propanol (BDH AR) was refluxed with excess of freshly burnt quicklime for 4 to 6 hours and then distilled.⁵⁾ The fraction distilling at 82°C was collected and its purity checked by gas chromatography.

Zinc chromium ferrite was prepared by the slurry method described by Batist.⁶⁾ A zinc oxide paste was made in distilled water and added to a mixture of $\text{Fe}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$ taken in distilled water and the whole mixture heated on a water bath for 4 hours keeping the total mass stirred vigorously. The solid was then filtered, dried overnight at 110°C and calcined at 1250°C for 16 hours. It was then characterized by XRD and chemical analysis.

The reactions were studied at atmospheric pressure using a flow reactor.⁷⁾ Liquid products were analysed by vapour phase chromatography making use of a carbowax column and hydrogen as a carrier gas.

2-propanol undergoes selective dehydrogenation on ZnCrFeO_4 . The 2-propanol reacted is computed from the acetone formed as determined by vapour-phase chromatography and also from the volume of hydrogen collected. When 2-propanol is reacted in mixture with acetic acid, in addition to undergoing dehydrogenation it reacts with acetic acid to form 2-propyl acetate.

Acetic acid alone does not react on the catalyst to give any products. In order to determine the amount of ester formed a known amount of the product is first titrated with standard sodium hydroxide to determine the unreacted acid. Then a known weight of the product is refluxed with excess alkali to hydrolyse the ester and the unreacted alkali determined by back titration. From these two titre values the amount of ester formed is calculated.

The catalyst is regenerated by passing CO_2 free air over it at 500°C for 3 hours.

Results and Discussion

The effect of partial pressure on the rate of dehydrogenation was studied using an inert diluent, nitrogen. At a given temperature the rate increases with increase in partial pressure of the alcohol and tends to level off near 1 atm. pressure indicating a saturation of the surface. (Fig. (1)). Acetic acid also tends to saturate the surface at atmospheric pressure. Hence when a mixture of acetic acid and 2-propanol is used, since the total pressure is 1 atmosphere, the surface is assumed to be completely covered by both together.

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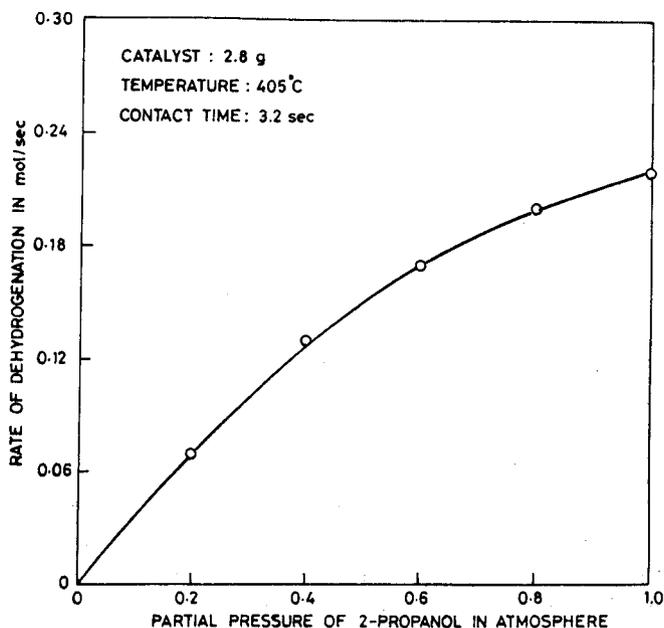


Fig. 1. Dehydrogenation of 2-propanol in presence of nitrogen.

Making use of the Langmuir expression for the surface coverage by 2-propanol, the kinetic expression for the dehydrogenation of 2-propanol assuming a unimolecular reaction is given by

$$V_i = \frac{k_1 b_A p_A}{1 + b_A p_A} \quad (1)$$

while for bimolecular reaction it is

$$V_i = k_2 \left[\frac{b_A p_A}{1 + b_A p_A} \right]^2 \quad (2)$$

Where V_i is the initial velocity of the reaction,
 b_A is the adsorption coefficient of 2-propanol,
 p_A is the partial pressure of 2-propanol,
 k_1 is the rate constant for the unimolecular reaction and
 k_2 is the rate constant for the bimolecular reaction.

Equations (1) and (2) can be rearranged as follows

$$\frac{1}{V_i} = \frac{1}{k_1} + \frac{1}{k_1 b_A p_A} \quad (3)$$

and

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$$\sqrt{\frac{1}{V_1}} = \frac{1}{\sqrt{k_2}} + \frac{1}{\sqrt{k_2 b_A p_A}} \quad (4)$$

A plot of $1/V_1$ versus $1/p_A$ according to equation (3) or $1/\sqrt{V_1}$ versus $1/p_A$ according to equation (4) must yield straight lines depending upon whether the dehydrogenation is a first order or second order reaction on the surface.

The results obtained at different partial pressures at a given temperature when plotted according to equations (3) & (4) yield straight lines in both cases (Fig. 2). The results satisfy both the first as well as second order rate expressions and do not permit an unambiguous choice between the two. This is due to the presence of two unknowns in the rate expressions, the rate constant ' k ' and the adsorption coefficient ' b '. In order to obtain the true orders an attempt was therefore made to study the reaction by employing the technique of competitive reactions⁸.

The esterification of acid and alcohol was chosen as the competing reaction. The manner in which the rate of dehydrogenation of 2-propanol is affected due to the presence of acetic acid shows that it is not a simple dilution effect like that of nitrogen. So the acetic acid is competing with

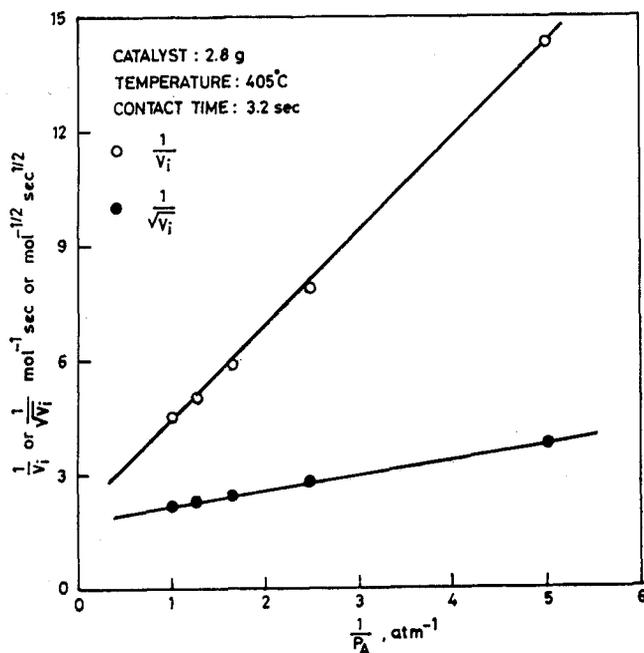


Fig. 2. Plot showing the relation between the velocity of dehydrogenation of 2-propanol and partial pressure according to Langmuir model.

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2-propanol for the adsorption sites on the catalyst surface.

If the esterification followed a Langmuir-Hinskelwood mechanism the rate expression

$$V_i = k_{\text{est}} \frac{b_A p_A \times b_M p_M}{(b_A p_A + b_M p_M)^2} \quad (5)$$

will give a maximum for ester formation when

$$\frac{b_{\text{alcohol}}}{b_{\text{acid}}} = \frac{p_{\text{acid}}}{p_{\text{alcohol}}} = x \quad (6)$$

where b and p are the adsorption coefficients and the partial pressure respectively, the subscripts A denoting alcohol and M denoting acid.

On the other hand if the Rideal-Eley mechanism is operative for the esterification we have from the rate expression (7),

$$V_i = k_{\text{est}} \frac{b_A p_A \times p_M}{b_A p_A + b_M p_M} \quad \text{OR} \quad k_{\text{est}} \frac{b_M p_M \times p_A}{b_A p_A + b_M p_M} \quad (7)$$

the condition for maximum as

$$\frac{b_A}{b_M} = \left[\frac{p_M}{p_A} \right]^2 = y \quad (8)$$

Thus, two values are obtained for b_A/b_M depending on the reaction model for esterification. Using these values of x and y for $b_{\text{alcohol}}/b_{\text{acid}}$, one can calculate theoretical curves for the dehydrogenation. Assuming the L-H model the rate expression is

$$V_i = k_{\text{dehydrogenation}} \left[\frac{b_A p_A}{b_A p_A + b_M p_M} \right]^2 \quad (9)$$

and for the R-E model the rate expression is

$$V_i = k_{\text{dehydrogenation}} \frac{b_A p_A^2}{b_A p_A + b_M p_M} \quad (10)$$

If the dehydrogenation is first order the expression is

$$V_i = k_{\text{dehydrogenation}} \frac{b_A p_A}{b_A p_A + b_M p_M} \quad (11)$$

In each of these expressions x and y can be substituted for $b_{\text{alcohol}}/b_{\text{acid}}$. Therefore six theoretical curves can be constructed. One can now find out to which of these theoretical curves the experimental points correspond and determine which model is applicable to the dehydrogenation reaction.

In Fig. 3 the relative velocities of the esterification are plotted as a

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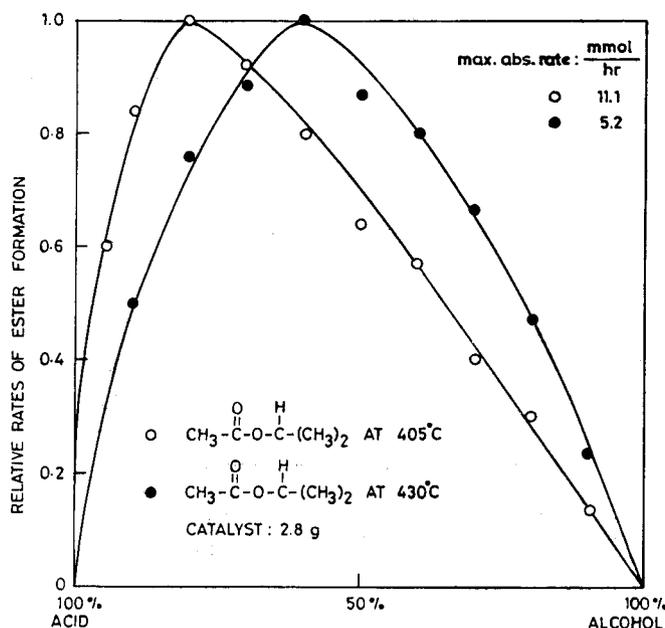


Fig. 3. Relative rates of formation of esters for reaction mixtures containing various proportions of 2-propanol and acetic acid.

function of the composition of 2-propanol and acetic acid at 405°C and at 430°C. The maximum rate of ester formation was found to be at a point where $p_{\text{acid}}/p_{\text{alcohol}}=4$ at 405°C and at a point where $p_{\text{acid}}/p_{\text{alcohol}}=1.5$ at 430°C.

In Fig. 4 the theoretical curves for the dehydrogenation of 2-propanol in the presence of acetic acid are shown along with the experimental results at 405°C. It is found that the experimental results for the dehydrogenation agree very well with the theoretical plot for a first order kinetics when the relative adsorption coefficient 4 is used. This also suggests that the true value of the relative adsorption coefficient of 2-propanol and acetic acid is four and the esterification reaction follows a Langmuir-Hinshelwood mechanism.

$k_{\text{dehydrogenation}}$ is calculated from equation 11 using the data given in Fig. (4). It is found to be 0.22 sec.^{-1} . The value calculated from equation (3) using the data given in Fig. (1) is 0.467 sec.^{-1} . The difference could be due to the mutual influence of reactants on each others adsorption. When nitrogen is the diluent no such effect is expected while when acetic acid is mixed with isopropanol there could be such an effect.

At 430°C the technique of competitive reactions could not be used

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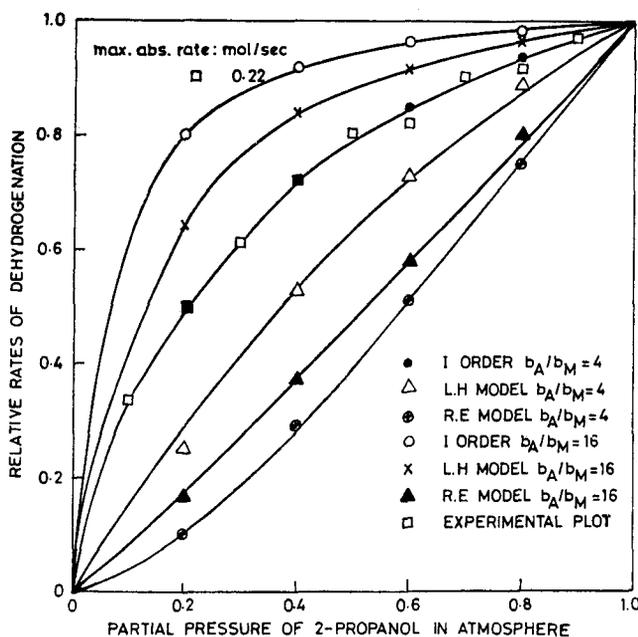


Fig. 4. Experimental and theoretical plots for the dehydrogenation of 2-propanol according to first order, Langmuir-Hinshelwood and rideal-eley models.

because the relative adsorption coefficient of 2-propanol and acetic acid is not of a suitable magnitude to permit a clear distinction between the mechanistic models.⁹ The method can be used only if the relative adsorption coefficient of the reactants is three or more.

From the relative adsorption coefficients at 405 and 430°C the difference in heat of adsorption is found to be 37 kcal. Since the value is so high it is most probable that one is dealing with practically a chemisorption of acetic acid corresponding almost to a salt formation. This would provide a high exothermicity from which when the normal heat of adsorption of 2-propanol is subtracted one still has a big number for the difference in heat of adsorption.

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