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Kinetic Study on the Mechanism of the Catalytic Conversion of Ethanol to Butadiene

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An investigation has been carried out on the mechanism of the one-step catalytic conversion of ethanol to butadiene on Al_2O_3:ZnO(60:40) catalyst, which has been reported earlier as the best catalyst in static as well as fluidized beds.

The formaiton of crotonaldehyde from acetaldehyde seems to be a relative slow step in the reaction sequence.

It has been further observed that the transformation of ethanol to butadiene, the ultimate product, is possible either by the selective hydrogenation of crotonaldehyde by ethanol or by direct reaction with hydrogen formed by the dehydrogenation of ethanol in the primary step. The former is more plausible, considering the energetics of the reactions.

INTRODUCTION

In a series of recent publications Bhattacharyya *et al.* (*1–4*) have reported remarkable success on the one-step catalytic conversion of ethanol to butadiene in the fixed as well as the fluidized bed, using Al_2O_3:ZnO (60:40) as the catalyst. In the present work the authors make a modest attempt to probe into the mechanism and kinetics of the reaction in the fixed bed.

From the mechanistic point of view, the one-step conversion of ethanol to butadiene is a complicated one and proceeds through a number of consecutive reactions. The reaction mechanism suggested by Gorin *et al.* (*5–8*) may be represented as follows:

$$C_2H_5OH \rightarrow CH_3CHO + H_2$$

$$CH_3CHO + CH_3CHO \rightarrow CH_3CHOHCH_2CHO$$

$$CH_3CHOHCH_2CHO \rightarrow CH_3CH{=}CHCHO + H_2O$$

$$CH_3CH{=}CHCHO + C_2H_5OH \rightarrow CH_3CH{=}CHCH_2OH + CH_3CHO$$

$$CH_3CH{=}CHCH_2OH \rightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2O$$

They claim that the formation of crotyl alcohol is the rate-controlling step. The American workers (*9*) in the field suggest almost a similar scheme but according to them the transformation of crotonaldehyde to butadiene occurs in one step and not via crotyl alcohol, which they have ignored.

THERMODYNAMICS

The thermodynamic feasibility of the individual steps of the suggested mechanism has been assessed by calculating ΔF and K_p with relation to different temperatures.

From the literature survey, some of the chemical data required for such calculations could not be traced. An attempt was made to calculate them by setting up stereochemical models, following the group contribution method described by Hougen and Watson (*10*). Such models were developed for acetaldol, crotonaldehyde, ethanol, and butadiene. Table 1 gives the ΔF (kcal/g mole) and K_p at different temperatures for the different consecutive reactions leading to the formation of butadiene and the same for the parallel mechanism of butadiene, suggested in the present work.

TABLE 1

Calculated Thermodynamic Data

No.	Reactions (Gaseous phase)	ΔF (kcal/g mole) at temperatures (°K):			K_p at temperatures (°K):			ΔH_{298} (kcal/g mole)
		298°	653°	733°	298°	653°	733°	
1	$C_2H_5OH \rightarrow CH_3CHO + H_2$	—	-1.1	-3.0	—	2.39	7.81	$+12.1$
2	$CH_3CHO + HCH_2CHO \rightarrow CH_3CHOHCH_2CHO$	$+2.6$	$+12.8$	$+14.3$	1.12×10^{-2}	5.21×10^{-5}	5.27×10^{-5}	-6.0
3	$CH_3CHOHCH_2CHO \rightarrow CH_3CH{=}CHCHO + H_2O$	$+1.0$	-20.9	-23.5	5.6	1.028×10^{7}	1.042×10^{7}	$+9.2$
4	$CH_3CH{=}CHCHO + C_2H_5OH$ $\rightarrow CH_2{=}CH{-}CH{=}CH_2 + CH_3CHO + H_2O$	$+1.7$	-7.3	-9.3	5.6×10^{-3}	2.8×10^{2}	6.07×10^{2}	$+9.0$
5	$CH_3CH{=}CHCHO + H_2$ $\rightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2O$	—	-5.1	-5.0	—	0.52×10^{2}	0.31×10^{2}	-4.2

EXPERIMENTAL

Preparation of Catalyst

The catalyst Al_2O_3:ZnO (60:40) was prepared by coprecipitating the mixed hydroxide gel by ammonia from a solution of nitrates of aluminum and zinc, mixed in the calculated ratio. All the chemicals used were Analar. The mixed hydroxide gel thus precipitated, was dried at 110°C for 24 hr and then decomposed at nearly 400°C for 6 hr. The final composition of Al_2O_3:ZnO (60:40) was ascertained by chemical analysis. The catalyst particle size was within mesh no. —100; +120 (BS 410/43).

Purification of Materials

Ethanol of about 99.4% purity was further purified by distillation with quick lime in a fractionating apparatus. The last traces of moisture were removed by distillation with magnesium ethoxide.

Acetaldehyde (Analar) was distilled and collected at 21°C.

Crotonaldehyde (Analar) was also distilled and collected at 102–103°C.

Apparatus and the Procedure

A flow-type reactor, operating at atmospheric pressure was used. The furnace and the catalyst tube were kept in an inclined position for the ease of liquid product recovery. The catalyst tube was 40 cm long and 2 cm wide, made of Pyrex glass, with a spiral wound around itself, so that the reactants could be preheated to the same temperature as that of the catalyst before entering the reactor. The catalyst was kept in the middle of the reactor and the remaining hollow space was filled up with Pyrex glass wool and glass beads. The thermocouple pocket was introduced in the middle of the catalyst bed from one end. The furnace was well insulated with asbestos packing.

The temperature was controlled within ±2°C by a Variac coupled with a voltage stabilizer and it was recorded by an iron–constantan thermocouple.

The arrangement for feeding the reactants was similar to the one used by Griffith *et al.* (*11*) with some modifications. Mercury from the reservoir (Fig. 1) passed through one of the capillaries C_1 and C_2 and entered the feeder F, in which the reactant (liquid) was kept, at the point P. The reactant was thus displaced by the mercury falling in the feeder, and entered the catalyst tube, at a rate determined by the height of the reservoir R from P, the

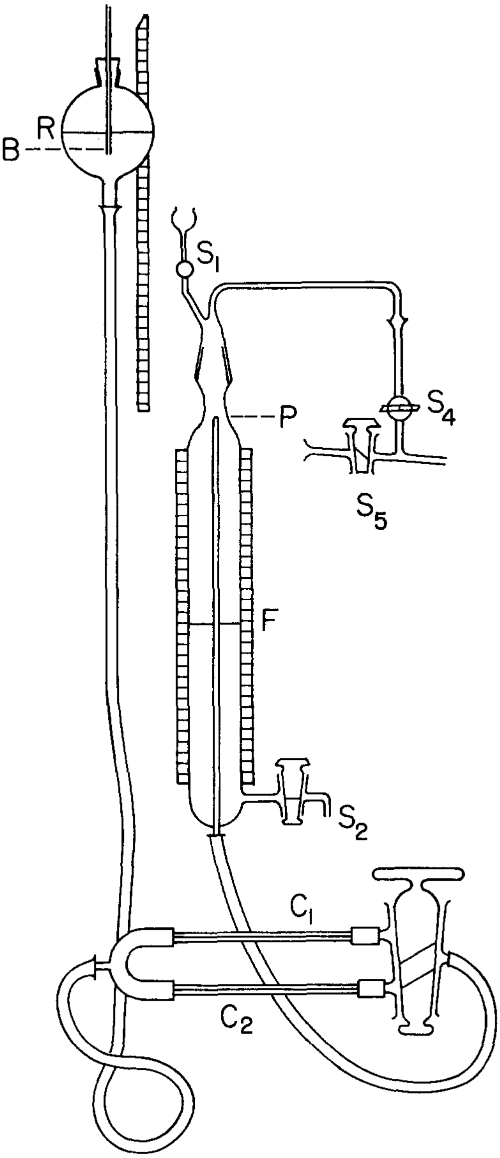

FIG. 1. Liquid feeding system.

diameter and the length of the capillary. The reservoir R was fitted with an airtight cork with an open glass tube dipped in mercury, so that when mercury flowed from the reservoir, it was replaced by air drawn at the point B. This produced a constant pressure head relative to the point P where the mercury entered the feeder. The feeder was of 25-cm height and about 2.5-cm width, and was calibrated for volume using a separate mirror scale attached to it. The stopcocks S_1 and S_2 served the purpose of filling the feeder with the reactant and taking out the mercury, or emptying the feeder, respectively.

With stopcocks S_4 and S_5 either the liquid reactant from the feeder or a gas (for reactivation, etc.) or both(reaction in presence of hydrogen) could be admitted to the reactor.

Analysis of Products

Liquids. The following compounds were successfully identified and estimated in the liquid condensate by vapor-phase chromatographic analysis (Perkin-Elmer Model 154B): acetaldehyde, acetone, water, diethyl ether, and traces of acetaldol (Table 2).

TABLE 2
CALIBRATION OF THE VAPOR FRACTOMETER FOR LIQUIDS

Column, F(P & E Co)
Column length, 4 meters Temperature, 60°C Inlet pressure, 15 psig
Chart speed, 0.4 inches/min Sensitivity, 64

Component	Retention time in min × chart speed (inches)	Calibration factor (C.F.)[a]
Diethyl ether	0.65	1.40
Acetaldehyde	0.75	1.20
Acetone	1.9	1.19
Ethyl alcohol	3.55	1.00
Ethyl acetate	3.75	1.25
Water	5.0	0.71
Acetaldol	8.4	—

[a] C.F. = (Alcohol peak area/Component peak area) for the same weight.

Analysis by IR spectroscopy revealed the presence of cortonaldehyde in the product.

Ethyl acetate was analyzed by the standard saponification method.

Gases. The gaseous products were analyzed by the modified Orsat analyzer with a combustion unit and were found to contain carbon dioxide, ethylene, carbon monoxide, hydrogen, and saturated hydrocarbon (expressed as CH_4).

Butadiene was identified in the product by gas chromatography and the quantitative analysis was carried out with maleic anhydride (*13*) using the apparatus of Bhattacharyya and Ganguli (*1*).

RESULTS AND DISCUSSION

In order to establish the mechanism, detailed investigation was carried out to study the influence of the intermediates on the overall conversion of ethanol to butadiene. The following different feeds, having varying compositions, were tried: (i) ethanol; (ii) ethanol–acetaldehyde; (iii) ethanol–crotonaldehyde; (iv) crotonaldehyle–hydrogen. The results, thus obtained, are discussed below.

(i) With the pure ethanol feed, all the possible intermediates leading to butadiene formation from ethanol, as reported by the Soviet and American workers (*5–9*) could be successfully identified, except the crotyl alcohol, whose presence could not be established beyond doubt either by vapor-phase chromatography or by IR spectroscopy. The total apparent activation energy for the conversion of ethanol to butadiene was found to be 20.7 kcal/g mole.

(ii) When the mixed ethanol–acetaldehyde feed in different mole ratios was fed the process yield of butadiene remained unaltered. The feed having maximum acetaldehyde concentration had the ethanol–acetaldehyde mole ratio in the proportion of 3/2. Other lower concentrations of acetaldehyde were also tried. This result indicated that acetaldehyde formation could not be rate-determining.

(iii) Formation of butadiene from ethanol can take place either by the selective reduction of crotonaldehyde, formed as an intermediate, with the excess ethanol, or by the reaction with the hydrogen formed by the primary reaction

TABLE 3

Effect of Addition of Crotonaldehyde to Ethanol Feed

Temp. (°C)	Mole fraction of croton-aldehyde	Contact time (sec)	Moles per 100 moles of mixture fed								Process yield of C_4H_6
			H_2	CH_3CHO	$CH_3COOC_2H_5$	CH_3COCH_3	C_2H_5OH conv.	CH_3CHO by direct dehydrogenation	C_4H_6	Total CH_3CHO accounted	
380°	0.046	0.40	12.6	11.9	6.8	2.8	60.8	9.8	0.72	31.1	—
380°	0.046	1.05	16.8	10.6	7.8	3.9	45.1	12.9	1.24	34.0	—
380°	0.046	1.40	21.3	9.2	6.7	9.2	41.5	12.1	2.0	41.0	—
420°	0.046	0.30	24.6	14.8	7.9	0.5	52.7	24.1	2.0	31.6	—
420°	0.046	0.90	32.0	14.6	6.9	2.3	52.0	29.7	3.8	33.0	—
420°	0.046	0.85	39.2	16.2	6.4	2.6	—	—	4.3	—	8.1
420°	0.15	0.85	56.2	10.7	6.8	1.3	74.8	—	7.2	-	11.0
420°	0.50	0.85	16.2	Liquid brown in color, not analyzed					4.8	—	6.4

of ethanol dehydrogenation. As such, both the mixtures, ethanol–crotonaldehyde and crotonaldehyde–hydrogen were fed and butadiene was obtained in each case.

The selective reduction of crotonaldehyde by ethanol over Al_2O_3, a dehydrating catalyst, resulting in the formation of butadiene had been reported earlier (*9*). The reaction can be represented as follows (No. 4 in Table 1):

$$CH_3CH{=}CH{-}CHO + C_2H_5OH \rightarrow CH_2{=}CH{-}CH{=}CH_2 + CH_3CHO + H_2O$$

Acetaldehyde was produced in the reaction. As the catalyst Al_2O_3:ZnO (60:40) had the dual function nature, the dehydrogenating effect could not be negligible. Thus, it was thought probable that an acetaldehyde balance, accounting for the formation of all other secondary products like ester and acetone, from it, could be conclusive in establishing the occurrence of reaction (1). The hydrogen (only by dehydrogenation of ethanol alone) produced on feeding the ethanol–crotonaldehyde mixture, indicated the equivalent acetaldehyde formed by the primary dehydrogenation of ethanol only. However, the total acetaldehyde accounted for, by considering that two molecules of the same were required separately for the formation of ester and acetone, showed a surplus over the equivalent acetaldehyde formed by dehydrogenation of pure ethanol (compare column 9 with 11 in Table 3). The excess acetaldehyde, in all probability, was formed by reaction (4) (Table 1), suggesting the possibility of selective reduction of crotonaldehyde by ethanol. The reaction has reasonable feasibility from the standpoint of thermodynamics (Table 1). The apparent activation energy of butadiene formation from an ethanol–crotonaldehyde mixture was 15.3 kcal/g mole, which was less in comparison to the total apparent activation energy for the formation of butadiene from ethanol. Thus the chemical resistance of the step is not much.

The effect of incorporation of crotonaldehyde in different mole ratio with ethanol was also studied. The maximum process yield was obtained with approximately 6/1 mole ratio (mole fraction of crotonaldehyde 0.15) (Table 3).

The process yield of butadiene (mole %) based on the theoretical yield as per the stoichiometric equations, was compared with pure ethanol, ethanol–acetaldehyde, and ethanol–crotonaldehyde feed on an equivalent basis at the same temperature and contact time as reported by Jones *et al.* (*12*) (Table 4). The increase in the process yield of butadiene, while ethanol-crotonaldehyde mixture was fed in the equivalent amount, might be due to the fact that the formation of crotonaldehyde was the rate-determining step. The marked increase in the process yield when approxi-

TABLE 4

COMPARISON OF PROCESS YIELD OF C_4H_6[a]

Feed	Process yield of C_4H_6 (Mole %)
Pure ethanol	7.2
Ethanol/acetaldehyde (3/1 mole ratio)	6.5
Ethanol/crotonaldehyde (6/1 mole ratio)	10.6

[a] On equivalent basis; temperature, 420°C; contact time, 0.9 sec.

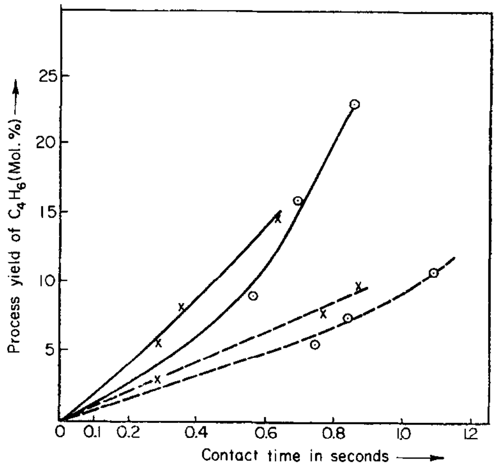

FIG. 2. Effect of incorporation of crotonaldehyde (5 mole %) with ethanol: ——, 440°C; - - - -, 420°C; X, ethanol–crotonaldehyde; ⊙, pure ethanol.

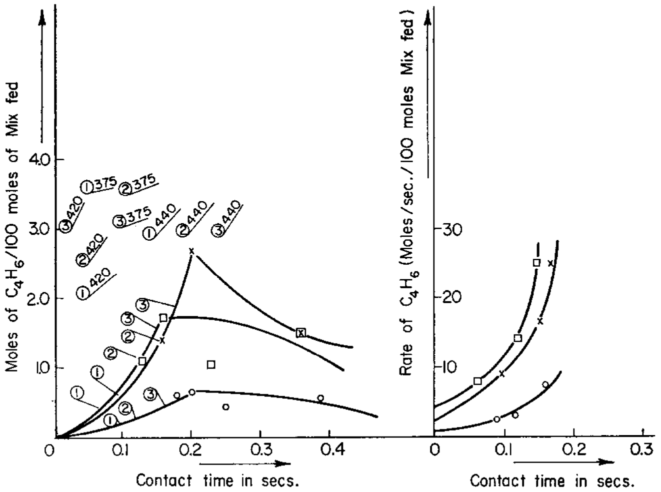

FIG. 3. Conversion (to C_4H_6) and rate of C_4H_6 formation feeding crotonaldehyde–H_2 mixture with variable contact times: □, 440°C; ⊙, 375°C; X, 420°C; circled numbers (1, 2, 3) indicate rate of formation of C_4H_6 (at different points) from slopes at different temperatures.

mately 5 mole % crotonaldehyde was admixed with ethanol, supports such an idea (Fig. 2).

(iv) Using crotonaldehyde–hydrogen as a feed mixture, butadiene could be identified successfully by vapor-phase chromatography. On injecting pure butadiene (99.9 mole %) into the vapor fractometer the product of retention time in minutes and the chart speed was found to be 0.6 inches [temp.: 48°C; sensitivity: 64; psig 10; column: F(P & E Co)]. One small peak of the gaseous products overlapped with that peak, on carrying out the analysis under identical conditions. The liquid product was dark brown and could not be identified by VPC. The variation of butadiene with contact time at different temperature is shown in Fig. 3. The apparent activation energy of butadiene formation was found to be 21.2 kcal/g mole, which was more than the same from ethanol-crotonaldehyde mixture. Thus, it appears that the mechanistic route of butadiene formation by the selective reduction of crotonaldehyde with ethanol appears to be more plausible, having less resistance.

The experimental establishment of this simultaneous mechanism for the formation of butadiene from ethanol over dual function catalyst has not been reported earlier.

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