Esterification of Some Organic Acids With Methanol and Ethanol Using Zirconium Tungstate As a Catalyst

A. S. ABOUL-MAGD

Department of Chemistry,
Faculty of Science, Al-Azhar University,
Nasr City, Cairo, Egypt

The catalytic esterification of formic, mono-, dichloroacetic, acetic, propionic, butyric, isobutyric, valeric and isovaleric acids with methanol/ethanol have been investigated using zirconium tungstate (H-form) as a catalyst.

INTRODUCTION

The esterification of alcohols with acids in presence of organic ion exchangers as catalysts have been reported by several workers[1-6]. The studies show that the rate of reaction was found to decrease with increasing the chain length of the alcohol or the acid, molecular weight or with their branching. However, data on the esterification of organic acids with alcohols in presence of zirconium tungstate are not reported elsewhere. The present study deals with the evaluation of the reaction of a group of organic acids with methanol and ethanol in presence of zirconium tungstate as a catalyst. The effects of the amount of catalyst, molar ratio, reaction temperature, added water as well as a dehydrating agent on the rate of esterification have been investigated. Preparation and evolution of such exchanger also have been carried out. The thermodynamic activation parameters: ΔG^*, ΔH^* and ΔS^* together with the activation energy for the esterification reactions have been computed.

EXPERIMENTAL

Zirconium tungstate was prepared as reported earlier[7]. It was treated by a double cycle (sodium-hydrogen) for exhaustion and regeneration using 1M NaCl solution and finally 10% HCl solution for about $\frac{1}{2}$ hr. By decantation the catalyst was washed three times with double distilled water. This final process was repeated five times, then the product was introduced in a suitable column, and eluted with 100 ml of 10% HCl solution at a rate of 1 ml/min. The catalyst was then washed several times with double distilled water to get free from Cl ions, then dried at 40°C, followed by heating at 120°C for 3 hrs, and kept in desiccator till the time of use.

The X-ray diffraction patterns for the prepared samples carried out in Cairo Electric Company, Central Laboratory Philips 1373 apparatus, showed that they are amorphous[8].

Evaluation of the synthesized exchanger: The resin was soaked for 24 hrs in different solutions at room temperature in H_2SO_4, HCl and HNO_3 solution (1M). The respective decrease in capacity was 0.076, 0.32 and 0.868 where in organic solvent the per cent decrease in capacity was of 0.056, 0.004, 0.036 and 0.018% in methanol, ethanol, propanol and butanol respectively. In case of formic, acetic, mono-, dichloroacetic, propionic, butyric, isobutyric, valeric and isovaleric acids, the maximum decrease in capacity reached 0.04920.

However, a much greater loss in capacity of 22.8% was obtained on soaking the resin in NaOH (1.0 M).

Thermal treatment was carried out by heating the samples previously prepared at 30–40°C till constant weight in a muffle furnace at different temperatures for about 3 hrs. The respective values of decrease in capacity are: 3.04×10^{-6}, 2.5×10^{-5}, 2.2×10^{-4}, 1.6×10^{-3}, 5.7×10^{-3}, 5.3×10^{-2} and 0.5 mequiv/g at temperatures of 80, 120, 240, 360, 480, 600, 780 and 900°C. It is also noticed that, there is no appreciable loss at temperatures from 80–120°C. At 240°C a continuous loss in weight is markedly recorded which is probably due to the removal of bound water present in the matrix.

Procedure and analysis: The capacity of the zirconium tungstate exchanger was 2.5 mequiv/g dry resin. Weighted amounts were soaked in the alcohol selected for esterification reaction and heated to its boiling point for 1 hr. The last procedure was repeated twice and the resin finally filtred off[6]. The resin was then covered with alcohol and left overnight, filtered again and dried at 60°C for $\frac{1}{2}$ hr., and finally placed in a desiccator. The esterification reaction was carried out in three-necked one litre flask placed in a constant temperature bath ± 0.1°C. The flask was initially charged with a portion of the studied alcohol, followed by addition of a whole calculated amount of acid. The catalyst and the remainder alcohol were then added. Aliquots of 2 ml were withdrawn from the flask at definite times, and titrated with 0.1N NaOH solution to analyse the formed acid in presence of excess alcohol[6].

RESULTS AND DISCUSSION

It is important to compute the data recorded in Tables 1 and 2 in terms of the activation parameters from Arrhenius plots Figs. (1–7/D). The change in free energy of activation ΔG^* was calculated according to Eyring's equation[9].

$$K_r = kT/h \exp (-\Delta G^*/RT) \tag{1}$$

where K_r is the specific rate constant, k is the Boltzman constant and h is the Plank's constant. The change in enthalpy ΔH^* is obtained from the relation:

$$\Delta H^* = E_a - nRT \tag{2}$$

TABLE 1
REACTION VELOCITY CONSTANTS, ENERGIES OF ACTIVATION AND THERMODYNAMIC ACTIVATION PARAMETERS FOR THE CATALYZED ESTERIFICATION OF METHANOL WITH VARIOUS CARBOXYLIC ACIDS

| Acid	Molecular weight	Temp °C	X_{Ao}	$K \times 10^{-4}$ Experimental	$K \times 10^{-4}$ Theoretical	Ea Cal mol^{-1}	ΔH^{*} Cal mol^{-1}	$-\Delta S^{*}$ (Cal deg^{-1} mol^{-1})	ΔG^{*} Cal mol^{-1}
Formic	46.026	60	0.96	53.2854	53.0681	5597.183	4273.841	54.343116	22370.098
		56	0.95	48.2138	47.8823		4289.737	54.313509	22158.881
		50	0.94	41.0113	40.8427		4313.581	54.282452	21846.812
Monochloro-acetic	94.50	64	0.87	11.1983	11.07207	6735.5932	5396.3552	54.288319	23691.518
		60	0.84	9.58228	9.50082		5412.2512	54.334224	23505.547
		55	0.83	8.00082	8.13542		5432.1212	54.354277	23260.324
Dichloro-acetic	128.94	64	0.82	7.96464	7.81233	6947.5524	5608.3144	54.336543	23919.729
		60	0.77	6.90856	6.89707		5624.2104	54.347874	23722.052
		55	0.74	5.86787	5.8771		5624.0804	54.324237	23462.43
Acetic	60.05	61	0.79	5.23414	5.2663	7147.482	5820.166	54.369309	23979.465
		56	0.75	4.44141	4.47131		5840.036	54.340491	23718.067
		51	0.70	3.69596	3.77721		5859.906	54.339932	23466.043
Propionic	74.08	62	0.75	4.01573	3.95656	7359.2592	6027.9692	54.333568	24229.714
		56	0.69	3.36681	3.23421		6051.8132	54.242795	23899.173
		52	0.67	2.73385	2.81583		6067.7092	54.36155	23735.212
Butyric	88.11	64	0.68	2.94674	2.76863	7642.3076	6303.0696	54.250983	24585.65
		60	0.65	2.53857	2.414		6318.9656	54.25116	24384.601
		55	0.60	2.14011	2.02435		6338.8356	54.210572	24119.903
Iso-butyric	88.11	64	0.66	2.52906	1.21357	7792.1568	6452.9188	54.110094	24688.02
		60	0.62	2.15033	1.92486		6468.8148	54.131019	24494.444
		55	0.58	1.7844	1.6086		6488.6848	54.114962	24238.392
Valeric	102.13	64	0.61	2.26877	2.11447	7822.8346	6483.596	54.199349	24748.776
		60	0.59	1.97095	1.83767		6499.492	54.212001	24552.088
		55	0.58	1.67438	1.53465		6519.362	54.147905	24279.874
Iso-valeric	102.13	64	0.57	1.05418	1.92726	7884.9205	6545.6825	55.573914	25274.091
		60	0.56	0.915776	1.67311		6561.5785	55.548844	25059.343
		55	0.55	0.760133	1.39523		6581.4485	55.528023	24794.64

TABLE 2

REACTION VELOCITY CONSTANTS, ENERGIES OF ACTIVATION AND THERMODYNAMIC ACTIVATION PARAMETERS FOR THE CATALYZED ESTERIFICATION OF ETHANOL WITH VARIOUS CARBOXYLIC ACIDS

| Acid	Molecular weight	Temp °C	X_{Ac}	$K \times 10^{-4}$ Experimental	$K \times 10^{-4}$ Theoretical	E_a Cal mol⁻¹	ΔH^* Cal mol⁻¹	$-\Delta S^*$ (Cal deg⁻¹ mol⁻¹)	ΔG^* Cal mol⁻¹
Formic	46.026	70	0.92	50.6034	49.7016	5809.9415	4446.8592	54.374302	23097.244
		64	0.91	41.2519	42.7039		4470.7035	54.443708	22818.233
		60	0.89	36.4393	38.478		4486.5995	54.459416	22349.287
Monochloro-acetic	94.50	75	0.84	10.73	10.9679	6952.4142	5569.4622	54.445768	24516.589
		70	0.82	9.23819	9.30016		5589.3322	54.423279	24256.516
		64	0.78	7.68088	7.75582		5613.1762	54.394212	23944.025
Dichloro-acetic	128.94	75	0.79	6.57831	6.46594	7305.147	5922.195	54.404501	24854.961
		70	0.75	5.63566	5.54321		5942.065	54.377105	24593.412
		64	0.70	4.67418	4.58033		5965.909	54.334596	24276.667
Acetic	60.05	75	0.74	3.0794	3.05877	7822.8346	6439.8826	54.425363	25379.908
		70	0.72	2.54939	2.5938		6519.7526	54.444283	25194.141
		64	0.68	2.12482	2.11447		6483.5966	54.365177	24804.66
Propionic	74.08	75	0.72	2.93338	3.1975	7792.1568	6409.2048	54.610061	25413.506
		70	0.67	2.51756	2.7132		6429.0748	54.558691	25142.705
		64	0.66	2.0247	2.21357		6452.9188	54.552128	24836.985
Butyric	88.11	75	0.45	1.45606	1.58121	8279.1666	6896.2146	54.60577	25899.022
		70	0.40	1.22245	1.32801		6916.0846	54.574552	25635.155
		64	0.35	0.991615	1.06977		6957.9286	54.525636	25333.067
Iso-butyric	88.11	75	0.44	1.23847	1.22567	8455.319	7072.367	54.418056	26009.85
		70	0.39	1.02721	1.02559		7092.237	54.406805	25753.771
		64	0.34	0.815784	0.822366		7116.081	54.390827	25445.789
Valeric	102.13	75	0.40	0.99011	0.991823	8601.7316	7218.7796	54.442127	26164.639
		70	0.36	0.825601	0.827361		7238.6496	54.414158	25902.705
		64	0.33	0.65532	0.660881		7262.4936	54.391645	25592.477
Iso-valeric	102.13	75	0.32	0.469005	0.472417	9114.6786	7731.7268	54.45308	26681.398
		70	0.31	0.391879	0.389844		7751.5968	54.399562	26410.646
		64	0.30	0.314578	0.307257		7775.4408	54.328033	26083.987
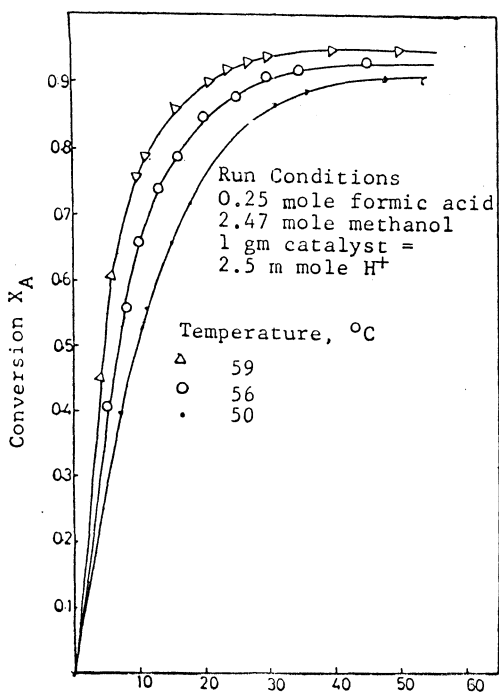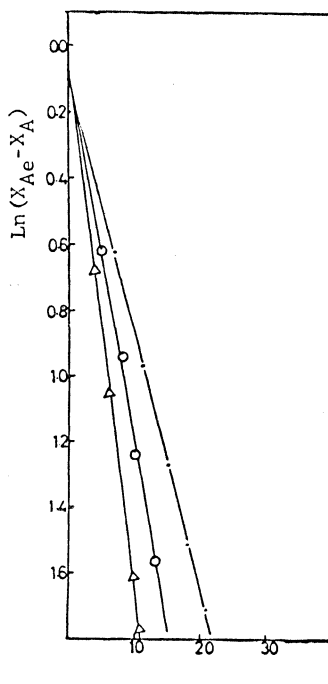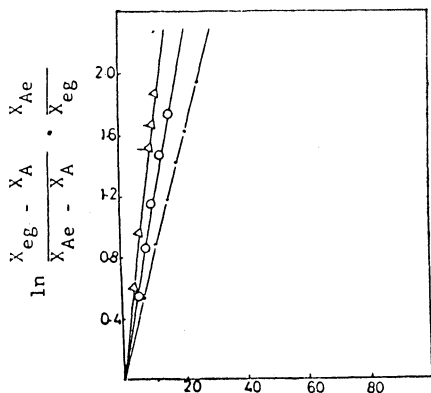
METHANOL-FORMIC ACID
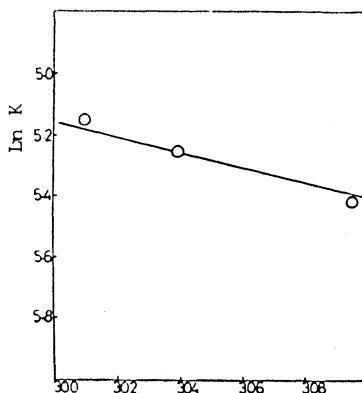

Fig. 1   Esterification of formic acid with methanol: (A) Effect of reaction temperature on the conversion of formic acid, (B) Linear transformation, (C) Determination of X_{Ae}, (D) Effect of temperature on reaction rate constant.
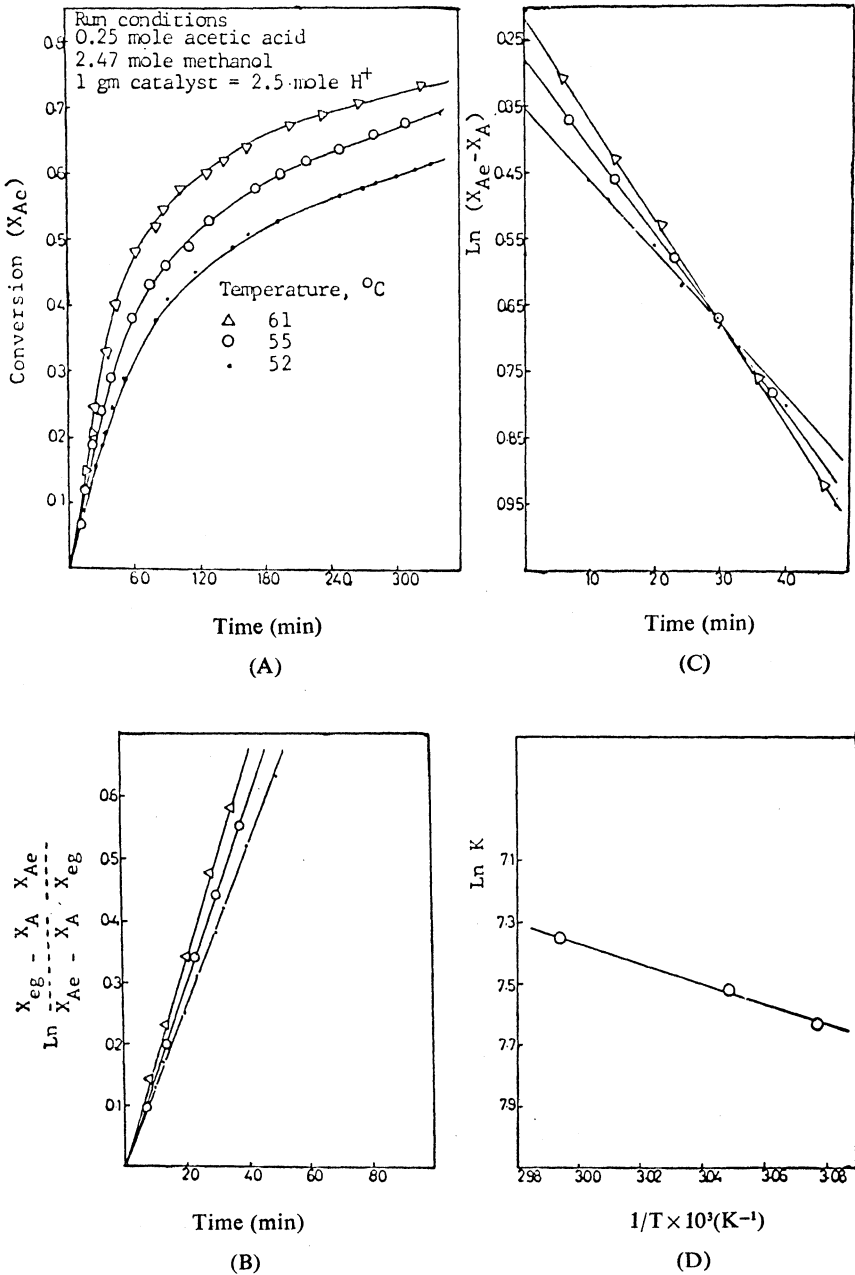
METHANOL-ACETIC ACID

Fig. 2 Esterification of acetic acid with methanol: (A) Effect of reation temperature on the convention of acetic acid, (B) Linear transformation, (C) Determination of X_{Ae}, (D) Effect of temperature on reaction rate constant.

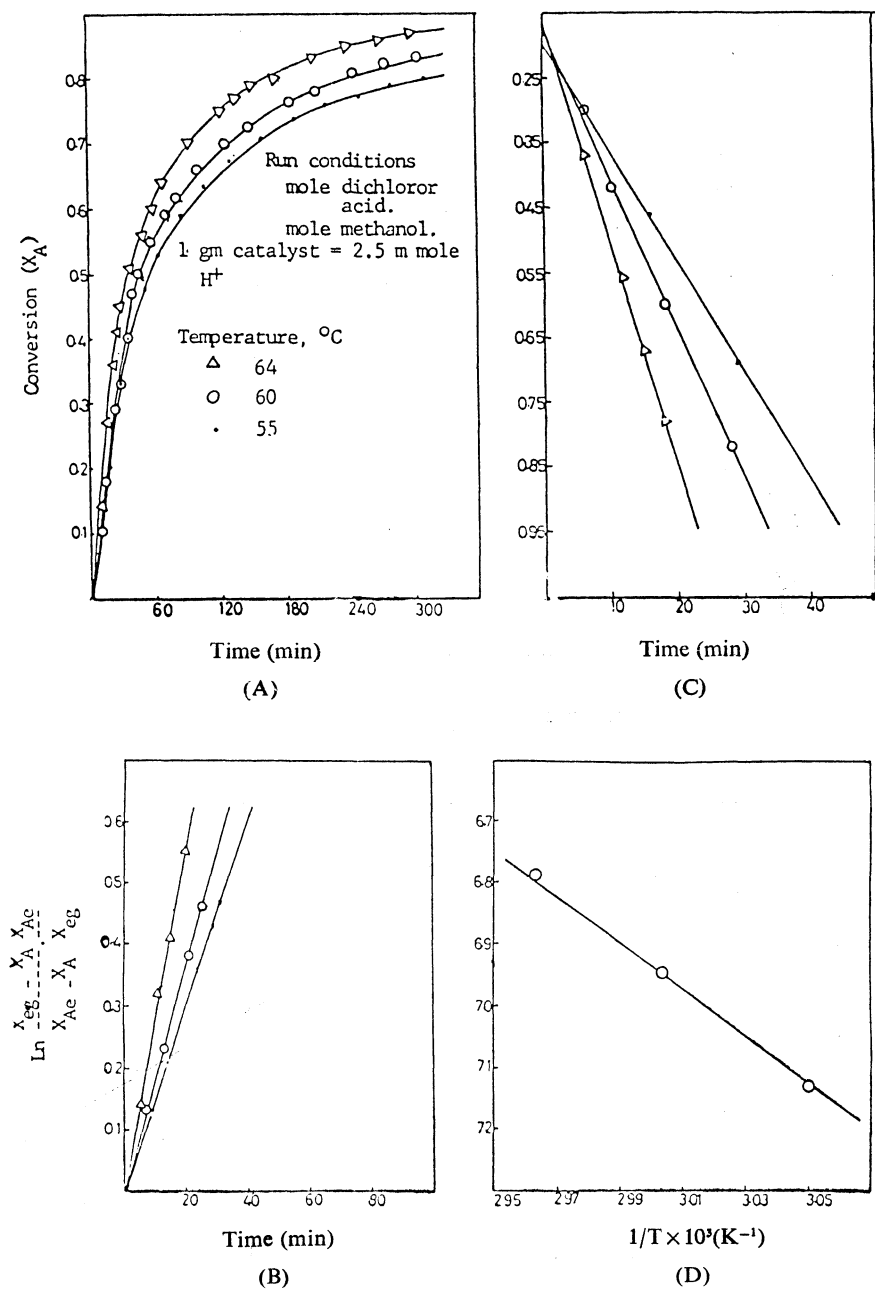## METHANOL-MONOCHLOROACETIC ACID

Fig. 3 Esterification of monochloroacetic acid with methanol: (A) Effect of reaction temperature on the conversion of monochloroacetic acid, (B) Linear transformation, (C) Determination of X_{Ae}, (D) Effect of temperature on reaction rate constant.
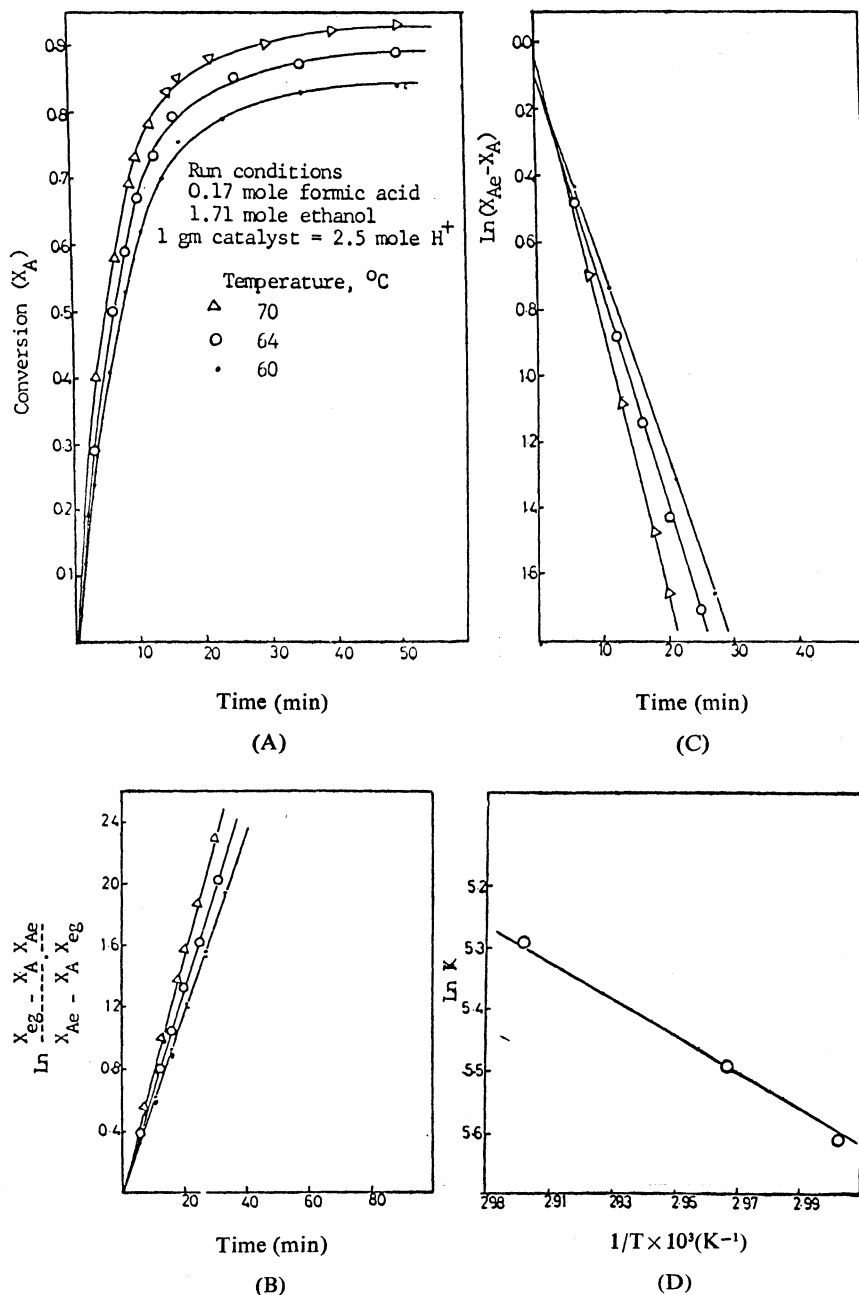
ETHANOL-FORMIC ACID

Fig. 4 Esterification of formic acid with ethanol: (A) Effect of reaction temperature on the conversion of formic acid, (B) Linear transformation, (C) Determination of X_{Ae}, (D) Effect of temperature on reaction rate constant.
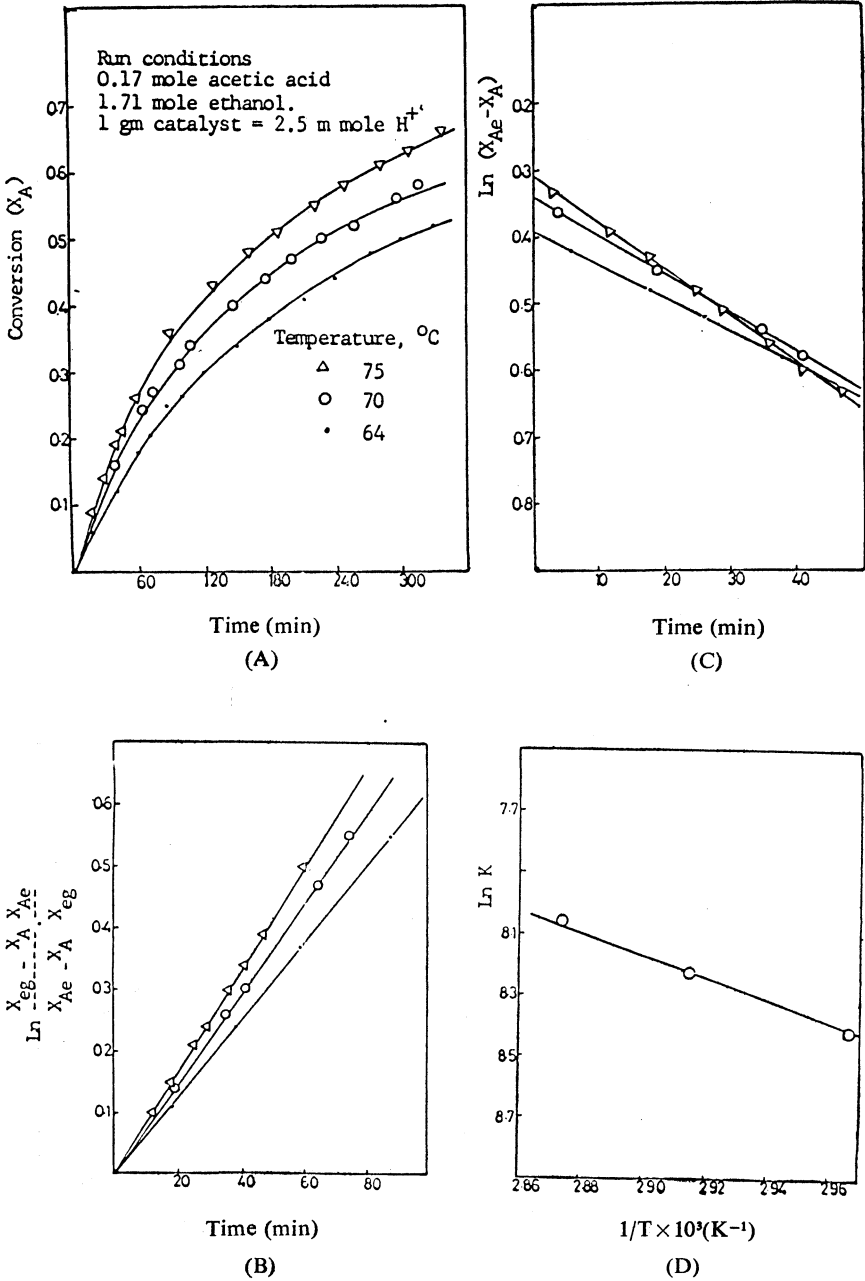
ETHANOL-ACETIC ACID

Fig. 5   Esterification of acetic actid with ethanol: (A) Effect of reaction temperature on the conversion of acetic acid, (B) Linear transformation, (C) Determination of X_{A_e}, (D) Effect of temperature on reaction rate constant.
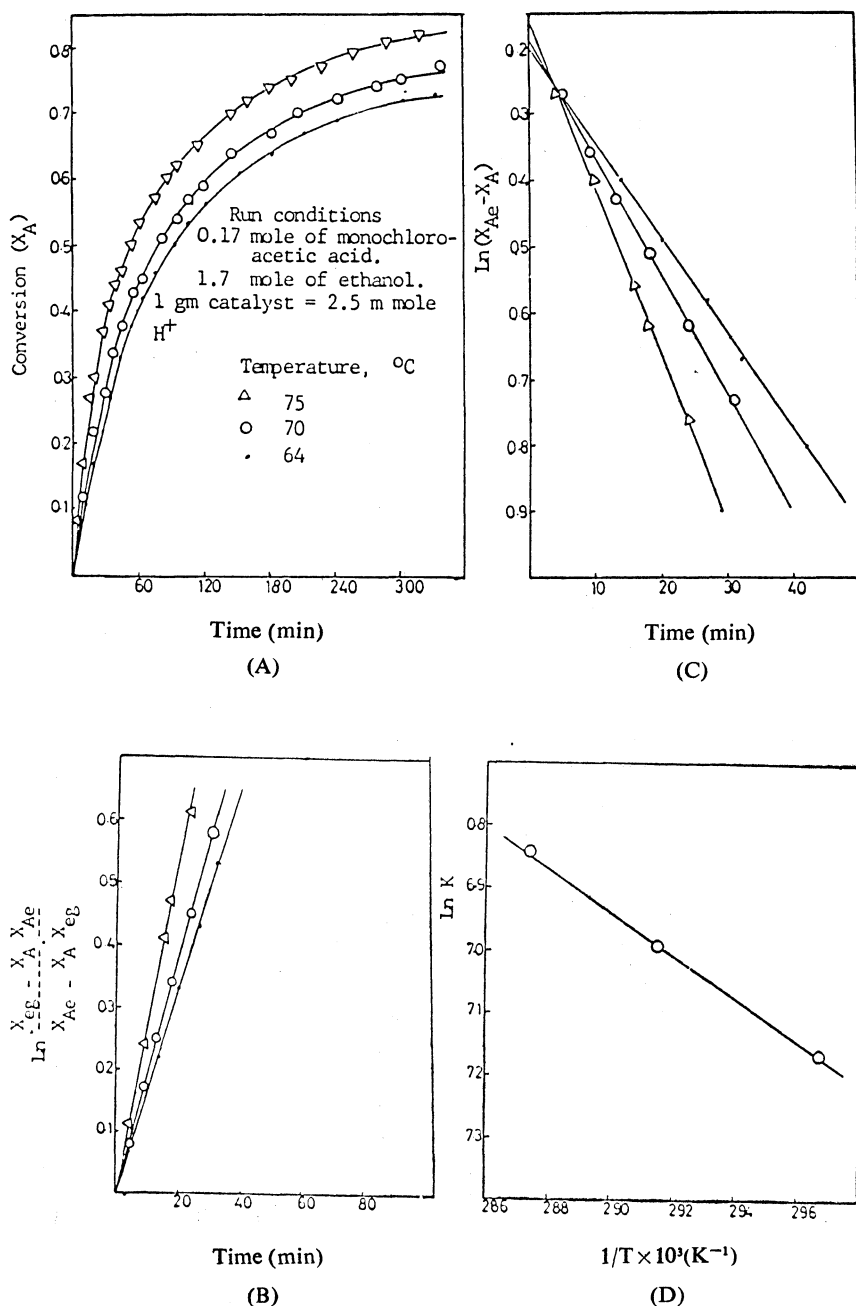
ETHANOL-MONOCHLOROACETIC ACID

Fig. 6 Esterification of monochloroacetic acid with ethanol: (A) Effect of reaction temperature on the conversion of monochloroacetic acid, (B) Linear transformation, (C) Determination of X_{A_e}, (D) Effect of temperature on reaction rate constant.
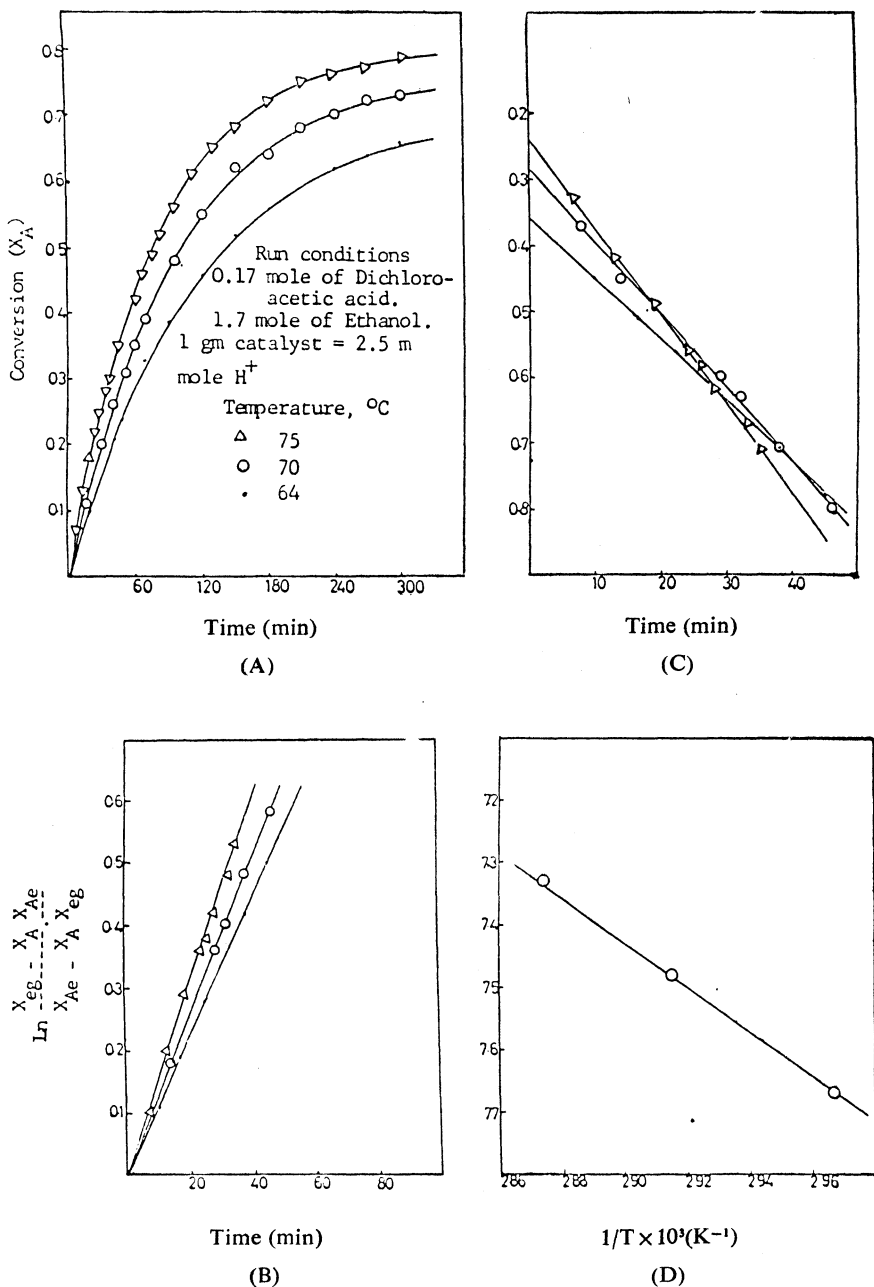
ETHANOL-DICHLOROACETIC ACID

Fig. 7   Esterification of dichloroacetic acid with ethanol: (A) Effect of reaction tem-
perature on the conversion of dichloroacetic acid, (B) Linear transformation,
(C) Determination of X_{Ae}, (D) Effect of temperature on the reaction rate constant.

The entropy changes were calculated from equation[10].

$$k_r = k \ T/h \ exp \ (\Delta S^*/R) \ exp \ (-E_a/RT) \qquad (3)$$

The values of activation energy for the esterification of methanol and ethanol with the use of acids lie in the range of esterification reaction i.e. between 5597.183 and 7884.92 Cal/mole for methanol and 5580.9415 and 9114.6788 Cal/mole for ethanol.

The correct value of X_{Ae} (fractional conversion at equilibrium is obtained either experimentally when equilibrium is attained or by fitting the experimental data in the equation Figs. (1–7/C).

$$X_A = X_{Ae} \ (1 - exp \ (-ht)) \qquad (4)$$

The values of X_{Ae} are assumed and then $log(X_{Ae} - X_A)$ is plotted against time t, where a linear relationship is obtained.

The activation energies calculated from Arrhenius plots have been used in equation 5 to calculate the theoretical values of specific rate constant of the used acids[6].

$$k_r = B/W \ mequiv. \ exp \ (-E_a/RT) \qquad (5)$$

The activation energies for the reaction of methanol and ethanol with the used acids given in Tables (1, 2), for a fixed value of W = amount of catalyst and B = molar ratio of reactants. It is assumed that W and B have no effect on the activation energy.

The specific rate constant k_r for the esterification of the studied acids with methanol and ethanol were calculated, using the following modified equation[6]:

$$ln\frac{X_{eg} - X_A}{X_{Ae} - X_A} \cdot \frac{X_{Ae}}{X_{eg}} = \frac{2B - (B + 1) \ X_{Ae}}{X_{Ae}} C_{Ao}k_r t \qquad (6)$$

where X_{eg} is a constant obtained by the relation:

$$X_{eg} = \frac{X_{Ae}}{(B + 1) \ X_{Ae} - B}$$

The kinetics of the catalyzed esterification of methanol and ethanol with formic, acetic, propionic, butyric, isobutyric, valeric, isovaleric, mono- and dichloroacetic acids were studied under of temperature as shown in Figs. (1–7/A), the conversion increases with increasing of temperature. From the values of E_a it can say that, it is probable that the esterification reaction of all the studied acids is controlled by the chemical reaction inside the particle of the catalyst. This means that the sorption equilibrium of the reacting species between the catalyst and solution phases is rapidly attained and is remained throughout the process[5].

The effect of initial water concentration on the rate of reaction is demonstrated in Table (3). It is apparent that the rate of conversion of acid decreases markedly with increase in initial water content. Since water

is being one of the product species in the esterification reaction, therefore the addition of water to the medium, together with the water resulting from esterification reaction may have a retarding effect on the percent of conversion[12].

TABLE 3

VALUES OF REACTION VELOCITY CONSTANT FOR THE ESTERIFICATION OF METHANOL AND ETHANOL WITH ACETIC ACID USING DIFFERENT VOLUME OF WATER AT 1 g AMOUNT OF CATALYST, MOLAR RATIO(B) 10 : 1 AND REACTION TEMPERATURE 61°C

Alcohol	X_{A_0}	Volumes of added H_2O (ml)	$k \times 10^{-4}$ dm^{-3} mol^{-1} sec^{-1}
Methanol	0.79	0.0	5.23414
	0.75	2.0	4.62884
	0.73	4.0	3.60021
	0.70	6.0	3.24019

The resulting effect of water is an agreement with the finding of Erilette et al.[11] as well as those of Levesque and Craig[12].

Preliminary water is found to be one of the products resulting from the esterification reaction, and according to Le-Chatelier Braun principle, its removal from the reaction medium leads to an increase in the reaction rate in the forward direction i.e. the reaction is enhanced. The rate of conversion of acetic acid is increased with increasing the amount of anhydrous $CaCl_2$ (Table 4).

TABLE 4

REACTION VELOCITY CONSTANTS FOR THE ESTERIFICATION OF ETHANOL WITH ACETIC ACID USING ANHYDROUS $CaCl_2$ AT 1 g AMOUNT OF CATALYST, MOLAR RATIO(B) 10 : 1 AND 75°C

X_{A_0}	Wt. of anhydrous $CaCl_2$ (g)	$k \times 10^{-4}$ dm^{-3} mol^{-1} sec^{-1}
0.74	1.0	3.0794
0.78	2.0	3.48106
0.81	3.0	3.63929
0.84	4.0	3.81259

The effects of the amount of catalyst on the fractional conversion of acid are shown in Tables (5,6). The m. equivalents of the H^+ ions used on all reactions were ranged from 2.5–10 meq/g dry resin/115 ml of reactants.

TABLE 5

REACTION VELOCITY CONSTANTS FOR THE ESTERIFICATION OF
METHANOL WITH DIFFERENT CARBOXYLIC ACIDS USING DIFFERENT
WEIGHTS OF CATALYST

Acid	Wt. of catalyst (gm)	Molar ratio(B)	X_{Ae}	T °C	$k \times 10^{-4}$ $(dm^{-3}\ mol^{-1}\ S^{-1})$
Acetic	1	10 : 1	0.79	61	5.23414
	2	10 : 1	0.80	61	6.48038
	3	10 : 1	0.81	61	8.10048
	4	10 : 1	0.82	61	9.25868
Propionic	1	10 : 1	0.75	62	4.01573
	2	10 : 1	0.78	62	5.14875
	3	10 : 1	0.79	62	5.61682
	4	10 : 1	0.80	62	6.1785
Butyric	1	10 : 1	0.68	64	2.94677
	2	10 : 1	0.69	64	3.63431
	3	10 : 1	0.70	64	3.89391
	4	10 : 1	0.71	64	4.54289
Valeric	1	10 : 1	0.61	64	2.26877
	2	10 : 1	0.62	64	2.64691
	3	10 : 1	0.63	64	2.80261
	4	10 : 1	0.64	64	2.97777

TABLE 6

REACTION VELOCITY CONSTANTS FOR THE ESTERIFICATION OF
ETHANOL WITH DIFFERENT CARBOXYLIC ACIDS USING DIFFERENT
WEIGHTS OF CATALYST AT REACTION TEMPERATURE OF 70°C

Acid	Wt. of catalyst (gm)	Molar ratio(B)	X_{Ae}	$k \times 10^{-4}$ $(dm^{-3}\ mol^{-1}\ S^{-1})$
Acetic	1	10 : 1	0.72	2.54939
	2	10 : 1	0.73	3.05927
	3	10 : 1	0.74	3.18674
	4	10 : 1	0.75	3.3253
Propionic	1	10 : 1	0.67	2.51756
	2	10 : 1	0.68	2.71122
	3	10 : 1	0.69	2.93715
	4	10 : 1	0.70	3.06485
Butyric	1	10 : 1	0.40	1.22245
	2	10 : 1	0.41	1.39848
	3	10 : 1	0.42	1.37106
	4	10 : 1	0.43	1.3447
Valeric	1	10 : 1	0.36	0.825601
	2	10 : 1	0.37	0.896368
	3	10 : 1	0.38	0.950684
	4	10 : 1	0.39	0.980403

It observed that for milliequivalent upto 10, the conversion of the acids increases. The increase of conversion rate with leading agrees well with the description of proton mechanism proposed by Tsoekove and Konevev[13].

In a previous work carried out by us and by several authors[5-7] on the esterification of organic acids in presence of exchange resin, the rate of coversion of acids is slightly increased by increasing the molar ratio of reactants. However in the present work, it is obvious that since we use a molar ratios of higher values a decrease in the rate of conversion of acids was obtained. This may be due to the fact that the presence of excess alcohol concentration leads to the production of deactivated protons, which decreasing the rate of ester formation[7].

TABLE 7

REACTION VELOCITY CONSTANTS FOR THE ESTERIFICATION OF
ETHANOL WITH ACETIC ACID AND PROPIONIC ACID IN PRESENCE
OF 1 gm CATALYST

Esterification reation	Molar ratio (B)	T°C	X_{A_e}	$k \times 10^{-4}$ (dm^{-3} mol^{-1} S^{-1})
Acetic acid + methanol	10 : 1	61	0.79	5.23414
	15 : 1	61	0.78	3.24318
	20 : 1	61	0.77	3.51571
	25 : 1	61	0.76	3.17469
Propionic acid + methanol	10 : 1	62	0.75	4.01073
	15 : 1	62	0.74	3.50952
	25 : 1	62	0.70	2.68591
Propionic acid + ethanol	10 : 1	75	0.72	2.93338
	15 : 1	75	0.70	2.38034
	20 : 1	75	0.68	1.8411

From the data given in Tables (1,2) for the esterification of mono-and dichloroacetic acids with studied alcohols, it is clear that, the values of activation energy, E_a, in case of dichloroacetic are higher as compared with monochloroacetic acid. This mean that monochloroacetic is the most reactive than dichloroacetic acid, although the latter one has the lower value of dissociation constant.

Consequently, acetic acid acquires the lowest molecular weight as compared with mono-, and dichlororoacetic acid, however the fractional conversion of acetic acid with the studied alcohols has lower values, it is probable that the lowering in the conversion may be due to the lower value of dissociation constant as compared with the studied other acids.

In all such cases, by plotting $\ln \dfrac{X_{eg} - X_A}{X_{Ae} - X_A} \cdot \dfrac{X_{Ae}}{X_{eg}}$ vs. time t, the values of k_r are obtained from the linear relation, and showed that the esteri-

fication of either ethanol or methanol with acids is a second order bimolecular reversible reaction Figs (1–7/B).

It is clear from Tables (1,2) that the values of ΔG^* increases with increase of temperature. The calculated values of ΔH^* and entropy changes of activation under identical conditions are higher for ethanol as compared with methanol when they reacted with the same acids. The rate constant values for ethanol are less than those for methanol, while the activation energies and entropies for the former reactions are higher than those of the latter. This indicates that ethanol has a higher energy barrier than methanol.

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