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Ion-Exchange Resin Catalysed Esterification of Isopropanol with Chloroacetic Acids

A. S. ABOUL-MAGD*, F. H. KAMAL, A. R. EBAID and A. M. BARAKAT

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

Studies have been made on the kinetics of the esterification of isopropanol with chloroacetic acids (mono-, di- and trichoro-acetic acids, using Imac 20Ar as a catalyst. The influence of chloro-substituted acid on the esterification has been investigated. The experimental data was found to befit a second order bimolecular kinetic equation.

INTRODUCTION

Heterogeneous catalytic esterification of alcohols with organic acids in presence of organic cation exchange resin in the H^+-form have been reported[1-6]. A few investigations of catalytic esterification concerning the effect of chloro-substituted acids on the rate of the esterification has been published[7].

The object of the present work is to evaluate the esterification reactions of mono-, di-, and trichloroacetic acids with isopropanol in presence of Imac 20 Ar as a catalyst. The thermodynamic function of activations viz, ΔG^*, ΔH^* and ΔS^* were calculated from Arrhenius plots for the two acids and compared.

EXPERIMENTAL

All chemicals used were of either BDH (AnalaR) or E. Merck (GR) grade. The cation exchanger Imac 20 Ar, mean diameter 0.035 cm, H^+-form, obtained from Imacti, Amsterdam, was employed.

The reaction was carried out in a three-necked one litre flask placed in a constant temperature bath. The acid and the portion of the alcohol were charged into the flask. The contents were kept thoroughly agitated for few minutes and lastly the catalysts were taken out at regular intervals for subsequent analysis using 0.1N sodium hydroxide solution as well as the methods described earlier[3].

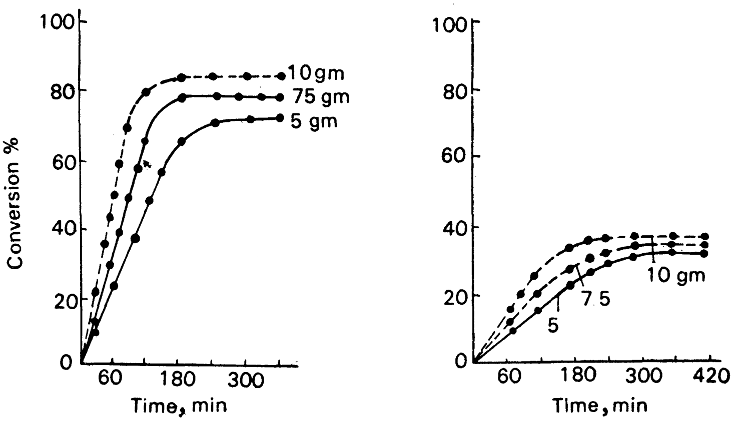
RESULTS AND DISCUSSION

The fractional conversion of mono- and dichloroacetic acids to isopropylmono- and dichloroacetate as a function of resin (expressed as the g catalyst/100 g reactants) studied.

The conversion-time data for the esterification of monochloroacetic acid with isopropanol with 5–10 g dry resin, molar ratio of alcohol to acid 10–20 and reaction temperature 60–82°C are represented in

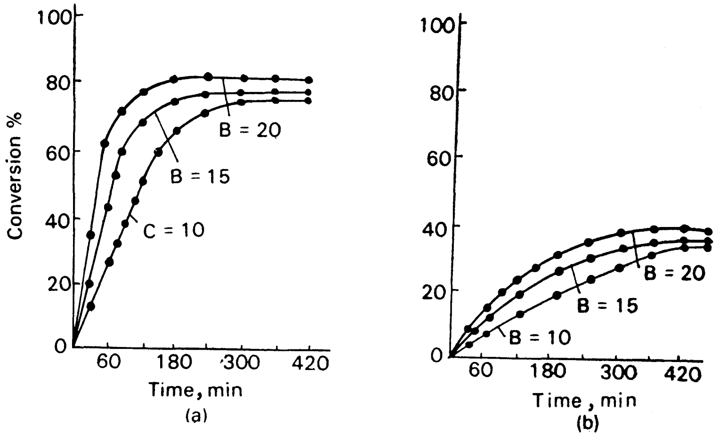
Figs (1a–3a). The rate of esterification reaction under these conditions was found to be markedly influenced with the amount of catalyst, reaction temperature and slightly with the molar ratio of reactants.

Figs (1b–3b) show that similar data concerning the effect of the above three variables mentioned upon the conversion of dichloroacetic acid when reacted with isopropanol are investigated. However, the reaction of trichloroacetic acid with isopropanol gave a negative result and no indication for conversion has ben observed under the influence of the above three variable conditions.



(a) (b)

Fig. 1. Effect of amount of catalyst on the per cent conversion for the esterifications of mono- (a) and dichloroacetic acids (b) with isopropanol



(a) (b)

Fig. 2. Effect of molar ratio (B) on the percent conversion for the esterification reactions of mono- (a) and dichloro aceticacids (b) with isopropanol

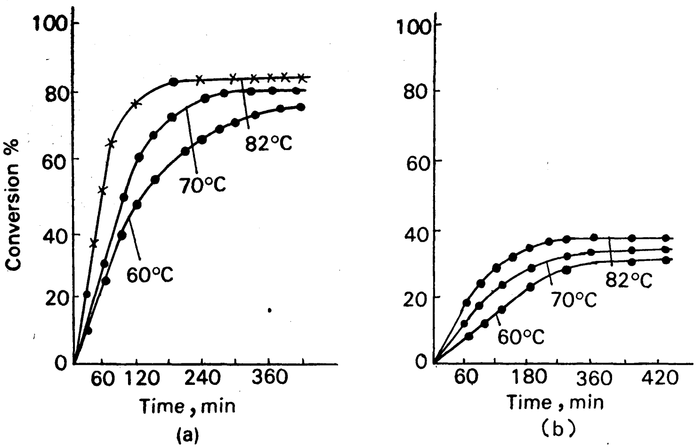


Fig. 3. Effect of reaction temperature on the per cent conversion for the esterification reactions of mono- (a) and dichloroacetic acids (b) with isopropanol

It is evident from Tables (1, 2) that the fractional conversion as well as the specfic rate constant (k_1) of monochloroacetic acid (MAA) when reacted with isopropanol assumed is higher than that assumed for dichloroacetic acid (DAA). It is suggested that (MAA) produces HCl during the reaction upon heating, therefore increasing the acidity of the reaction

TABLE 1

REACTION VELOCITY CONSTANT AND THERMODYNAMIC PARAMETERS FOR THE ESTERIFICATION REACTION OF (MAA) WITH ISOPROPANOL USING ION-EXCHANGE RESIN

Weight of catalyst, g.	Molar ratio (B)	Reaction velocity constant		T, °C	X, %	G^*	H^* —	S^*
		k_1, exp	k_1^* theo $\times 10^{-6}$			(Kcal/mole;	Kcal/mol.	deg.)
5	25	2.295	2.189	82	70.2	30.061		
7.5	25	3.425	3.285	82	77.9	29.779		
10.0	25	4.523	4.376	82	83.0	29.583		
10.0	10	1.751	1.751	82	73.2	30.252		
10.0	15	2.850	2.627	82	77.4	29.908		
10.0	20	3.672	3.502	82	80.1	29.703		
10.0	25	1.555	1.432	60	78.0	29.027	11.337	0.053
10.0	25	2.565	2.434	70	80.0	28.946	11.317	0.051
10.0	25	4.523	4.378	82	83.0	29.583	11.293	0.051

TABLE 2

REACTION VELOCITY CONSTANT AND THERMODYNAMIC PARAMETERS FOR THE ESTERIFICATION REACTION OF (DAA) WITH ISOPROPANOL USING ION-EXCHANGE RESIN

Weight of catalyst, g	Molar ratio (B)	Reaction velocity constant		T, °C	X, %	G^*	H^* —	S^*
		k_1 exp.	k_1^* theo $\times 10^{-6}$			(Kcal/mole;	Kcal/mole.	deg.)
5	25	8.25	8.158	82	29.0	30.783		
7.5	25	12.367	12.238	82	34.5	30.497		
10.0	35	16.564	16.310	82	36.5	30.291		
10.0	10	4.523	4.522	82	32.0	31.191		
10.0	15	9.884	9.790	82	34.5	30.655		
10.0	20	13.092	13.050	82	36.1	30.457		
10.0	25	5.211	5.000	60	28.0	29.750	12.037	0.053
10.0	25	8.858	8.725	70	31.5	29.671	12.017	0.051
10.0	25	16.564	16.310	82	36.5	29.583	11.993	0.049

medium, promoting thus the catalytic process as well the following equation.

$$CH_2ClCOOH + H_2O \rightarrow CH_2OHCOOH + HCl$$

Thus, experiments were carried out to investigate the evolution of HCl from (MAA), (DAA) and (TAA) where 6.9 g, 5.0 g and 6.5 g respectively were treated with 100 ml water at different temperatures.

It is noticed from the data that the rate of acidity increases in the case of (MAA) whereas for (DAA) no appreciable increase in the quantity of sodium hydroxide solution, necessary for neutralization was observed, which indicates no significant production of HCl from this acid. However for (TAA) an interaction of this acid with water by time to proceed with the formation of nonacidic production or may be destroyed during the reaction, therefore the acidity of the medium decreased with time.

The absence of induction period in each case is probably due to the absence of water contained in the resin[3].

In all cases, however, the rate (Tables 1, 2) obtained in the esterification reaction of mono- and dichloroacetic acids with isopropanol have been satisfactorily correlated by the second order bimolecular reaction[3].

The equilibrium conversion of the esterification reaction (X_{Ae}) of isopropanol with the above mentioned acids are obtained by fitting the experimental data.[3]

$$X_A = X_{Ae}(1 - e^{-\mathrm{ht}}) \qquad (1)$$

The values of X_{Ae} were assumed and log $(X_{Ae} - X_A)$ was plotted against time t. The corrected value and that obtained from the intercept of the linear plot coincide.

The specific rate constant k_1 for the esterification of the studied acids with isopropanol was calculated, using the simplified equation (2).

$$\ln \frac{X_{eg} - X_A}{X_{Ae} - X_A} \cdot \frac{X_{Ae}}{X_{eg}} = \frac{2B - (B + 1)}{X_{eg}} k_1 C_{A_0} t \qquad (2)$$

where,

$$X_{eg} = \frac{BX_{Ae}}{(B + 1)X_{Ae} - B} \qquad (3)$$

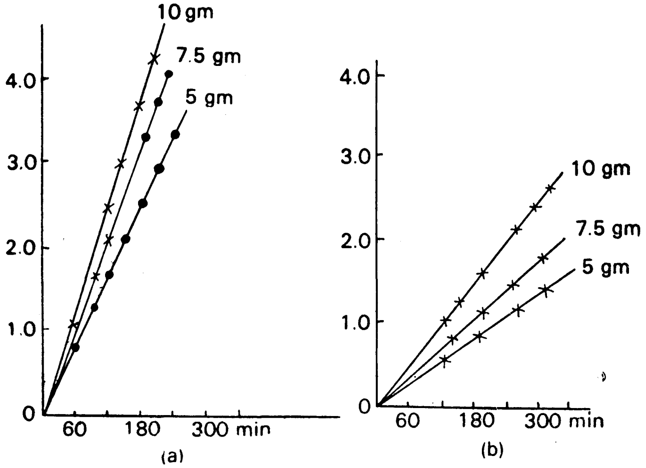


Fig. 4. Effect of amount of catalyst on the fraction conversion for the esterification of mono- (a) and dichloroacetic acids (b) with isopropanol (a linear transformation)

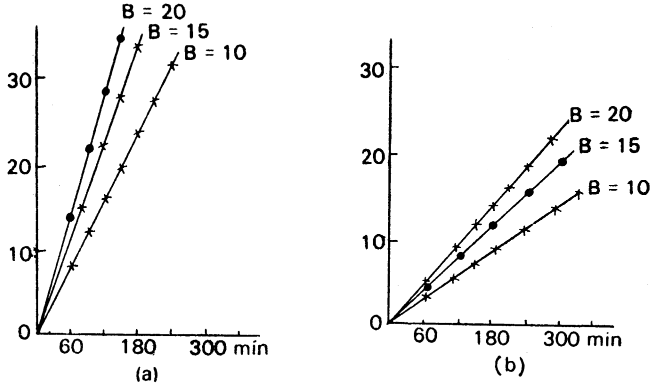
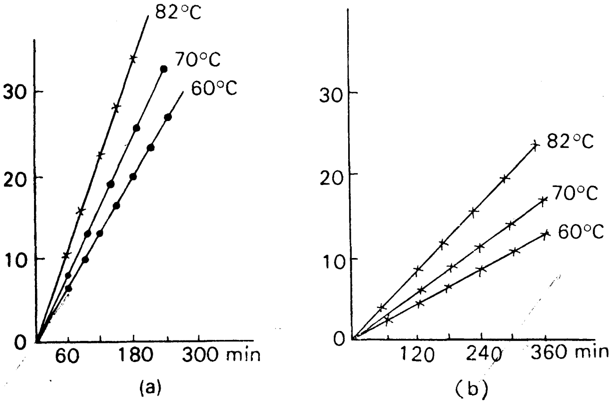


Fig. 5. Effect of molar ratio (B) on fraction conversion for esterification of mono- (a) and dichloroacetic acids (b) with isopropanol (a linear transformation)

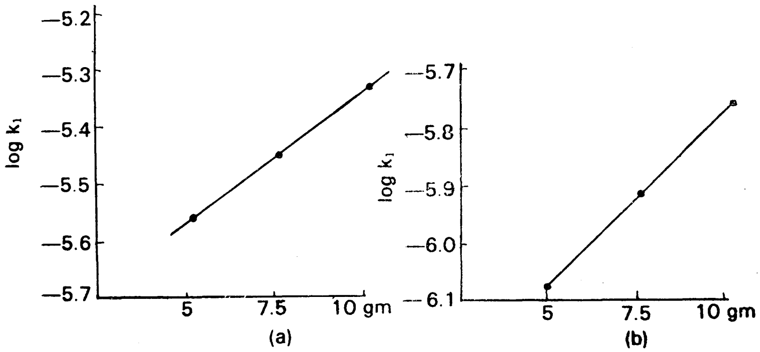
By plotting,

$\ln \dfrac{X_{eg} - X_A}{X_{Ae} - X_A} = \dfrac{X_{Ae}}{X_{eg}}$ against time t, value of k_1 from the rectilinear relation, and representing that the esterification of isopropanol with the studied acids, in presence of Imac 20 Ar cation exchanger is a second order bimolecular reversible reaction Figs (4a,b–6a,b).



(a) (b)

Fig. 6. Effect of reaction temperature on fraction conversion for esterification of mono- (a) and dichloroacetic acids (b) with isopropanol (a linear transformation)



(a) (b)

Fig. 7. Relation between log k_1 and amount of catalyst (a linear relationship) for mono- (a) and dichloroacetic acid (b)

The rate of acid catalysed esterification is proportional to acid concentration is confirned by the data presented in Fig. (7a,b). The plot of log k_1 against molar ratio of the reactants in Fig. (8a,b). It is clear that the value of k_1 varied little with B, this is in agreement with the results of Sharma et al[3]. The increase in the specific rate constant with the reaction temperature is probably, due to the increasing the mobility of the ion or molecules in the solution[8] Fig. (9a, b).

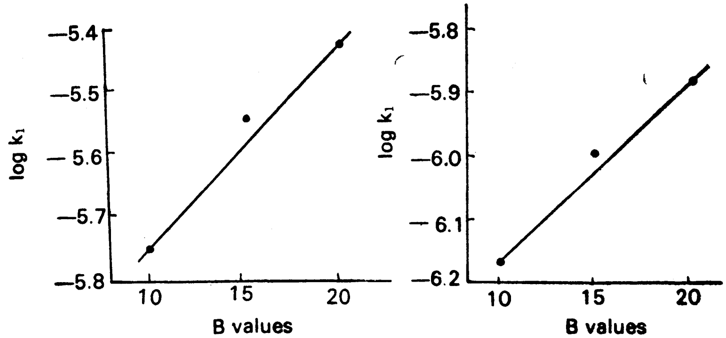


Fig. 8. Relation between log k_1 and molar (B) (a linear relationship) for mono- (a) and dichloroacetic acids (b)

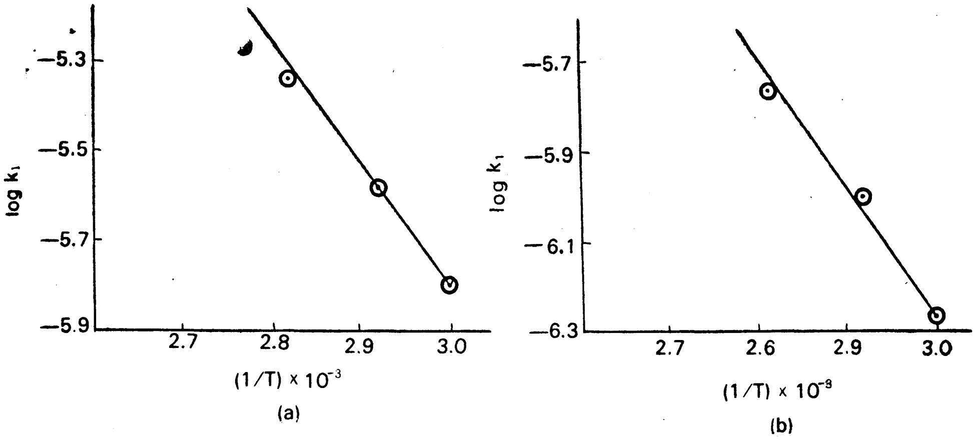


Fig. 9. Relation between log k_1 and $1/T$, for mono- (a) and dichloroacetic acids (b)

The activation energy (E_a) obtained from Arrhenius plots, gave a linear relationship. The calculated values of E_a for (MAA) and (DAA) with isopropanol are found 12.0031 and 12.7039 Kcal/mole respectively, at fixed value of $W = 10$ and $B = 25$.

Assuming that W and B have no effect on the activation energy, the value of E_a can be substituted in equation

$$k_1^* 1 = B/W \text{ mequiv. } \exp(-E_a/RT) \quad (4)$$

to calculate the corresponding theoretical values of k_1^*. The values of the reaction velocity constants calculated from equation (2) and equation (4) are given in Tables 1, 2.

Tables 1, 2 also indicate the values of ΔG^* decrease with increasing the resin quantity and molar ratio of the reactants. However, this value decreases with the reaction temperature for both acids. The thermodynamic functions of activation ΔH^*, ΔG^* and ΔS^* under identical conditions are higher for (DAA) as compared with (MAA).

It has been found that the value of specific rate constant k_1 for MAA and DAA increased by a values 9% and 6% respectively with silical gel additions.

Nomenclature:

B = the molar ratio of alcohol to acid

C_{A_0} = initial concentration of actid in the bulk, g mole/litre

k_1 = the reaction velocity constant, litre g/mole sec.

k_1^* = the reaction velocity constant, litre g/mole sec. (eq. 4)

t = time sec.

T = temperature; K

X_A = fraction conversion of acid

X_{Ae} = fraction conversion of acid at equilibrium

X_{eg} = constant

W = g catalyst/100 g reactants

ΔH^* = enthalpy change, cal/g mole

ΔG^* = free energy change, cal/g mole

ΔS^* = entropy change, cal/g. mol deg.

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