

HETEROGENEOUS CATALYSIS FOR THE ESTERIFICATION OF CHLOROACETIC ACIDS WITH *n*-BUTANOL AND ISOBUTANOL USING DOWEX HCR-S

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The formation of *n*-butyl- and isobutylmono-, di-, and trichloroacetate (esters) using Dowex HCR-S (8% crosslinking) sulphonated polystyrene copolymer as catalyst. It was found that the rate of esterification was accelerated when the exchanger was used in combination with silica gel as dehydrator in amounts equal to 7.2%, 7% and 9.5% for monochloro-, dichloro- and trichloroacetic acids in the case of *n*-butanol and 8%, 8.5% and 10.3% in case of isobutanol respectively. The rate of reaction is found to increase significantly with the quantity of catalyst, molar ratio of reactants and reaction temperature.

INTRODUCTION

In the preceding article [1], the kinetics of esterification of isopropanol with mono-, and dichloroacetic acids were investigated using Dowex HCR-S cation-exchanger. However, no indication for conversion was observed when isopropanol was esterified with trichloroacetic acid.

Various reports concerning the increase of the rate constant with temperature, amount of catalyst, and molar ratio of reactants have been reported for heterogeneous catalytic reactions [2,6]. The external and internal diffusion and the stirring rate are claimed to have no effect upon the reaction rate constant [3]. However, increasing molecular weights [4] branching of alcohols or acids have a retarding effect on the rate of esterification [5].

The present study is an extension of previous work [1], which aims at studying the kinetics of esterification of mono-, di- and trichloroacetic acids with *n*-butanol and isobutanol in the presence of Dowex HCR-S (H^+ - form) as catalyst. The factors affecting the reaction rate constant, and the fractional conversion, viz. the molar ratio of reactants, quantity of catalyst and reaction temperature were evaluated.

The effect of some physical constants of the reacting alcohols, viscosity and dielectric constant was also mentioned. The thermodynamic functions, viz. ΔG^* , ΔH^* and ΔS^* for the esterification of the two alcohols were calculated and compared.

MATERIALS AND METHODS

Materials: All chemicals were of AR-grade (for spectroscopy) and used without purification. The cation exchanger, Dowex HCR-S, was a product of Prolabo (capacity 4 m. eq./g).

The methods and technique were the same as described in the previous paper [1].

RESULTS AND DISCUSSION

The conversion of (MAA), (DAA) and (TAA) to *n*-butyl as well as isobutyl-mono-, di- and trichloroacetate were investigated in the presence of cation-exchanger Dowex HCR-S as catalyst under variable conditions.

The effect of the amount of catalyst (g catalyst/100 g reactants), molar ratio of reactants (alcohol/acid) and temperature on the fractional conversion of *n*-butyl alcohol are illustrated in Fig. 1_b - 9_b. The reaction in the case of isobutyl alcohol was also investigated with the above mentioned acids, and the results are given in Fig. 1_b - 9_a.

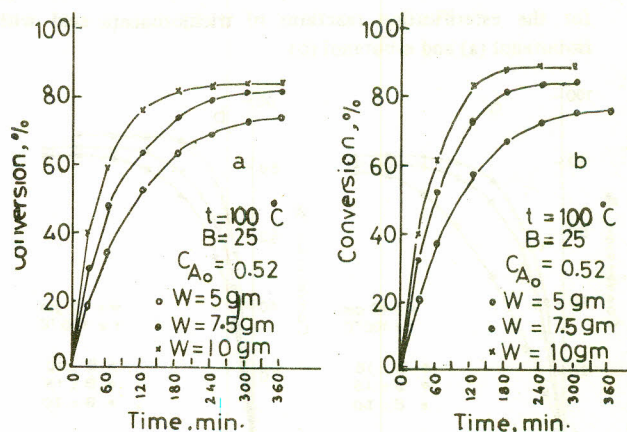


Fig. 1. Effect of amount of catalyst on the percent conversion for the esterification reactions of monochloroacetic acid with isobutanol (a) and *n*-butanol (b)

The fractional conversion of acids to the respective esters when esterified with *n*-butanol increase markedly with the amount of catalyst, molar ratio of alcohol: acid and reaction temperature (of. Fig. 1_b - 9_h).

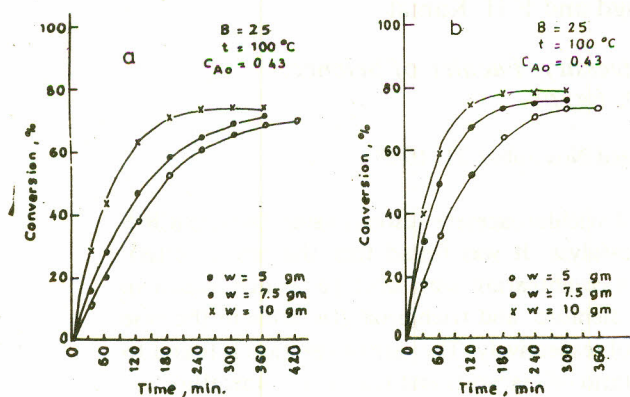


Fig. 2. Effect of amount catalyst on the percent conversion for the esterification reactions of dichloroacetic acid with isobutanol (a) and *n*-butanol (b).

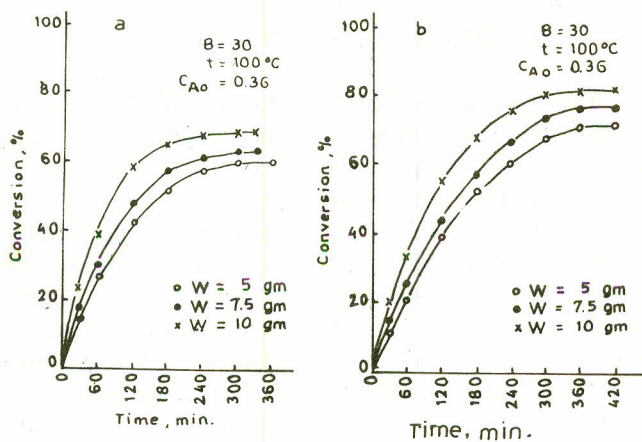


Fig. 3. Effect of amount of catalyst on the percent conversion for the esterification reactions of trichloroacetic acid with isobutanol (a) and *n*-butanol (b).

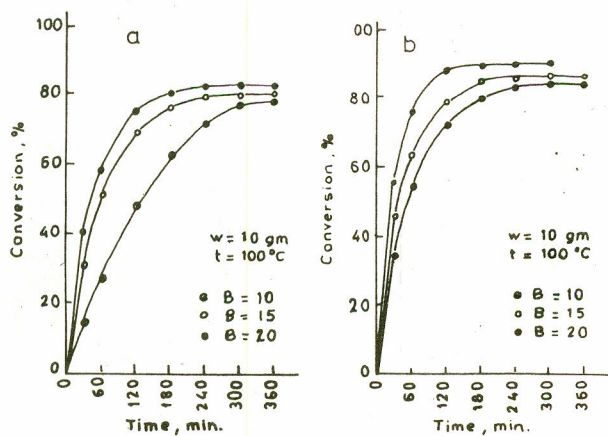


Fig. 4. Effect of molar ratio of reactants on the percent conversion for the esterification reactions of monochloroacetic acid with isobutanol (a) and *n*-butanol (b).

Similar data concerning the influence of the above mentioned variable upon the conversion of isobutanol when reacted with all acids are given in Fig. 1_a - 9_a.

However, the values of percent conversion at equi-

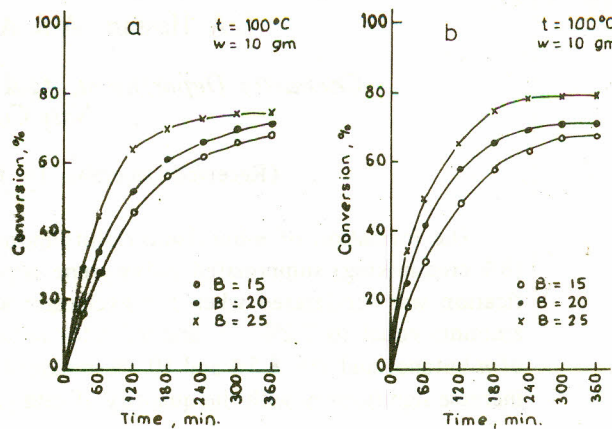


Fig. 5. Effect of molar ratio of reactants on the percent conversion for the esterification reactions of dichloroacetic acid with isobutanol (a) and *n*-butanol (b).

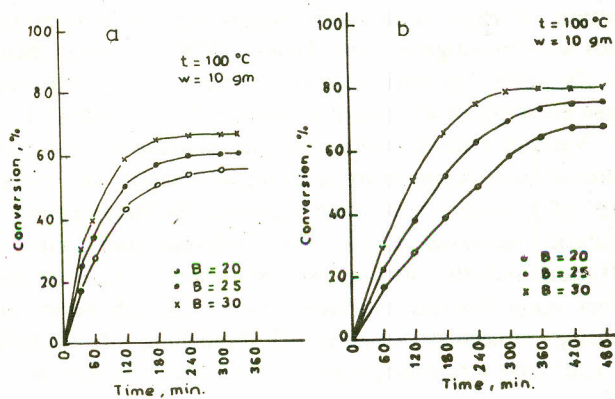


Fig. 6. Effect of molar ratio of reactants on the percent conversion for the esterification reactions of trichloroacetic acid with isobutanol (a) and *n*-butanol (b).

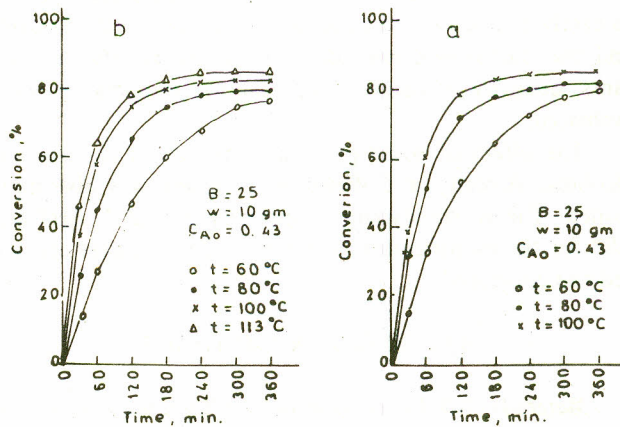


Fig. 7. Effect of temperature on the percent conversion for the esterification reactions of monochloroacetic acid with isobutanol (a) and *n*-butanol (b).

bromium X_{Ae} at all studied resin quantity, molar ratio of reactants temperature are lower in the case of *isobutanol* as compared with those obtained in case of *n-butanol*.

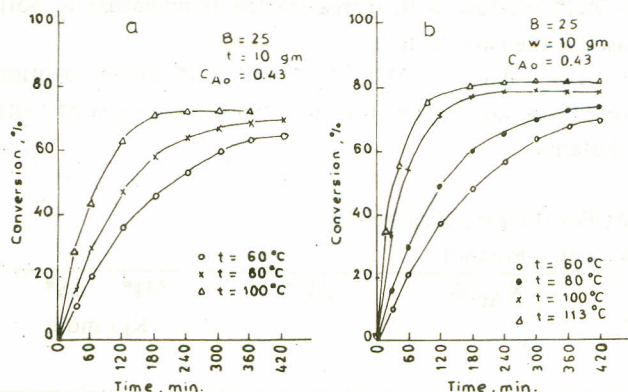


Fig. 8. Effect of temperature on the percent conversion for the esterification reactions of dichloroacetic acid with *isobutanol* (a) and *n-butanol* (b)

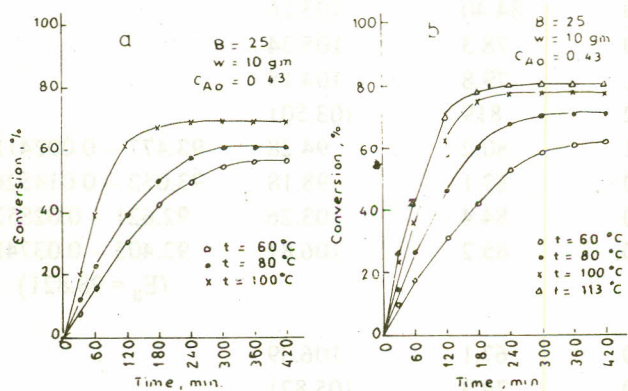


Fig. 9. Effect of temperature on the percent conversion for the esterification reactions of trichloroacetic acid with *isobutanol* (a) and *n-butanol* (b)

It is probable that the higher values of viscosity (η) [7] and dielectric constant (D) [9] for *isobutanol* is 2.3001 and 2.75 as compared with *n-butanol* = 2.271 and 1.66 respectively at the same values of molar ratio of B , resin quantity and rate of stirring, affect the rate of mixing of the reactants, leading to relatively lower values of percent conversion at equilibrium in the case of *isobutanol*.

The effect of the structure of alcohol or acid on the percent conversion in the esterification reaction has been studied by authors [3,8]. It is mentioned that the rate of reaction decreases as the alcohol chain length or branching increases, and also with increasing the branching of the side chains of both alcohol and acid. Such branching in the *isobutanol* molecule (secondary alcohol) probably imparts a steric hindrance, which decrease the rate of esterification, lowering therefore the percent conversion in the case of *isobutanol*.

The absence of induction period in each cases is probably due to the absence of water contained in the resin, [6].

In all cases however, the conversion data obtained either in the esterification reaction of *n-butanol* and also *isobutanol* with the above mentioned acids can be fairly well correlated by a bimolecular reversible kinetic equation [6].

The calculated values of the reaction velocity constant (K_1) given in Table 1 are higher for *n-butanol* as compared with *isobutanol* (c.f. Table 2) using the following equation 6.

$$\ln \frac{X_{eg} - X_A}{X_{Ae} - X_A} \cdot \frac{X_A}{X_{eg}} = \frac{2B - (B-1)X_{Ae}}{X_{Ae}} K_1 C_{Ao} t \quad (1)$$

$$\text{Where ; } X_{eg} = \frac{BX_{Ae}}{(B-1)X_{Ae} - B}$$

The plots of line $\frac{X_{eg} - X_A}{X_{Ae} - X_A} \cdot \frac{X_A}{X_{eg}}$ against time t (min.); the value of K_1 can be obtained from the resulting linear transformation.

The activation energies were calculated from the Arrhenius plots (Fig.10-12), and substituted in equation (2) to calculate the theoretical values of specific rate constant

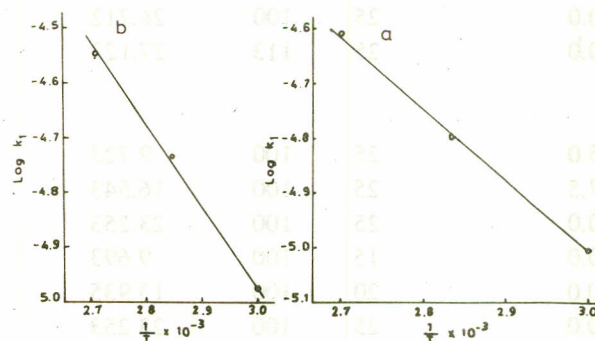


Fig. 10. Relation between $\log K_1$ vs. $\frac{1}{T}$ for the esterification reaction of monochloroacetic acid with *isobutanol* (a) and *n-butanol* (b)

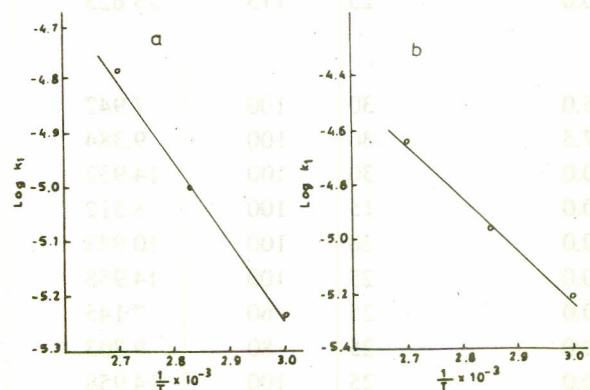


Fig. 11. Relation between $\log K_1$ vs. $\frac{1}{T}$ for the esterification reactions of dichloroacetic acid with *isobutanol* (a) and *n-butanol* (b)

$$K_1 = \frac{B}{W} m.e.q.e^{-E/RT} \text{ equation(2) [6]}$$

$$K_1 = \frac{25}{10} m.e.q.e^{-98821/RT} \text{ for } n\text{-butanol with MAA as for example}$$

$$K_1 = \frac{25}{10} m.e.q.e^{-99794/RT} \text{ for isobutanol with MAA as for example}$$

at fixed values of $W=10$ and $B=25$, assuming that W and B have no effect on the activation energy.

The results given in Table 1 and 2 in general, show that the values of ΔG^* decrease with increasing the resin quantity and molar ratio of alcohol to acid. However, the values of ΔG^* increase with increasing the temperature in both cases of the two alcohols.

The values of ΔH^* , ΔG^* and ΔS^* under identical conditions are higher for isobutanol as compared with n -butanol.

Table 1. Reaction Velocity Constants For the Esterification Of (MAA), (DAA) And (TAA) with n -butanol.

Weight of Catalyst, gm.	Molar Ratio B	Temp. °C	Reaction Constant k exp.	Velocity $k_1 \times 10^6$ k calc.	$X_{Ae}, \%$	ΔG^*	ΔH^* ΔS^* Kj / mole
5.0	25	100	12.959	12.9321	75.8	105.49	
7.5	25	100	20.101	20.2240	81.0	104.13	
10.5	25	100	26.712	26.6120	84.40	103.26	
10.0	10	100	13.606	13.5420	78.3	105.34	
10.0	15	100	19.970	20.0021	79.8	104.15	
10.0	20	100	24.623	25.0142	81.9	103.501	
10.0	25	60	11.130	11.2341	80.2	94.28	93.477 - 0.002411
10.0	25	80	21.572	21.5320	82.1	98.18	93.052 - 0.014526
10.0	25	100	26.712	26.6120	84.4	103.26	92.621 - 0.02852
10.0	25	113	27.123	27.1340	85.2	106.81	92.405 - 0.03741 ($E_a = 98.821$)
5.0	25	100	9.723	9.8210	67.1	106.39	
7.5	25	100	16.543	16.5630	74.3	105.821	
10.0	25	100	23.253	23.2430	77.2	105.679	
10.0	15	100	9.693	9.7930	67.1	106.391	
10.0	20	100	13.935	14.0121	71.6	105.266	
10.0	25	100	23.253	23.2430	77.2	103.679	
10.0	25	60	6.214	6.2431	68.3	95.886	94.298 - 0.004768
10.0	25	80	9.432	9.5230	71.8	100.605	93.775 - 0.019348
10.0	25	100	23.253	23.2430	77.2	103.679	93.442 - 0.027444
10.0	25	113	25.623	25.6920	78.9	107.082	93.226 - 0.035989 ($E_a = 99.642$)
5.0	30	100	7.942	7.9320	70.9	107.009	
7.5	30	100	9.384	9.2840	76.1	106.525	
10.0	30	100	14.952	14.8410	77.8	105.071	
10.0	15	100	8.512	8.6212	63.8	106.790	
10.0	20	100	10.933	10.9210	71.4	106.019	
10.0	25	100	14.958	14.8420	77.8	105.007	
10.0	25	60	7.145	7.1324	61.4	95.803	100.78 + 0.01494
10.0	25	80	9.803	9.9120	68.3	100.807	100.45 - 0.00101
10.0	25	100	14.958	14.8410	76.1	105.077	100.12 - 0.013289
10.0	25	113	15.721	15.8440	77.3	108.634	99.897 - 0.022693 ($E_a = 106.321$)

Table 2. Reaction velocity constants for the esterification of (MAA) (DAA) and (TAA) with *isobutanol*.

Weight of catalyst, gm.	Molar ratio B	Temp., °C	Reaction constant k exp.	Velocity $k_1 \times 10^6$ k calc.	$X_{Ac}, \%$	ΔG^* KJ/mole	ΔH^*	ΔS^*
5.0	25	100	10.87	10.92	72.8	106.03		
7.5	25	100	17.50	17.59	79.6	104.55		
10.0	25	100	24.52	24.51	83.9	103.51		
10.0	10	100	11.24	11.23	77.2	105.93		
10.0	15	100	19.97	19.96	79.4	104.15		($E_a = 99.794$)
10.0	20	100	21.35	21.29	81.2	103.94		
10.0	25	60	9.92	9.95	79.4	94.59		94.45 - 0.00042
10.0	25	80	16.23	16.37	80.3	99.01		93.92 - 0.01441
10.0	25	100	24.52	24.51	83.9	103.51		93.59 - 0.02659
5.0	25	100	9.00	9.02	66.7	106.62		
7.5	25	100	13.93	14.01	71.6	105.26		
10.0	25	100	16.37	16.53	74.2	104.73		
10.0	15	100	9.00	9.02	66.70	106.62		
10.0	20	100	10.24	10.24	70.1	106.20		($E_a = 101.272$)
10.0	25	100	16.37	16.53	74.2	104.73		
10.0	25	60	5.91	5.92	66.3	96.03		95.92 - 0.00033
10.0	25	80	9.29	9.29	69.4	100.64		95.40 - 0.01484
10.0	25	100	16.54	16.53	74.6	104.73		95.07 - 0.02589
5.0	30	100	7.56	7.55	61.1	107.20		
7.5	30	100	8.64	8.56	63.4	106.68		
10.0	30	100	12.82	12.90	69.4	105.70		
10.0	15	100	7.14	7.13	57.5	107.11		
10.0	20	100	9.20	9.14	64.1	106.40		($E_a = 107.272$)
10.0	25	100	13.64	13.50	69.0	105.10		
10.0	25	60	6.86	6.94	57.5	95.62		101.73 + 0.01834
10.0	25	80	8.82	8.71	64.1	100.54		101.57 + 0.00291
10.0	25	100	13.64	13.50	69.0	105.10		101.37 + 0.01

Table 3. Effect of silica gel (2 g) on the esterification reactions of (MAA), (DAA) and (TAA) With *n*-butanol and *isobutanol* respectively.

Alcohol	Molar ratio B	Wgm	$K_1 \times 10^6$	$X_{Ac}, \%$	ΔG^*	(Acid)
<i>n</i> -butanol	25	10	28.615	85.9	107.81	(MAA)
<i>isobutanol</i>	25	10	26.48	85.2	103.52	
<i>n</i> -butanol	25	10	24.88	79.1	103.45	(DAA)
<i>isobutanol</i>	25	10	17.89	76.9	104.50	
<i>n</i> -butanol	25	10	16.37	78.4	105.72	(TAA)
<i>isobutanol</i>	25	10	15.04	70.2	104.02	

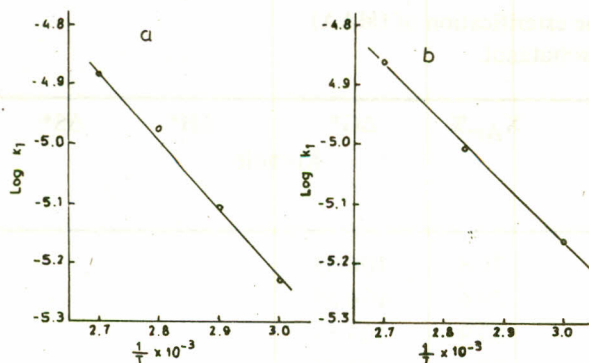


Fig. 12. Relation between $\log K_1$ vs. $\frac{1}{T}$ for the esterification reactions of trichloroacetic acid with *isobutanol* (a) and *n-butanol* (b).

It is evident from Table 3 that the rate of formation of *n-butyl* and *isobutyl* (MAA), (DAA) and (TAA) are higher when silica gel (2g.) is used as dehydrator.

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