
KINETICS AND ADSORPTION ON ACID CATALYSTS. III.*
STRUCTURE EFFECTS IN REESTERIFICATION OF ESTERS
WITH ALCOHOLS

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Reactivity and adsorptivity of the reaction components were correlated with polar and steric constants of substituents in the reesterification of esters with alcohols in the gaseous phase, catalyzed by a sulphonated organic ionex at 120°C. The studied reactions were reesterification of ethyl acetate with methanol, 1-propanol, 2,2-dimethylpropanol and 2-methoxyethanol, as well as reesterification of ethyl formate, acetate, methoxyacetate and isobutyrate with 1-propanol.

In our laboratory we have been studying heterogeneous catalytic reactions on macroreticular ion exchangers. The aim of the so far performed studies¹⁻⁴ was to test the applicability of the values of the constants of kinetic equations of the Langmuir-Hinshelwood type to different reaction systems; the acidic catalyst used was considered ideal, in the sense that it contained active sites of the same kind. One of the studied types of reactions were reesterifications of aliphatic esters with alcohols¹, and that the reesterification of ethyl acetate with three alcohols (methanol, 1-propanol, and 2,2-dimethylpropanol) and the reesterification of three ethyl esters (formate, acetate, and isobutyrate) with 1-propanol. The reaction partners were selected so as to ensure difference in reaction rates as great as possible, with the aim to evaluate the validity of kinetic adsorption coefficients also at broad range of rate constants. As obvious from Table I, this goal has been achieved. When attempting to use these results¹ for correlations with structure effects of reactants, it turned out to be necessary to extend this series of esters and alcohols to other members, such in which steric effect of substituent markedly differs from its inductive effect. For that reason we have further measured the systems ethyl acetate-2-methoxyethanol and ethyl methoxyacetate-1-propanol.

All these reesterification reactions were subjected to kinetic analysis. We used a glass flow microreactor with reactants in gaseous phase; the reaction temperature was 120°C, the range of partial pressures of individual reactants 0.02-0.81 atm, and the range of total pressure of reaction components was 0.1-0.9 atm. Further ex-

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TABLE I
Values of the Constants of Rate Equation (1)

Second reaction component	Separate calculation			Joint calculation			Substituent
	k	K_A	K_B	k	K_A	K_B	
Reaction of ethyl esters (A) with 1-propanol (B)							
Formate	37 050 ¹	0.41	1.8	24 650	0.56	2.8 ^a	$\left\{ \begin{array}{l} \text{H} \\ \text{CH}_3 \\ (\text{CH}_3)_2\text{CH} \\ \text{CH}_3\text{OCH}_2 \end{array} \right.$
Acetate	284 ¹	1.01	2.8	280	1.03		
Isobutyrate	56 ¹	0.55	3.1	59	0.55		
Methoxyacetate	1 500	1.81	0.5	431	3.00		
Reaction of ethyl acetate (A) with alcohols (B)							
Methanol	2 620 ¹	1.30	0.3	5 480	1.0 ^a	$\left\{ \begin{array}{l} 0.1 \\ 2.6 \\ 8.3 \\ 3.5 \end{array} \right.$	$\left\{ \begin{array}{l} \text{H} \\ \text{C}_2\text{H}_5 \\ (\text{CH}_3)_3\text{C} \\ \text{CH}_3\text{OCH}_2 \end{array} \right.$
1-Propanol	284 ¹	1.01	2.8	293			
2,2-Dimethylpropanol	80 ¹	0.90	7.6	74			
2-Methoxyethanol	1 360	0.34	1.1	391			

^aChosen.

perimental details are in the preceding work¹. For each of the reactions studied we measured 30 values of initial reaction rates at different partial pressures in the above range (except for the reaction of ethyl methoxyacetate whose vapour pressure allowed to carry out the measurements only to 0.5 atm; only 15 values of initial reaction rates were therefore determined). By the use of a combined linear and non-linear regression the best kinetic equation of the Langmuir-Hinshelwood type was selected and its constants calculated. It has been found that all the reactions studied are best described by Eq. (1)

$$r^0 = kK_A K_B p_A^0 p_B^0 / [1 + K_A p_A^0 + (K_B p_B^0)^{1/2}]^3, \quad (1)$$

where r^0 is the initial reaction rate [$\text{mol h}^{-1} \text{kg}_{\text{catalyst}}^{-1}$], k the rate constant [$\text{mol} \cdot \text{h}^{-1} \text{kg}_{\text{catalyst}}^{-1}$], K_i the adsorption coefficient [atm^{-1}], and p_i^0 the initial partial pressure [atm]; the indices A and B denote an ester and an alcohol, respectively.

In order to evaluate structure effects of the reactants, the experimental rate constants and adsorption coefficients (Table I, the column separate calculation) were treated by the method of linear free energy correlations, which, under certain circumstances, can also be applied to heterogeneous catalytic reactions⁵. As it is seen from Table I, one can observe a certain fluctuation of the values of adsorption coefficients of the common reagent, although these should have been constant. This is particularly distinct in the reactions of the methoxyacetate and the methoxyethanol. In both

cases this quantity is appreciably smaller, relative to other reactions. We have therefore attempted to eliminate the effect of fluctuation of the adsorption coefficients of the common component by regarding these values as constant for the whole series of esters and alcohols. In the calculation we have used the values found for the reaction of ethyl acetate with 1-propanol, as these were close to the mean values for the first three members of the series. By regression method, the two remaining constants of the kinetic equation (1) were then re-calculated (Table I, the column joint calculation). The results showed, however, that the corrections achieved are not significant.

With the same aim we have therefore employed a simpler procedure, using as a kinetic parameter expressing reactivity the product of rate constants and the corresponding adsorption coefficient of the common reagent, which could be expected to be constant (kK_B or kK_A). The values of the so defined reactivities, along with the adsorption coefficients in both series (esters and alcohols) were correlated by Taft equation

$$\log \kappa = \text{const.} + \rho\sigma^* \quad (2)$$

to express the influence of inductive effect, and by the relation

$$\log \kappa = \text{const.} + sE_s \quad (3)$$

to evaluate the influence of steric effect (κ is the corresponding kinetic or adsorption parameter). The values of constants σ^* and E_s were taken from the literature⁶ for the groups specified in the last column of Table I. The results of the most successful

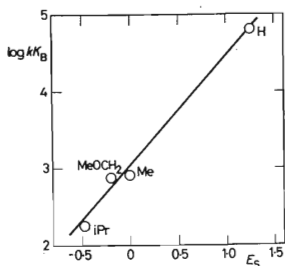


FIG. 1

Correlation of the Reactivity of Esters kK_B with Steric Parameter E_s ($\rho = 1.4$)

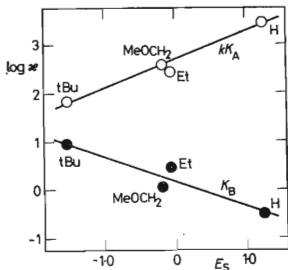


FIG. 2

Correlation of the Reactivity kK_A ($\rho = 0.6$) and of the Adsorptivity K_B ($\rho = -0.4$) of Alcohols with Steric Parameter E_s

correlations are graphically represented in Figs 1 and 2. With alcohols we made also an attempt to correlate the data under the assumption that the reaction center is the hydroxyl group itself. In this way, however, better results have not been obtained than in the case where the $-\text{CH}_2\text{OH}$ group was considered as the reaction center.

Summarizing, the kinetic parameters yield better correlation with steric constants E_s than with polar constants σ^* . The adsorption coefficients of the esters did not correlate either with σ^* or with E_s . The better correlation of this quantity has been obtained in the case of alcohols (Fig. 2); however, there is no significant difference between the correlation with inductive effects and that with steric effects.

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