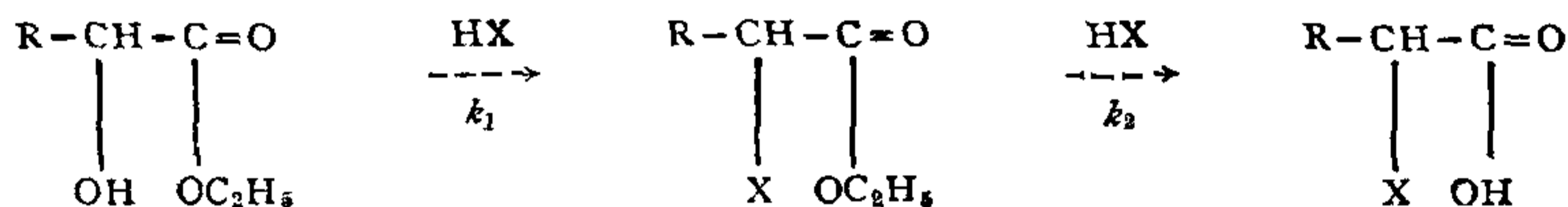


## A KINETIC STUDY OF THE REACTION OF $\alpha$ -HYDROXY ACIDS AND THEIR ESTERS WITH HALOGEN HYDRACIDS

CLEAVAGE of esters and substitution in mono- and dihydric alcohols with halogen hydracids as cleaving or substituting agent have been reported earlier<sup>1-3</sup>. It was found worthwhile to investigate the action of halogen hydracids on  $\alpha$ -hydroxy acids and  $\alpha$ -hydroxy esters primarily to follow the two steps of the consecutive reactions and also to fix up which step is the first one—whether displacement of the  $-\text{OH}$  or the cleavage of the ester.

With this object in view, the two substrates *dl*-ethyl lactate and *dl*-ethyl mandelate were chosen. Reactions of these two esters with HCl, HBr and HI (aq.) have been studied at 80° C in glacial acetic acid. The two steps can be represented as :



The rate constants of the two steps are given in Table I.

TABLE I

Temperature: 80° C  $10^3 \times k$  (litre mole<sup>-1</sup> min<sup>-1</sup>)

Substrate	HCl		HBr		HI	
	$k_1$	$k_2$	$k_1$	$k_2$	$k_1$	$k_2$
<i>dl</i> -ethyl lactate	1.42	3.184	2.634	5.855	4.88	11.65
<i>dl</i> -ethyl mandelate	1.081	2.192	2.13	4.66	3.987	10.09

It can be seen that the second step is consistently higher in all the cases. The order of reactivity of the halogen hydracids is also in accordance with their increasing nucleophilicity.

To confirm the mechanism visualised above, the substitution reactions of *dl*-lactic acid and *dl*-mandelic acid and cleavage of ethyl  $\alpha$ -bromo propionate with HBr were studied under the same conditions. The rate constants are collected in Table II.

TABLE II

Temperature: 80° C  $10^3 \times k$  (litre mole<sup>-1</sup> min<sup>-1</sup>)

Substrate	$k$
<i>dl</i> -lactic acid	2.469
<i>dl</i> -mandelic acid	1.992
ethyl- $\alpha$ -bromo propionate	5.884

It can be seen that the rate constants for the substitution in the two  $\alpha$ -hydroxy acids are almost equal to the first step of the two  $\alpha$ -hydroxy esters, the slight difference being due to the adjacent  $-\text{COOH}$  in one and the  $-\text{COOC}_2\text{H}_5$  in the other. Again the rate constant for the cleavage of ethyl- $\alpha$ -bromo propionate agrees well with the rate constant for the second step of cleavage of ethyl lactate with HBr. Thus it is the  $-\text{OH}$  that is substituted first and then the ester is cleaved.

The higher rate for the cleavage (first step) than the substitution (second step) in each case can also be expected from the fact that the second step involves the cleavage of  $\alpha$ -halogen esters that are formed in the first step. A halogen atom at the  $\alpha$ -position being an electron attracting substituent enhances the rate of the second step—which

involves an  $A_{AL} 2$  mechanism, as reported earlier in the study of ester cleavages (*loc. cit.*).

The substrates were of guaranteed quality from Fluka or were purified by the usual procedure and redistilled before use. Ethyl- $\alpha$ -bromo propionate was prepared by the Hell-Volhard-Zelinsky reaction<sup>4</sup> and purified by distillation under reduced pressure. The solvent was purified by the usual procedure and distilled before use. The halogen hydracids were azeotropic mixtures (with water) distilled just before use.

The kinetics has been followed by the usual argentimetric procedure, *i.e.*, Volhard's method.

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