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REGARDING THE FRONT SIDE PARTICIPATION OF THE ACETOXY GROUP IN THE CATALYTIC EFFECT OF ACETIC ACID ON THE REACTIONS OF GLYCOLS WITH HYDROGEN HALIDES

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We have been recently interested in the kinetics of the reactions of glycols with halogen hydracids in acetic acid medium and in the cleavages of esters in acetic acid medium[1]. For the first displacement of reactions with the halogen hydracids in acetic acid, we postulated a mechanism involving neighbouring hydroxyl group participation consistent with our results wherein we found that the first displacement rates are of the order, ethylene glycol > propylene glycol > 1,3 butane diol > 1,4 butane diol. We also found that the second displacement rates are very slow compared to the rates of first displacement. In the case of 1,4 butane diol we could compute the rates of both the displacements using Frost-Schwemer treatment.

We wish to comment on the statements made by Winstein and others[2] in their synthetic work on reactions of glycols with halogen hydracids in acetic acid. They postulated an immediate esterification of the hydoxyl group to an acetoxy derivative followed by cleavage leading to the dihalo compound or the halohydrin depending of the hydracid employed. Our contention is that these reactions are facile in acetic acid due to general solvent effects and they need not go through acetoxy derivative and our arguments in favour are:

1. The rate of esterification of methanol with acetic acid (6.6×10^{-6} 1. moles^{-1} sec^{-1}) and rate of substitution of methanol with HBr in acetic acid (1.57×10^{-4} 1. moles^{-1} sec^{-1}) show that the substitution reactions are very much faster than the esterification reactions. Hence the question of immediate esterification does not arise. These two are independent reactions which take place depending on the conditions employed. The rates of monohydric alcohols are chosen for purposes of comparison as a model for the first esterification of glycols.

2. If there is immediate esterification followed by cleavage as Winstein has postulated, then the rates of ester cleavages by hydrobromic acid in glacial acetic acid should be almost identical. A glance at the following table would indicate that it is not so.

The above arguments '1' and '2' rule out the possibility of immediate esterification of the alcohols. Extending it to glycols as well, we may safely assume that here also there is no likelihood of immediate esterification as assumed by Winstein. This comparison is relevant as this clearly brings out that substitution of alcohols and ester cleavages go at different rates. Hence immediate esterification of glycols is not the essential routes for this reaction.

3. We have carried out the reactions with pure phenol as solvent in which they are faster than in pure acetic acid. The facile reaction in phenol as solvent indicates that acetoxy derivative formation is not likely in this reaction as any such presumption of

Second Order Rate Constants (1. moles^{-1}min^{-1} x 10^3) for the cleavages of Esters and substitutions of corresponding Alcohols with Hydrobromic acid at 80°C in glacial acetic acid.

Methyl acetate	19.78	Methanol	9.416
Ethyl acetate	5.862	Ethanol	3.72
n-Butyl acetate	4.987	n. Butanol	2.571
Cyclopentyl acetate	8.569	Cyclopentanol	15.96
Bornyl acetate	1.412	Borneol	3.962

the possibility of esterification does not arise in phenol as solvent. The second order rate constants (1. moles^{-1}min^{-1}) in respect of reactions of ethanol and ethylene glycol with HBr at 80°C are o.115 and 14.5 in pure phenol, respectively, and 0.00372 and 5.93 in pure acetic acid, respectively.

4. The reactions are facile in pure propionic acid medium and are faster than in acetic acid medium. It is well known that the rate of esterification, if any, should be less with propionic acid and if it were going through the ester, the reaction should have been slower than in acetic acid which is not the observed fact. Hence the effect is only a medium effect. The second order rate constants (1. moles^{-1}min^{-1}) for the reactions of ethylene glycol and propylene glycol at 80°C with HBr are 5.93 and 2.35 in pure acetic acid; and 51.7 and 10.9 in pure propionic acid respectively.

5, Another noteworthy feature which should be mentioned is that when the medium is changed from pure acetic acid to acetic acid - hydrocarbon mixtures, the reactions are faster. The overall rate corresponds to 2nd order - 1st order with respect to HBr and 1st order with respect to the substrate. Evidently the acetoxy group formation cannot be the route as is seen from the solvent effect.

6. Yet another feature of these reactions is that they virtually stop with a water content of 7.5% (v/v). The competition of H^+ for H_2O rather than for the OH group leads to the stoppage as water content is increased. The effect of water on the reaction of ethylene glycol with hydrobromic acid in acetic acid medium at 80°C is shown in the following table:

Second Order Rate Constants (1. moles^{-1}min^{-1}) for reactions of Diols with HBr at 80°C in acetic acid- hydrocarbon mixtures (v/v).

	k_1				
	100% HAc	80% HAc 20% C_6H_6	80%HAc 20% $C_6H_5CH_3$	80% HAc 20% DPM	80% HAc 20% CCl_4
Ethylene Glycol	5.93	10.91	11.99	15.50	13.33
Propylene Glycol	2.35	8.05	8.00	-	7.33
1,3 Butane Diol	0.2101	1.47	2.354	-	2.22

Second Order Rate Constants (l. moles^{-1} min^{-1}) for the reaction of Ethylene Glycol with HBr at 80°C in acetic acid - water mixtures (%v/v).

Solvent Composition		
Acetic acid	Water	k_1
100	-	5.93
97.5	2.5	1.00
95	5	0.06
92.5	7.5	no reaction

Hence according to us the mechanism postulated by Winstein is unlikely as it presupposes the formation of an acetoxy derivative and assumes that acetic acid acts catalytically. We suggest that the effect of acetic acid, as in the case of phenol or propionic acid or the hydrocarbons, is only a solvent effect.

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