Interferences.—Tartaric acid did not interfere with the determination of zinc. However, the precipitation was partially inhibited by oxalic acid, citric acid and completely so by disodium-EDTA and thioglycollic acid.

Precision and Accuracy.—The average error for several determinations of 5–32 mg of zinc (II) in a volume of 200 ml was found to be better than $\pm 0.4\%$.

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CONCERNING SOLVENT EFFECTS ON THE REACTIVITY OF LACTONES TOWARDS ALKALINE HYDROLYSIS

The enhanced reactivity of lactones over the corresponding open chain esters towards alkaline hydrolysis was attributed to the absence of repulsion between the attacking hydroxide ion and the 'lone pair' dipole on the cyclic oxygen atom because of the rearside attack of the OH^- ion on the carbonyl group which is not possible in the corresponding open chain esters[1]. This was schematically represented as follows :
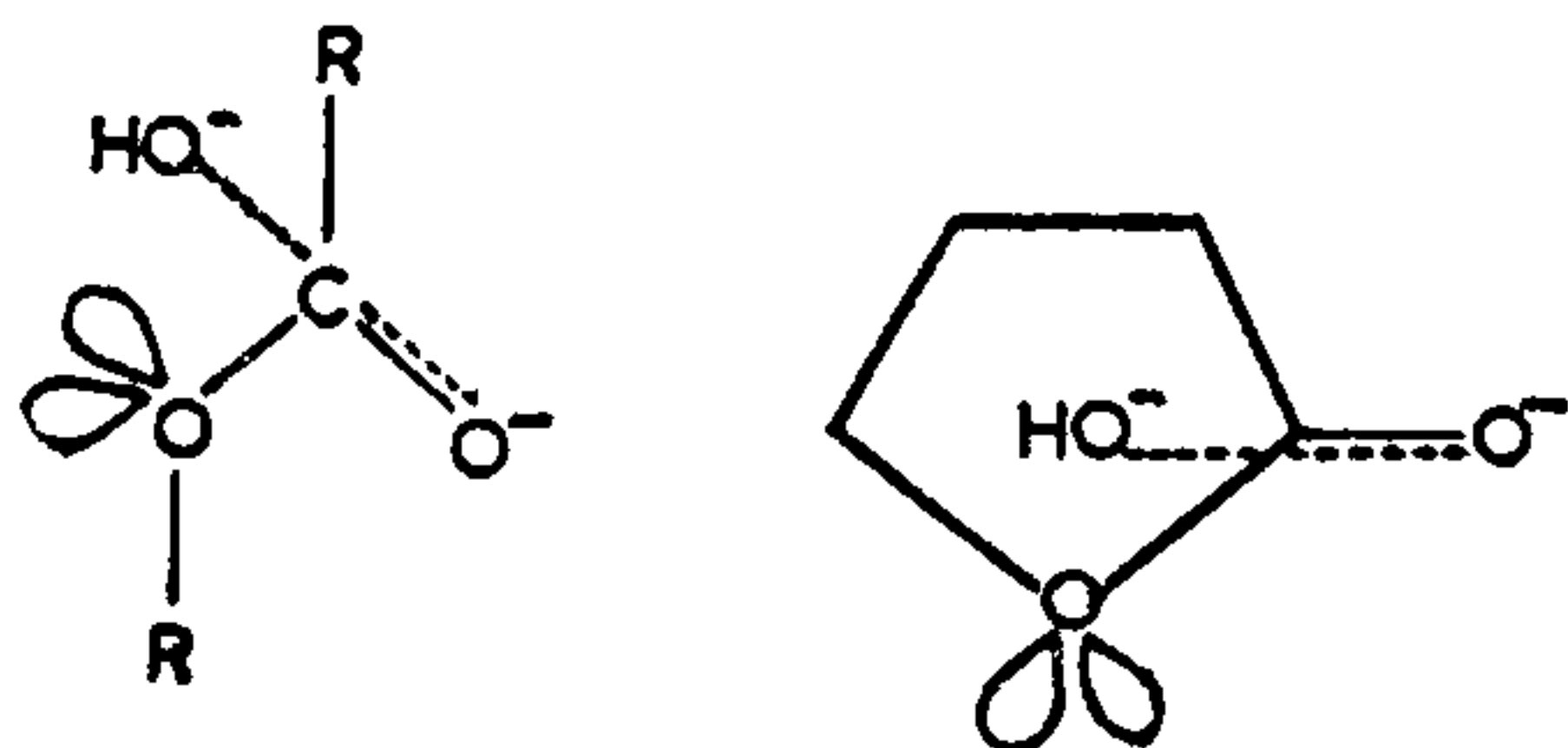
This mechanism of rearside attack was, however, questioned by Bender[2] according to whom the best approximation to the transition state is the one in which the attacking OH^- ion is perpendicular to the carbonyl bond. Bender added that the results of Hall and co-workers could be explained on the

basis of this perpendicular attack still invoking a difference in electrostatic repulsion between the attacking hydroxide ion and the lone pair dipole. He could not, however, rule out the possibility of the repulsion being responsible for the increased rates of hydrolysis of lactones over that of the corresponding open chain esters. Further studies on basic hydrolysis of lactones also could not exclude this possibility[3].

We have now employed solvent effects as a diagnostic tool in testing out the above hypothesis. To our knowledge, this is the first report on the differential effects of solvents on lactone saponification.

The present study concerns the alkaline hydrolysis of some γ-lactones, aliphatic and aromatic, and their open chain analogues. The kinetics of these reactions were studied in solvent mixtures of DMSO-water, ethanol-water and acetone-water. In Table I are presented the kinetic data in the form of $k_{lactone}/k_{ester}$ values for the various pairs and in various solvent mixtures.

TABLE I

$k_{lactone}/k_{open\ chain\ ester}$ *for the following pairs at 30° C*

(I) γ-butyrolactone and ethyl acetate
(II) γ-valerolactone and isopropyl acetate
(III) phthalide and methyl benzoate
(IV) 3-phenyl phthalide and benzyl benzoate

Solvent (v/v)	(I)	(II)	(III)	(IV)
60% DMSO	7	20	7	..
70% DMSO	7	22	5	..
80% DMSO	11	22	6	..
60% EtOH	15	26	17	..
70% EtOH	15	32	19	..
80% EtOH	15	30	26	27
70% Acetone	11	..	7·5	..
80% Acetone	13	..	8·0	..

It is a well established fact that the OH^- ion is poorly solvated in aqueous DMSO and consequently very active in these solvent systems[4]. So the repulsion between the attacking OH^- ion and the 'lone pair dipole' on oxygen should be greater in aqueous DMSO. This would lead to considerable diminution in the rate of hydrolysis of open chain esters and as a consequence the ratio $k_{lactone}/k_{ester}$ should have a greater value in aqueous DMSO relative to aqueous ethanol. Such a situation exists

indeed in the alkaline hydrolysis of dicarboxylic esters, where the ratio k_I/k_{II} increases on transfer from aqueous ethanol to aqueous DMSO[5] (k_I and k_{II} being the rate constants for the first and second steps of saponification of the dicarboxylic ester). This was attributed to the repulsion between a poorly solvated OH⁻ ion and the half ester anion leading to a considerable drop in the value of k_{II} in aqueous DMSO. What is observed in the present studies is a decrease in the ratio $k_{lactone}/k_{ester}$ instead of an increase on solvent change from aqueous ethanol to aqueous DMSO.

Further perusal of the data also shows that even in a solvent system, variation in the content of one of the components does not produce any significant change in the ratio. Thus the rate ratio for the pair γ-butyrolactone and ethyl acetate has the same value of 15 in 60% EtOH, 70% EtOH and 80% EtOH. If the repulsion had been an important factor, one should have noticed a decrease in the ratio of $k_{lactone}/k_{ester}$ with decrease in the dielectric constant of the medium as was observed in the case of dicarboxylic ester hydrolysis[6,7]. The solvent effects thus prove that the repulsion between the attacking OH⁻ ion and the 'lone pair dipole' is of minor importance in controlling the rates of hydrolysis of lactones.

We attribute the increased reactivity of lactones over that of the corresponding open chain esters to the increased polarity of the lactone carbonyl resulting from the 'cisoid' arrangement of the lone pair on etherial oxygen and the carbonyl group[8,9], since in the $B_{AC}{}^2$ ester hydrolysis, the rate determining step is the attack of the OH⁻ ion on the ester carbonyl group. These structural features contribute to a greater localisation of the negative charge on the carbonyl oxygen in the transition state for lactone hydrolysis (relative to the open esters), a situation favoured by aqueous ethanol. The situation is reversed with respect to the open esters, the resultant transition state structures being stabilised by the aprotic solvents DMSO and acetone. Thus one observes a drop in the rate ratio on solvent transfer from aqueous ethanol to aqueous DMSO or aqueous acetone.

If the *repulsion* had been important, then one would not have observed a drop in the ratio for the pair phthalide and methyl benzoate from 26 to 8 and from 27 to 5 for the pair 3-phenyl phthalide and benzyl benzoate on solvent transfer from 80% ethanol to 80% acetone. It will be pertinent to point out here that the k_I/k_{II} ratio for the dicarboxylic ester hydrolysis does not vary much when the solvent is changed from aqueous ethanol to aqueous acetone[6,7].

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USE OF NH₄F AS A MASKENT IN THE COMPLEXOMETRIC DETERMINATION OF SOME DIVALENT CATIONS IN PRESENCE OF CALCIUM

THE need for a very rapid and accurate method for the estimation of some divalent cations in presence of calcium was felt necessary for a study of the kinetics of $Ca^{2+} \rightarrow M^{2+}$ (where M = Pb or Zn or Cd or Hg or Fe) exchange reactions on hydroxylapatite (CaHA), $Ca_{10}(PO_4)_6(OH)_2$, an important inorganic component of human skeletal system. The novel feature of this method over other previous methods[1-3] was that without the actual separation of the cations from one another from the sample solution it was possible to determine their contents complexometrically by using NH₄F as a maskent for calcium.

Procedure.—The Chemicals used were of AR (BDH) grade and the sample solutions were prepared in double distilled water tested for the absence of Ca^{2+} and preserved in polyethylene bottles. Since the presence of phosphate interferes with the determination of a mixture of calcium and a divalent cation mentioned above it was separated from the sample solution as ammonium molybdophosphate first of all and removed filtration through 1G₄ crucible. There is no effect of molybdate solution on the determination of the above-mentioned divalent cations.

The filtrate after the separation of phosphate was made upto a known volume. Convenient volume of the filtrate containing a mixture of calcium and lead (or Cd^{2+} or Zn^{2+}) was titrated against standard 0·01 M EDTA solution using 4 drops Eriochrome Black T as indicator at a pH ~ 10 till the colour