Hydrolysis of Esters and Ester-anions by a Polymeric Quaternary Ammonium Hydroxide

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Summary Rates of hydrolysis of uncharged aliphatic esters with poly(vinylbenzyltriethylammonium hydroxide) do not differ greatly from those with sodium hydroxide, but for the monoethyl ester-anions of dicarboxylic acids the rates with the polymer are greater than those with sodium hydroxide by factors of 2—5; the increase is ascribed to migration of the ester-anions into the hydroxylic counter-ion layer of the polymeric alkali.

HYDROLYSABLE compounds, bearing amino-groups which become converted in acid solution into ammonium ions, exemplified by peptides and proteins[1] and methyl 2-amino-2-deoxy-β-D-glucopyranoside,[2] undergo hydrolysis with poly(vinylsulphonic acid) and poly(styrenesulphonic acid) at rates markedly greater than those with sulphuric acid and hydrochloric acid. For uncharged substrates the difference in rates with the two types of acid is small. The increased rate observed with a positively-charged substrate is attributed to its migration to the vicinity of the polyanions of the polymeric strong acid, where it encounters the relatively high concentration of hydrogen ions constituting the counter-ion layer.[3]

We have examined a series of alkaline hydrolyses analogous to the above acid hydrolyses. For the esters and monoethyl ester-anions shown in the Table, rates of hydrolysis with poly(vinylbenzyltriethylammonium hydroxide) and with sodium hydroxide have been determined. All reactants were in homogeneous aqueous solution. The effect of the polycation is indicated by the macromolecular rate-factor, μ, the ratio of the rate-constant with the polymer to that with sodium hydroxide.

For the uncharged esters, values of μ range from 0·73—1·05; those for the ester-anions range from 2·03—5·02. The increased rates of hydrolysis of the negatively-charged substrates, when the polymeric quaternary ammonium hydroxide is used, are ascribed to the migration of the ester-anions into proximity to the polycations. They thus enter the counter-ion layer of increased hydroxide-ion concentration, and hydrolysis proceeds at an augmented rate.

Hydrolyses of esters at 0·0° *and of ester-anions at* 25·0°

Substrate	NaOH 10^2k	Polymer 10^2k	μ
	(l. mole^{-1} sec.$^{-1}$)		
Ethyl acetate	2·04	1·76	0·86
Propyl acetate	1·72	1·55	0·90
Butyl acetate	1·56	1·64	1·05
Ethyl propionate	1·91	1·39	0·73
Propyl propionate	1·56	1·52	0·97
Ethyl butyrate	1·10	1·04	0·95
Potassium ethyl			
oxalate	77·7	158	2·03
malonate	2·02	6·68	3·31
succinate	3·33	16·7	5·02
glutarate	4·30	14·5	3·37
adipate	4·07	13·8	3·39

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[1] W. Kern, W. Herold, and B. Scherhag, *Makromol. Chem.*, 1956, **17**, 231; W. Kern and B. Scherhag, *ibid.*, 1958, **28**, 209.

[2] T. J. Painter and W. T. J. Morgan, *Chem. and Ind.*, 1961, 437.

[3] Effects pertaining to macromolecular reactions have been reviewed by H. Morawetz, *Svensk kem. Tidskr.*, 1967, **79**, 309.