In studying the adsorption of sugars, two synthetic mixtures of sugars and acids were passed through small columns (5 gm. air-dry resin) of 'Amberlite IR-4B'. One column had been used many times to collect acids from fruits, the other was freshly packed from a different batch of resin. The mixtures of sugars (glucose, fructose and sucrose) and acids (malic, citric, quinic, galacturonic and phosphoric[3]) were similar in composition to those obtained after removing the cations from extracts of pears and peaches. The aliquot used for each experiment contained two or four milli-equivalents of mixed acids and 3 gm. of sugars including 0·4 or 2·6 gm. of sucrose. Following the passage of the sugars and acids, the column was washed with water. The first 100 ml. was discarded. The rest of the washings was collected in fractions some of which were concentrated (usually 100 : 1) under reduced pressure for paper chromatography.

All the fractions run on paper gave a good glucose spot, even after the column had been washed with two litres of water. In the case of the mixture with the high sucrose concentration, early fractions gave a good sucrose spot, otherwise only traces of sucrose and fructose were detected. All fractions contained quinic or galacturonic acid, or both, depending on their relative proportions in the mixture ; the other (stronger) acids were not detected. Similar results were obtained with both columns, with rates of washing varying from 0·25 to 2 ml. per minute, and after regeneration of the resin with 2 N ammonia or 2 N sodium carbonate.

Some quantitative work was done using solutions of glucose. Aliquots were run through the columns, followed by 200 ml. of water and then by 50 ml. 2 N ammonia or 50 ml. 2 N hydrochloric acid. The water wash recovered 98–100 per cent of the glucose used, the ammonia a further 0·01–0·1 per cent, the acid a further 0·3 per cent. Successive washings with 2 N hydrochloric acid, allowing the acid to stand on the column, eluted altogether 0·7–1·0 per cent of the glucose used. The glucose was estimated by reaction with anthrone[4], using a solution of glucose in 2 N hydrochloric acid as a standard in appropriate cases. It was necessary to wash the new column thoroughly with 2 N hydrochloric acid to obtain a satisfactory blank.

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Energy of Activation for the Acid-catalysed Hydrolysis of Esters

ACTIVATION energies of the order of 30 kcal./mol. have been found for the acid-catalysed hydrolysis of tert.-butyl 2 : 4 : 6 trimethylbenzoate and tert.-butyl benzoate, for which the reaction has been shown to proceed by alkyl–oxygen fission[1], and of tert.-amyl 2 : 4 : 6 trimethylbenzoate, tert.-amyl benzoate,

diphenylmethyl 2 : 4 : 6-trimethylbenzoate and α-methylallyl 2 : 4 : 6-trimethylbenzoate, where the same mode of fission may be predicted. This value is significantly higher than that found for the hydrolysis of esters by acyl–oxygen fission, and seems to be characteristic of this mechanism.

The rate of hydrolysis with acyl–oxygen fission increases markedly from benzoates to acetates, and the transition in mechanism would be expected to occur in the region of tert.-butyl acetate. This appears to be the case, for the Arrhenius equation is not followed in the hydrolysis of tert.-butyl acetate, the activation energy varying from 26 to 30 kcal./mol. between 50° and 100°, which implies, however, predominantly alkyl–oxygen fission, in agreement with the results of Bunton, Comyns and Wood[2]. Preliminary experiments on tert.-butyl formate give an activation energy of c. 16 kcal./mol., which is normal for the acyl–oxygen fission of esters of aliphatic acids. This is consistent with the behaviour of diphenylmethyl formate mentioned by Day and Ingold[3].

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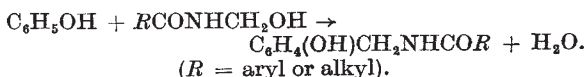Armidale,
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A General Method of Aminomethylation

EINHORN discovered that methylolamides condense with phenol (in concentrated sulphuric acid), in accordance with the equation :

$$C_6H_5OH + RCONHCH_2OH \rightarrow$$
$$C_6H_4(OH)CH_2NHCOR + H_2O.$$
$$(R = aryl \text{ or } alkyl).$$

It has now been shown that the above reaction is a general one which can be used to introduce CH_2NH_2 groups into many aromatic compounds. Thus benzene can be condensed, according to the conditions of the experiment, with one or two molecules of the methylolamide giving $C_6H_5CH_2NHCOR$ or $C_6H_4(CH_2NHCOR)_2$. These compounds are readily hydrolysed, with alcoholic hydrochloric acid, to the hydrochlorides $C_6H_5CH_2NH_2HCl$ and p-$C_6H_4(CH_2NH_2)_2 2HCl$ (and another isomer). Some methylated benzenes (toluene, the xylenes and mesitylene) have also been condensed. In each case three CH_2NHCOR groups can be introduced into the molecule.

Naphthalene also reacts, but the products obtained are difficultly soluble and have not yet been separated.

The reaction was successful with the following mono-substituted benzenes : chloro-, bromo-, iodo-, cyano-, sulphamido-. In each case only one CH_2NHCOR group was introduced. Nitrobenzene, benzamide and acetophenone did not react. From thiophene the compounds $C_4H_3S.CH_2NHCOR$-2 and $C_4H_2S(CH_2NHCOR)_2$ were prepared.

Details of these experiments will be published elsewhere.

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