Material. The sample of pollen from rye (*Secale cereale*) was obtained from AB Cernelle, Vegeholm, Sweden.

Air-dried pollen (100 g) was extracted with chloroform-methanol 2:1, in a non-siphoning solid extractor under boiling for several hours. The solvent was then evaporated and the extractable fraction weighed. An amount of 10.6 g (10.6 %) was obtained.

Chromatography on silicic acid. Silicic acid (Baker AR, Lot. No. 23043) with particles passing a 325 mesh sieve was used. The pretreatment of the silicic acid was the same as earlier described [11,12]. A 60 g column was packed in light petroleum (b.p. 60—80°) and rinsed with the same solvent. An amount of 1.385 g of lipid material was applied to the column. The hydrocarbon fraction was eluted with light petroleum. The yield was 0.173 g (12.5 %).

Hydrogenation. About half of the hydrocarbon fraction was hydrogenated using Adams' catalyst in an amount of 10 mg in 3 ml of ethyl acetate at 40°. The catalyst was removed by filtration. The completeness of hydrogenation was checked by GLC.

Conditions for gas-liquid chromatography I. Chromatograph: Perkin-Elmer, Model 116 equipped with flame ionization detector. *Column dimensions:* 150 × 0.6 cm o.d. aluminium tubing. *Solid support:* Gas Chrom P (100—120 U.S. mesh) Applied Science Laboratories, Inc., Pennsylvania, treated with dimethyldichlorosilane. *Stationary phase:* Silicone elastomer SE-30, General Electric (1 % by weight of the solid support), 0.27 % polyethylene glycol M. 20000 added. *Temperatures:* Injection: 300°. Detector and column: 216°. (All temperatures measured with mercury thermometer.) *Carrier gas:* He at 70 ml/min. Inlet pressure: 1.5 kp/cm². Outlet pressure: atmospheric. *Recorder:* 2 mV; 1 sec; 1.3 cm/min. *Detector:* Flame ionization detector, one flame hydrogen detector, model Bodenseewerk. *Sample size:* 0.10 μl of a diluted solution in carbon tetrachloride. *Analysis time:* About 19 minutes to hentriacontane.

Conditions for gas-liquid chromatography II. Chromatograph: See I. *Column dimensions:* 180 × 0.6 cm o.d. aluminium tubing. *Solid support:* See I. *Stationary phase:* Apiezon L grease, manufactured by Metropolitan—Vickers Electrical Co., Ltd., England, (1 % by weight of solid support), 0.1 % polyethylene glycol M. 20000 added. *Temperatures:* Injection: 300°. Detector and column: 217°. *Carrier gas:* He at 80 ml/min. Inlet pressure: 1.8 kp/cm². Outlet pressure: atmospheric. *Recorder:* 2.5 mV; 1 sec; 0.52 cm/min. *Detector:* See I. *Sample size:* 0.15 μl of a diluted solution in hexane. *Analysis time:* About 90 min to hentriacontane.

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The Hydrolysis of Sodium Acetate

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Danielsson and Suominen [1] have recently used the cell with liquid junction

− glass	(3—x) M NaCl x M NaA y M HA	3 M NaCl	Ag, AgCl 3 M NaCl +

to study the hydrolysis of sodium acetate in a 3 M Na(Cl) medium at 20°C. Average degrees of protonation $0 \geqslant \bar{n}_H \geqslant 0.1$ for total acetate concentrations $0.3 \geqslant A \geqslant 3.0$ M proved to be a unique function of a quantity considered to be log [OH^-], and it was concluded that "The hydrolysis . . . . is accurately defined by only one equili-

brium constant" *. However, it was not pointed out that the data $\bar{n}_H$ ($\log[OH^-]$)$_{A=0.3}$, which are the only set in which $\bar{n}_H$ extends up to unity, are only consistent with the hydrolysis constant (pK_h = 9.401) up to $\bar{n}_H \sim 0.37$. For $\bar{n}_H < 0.63$, the data are more in accord with $pK_h - 9.45$. This small discrepancy is far larger than the experimental error of ± 0.2 mV.

In calculating values of log [OH^-] from the equation

$$E = E_o + E_j + 58.16 \log \gamma_{OH} + 58.16 \log [OH^-] = E_o' + 58.16 \log [OH^-]$$

Danielsson and Suominen follow Ingri *et al.*[2] in assuming that the appropriate value of E_o' depends upon the exchange of the medium anion for the reacting anion. Their results imply that $\Delta E_o'$ is about + 8.3 mV per mole chloride replaced by acetate. Our results [3] for a 3 M $Na(ClO_4)$ medium at 25°C confirm the precise magnitude of this effect, since $\Delta E_o'$ is + 5.85 mV per mole perchlorate replaced by acetate and −2.4 mV per mole perchlorate replaced by chloride. However, an additional correction is required to allow for the effect of undissociated acetic acid on the ionic medium. This amounts to −3.42 mV per mole undissociated acetic acid added to 3 M $Na(ClO_4)$ at 25°C. Consequently, in calculating log [OH^-] at a constant value of A, E_o' cannot be assumed to be constant, since it must vary appreciably with $\bar{n}_H$.

Our original data [4] have been corrected for the effects of both acetate ions and undissociated acetic acid on E_o'. Within the experimental error of ± 0.2 mV, each set $\bar{n}_H$ ($\log [H^+]$)$_A$ is consistent with a monuclear protonation constant, K_{11}. However, the values so found increase from $\log K_{11} = 5.02$ at low values of A to 5.06 at A = 1 M. This increase implies a decrease in the stoichiometric activity coefficient of acetic acid (*cf.* the salting in of acetic acid by sodium acetate), and may be represented by the model of polynuclear complex formation. Our corrected data [3] are consistent with the formation of HA_2^- and H_2A_2, although the relevant overall formation constants are smaller than our preliminary values [4,5]. Thus we now find for

$$HA + A^- \rightleftharpoons HA_2^-; \quad \log K_{12} = -1.0 \pm 0.1$$

and for

$$HA_2^- + H^+ \rightleftharpoons H_2A_2; \quad \log K_{22} = 5.06 \pm 0.05.$$

The revised value of the dimerisation constant of acetic acid ($\log K_d = -0.96 \pm 0.15$) is in fair agreement with a value of −0.80 obtained by Katchalsky *et al.*[6], and of the same order of magnitude as those of other workers [7-9], who have used a variety of experimental techniques.

It will be clear that the effects under discussion are so small that it is difficult to assert that polynuclear species definitely exist in aqueous solution. However, we do assert that it is not at present possible to describe the hydrolytic equilibria in sodium acetate solutions by means of a single parameter.

* In the following, A corresponds to their B and $\bar{n}_H$ to their Z.

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