For comparison, the results obtained when using chloroform as proton donor, are also included.[4] It is seen that pentafluorobenzene forms a weaker association complex than does chloroform, as expressed by the respective values of K and ΔH. Nevertheless, there is no doubt that pentafluorobenzene exhibits considerable proton donor properties, a result which should be born in mind when dealing with ethylenic protons in a medium having electron donor properties.

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Diacetyl and Formic Acid as Decomposition Products of 2-Acetolactic Acid

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In fermentation solutions, 2-acetolactic acid appears as an intermediate in valine synthesis; it is unstable, and decarboxylates readily to acetoin, both enzymatically [1–3] and under the influence of strong mineral acids.[2–4] Acetolactic acid also tends towards spontaneous decomposition, with or without the contribution of certain metal cations,[5,6] and also in fermentation solutions;[7] one of the products of spontaneous decomposition is diacetyl.[5–7] Quite recently, the formation of diacetyl from 2-acetolactic acid, and the reaction mechanism, have been studied more thoroughly by us,[8,9] and by Japanese researchers.[10–13] Inoue *et al.*[10–13] have interpreted the reaction of diacetyl formation from 2-acetolactic acid as a "spontaneous oxidative decarboxylation". According to Lewis,[14] the redox potential for the oxidative decarboxylation in a commercial brew is likely to be suitable for 2-acetolactate conversion only at the beginning of fermentation; at the time when diacetyl is produced, strong reducing conditions should exist, and consequently 2-acetolactate should be stable. Our experiments made by application of the headspace technique have shown that 2-acetolactic acid decomposes in solutions at a definite velocity under aerobic [9] and anaerobic [8] conditions, as well as in fermentation solutions;[8,9] moreover, the rate of decomposition increases when the pH is lowered, or the temperature raised. The concentration of diacetyl in the fermentation solutions is near zero during fermentation, as diacetyl is consumed by the yeast to the extent that it is split off from the 2-acetolactic acid.[8,15] After the yeast has been removed, the level of diacetyl in the solution increases, but again diminishes rapidly when the yeast has been added to the solution.[8]

We have continued studies of the spontaneous decomposition of 2-acetolactic acid, and our attention has further been directed towards the carboxylic acids formed in addition to diacetyl.

The ethyl ester of 2-aceto-2-acetoxypropionic acid (b.p. 96°/7 mmHg) was prepared from 2-methyl-substituted ethyl acetoacetate (*cf.* Ref. 9) (*pract.*, Fluka AG, Buchs, Switzerland). The synthesised ester was hydrolysed by means of 0.1 N NaOH solution at a temperature of 4°C. Both the carboxyl and the α-hydroxyl are released from the ester-form by alkaline hydrolysis, and consequently a base solution of 2-acetolactate can be prepared in this way. For this purpose, 53.0 mg (0.262 mmol) of the ethyl ester of 2-aceto-2-acetoxypropionic acid was weighed, and dissolved in 7.5 ml of cold (4°C) 0.1 N NaOH solution; the total volume was regulated to 50 ml with cold (4°C) distilled water. This base solution was allowed to stand overnight at 4°C. Samples of 1 ml (containing 5.24×10^{-3} mmol of acetolactate) and 2 ml (containing 10.5×10^{-3} mmol) were taken from this solution, and acidified to pH 5–6 with a buffer (phosphate or citrate) or 0.001 N HCl solution, and diluted with water to 25 ml. These solutions were kept in a constant-temperature bath at 40°C for

24 h, and in some parallel experiments for as much as 50 h. The diacetyl formed was determined by gas chromatography, with the head-space technique and an electron capture detector, as described earlier.[8,9]

Acids were isolated from the sample solutions with slightly alkaline anion exchanger, Ion-exchanger II (for analytical purpose, E. Merck AG, Darmstadt, West Germany). After the sample solution had been run through the column, it was rinsed with water (100 ml, eluate 1) and eluted with 1.0 N NH_4OH solution (300 ml, eluate 2). Another ammonia fraction of 200 ml was collected (eluate 3), and following this the column was washed with water, and used for a fresh experiment. One ml of 0.1 N NaOH solution was added to each of the three eluates collected, in order to convert ammonium salts of carboxylic acids to sodium salts, and to preclude their evaporation by evaporation of the solvent. Each eluate was vaporised to dryness with a rotavaporizer. The remainder was dissolved in a small amount of water, and transferred to a small (20 ml) ampoule, from which the water was driven away by keeping the ampoule at 120°C overnight. The salts of acids were converted to ethyl esters by diethyl sulphate[16] (*puriss.*, Fluka AG, Buchs, Switzerland), adding 1 ml of this ester to the salts, and heating the bottom of the closed ampoule for 2 h in an oil bath at 160°C. After the ampoule had been cooled, the esters in the solution were analysed by gas chromatography with a 4 m DEGA column and flame ionisation detector (*cf.* Ref. 17). Of the fractions collected by ion exchange, only eluate No. 2 contained carboxylic acids.

Fig. 1 presents two chromatograms; the upper one relates to the acids isolated from the decomposition mixture of hydrolysed 2-aceto-2-acetoxypropionic acid ester, and the lower one the corresponding reference mixture of formic and acetic acid (mol relation 0.4). On the esterification of organic acid salts with diethyl sulphate, the latter partly decomposes, giving two peaks of which the higher (peak No. 2) is diethyl ether. In this case, the diethyl sulphate itself does not form any peak; this is a consequence of the low temperature (86°C) of the gas chromatographic oven.

According to the head-space analyses, acetolactic acid decomposes within the range of pH 5–6, giving 40–60 mol % of diacetyl as calculated from the starting material. The percentage of corresponding formic acid is often lower than that of

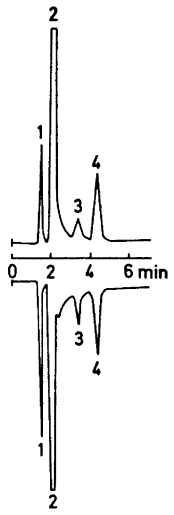

Fig. 1. Gas chromatogram (upper) of esterified acids isolated from the solution by ion exchange after the hydrolysis of 2-aceto-2-acetoxypropionic acid ethyl ester, and after decomposition of the 2-acetolactic acid formed; and a gas chromatogram (lower) of the corresponding reference mixture of formic and acetic acid (mol relation 0.4), isolated and esterified as above. Conditions: column 4 m, liquid phase DEGA on the Chromosorb W; carrier gas helium, flow rate 34 ml/min, inlet pressure 1.5 kp/cm^2; temperature 86°C. 1, 2. Pyrolysates of the solvent. 3. Ethyl formate. 4. Ethyl acetate.

diacetyl, by virtue of the method of isolation and analysis applied; in some cases, however, we have found equivalent contents of diacetyl and formic acid. The starting material, the ethyl ester of 2-aceto-2-acetoxypropionic acid, gives on hydrolysis one mol of acetic acid + one mol of acetolactic acid in addition to one mol of ethanol. The content of acetic acid, however, is in most cases higher than that calculated. Thus, in a slightly acidic medium, acetolactic acid may also partly decompose in the direction of acetic acid + lactic acid. Lactic acid itself does not decompose to formic acid during the course of the procedure, and neither has formaldehyde been identified as a possible precursor of formic acid. The formation of acetoin at this pH-limit seems to be prevented,

and only traces of this compound are identifiable.

We conclude that one of the spontaneous decomposition reactions of 2-acetolactic acid, produces, also in fermentation solutions, diacetyl together with formic acid.

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On the Crystal Structure of $Nd_4Re_2O_{11}$

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Several rare earth-rhenium oxides have been described.[1-4] Only one of these compounds, the complex oxide $La_4Re_6O_{19}$, has been characterized by a crystal structure determination.[5-6]

One of the present authors [2,3] recently made a study comprising several compounds near the Ln_2ReO_5 stoichiometry (Ln=rare earth metal, Nd, Sm, Gd, Dy, Er, Yb, Y). Well developed crystals of an Nd compound were prepared by using a starting mixture of Ln_2O_3 and ReO_2 with ~20 % excess ReO_2 over the stoichiometric requirement. The mixtures were heated for several days at 1100—1300°C in closed Pt-10Rh capsules. The analysis of several samples indicated that the compound obtained presumably is richer in oxygen than Nd_2ReO_5 and the formula β-Nd_2ReO_{5+x} ($x \approx 0.3$) was suggested. To establish the composition unambiguously a structure determination of the product has now been performed. This article is a preliminary report of this work.

The unit cell dimensions of the tetragonal cell, calculated from a powder pattern, obtained with a Hägg-Guinier camera, are in excellent agreement with those reported earlier.[2,3]

$a = 12.676(\pm 2)$ Å, $c = 5.601(\pm 1)$ Å,
$V = 899.9$ Å^3

The previously observed density, 8.14 g cm^{-3}, indicated a cell content of eight formula units Nd_2ReO_5 (calc. 8.18 g cm^{-3}). Rotation and Weissenberg photographs [2,3] of a single crystal along the a and c axes had revealed the Laue symmetry $4/m$ and shown the following extinctions: $h+k=2n+1$ for the $hk0$ reflections and $l=2n+1$ for $00l$ reflections. These observations were confirmed