Oxygen consumption studies on the formation of the oxidized complexes similar to those described in the study of the thioglycolic acid complexes show that one equivalent of oxygen is taken up for each mole of cobalt.

Summary

A number of cobalt complexes of cysteine in both reduced and oxidized states have been crystallized and their chemical constitutions, properties and interrelationships discussed.

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LEVULINIC ACID. III. THE HYDROGENATION OF CERTAIN OF ITS ALKYL ESTERS IN THE PRESENCE OF PLATINUM CATALYST

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The discovery[1] that levulinic acid readily may be converted to γ-hydroxy-n-valeric acid with hydrogen in the presence of platinum catalyst logically leads to a study of the behavior of its alkyl esters under similar conditions. The resulting compounds of such a reaction, the esters of γ-hydroxy-n-valeric acid, have not yet been described. Neugebauer[2] reported the synthesis of the ethyl derivative from the silver salt of the acid and ethyl iodide. On attempting to purify the resulting ester by fractional distillation, he found, however, that it underwent decomposition with the formation of ethanol and n-valerolactone, as follows

$$CH_3CHOHCH_2CH_2COOC_2H_5 \longrightarrow CH_3CHCH_2CH_2CO + C_2H_5OH$$
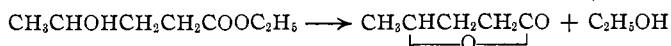
This observation is of interest in that it suggests that the alkyl esters of γ-hydroxy-n-valeric acid show that same instability which is characteristic of the parent acid.

That this instability is not alone a property of the ethyl ester and that the rate of hydrogenation is a function of the size of the alkyl residue and the solvent employed, if any, have been demonstrated in this Laboratory. The presentation of pertinent data is the object of this communication.

Rate of Hydrogenation.—Two series of hydrogenations of the methyl, ethyl, n- and isopropyl, and n- and isobutyl esters[3] of levulinic acid were carried out with portions of the same preparation of catalyst[4] in the usual mechanical shaker operating with hydrogen under a pressure of two to three atmospheres and at a temperature of 22–24°. No solvent was em-

[1] Schuette and Thomas, THIS JOURNAL, **52**, 3010 (1930).

[2] Neugebauer, *Ann.*, **227**, 101 (1885).

[3] Schuette and Cowley, THIS JOURNAL, **53**, 3485 (1931).

[4] Voorhees and Adams, *ibid.*, **44**, 1397 (1922).

ployed in one series of experiments but the other was carried out in the presence of 150 cc. of anhydrous diethyl ether because it had previously been found to be very satisfactory when hydrogenating the parent acid of these esters. In carrying out these hydrogenations, in every instance 0.3 g. of catalyst was suspended in one-fourth mole of ester. The reaction was allowed to proceed until the theoretical amount of hydrogen had been absorbed or until it was apparent that the reaction had ceased. Pertinent data are presented graphically (Fig. 1).
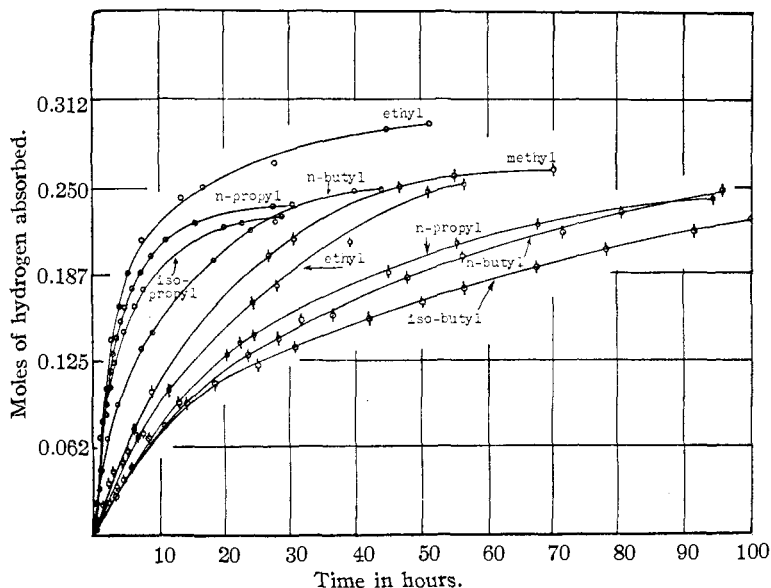

Fig. 1.—Rate of hydrogenation of alkyl esters of levulinic acid: O, in diethyl ether; ◊, without solvent.

It was found that the rate of the reaction varied inversely with the size of the alkyl residue in the ester molecule and that one containing a branched chain alcohol group reacted slower than the corresponding straight chain compound. In seeking an explanation for this phenomenon, the thought suggests itself that this difference of reaction rate is probably traceable to steric hindrance, for the space arrangement of the atoms is such that the alcohol residue lies in close proximity to the carbonyl group which is undergoing hydrogenation. A variation in the size of the alcohol group might well be expected under these circumstances to affect the rate at which hydrogenation proceeds.

The relative rates of reaction for each series of hydrogenations were the same both in the presence and in the absence of a solvent, but in general the reaction proceeded much more satisfactorily in the presence of diethyl

ether than without it.   The ethyl ester, for example, absorbed the theoretical amount of hydrogen in sixteen hours when it was dissolved in ether, whereas in the absence of this solvent about fifty-six hours were required. Attention is also called to the fact that in the first series of hydrogenations the reduction curve for the ethyl ester rises above the point corresponding to complete conversion of the carbonyl group to secondary alcohol, or 0.25 mole of hydrogen.   This would indicate that there is some tendency for the reaction to proceed to complete hydrogenation of the carbonyl group.   This was later found to be the case.

Stability of Esters.—Attempts were made to purify by distillation, both at atmospheric and at reduced pressures, all the esters in question after removal of the catalyst by filtration and the ether, when present, by evaporation at 60° on a water-bath.   The behavior of the methyl and ethyl esters on distillation *in vacuo* (2.5 mm.) and the *n*-propyl derivative at atmospheric pressure will serve to illustrate typical conditions met in these experiments.

Three fractions were collected from the reaction mixture containing the hydrogenated ethyl ester, *viz.:* 40–65°, 65–70° and 70–72°.   The low-boiling fraction contained ethyl valerate in small amounts.   It was identified by preparing from it the *p*-toluide of *n*-valeric acid.   Attempts to derivitate ethyl alcohol as the 3,5-dinitrobenzoate from this fraction were not successful.   This is to be expected, however, because the relatively high vapor pressure of this alcohol would result in its removal from the system in the vapor state as the distillation proceeds.   This conclusion is supported by the fact that the higher alcohols were identified in the lower-boiling fractions when the corresponding esters were distilled.

Ethyl levulinate boils at 78.5–79.5° (2.5 mm.).[3]   It is to be expected that hydrogenation of the carbonyl group to a secondary alcohol group will raise the boiling point, hence the major portion of the hydroxy ester would be in the higher-boiling fraction.   That the observed boiling point of the third fraction was lower than that of pure ethyl levulinate was due to the fact that it contained *n*-valerolactone, b. p. 52.3° (2.5 mm.).   This fraction did not react with phenylhydrazine reagent, showing that none of the unhydrogenated ester was present.   On saponification there were obtained ethyl alcohol (identified through its 3,5-dinitrobenzoate) and the sodium salt of γ-hydroxy-*n*-valeric acid.   The latter was identified by preparing from it the corresponding silver salt (Ag found: 47.84); calcd. for $(C_5H_9O_3)Ag$, 47.97).

The effect of a second distillation upon esters of this type was studied by redistilling the combined distillates from the first operation.   To that end hydrogenated methyl levulinate was distilled at 2.2 mm., two main portions boiling at 61–63° and 63–64° being collected.   They were then subjected to a second distillation.   The first fraction, comprising about

one-third of the total distillate, boiled at 52.5–53.5° (2.5 mm.). The second fraction distilled at 53.5–54.5° (2.5 mm.), and the third at 54.5–55.0° (2.5 mm.). The boiling point of the ester before hydrogenation was 72.3–73.8° (2.3 mm.).[3] Continued distillation evidently tends toward complete decomposition of the ester, for the first fraction collected on redistillation had a boiling point which was almost identical with that of *n*-valerolactone, b. p. 52.3° (2.5 mm.).

These esters undergo a decomposition which is complete when they are distilled at atmospheric pressure. This was shown by the fact that a sample of hydrogenated *n*-propyl ester (b. p. of keto ester 221.2°)[3] on distillation yielded fractions with a maximum boiling point of 203°, which is only slightly lower than that of *n*-valerolactone at atmospheric pressure (206°). In this case the lower-boiling fraction contained appreciable quantities of *n*-propyl alcohol, which was identified by means of its 3,4-dinitrobenzoate. The higher-boiling fraction on saponification yielded no alcohol. There was prepared from it, however, the silver salt of γ-hydroxy-*n*-valeric acid—proof of the presence of *n*-valerolactone and the absence of undecomposed ester.

The behavior of the other esters under similar conditions was such that decomposition took place, the products being alcohol and *n*-valerolactone. The degree of decomposition was dependent upon the temperature and the rate of distillation.

Summary

In a study of the behavior of the alkyl esters of levulinic acid and hydrogen in the presence of a platinum catalyst[4] it has been found that they are converted to the corresponding γ-hydroxy esters which when distilled at atmospheric pressure appear to undergo complete decomposition into *n*-valerolactone and alcohol. When distilled at reduced pressure this decomposition is not complete for some hydroxy ester will be found in the higher-boiling fractions. Repeated distillation, however, will bring about complete destruction of the molecule. It follows, therefore, that pure γ-hydroxy esters of *n*-valeric acid cannot be prepared by methods which involve fractional distillation.

It has also been observed that the rate at which these alkyl esters will absorb hydrogen under the influence of the platinum catalyst stands in an inverse ratio to the size of the alcohol residue which they contain, an ester of a branched chain alcohol hydrogenating slower than its corresponding straight chain compound.

There appears to be a slight tendency for the reaction to proceed to complete hydrogenation of the ketone group.

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