

Titration of Amides in Acetic Anhydride with Perchloric Acid

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Wimer¹ has demonstrated that a representative number of amides can be titrated with perchloric acid using acetic anhydride containing less than 10 % of acetic acid as a solvent. The titration was carried out potentiometrically using a modified calomel-glass electrode couple. The method is now adopted in *Handbook of Analytical Chemistry*.²

In titrating several primary amides according to Wimer we found that the results were not accurate. The procedure was reproducible but it was impossible to obtain a purity of about 100 % even if highly purified samples were analysed.

It is now proved that there is a systematic error in the titration; this is most probably due to a slight acetylation of the primary amide. If the potentiometric titration is carried out within a period of 4–5 min about 2–3 % of the amide is acetylated. The secondary amide formed is too weak a base to be titrated. With a titration time of about 11 min as much as 5–10 % of acetylation takes place. The following data can be reported:

	Purity (%) found with a titration time of	
	ca. 5 min	ca. 11 min
Acetamide	97.2	94.9
Propionamide	96.9	91.7
Isobutyramide	94.1	88.8

In order to make sure that the time dependence was not due to an apparatus factor the purity of potassium hydrogen phthalate was determined by the same method and it was found that the result was independent of the titration time. We therefore conclude that Wimer's procedure cannot be used safely for the determination of unsubstituted amides. The method has not been checked with other types of amides.

All attempts to modify the procedure so as to avoid the acetylation have failed.

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The Behaviour of Lignin in Alkaline Pulping

I. Model Experiments with Phenylcoumarans

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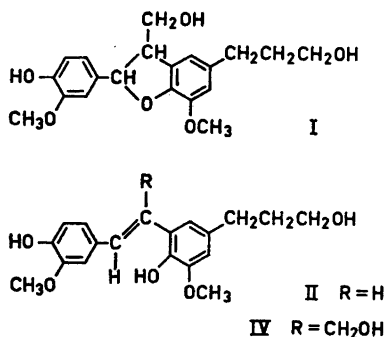
Some years ago a study of the behaviour of lignin in the alkaline pulping processes was initiated in this laboratory. Our main interest was to elucidate the reactions of lignin in the "kraft" or "sulphate" process, in which a cooking liquor containing sodium sulphide in addition to sodium hydroxide is used. Extensive studies on the reactions of lignin model compounds and of isolated lignin on heating with aqueous sodium hydroxide ("soda cooking" conditions) were recently reported by Gierer *et al.*¹ and work on the sulphate cooking process is being published by the same group.^{2,**} In the present paper and two following communications we wish to give a brief account of some of our own results.^{***}

The comparatively high content of phenolic hydroxyl groups found in lignin isolated from soda or sulphate "black liquors" indicates that cleavage of aryl alkyl ether linkages is a characteristic feature of alkaline lignin dissolution processes.³ Two types of such ether linkages have been shown to occur in lignin, *viz.*, the benzyl aryl ether linkage and the arylglycerol- β -aryl ether linkage. The present communication deals with the behaviour of the cyclic benzyl aryl ether I, dihydro-dehydrodiconiferyl alcohol,⁴ a model of the dimeric units of phenylcoumaran type which make up about 18 % of the average lignin molecule.⁵

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*** For preliminary data see Falkehag, I. *Paper and Timber (Finland)* **43** (1961) 655.



The solution of substance I (C₂₀H₂₄O₄; 190 mg) in 8 ml of a "cooking liquor" containing 3.4 g of NaOH and 1.56 g of Na₂S per 100 ml of H₂O was heated for 4 h at 170° (nitrogen atmosphere). Ether extraction of the neutralized reaction mixture gave an oil (167 mg), which after purification on a silica gel column (elution with benzene-acetone 3:1) yielded chromatographically pure, colourless crystals with the composition C₁₈H₂₂O₅ (m.p. 113.5–114°, 133 mg, *i.e.* 76%). (Found: C 69.09; H 6.70; O 24.43; OCH₃ 19.26. Calc.: C 69.07; H 6.72; O 24.21; OCH₃ 18.78). Quantitative acetylation indicated 3 OH groups (triacetate, m.p. 121.5–122°; OCH₃ calc. 13.60, found 13.75). The product showed a strong blue fluorescence in UV light, and an IR absorption band of medium intensity at 960 cm⁻¹ indicating the presence of the –CH=CH– grouping of a *trans*-stilbene.⁶ Furthermore, the UV spectrum of the substance in ethanol (λ_{\max} 222 m μ , ϵ 25 600, and 327 m μ , ϵ 26 600) and the strong bathochromic shift of the long-wave maximum in 0.1 N NaOH (λ_{\max} 378 m μ , ϵ 24 300), when compared with the similar properties of *trans*-4,4'-dihydroxy-3,3'-dimethoxystilbene* and *trans*-2-hydroxy-3-methoxystilbene,⁵ are in harmony with the structure of a phenolic *trans*-stilbene lacking substituents at the α,α' -positions.⁷ These data show that the hydrofuran ring of I was opened and its methylol substituent removed (as formaldehyde), the resulting pro-

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duct of m.p. 113.5–114° being *trans*-2,4'-dihydroxy-3,3'-dimethoxy-5-(3-hydroxypropyl)-stilbene (II).

The monomethyl ether of I (CH₃O instead of the phenolic OH)⁴ remained essentially unaffected when heated with the kraft cooking liquor.

As reported by Gierer *et al.*, heating of dihydro-dehydrodiisoeugenol (III = I, CH₃ instead of CH₂OH) with sodium hydroxide solution^{1a} or with kraft cooking liquor^{2b} also resulted in the cleavage of the hydrofuran ring, the corresponding α -methyl-substituted stilbene being formed. Methylation of the phenolic hydroxyl of III again stabilized the phenylcoumaran system towards the reagents mentioned.

The alkaline cleavage of the hydrofuran ring of I and III was suggested^{1a} to proceed *via* a quinonemethide. The loss of a methylol group (presumably as formaldehyde) in the conversion I → II then might be understood as a reverse (vinylogous) aldol reaction of the quinonemethide intermediate, or as a reverse Lederer-Manasse reaction of the stilbene IV, a vinylogous phenol alcohol which may arise from the quinonemethide.

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