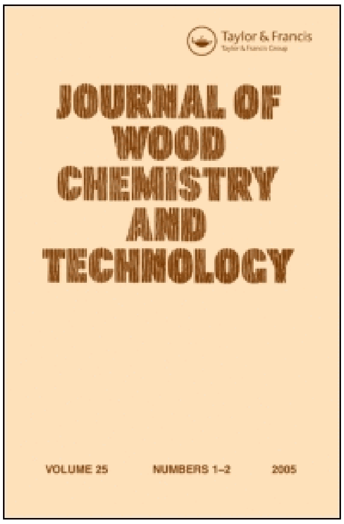

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Kyostl V. Sarkanen[a]; Lin H. Hoo[a]
[a] University of Washington, College of Forest Resources, Washington

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KINETICS OF HYDROLYSIS OF ERYTHRO-GUAIACYLGLYCEROL β-(2-METHOXYPHENYL) ETHER AND ITS VERATRYL ANALOGUE USING HCl AND ALUMINUM CHLORIDE AS CATALYSTS

Kyosti V. Sarkanen and Lin H. Hoo
University of Washington, College of Forest Resources
Seattle, Washington 98195

ABSTRACT

The rates of hydrolysis of the β-aryl ether bond were determined in the temperature range 130° to 155°C for guaiacylglycerol-β (2-methoxyphenyl) ether and its veratryl analogue using both HCl and $AlCl_3$ as catalysts in a mixed ethanol-water medium. The data, based on quantitative determinations of guaiacol liberated in the process, demonstrate the absence of competing intramolecular condensation processes. The rates of HCl-catalyzed hydrolyses are first-order with respect to both catalyst and substrate concentrations, higher in dioxane-water than in aqueous or ethanol-water media, and the activation energies were nearly identical for both model compounds, 36.1 and 35.5 kcal/mol, respectively. In general, the hydrolysis of the guaiacyl model was four times faster than that of the veratryl analogue. The catalytic effect of $AlCl_3$ appears to be based on HCl released at higher temperatures by gradual hydrolysis.

INTRODUCTION

Arylglycerol-β-ether linkages account for approximately 47 per cent of all intermonomeric linkages in softwood lignins and for 60 per cent of corresponding linkages in hardwood lignins.[1] The mechanism of the acid-catalyzed hydrolysis of these bonds as well as the products formed, such as the "Hibbert's ketones" structures, are known in great detail.[1-4] The kinetics of this important reaction have not, however, been subjected to a systematic study. Consequently, erythro-guaiacylglycerol-β-(2-methoxyphenyl) ether 1 and erythro-veratrylglycerol-β-(2-methoxyphenyl) ether 2, two compounds frequently used in previous studies as models for phenolic and etherified arylglycerol-β-arylether structures in lignin, were subjected to a kinetic study in ethanol-water, using HCl and $AlCl_3$ as catalysts.

EXPERIMENTAL

Materials and Methods

Dioxane (tech. grade) was purified by the method described by Vogel[5].

Proton NMR spectra were recorded on a Varian A-60 instrument with TMS as internal standard and $CDCl_3$ as solvent. Carbon-13 NMR spectra were kindly measured by Dr. L.W. Amos from Weyerhaeuser Technology Center, Tacoma, WA. UV spectra were determined using a Perkin-Elmer Model 571 UV-visible spectrophotometer.

Synthesis and Model Compounds

Erythro-guaiacylglycerol-β-(2-methoxyphenyl) ether 1 was prepared using the procedure described by Higuchi *et al*.[6]. M.p. 89-91°C (Lit. m.p. 90-92°C)[6,9].

Erythro-veratrylglycerol-β-(2-methoxyphenyl) ether 2 was synthesized likewise by the method described by Higuchi et al.[6] The product was obtained as a pale yellow viscous liquid that failed to crystallize and apparently contained the threo-isomer as an impurity. Consequently, a simple method for the enrichment of the erythro-isomer was developed, based on countercurrent equilibration between an organic solvent and aqueous potassium borate, known to form stronger complexes with the erythro-isomer[7,8]. In a typical experiment, 20 g of the oil in ethyl ether (200 ml) was equilibrated in a 500 ml separatory funnel successively with five 50 ml portions of 7% $K_2B_4O_7.4H_2O$-solution. Each borate solution was, in turn, equilibrated in four additional separatory funnels (numbered 2 to 5) containing 250 ml of ethylacetate each. The ethylacetate solutions from separatory funnels 2 to 5 were combined, dried over anhydrous sodium sulfate and evaporated to dryness. The remaining oil, dissolved in ethyl acetate-hexane, crystallized in a freezer over a period of several weeks. Additional crystals were recovered from the ether solution in separatory funnel 1 in the same manner. Total yield of crystals was 8-9 g, m.p. 96-97.5°C (lit. m.p. 98-99°C)[9].

^1H NMR (after deuterium exchange of hydroxyl groups) δ (ppm, $CDCl_3$): 3.68-3.80 (2H,m), 3.82 (9H,s), 4.08-4.30 (1H,m), 5.0 (1H, d,J = 4.5), 6.83-6.94 (7H,m). ^{13}C NMR, δ (ppm, $CDCl_3$): 55.82 (^{C}OMe), 60.91 (Cγ), 72.81 (Cα), 86.57 (Cβ), 109.69, 111.06, 112.23, 118.71, 120.11, 121.49, 123.66, 133.18, 147.14, 148.42, 148.91, 151.23. The chemical shifts for the three side-chain carbons are essentially identical with those reported for erythro-guaiacylglycerol-β-guaiacyl ether[10].

Kinetic Runs

Solutions of substrate (.003 to .015 M) containing the catalyst (HCl or $AlCl_3$) were injected in 3 ml quantities in 6 ml glass ampoules which were sealed and heated in a thermostatically controlled oil bath. After selected reaction periods, the ampoules were chilled in a dry-ice acetone bath. Two separate methods were used to determine the guaiacol released in the hydrolysis process:

a. Method I was applied for the veratryl model <u>2</u> only and was based on the neutral-alkaline difference spectrum of reaction mixture. The contents of the ampoule (0.015 M initial substrate concentration) were transferred quantitatively to a 10 ml volumetric flask and water added to the mark. An 8 ml aliquot of this solution was neutralized with four to eight ml of 0.1 N NaOH in a

25 ml volumetric flask, 4 ml of 0.2% $NaBH_4$ solution added and the flask filled to the mark with water. A 24 hour reduction period was satisfactory for the reduction of carbonyl functions present in Hibbert's ketones. Aliquots of the reduced solution were used to determine the alkaline-neutral difference spectrum by the method described by Goldschmid[11]. The amount of guaiacol was computed from the ΔA_{max}-value at 292 nm, using the separately determined $\Delta\varepsilon_{292}$-value for guaiacol, 3363, on a molar basis.

b. Method II was based on the separation of guaiacol from the reaction mixture by steam distillation prior to its spectral determination. This method was used exclusively for kinetic runs on the guaiacyl model 1, although it also gave concordant results with Method I, when applied to the hydrolysis of the veratryl model 2.

The contents of the ampoule were transferred to a 100 ml three-necked flask, 5% sodium acetate (4 ml) and water (15 ml) were added to adjust the pH to about 5-6. Distillation was then started, replacing the evaporated volume continuously by water from a dropping funnel. The distillate was collected through a condenser in a 25 ml volumetric flask. Approximately 23 ml of collected distillate was sufficient for complete transfer of guaiacol to the receiving flask. In case of the guaiacyl model 1, the amount of codistilled Hibbert's ketones was negligible and after filling the 25 ml flask to the mark, the amount of guaiacol could be determined from the absorbance at 276 nm (ε_{276} = 2400 for guaiacol). Minor amounts of Hibbert's ketones released from the veratryl model 2 codistil with guaiacol and consequently, alkaline-neutral difference spectra, unaffected by the presence of Hibbert's ketones, are more reliable for use in the determination of the guaiacol content in this case.

RESULTS AND DISCUSSION

The mechanism of hydrolysis of models 1 and 2 is depicted in Figure 1[2,3]. The rate-determining step of this reaction is the

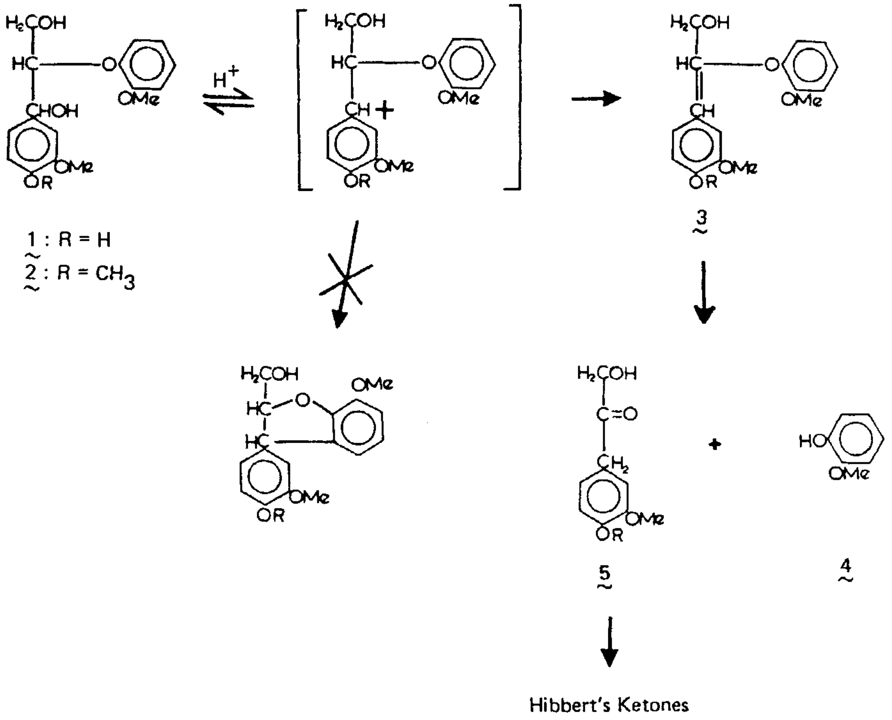

FIGURE 1 Mechanism of acid-catalyzed hydrolysis of model compounds 1 and 2.

formation of the enol ether intermediate 3 which is rapidly hydrolyzed to guaiacol 4 and the α-ketocarbinol 5. The latter is gradually converted to a mixture of four compounds called "Hibbert's ketones" via allylic rearrangement and intermolecular redox reactions.

The rate of the hydrolysis process is measured conveniently by determining the amount of guaiacol generated. In case of the veratryl model 2, the measurement of the alkaline-neutral difference spectra of the reaction mixtures was used for this purpose after borohydride reduction (Method I). The reductive pretreatment was necessary to eliminate the potential contribution of the enolate of 5 to the difference spectra.

Method I is not applicable to the hydrolysis of the guaiacyl model 1, because both the starting material and the Hibbert's ketones formed contribute to the difference spectrum. Consequently, guaiacol was separated from the rest of the reaction mixture by controlled steam distillation for spectral determination (Method II). This method was found to be both more accurate and more convenient than analysis based on gas-liquid chromatography.

Conceivably, the condensation of the intermediate carbonium ion with position 6 of the 2-methoxyphenyl group could compete with the hydrolysis process (Figure 1). In order to determine the extent of this potential side-reaction, prolonged hydrolysis runs were conducted in ethanol-water using both HCl and $AlCl_3$ as catalysts. Results obtained for the veratryl model 2 demonstrate clearly (Figure 2) the quantitative recovery of guaiacol after completed hydrolysis. Thus, intra- and intermolecular condensations do not interfere with the determination of the kinetics of the hydrolysis process.

(1). HCl-Catalyzed Hydrolysis

The rate of hydrolysis of the veratryl model 2 in ethanol-water media was found to be first-order in respect to the substrate- (Figure 3) and the HCl-catalyst concentrations (Figure 4):

$$\text{Rate} = k_{obs}\ [\text{Substr.}] = k\ [H_3O^+]\ [\text{Substr.}]$$

The same kinetic pattern was also confirmed for the guaiacyl model 1.

The activation energies for models 1 and 2, determined in ethanol-water (1:1 by volume) are nearly identical (Figure 5), 36.1 and 35.5 kcal/mol, respectively. Consequently, the ratio of the respective rate constants (k'/k) is also essentially independent of the temperature, having the average value of 3.9 (Table 1). A higher rate for the phenolic model 1 has also been found by Lundquist[3] for the acidolysis in dioxane-water.

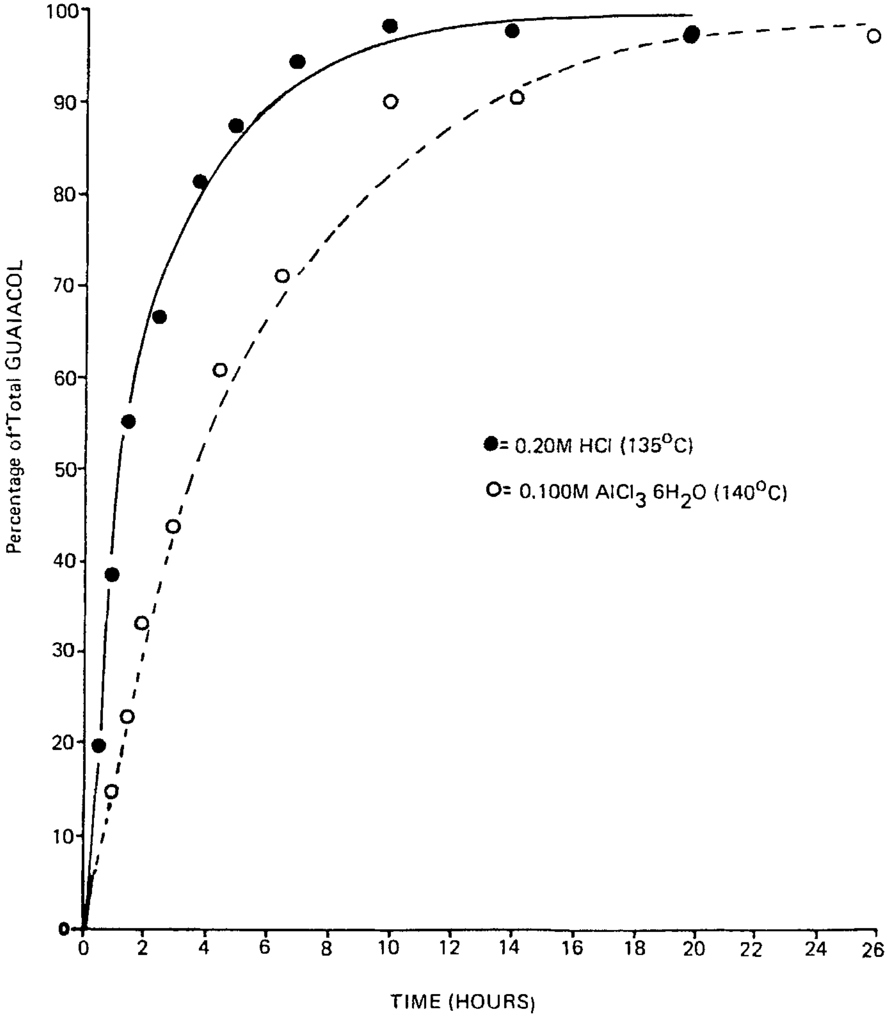

FIGURE 2 Guaiacol liberated in prolonged HCl- and $AlCl_3$-catalyzed hydrolysis of erythro-veratrylglycerol-β-(2-methoxyphenyl) ether 2 in ethanol-water as a function of reaction time, expressed as percent of maximum theoretical release.

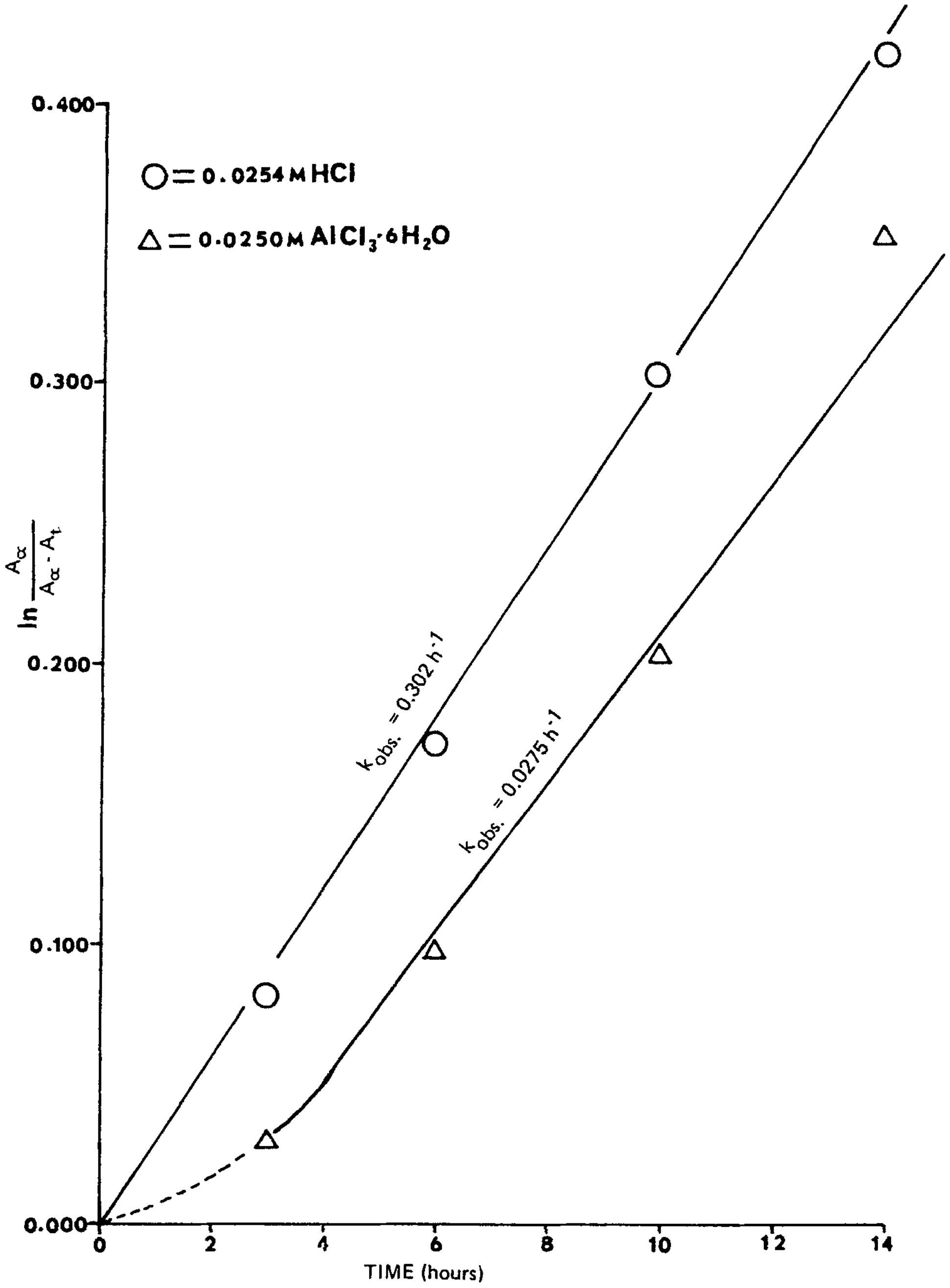

FIGURE 3 First-order rate plots for the hydrolysis of erythro-veratrylglycerol-β-(2-methoxyphenyl) ether 2 in ethanol-water (1:1 by volume), using HCl and AlCl$_3$ as catalysts at 130°C.

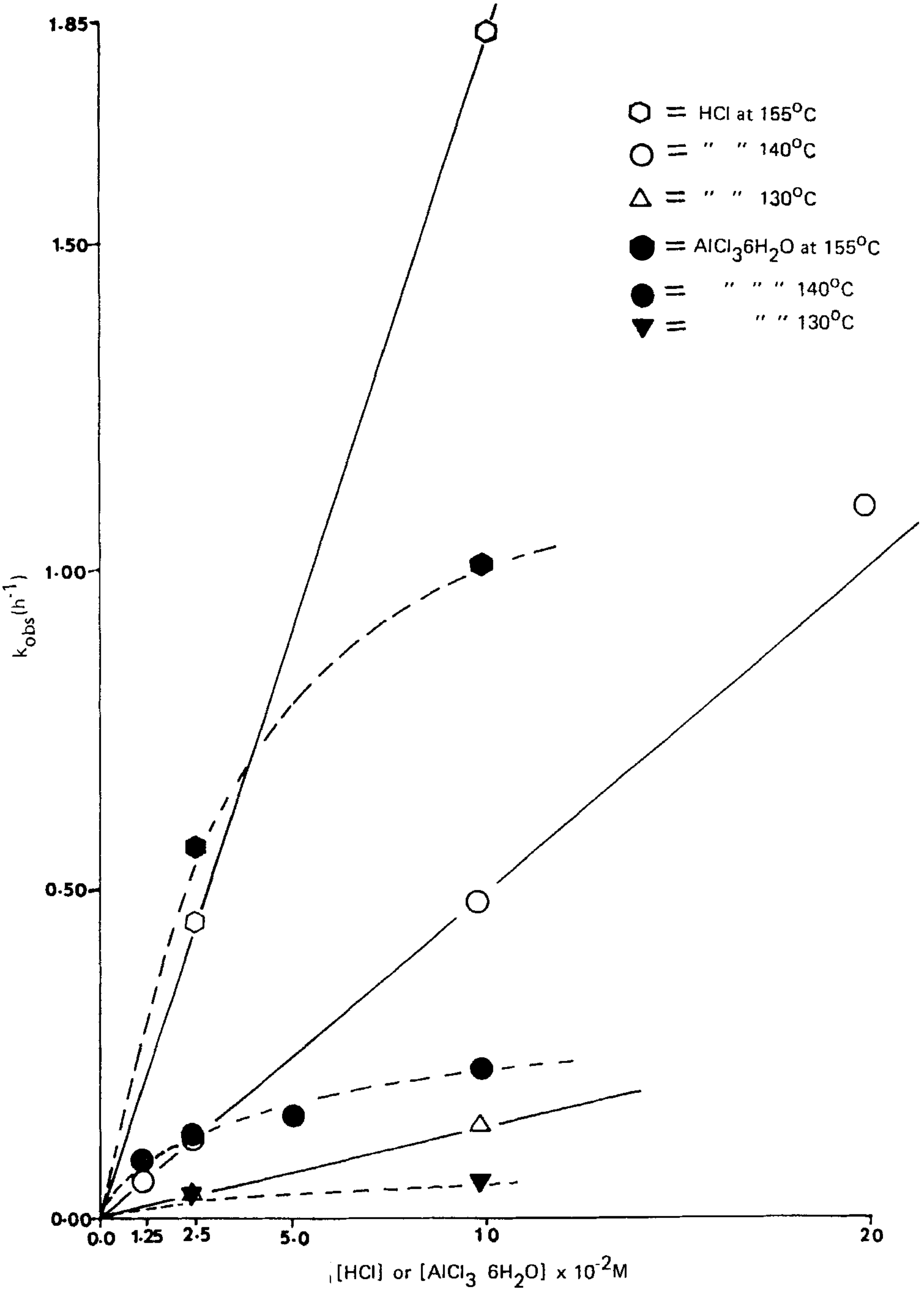

FIGURE 4 Observed first-order rate constants as a function of catalyst concentration. Hydrolysis of model compound 2 in ethanol-water, with HCl and AlCl$_3$ as catalysts, at 130°, 140° and 155°C.

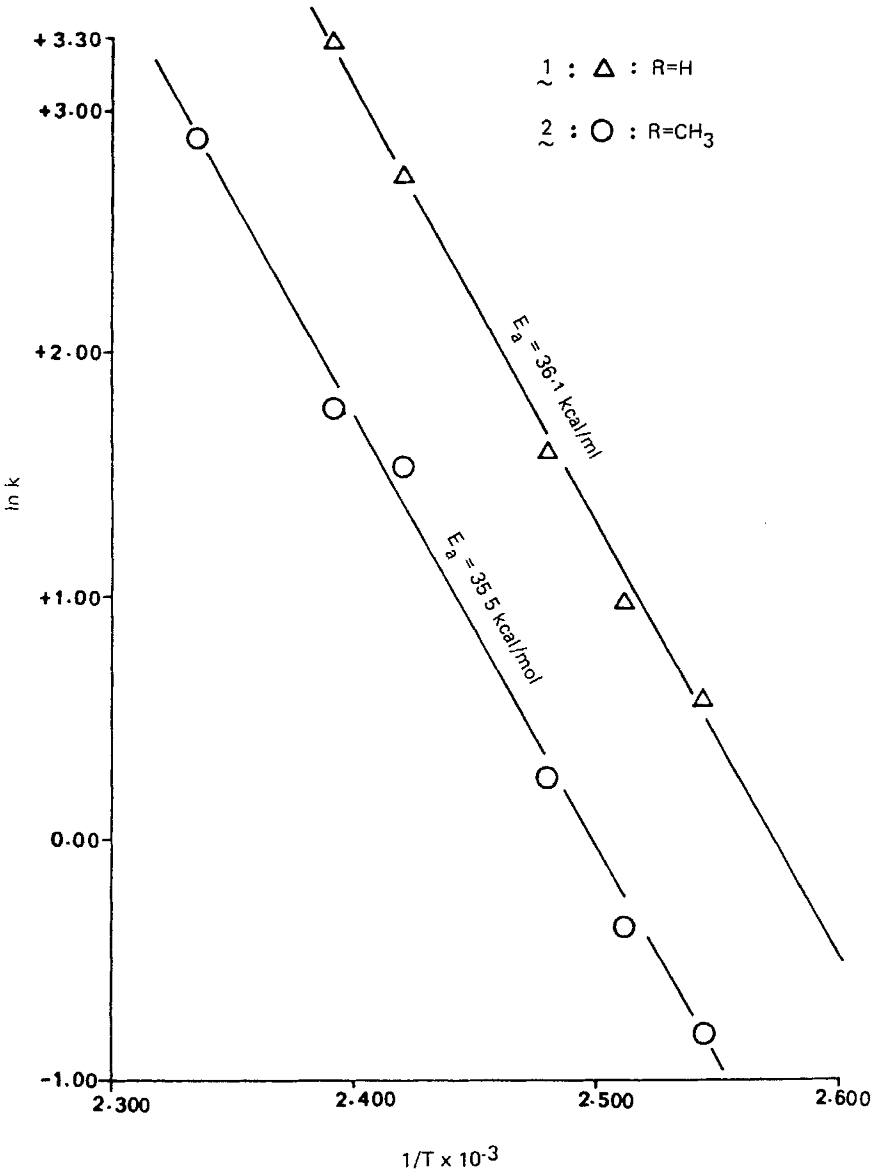

FIGURE 5 Activation energy plots for the HCl-catalyzed hydrolysis of erythro-guaiacylglycerol-β-(2-methoxyphenyl) ether 1 and its veratryl analogue 2.

TABLE 1

Typical Rate Data for the Hydrolysis of Erythro-Guaiacylglycerol-β-(2-methoxyphenyl) ether 1 and its Veratryl Analogue 2 in Ethanol-water (1:1 by Volume).

Temperature (C°)	HCl-catalyzed hydrolysis			Hydrolysis catalyzed by 0.1 M $AlCl_3$		
	$k'(h^{-1})$ (Cpd. 1)	$k\ (h^{-1})$ (Cpd. 2)	k'/k	$k'_{obs}(h^{-1})$ (Cpd. 1)	$k_{obs}(h^{-1})$ (Cpd. 2)	$\frac{k'_{obs}}{k_{obs}}$
120	1.77	0.442	4.0	0.038	-	-
125	2.67	0.689	3.9	-	-	-
130	4.92	1.29	3.8	0.133	0.050	2.68
140	15.4	4.56	3.4	0.548	0.231	2.37
145	26.7	5.89	4.5	-	-	-
155	-	18.0	-	-	1.04	-
		Average = 3.9			Average = 2.5	

In general, the hydrolysis rate is lower in ethanol-water than in pure water, particularly when the ethanol concentration exceeds 30 vol. % (Figure 6). This behavior is probably due to the rapidly established equilibrium between the models and their benzyl ethyl ethers[1].

Hydrolysis in dioxane-water mixtures was shown to conform with the kinetics expressed by equation (1) and to proceed faster than in pure water (Figure 6).

(II). Hydrolysis with $AlCl_3$ as Catalyst.

Aluminum chloride and sulfate have been found to act as catalysts in organosolv delignification of wood in ethanol-water mixtures. The catalytic activities appear to exceed the H_3O^+-ion concentrations prevailing in their solutions[12]. It was therefore, of interest to compare the catalytic action of $AlCl_3$ with that of HCl in ethanol-water mixtures.

The $AlCl_3$ - catalyzed hydrolysis of the veratryl model 2 follows generally first-order kinetics, except at low reaction temperatures, where an initial retardation effect is observed (Figure 3). However, the relationship between hydrolysis rate and catalyst concentration is not linear (Figure 4). In comparison with the HCl-catalyzed process, .025 M $AlCl_3$ is about equally effective a catalyst as .025 M HCl. The measured pH of .025 M $AlCl_3$ is 3.20 at ambient temperature, corresponding to the molar H_3O^+ concentration of 6.3×10^{-4}. Thus the observed hydrolysis rate is approximately by a factor of forty higher than expected on the basis of the initial hydronium ion concentration. It follows that either the initially measured hydronium ion concentration is substantially lower than that prevailing at the reaction temperature or, alternatively, that the aluminum cation accelerates, in some manner, the rate of the process.

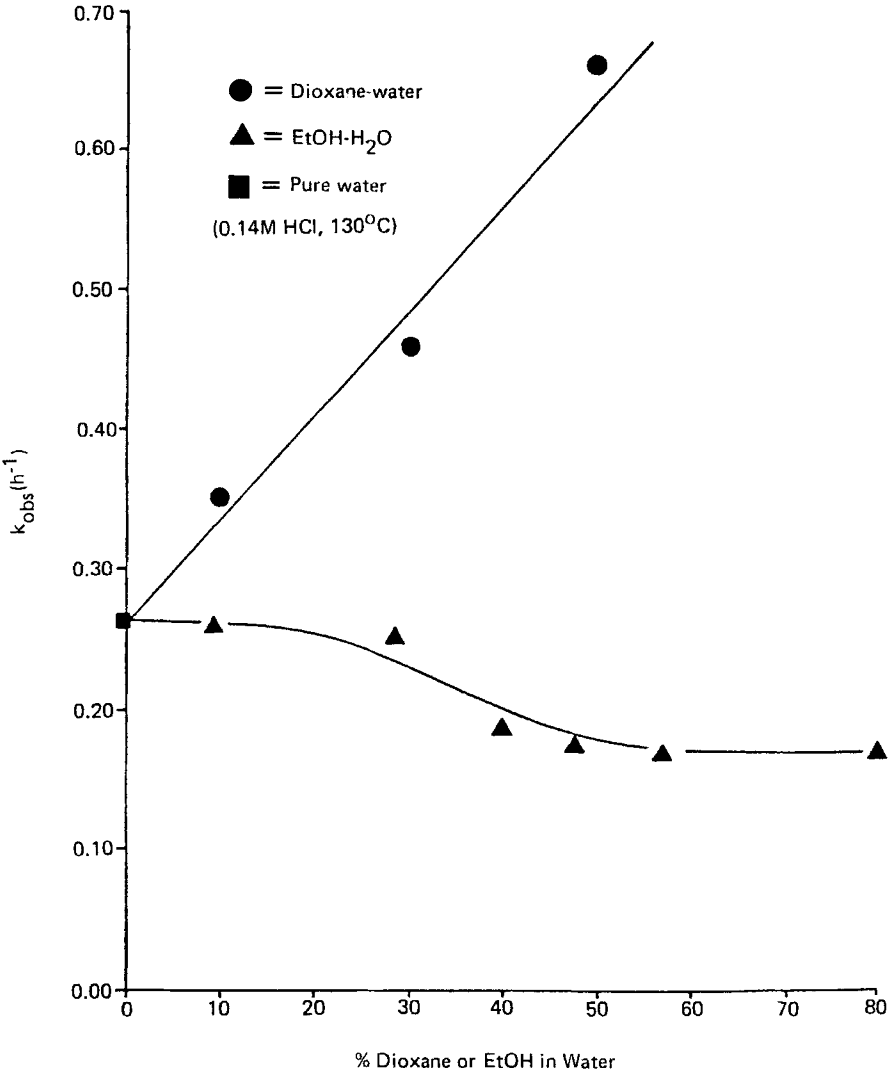

FIGURE 6 Effect of solvent composition on the rate of HCl-catalyzed hydrolysis of the veratryl model 2 in dioxane-water- and ethanol-water mixtures.

In order to explore the validity of the first alternative, aluminum chloride solutions, without substrate, were heated to the reaction temperatures used in kinetic runs and the pH determined after rapid cooling, of the ampoules. The results (Table 2) demonstrated that heating caused a 10- to 20- fold irreversible increase in hydronium ion concentration. The increase in acidity may be ascribed to the formation of polymeric hydrated aluminum ion complexes releasing hydrochloric acid[13]. This process appears to be more extensive at 155° than at 130°C.

Thus, it appears likely that the effect of $AlCl_3$-solutions is simply based on the liberation of HCl. At 130°, the release is probably not instantaneous, resulting in the acceleration effect shown in Figure 3. The apparent activation energies determined for the $AlCl_3$-catalyzed hydrolysis were higher than those for the HCl-catalyst, 43.0 and 41.2 kcal/mole, for models <u>1</u> and <u>2</u>, respectively. This effect is understandable in view of the more extensive release of HCl at higher reaction temperatures. The identity of $AlCl_3$-and HCl-catalyzed processes was further supported by HPLC-analysis of hydrolysis products, indicating no discernible differences in the nature and distribution of individual components.

TABLE 2

Change in the pH-value of .025 M $AlCl_3$ in Water and in Ethanol-water (1:1 by Volume) after Heating the Solution at 130°C.

Heating time, min.	pH, measured in			
	Ethanol-water		Water	
	After heating	Additional 1 wk. storage	After heating	Additional 1 wk. storage
No heating	3.20	3.20	3.50	3.50
20	2.25	2.50	2.95	-
180	2.20	2.30	2.35	2.70

On the other hand, the ratio of rate constants (k'_{obs}/k_{obs}) for model 1 and 2 was only 2.5 in $AlCl_3$-catalyzed hydrolysis and clearly lower than the value 3.9 obtained for the HCl-catalyst (Table 1). This difference is significant and makes it unjustifiable to eliminate the role of the aluminum cation in the hydrolysis altogether.

CONCLUSION

The kinetic results obtained are of interest for the understanding of acid-catalyzed hydrolytic degradations of biomass lignins in dioxane-water ("acidolysis")[2,4], in ethanol ("ethanolysis")[14] and in aqueous ethanol ("organosolv pulping")[15]. The results suggest that, other conditions being equal, the reaction proceeds faster in dioxane-water than in water or aqueous ethanol. Generally, phenolic β-O-4-linked units appear to hydrolyze faster than corresponding etherified units. The activation energy obtained in aqueous ethanol, 36 kcal/mol, is very close to the range of activation energies obtained for the acid-catalyzed hydrolysis of glycosidic bonds, 32 to 35 kcal/mol[16]. Consequently, it appears unlikely that variation of reaction temperature in acid-catalyzed biomass hydrolysis would significantly change the selectivity of lignin hydrolysis in comparison with the hydrolysis of polysaccharide components.

On the other hand, it should be noted that overall, the hydrolysis of biomass lignins is a much more complex reaction than that of other natural polymers, due to the presence of a variety of hydrolyzable bonds, such as α-aryl ether linkages which represent about 7 per cent of intermonomeric bonds and are hydrolyzed more rapidly than the β-aryl ether (β-O-4) linkages[17]. Lignin-carbohydrate bonds[18] and competing condensation reactions also exert an effect on the release of lignin hydrolysis products from the biomass matrix.

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REFERENCES

1. E. Adler, Wood Sci. Technol., 11, 169 (1977).
2. E. Adler, K. Lundquist and G.E. Miksche, Adv. Chem. Ser., 59, 22 (1966).
3. K. Lundquist and R. Lundgren, Acta Chem. Scand., 26, 2005 (1972).
4. K. Lundquist, Appl. Polym. Symp., 28, 1393 (1976).
5. A.I. Vogel, A Textbook of Practical Organic Chemistry, p.177, 3rd ed., Wiley-Interscience, New York, 1966.
6. T. Higuchi, F. Nakatsubo and K. Sato, Holzforschung, 29, 165 (1975).
7. J. Gierer and I. Noren, Acta Chem. Scand., 16, 1976 (1962).
8. K. Lundquist and I. Berndtsson, Acta Chem. Scand., B 31, 725 (1977).
9. G.E. Miksche, J. Gratzl and M. Fried-Matzka, Acta Chem. Scand., 20, 1038 (1966).
10. S. Hosoya, K. Kanazawa, H. Kaneko and J. Nakano, Mokuzai Gakkaishi, 26, 118 (1980).
11. O. Goldschmid, Anal. Chem., 26, 1421 (1954).
12. J.S. Sanwal, G. Meshitsuka, L. Wu and K.V. Sarkanen "Catalytic Effects in Organosolv Pulping", Paper presented at the Tappi Wood Chemistry Conference, Appleton, Wisconsin, May, 1978.
13. C. Brosset, Acta Chem. Scand., 6, 910 (1952).
14. W.B. Hewson, J.L. McCarthy and H. Hibbert, J. Am. Chem. Soc., 63, 3041 (1941).
15. T.N. Kleinert, Tappi, 57, 99 (1974).

16. T. Timell, Can. J. Chem., 42, 1456 (1964).

17. G.E. Miksche, Acta Chem. Scand., 26, 289 (1972).

18. O. Eriksson and B.O. Lindgren, Svensk Papperstidn., 80, 59 (1977).