constant for at least 50% of complete reaction. The surface reaction could be catalyzed by rinsing the cold clay reaction tube with concentrated sulfuric acid and heating until no more sulfur trioxide was evolved at the temperature of use. In a treated tube the heterogeneous reaction rate for carbon monoxide/nitric oxide ratios of from one to four could be expressed by the equation moles $CO_{2/\text{sec.}} = 85\ e^{-36,900/RT}$. In an untreated clay tube, the constant reaction velocity at 1317° was only one-third as great as that observed in the treated tube. At 1380° and at higher temperatures, acceptable third order constants were obtained and an acid treated and untreated tube gave the same results.

The values of the observed reaction constant were calculated from the equation

$$k_{(\text{obs.})} = \frac{1}{t[(CO_0) - (NO_0)]} - \left[\frac{1}{(NO_0) - (CO_2)} - \frac{1}{(NO_0)} - \frac{2.3}{(CO_0) - (NO_0)} \log \frac{(NO_0)[(CO_0 - CO_2)]}{(CO_0)[(NO_0) - (CO_2)]}\right]$$

where

t = residence time of the gas in the heated zone

(CO_0), (NO_0) = initial moles/liter of CO, NO at the temperature and pressure of the reaction tube

(CO_2) = moles/liter of CO_2 formed in time t.

The data obtained are collected in Table I. In each case, k (calcd.) is obtained from $k = 2 \times 10^{10}\ e^{-49,600/RT}$ sec.$^{-1}$ mole^{-2} liter^2.

TABLE I

Initial moles/liter $\times 10^3$ NO	CO	N_2	Residence time, sec.	CO_2 formed, moles/liter $\times 10^3$	k(obs.)	k(calcd.)	Temp., °C.
0.93	2.33	4.70	1.50	0.019	6.7×10^3	6.0×10^3	1383
			3.30	.035	5.2		
			5.25	.055	6.8		
2.08	5.18	0	0.57	.076	5.9		
			1.21	.17	5.6		
			1.63	.20	6.5		
			3.90	.37	5.3		
2.91	4.36	0	1.48	.37	7.9×10^3		
			2.00	.43	6.9		
			3.88	.68	6.6		
3.01	3.51	0.56	1.67	4.62	12.3×10^3	10.7×10^3	1450
			2.66	.606	9.7		
			3.56	.804	10.6		
1.28	5.49	0	0.82	.129	17.9×10^3	19.9×10^3	1527
			1.35	.23	22.4		
			2.28	.333	21.4		
			3.80	.422	18.3		
2.28	4.49	0	1.74	.62	21.7		
			3.66	.97	21.2		
			3.84	.99	21.1		
			6.40	1.16	19.4		
0.80	5.76	0	1.34	0.13	31.6×10^3	29.7×10^3	1581
			1.48	.138	31.0		
			2.32	.19	29.8		
			3.45	.238	27.0		
2.85	2.81	1.49	0.73	.49	27.3		
			1.06	.73	34.0		
			1.40	.89	35.4		
			2.99	1.22	32.0		

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Acetylation of Alkyl Phenyl Ethers

BY ALVIN I. KOSAK[1] AND HOWARD D. HARTOUGH

It has recently been shown that thiophene and furan can be acylated by acid anhydrides and acyl halides in the presence of catalytic amounts of iodine and hydriodic acids,[2] zinc chloride,[3] strong inorganic oxyacids,[4] and silica–metal oxides.[5]

The use of these catalysts has been extended to the acetylation of alkyl phenyl ethers which, likewise, have a reactive hydrogen on the nucleus. Anisole, phenetole and *o*-methoxydiphenyl upon reaction with acetic anhydride yielded the corresponding methyl ketones para to the ether linkage; diphenyl oxide did not react.

The procedures employed were similar to those described in the references cited above. The following catalysts were tested and found to be effective: zinc chloride, iodine, 96% sulfuric acid, dihydroxyfluoboric acid, 85% phosphoric acid and Super-Filtrol (an activated montmorillonite clay).

Phosphoric Acid Catalyst.—A mixture of 108 g. (1 mole) of anisole, 161 g. (1.5 mole) of 95% acetic anhydride, and 7 g. of 85% orthophosphoric acid was heated at the reflux temperature with stirring for three hours. The product was washed with water and dilute sodium carbonate solution, dried over activated alumina and distilled. Sixty-eight grams (45% of theory) of *p*-methoxyacetophenone boiling at 124° (6 mm.) was collected. The 2,4-dinitrophenylhydrazone melted at 232–233°.[6] The semicarbazone melted 197–198°.[7]

Silica-Metal Oxide Catalyst.—A mixture of 102 g. (0.95 mole) of 95% acetic anhydride, 84.8 g. (0.79 mole) of anisole and 15 g. of Super-Filtrol was refluxed with stirring for six hours. The product was worked up as in the preceding example; yield was 13.5 g. (11.4%) of *p*-methoxyacetophenone boiling at 124° (6 mm.).

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[1] Present address: Department of Chemistry, The Ohio State University, Columbus, Ohio.

[2] Hartough and Kosak, THIS JOURNAL, **68**, 2639 (1946).

[3] Hartough and Kosak, *ibid.*, **69**, 1012 (1947).

[4] Hartough and Kosak, *ibid.*, **69**, 3098 (1947).

[5] Hartough, Kosak, and Sardella, *ibid.*, **69**, 1014 (1947).

[6] Borsche and Barthenheier, *Ann.*, **553**, 250 (1942), report 233–234°.

[7] Wahl and Silberzweig, *Bull. soc. chim.*, [4] **11**, 69 (1912), give the melting point of the semicarbazone as 197°.

RESEARCH AND DEVELOPMENT DEPARTMENT
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Destructive Distillation of Douglas Fir Lignin

BY T. L. FLETCHER AND E. E. HARRIS

The destructive distillation of lignin from wood has been investigated sporadically during the last thirty years. The only systematic, though partial, work on lignin distillation was carried out by Phillips and Goss[1] and by Bridger[2] on corncob alkali lignin. Recently, modified distillation of wood lignin has been reported from Germany.[3]

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[1] Phillips and Goss, *Ind. Eng. Chem.*, **24**, 1436 (1932).

[2] Bridger, *ibid.*, **30**, 1174 (1938).

[3] Freudenberg and Adam, *Ber.*, **74B**, 387 (1941); Suida and Prey, *ibid.*, **75**, 1580 (1942).

The investigation discussed here was undertaken by the Forest Products Laboratory to obtain a more complete knowledge of the pyrolysis of lignin from wood, specifically from Douglas fir by the Madison wood-sugar process. Elucidation of the chemistry of Douglas fir lignin is highly pertinent because great quantities may remain from saccharification. The literature reports no systematic destructive distillation of lignin from any species isolated by this method.

For comparison with previous work and to lay groundwork for the ramification of lignin pyrolysis investigations, six batches of Madison wood-sugar lignin totaling 199.2 pounds were distilled at atmospheric pressure at a final retort temperature of 375 to 392°.[4] The yield of charcoal (55 to 66%) decreased with increasing amounts of residual cellulose, and decreased an extra amount in each of the three runs where the lignin had been washed free of the approximately 1.3% sulfuric acid remaining in it.

The yield of aqueous distillate (13 to 21%) and settled tar (5.2 to 8.9%) increased with increasing amounts of residual cellulose, and increased an extra amount in the distillations of acid-free lignin. Conventional methods show the presence in the aqueous distillate of 0.3 to 0.5% methyl alcohol, 0.15 to 0.25% acetone, 0.14% formic acid, and 0.2 to 0.4% acetic acid on the basis of dry acid-free lignin. There is reason to believe, however, that these methods give only approximations.

Since some of the settled tar appeared to be crystalline, the effect of various solvents was observed. It was found that 82% of the tar, including the solid material, was extractable with petroleum ether. Evaporation of the solvent, cooling and filtration led to recovery of some white crystalline material (about 3.5% of the settled tar), which appears to be a mixture of long chain aliphatic acids in the C_{18}-C_{22} range. The extracted oil was then separated into phenolic (35.5% of the settled tar), neutral (32%) and acid fractions (7 to 8%). The residual tar was also separated into various fractions, including a basic mixture.

Each of the foregoing mixtures was further separated by steam-distillation. Thus far the presence of the following phenols has been demonstrated in the steam-volatile fraction after vacuum distillation through a 4-foot Fenske-type column: phenol, *o*-cresol, *p*-cresol, guaiacol, 2,4-xylenol, 4-methylguaiacol, and 4-ethylguaiacol. The 4-methylguaiacol was identified as its aryloxyacetic acid, m. p. 117–118.5°; known compound, m. p. 117–118°; mixed m. p. 117.5–118.5°. This agrees with J. H. Fletcher and Tarbell,[5] m. p. 115–116°. Bridger[2] reported the melting point of this aryloxyacetic acid as 86°, but reported no mixed melting point.

Further work is being done on the phenols, and the other fractions are being investigated.

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(4) The distillations were carried out by E. Beglinger and L. D. Pennington.

(5) THIS JOURNAL, **65**, 1431 (1943).

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RECEIVED JUNE 19, 1947

Evidence for the Presence of Streptothricin in Streptolin Culture Filtrates

BY D. H. PETERSON, D. R. COLINGSWORTH, L. M. REINEKE AND C. DEBOER

An antibiotic fraction similar to streptothricin has been isolated from a culture filtrate of a *Streptomyces sp.*[1] which produces streptolin.[2] The culture was grown according to the procedure described by Rivett and Peterson.[2] A high potency streptolin (Fraction A) was prepared by the streptomycin procedure of Vander Brook, *et al.*,[3] which involved adsorption of the active material on 1% Darco G-60 at *p*H 6.5–7.0. However, in order to prepare the streptothricin antibiotic (Fraction B) relatively free of streptolin, it was first necessary to remove the streptolin by adsorption on 2% Darco G-60 at *p*H 6.5–7.0. This step also removed some of fraction B from the culture filtrate. The *p*H of the filtrate was adjusted to 8.0 and the remainder of the second antibiotic (Fraction B) adsorbed on 1% Darco G-60. The steps which followed were essentially those for the preparation of streptomycin,[3] *viz.*, the carbon was eluted with dilute acetone at *p*H 2.5, the acetone concentration of the eluate increased to 75% to precipitate the active fraction, the precipitate leached with water, the *p*H adjusted to 7.2 and the aqueous solution lyophilized to give a powder. Two hundred and sixty liters of culture filtrate yielded 4.8 g. of crude Fraction B assaying 95 units per mg. (see footnote *a*, Table I). Aluminum oxide chromatography increased the activity to 325 units per mg.

TABLE I

	Streptothricin-like (Fraction B)	Streptothricin	Streptolin (Fraction A)	Streptomycin
Agar plate assay, units per mg.[a]	325	437	24	400
Broth Dilution Activities[b]				
B. subtilis (Illinois)	8700	10,600	113,000	3500
E. coli (ATCC 26)	1650	1,480	5,200	760
S. marcescens (ATCC 60)	2800	2,600	8,000	7100
S. albus (ATCC 151)	3000	2,600	57,000	2250
S. aureus (FDA 209)	6450	10,100	42,000	7700
B. cereus (ATCC 9139)	62	82	1,200	2100
P. vulgaris (ATCC 8427)	4750	7,500	20,000	1900
S. schottmuelleri (ATCC 9149)	2800	3,400	9,900	490
PCI-3[c]	1100	1,060	2,000	10
T. R.-160[d]	45	41	3,800	210
Toxicity intravenously, LD-50 per 20 g. mouse				
Mg./mouse	4	7.5	0.11	9
Units/mouse	1300	3,280	2.6	3600

[a] Agar plate method of Loo, Skell, Thornberry, Ehrlich, McGuire, Savage and Sylvester, *J. Bact.*, **50**, 701 (1945). The unit employed is based on the activity of 1 microgram of streptomycin. [b] Figures represent highest dilutions of 1 mg. which inhibited test organisms in peptone yeast extract medium at *p*H 7.25. [c] Culture obtained from F.D.A. [d] *B. subtilis* (Illinois) made resistant to streptothricin.

The results in Table I indicate that Fraction B is similar to streptothricin but differs from streptolin and streptomycin. The inhibition of growth of the ten bacteria in broth medium by Fraction B is practically identical with that shown by streptothricin, but differs from the inhibition by streptolin and streptomycin. Additional spectra studies

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(1) The Streptomyces culture was received from Prof. W. H. Peterson of the University of Wisconsin.

(2) Rivett and Peterson, THIS JOURNAL, **69**, 3006 (1947).

(3) Vander Brook, Wick, DeVries, Harris and Cartland, *J. Biol. Chem.*, **165**, 643 (1946).