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 $CO_{2/sec.} = 85 \ e^{-36,900/RT}$. 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

$$k_{\text{(obs.)}} = \frac{1}{t[(\text{CO}_0) - (\text{NO}_0)]} - \left[\frac{1}{(\text{NO}_0) - (\text{CO}_2)} - \frac{1}{(\text{NO}_0)} - \frac{2.3}{(\text{CO}_0) - (\text{NO}_0)} \log \frac{(\text{NO}_0)[(\text{CO}_0 - \text{CO}_2)]}{(\text{CO}_0)[(\text{NO}_0) - (\text{CO}_2)]}\right]$$

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

= moles/liter of CO₂ formed in time t. (CO_2)

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

Table 1	[
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Initia	l mole	s/liter	Resi- dence	CO2 formed moles/	3		Temp
NO	ĉõ	Nı	sec.	× 10*	k(obs.)	k(calcd.)	°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 X 10•		
			2.00	.43	0.9		
9.01	0 51	0 50	3.88	.08	0.0	10 7 1 101	1450
3.01	3.51	0.00	1.07	4,02	12.3 × 10*	10.7 X 10	1400
			2.00	.000	9.1 10.6		
1 00	5 40	0	0.00	120	17.0×101	10.0 ~ 101	1597
1.20	0.49	U	1 35	.125	22.4	19.9 × 10.	1021
			2 28	333	21.4		
			3 80	422	18.3		
2 28	4 49	n	1.74	62	21.7		
~	1.10	Ū	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		

BALLISTIC RESEARCH LABORATORIES ABERDEEN PROVING GROUND, MD.

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Acetylation of Alkyl Phenyl Ethers

BY ALVIN I. KOSAK¹ 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 dissolution is a set of 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.).

(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

SOCONY-VACUUM LABORATORIES

(A DIVISION OF SOCONY-VACUUM OIL CO.)

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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 Goss¹ and by Bridger² on corncob alkali lignin. Recently, modified distillation of wood lignin has been reported from Germany.³

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

 Bridger, *ibid.*, **30**, 1174 (1938).
Freudenberg and Adam, *Ber.*, **74B**, 387 (1941); Suida and Prey, ibid., 75, 1580 (1942).