TABLE I

WAX FROM DOUGLAS FIR AND DOUGLAS FIR LIGNIN RESIDUE

Material	M. p., °C.	Sp. gr., 20 per 20	Sapon. value,	Acid value,	Ester value,	Acetyl value,	Iodine (Hanus), I_2 per 100 g.	Reichert Meissl, ml. 0.1 *N* KOH per 5 g.
				mg. KOH per g.				
Hogged woodbark	53	1.05	176.8	46.1	130.7	76.8	42.3	0.43
Bark	55	1.05	194.9	46.8	148.1	80.6	37.4	.14
Lignin	61	1.05	170.4	74.2	96.2	77.1	27.8	6.7

Extraction of dried lignin residue with benzene yielded 3.9% extractives. A similar extraction with acetone yielded 7.1% extractives of which 3.6% (dry lignin basis) was benzene-soluble, the rest being soluble lignin and other materials. Extraction of wet lignin residue with acetone yielded 10.8% extractives, of which 6.9% (dry lignin basis) was benzene-soluble. Increased yields by acetone extraction of wet lignin may be attributed to improved solvent diffusion into undried cellular structure.[2] Benzene extraction of the original dried, hogged Douglas fir waste, which contained approximately 30% bark yielded 1.5% extractives. Similar extraction of sapwood alone yielded 1.1% extractives.

Benzene-soluble extractives obtained were wax-like brown and black substances. They consisted of a mixture of long chain aliphatic acids, alcohols, esters, and unidentified materials. The customary values for waxes were determined for Douglas fir wax (Table I). A petroleum ether separation of benzene extractive yielded a light brown petroleum ether-soluble fraction having lower acetyl and saponification values and a petroleum ether-insoluble fraction of higher melting point and saponification value.

A separation of a sample of 180 g. of benzene extractives by saponification and subsequent solvent extraction of the salts yielded 66% wax-saponifiable materials, 12% water-soluble materials, and 22% unsaponifiable material.

Behenic acid, lignoceric acid, and a C_{15} alcohol have been identified in the hydrogenation product from the lignin residue. These are believed to have been present originally as extractives. Further separation and characterization of the extractives is now in progress to check this.

[2] A. J. Stamm and L. A. Hansen, *Ind. Eng. Chem.*, **38**, 413–416 (1946).

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The Homogeneous Reaction of Nitric Oxide and Carbon Monoxide

BY CHARLES P. FENIMORE

Although the interaction of carbon monoxide and nitric oxide has been studied in the neighborhood of 900°,[1] no homogeneous gas phase reaction of these compounds is reported in the literature.

$$2NO + 2CO \longrightarrow N_2 + 2CO_2 \qquad (1)$$

At 1380 to 1580° and one atmosphere pressure, a slow homogeneous reaction has been found to occur. The reaction is first order with respect to carbon monoxide and second order with respect to nitric oxide. This dependence on composition is the same as that which characterizes all other known homogeneous reactions of nitric oxide.

$$dNO/dt = -k[NO]^2[X] \quad X = Cl_2,\ O_2,\ Br_2,\ H_2 \qquad (2)$$

The temperature required is so high that no great accuracy in temperature measurement can be claimed. The data obtained are best correlated by

$$k = 2 \times 10^{10}e^{-49,600/RT}\ \text{sec.}^{-1}\ \text{mole}^{-2}\ \text{liter}^2$$

Nitric oxide and carbon monoxide were prepared by reduction of nitrite ion and dehydration of formic acid, respectively.[3] The gases, either alone or sometimes with added nitrogen, were stored briefly over an aqueous sodium hydroxide solution, then by displacement of the solution forced to flow through a train consisting of calcium chloride drying tube, flowmeter and reaction tube. A sample of the unreacted gas was analyzed for nitric oxide by absorption in a dilute sulfuric acid solution of ferrous sulfate and for carbon monoxide by subsequent combustion with excess oxygen. After a steady flow rate had been established through the reaction tube and a volume of gas had been passed equal to at least ten times the volume of the tube, the extent of reaction was determined by absorption of carbon dioxide in ascarite from a known volume of gas. Before using the ascarite, air was displaced from the absorption bulb by nitrogen.

The reaction tube was of clay, ten inches long, one inch inside diameter, heated in a glowbar furnace. Temperature was measured with platinum-platinum rhodium thermocouple, uncalibrated in the temperature region of interest, using e. m. f. values from tables.[4]

The residence time of the gas in the reaction tube was calculated by dividing the volume of the tube by the volume of gas at the prevailing temperature and pressure. Inasmuch as a volume change accompanies the reaction, an average was struck between the volumes of the unreacted and the reacted gas for this calculation. Between 1000 and 1300° only a zero order surface reaction was observed. At 1317°, the reaction velocity was

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[1] Musgrave and Hinshelwood, *J. Chem. Soc.*, **56** (1933).

[2] Schumacher, "Chemische Gasreaktionen," Edwards Bros., Ann Arbor, Michigan, 1943, p. 311.

[3] Farkas and Melville, "Experimental Methods in Gas Reactions," The Macmillan Co., New York, N. Y., 1939, chapt. III.

[4] Lange, "Handbook of Chemistry," 5th ed., p. 845.

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

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

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

(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 $\times 10^3$			Residence time, sec.	CO_2 formed, moles/liter $\times 10^3$	k(obs.)	k(calcd.)	Temp., °C.
NO	CO	N_2					
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°.

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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).