

Cyclopentanones from Black Liquor Heated with Alkali

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Cyclopentanone, its 2-methyl-, 3-methyl-, and 2,4-dimethyl derivatives, and guaiacol were identified among the volatile products from kraft black liquor heated with alkali at diminished pressure. Infrared and mass spectra of the cyclopentanones are presented.

One of us (T.E.) and his coworkers have carried out a series of demethylating heatings of kraft black liquor with added alkali at 250–300° and at atmospheric or diminished pressure.¹⁻⁴ In this treatment, pyrocatechol and other phenols, and phenolcarboxylic, acetic, formic, succinic, and oxalic acids are formed, but remain as salts in the alkaline medium and are recovered after acidification. Water and a restricted amount of organic substances, among them especially dimethyl sulfide and methyl mercaptan in amounts of up to 4 and 2.7 %, respectively, of the organic matter in the black liquor, distill off already during the heating of the alkaline reaction mixture. In addition, small amounts of phenols and volatile neutral substances distill off. The present paper describes the identification of cyclopentanone and three of its homologs among the volatile ketonic bodies. It may be mentioned that cyclopentanone, 2-methylcyclopentanone, and two compounds described as dimethyl- and trimethyl-cyclopentanone without characterization have been detected earlier in dry distillates of wood.⁵

MATERIALS AND METHODS

Starting material. Four-kilogram portions of a commercial kraft black liquor derived from a cook of a wood mixture composed of about 2/3 of pine and 1/3 of spruce wood and containing 51.9 % of dry matter, 21.1 % of ash and approximately 42 % of organic substances (cf. Ref. 6) were heated with commercial 77.1 % sodium hydroxide in a 12-l vessel at diminished pressure as follows:

Digestion L 1002, 550 g of comm. NaOH, 1 h at about 295°C; digestion L 1054: 500 g, $\frac{1}{2}$ h, 280°C. The distillates were condensed in two common Liebig condensers, cooled with water, and extracted with ether. The yield of moist ether extract from digestion L 1054 was 8.79 g. The yield after drying with sodium sulfate was 7.73 g, or 0.46 % of the organic matter in the starting material. This ether extract was distilled in a 70-cm spinning-band column of the type designed by Björkman.⁷ The distillation was performed at

normal pressure up to 142°C, and then at 7–10 torr: the reflux ratio varied from about 1.5 to 10, and the rate of distillation was about 3.5 ml/h.

The *gas chromatographs* used were Perkin-Elmer F 6 and 800 and Varian 200, all fitted with flame ionization detectors. Columns: A, Apiezon M, 15 %, 2 m long, 2 mm i.d., for distillate fractions; B, as A, except that the i.d. was 4 mm, for preparative isolations; C, trimethylene propane triple argonate, 15 %, 2 m, 4 mm i.d., for preparative isolation; D, butanediol succinate, 8 %, 1.8 mm i.d.; E, silicone S 30, 10 %, 1.8 mm i.d.; F, polyethyleneglycol 1500, 15 %, 1.8 m, 1.8 mm i.d. Carrier gas N₂ in all cases.

In the gas chromatographic isolation of components, about 99 % of the carrier gas was led past the detector, and the components were condensed in a glass test tube at liquid nitrogen temperature. The tube was centrifuged at 10³ g to collect the condensate. When large amounts were chromatographed, the condensation took place at room temperature. The temperature needed to condense a particular component may be approximately calculated from

$$\text{Grams of substance remaining in vapour phase at } T = \frac{3 \times p_T \times M \times w \times u}{2 \times 760 \times 22.4}$$

T = temperature of condensation vessel, °K.

p_T = vapour pressure of the substance at T in mm Hg.

M = molecular weight of the substance

w = width of elution band in minutes

u = rate of flow of carrier gas, l/min

Fractions isolated on column B were rechromatographed on column C before spectrometry.

Paper chromatography of phenols was carried out on Whatman No. 4 paper impregnated with formamide using chloroform or ligroin-xylene, 95:5, as eluents, and the paper was sprayed with diazotized *p*-nitroaniline as described in Refs. 10 and 11.

Dicarboxylic acids formed by oxidation of the isolated substances were resolved by the descending technique on Whatman No. 4 paper with 2-propanol-25 % NH₃ (4:1 v/v) during 48 h. 0.5 % bromocresol green in ammoniacal ethanol-water was used to render the spots visible.

Thin layer chromatography of 2,4-dinitrophenylhydrazones (DNP) was performed on 0.5-mm layers of Kieselgel G, 10–25 μ (E. Merck AG), activated at 120°C. The solvent (petroleum ether-benzene, 1:1 v/v)⁸ was allowed to ascend five times, the plate being dried between the runs. For preparative separations, the Kieselgel was washed with chloroform: methanol (1:1 v/v) before preparing the plates.

Infrared absorption spectra were measured on a Perkin-Elmer 237 spectrometer using the KBr-pellet and capillary-film techniques. Mass spectra were measured on a modified CEC and an LKB instrument.

Reference compounds. Cyclopentanone was synthesized by dry distillation of adipic acid. Its 2-methyl, 3-methyl and 2,4-dimethyl derivatives were synthesized according to Blanc⁹ by distillation of the anhydrides of 2-methyl-, 3-methyl-, and 2,4-dimethyl-adipic acids at 200–250°. The adipic acids were prepared by oxidation of the 2-methyl-, 4-methyl-, and 3,5-dimethyl-cyclohexanols (Fluka AG) with nitric acid. In the conditions used (65 % HNO₃, 55–65°C), 2-methylcyclohexanol gives 30–40 % adipic acid, which was separated by crystallization. 2-Methyladipic acid was isolated in about 50 % yield by extraction of the partially neutralized (pH 3) reaction mixture with ether and crystallized from benzene. The dimethylcyclohexanol was stereochemically inhomogeneous, and hence the dimethylcyclopentanone must have been a mixture of stereoisomers.

The 2,4-dinitrophenylhydrazones were precipitated from solutions 1 N in aqueous hydrochloric acid and purified by TLC before the recording of their IR spectra.

One of the products isolated by gas chromatography (2,4-dimethylcyclopentanone) was oxidized by leading the emerging gas stream onto the surface of 0.1 ml of 65 % HNO₃ in a tube. After heating the tube at 100° for 2 min and diluting the mixture with cold water, the products were isolated by extraction with ether and the ether evaporation on a water bath. Synthesized 2-methylcyclopentanone was oxidized in the same way.

Table 1. Main distillate fractions.

Fraction	B.p.	Wt. % of total distillate
4	80–100° (760 mm)	2.6
5	132–142° (760 »)	7.7
6	48–49° (7 »)	3.4
8	53–57° (7 »)	4.7
13	79–81° (7 »)	3.8
15	88–89° (7 »)	6.0
16	93–96° (7 »)	3.4
18	101–104° (8 »)	4.8
20–22	112–115° (9 »)	7.7
24	123–124° (8 »)	4.2
29–30	148–150° (9 »)	6.2
33	174–175° (10 »)	4.2
37–38	193–205° (10 »)	8.5
Total		67.2 %

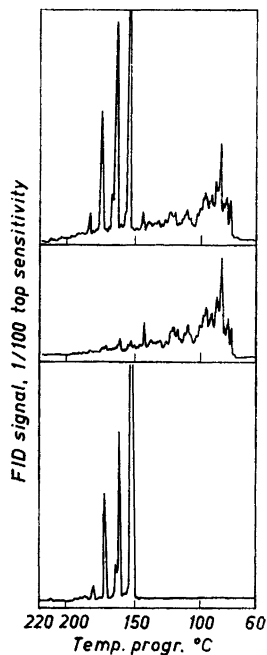


Fig. 1. Programmed temperature GLC on a BDS column. From top to bottom: total distillate, neutral + alkaline fractions, alkali-soluble fraction.

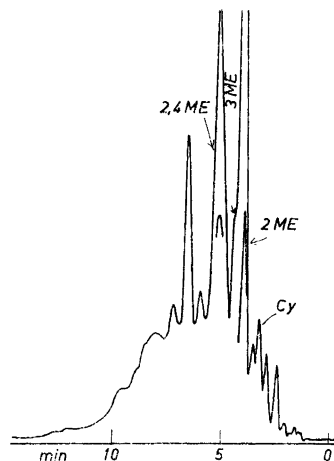


Fig. 2. Gas chromatogram at 150°C of the distillate fraction 5 (Table 1). Horizontal axis = retention time. Cy = cyclopentanone; 2 ME = 2-methylcyclopentanone; 3 ME = 3-methylcyclopentanone; 2,4 ME = 2,4-dimethylcyclopentanone.

RESULTS AND DISCUSSION

In the distillation in the spinning band column, 38 fractions were collected. The total yield of distillate boiling up to 200°C at 10 mm was 74.2 % of the weight of the original oil. No sharp separations were achieved by distillation alone. The largest fractions are presented in Table 1; each contained 4–6 different compounds.

Phenols. For comparison, temperature-programmed gas chromatography was carried out on the total distilled matter as well as on the phenolic and neutral+basic fractions of the volatile oil from the digestion L 1002. These fractions were resolved by shaking the total distillate with ether and N sodium hydroxide solution. The results (Fig. 1) indicate that the neutral matter was present mainly in the low-boiling fractions 3–8 (b.p. <55° at 7 mm), whereas the fractions boiling between 70 and 125° at 8 torr contained monohydric phenols and guaiacol and its homologs. Paper chromatography

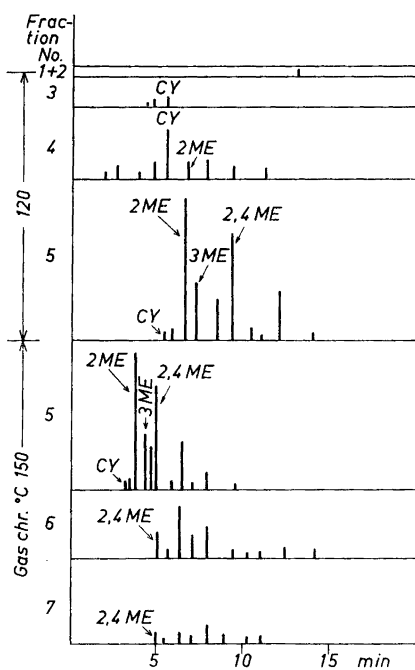


Fig. 3. Schematic gas chromatograms for fractions 3–8 (Table 1). See p. 3204.

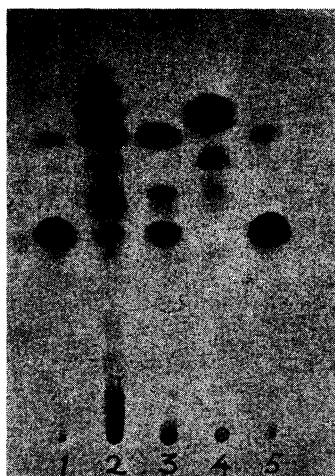


Fig. 4. Thin layer chromatograms of 2,4-dinitrophenylhydrazones of cyclopentanone and its homologs (see p. 3206). 1 and 5: cyclopentanone-DPN. 2: DPN:ones from distillate fraction 5 (Table 1 and Fig. 2). 3: 2-methylcyclopentanone-DNP containing also cyclopentanone-DNP. 4: 2,4-dimethylcyclopentanone.

indicated that catechol and its homologs begin to appear in the distillate fractions from number 16 (b.p. 93° at 7 torr) upwards.

The identification of the phenolic compounds was only preliminary.

By comparing gas chromatographic retention values of the isolated compounds on column A (at 175°C, $u=40$ ml/min) with those of known compounds, it was concluded that fractions 13–15 contained *phenol* ($t_r=4.3$ min), and *guaiacol* ($t_r=8.3$ min), fractions 13–16 *o-cresol* ($t_r=6.3$ min), fractions 15–18 *m-* and/or *p-cresol* ($t_r=12.8$ min), fractions 16–18 *p-ethylphenol* ($t_r=9.0$ min), fractions 17–22 *p-propylphenol* ($t_r=15.0$ min) and fraction 22 possibly also *ethylguaiacol* ($t_r=18.3$ min). Of these compounds, only guaiacol was isolated by preparative gas chromatography and identified by its infrared spectrum.

Low-boiling neutral substances. Fig. 2 shows, as an example, a gas chromatogram of the distillate fraction 5. Fig. 3 shows schematic gas chromatograms for the fractions 3–8. The heights of the lines are proportional to the areas of the peaks, and their abscissæ indicate the retention times.

A compound was isolated by preparative gas chromatography from fraction 4, and as its DNP:one by TLC (Fig. 4). It was concluded from its IR spectrum to be *cyclopentanone*.

From the DNP:ones obtained from fraction 5, a compound was isolated by TLC which had the same retention time as 3-methylcyclopentanone-DNP:one (Fig. 4). The infrared spectra were identical. Gas chromatograms of fractions 4–6 had a peak with the same retention time as 3-methylcyclopentanone (Table 2).

Another compound isolated from the same fraction by GLC was identified as 2-methylcyclopentanone by means of its infrared (Fig. 5b) and mass spectra (Fig. 6a) and by the mixed melting point of its semicarbazone with that of the synthetic compound.

A fourth compound isolated by GLC from fractions 5 and 6 had an IR (Fig. 5d) and a mass spectrum (Fig. 6b) suggesting that it was a homolog of methylcyclopentanone. Paper chromatograms of the product obtained on nitric acid oxidation showed the presence of two acids. Neither of these was glutaric or α -methylglutaric acid, $R_G=0.75$: X_1 , $R_G=1.1$: X_2 , $R_G=1.6$. Assuming that methylcyclopentanones would react in a similar way as 2-methylcyclohexanols when oxidized with nitric acid and give a mixture of an α -methyldicarboxylic acid and a dicarboxylic acid lacking the α -methyl group, the retention times seemed to indicate that of the possible homologs of methyl-

Table 2. Gas chromatographic retention times in minutes.

Column	A	E	F
Temperature, °C	120	80	75
Flow rate, ml/min	40	30	30
Cyclopentanone	5.5	7.8	5.8
2-Me-cyclopentanone	6.6	10.6	5.8
3-Me-cyclopentanone	7.4	11.0	7.1
2,4-Dime-cyclopentanone	9.4	15.8	7.1

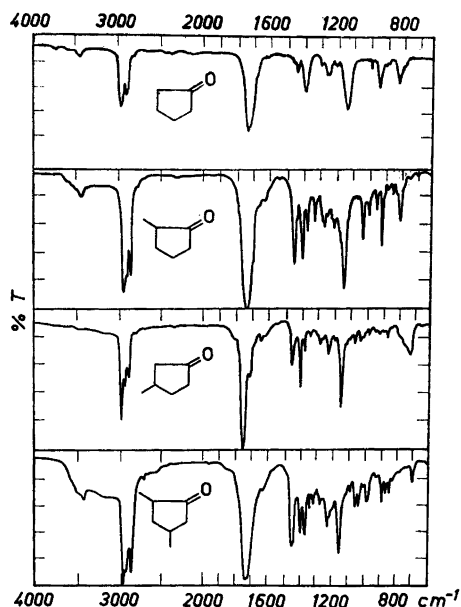


Fig. 5. IR spectra, capillary film. From top to bottom: cyclopentanone, 2-methyl-, 3-methyl-, and 2,4-dimethylcyclopentanone.

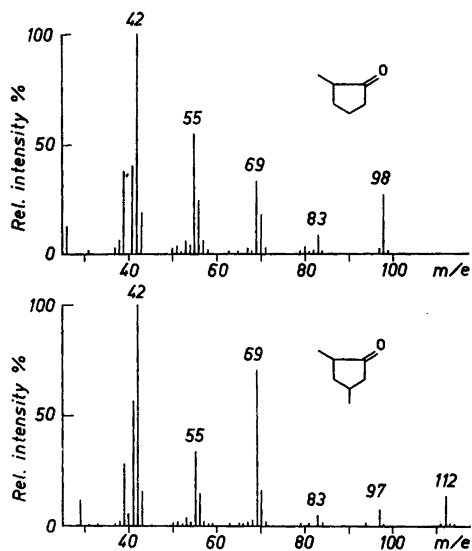


Fig. 6. Mass spectra. Upper, 2-methylcyclopentanone, CEC. Lower, 2,4-dimethylcyclopentanone, LKB.

cyclopentanone, the isolated product is most probably either the 2,4-dimethyl- or the 3-ethyl compound. Its IR spectrum was identical with that of 2,4-dimethylcyclopentanone.

The contents of cyclopentanones in the distillate were estimated (Fig. 3) to be: cyclopentanone, 1.1 %; 2-methylcyclopentanone, 2.8 %; 3-methylcyclopentanone, 1.1 %; 2,4-dimethylcyclopentanone, 3.1 %, or together about 8 % of the total distillate, or 5.9 % of the oil distilled.

The IR spectra of all four cyclopentanones described show a strong absorption band at 1150 cm^{-1} (Fig. 5). The carbonyl group absorbs at a relatively high wavenumber as shown by Castinel¹² for cyclopentanone and its 3-methyl derivative.

The mass spectra of 2-methylcyclopentanone (Fig. 6) are similar to the spectrum of cyclohexanone. Though no attempts were made to investigate the mechanisms of fragmentation of these substances, they seem to be easily explained by the work of Seibl¹³ and Natalis¹⁴ on cyclohexanone and cyclopentanone, the fragment with $m/e=69$ possibly being $\text{H}_3\text{C}-\text{C}(=\text{CH}_2)-\text{C}^+=\text{O}$ for both compounds, and the base peak with $m/e=42$ possibly due to the ketene ion $\text{H}_2\text{C}=\text{C}^+=\text{O}$.

Some possible mechanisms for the formation of cyclopentanone and its homologs on heatings of black liquor with alkali will be discussed by G. Nordman in a separate paper.

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