

STRUCTURE AND REACTIVITY OF A WYODAK SUBBITUMINOUS COAL

Shuyen L. Huang and Ramani Narayan

Laboratory of Renewable Resources Engineering
and
Coal Research Center
A. A. Potter Engineering Center
Purdue University
West Lafayette, IN 47907

INTRODUCTION

The linkages in coal which are susceptible to attack and cleavage are the ether, thioether, and diaryl alkane linkages (1-3). Most approaches to cleave linkages in coal involve reacting coal under severe conditions of temperature and pressure. These severe processing conditions often result in non-specific bond cleavages and retrogressive (bond-forming) reactions. In this paper, we report on the reaction of a Wyodak subbituminous coal with a powerful site-specific reagent, namely potassium-crown ether (K-CE) under thermally mild conditions of room temperature and atmospheric pressure. The selective cleavage of ethers (4-6), sulfides and sulfones (7) by solvated electrons is documented. The solvated electrons generated by K-CE in THF can transfer onto the aromatic substrates in coal. This results in the formation of aromatic radical anions or dianions which undergo cleavage reaction at aryl ether and diaryl alkane linkages (8,9,10). The crown ethers also function as phase transfer catalysts and promote the electron transfer to the coal. The cleavage of ether linkages can render coal soluble with the formation of "coal oligomer" fragments. In this paper, the solubility of K-CE treated Wyodak coal in THF and aqueous alkali solution is reported. The analysis of the solubilized coal by IR, 1H and ^{13}C NMR is also described.

EXPERIMENTAL

Reaction of Wyodak Coal with K-CE Reagent

A 500 ml round bottom flask was flame dried and flushed with nitrogen. Potassium metal (12 g, 307 mmole) was transferred into the flask in a glove box under nitrogen atmosphere. 350 ml of THF solution of crown ether (16.2 g, 61 mmole) was added to the potassium metal via a double-ended needle at 0°C when a dark blue solution was obtained. Four gram of Wyodak coal (C = 70.20%; H = 4.69%; O = 23.76%; N = 0.86%; S = 0.39%; 100 mesh; prewashed with methanol, pentane and dried under vacuum at 105°C for 24 hrs) was added to the K-CE/THF solution. The reaction mixture was stirred for 24 hours (or 5 days in some runs) at room temperature under nitrogen atmosphere. It was then cooled to 0°C and quenched with water. The THF was removed by rotoevaporation and the remaining aqueous slurry of coal was freeze dried to remove the water. The work up of the reacted coal is shown in Figure 1.

NMR Spectroscopic Analysis

1H NMR spectra were obtained with a Nicolet NTC-470 spectrometer (470 MHz) at ambient temperature. Coal samples (15 mg) were dissolved in 0.5 ml of chloroform- d_3 or DMSO- d_6 . Proton decoupled ^{13}C NMR spectra were obtained with a Nicolet NTC-200 at 50 MHz at ambient temperature (or 40°C) using a 12 mm probe. The sample concentration was 100 mg/ml of NMR solvent. For the THF-1 fraction chloroform- d_3 was used, for the THF-2 fraction and the alkali-methylated coal DMSO- d_6 was used, and for the alkali-soluble fraction NaOD/ D_2O was used.

Infrared Spectra

Figure 2 showed the infrared spectra of various extracts obtained from the K-CE reaction with the coal. IR spectrum of the THF-1 fraction shows sharp aliphatic C-H stretching bands below 3000 cm^{-1} , and aliphatic C-H bending bands at 1450 and 1375 cm^{-1} suggesting that this extract contains predominantly aliphatic material. In addition to the C-H stretching bands below 3000 cm^{-1} , the spectrum of the THF-2 fraction shows a broad OH stretching vibration in the $3100\text{-}3200\text{ cm}^{-1}$ region and two vibration bands at 1410 cm^{-1} and 1375 cm^{-1} corresponding to the C-O stretching vibrations. Thus, the THF-2 extract also contained aliphatic material which may be attached to a hydroxy aromatic ring system.

Except for the untreated Wyodak coal, the IR spectra of all the extracts showed absorption bands for carbonyl at 1725 and 1710 cm^{-1} . Using β -naphthol as a model compound to react with K-CE, the results showed that β -tetralone, 5,8-dihydro-2-naphthol and 5,6,7,8-tetrahydro 2-naphthol were the major products. This indicated that in addition to cleavage reactions, reduction of the coal phenolic units to carbonyl units is occurring. This explains the observed 1725 cm^{-1} carbonyl bands in the IR spectra of the K-CE treated coal fractions. In the alkali-soluble fraction an additional carbonyl band at 1710 cm^{-1} along with the broad stretching vibration extending from 3500 cm^{-1} suggested the presence of -COOH groups. The IR spectrum of the methylated product of the alkali-soluble fraction (spectrum not shown here) showed the carbonyl absorption was shifted to 1730 cm^{-1} corresponding to the carbonyl of ester groups. This supported the presence of carboxyl groups in the alkali-soluble fraction. The carboxylated coal fragments may have arisen by cleavage of ester linkages in the coal by the K-CE reagent. In fact, it has been suggested that as much as 58% of the oxygen in this coal is present as ester linkages (11). However, more work needs to be done to quantify how much of the -COOH groups in the alkali fraction arise from ester cleavage and how much were originally present. Interestingly, 10% of Wyodak coal can be solubilized in aqueous NaOH at room temperature and the IR spectrum of the solubilized product showed carbonyl absorption bands, suggestive of ester linkages being hydrolyzed.

^1H and ^{13}C NMR Spectra

Proton NMR spectra of the soluble fractions are shown in Figure 3. The spectrum of THF-1 (Figure 3A) confirmed the presence of predominantly aliphatic material in this extract. The dominant sharp signal at 1.3 ppm is characteristic of methylene protons of long chain polymethylenes. The sharp signal at 1.0 ppm corresponds to paraffinic CH_2 or CH_3 groups gamma or further from an aromatic ring. The spectrum of THF-2 also showed the presence of long-chain polymethylene. The group of signals in the 2-3 ppm region can be assigned to dihydro aromatic protons or protons α to an aromatic ring. Based on the mechanism of the K-CE reaction, reduction of aromatic rings to dihydro and even tetrahydro aromatics was expected and the NMR evidence nicely corroborates it.

The phenolic proton (5-7 ppm or 8.5-11 ppm) and carboxylic proton signals (8.5-11 ppm) were found in the spectrum of the alkali-soluble fraction (Figure 3C). The spectrum of the methylated product of the alkali-soluble fraction (Figure 3D) showed the disappearance of the phenolic or carboxylic protons. Instead, a broad signal appeared at 3.8-4.2 due to the $-\text{OCH}_3$ protons of methoxyl ester or phenolic methyl ester. The ^{13}C NMR spectrum of the methylated product (spectrum not shown) also showed two distinct signals at 52 ppm and 56 ppm corresponding to methoxyl of phenolic and aromatic esters, respectively. The broad signal at 12 ppm in Figures 3B, 3C and 3D, could probably be due to strongly intramolecular H-bonded -OH groups.

Proton decoupled ^{13}C NMR spectra of the THF-1 fractions from three successive K-CE reactions are shown in Figure 4. The ^{13}C NMR spectra also strongly support the presence of long chain polymethylene groups in the extract. The most intense signal is at 30.2 ppm which is generally assigned to the internal methylene carbons of straight-chain alkanes (an average carbon chain length of approximately 8). The presence of a broad spectral envelope in the 15-50 ppm region in addition to the sharp alkane lines is indicative of the extract's complexity arising out of the presence of only small amounts of these polymethylene-type compounds. The broad band on the 120-140 ppm region is due to the aromatic and polycyclic aromatic species of the extract.

RESULTS AND DISCUSSION

Solubility of Wyodak Coal

After the reaction with K-CE, the Wyodak subbituminous coal was fractionated into THF soluble fractions (THF-1 and THF-2) and an alkali-soluble fraction according to the work-up shown in Figure 1. Due to the limitation of diffusion of solvated electrons into the coal, the insoluble coal residue after each K-CE reaction was subjected to second and third K-CE reactions. The successive K-CE reactions with coal solubilized additional coal. It was expected that the analysis and comparison of soluble fractions among each successive K-CE reaction may indicate whether or not coal is composed of some common major structural fragments (coal oligomers) which are linked together to form the coal network.

Using conditions described in the experimental section, for each K-CE reaction, 20-30% of the coal was solubilized into the THF and aqueous alkali fractions. However, it was found that the solubility of coal depends on the amount of potassium and crown ether used and the length of the reaction time. Table 1 summarizes the results of various K-CE and coal reactions using different reagent stoichiometries and reaction times. The results show the alkali-soluble fraction increased significantly with a long reaction time. This suggested that more of the phenolic-type ether linkages were cleaved, thus increasing the alkali-soluble materials. When the amount of crown-ether was increased, the THF-1 soluble fraction increased 3- to 6-fold. The increase in the concentration of solvated electrons, due to the presence of more crown-ether, increased the amount of aromatic ring systems and phenolic or naphthol-type structures, being reduced, thus increasing the THF solubility. When the ratio of potassium to coal was decreased, by using a large quantity of coal, the solubility of coal decreased significantly. This could be attributed to limitations in diffusion rates and availability of sufficient solvated electrons.

Table 1. Solubility of Wyodak Coal

Reaction	Ratio of k/coal (g)	Ratio of K-CE (mole)	Reaction Time	THF-1 (%)	Alkali-Soluble (%)	THF-2 (%)
One K-CE Reaction	3	5	4 days	2	47	3
Total of two K-CE Reactions	3	5	4 days	2	59	5
Total of two K-CE Reactions	3	3	20 hr	6	40	3
Total of two K-CE Reaction	3	2	20 hr	12	35	4
Total of three K-CE Reaction	1	5	2 days	2	34	10

Microanalysis

Elemental compositions of the soluble fractions, the insoluble fraction and the original Wyodak coal are shown in Table 2. The results show that after each K-CE reaction of coal there was an increase in the number of hydrogen atoms. The THF-1 fraction showed high H/C ratio indicating the fraction is rich in aliphatic material. IR and NMR spectra of the THF-1 fraction demonstrated the presence of long chain methylene groups. The hydrogen uptake is due to reactions such as Birch-Huckel-type reduction, and cleavage of aliphatic bridges and ether linkages occurring during the K-CE reaction with coal.

Table 2. Results of Elemental Analysis of Wyodak Coal

Coal Samples	C	H	O	N	S	Ash	H/C
Wyodak Coal	70.29	4.69	23.76	0.86	0.39	5.68	0.80
THF-1 Fraction	77.63	9.78	11.68	0.36	0.54	0.58	1.51
Alkali-Soluble	68.38	4.95	25.50	0.93	0.33	0.39	0.87
Insoluble Fraction	71.68	5.36	21.95	0.59	0.42	2.87	0.90

The similarity between the spectrum of the THF-1 fractions from each successive K-CE reaction, strongly suggest that the major components of THF-1 solubles are a integral part of the coal network and not just "trapped molecules". The results also indicated that coal is composed of some common structural fragments (coal oligomers). Upon each K-CE reaction, some part of the coal network was being snipped releasing these soluble coal oligomer fragments.

Figure 5 shows the ^{13}C NMR spectra of alkali-soluble fractions. The broad signals in the spectra again shows the complexity of the compounds in the extracts. Broad signals at 0-50 ppm correspond to aliphatic carbons. Aromatic carbons bonded to oxygen appeared between 150 and 160 ppm (aryl ethers and phenols). The region between 100 and 130 ppm corresponds to protonated aromatic carbons. Olefinic carbons are also observed.

SUMMARY

The K-CE reagent has provided a way to dismantle the coal network and release soluble coal oligomer fragments, without recourse to any thermal or pressure effects. Up to 50% of Wyodak coal can be solubilized into THF and the alkali-soluble fractions with the alkali-soluble fraction accounting for 90% of the total solubles. The THF-1 fraction is rich in aliphatic material, and polymethylenes were shown to be the predominant component. Alkali-soluble fraction contained primarily phenolic and carboxy groups due to the nature of the extract. In addition to ether cleavage reactions, a major reaction pathway in the coal/K-CE reaction was the reduction of phenolic groups to carbonyls. The results of successive K-CE/coal reactions showed that the structural components of the extracts from each reaction are very similar, suggesting common building blocks for the coal network.

FIMS and MS/MS analysis of the extracts are under investigation to reveal more details about the structural features of the coal.

ACKNOWLEDGMENTS

Funding for this work was provided by the Electric Power Research Institute under Contract No. RP8003-1. We are grateful to the Purdue University Biomagnetic Resonance Laboratory supported by NIH Grant No. RR01077 for the NMR spectra reported here.

REFERENCES

1. D.D. Whitehurst, in "Organic Chemistry of Coal," ed., J.W. Larsen, ACS Symp. Ser., 71, 1 (1978).
2. W. Wiser, preprints Fuel Division ACS Meeting, 20(2), 122 (1975).
3. HW. Sternberg, C.L. DelleDone, P. Pantages, F.C. Moroni, and R.E. Markbly, Fuel, 50, 432 (1971).
4. B. Weinstein and A.H. Fenselan, J. Org. Chem., 34, 126 (1969).
5. J.A. Marshall, and N.H. Anderson, J. Org. Chem., 30, 1291 (1965).
6. D.H. Eagle, Jr., J. Org. Chem., 12, 1918 (1967).
7. H.O. House, in "Modern Synthetic Reaction," W.A. Benjamin, Inc., Ch. 3, p. 145 (1971).
8. L. Schanne and M.W. Haenel, Tet. Letters, 44, 4245 (1979).
9. C.J. Collins, H.P. Hombach, B.E. Maxwell, N.C. Woody, and B.M. Benjamin, J. Amer. Chem. Soc., 102, 851 (1980).
10. S. Huang, K. Wood, and R. Narayan, Amer. Chem. Soc., Div. Fuel Preprints, 32 (1986).
11. K. E. Chung, I. B. Goldberg, and J. J. Ralitto, Proceedings: Ninth Annual EPRI Contractors Conference on Coal Liquefaction, p. 381, March (1985).

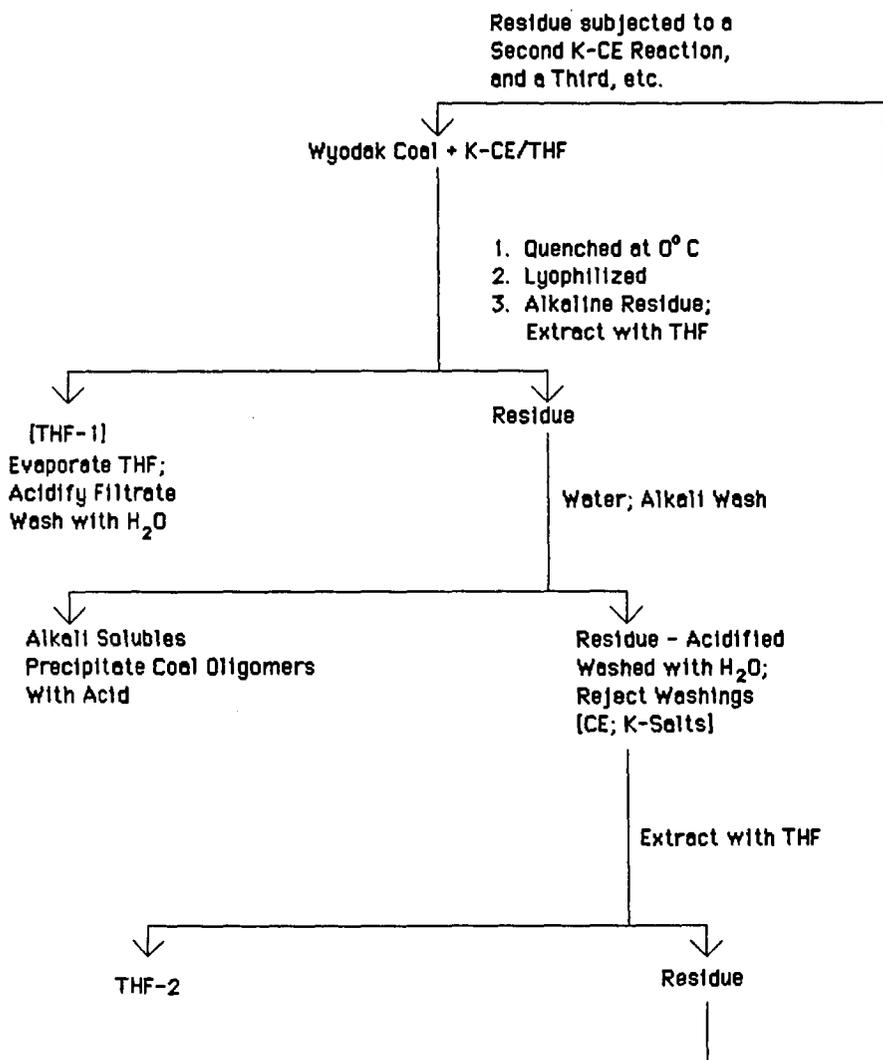


Figure 1. Work-Up of the Coal/K-CE Reaction.

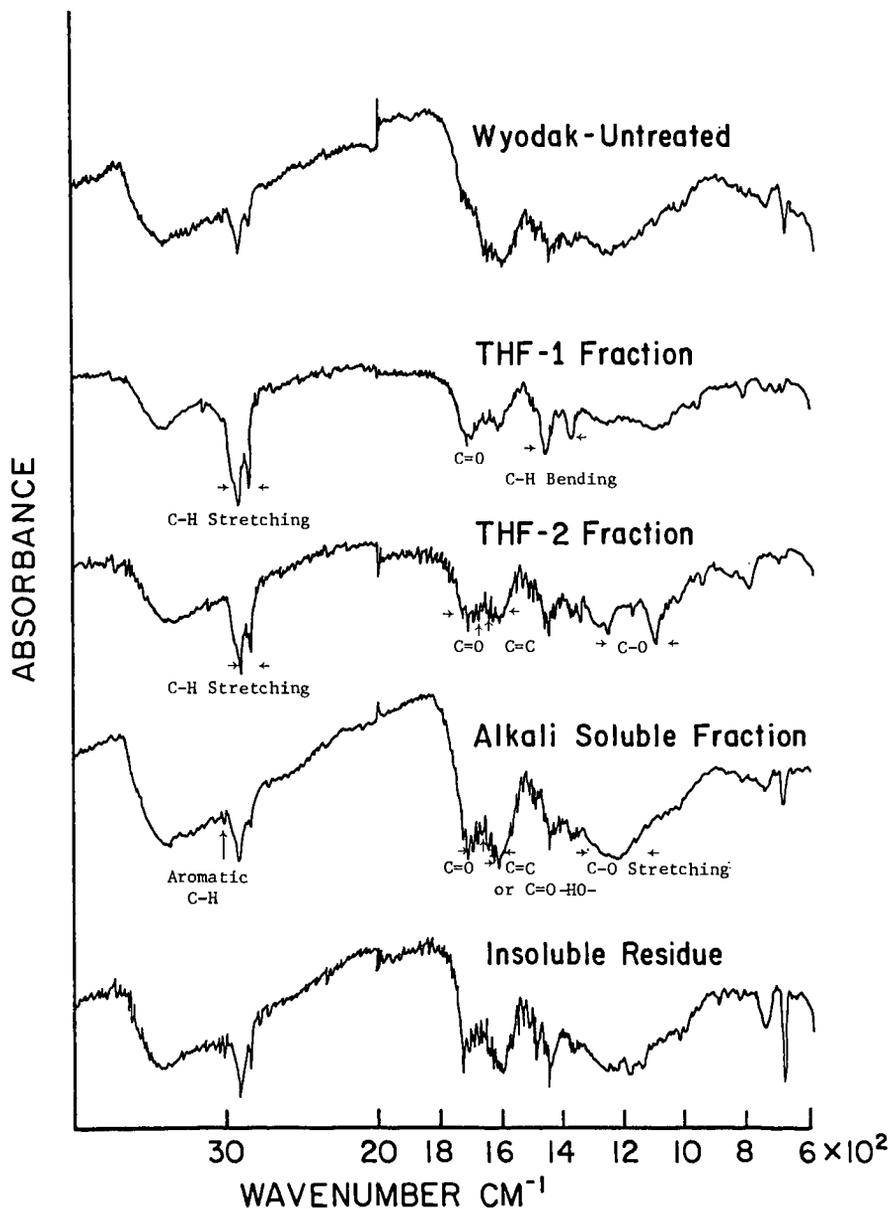


Figure 2. IR spectra of various fractions of K-CE treated Wyodak subbituminous coal.

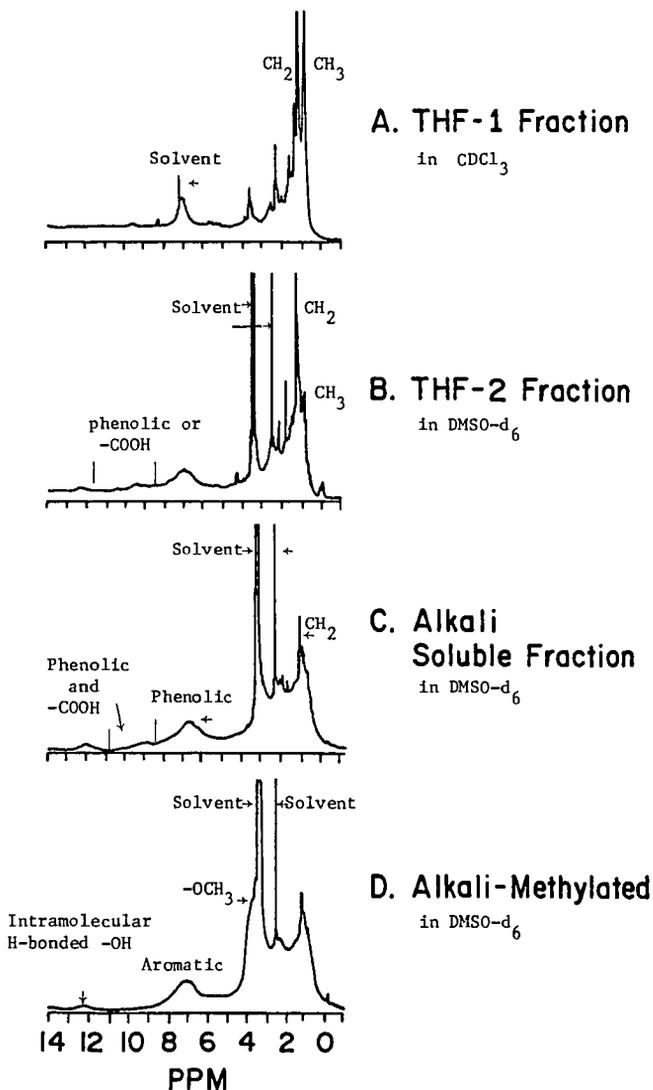


Figure 3. 470 MHz ^1H NMR spectra of extracts from reaction of Wyodak coal with K-CE.

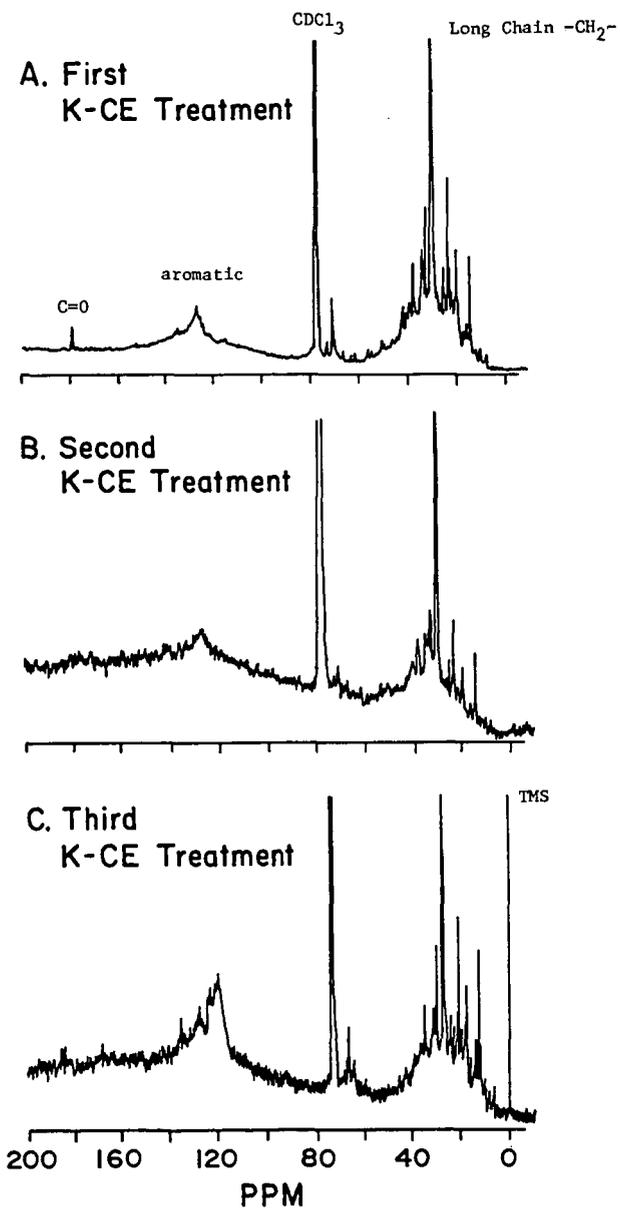


Figure 4. Proton decoupled ¹³C NMR spectra (50 MHz) of THF-1 in chloroform-d.

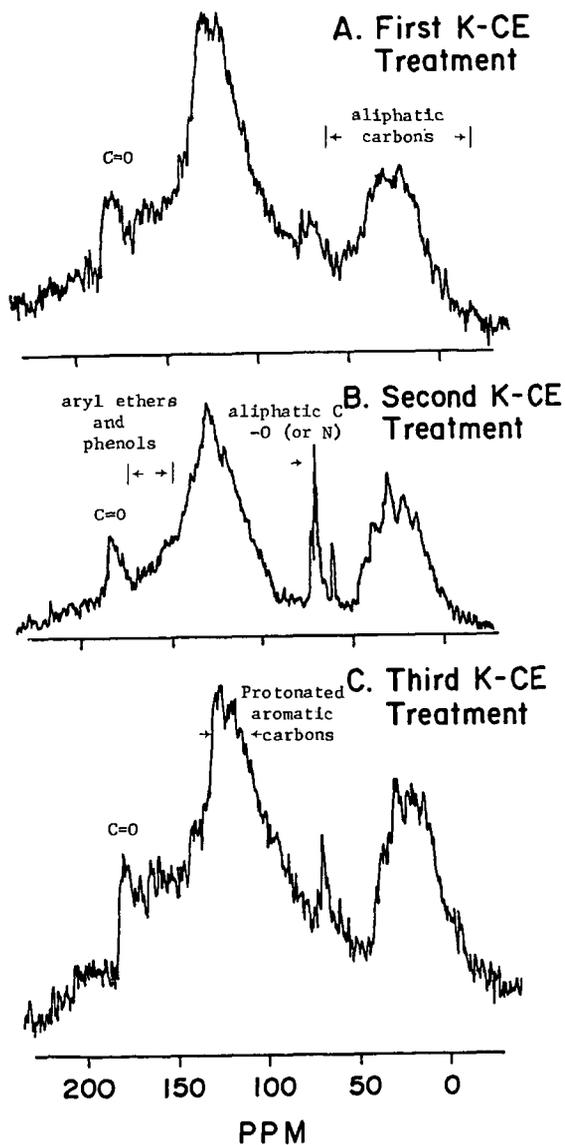


Figure 5. Proton decoupled ^{13}C NMR spectra (50 MHz) of alkali-solubles in $\text{NaOD}/\text{D}_2\text{O}$.