

Characterization of Hydrolytically Solubilized Coal

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INTRODUCTION

In a search for relatively mild methods for solubilizing coal, we have found that treating a bituminous coal with potassium hydroxide in ethylene glycol at 250°C is quite effective. The use of alkali in protic solvents is not new. Recently, Ouchi and co-workers (1) have reported in detail the reaction of coal with ethanolic KOH from 260° to 450°C. Also, Ross and Blessing have looked at both iPROH/iPROK (2) and MeOH/KOH systems at 400°C (3). In an early study Pew and Withrow found that the yield of 2-ethoxy-ethanol extract at 135°C for a bituminous coal increased from 9.4% to 31.3% with the addition of KOH (4). In general at lower temperatures (< 250°C) it has been found that only low rank coals are appreciably solubilized (1). We feel that the glycol is playing a special role in producing a soluble product and have characterized this product in order to understand the chemistry involved. Our conclusions are similar to those given by Ouchi (1).

We decided to use glycol as a solvent for several reasons. First, the results of Pew and Withrow (4) indicate that glycol and KOH have special properties and therefore more drastic conditions could give improved extract yields. It is easier to obtain higher reaction temperatures with glycols without using an autoclave. Finally, cleavage of C-C bonds has occurred as side reactions in Wolf-Kishner reductions (5). Also, alkaline hydrolysis at high temperatures (> 200°C) will cleave ethers (6,7) and carbonyls (7). The original objective of these experiments was to cleave these linkages and to determine their importance in the structure of coal. However, as observed by Ouchi (1) and Ross (2,3) apparently reduction is involved also as seen in the increased H/C ratio and decrease in aromatic carbons. We shall show that this is a true reduction of aromatic rings in the coal, not just an attachment of the solvent.

In the analysis of the glycol solubilized coal we have applied all the techniques used in our studies on coals, SRC and SRL products (8). The effect of the reaction on the aromatic units was shown by comparing selective oxidation products from the coal and its hydrolytic product. These results were compared with the aromaticity of the product determined by C-13 nmr. The molecular size distribution was determined using gel permeation chromatography (GPC). Also, we compared the products from glycols to those from water and alcohol alkaline hydrolysis.

EXPERIMENTAL

In a typical reaction 15 g of Illinois #2 high volatile bituminous coal [73.9% C, 5.2% H, 1.4% N, 3.4% total S (1.2% organic S), 16.1% O (by difference) on a maf basis] which was extracted by refluxing

with benzene/MeOH (3/1) was mixed with 20 g potassium hydroxide and 200 g of solvent and heated at 250°C in a rocking autoclave for 2-3 hours. With triethylene glycol the reaction was also run at atmospheric pressure under a nitrogen sweep. The autoclave was cooled and the gases produced were collected for mass spectrometric analysis. The homogeneous, alkaline, reaction mixture was poured into water, acidified with conc. HCl, filtered and dried *in vacuo* at 100°C. The product was successively extracted with hexane, benzene-methanol (1:1) and pyridine under reflux with the results shown in Table 1.

The hexane insoluble product from Reaction No. 1 and the original coal were derivatized with d₆-dimethylsulfate and oxidized with aq. Na₂Cr₂O₇ at 250°C for 38-48 hours (8). The resulting aromatic acids were derivatized with diazomethane and analyzed by gas chromatography mass spectrometry. The identifications of the esters were confirmed from retention times and mass spectra of authentic compounds, from published data and from high resolution mass spectrometric analysis of the mixture.

The molecular size distribution was determined using gel permeation chromatography with a series of four μ-styragel columns (500 Å, 3 x 100 Å). Tetrahydrofuran was used as the elution solvent with a UV detector set at 254 nm (see Fig. 1, Reaction 1 product). Calibration curves (Figure 2) were obtained under the same conditions for linear polymers and a series of aromatic hydrocarbons.

The C-13 nmr spectra were obtained on a Bruker WP-60 at 15.08 MHz, with 3 sec delays, no decoupling and typically 50,000 scans. The samples of chloroform soluble product were made up to 50% (w/v) in deuteriochloroform.

RESULTS AND DISCUSSION

In the initial experiments with triethylene glycol (TEG) it was noticed that the H/C of the product (1.08) was significantly higher than that of the coal (0.84). This would indicate that either reduction or solvent attachment or both were occurring. Also, the yield of solid product was greater than the amount of the original coal. The hexane extract, which was significant in this case (11.9%), was shown by solid probe MS and GCMS to be mostly glycol degradation products. When ethylene glycol was used there was no increase in weight and the amount of hexane extractable material was reduced. Both Ouchi (1) and Ross (2,3) observed an H/C increase with the alcohols.

With the increase in H/C ratio one would expect a decrease in the fraction of aromatic carbons (fa). From the C-13 nmr spectra (Fig. 3) the fa for product #1 was determined to be 0.50. This same coal has been shown by fluorination to have an fa of approximately 0.69 (9). The attachment of ethylene glycol groups (ROCH₂CH₂-O-COAL) has been determined to be 5.1% of carbons from the integration of the peaks from 55-65 ppm. We have found these peaks to be absent in other coal products such as SRC. Also, the importance of the carbonyl carbon peak at 215 ppm will be discussed later. However, these data do not exclude the reaction of ethylene (CH₂=CH₂) with the coal as mentioned by Ouchi (1).

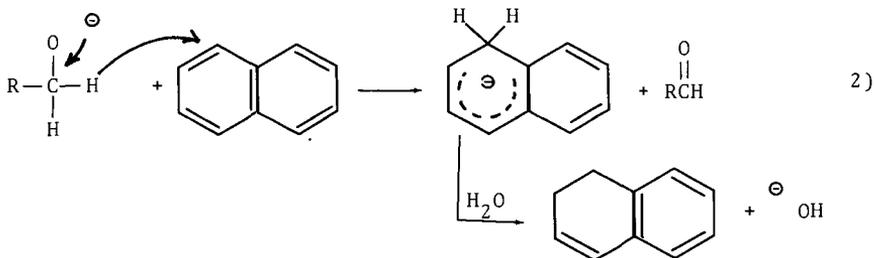
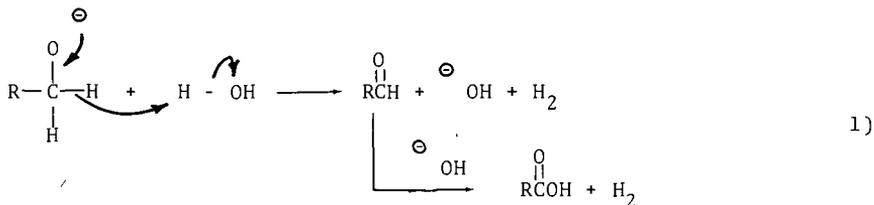
The best evidence for the occurrence of polycyclic aromatic ring reduction is the comparison of the aq. Na₂Cr₂O₇ oxidation products of the hydrolytic product with those of the original coal (Table 2).

The gas chromatogram for the volatile methyl esters from the original coal oxidation is shown in Figure 4 with identification in Table 3. As we have shown before a significant amount of polycyclic aromatics such as phenanthrene and naphthalene carboxylic acids and hetero-aromatics including dibenzofuran and xanthone carboxylic acids were isolated (8). Figure 5 is the gas chromatogram for the oxidation products from the hydrolytic product with peak identification in Table 3. The major products are benzene, methoxybenzene, and methyl-benzenecarboxylic acids. The acids from the coal and hydrolytic product are compared in Table 2. It is obvious that the polycyclic aromatics and heteroaromatics have been reduced and degraded. As expected the furan ring in dibenzofuran was destroyed. Since aqueous alkali treatment has been used as a method for removal of sulfur from coal (10), it is not surprising that in Reaction #1 the total sulfur was reduced from 3.5% (1.2% organic) to 0.72%. Most of the loss was due to the removal of inorganic sulfur, but a significant amount of organic sulfur including dibenzothiophene was removed. The yield of phenanthrene and anthracene (isolated as anthraquinones) carboxylic acids has been reduced to a nondetectable level. We and Ross (3) have observed independently that anthracenes are reduced with alcoholic alkali. The greater amount of hydroxybenzene compounds in the product indicate that as expected aryl and arylalkyl ethers have been cleaved. The exception to this is the aryl methyl ethers which from the labeling experiments with d_6 -dimethylsulfate appear to be stable.

Other characteristics of the hydrolytic product can be seen in the gel permeation chromatogram shown in Figure 1. For comparison it has been superimposed on a chromatogram for a SRC (11) using the same amount of sample. The hydrolytic product has a higher molecular weight distribution than the SRC. Using the aromatic hydrocarbon curve from Figure 1, the M.W. runs from approximately 350 to 1500. Because of the lower temperature of the reaction (250° compared to 450°C), this coal has not been so extensively fragmented. The lower UV absorption of the hydrolytic product (HSC) again indicates a lower aromaticity compared with the SRC which has an $f_a = 0.85$ from C-13 nmr data. Figure 2 demonstrates a problem encountered in using GPC for coal product analysis, that is which standards should be used. We chose the aromatic hydrocarbons because they were more representative of the hydrolytic product than linear polymers.

From examination of Table 1 it is evident that glycol is superior to other protic solvents for hydrolysis. There are at least two possible reasons for this. First, the glycol is better at solvating the positive ion. Secondly, the glycol may be more effective for reducing the aromatics in coal. Even in a nonpolar solvent such as toluene (Reaction #3) TEG brought the KOH into solution and gave a substantial yield of soluble product. The effects of base strengths were examined by changing the alkali metal using Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ . However, no trends were found in the extraction yields and the GPC indicated a possible increase in M.W. with increase in size of the ion.

The alkaline oxidation of alcohols and glycols is thought to involve hydride transfer with the intermediate formation of the corresponding aldehyde (7,12) (Eq. 1).



Therefore, a possible pathway for reduction is by a hydride transfer to an activated aromatic ring (Eq. 2). Hydrogenation with H_2 can be ruled out for two reasons. First, there are no active catalysts available. Secondly, the triethylene glycol reactions were conducted in an open system so that the H_2 could escape and yet the decrease in aromatic carbon was observed. Also alkaline oxidation of reduced phenols and alcohols could account for the carbonyls seen in the C-13 nmr spectra.

CONCLUSIONS

From the characterization of the hydrolytically solubilized coal with glycols the following observations can be made: 1. The polycyclic aromatic rings are being reduced. A possible mechanism is hydride transfer from the solvent. Also oxygen heteroaromatics are destroyed. 2. Arylalkyl ethers are being cleaved by this process. 3. The ability of the glycols to chelate the positive alkali metal ion could contribute to the enhanced yields of soluble coal compared to other protic solvents.

This study demonstrates the utility of using a multi-pronged analytical and chemical approach to the study of non-volatile coal products.

ACKNOWLEDGEMENTS

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Table 1
Yields and Solubilities of the Hydrolytic Coal Products in Weight Percent^a

Reaction #	Solvent	Yield	Hexane	Benzene/ MEOH(1/1)	Pyridine	Insoluble
1	Triethylene glycol (TEG)	123	11.9	46.8	37.3	4.1
2	Ethylene glycol	90	1.3	48.9	42.2	7.4
3	Toluene-TEG ^b	124	0.6	46.6 ^c	35.1	17.7
4	Water	86	---	18.5	12.0	69.7
5	Methanol	90	0.8	37.3 ^c	7.8	54.0

^aAll reactions at 250°C; ^b1:1 mole ratio of TEG and KOH; ^cIncludes solids soluble in the reaction solvent.

Table 2
Relative Mole Abundances from the GC Data of the Volatile Aromatic Carboxylic Acids from the Oxidation of the Coal and its Hydrolytic Product

Carboxylic acids of:	Illionois #2 Bituminous Coal	Hydrolytic Product from Reaction #1 (Table 1)
Benzene	100	100
Hydroxybenzene	1.4	10
Methylbenzene	2.3	7
Naphthalene	7.2	1
Phenanthrene	1.1	---
Dibenzofuran	1.5	0.4
Xanthone	1.3	---
Dibenzothiophene	0.5	---
Other Heteroaromatics	2.8	<1

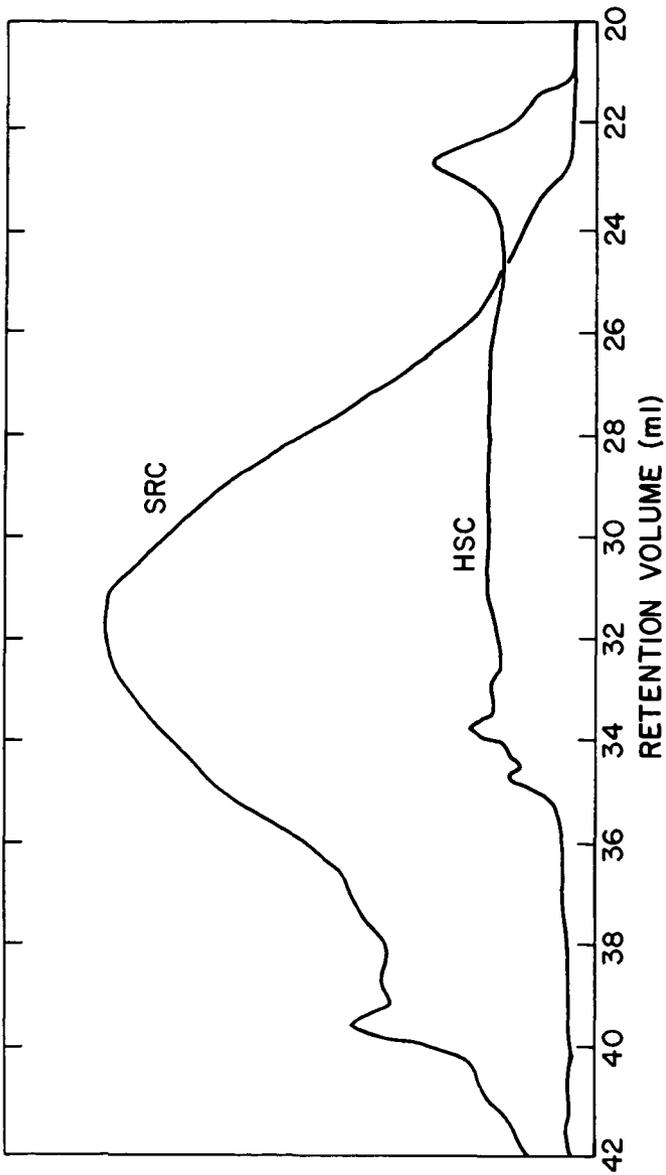
--- not detected.

Table 3
Methyl Esters of the Oxidation Products from Coal (Figure 4) and the Hydrolytic Product (Figure 5)

Peak No.		Compound	
Coal	Product		
	1	Methyl	succinate
	2	Methyl	methylsuccinate
	3	Methyl	benzoate
	4	Methyl	methylfurancarboxylate
	5	Methyl	methylbenzoate
	9	Methyl	methoxybenzoate (+d ₃ -methoxy)
	11	Methyl	methoxymethylbenzoate
	12	1	Methyl furandicarboxylate
	13	2	Methyl 1,2-benzenedicarboxylate
	14	3	Methyl 1,4-benzenedicarboxylate
	15	4	Methyl 1,3-benzenedicarboxylate
	5,7,8	Methyl	methoxy-(methoxy-d ₃)-benzoate(T)
	16	6,9,10	Methyl methylbenzenedicarboxylate
	17	Methyl	naphthalenecarboxylate
	11	Methyl	pyridinedicarboxylate
	19	13	Methyl methoxybenzenedicarboxylate (+d ₃ -methoxy)
	12,14	Methyl	(methoxy-d ₃)-benzenedicarboxylate
		Methyl	dimethylfurandicarboxylate
		Methyl	biphenylcarboxylate
	16	Methyl	1,2,4-benzenetricarboxylate
	17	Methyl	1,2,3-benzenetricarboxylate
	18	Methyl	unidentified m/e 261,230
	19	Methyl	1,3,5-benzenetricarboxylate
	20-23	Methyl	methylbenzenetricarboxylate
	26	Methyl	dibenzofurancarboxylate
	24,25	Methyl	naphthalenedicarboxylate
		Methyl	pyridinetricarboxylate
	26	Methyl	methoxybenzenetricarboxylate (+d ₃ -methoxy)
	27-29	Methyl	(methoxy-d ₃)-benzenetricarboxylate
		Methyl	fluorenonecarboxylate
	30	Methyl	1,2,4,5-benzenetetracarboxylate
	31	Methyl	1,2,3,4-benzenetetracarboxylate
	32	Methyl	1,2,3,5-benzenetetracarboxylate
	33,34	Methyl	methylbenzenetetracarboxylate
		Methyl	phenanthrenecarboxylate
		Methyl	dibenzothiophenecarboxylate
		Methyl	xanthonecarboxylate
		Methyl	anthraquinonecarboxylate
	35,36	Methyl	naphthalenetricarboxylate
		Methyl	methylxanthonecarboxylate
	37	Methyl	dibenzofurandicarboxylate
	38	Methyl	benzenepentacarboxylate
		Methyl	benzoquinolinecarboxylate
		Methyl	phenanthrenedicarboxylate
		Methyl	carbazolecarboxylate
		Methyl	xanthonecarboxylate

T indicates that identification is tentative.

Figure 1. Gel permeation chromatogram of hydrolytic product (HSC) from Reaction #1 and of a solvent refined coal (SRC) from Wilsonville, Alabama.



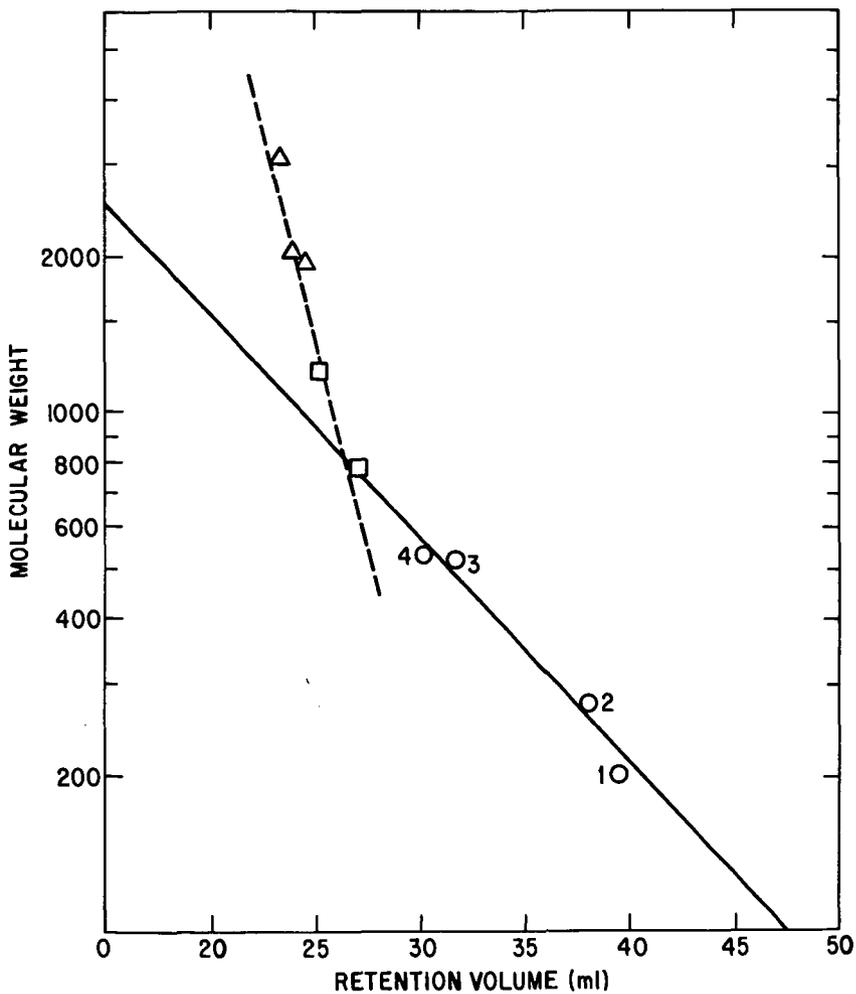


Figure 2. Calibration curves for GPC. O - aromatics, □ polyethylene standard, and Δ polystyrene standard.

Figure 3. C-13 nmr spectra of hydrolytic product from Reaction #1, in ppm from TMS.

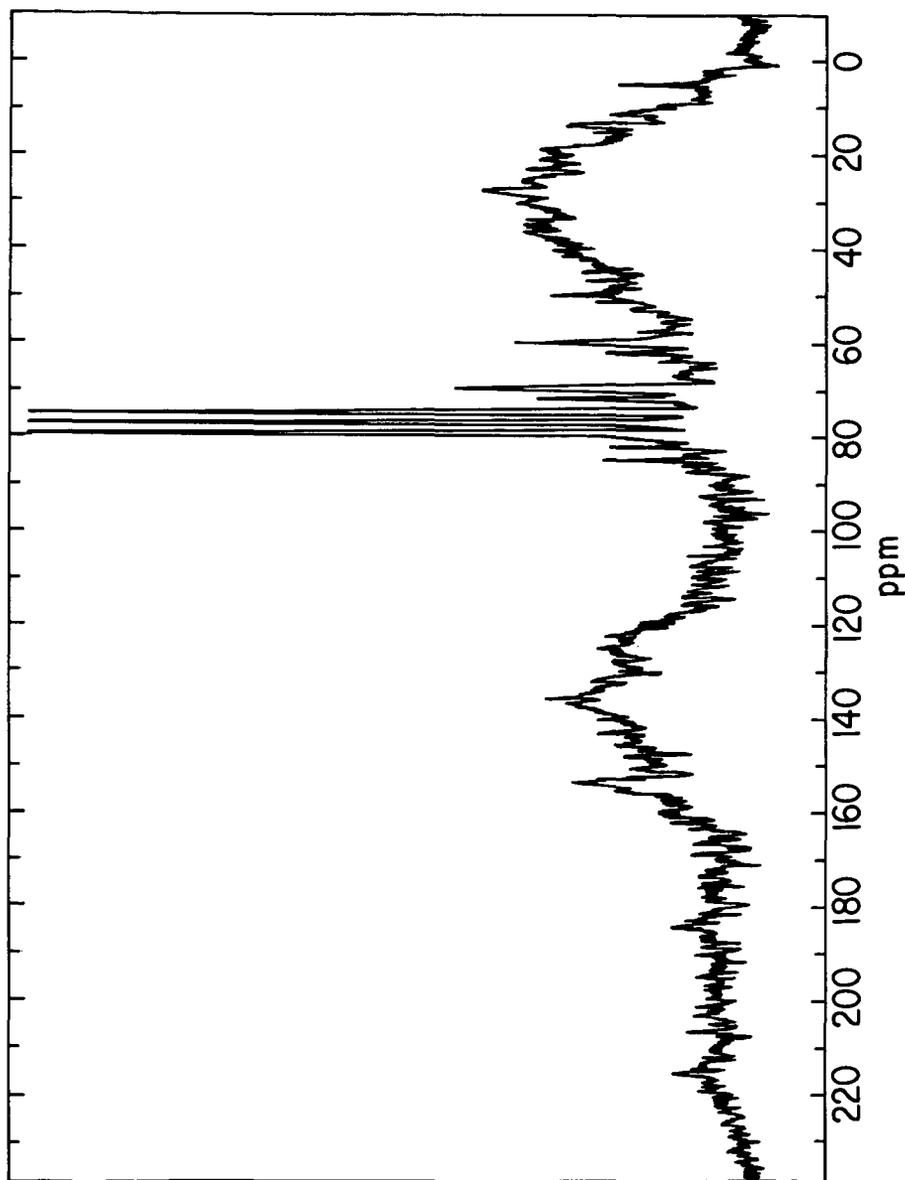


Figure 4. Gas chromatogram of methyl esters from the oxidation of Illinois #2 bituminous coal. Separated on an OV-17 support coated open tubular column (SCOT), temperature programmed at 100-250°C at 4°/min.

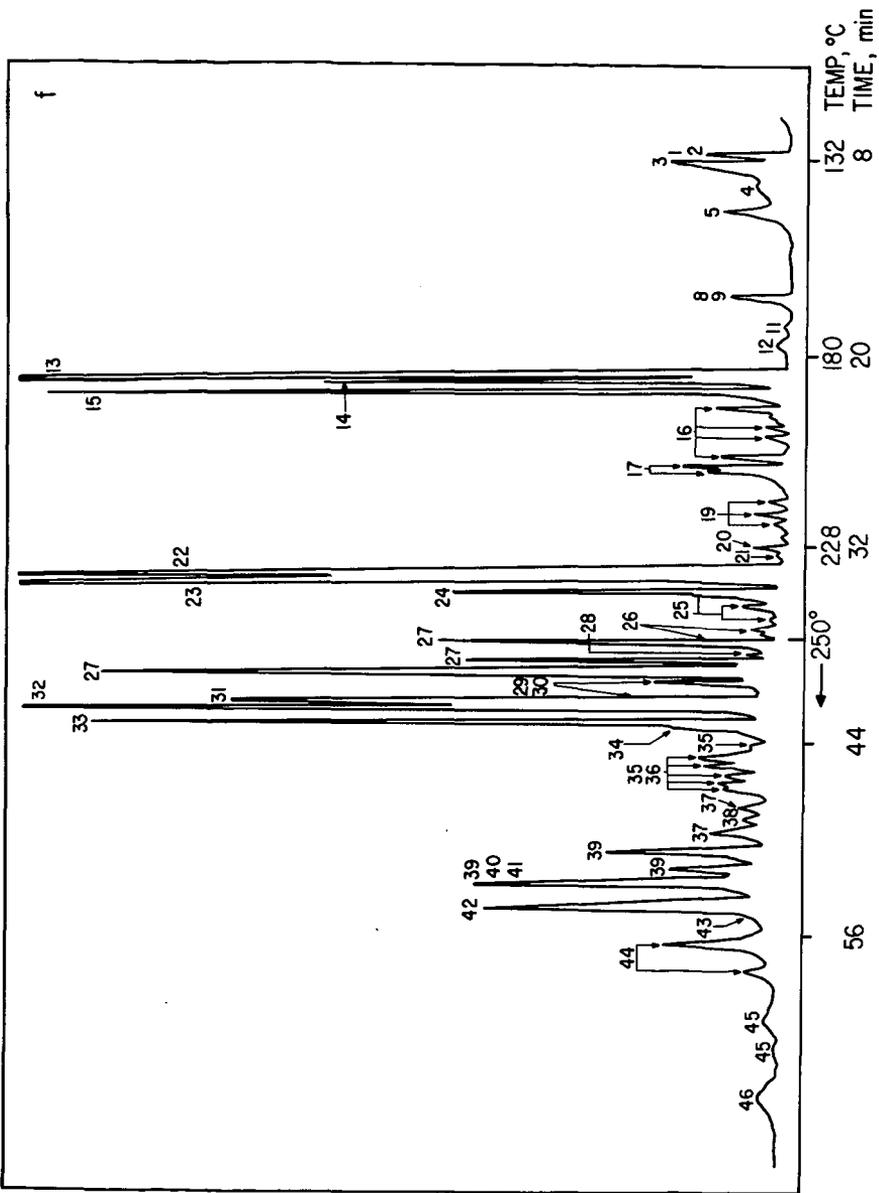


Figure 5. Gas chromatogram of methyl esters from the oxidation of the hydrolytic product from Reaction #1. Same conditions as Figure 4.

