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CHEMISTRY OF LIGNITE LIQUEFACTION

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II. Objective Scope of Work

The Fuel Committee was established in 1974, as an interdisciplinary group of chemists and engineers at the University of North Dakota to investigate the chemistry associated with lignite liquefaction in cooperation with the UND Chemical Engineering Departments's efforts on liquefaction and, later, with the Grand Forks Energy Research Center. The ultimate goals of the present work are to develop rapid analytical methods for the structural analysis of SRL and its reduction products, apply the developed analytical methods to these materials, and do catalyst testing and mechanistic studies on the $CO-H_2O-H_2$ and $CO-H_2O$ reducing systems.

III. Summary of Progress to Date

Solvent refined lignite (SRL), obtained by treating lignite with carbon monoxide-hydrogen-water at 1,500 - 2,500 psi at ca. 400°C, has an average molecular weight of ca. 460 with about 89% carbon, 6% hydrogen, 3% oxygen, 1% nitrogen and 1% sulfur with no inorganic material. Based on nuclear magnetic resonance studies, SRL is highly aromatic with one acid group and 0.1 base groups per average molecule.

SRL is similar to solvent refined coal (SRC's from bituminous and subbituminous coals in C, H and S elemental analysis, acid content, nmr and uv spectra, but lower in nitrogen and base content. (N. F. Woolsey, et al., submitted). The average molecular weights of SRC's and SRL's are dependent upon the conversion conditions. The electron spin resonance g and ΔH values, as well as the radical concentrations, are the same for SRL's and SRC's as determined by spin resonance. Ultraviolet spectra of SRL gel permeation fractions show the same aromatic chromophores are present in both larger and smaller molecular weight fractions of SRL with the nmr spectra showing the lower molecular weight fractions to contain methyl carbons while the larger molecular weight fractions include cyclic aliphatic groups.

The average molecule of SRL has 0.86 atoms of oxygen, 0.33 atoms of nitrogen and 0.14 atoms of sulfur. Half of the oxygens are ethers and the other half are phenolic. There are no detectable alcohol-type oxygens.

Gel permeation chromatographic (GPC) separations, using pyridine as the eluent, show the range of molecular weights of SRL to be 4000 to 160 gm/mole. The data are consistent with SRL having monomeric molecules in pyridine. Thus, GPC can be used to examine SRL for structural changes with interactions. It is assumed that adsorption and partitioning processes do not occur during the separation.

A method has been developed for determining the percent of acidic hydrogens present in SRL and SRC samples based on acetylation and silylation coupled with nmr proton analysis. For one sample of SRL the percent acidic hydrogens is 2.7% (average of four determinations). This agrees with the 2.65 percent acidic protons determined by titration for this sample.

A second method has been developed for determining the percent of phenolic acid hydrogens present in SRL and SRC using silylation with subsequent analysis by proton nmr. For the same sample used for the acetylation method development, it was found that an average percentage figure for the phenolic hydrogens is 1.9% which leaves the carbazole type hydrogens percentage at 0.8%.

Hydrogen bonding has now been documented as one of the major forces determining benzene solubility of SRL. The solubility of an SRL sample in benzene was increased from ca. 50% to ca. 90% by either silylation or acetylation of the sample. Since silylation destroys the hydrogen bonding capability of phenols and acetylation for both phenols and carbazoles, the conclusion was reached that hydrogen bonding causes intermolecular association among the SRL molecules.

The kinds of hydrogens present in the soluble portions of SRL samples in various solvents vary from the insoluble portion. However, the aromaticity does not vary much between the soluble and insoluble portions. Consequently, the soluble portions of SRL from various solvents reflect the aromaticity for the whole sample to a very high degree. Dioxane is the most selective solvent and chloroform is the least. Thus, chloroform is the superior solvent to use for nmr solvents of partially soluble samples.

As determined by large angle X-ray diffraction studies, SRL and SRC have crystallites present in the solid phase with about 15 Å diameter with the SRL having an average stack of four aromatic planes separated by 3.7 Å. The SRC stack contains an average of three. Low angle X-ray scattering studies on the SRL sample in pyridine solution show particles present having an 18 Å average radius of gyration.

Solvent refined lignite can be 90% converted by catalytic hydrogenation into ca. 20% light liquids, 15% light oil, 20% heavy oil and gases. (Low, et al., 1976). A series of commercially available Ni-Mo, Co-Mo, Ni-W, Pt, and Cr catalysts on Al_2O_3 and SiO_2 supports, and a series of synthesized Ni-Mo/fibrous Al_2O_3, TiO_2 (α or β), ZrO_2 and SiO_2 catalysts have been tested in hydrotreating of SRL into liquids. The temperature (450°) and pressure (3,500 psi) have been optimized. Ni-Mo/Al_2O_3 is the best catalyst overall, but we have determined that on a surface area basis, the Ni-Mo/ZrO_2 and Ni-Mo/TiO_2 catalysts are extremely good. Ni-Mo/ZrO_2 is particularly promising, probably due to the dual acid-base character of the ZrO_2 support.

Phenol, ethylbenzene, diphenylether, diphenylmethane, dibenzothiophene and carbazole are difficult to reduce under carbon monoxide-water conditions at 425°C in batch autoclaves. These conditions readily convert benzophenone, diphenyl sulfide, thioanisole, phenylbenzyl ether, benzhydrol, quinoline, anthracene and 1,2-diphenylethane into a variety of products. For 1,2-diphenyl-

ethane, benzophenone, quinoline and benzylphenyl ether, the presence of tetralin had no effect on conversions, it had a negative effect on the conversions of thioanisole, diphenylsulfide and n-decanol; and a positive one on the anthracene reduction. Sodium carbonate aids the CO-H_2O conversions of n-decanol, benzophenone and quinoline, has no effect on the reductions of 1,2-diphenylethane and anthracene and a negative effect on the thioanisole and diphenylsulfide runs. Iron oxide aided the conversions of the benzophenone and quinoline reductions, and ferrous sulfide favored the conversion of the quinoline and the thioanisole reduction, but it had no effect on the 1,2-diphenylethane and benzylphenyl ether runs and a negative effect on the diphenylsulfide, n-decanol and anthracene ones. For all but the quinoline reaction, where hydrogen was superior, a blend of carbon monoxide-water and hydrogen was the optimum set of reducing gases. Carbon monoxide and water outperformed hydrogen for the benzophenone and benzhydrol reductions.

A new mechanism for the reduction of organic molecules by carbon monoxide, in which there is a transfer of electrons from the catalyst surface to carbon monoxide prior to reaction with the organic molecules, is now more plausible.

The catalytic activity of metal oxides for the reduction of benzophenone using carbon monoxide and water parallels the ability of the metal oxide to transfer electrons to carbon monoxide on its surface under anhydrous conditions,

Related to CO-H_2O as a reducing medium, a host of metal oxides (possible in situ catalysts in coal) has been tested by electron spin resonance for activity in electron transfer processes to carbon monoxide to form surface bound $CO\cdot^-$. Only the alkaline earth oxides have shown activity (MgO, CaO, BaO, SrO). Currently, we believe carbon monoxide is adsorbed efficiently on Lewis base sites (two electron donors) and then migrates to one electron reducing sites.

The interaction of carbon monoxide with metal oxide surfaces has been shown to be dependent upon the prior heat treatment temperature for the metal oxide. The interaction is measured by electron spin resonance.

Presentations and Publications

1. V. I. Stenberg, R. J. Baltisberger, N. F. Woolsey and K. J. Klabunde, Chemistry of Lignite Liquefaction, Sept. 15, 1976, Lignite Briefing for Legislators, University of North Dakota.

2. K. J. Klabunde, R. J. Baltisberger, N. F. Woolsey and V. I. Stenberg, Chemical Characterization of Solvent Refined Lignite, Fuels Science, Gordon Research Conference, July 1976, New Hampton, NH.

3. V. I. Stenberg, R. J. Baltisberger, N. F. Woolsey, K. J. Klabunde, Chemistry of Lignite Liquefaction, 1976 ERDA/NSF/EPRI Principal Investigator's Conference - Coal Research, Golden, Colorado, September 3-4, 1976.

4. N. F. Woolsey, K. J. Klabunde, R. J. Baltisberger, V. I. Stenberg and R. Kaba, Characterization of Solvent Refined Lignite and Solvent Refined Coal. Computerized Methodology Development, ACS Fuel Division Preprints, 21, 33 (1976). (Storch Award Invitation Lecture given by K. J. Klabunde).

5. N. F. Woolsey, R. J. Baltisberger, K. J. Klabunde, V. I. Stenberg and E. J. O'Reilly, Approaches to the Analytical Analysis of Solvent Refined Lignite, Coal Chemistry Workshop, Stanford Research Institute, August 26-27, Menlo Park, CA (lecture given by N. F. Woolsey), 1976.

6. K. J. Klabunde, D. S. Jones, D. H. Ralston, K. Tanabe, M. Govek, V. I. Stenberg, N. F. Woolsey, and R. J. Baltisberger, Production of Clean Liquid Fuels from Lignite: Catalytic Hydrotreating of Solvent Refined Lignite Employing Low Surface Catalysts and Commercial Catalysts, Lignite Symposium, May 18-19, 1977, Grand Forks, ND.

7. R. J. Baltisberger, N. F. Woolsey, K. J. Klabunde and V. I. Stenberg, Carbon Monoxide Catalysts and the Reduction of Lignite Model Compounds, COLL. 18, Second Joint Conference, Chemical Institute of Canada and American Chemical Society, (Symposium Speaker), May 31, 1977, Montreal, Quebec, Canada.

8. V. I. Stenberg, (Invited Lecture), Summer Institute in Energy Economics and Mining Ecology for Educators, (high school science teachers), University of North Dakota, Grand Forks, ND, June 17, 1977. Chemistry of Lignite Liquefaction.

9. J. Y. F. Low, K. J. Klabunde, D. E. Severson, N. F. Woolsey, R. J. Baltisberger, M. Govek, M. J. Wolf, J. Rice, S. Switzer, M. L. Mannering, and V. I. Stenberg, Batch Autoclave Hydrogenation of Solvent Refined Lignite, ACS Fuel Division Preprints, 20 (1), 122 (1975).

10. James Y. F. Low, K. J. Klabunde, N. F. Woolsey, R. J. Baltisberger, M. Govek, and V. I. Stenberg, Catalytic Hydrogenation of Solvent-Refined Lignite to Liquid Fuels, Energy Sources, 3, 19 (1976).

Presentations and Publications (continued)

11. V. I. Stenberg, R. J. Baltisberger, N. F. Woolsey, and K. J. Klabunde, Chemistry of Lignite Liquefaction, 1977 ERDA/NSF/EPRI Principal Investigator's Conference-Coal Research, Pittsburgh, Pennsylvania, August 25, 1977.

12. R. J. Baltisberger, K. J. Klabunde, V. I. Stenberg, N. F. Woolsey, K. Saito and W. Sukalski, Comparison of Solvent Refined Lignites with Solvent Refined Bituminous Coals, ACS Fuel Division Preprints, 22 (5), 84 (1977).

13. V. I. Stenberg, R. J. Baltisberger, N. F. Woolsey and K. J. Klabunde, Chemistry of Lignite Liquefaction, Seminar at North Dakota State University, October 25, 1977.

14. D. Jones, R. J. Baltisberger, K. J. Klabunde, N. F. Woolsey and V. I. Stenberg, Carbon Monoxide-Hydrogen-Water: Reduction of Benzophenone, Diphenylcarbinol and Diphenylmethane, J. Org. Chem., 43, 175 (1978).

15. R. J. Baltisberger, R. A. Kaba, K. J. Klabunde, K. Saito, W. Sukalski, V. I. Stenberg and N. F. Woolsey, "Comparison of Solvent Refined Lignite with Solvent Refined Bituminous Coals", Fuels, accepted.

16. V. I. Stenberg, J. Wang, R. J. Baltisberger, K. J. Klabunde, R. Van Buren and N. F. Woolsey, Carbon Monoxide-Hydrogen-Water: Reduction of Anthracene, Dihydroanthracene, and Quinoline, J. Org. Chem., 43, 2991 (1978).

17. K. J. Klabunde, R. A. Kaba, and R. M. Morris, "Carbon Monoxide-Metal Oxide Interactions. Surface Site Requirements for Electron Transfer Processes. Chemistry Related to Low Rank Coal Liquefaction", plenary lecture, Symposium on Inorganic Compounds with Unusual Properties. II. Molecular Catalysis and the Conversion, Production, and Storage of Energy, Athens, Georgia, February 1-4, 1978, paper in press.

18. K. J. Klabunde, R. A. Kaba, and R. M. Morris, "Highly Efficient Electron Transfer Processes Over Thermally Activated Alkaline Earth Oxides. Monolayer Anion Radical Formation with Nitrobenzene-MgO and High Concentration of CO Radicals over MgO, CaO, SrO, BaO, and ThO_2", Inorg. Chem., submitted.

19. K. J. Klabunde, R. A. Kaba, and R. M. Morris, "Carbon Monoxide-Metal Oxide Interactions. II. Surface Site Requirements for the Formation of Paramagnetic Species on Thermally-Activated Magnesium Oxide", J. Amer. Chem. Soc., submitted.

20. K. J. Klabunde, R. A. Kaba, and R. M. Morris, "Carbon Monoxide-Metal Oxide Interactions. Surface Site Requirements for Electron Transfer Processes", ACS, Advances in Chemistry Series books, in press.

21. R. J. Baltisberger, K. J. Klabunde, V. I. Stenberg, N. F. Woolsey, K. Saito, and W. Sukalski, "Comparison of Solvent Refined Lignites with Solvent Refined Bituminous Coal", in Organic Chemistry of Coal, ed. J. W. Larson, ACS Symposium Series 71, pg. 294 (1978).

22. Stenberg, V. I., Baltisberger, R. J., Woolsey, N. F., Klabunde, K. J., Chemistry of Lignite Liquefaction, 1978 Department of Energy Principal Investigator's Conference-Coal Research, Lexington, Kentucky, August 23-24, 1978.

23. V. I. Stenberg, J. Wang, R. J. Baltisberger, K. J. Klabunde, R. Van Buren, and N. F. Woolsey, Carbon Monoxide-Hydrogen-Water: Reduction of Anthracene, Dihydroanthracene and Quindine, Abstracts, Proceedings of the North Dakota Academy of Science, 32, 34 (1978).

24. D. Ralston, M. Govek, C. Graf, D. S. Jones, K. Tanabe, K. J. Klabunde, N. F. Woolsey, R. J. Baltisberger, and V. I Stenberg, "Catalytic Activities and Selectivities of MoO_3NiSO_4 Supported on Various Oxides for Hydrocracking of Solvent Refined Lignite; Novel Surface Area Active Catalysts, Fuel Processing Tech., 1, 143 (1977).

Detailed Description of Technical Progress

Task I

Structural Comparisons of SRL and SRC

(a) Objectives

To aid in the development of analytical methods to generate average molecular structures of SRL, SRC and their heavy liquids. To compare SRL and SRC as to their structural and chemical differences.

A. Use of Silylation and Acetylation Technique for Structural Examinations

(b) Introduction

Chemical structure of coal is a riddle that has long defied solving, but in the past decade excellent work has been done which contributes to a better understanding of the basic structure of coal. An impressive array of chemical and physical methods has been applied, building up useful data bit by bit. The determination of phenolic and carbazole type moieties by acetylation has been used routinely for several years.[1,3,4,5,6,7,8] Recently several groups have used silylation in combination with infrared[11], proton NMR[2], and atomic adsorption spectroscopy[3] to determine phenolic and alcoholic content of coal and coal derived products. Our interest in studying the structure and properties of SRL and SRC has led us to determine the oxygen distribution for various samples. Acetylation and silylation were used for the determination of functional oxygen groups.

(c) Results

Acetylation:

Acetylation by acetic anhydride affords a method for determining phenols, alcohols, amines and thiophenols in coal and coal derived products.

In a typical experiment the SRL (M11A)(1.0 g) was allowed to react with acetic anhydride (3 ml) in 15 ml pyridine at reflux temperature for 24 hr. The acetylated

SRL was then diluted with 2 liters of water. A 5μ teflon filter was used for filtering and the filtrate washed with water (ca. 5 liters) until the effluent was free of acetic acid. The acetylated SRL was then dried at 64° in vacuum for 24 hr. The dried sample was freeze-dried with benzene and the sample was again dried in vacuum at 64° for 24 hr.

Proton NMR data of acetylated M11A and that of M11A were used for the calculation of percent acidic hydrogen (OH and NH type). The formula (1) was used for the calculation:

$$\text{Percent acidic hydrogen} = 100 \times \frac{R_2 - R_1}{2R_1 + 1} \qquad (1)$$

where R_1 is a fraction of aromatic protons in acetylated M11A and R_2 is a fraction of aromatic protons in M11A.

Tables 1 and 2 summarize the results.

Table 1. Percent Aliphatic and Aromatic Hydrogen in M11A

Run	$H_{aliphatic}$	$H_{aromatic}$	H_{alip}/H_{aro}
1	45.9%	54.1%	0.85
2	45.2	54.8	0.82
Average	45.6	54.4	0.84

Table 2. Percent Aliphatic, Aromatic and Acidic Hydrogen in Acetylated M11A

Run	$H_{aliphatic}$	$H_{aromatic}$	H_{ali}/H_{aro}	H^*_{acidic}
1	51.5%	48.5%	1.06	2.6%
2	51.4	48.6	1.06	2.8
3	51.1	48.9	1.05	2.6
4	51.1	48.9	1.05	2.6
Average	51.3	48.7	1.05	2.7

*Calculated using formula 1

The result agrees with that of the titration result which calculates out to be 2.7% acidic hydrogen.

It should be pointed out that in deriving formula 1, it was assumed that all acidic type protons (phenolic and carbazole type) in M11A have chemical shifts between 6 and 9 ppm (i.e., in aromatic region) in pyridine-d_5 solvent. So after acetylation of M11A, the decrease in the area of aromatic hydrogen is due to acetylation of those acidic hydrogens.

The nmr of acetylated M11A did not show a sharp peak at ∿1.97 ppm, which corresponds to acetate hydrogen ($-O-\overset{O}{\overset{\|}{C}}-CH_3$). However, when acetylated M11A was fractionated on GPC column (Bio-Beads, SX-3; exclusion limit 2000 mw; column size 19" X 3/4") using pyridine, fraction 1 through 8 showed a sharp peak at ∿ 1.97 ppm. Peak intensity increases from fraction 1 to 5 and then decreases. It appears that fraction 5 has maximum amount of acidic proton. Besides a sharp peak at ∿ 1.97 ppm, two broad peaks were observed at 3.1 ppm and at 3.5 ppm. The peaks intensity are maximum in fraction 5. It seems at this point that there is a definite relationship between acetate peaks and these two broad peaks.

Solvent effect in NMR was studied on fractions 6, 7 & 8 and found that the peak at 3.1 ppm shifted to 3.25 ppm in $CDCl_3$. It clearly indicates that

these two peaks are not coupled with each other.

Also, the fractions 7 and 8 showed a sharp peak at ∿2.7 ppm corresponding to carbazole-acetate type protons. Fraction 9 has no acetate peak at ∿2.00 ppm but had a peak at 2.7 ppm. Again peak intensity increases from fraction 6 to 9 and maximum in fraction 9. This suggests that carbazole type compounds are concentrated in low molecular weight fractions. It should be pointed out that condensed aromatic nuclei are found in lower molecular weight fractions.

The infrared spectra of acetylated M11A and all the fractions were recorded and all showed absorptions at ∿ 1200 $\cdot Cm^{-1}$ ($\cdot C$ - O-C stretch) and at 1765 Cm^{-1} (C = O stretch).

We thought that the peaks at 3.1 ppm and at 3.5 ppm in all fractions may be due to $R\text{-}\underline{CH_2}\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3$ hydrogen and that this moiety may have formed during the acetylation conditions by ether cleavage. To confirm this theory the acetylation of benzyl ether was investigated. Benzyl ether was allowed to react with acetic anhydride in pyridine for 24 hr at reflux temperature. The reactions were also carried out using equivalent amounts of acetic acid and hydrochloric acid as catalyst. However, in all these reactions benzyl ether recovered completely. Aliphatic ether can be cleaved by treatment with pyridinium hydrochloride in acetic anhydride.[18,19] At this point the only possible explanation that seems logical for the sharp peak at 1.97 ppm for acetate protons and two broad peaks at 3.1 ppm and at 3.5 ppm, in the nmr spectra of fractions 1 through 8 is that the acetylation of M11A may be breaking loose some paramagnetic material which may have filtered off during GPC separation.

Silylation:

Silylation of SRL and SRC will enable us to study the hydroxyl groups by proton nmr spectroscopy.

The M11A was silylated in dry benzene using 1,1,1,3,3,3-hexamethyldisilazane (HMDS) as a silylating reagent and N-trimethylsilyldimethylamine (TMSDMA) as catalyst at reflux temperature for 1 hr. The silylated M11-A was then freeze dried with benzene. Proton NMR analysis (in pyridine-d_5 using s-trioxane internal standard) of this silylated sample indicated that besides silyl ethers there was a small peak corresponding to trimethylsilanol. Attempts to remove trimethylsilanol by placing the sample in vacuum ($\sim$ 0.1 mm) at 64^{o} for 24 hr failed. In spite of a very small impurity the calculation was done for the percent phenolic hydrogen from NMR. Table 3 shows these results. Also the percent acidic hydrogen (OH type) was calculated by formula (2).

$$\text{Percent phenolic hydrogen} = 100 \times \left(\frac{R_2 - R_1}{8\ R_2 + 1}\right) \qquad (2)$$

where R_1 is a fraction of aromatic protons in silylated M11-A; and R_2 is the fraction of aromatic protons in M11A.

Table 3. Percent Aliphatic, Aromatic and Phenolic Hydrogen in Silylated M11A

Run	$H_{aliphatic}$	$H_{aromatic}$		H_{ali}/H_{aro}	H_{OH}*	H_{OH} **
1	44.70%	53.00%		0.86	2.30%	1.80%
2	43.90	54.00		0.82	2.10	2.09
Avg.	44.3	53.50	0.84	0.84	2.20	1.90

* Based on integration of silyl ether peak

** Calculated using formula (2)

The 1.9 percent acidic proton may correspond to the percentage of phenolic hydrogen in the sample. The total acid titration gives 2.7% acidic protons which compares favorably with the 2.65% acidic protons measured by acetylation. It appears then that acetylation measures the carbazole and phenol type hydrogens while the silylation measures the phenolic hydrogen.

The GPC (Bio-Beads SX-3 exclusion limit 2000 mw) fractions of M11A were also silylated and attempts were made to find phenolic content of each fraction by NMR and to determine the change in number average molecular weight, but due to a large amount of impurities of HMDS and trimethylsilanol reliable values were difficult to obtain.

Silylated M11A was also fractionated on GPC (SX-3) column and NMR of each fraction was recorded. In this experiment most of the silyl ether had hydrolyzed during GPC separation and freeze-drying.

It is clear from titration, elemental analysis, acetylation and silylation experiments that M11A has about 1.0% carbazole type hydrogen which is also acidic in nature.

B. Hydrogen Bonding Study Via Acetylation and Silylation of SRL & SRC

(a) Introduction

Intramolecular association forces have long been acknowledged as fundamental forces for stacking of aromatics in the coal. Sternberg[13] has shown that alkylation of coal with alkyl halides($n\text{-}C_4H_9I$) using lithium and liquid ammonia increased the solubility of bituminous coal up to 90% in benzene. His conclusion was that the stacking process was reduced by alkylation, since the solubility was highest with sec.-butylhalide and lowest with methylhalide as the alkylating agent. Schlosberg, Gorbaty and Aczel[14] have shown that Friedel-Crafts isopropylation of a bituminous coal had higher solubility in benzene and pyridine than untreated coal.

Recently[15,16,17] many authors have indicated that intermolecular hydrogen

bonding is a measure of the association force in coal. Ignasiak[15] has studied infrared spectra of Athabasca asphaltene in carbon tetrachloride and also molecular weight measurement of athabasca asphaltene and its acetylated, methylated and silylated derivatives. He found that the molecular weight in fact decreased when asphaltene was acetylated, silylated and methylated. He concluded that hydroxy groups exist almost entirely as hydrogen-bonded complexes and that the hydrogen bonding is intermolecular in character. Moschopedis and Speight[16] have also indicated by infrared study of asphaltene and acetylated asphaltene that oxygen exists as phenolic hydroxyl groups and that a considerable portion of these groups may occur as collection of two or more functions on the same aromatic rings or on adjacent sites in a condensed aromatic system. Barbour and Petersen[17] have also studied infrared spectra of asphalt in different conditions. His data on methylation of an asphalt and asphaltene fractions with diazomethane suggest the occurrence of molecular aggregation via hydrogen bonding.

(b) Results

We have studied the effect of acetylation and silylation on M11-A and found that the soubility was increased almost 100%. The data shown in Table 4 reflects this phenomenon for benzene.

Table 4. Effect of Silylation and Acetylation on the Solubility of Solvent Refined Lignite (M11A) in Benzene

Run	Solubility in benzene, Central Sample	Solubility in benzene, after Silylation	Solubility in benzene after Acetylation
1	52.0%	89.0%	85.0%
2	47.0	88.0	85.0
3	48.0	87.0	
4	51.0*	88.0	
5		91.0	
Average	50.0%	89.0%	85.0%

* The control sample duplicates the acetylation conditons.

We have also measured number average molecular weight for acetylated M11A and found no increase in number average molecular weight.

(A) Number Average Moleular Weight of M11A 500 g/mole.

(B) Number Average Molecular Weight of Acetylated M11A 506 g/mole.

We have demonstrated unequivocally that acetylation and silylation has increased solubility of M11A and that increase in solubility and no change in number average molecular weight can be correlated with the intermolecular hydrogen bonding phenomenon.

Experimental detail on silylation acetylation and solubility measurement are given below.

(c) Experimental

Silylation of SRL (M11A)

One gram of SRL was weighed into a 25 ml flask. To this were added 10 ml of dry benzene, 0.5 ml of 1,1,1,3,3,3-hexamethyldisilazane and 0.5 ml of N-trimethylsilyldimethylamine. The sample flask was then placed in an oil bath and the mixture was refluxed for 1 hr under argon atmosphere. Following cooling to room temperature the insoluble M11A was filtered, dried and weighed. The amount of benzene remaining in the dried samples was determined to be negligible (< 10 ppm) by NMR measurements.

Control Solubility Measurement in Benzene

The one gram of M11A was mixed with 10 ml of dry benzene in a 25 ml round bottomed flask. The solution was refluxed for 1 hr under inert atmosphere. The insoluble portion was filtered, dried and weighed.

Acetylation

The SRL (1.0 g) was allowed to react with acetic anhydride (2 ml) and 200µl pyridine in 10 ml of benzene at reflux temperature for 24 hr under inert atmosphere. The mixture was then cooled and filtered on a 5µ Teflon filter paper. The insoluble residue was dried in vacuum and weighed.

Control for Acetylation

One gram of SRL (M11A) was dissolved in 10 ml dry benzene and 200μl pyridine. The solution was refluxed for 24 hr while it was stirring. The insoluble portion was filtered and weighed after drying.

C. Structural Variation of SRL with Molecular Weight

(b) Introduction

This section involves the study of what information can be obtained about the structure of a coal derived liquid using gel permeation chromatographic techniques (GPC). In the course of this investigation several important features have been discovered and are as follows:

(1) Pyridine serves well as a chromatographic solvent when the coal derived liquids contain large quantities of preasphaltenes. In the case of our SRL sample this was over 40% by weight. Approximately 100% recovery was obtained from a column of Bio-Beads SX3, a styrene-divinyl benzene copolymer gel.

(2) For the most part, all fractions separated on the GPC remain soluble in pyridine except the first two very high molecular weight fractions (2000 - 4000 gm/mole). These fractions have a lower acid content than the later fractions and may require a more acidic solvent to remain soluble.

(3) The number average molecular weight distribution of an SRL (M11A) was from 200 to 4000 gm/mole. The number average molecular weight $\overline{M}_n$ of the original sample, 406, agrees well with the weighted sum of the individually collected fractions, 440. There apparently is no major change in association between SRL molecules during separation or there is little association in pyridine at all.

(4) UV spectral analysis of the individual GPC fractions shows that at 280 nm there is a slight increase in $E^{1\%}_{1cm}$, absorbtivity, as one goes to the

lower molecular weights. This would be consistent with a slight increase in total aromaticity or a shift of the low weights to more polynuclear systems.

(5) The acid content of the GPC fractions maximizes in the middle molecular weight ranges ($\sim$ 600 gm/mole).

(6) The ratio of alpha aliphatic protons (H_α) to other aliphatic protons (H_o) increases as one goes to low molecular weights. This is consistent with loss of cyclic aliphatic rings in the molecules ending up with methyl substitution on larger aromatic molecules.

Earlier Quarterly Reports describe the detailed results of the above work. This Quarterly Report provides further information about the nature of the structure.

(c) Results

Acid Content

The original acid titration data was measured on GPC fractions isolated from 1200 gm/mole exclusion gel, SX4. Because the SRL samples contained a sizeable portion of weights above this limit, a higher exclusion gel, SX3 (2000 gm/mole) was chosen to be used in all our work. Because of this change we felt it was necessary to repeat the acid analysis. Table I shows the results of this analysis carried out two ways. The fourth column in the Table shows the acidity measured by nonaqueous titration of the fractions. Column six reports the percentage of hydrogen relative to the total hydrogen as measured by nmr. In this case the percentage is equal to:

$$OH\% = \frac{R_2 - R_1}{2R_2 + 1} \quad (100)$$

where R_2 is the fraction of aromatic protons in a nonacetylated SRL sample and R_1 is the fraction of aromatic protons in an acetylated sample. The

assumption in this equation is that all the acidic protons lie under the aromatic region and these shift to the aliphatic region upon acetylation. Details of this procedure are described in the acetylation section. The results agree closely when one includes the percentage of hydrogen in the calculation to convert the meq/gm SRL to mole percent of hydrogen.

$$OH\% \text{ mole} = \frac{\text{meq acid/gm } (100)}{(H\%)\ (1000 \text{ mg/gm})} \qquad (1)$$

Fraction four contains 4% acidic protons as measured by nmr which compares well to 3.8% as calculated from equation one using 5% as the percentage hydrogen in the fraction. Data in the acetylation section supports the fact that we are acetylating all of the acidic protons.

It is apparent from the table that acidity maximizes between 700 and 300 gm/mole molecular weight. A possible explanation of this fact could be that the liquefaction process involves mechanisms in which ethers present in the high molecular weight portions are cleaved to produce lower weight units containing more acidic groups:

This point will be investigated further. In particular, we plan to measure the total oxygen distribution over the fractions in order to determine if the high molecular weight ends contain a larger portion of nonacidic oxygen (probably as ethers).

Table 1. GPC Separation XXV M11A on Bio Beads SX-3

Fraction	Mole Wt.	Wt % Recovery	Meq acid/gm	$(OH\ \%)_{mole}$ NMR	f_a
1	4526	7.2	1.10	1.0	—
2	3533	12.5	1.09	—	0.47±0.01
3	1151	6.2	1.13	5.4	0.73±0.01
4	716	9.0	1.92	4.1	0.783±.006
5	608	13.0	1.60	—	0.815±.006
6	488	14.2	1.74	3.0	.821±.008
7	329	12.7	1.69	1.4	.818±.006
8	369	15.7	0.84	—	—
9	92	4.6	0.64	—	—
10	198	3.6	0.15	—	—
11	56	0.3	—	—	—

Aromatic Content

The fraction of aromatic carbons (f_a) in the GPC fractions was measured by C^{13} nmr and reported in Table 1. There is only a slight increase in f_a in going from high to low molecular weights. A problem in fraction two is that we experienced solubility problems for fractions 1 and 2 in s-triazine, our nmr solvent. All other fractions were quite soluble in the solvent. Since one observed no marked change in aromatic content with weight, the observed $E^{1\%}_{1cm}$ increase at low molecular weight values could be due to a shift in the type of aromatic groups to more polynuclear systems.

Recovery of Acetylated GPC Fractions

Several acetylated SRL samples were run through the GPC separation using pyridine as the solvent. The objective in this case was to hopefully solublize the high molecular weight fractions through acetylation of their acid groups.

Compared to a non-acetylated separation, only 90% recovery of acetylated sample was obtained relative to about 100% for a typical non-acetylated run. A fine black powder was left on the column. This behavior could be consistent with a loss of pyridine solubility by acetylation of the acid site thus reducing the hydrogen bonding ability of the SRL molecules making it insoluble in pyridine. We are presently testing a series of solvents which might dissolve this precipitated material. The remainder of the soluble acetylated SRL passed through the GPC column without a problem. A molecular weight fractionation was still obtained as shown in Table 2.

Table 2. GPC Separation of Acetylated SRL on Bio-Beads SX-3

Fraction	M.W. (Acetylated)	M.W. (non-acetylated)
1	3487	4526
2	1997	3533
3	1279	1151
4	736	716
5	670	608

Compared to the original SRL, there is a decrease in the high molecular weight ends which probably is due to a better solubility in pyridine leading to a more correct VPO molecular weight measurement. The lower molecular weight fractions are slightly larger indicating the additional weight of the acetyl groups added to the molecules. In conclusion, acetylation does not solve the problem of solublizing the high molecular weight ends. We plan to investigate this problem during the next quarter.

D. The Variation of Structural Parameters in the Soluble and Insoluble Portions of SRL from Different Solvents

(a) Introduction

In order to determine the structural characteristics of an SRL sample, the spectrum must be obtained on the whole sample in a solution or in solid state. The ^{13}C-NMR spectra in the solid state can answer this question, but due to low precision and the unavailability of commercial equipment this is not yet practical. Many structural parameters for SRL have been derived from the 'H and ^{13}C-NMR spectra and the elemental analysis data of the soluble portions in many kinds of solvents. The most common solvents are carbon disulfide, chloroform and dioxane, etc. However, it is not clear how different the parameters for the soluble portion of a solvent are from those of the whole sample or how the structural parameters vary in the soluble and insoluble portions of different solvents. Therefore, it is very important to learn to what extent the soluble portions of SRL (SRC and coals) in different solvents reflect the features of the whole sample as well as to develop new solvents which can dissolve the whole SRL sample completely, almost completely, or at least unselectively.

We have examined many kinds of compounds to find the solvent for the ^{13}C-NMR of SRL and found s-triazine to be a desirable solvent (cf. the previous Quarterly Report). In the present report we describe the variation of structural parameters for the soluble and insoluble portions of SRL from five different solvents which are used commonly as solvents for SRL, SRC and some coals.

(b) Experimental

SRL (M11A, undeashed) (1.0 g) was added to the solvent (10 ml) (SRL, 2.0 g and 15 ml of dimethylsulfoxide was used). The mixture was stirred with a magnetic stirring bar for 1 hr at room temperature. In some cases, ultrasonification was applied to the mixture for about half an hour besides stirring. Then

the mixture was separated into the soluble (filtrate) and insoluble portion (precipitate) by filtration through a filter followed by drying under reduced pressure at up to $130^{o}C$ to remove the solvent, then both filtrate and precipitate samples were weighed. The recovery of SRL was more than 98% except 90% for dimethylsulfoxide. Both portions were dissolved into pyridine-d_5 and s-triazine for ^{1}H and ^{13}C-NMR runs respectively. (Some precipitates didn't dissolve completely in s-triazine.)

(c) Results

(1) Solubility of SRL (M11A) in Different Solvents

The solubilities of SRL (M11A) in five different solvents decrease in the following order: dioxane (77.9%) > dimethylsulfoxide (71.5%) > chloroform (63.7%) > benzene (49.2%) > carbon disulfide (48.8%) and are summarized in Table I. Application of ultrasonification improved the solubilities about 10% in absolute percentage (in dioxane 77.9 to 86.3% and in carbon disulfide 48.8 to 60.1%).

(2) The Change of Elemental Analysis Data

The soluble portion of SRL (M11A) from dioxane has less carbon and more hydrogen than the insoluble portion from dioxane. The weighted averages of carbon, hydrogen and total sum of both elements agree with the corresponding values of the whole sample within 0.4 wt % error (cf. Table I). The soluble portion from carbon disulfide has more carbon and hydrogen than the insoluble portion. The weighted average of the total sum of carbon and hydrogen is different by about 1.2% from the value for the original whole sample. This seems to be a problem of the reliability of commercial analysis and is being checked.

(3) Hydrogen Distribution

The hydrogen distribution varies in the soluble portions and the insoluble portions of SRL (M11A) from different solvents (Table I), but some

Table I

Solvent	Portion, Wt.%	Elemental Analysis			Hydrogen Distribution - ^{1}H-NMR				Brown-Ladner's Structural Parameters			^{13}C-NMR
		C	H	Total	H_{ar}	H_α	H_o	$H_{ar}/H_\alpha+H_o$	F_a	σ	H_{aru}/C_{ar}	$C_{ar}/C_{tot.}$
Dioxane	Soluble 77.9	88.99	5.56	94.55	.518	.355	.127	1.07	.821	.316	.686	.820±.005
	Insoluble 22.1	90.66	4.78	95.44	.593	.270	.137	1.46	.872	.248	.567	.852±.004
	Average weighted	89.36	5.39	94.75	.534	.336	.129	1.16	.832	.301	.660	.827
	Soluble 86.3 *				.517	.362	.121	1.06				
	Insoluble 13.7				.602	.299	.098	1.51				
	Average weighted				.528	.353	.117	1.12				
Dimethyl Sulfoxide	Soluble 71.5				.548	.345	.108	1.21				
	Insoluble 28.5				.531	.309	.160	1.13				
	Average weighted				.543	.336	.123	1.19				
Chloroform	Soluble 63.7				.532	.350	.119	1.13				.826±.003
	Insoluble 36.3				.589	.312	.099	1.43				.826±.004
	Average weighted				.553	.336	.112	1.24				.826
Benzene	Soluble 49.2				.590	.316	.094	1.44				.811±.003
	Insoluble 50.8				.531	.351	.118	1.13				.824±.006
	Average weighted				.560	.334	.106	1.28				.818
Carbon Disulfide	Soluble 48.8				.513	.355	.133	1.05				
	Insoluble 51.2				.598	.306	.099	1.48				
	Average weighted				.557	.330	.116	1.27				
	Soluble 60.1 *	89.28	5.68	94.96	.515	.353	.132	1.06	.816	.310	.693	.821±.006
	Insoluble 39.9	87.35	4.97	92.32	.574	.317	.109	1.34	.855	.308	.656	.833±.009
	Average weighted	88.51	5.40	93.91	.539	.339	.123	1.17	.832	.309	.678	.826
Pyridine	Soluble 100	89.31	5.81	95.12	.540	.340	.120	1.17	.822	.292	.719	.811-.824

* sonicated

trends are found. In three solvents, carbon disulfide, chloroform and dioxane, the ratios of aromatic to total protons, H_{aro}/H_{total}, of all soluble portions are smaller than those of the insoluble portions, while the values of H_{α}/H_{total} and H_{o}/H_{total} of the soluble portions are bigger than those of the insoluble portions. In the soluble and insoluble portions, the hydrogen distribution is completely different for the three solvents mentioned above and it is reversed between the soluble and the insoluble portions. In the soluble and insoluble portions from dimethylsulfoxide H_{aro}/H_{total} does not change much while H_{α}/H_{total} increases in the soluble portion and H_{o}/H_{total} increases in the insoluble portion.

The ratios of aromatic to aliphatic hydrogen indicate that benzene, the only aromatic solvent in Table I,can selectively dissolve the aromatic proton-rich components of SRL (M11A), but that the soluble portions from the other solvents (except dimethylsulfoxide) are composed of more aliphatic proton-rich components than the corresponding insoluble portions. The difference of $H_{ar}/H_{\alpha} + H_{o}$ between the soluble and insoluble portions decreases as follows: dioxane (0.35 - 0.45) $\geq$ carbon disulfide (0.43 - 0.28) > benzene (0.36) > chloroform (0.30) > dimethylsulfoxide (0.08). In other words, the latter compounds are less selective solvents as determined by the hydrogen distribution in the soluble and insoluble portions.

(4) Aromaticity, f_a and C_{ar}/C_{total}

The aromaticities, the ratios of aromatic to total carbons of the insoluble portions from different solvents,are higher than those of the soluble portions. The biggest difference in C_{ar}/C_{total} is found between the soluble and insoluble portions from dioxane (0.820 and 0.852), but the same value of C_{ar}/C_{total} (0.826) is observed between the portions from chloroform in spite of their different hydrogen distributions. It is interesting that all soluble portions have the same C_{ar}/C_{total} value

within experimental error. 0.82 ± 0.01, which agrees with the value (0.82) for a whole sample, regardless of the different solvents and solubilities.

The values of f_a calculated by Brown-Ladner's equation for the insoluble portions are bigger than those from ^{13}C-NMR. One of the possible causes is incomplete solubility of the samples in s-triazine.

In conclusion, hydrogen distribution varies in the soluble and insoluble portions depending on the kind of solvents and solubilities of SRL (M11A). The aromaticity does not vary much in any of the soluble portions for different solvents and it is close to that for a whole SRL (M11A). This means the soluble portions of SRL from different solvents reflect the aromaticity for a whole sample to a very high degree. Dioxane is the most selective solvent. Chloroform gives the same aromaticity for the soluble and insoluble portions which have different hydrogen distributions.

(d) Work Forecast

(1) Acetylation on other SRL and SRC samples will be investigated and a detailed study of acetylated samples will be carried out using proton, ^{13}C nuclear magnetic resonance spectroscopy, solubility measurement, GPC analysis and molecular weight measurement.

(2) Radio-labeled acetylation methods for coal will be developed.[12]

(3) Silylation of other SRL and SRC samples will be studied in detail.

(4) Also, O-methylation of phenol will be carried out to develop a method for alkylation of phenols in coal.

(5) The remaining data (combustion analysis) will be obtained to complete Table 1.

(6) A re-examination of the carbon-13 nmr quaternary carbon problem utilizing some new model compounds is now underway.

References

1. Zeinab Abdel-Baset, P. H. Given and R. F. Yarzab, Fuel, 57, 95 (1978).

2. F. K. Schweighardt, H. L. Retcofsky, S. Friedman and M. Hough; Anal. Chem. 50, 368 (1978).

3. U. Hasegawa, S. Ueda, S. Yokoyama, Y. Yoshida, Y. Maekawa, Nenryo Kyokai-shi (Japan); 53, 995 (1974).

4. T. Ignasiak, O. P. Strausz and D. S. Montgomery, Fuel, 56, 359 (1977).

5. L. Blom, L. Edelhausen and D. W. Van Krevelen, Fuel, 36, 135 (1956); also Fuel, 38, 537 (1959).

6. P. H. Given, ACS Fuel Division Preprints, 55-60 (1962).

7. C. W. DeWalt, Jr. and R. A. Glenn; Anal. Chem., 24, 1789 (1952).

8. R. A. Glenn, E. D. Olleman; Anal. Chem., 26, 350 (1954).

9. R. V. Barbour and J. C. Peterson, Anal. Chem., 46, 273 (1974).

10. J. F. McKay, T. E. Cogswell, J. H. Weber and D. R. Latham, Fuel, 50 50 (1975).

11. S. Friedman, M. L. Kaufman, W. A. Steiner and I. Wender, Fuel, 40, 33 (1961).

12. K. Patel, W. Kisieleski, Int. Journal of Applied Radi and Isotopes, 28, 425 (1977).

13. Sternberg H. W., Delle Donne C. L., Pantages P., Moroni E. C. and Markby R. E., Fuel, 50, 432 (1971).

14. Schlosberg R. H., Gorbaty M. L., and Aczel T., J. Am. Chem. Soc., 100, 4188 (1978).

15. Ignasiak T., Strausz O. P., Montgomery D. S., Fuel, 56, 359 (1977).

16. Moschopedis S. E. and Speight J. G., Fuel, 55, 187 (1976), Fuel, 55, 334 (1976).

17. Barbour R. V. and Petersen J. C., Anal. Chem., 46, 273 (1974).

18. Ireland R. E., Mander L. N., J. Org. Chem., 34, 142 (1969).

19. Peet N. P., Cargill R. L., J. Org. Chem., 38, 1215 (1973).

Task II

(a) Objective

The objective of this task is to catalytically hydrotreat SRL to produce light liquid fuel and gases, determine the best catalysts, and study in some detail the chemical features of the product fuels.

(b) Results

This task is complete to the extent that we have successfully hydrotreated SRL and SRC to give 90% distillable liquids and gases. A number of catalysts have been tested and we have determined a $NiO\text{-}MoO_3/Al_2O_3$ system is best. However, a series of low surface $NiO\text{-}MoO_3$ catalysts we synthesized and tested were very good, particularly $NiO\text{-}MoO_3/ZrO_2$. These results have been reported in previous Quarterly Reports along with detailed data on experiments at varying reaction conditions.

Currently we are carrying out detailed spectroscopic and analytical studies on the liquid fractions from $NiO\text{-}MoO_3/Al_2O_3$ hydrotreating of SRL. We have completed U.V., NMR, C,H,S,N analyses. We are still in the process of collecting mass spectral type analyses in conjuntion with the Grand Forks Energy Research Center. All of these results will be tabulated, analyzed, and summarized in a final report when studies are complete.

Task III

1. The Reduction of Model Compounds Under the COSteam Conditions

(a) Objectives

To understand both the function of the hydrogen donor solvent and the role of mineral matter in lignite during the formation of solvent refined lignite using and comparing the reducing gas mixtures H_2; H_2, CO-H_2O and CO-H_2O.

(b) Introduction

A mixture of carbon monoxide, hydrogen and water is regarded to be superior to either carbon monoxide-water or hydrogen as reducing gases for the liquefaction of lignites. The role of carbon monoxide as a reducing agent for coal and lignite reduction is not well defined. In contrast, a considerable volume of literature and knowledge is available on the subjects of converting carbon monoxide into methane, methanol and hydrocarbons and on the water gas reaction.

It is known that a combination of bases and carbon monoxide is effective in the reduction of aromatic carbonyl compounds, and this is likely to proceed though the formate ion. The reduction of other compounds with carbon monoxide is ill-defined both in terms of products as well as mechanism.

Reactions 1-8 are known or postulated pertinent reactions regarding carbon monoxide chemistry. The reactions are as follows:

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (1)$$

$$2CO \rightarrow C + CO_2 \qquad (2)$$

$$Na_2CO_3 + H_2O \rightleftarrows NaHCO_3 \qquad (3)$$

$$NaOH + CO \xrightarrow[100\ psi]{120 - 150^{o},} NaOCOH \qquad (4)$$

$$2NaOCOH \xrightarrow{360^{o},\ base} Na_2C_2O_4 + H_2 \qquad (5)$$

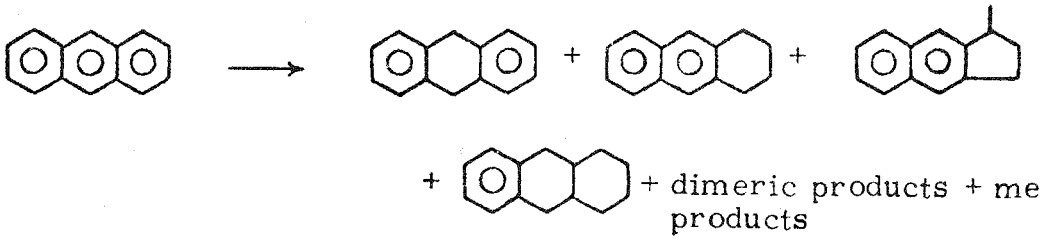
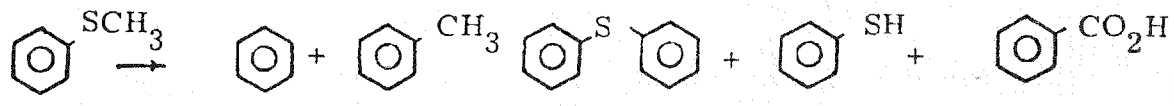
$$HCO_2H \rightarrow H_2 + CO_2 \qquad (6)$$

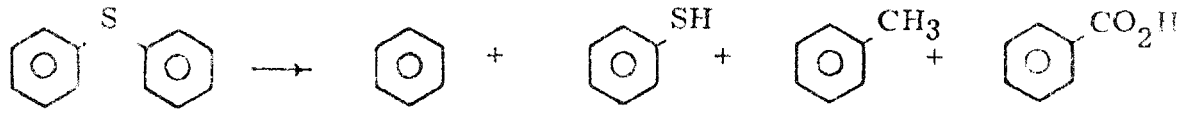
$$HCO_2H \rightarrow H_2O + CO \qquad (7)$$

$$2HCO_2H \rightarrow CH_2O + H_2O + CO \qquad (8)$$

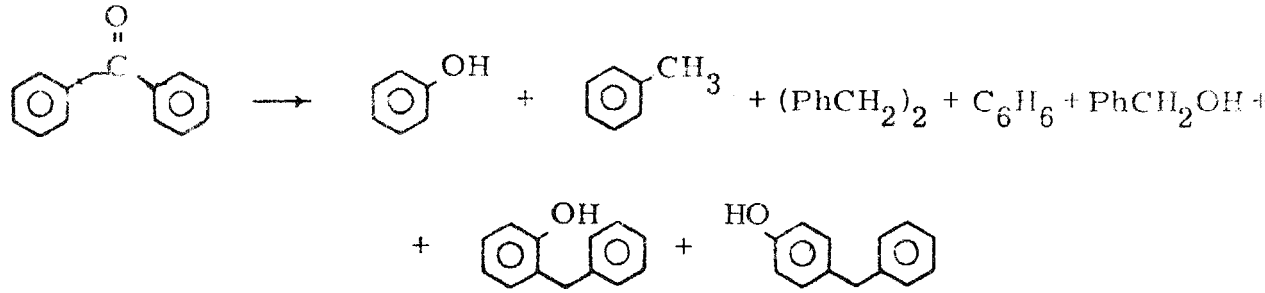
We have previously determined that phenol, diphenylether, ethyl benzene, carbazole and diphenylmethane are converted into reaction products via the reducing gases H_2; $H_2.CO$-H_2O and CO-H_2O in low yields in batch autoclave experiments. The conditions are two hours at reaction temperature of 425°C and pressure of ca. 3500 psi.

Earlier results have shown that 1,2-diphenylethane, benzophenone, benzhydrol, anthracene, quinoline and thioanisole are reactive. The products, which are condition dependent, are as follows:

1. $PhCH_2CH_2Ph \rightarrow PhCH_3 + PhH + PhC_2H_5 + PhCH{=}CHPh + Ph_2CHCH_3$
2. $Ph_2CO \rightarrow Ph_2CHOH + Ph_2CH_2 + PhCH_3 + PhH$
3. $Ph_2CHOH \rightarrow Ph_2CH_2 + Ph_2CO + PhCH_3 + PhH$
4.  + dimeric products + methylated products
5.  + dimeric products + methylated products + other alkylated anilines
6. 

7. 

8. 

9. 

10. $CH_3(CH_2)_9OH \rightarrow C_6 + C_7 + C_8 + C_9 + C_{10}$ hydrocarbons + nonanol (C_9 predominates)

In the course of these model compounds studies, several unique and important features have been discovered and each merits further detailed studies. These conclusions are in addition to the conclusions given in tabular form in Table I. The other features are:

1. Carboxylation occurs during the course of the carbon monoxide reductions. For the outstanding example, benzoic acid is formed in 30% yield during the reduction of diphenylsulfide using carbon monoxide and water with sodium carbonate as the catalyst. Sodium carbonate is not necessary. At this time, it is not known if carbon monoxide or carbon dioxide is reponsible for the carboxyl carbon.
2. Dimerization of the model compounds occurs in less than 5% yields in many of the reductions. This potentially provides a mechanism for repolymerization which occurs during liquefaction. It is not known whether these are radical or ionic type dimerizations.

3. Ferrous sulfide is as good as sodium carbonate as a conversion catalyst for the carbon monoxide-water reduction and appears to do a better job of cracking the model compounds.

An overall summary table is provided herein (Table I) updated to include the results of this report. Earlier Quarterly Reports and publications therefrom describe the detailed results. This Quarterly Report provides new information on the model compound, n-decanol.

(c) Results

Results from our laboratory on electron spin resonance studies imply that the alkaline earth metal oxides are possible catalysts of the carbon monoxide-water reactions. It has been shown that these metal oxides generate radicals with carbon monoxide at room temperature. At 500°C, the order of the ability to generate radicals with carbon monoxide is MgO > CaO > SrO > BaO.

The next step in this investigation was to determine whether the order originating from electron spin resonance studies had any basis of fact in the actual catalysis process. Thus it was necessary to select two structurally different model compounds (for coal conversion) which had previously been studied. These are benzophenone and bibenzyl.

The dilemma of whether to use mole ratios or weight ratios of the metal oxides are resolved by doing both. At the reaction temperature used in these experiments (425°C), the water is above its critical point. Therefore solubility of the metal oxide is not a factor in the data analysis except at the lower temperatures. This reasoning leads to the conclusion that the catalyst mass is more important than the number of moles present. Water disturbs the surface of the heavier metal oxides because of their greater solubility at room temperature (MgO - 0.00062 g/100cc (rt); CaO - 0.131 g/100cc (10°); SrO - 0.69 g/100cc (20°C); and BaO - 3.48 g/100cc (20°C)). The oxides were added

as finely divided solids and silica (not very active) and sodium carbonate (active) runs were made at the same conditions as controls.

The reaction results of bibenzyl with carbon monoxide and water are described in Table 2. For conversion, silica is the worst performer and sodium carbonate is the best and the alkaline earth oxides are intermediate in catalytic activity. Based on products, there are two major paths for the conversion of bibenzyl:

Path A: $PhCH_2CH_2Ph \rightarrow 2\ PhCH_2CH_3$

Path B: $PhCH_2CH_2Ph \rightarrow PhH + PhCH_2CH_3$

Of the catalysts, sodium carbonate is the best for favoring Path B. For this catalyst, the two pathways are equally favored (Run 1), whereas on the opposite end of the scale, silica favors Path A over Path B by 6:1 (Run 2). The presence of benzaldehyde presumably comes from oxygen present in the reactor.

The benzophenone reaction results are illustrated in Table 3. Again silica is the poorest performer for conversion, whereas magnesium oxide is the best. From these data, it appears that weight ratios is the best way to report the data because real differences come to the forefront then, which are hidden with mole ratios. To support this conclusion, it must be remembered that the material is expected to be solid since the water is a gas at reaction temperature so analysis by weight ratios make the most sense. With weight ratios and for conversions the order of catalyst effectiveness is: MgO >CaO > SrO >Na_2CO_3 >BaO > SiO_2 which defies explanation on the basis of basicity. This argues against the formate intermediate with its hydride transfer[1-3] as the sole and perhaps not even major reaction pathway of benzophenone conversion. The electron transfer mechanism from the metal oxide to carbon monoxide (Klabunde and Kaba, unpublished data, University of North Dakota) must be ex-

plored further because the ability of the metal oxide to donate electrons parallels the catalytic activity. Further, the metal oxides are better at converting the intermediate into diphenylmethane. Earlier work has shown that this occurs by a disproportionation.[4]

(d) Work Forecast

The next quarter will be used to evaluate fly ash from different coal-fired electrical generating plants as disposable catalysts for liquefaction and to give new leads for promising catalysts. Two compounds of widely differing chemical bond types will be used in the evaluation. The results will be obtained by quantitative glpc analysis of the reaction solutions from 250-ml batch autoclaves.

References

1. H. R. Appell and I. Wender, Am. Chem. Soc., Div. Fuel Chem. Prepr., 12, No. 3, 220 (1968).

2. H. R. Appell, I. Wender, and R. D. Miller, Am. Chem. Soc., Div. Fuel Chem. Prepr., 13, No. 4, 39 (1969).

3. H. R. Appell, I. Wender, and R. D. Miller, Chem. Ind. (London), 1703 (1969).

4. D. Jones, R. J. Baltisberger, K. J. Klabunde, N. F. Woolsey and V. I. Stenberg, J. Org. Chem., 43, 175 (1978).

Table I. Brief Summary of Batch Autoclave Studies of Model Compounds[a]

	Reducing gas effectiveness for conversion	$CO-H_2O$, Catalytic effect Na_2CO_3	$CO-H_2O$, Catalytic effect of FeS	$CO-H_2O$, Catalytic effect of Fe_2O_3	Effect of tetralin
$PhCH_2CH_2Ph$	$CO-H_2O \cong H_2$, $CO-H_2O \cong H_2$	no effect	no effect	unavailable	no effect on conversions conv. to naphthalene
Ph_2CO	$CO-H_2O, H_2 > CO-H_2O > H_2$	+	unavailable	+	no effect
Ph_2CHOH	$CO-H_2O \cong CO-H_2O, H_2 > H_2$	---------- all give 100% conversion ----------			unavailable
Anthracene	$H_2 \cong H_2$, $CO-H_2O \cong CO-H_2O$	no effect	-[b]	unavailable	+[b]
Quinoline	$H_2 > H_2$, $CO-H_2O > CO-H_2O$	+	+[b]	+	no effect
Thioanisole	$H_2 \cong H_2$, $CO-H_2O > CO-H_2O$	-	+	unavailable	-
Diphenylsulfide	$H_2 \cong H_2$, $CO-H_2O > CO-H_2O$	-	-	unavailable	-
Benzylphenyl ether	$CO-H_2O, H_2 > H_2 > CO-H_2O$	no effect[b]	no effect[b]	unavailable	no effect[b]
n-Decanol	$CO-H_2O, H_2 \gg H_2 > CO-H_2O$	+[c]	+[c]		no effect

- represents lowered conversions, + increased conversions and "no effect" means no change in the conversions.

The product distributions do change and this can be examined via the individual Tables.

[b] Promoted cracking

[c] $CO-H_2O > H \gg CO-H_2O, H_2$

Table 2. The Effectiveness of the Alkaline Earth Oxide Catalysts for the Reduction of Bibenzyl with Carbon Monoxide and Water

Run	Catalyst	Catalyst quantity	Benzene	Toluene	Ethyl-benzene	Benzyl-dehyde	Unknown no. 1	Unknown no. 2	1,1-Diphenyl-ethane	Stilbene	Conversion[1,2]
1	Na_2CO_3	2.3 g	11.1	19.2	10.5	.7	1.3	1.2	.8	.4	45.2
2	SiO_2	2.3 g	1.6	15.6	.8	.8	T[2]	T	T	6.5	25.3
3	MgO	2.3 g	3.4	18.1	4.7	.4	1.3	.7	.3	2.3	31.2
4	CaO	2.3 g	4.7	20.7	3.8	T	1.3	T	T	2.6	33.1
5	SrO	2.3 g	2.2	15.6	2.7	.1	.5	.4	.1	2.6	24.2
6	BaO	2.3 g (.015m)	3.1	16.9	1.8	1.1	1.0	.3	T	2.2	26.4
7	Na_2CO_3	.015 m	9.1	20.5	8.0	.6	1.5	T	.6	.9	41.2
8	SiO_2	.015 m	2.4	12.9	.6	3.4	T	1.2	T	4.1	24.6
9	MgO	.015 m	2.4	13.8	1.2	1.4	1.7	1.3	T	2.3	24.1
10	CaO	.015 m	3.1	17.4	2.2	.9	.9	1.1	.4	2.7	28.7
11	SrO	.015 m	3.9	21.7	3.0	.6	.2	T	T	2.7	32.1

[1] Styrene and diphenylmethane exist in all bibenzyl runs in trace amounts; all results are reported in weight percent. The water present was 10.8 ml, carbon monoxide initial pressure 750 torr, argon 750 torr and 2.73 g (0.015 m) of bibenzyl.

[2] Trace (T)

Table 3. The Effectiveness of the Alkaline Earth Oxide Catalysts for the Reduction of Benzophenone With Carbon Monoxide and Water

Run	Catalyst	Catalyst quantity	Diphenyl methane	Benzohydrol	Conversion[1,2]
1	Na_2CO_3	2.3 g	13.8	13.3	27.1
2	SiO_2	2.3 g	1.9	T[2]	1.9
3	MgO	2.3 g	65.7	2.2	67.9
4	CaO	2.3 g	58.1	1.5	59.6
5	SrO	2.3 g	44.6	T	44.6
6	BaO	2.3 g (.015m)	18.2	1.2	19.4
7	Na_2CO_3	.015 m	10.4	18.6	29.0
8	SiO_2	.015 m	2.4	T	2.4
9	MgO	.015 m	36.0	1.1	37.1
10	CaO	.015 m	34.4	T	34.4
11	SrO	.015 m	32.5	T	32.5

[1] Benzene and toluene exist in all benzophenone runs in trace amounts; all results are reported in weight percent. The water present was 10.8 ml, carbon monoxide initial pressure 750 torr, argon 750 torr, and 2.73 g (.015m) of benzophenone.

[2] Trace (T)

Task IV

1. Mechanism of the CO Reducing System

(a) Objective

To investigate the mechanism of solvent refining and its related processes under the system of $CO-H_2O$ or $CO-H_2O-H_2$ in the presence of constituents possibly present in the mineral matter of lignite.

(b) Introduction

This task deals with the possible modes of activation of carbon monoxide and carbon monoxide-water over minerals present in lignite and, possibly, acting as catalysts in the $CO-H_2O-H_2$ solvent refining or COSteam liquefaction processes. Since the $CO-H_2O$ system is very effective in the liquefaction of lignite (moreso than H_2 alone), we sought unusual activation mechanisms. One such mechanism is the initiation of radical processes when CO adsorbs on metal oxides.

In previous Quarterly Reports we have reported that well degassed surfaces of MgO, CaO, SrO, BaO, and ThO_2 give rise to a paramagnetic CO derived species upon exposure to a CO atmosphere. All other oxides examined did not yield observable radical species under similar conditions.

The activity of the alkaline earth oxides, heat-treated at 600°, toward formation of a paramagnetic species upon CO exposure has been shown to follow a systematic pattern: MgO>CaO>SrO>>BaO. However, this trend is changed (i.e., SrO $\sim$ CaO $\sim$ MgO) when the activity is corrected for surface area. When heat treated at 800°, the initial results give no such systematic pattern but rather MgO $\sim$ SrO < CaO. The order, when corrected to unit surface area, is SrO > CaO > MgO. These trends correlate roughly with either the number of Lewis basic or reducing sites.[1,2] A basic site could be an electron pair from oxygen or isolated hydroxyl groups, whereas a one electron reducing site might be an area of high electron density; for example, a cationic vacancy. Thus, the order of activity/area could be explained by either the number of basic or reducing sites.

Heat treatment of the alkaline earth oxides can affect the number of both the Lewis basic[3] and reducing sites.[1,3] The effect of the heat treatment temperature on the number of reducing sites on MgO and SrO has been examined in detail. The related study of the number of basic sites on MgO or SrO as a function of heat treatment temperature has met with no success to date.

We have examined in detail the relationship between the heat treatment temperature and the formation of radicals in both the MgO/CO and SrO/CO systems. The trends in both the MgO/CO and SrO/CO systems and the number of reducing sites on the respective alkaline earth oxides as a function of the heat treatment temperature correlate very strongly and, thus, support our earlier contention that the primary site for CO radical formation is a reducing site. In earlier Quarterly Reports we have speculated that the basic sites also play a role as a site for nonradical CO adsorption with, perhaps, later migration to a reducing site. Thus it appears that both basic and reducing sites are important in CO adsorption and radical formation on the alkaline earth oxides.

(c) Results and Discussion

(A) Oxide Survey. The oxide survey was completed in the January-March, 1978 reporting period. Only the alkaline earth oxides (excepting BeO) and ThO_2 gave rise to a paramagnetic species upon exposure to carbon monoxide under our experimental conditions.[4] The most compelling characteristic common to the oxides that form paramagnetic species upon CO adsorption is that they all possess both basic and reducing sites.

(B) Chemistry of the CO-Derived Surface Species. A study of the effect of the heat treatment teperature of MgO[5,6] on the relative amount of radical formed upon exposure to carbon monoxide or nitrobenzene has been completed and is discussed in the January - March, 1978 Quarterly Report. MgO samples were heat treated at 400 - 1000°C in 100°C intervals. These samples were then exposed to either 150 torr of CO or ca. 0.25 torr of nitrobenzene. Radical growth was then monitored

until a constant radical concentration was obtained. The results[7] of the MgO/CO and MgO/nitrobenzene systems as a function of the heat treatment temperature are shown in Figure I.

A similar study on the effect of heat treatment temperature on SrO has also been carried out and completed this past Quarter. Procedures were the same as used for the MgO systems.[5,6] The results of this study are shown in Figure II. A maximum radical concentration is obtained at a heat treatment temperature of 800°C in both the SrO/CO and SrO/nitrobenzene systems. Except for the 900° run[8] the curves for both the SrO/CO and SrO/nitrobenzene systems are very similar.

As can be seen from Figures I and II, the [CO·] and [$C_6H_5NO_2^-$] curves as a function of the heat treatment temperature are very similar for each individual alkaline earth oxide. In as much as the epr spectra in the MgO/nitrobenzene system is that of the nitrobenzene anion radical,[2,9,10] $C_6H_5NO_2^-$, it seems reasonable that the active site for nitrobenzene radical formation is one electron reducing site. The similarity of the two curves in both Figures I and II strongly suggest that the active, primary site for CO radical formation is also a reducing site. The number of CO radicals formed on MgO or SrO is about a factor of 10 - 20 lower relative to the corresponding data point for the nitrobenzene systems. Thus for CO radical formation more stringent site requirements are indicated. This may also be related to differences in the electron affinities of CO and nitrobenzene. In comparison the number of radicals, either CO· or $C_6H_5NO_2^-$, formed on SrO is generally a factor of ten lower than in the corresponding MgO system.[11]

During the study of the effect of the heat treatment temperature of SrO exposed to CO an interesting phenomenon was observed. When SrO is heat treated at 600° and exposed to CO then either (1) two different radicals are formed or (2) similar radicals are formed on two different surface sites. At all other heat treatment temperatures only one species has been observed.[12] The two species on

the radicals on two different sites with SrO heat treated at 600 had different saturation and desorption with heat characteristics.

Several SrO samples were prepared in special quartz epr cells for use in the Bruker B-ER 400 HT ultra high temperature resonator system. These samples, heat treated at 600^{o} and 800^{o}, were exposed to ca. 150 torr of CO and then sealed. The samples were kept at room temperature until a constant radical concentration was obtained. Samples were then heated in the ultra high temperature cavity to the desired temperature during which time changes in the epr spectra could be noted. The two species or radical sites on SrO samples heat treated at 600^{o} can be labeled as "low-field" and "high-field" lines in the epr spectra. As soon as the temperature is increased the "high-field" signal begins to decrease in intensity at ca. 500^{o} and by 800^{o} is reduced to ca. one-half of its orignial intensity. For these samples originally heat treated at 600^{o}, exposed to CO, and then heated to $600\text{-}800^{o}$ in the presence of the CO atmosphere the signal regrows to ca. 60-100% of its original, maximum value. The desorption of the radical from a SrO sample heat treated at 800^{o} and exposed to CO is very different, however. The single observable epr line from the 800^{o} sample begins to decrease in intensity at ca. $500\text{-}600^{o}$ and disappears almost completely by 850^{o}C. Later signal regrowth is less than 10% of its original maximum signal intensity. After heating all samples in the presence of the CO atmosphere there was only one radical species or radical site observed in later regrowth experiments independent of the original heat treatment temperature. Work of this interesting phenomenon exhibited with SrO and CO will be continued during the next reporting period.

Some work this past reporting period has also been done on the MgO/CO systems which has been discussed in detail in earlier Quarterly Reports. The results of these investigations, which extend or complete the earlier results, will be briefly summarized.

Using normal pressure-volume measurements it has been determined that ca.

1×10^{19} molecules of CO are adsorbed per gram of MgO heat treated at 500^{o}, 600^{o}, or 800^{o}. These measurements were carried out using large sample (1.0 - 1.5 gr MgO); the final pressure after heat treating was generally a factor of ten higher (i.e., 1×10^{-5} torr) than in the case of normal epr samples (final pressure, 1×10^{-6} torr and sample sizes of ca. 10-100 mg). Based on the number of spins per gram from Figure I it can be concluded that ca. 10-35% of adsorbed CO or MgO is in a paramagnetic form. There were no differences detected concerning the amount of CO adsorbed based on the length of time the surface was exposed to the CO atmosphere.

The activity of the various alkaline earth oxides heat treated at 600 and 800^{o} towards CO radical formation has been determined and the results are listed in Table I. In order to determine the number and trends of the reducing sites on the alkaline earth oxides a corresponding study with nitrobenzene has been carried out. The final results are given in Table II. The trends between the CO and nitrobenzene systems at heat treatment temperature of 600^{o} correlate closely. For example, for the (spins/gr) data $[CO]_{rel}$ and $[\phi NO_2^{-}]_{rel}$ both follow the pattern MgO > CaO > SrO. When this data is corrected for surface area similar patterns evolve for both data sets, namely MgO $\sim$ CaO $\sim$ SrO. The situation for the 800^{o} heat treatment studies is by no means as clear although some common trends can be noted between the CO and nitrobenzene data sets. For example, the (spins/gr) data for both systems at 800^{o} heat treatment temperature show the same pattern: SrO < MgO < CaO. When the data is corrected for surface area, however, the activity order for the two systems differ (for the CO system, MgO < CaO < SrO; for the nitrobenzene system, MgO < SrO < CaO). These differences are now under study.

Table I. Activity of the Alkaline Earth Oxides Towards CO Radical Formation. Heat Treatment Temperatures of 600 and 800°

Sample	$[CO]_{rel}$, (spins/gr)		$[CO]_{rel}$, (spins/m^2)*	
	600°	800°	600°	800°
MgO	12.4	8.4	0.9	0.6
CaO	7.7	8.8	1.3	1.5
SrO	1.0	6.5	1.0	6.5

*Calculated using the following surface areas: MgO, ∿ 140 m^2/gr; CaO, ∿ 60 m^2/gr; SrO, ∿ 10 m^2/gr.

Table II. Activity of the Alkaline Earth Oxides Towards $\phi NO_2^{\cdot-}$ Radical Formation. Heat Treatment Temperatures of 600 and 800°

Sample	$[\phi NO_2^{\cdot-}]_{rel}$, (spins/gr)		$[\phi NO_2^{\cdot-}]_{rel}$, (spins/$m^2$)*	
	600°	800°	600°	800°
MgO	11.7	11.7	0.8	0.8
CaO	3.4	15.5	0.6	2.6
SrO	1.0	1.7	1.0	1.7

*Calculated using the following surface areas: MgO, ∿ 140 m^2/gr; CaO, ∿ 60 m^2/gr; SrO, ∿ 10 m^2/gr.

Several inorganic and organic molecules have been added to a well degassed, thermally activated MgO surface (heat treated at 800^{o}). The organic compounds were added by using their vapor pressure at room temperature or, in cases when the vapor pressure is extremely low, by use of a break seal attached directly to the epr tube such that the surface can remain exposed to the organic vapor for whatever period of time required. The results of this study to date are given in Table III. Work on the addition of organic molecules to MgO will continue in the next Quarter. We hope to relate the results of this study to the electron affinity of the organic molecules.

Table III. Interaction of Organic Substrates on Thermally Activated (800^{o}C) MgO Surfaces

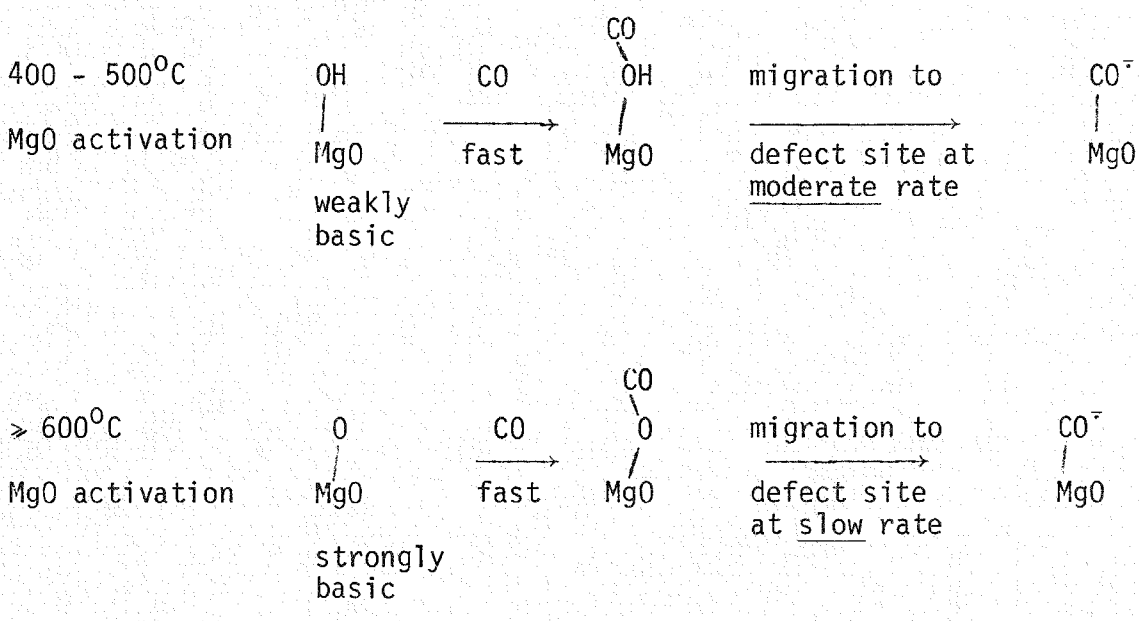
Substrate	Color of Surface	EPR Signal
Acetaldehyde	No change	No
Acetonitrile	No change	No
Benzonitrile	No change	Yes (at 77^{o}K; g=2.0030)
Benzene	No change	No
1,4-Benzoquinone	Dark bluish black	Yes (g=2.0046)
Benzophenone	Sky blue	Yes
Trifluoro methylbenzene	No change	Yes*
1,3-Di(trifluoro-methyl) benzene	No change	No
Perfluorobenzene	No change	Yes*

*Only small epr signal observed; needs to be duplicated

In summary, we feel that all of the data generated to date (described here and in earlier Quarterly Reports) concerning the CO radical formation on alkaline earth oxides can be explained by the following conclusions.

(1) The same sites that are responsible for the formation of the nitrobenzene anion radical are probably important in the formation of the paramagnetic species formed when well-degassed, thermally activated MgO, CaO, or SrO surfaces are exposed to CO. These sites are one-electron reducing sites (nonparamagnetic). Thus, one would predict that the CO radicals resemble CO^{-} more than CO^{+}. The actual physical appearance of the reducing site probably resembles crystalline defects where Mg^{2+} vacancies, and thus high electron density,[13] exists.

(2) The Lewis base sites on MgO[14] are also important. The data suggest that nonparamagnetic CO can be adsorbed on a base site and then later migrates to a reducing site or somehow interacts with a nearby reducing site, forming the observed paramagnetic species. The following scheme would explain our current results with MgO surface exposed to CO:



(d) Work Forecast

Work will continue on the detailed surface chemistry of adsorbed radicals on MgO, CaO, SrO, BaO, and ThO_2.

(1) Determination of initial rate constant for the growth of CO radical on MgO samples heat treated at various temperatures.

(2) Develop a method for base site determinations.

(3) Begin studying $^{13}CO/MgO$, $^{13}CO/MgO/H_2O$, and related system. The ^{13}CO needs to be purified by exposing to Zn metal film at $400^{o}C$.

(4) Continue study of addition of small organic molecules to well degassed surfaces of alkaline earth oxides.

(5) IR study of CO on MgO.

References and Footnotes

1. Private communications with K. Tanabe, Distinguished Foreign Scientist, University of North Dakota (1976).

2. T. Iizuka, H. Hattori, Y. Ohno, J. Sohma, and K. Tanabe, J. Catal., 22, 130 (1971).

3. K. Tanabe, "Solid Acids and Bases," Academic Press, New York-London, (1970).

4. Briefly the experimental conditions were as follows: (1) A water-washed, dried sample of the oxide was heat treated at 600° in vacuo (10^{-6} torr) for about 10-18 hrs. (2) After checking for background epr signals, ca. 150 torr CO was added to the oxide sample. (3) The sample was checked immediately and ca. 1 week later for paramagnetic species. See Quarterly Report, April - June, 1977, and Quarterly Report, July - September, 1977, for more details and a list of the oxides surveyed.

5. Samples were heat treated at a given temperature for ca. 12-18 hrs in vacuo. The final pressure was generally ca. 10^{-6} torr.

6. For experimental details see Quarterly Reports, July - September, 1977 and January - March, 1978.

7. These results are slightly different from those reported earlier in that an error was discovered in the radical concentration calculations. However, this error did not affect any trends that have been noted in the data.

8. The 900° run with SrO exposed to nitrobenzene is being duplicated.

9. H. Hattori, M. Itoh, and K. Tanabe, J. Catal., 38, 172 (1975).

10. A. J. Tench and R. L. Nelson, Trans. Faraday Soc., 63, 2254 (1957).

11. The number of radicals formed in the SrO systems is lower by a factor of 2-20 related to the MgO systems if comparisons are made at each individual heat treatment temperature.

12. It is possible that one radical species or surface site may predominate at heat treatment temperatures below 600° and the other radical or site at more elevated temperatures. This possibility will be investigated in the near future by determining the g-values of the radical species as a function of the heat treatment temperature.

13. K. J. Klabunde, R. A. Kaba, and R. M. Morris, Inorg. Chem., in press; and see also earlier Quarterly Reports.

14. There is insufficient data to discuss the possible importance of basic sites in the other alkaline earth oxides at the present time.

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