Basic Properties of Coals and Other Solids
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Yearly Report #2 for September 1, 1990 - August 30, 1991

Title: Basic Properties of Coals and Other Solids

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I. Abstract

Results are reported here for the heats of immersion of samples of polyvinylpyridine and the following coals: Exxon Rawhide, Argonne Wyodak, Illinois #6, Pittsburgh #8 in solutions of twelve sulfonic and carboxylic acids and boron trichloride. Heats of immersion in the different types of acids vary considerably from one solid system to another and the simple solid base polyvinylpyridine is a poor model for the more complex coals. The coals show varying degrees of correlation with each other.

An important feature of the second half of the year has been an extensive comparison of titrametric heats of reaction of the different acids with several coal liquids and the coals from which they were derived.

II. Background

From the standpoint of the work to be discussed here the most important result from last year's report was the excellent correlation obtained between titrametric heats of interaction between a series of eleven strong acids (0.25 M in acetonitrile) with poly 4-vinylpyridine slurries and pyridine solutions at 25 °C. Figure 1 reiterates those results which will be important for comparison with comparable investigations using coals in this year's report. Figure 2 reiterates an equivalent plot from our previous grant which compared the response of solid sulfonic acid resin with *p*-toluene sulfonic acid in their response to a series of bases. An alternative thermochemical method employs heats of immersion of solids into liquid acids or their solutions. As we showed in last year's report, there is a very poor correlation between heats of immersion and titrametric heats. Since both types of thermochemical results will be presented in this report it is important to bear in mind the considerable difference between the two sets of properties.

Titrametric heats of interaction are obtained, as the name implies, by titrating a solution of the acid into a stirred slurry of the basic solid or solution of the liquid base. This method measures the heat of interaction first of the most accessible and most basic sites of the solid with the acid, and then after they are neutralized subsequent increments of acid neutralize progressively weaker sites at progressively less accessible positions. The heat of immersion experiment involves the sudden release of the solid into an excess of liquid acid or its solution with an immediate neutralization of all readily accessible basic sites, both strong and weak, followed by the gradual neutralization of the rest as the liquid penetrates into the solid. The important components that determine the shape of the heat of immersion thermogram are again the number and strength of the basic sites most available at the surface, the porosity, the permeability of the solid, the extent to which it is swollen, and the degree to which the acidic and basic sites in the coal are involved in hydrogen-bonding with each other since hydrogen-bonding interactions must be broken endothermically in order to release any exothermic interaction

between the penetrating acid or base solution.

III. Experimental:

The experimental procedure for handling the coals described below is taken verbatim from the fifth quarterly report. The calorimetric procedures have been described in previous reports and are routine.

The coal samples were mostly obtained in sealed ampules from the Argonne Laboratories Coal Bank. Each ampule was broken inside the Vacuum Atmospheres dry box under an argon atmosphere. A sample was transferred to a glass jar, screw-capped and left stored in the dry box. Small amounts of this sample (about 150 mg) were removed from the dry box in sample vials and out-gassed at 110° C in the vacuum oven for about 16 hours prior to each ΔH_{imm} measurement in the acid solutions. The literature provided by Argonne stresses the point that samples of some coals are highly susceptible to atmospheric oxidation if left exposed to the air. They also recommend that samples should be used immediately after opening the ampules and give little assurance concerning the stabilities of the samples after opening. However, since it would be wasteful to open a fresh 5 g ampule for each ΔH_{imm} measurement, which only requires 100 mg of sample, we believe that the careful protection of the open ampule in a screw-capped container in the dry box should be adequate protection. We have checked this question for our present sample by repeating experiments after various periods of time. The majority of the average values taken from 2 or 3 measurements for a typical acid/coal system, sometimes spread as far as 2-3 weeks, show a relative mean deviation of only $\leq 5\%$. A letter from Dr. Charles Cantrell of S.E.I Wilsonville is attached which provides analytical data for the coal liquids.

The Wyoming Rawhide CMEV sample was obtained from Exxon, stored in a glass jar as

supplied, and apparently is only slightly susceptible to oxidation. We have handled this outside the dry box, but have used freshly out-gassed samples for each ΔH_{imm} measurement.

Sharp thermograms showed that interactions of the acids with the coal samples did not involve processes with long term heat evolution, such as would be expected by exothermic swelling, or the attack of acid on the solid matrix such as that observed previously with polyvinylpyridine.

Solutions of the purified acids in acetonitrile at 0.60 - 0.70 M were used as described in the first yearly report.

IV. Results and Discussion

Two types of experiments will be reported here. 1) Comparison of titrametric heats of interaction of three coal slurries with solutions of various acids and the corresponding titrametric heats of coal liquids derived from the same types of coals. These experiments are comparable to those on which Figures 1 and 2 are based whereby the homogeneous solution of acid or base is titrated with a series of basic or acid solutions and compared to a slurry of a comparable solid acid or base. Figures 1 and 2 are the relevant models which provide the basis for subsequent comparisons of coals and coal liquids. Figures 3-6 present the incremental titration of slurries of Exxon Rawhide, subbituminous; Illinois, bituminous; Black Thunder, subbituminous; and Pittsburgh #8, bituminous with several coal liquids derived from comparable types of coal using acetonitrile solutions of benzenesulfonic acid, trifluoromethane sulfonic (triflic) acid, methanesulfonic acid and trifluoroacetic acid. Each point is the result of a separate calorimetric titration of a small increment of the acid solution into the coal or coal liquid. Since the increments of acid are small compared to the excess of basic liquid and solid, one would obtain a horizontal line representing equivalent titrametric heats of neutralization if all sites that were

being reached by successive increments of acid were equally strong and accessible. What is remarkable about Figures 3-6 is the general similarity of patterns with the different titrations although (Figure 6) there are some differences especially as the later increments of acid are added to the samples of coal liquid. In general, and not surprisingly, the coal liquids give more exothermic interactions than the coal slurries since many of the hydrogen-bonds are already ruptured in the former. Furthermore, their heats of interaction maintain more constant values as the cumulative amount of acid becomes greater. The most exothermic results are obtained with triflic acid, by far the strongest of the series, and are less exothermic for trifluoroacetic acid or methanesulfonic. In Figures 7-10 the results are replotted, each point for each acid being taken from those on Figures 3-6. When presented in this way the differences between the different coal liquids and the solid parents are dramatic. Figure 7 shows a general correlation in terms of the behavior, not only of different increments, but also for the four different acids. Figure 10 comparing coal liquid R 259 with Pittsburgh #8 is an extreme of complexity.

In contrast to the results of thermometric titrations described above, Table I lists the heats of immersion of four coal samples and polyvinylpyridine in solutions of twelve strong Brönsted acids in acetonitrile and the very strong Lewis acid, boron trichloride in hexane. Figures 11-16 compare the heats of immersion of Exxon Rawhide, Illinois #6, Wyodak and polyvinylpyridine. Obviously polyvinylpyridine is an overly simplistic model for the behavior of these coals as complex solids in their interactions with this series of acids.

Comparing the coals with each other provides some better correlations and in fact, improves the credibility of the whole exercise. Figure 12 shows a rather good correlation between the interactions of Exxon Rawhide coal and Wyodak. In view of the fact that these are both taken from the same subbituminous coal field, this is perhaps not surprising. On the other hand they are different samples taken from different areas at different times and it might not be surprising if they were quite different. Figure 13 and 14 compare the two Wyoming coals with

Illinois #6 bituminous. The interesting feature of both plots is the clear dispersion between aliphatic acids and the series of benzenesulfonic acids. Presumably this is due to a pi-pi interactions between the aromatic portions of the acids with aromatic portions of the coals which differentiate them from the aliphatic ones as do Figures 15 and 16.

V. Presentations

1. Invited paper "Comparison of the Strengths of Solid Acids and Bases by a Thermochemical Method", E.M. Arnett and T. Ahsan at Symposium on Heterogeneous Organic Reactions, ACS Southeast-Southwest Combined Regional Meeting, New Orleans, December 7, 1990.

2. Presentation of results at the University Contractor's Review Meeting in Pittsburgh on Wednesday, June 26, 1991.

3. Invited paper "Acid-Base Properties of Coals and Coal Liquids" by E.M. Arnett and T. Ahsan at Symposium on "Novel Analytical Techniques for Fossil Fuels" sponsored by the Division of Fossil Fuel Chemistry at the National ACS Meeting in New York, Tuesday, August 27, 1991.

4. Presentation by Dr. Ahsan at the 65th ACS Colloid and Surface Science Symposium, University of Oklahoma, June 17, 1991, "Calorimetric Study of the Reactivity of Commercial Silica with Strong Brönsted and Lewis Acids".

VI. Personnel

Contributions to this work were made primarily by Dr. Tanweer Ahsan with assistance

from two graduate students, Steven Truckenbroad and Eric Olson.

VII. Publications

E.M. Arnett and T. Ahsan, "Heats of Interaction of Strong Brönsted Acids with Silica", J. Am. Chem. Soc. (in press).

E.M. Arnett, T. Ahsan and K. Amarnath, "Thermochemical Comparisons of Solid and Homogeneous Acids and Bases---Pyridine and Polyvinylpyridine as Prototype Bases", J. Am. Chem. Soc. (in press).

VIII. Future Work

During the coming year we hope to focus primarily on applying the thermochemical comparison method to various coals and their derived coal liquids. Permission has been requested from Dr. Kenneth Jones, the Project Officer, to measure the acidic properties of coal liquids by thermometric titration used with our previous DOE grant to compare the acidic properties of various coals. This will extend the original proposed work by comparing coal liquids as homogeneous analogues of the coals, and through titration with bases to measure the acidic properties of the coal liquids. Neither of these types of studies with coal liquids have been included in the original proposal for the present grant.

Table-1. Heats of immersion (ΔH_{imm}) of coals and Polyvinylpyridine in (0.65M) acid solutions in acetonitrile.

Acids	pka ^a	PVP	- ΔH_{imm} (cal/g)		Wyodak	IL#6	Pittsburgh#8
Ethanesulfonic	-1.68	148.33 $\pm$ 17.0	37.35 $\pm$ 0.84	44.62 $\pm$ 1.56	22.86 $\pm$ 0.48		
Methanesulfonic	-1.92	147.55 $\pm$ 1.47	37.99 $\pm$ 1.46	44.79 $\pm$ 2.00	21.56 $\pm$ 0.24	21.98 $\pm$ 1.19	
Triflic	-5.90	130.54 $\pm$ 9.54	59.16 $\pm$ 2.85	60.16 $\pm$ 1.61	45.08 $\pm$ 2.36	29.39 $\pm$ 1.47	
Trifluoroacetic	0.54	85.75 $\pm$ 0.72	32.19 $\pm$ 0.86	35.69 $\pm$ 1.15	18.53 $\pm$ 0.48	12.62 $\pm$ 0.60	
Trichloroacetic	0.69	80.82 $\pm$ 1.40	28.17 $\pm$ 0.03	23.89 $\pm$ 0.88	14.71 $\pm$ 0.72		
Difluoroacetic	1.30	74.99 $\pm$ 1.89	29.73 $\pm$ 0.56	31.55 $\pm$ 0.66	16.44 $\pm$ 0.45		
Dichloroacetic	1.36	70.56 $\pm$ 0.82	29.06 $\pm$ 0.22	26.52 $\pm$ 0.49	16.38 $\pm$ 0.38		
4-Toluenesulfonic	-6.55	66.89 $\pm$ 1.99	24.81 $\pm$ 1.02	24.81 $\pm$ 0.95	20.39 $\pm$ 0.41		
Benzenesulfonic	-2.70	62.08 $\pm$ 0.53	30.55 $\pm$ 0.94	29.30 $\pm$ 0.22	23.79 $\pm$ 1.87		
Chloroacetic		60.00 $\pm$ 0.82	27.25 $\pm$ 0.07	26.72 $\pm$ 0.94	16.75 $\pm$ 0.59		
4-Chlorobenzenesulfonic		53.26 $\pm$ 1.37	24.89 $\pm$ 0.94	24.09 $\pm$ 1.21	19.14 $\pm$ 0.98		
4-Nitrobenzenesulfonic	-4.00		23.24 $\pm$ 0.27	26.23 $\pm$ 1.00	20.81 $\pm$ 0.79		
Boron trichloride ^b			12.09 $\pm$ 0.58	11.34 $\pm$ 1.36	33.78 $\pm$ 2.23		

^a Acidic dissociation constants of sulfonic acids in water at 25 °C from Grunrine et al; *J.Org.Chem.* 1986,51,25,5013. and J.P.Guthrie; *Can.J.Chem.* 1978,56,2342. which describes the unusual difficulties of comparing the strengths of very strong acids. ^b Hexane as solvent.

Fig.1 Plot of ΔH_{PVP} vs. ΔH_{PYR} with some strong acids at 25 °C

Fig.2 Plot of ΔH_{Dowex} vs. ΔH_{PTSA} with some strong bases at 25 °C

Fig.3 $\Delta H_{\text{titr.}}$ profile for coal liquid(ExxonYP35) and coal slurry(Exxon Rawhide) with some strong acids in acetonitrile

Fig.4 $\Delta H_{\text{titr.}}$ profile for coal liquid(V182) and coal slurry(IL#6) both from Wilsonville with some strong acids in acetonitrile.

Fig.5 $\Delta H_{\text{titr.}}$ profile for coal liquid(V182) and coal slurry(Blk.Thunder),¹
both from Wilsonville, with some strong acids in acetonitrile

METHANESULFONIC ACID

TRIFLIC ACID

TRIFLUOROACETIC ACID

Fig.6 $\Delta H_{\text{titr.}}$ profile for coal liquid(V182) and coal slurry(Pitts#8), both from Wilsonville, with some strong acids in acetonitrile

Fig.7 Comparison plots for coal liquid(ExxonYP35) and coal slurry(Exxon Rawhide) acid titrations

Fig.8 Comparison plots for coal liquid(V182) and coal slurry(IL#6)titrations

Fig.9 Comparison plots for coal liquid(V182) and coal slurry(Blk.Thunder) acid titrations

Fig.10 Comparison plots for coal liquid (V182) and coal slurry(Pitts#8) acid titrations

Fig.11 Comparison of ΔH_{imm} of Argonne Wyodak coal and PVP in strong acids

Fig.12 Comparison of ΔH_{imm} of Argonne Wyodak and Exxon coals in strong acids

Fig.13 Comparison of ΔH_{imm} of Argonne Wyodak and Argonne IL#6 coals in strong acids

Fig.14 Comparison of ΔH_{imm} of Argonne IL#6 and Exxon Rawhide coals in strong acids

Fig.15 Comparison of ΔH_{imm} of Exxon Rawhide and PVP in strong acids

Fig.16 Comparison of ΔH_{imm} of Argonne IL#6 and PVP in strong acids

SEI

May 3, 1991

Dr. Edward M. Arnett
Chairman and R. J. Reynolds
Professor of Chemistry
Duke University
Durham, North Carolina 27706

Dear Dr. Arnett:

I will be glad to supply you with the requested coal samples and they should be arriving in a few days. I'll try to answer your questions regarding pretreatment of the coals. Perhaps the most significant factor is air oxidation of which we make no attempt to quantify. Basically, the coals follow this route before they are liquefied. A small amount of washing occurs at the mine. This removes mostly mineral matter and puts the respective coals on a consistent moisture and ash level. The coal is then trucked to Empire Coke near Tuscaloosa, Alabama where it is placed on the ground in piles for storage. A typical particle size is 4" x 4" and some smaller at perhaps 1/4". Residence time on the ground is variable but two months is nominal. When an experimental run is ready to be made, the grinder, Empire Coke, is notified and the coal is pulverized to approximately 75 microns and stored in large metal bins. Each bin holds about two tons of coal and they are blanketed with nitrogen. The grinding process reduces the moisture some. Bituminous coals having about ten percent moisture will have been reduced to approximately two percent while subbituminous coals coming in at thirty percent will leave with about two percent moisture. Then about fourteen bins of the pulverized coal are shipped by truck to the pilot plant at Wilsonville. Within two weeks all of the coal will have been liquefied but the grinder is notified to have more ready before the fourteen bins have been consumed. A typical experimental run continues for twelve weeks and therefore it is entirely possible that some of the coal experiences, two to three months weathering before liquefaction. Oxidation no doubt influences performance and we are hoping in the near future to eliminate that factor by having grinding facilities on site.

I've included a Table of typical physical and chemical properties for each coal that you obtained distillates. I checked to make sure for which Pittsburgh coal distillate you received because for that coal we did process some heavy media cleaned coal. Your

samples came from what I describe as typical Pittsburgh seam coal. It contained about fourteen percent ash and received typical physical cleaning at the mine. However, a large batch of this coal was sent to CQ Incorporated at Homer City, Pennsylvania for heavy media cleaning which reduced the ash level to four percent. Both coals were liquefied in the same experimental Run 259. If you would like to have Pittsburgh distillates from the low ash coal, please let me know and I will supply both the coal and the distillates. I hope the additional information causes no confusion and in essence to answer your questions the coal is not purposely dried in any way and storage is outside at ambient conditions. However, the fine, pulverized coal is stored in bins under nitrogen until liquefied. Those are the type samples you will be receiving. If you have any questions, please call me at 205-669-6747.

Sincerely,

Charles Cantrell

CC/md

April 17, 1991

Dr. Edward Arnett
Department of Chemistry
Duke University
Durham, North Carolina 27706

Dear Dr. Arnett:

I have summarized below some typical properties of liquefaction oils I recently sent to you. The total oil is a combination of the V161 and V182 samples with about 40 wt% coming from the V161. Just guessing. I would think it to be more acidic, maybe due to phenols, and the V182 to be more basic, possibly because of higher nitrogen content. If you have any questions, please give me a call at 205-669-6717.

Run 259- Pittsburgh # 8 coal (bituminous)

Sample	%C	%H	%N	%S	Boiling Range, F
V161	84.1	13.2	0.1	0.05	75-500
V182	85.2	10.4	0.2	0.02	500-800
Total	85.5	11.9	0.3	0.04	75-800

Run 260-Black Thunder coal (subbituminous)

V161	85.1	12.6	0.2	0.04	75-500
V182	87.5	10.5	0.4	0.04	500-800
Total	87.1	11.9	0.4	0.02	75-800

Run 261-Illinois #6 coal (bituminous)

V161	86.7	13.1	0.1	0.03	75-500
V182	88.8	10.5	0.2	0.02	500-800
Total	87.5	11.4	0.2	0.03	75-800

Sincerely,

Charles Cantrell

Charles Cantrell

Table 1. Coal Analysis

Coal Mine	Black Thunder Burning Star 2	Black Thunder Black Thunder	Pittsburgh No. 8 Ireland
Moisture, wt %	5	25	3
<u>Ultimate Analysis, MF wt %</u>			
Carbon	70.6	68.7	69.8
Hydrogen	4.8	5.1	4.8
Nitrogen	1.5	1.0	1.1
Sulfur	3.4	0.4	4.5
Ash	11.5	6.1	14.5
Oxygen (by diff.)	8.2	18.7	5.3

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