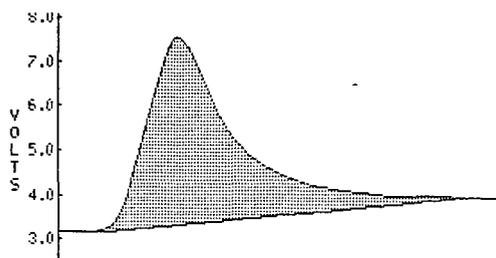
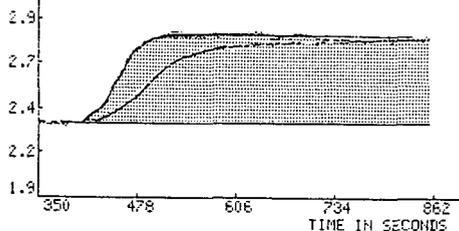


FLOW DIAGRAM

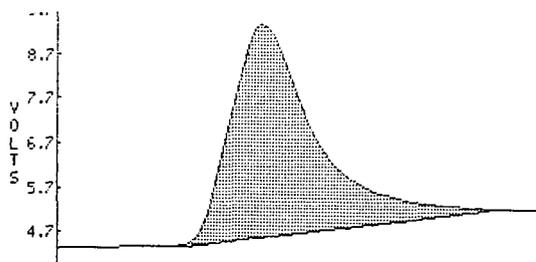
Figure 1. Diagrammatic sketch for lay-out of flow microcalorimeter with UV detector.



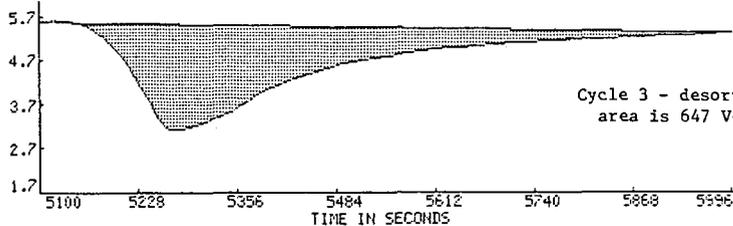
Cycle 2 - adsorption exotherm
area is 571 V-secs



Cycle 2 - UV absorption
Empty bed 201 V-sec
Coal bed 165 V-sec



Cycle 3 - adsorption exotherm
area is 596 V-sec



Cycle 3 - desorption endotherm
area is 647 V-sec

Figure 2. Flow microcalorimeter records of adsorption-desorption cycles for 25.4 mM 4-t-butylpyridine in iso-octane interacting with bed of heat-treated 170-230 mesh low-ash bituminous coal (PSOC #11).

chloroform and its shift upon complexation with bases (12).

The spectral shifts were determined with a Mattson FTIR spectrometer used in the transmission mode, operated to provide resolutions of one wave-number for OH and CD shifts, and about 0.3 wave-numbers for carbonyl shifts.

Surface Areas by Gas Adsorption

The specific surface areas of all coal samples were determined by nitrogen adsorption with the BET analysis, using the gas chromatography method with a Quantichrome Monosorb Surface Area Analyzer and the classical static equilibrium method with a Numinco-Orr Surface Area-Pore Volume Analyzer. The Numinco-Orr Analyzer was also used for adsorption studies with 2,2'-dimethylbutane and with carbon dioxide, both at 25 C. The adsorption data for dimethylbutane were analyzed with the BET method, and the carbon dioxide data were analyzed by both the BET and the Dubinin-Polanyi method (13).

Materials Used in this Investigation

Coal powders prepared from five different coal samples were investigated. Four came from the Pennsylvania State University coal bank, and we also tested a more recently mined bituminous coal from Bethlehem Steel Company (Van-131). The properties of these coals were as follows:

<u>Identification</u>	<u>Rank</u>	<u>% Carbon</u>	<u>% Moisture</u>	<u>% Ash</u>	<u>% Volatiles</u>
PSOC #11	Bituminous	81.62	1.50	2.04	35.62
PSOC #213	Bituminous	65.12	8.93	8.52	35.91
PSOC #870	Anthracite	89.52	3.84	2.46	2.93
PSOC #868	Anthracite	63.34	3.82	25.00	4.06
Van-131	Bituminous	80.4		5.00	39.60

The coals were obtained as coarse powders, were riffled to provide more uniform samples and were stored in the dark in argon-filled glass desiccators. They were subsequently ground to enhance the amount of surface available in the adsorption bed. Most of the grinding was done with a micro-mill from Technilab Instruments; the coal was micro-milled in air for two minutes in the water-cooled chamber. Other samples were ball-milled, and some Van-131 samples were π -milled to much higher specific surface areas.

A major consideration in the selection of the carrier solvent and of the test acids and bases was their tendency to penetrate into the bulk region of the coal particles; we wished to sample only the surface region. This point will be discussed in more detail, but we have chosen to use iso-octane as carrier solvent and t-butylated acids and bases as "limited penetration" test probes for surface acidity and basicity. The iso-octane was Purified grade from Fisher, the pyridine and phenol were ACS Reagent grade from Fisher, and the t-butylated acid-base probes (4-t-butylphenol, 3,5-di-t-butylphenol, 2,6-di-t-butylphenol, 4-t-butylpyridine, 2,6-di-t-butylpyridine and 4-t-butylcyclohexanone) were all Aldrich Reagent grade. Some gas adsorption studies were made with 2,2'-dimethylbutane (98%) which we obtained from Aldrich Chemical Co.

Results and Discussion

Limited-Penetration Acid-Base Probes.

Pyridine is known to swell coal very considerably, but in studies of the equilibrium swelling of coal by pyridine and its derivatives, Larsen and co-workers found that the derivatives with side chains cause less swelling and that t-butyl derivatives cause the least swelling, about 10% of that observed with pyridine (1). Perhaps the most important effect of the t-butyl groups is on the rates of swelling; Aida, Squires and Hansen found that the t-butyl groups retarded the rates of penetration by a factor of a thousand or more (14).

An important consideration is the effect of t-butyl substitution on the strength of the acidity or basicity of a test molecule, so we investigated the heats of acid-base complexation of the candidate test acids and bases in a neutral organic solvent, using infrared spectral peak shifts measured in the presence of various excess concentrations of reactant. For example, the peak shift of 3,5-di-t-butylphenol was measured with a 17.5 mM solution in cyclohexane, and in the presence of a 3-fold, 10-fold and 30-fold excess of pyridine the spectral shift was -434 cm^{-1} in each case, showing none of the concentration-dependence reported by Drago and co-workers (4). The details of these measurements will be shown in the forthcoming publication. It was found that substitution of t-butyl groups in the 2-, 4-, or 3,5- positions do not affect the acid or base strength of phenol or pyridine appreciably, but in the 2,6- positions the t-butyl groups completely blocked any reactions of the phenol or pyridine sites.

In our flow microcalorimetry measurements the bed of powdered coal is exposed to test acid or base solutions for only about 5 to 10 minutes. In another few minutes pure solvent is pumped through the bed to desorb the adsorbed probe. If the probe is pyridine or phenol some of it tends to penetrate into the coal during the 5 to 10 minutes of exposure, but with t-butyl derivatives the degree of penetration is negligible. Table 1 illustrates this effect by comparing heats of adsorption and desorption in several successive adsorption-desorption cycles with phenol, pyridine, and their t-butyl derivatives adsorbing from iso-octane at 40 C onto low-ash anthracite (PSOC #870) and onto low-ash bituminous coal (Van-131) powders.

The penetration of pyridine into low-ash anthracite (PSOC #870) is illustrated in Figure 1. The heat of adsorption of pyridine was so excessive that the recorder went way off scale on the first adsorption cycle, and the subsequent heat of desorption was still quite large (+2130 Joules/kg); in the subsequent cycles only about half as much heat was evolved, with the heats of adsorption exceeding the heats of desorption by about 10%. On the same anthracite powder 4-t-butylpyridine is seen to desorb quantitatively, with an average heat of adsorption of -825 Joules/kg and an average heat of desorption of $+827\text{ Joules/kg}$.

The flow microcalorimetry results for phenol in Table 1 also shows much penetration into anthracite. The heats of adsorption are about double the heats of desorption, and the heats for the second adsorption-desorption cycle are much less than for the first cycle. The limited penetration of phenol with 3,5-di-t-butyl substitution is quite remarkable; the initial heat of adsorption (-237 Joules/kg) is exactly equal to the average of the five cycles, and the standard deviation for the five heats of adsorption and five heats of desorption is only 3.6%.

In Table 1 it is shown that 2,6-di-t-butylphenol has weak exothermic interactions (-4 to -6.6 kJoules/mole) with the surface of coal, even though FTIR studies showed that the phenolic group cannot interact with pyridine. Perhaps the weakly basic aromatic ring is the site of exothermic acid-base interaction with acid sites of coal.

The basic probes used in this study included two oxygen bases, ethylacetate and 4-t-butylcyclohexanone; their heats of acid-base interaction are -5.0 and -5.7 kcal/mole with phenol, as compared to the -8.1 kcal/mole for 4-t-butylpyridine. The 4-t-butylcyclohexanone performed well as a limited-penetration probe for acidic sites on Van-131 coal powders.

Statistical Significance of the Flow Microcalorimetric Measurements

The data in Table 1 illustrate the statistical significance of the flow microcalorimetric measurements. With the limited-penetration probes the heats of desorption are seen to be very close to the heats of adsorption; the average difference is only 2.7%. The standard deviations in the heats of adsorption and desorption (measured in Joules/kg) in repeat runs were found to be about 5% in all cases for the low-ash anthracite and about 15% in all cases for the low-ash bituminous coal.

The measurements of amounts adsorbed determined from the UV absorption were much less repeatable, and the molar heats of adsorption derived therefrom were also less repeatable. With the low-ash anthracite (PSOC #870) and with the low-ash

Table 1. Adsorption and Desorption of Acid-Base Probes on Low-Ash Coal Powders.

Coal	(m ² /g)	Acid-Base Probe	Cycle	Joules/kg		kJ/mole	
				mmoles/kg adsorbed	adsorbed desorbed		
PSOC #870	1.85	Phenol	1	37.2	-2438	+1295	-65.5
			2	27.8	-1808	+1100	-65.0
		3,5-di-t-Butylphenol	1	7.8	-232	+242	-29.9
			2	6.8	-238	+265	-35.2
			3	6.5	-237	+243	-36.5
			4	8.1	-242	+229	-30.0
			5	7.3	-236	+249	-32.2
		2,6-di-t-Butylphenol	1	16.9	-111,	+119	-6.6
			2	26.2	-112	+129	-4.3
			3	26.4	-135	+114	-5.1
			4	26.3	-123	+139	-4.7
			5	20.5	-91	+125	-4.5
		Pyridine	1		-????	+2130	
			2	34.6	-1477	+1375	-42.7
			3	38.1	-1392	+1270	-36.5
			4	37.0	-1432	+1242	-38.7
		4-t-Butylpyridine	1	37.4	-871	+863	-23.3
			2	28.7	-815	+864	-28.4
			3	27.0	-709	+817	-26.3
			4	31.1	-862	+782	-27.7
5	37.5		-868	+809	-23.1		
PSOC #11	1.81	3,5-di-t-Butylphenol	1	13.4	-391	+388	-29.2
			2	22.0	-481	+487	-21.9
			3	24.0	-570	+559	-23.8
			4	20.2	-617	+588	-30.5
		4-t-Butylpyridine	1	35.6	-893	+864	-25.1
			2	40.5	-1081	+1025	-26.7
			3	44.3	-1096	+1059	-24.7
			4	39.4	-1194	+1232	-20.3
			5	44.5	-1130	+1130	-25.4
Van-131	0.62	Pyridine	1		-536	+334	
			2		-668	+460	
			3		-572	+390	
	1.57	3,5-di-t-Butylphenol	1	12.1	-158	+184	-13.0
			2	9.9	-162	+155	-16.4
			3	4.2	-161	+162	-38
			4	4.7	-122	+127	-26
			5		-129	+128	
			6		-117	+105	
	4-t-Butylphenol	1		-176	+221		
		2		-257	+258		
		3	15.4	-260	+259	-16.9	
		4	15.0	-250	+263	-16.7	

bituminous coal (PSOC #11) the standard deviations for repeat runs in the number of micromoles adsorbed per square meter varied from 10 to 20%, but with the Van-131 bituminous coal these deviations were much greater. In other flow microcalorimetric studies with this same instrument (15) we have achieved standard deviations between the heats of adsorption in successive repeat runs of about 2%, so we are encountering coal-related analytical difficulties in determining the concentration of the acid-base probes in the eluent. The UV flow detector is very sensitive to air bubbles, and as the solution flows through the calorimeter bed at 40 C, there is a tendency for bubble-formation; we have switched to 30 C, and this helps. There is also a tendency for small coal particles to be carried out of the bed and through the UV detector cell; we have introduced a micro-pore filter at the base of the bed, and this also helps. Nevertheless, there is a tendency for some aromatic components of coal to be leached out despite our use of iso-octane as a carrier liquid with of minimal solubility for aromatics. Perhaps a branched saturated hydrocarbon of higher molecular weight or some Freon-type solvent would give a cleaner eluent.

Differences in the Surface Properties of Coals

In the studies with low-ash coals, the heats of adsorption of limited-penetration acid-base probes are appreciably greater for the pyridine derivatives than for the phenol derivatives, and this is shown to result from higher surface concentrations of acidic surface sites in the three low-ash coals investigated, whether anthracite or bituminous coal.

Table 2. Heats of Adsorption of Test Probes on High-Ash Coal Powders

Coal	Milled	Acid-Base Probe	Cycle	mmoles/kg			Joules/kg	
				adsorbed	adsorbed	desorbed	adsorbed	desorbed
PSOC #213	no	3,5-di-t-Butylphenol	1	25.3	-536	+532	-23.1	
			2	26.9	-649	+532	-24.1	
			3	31.4	-649	+615	-20.7	
	yes	"	1	36.6	-1351	+933	-37.9	
			2	35.4	-1021	+874	-28.8	
			3	29.8	-1067	+824	-35.8	
			4	32.7	-1092	+1096	-33.4	
	no	4-t-Butylpyridine	1	46.1	-1331	+636	-28.9	
			2	35.6	-782	+619	-22.0	
			3	43.3	-703	+678	-16.2	
	yes	"	1	34.0	-1745	+1163	-51.5	
			2	58.9	-1251	+1276	-21.3	
3			60.3	-1318		-21.8		
PSOC #868	no	3,5-di-t-Butylphenol	1	41.8	-540	+389	-12.9	
			2	43.6	-494	+406	-11.3	
			3	45.7	-439	+439	-9.6	
	yes	"	1	26.0	-916	+385	-35.2	
			2	37.5	-607	+523	-16.2	
			3	30.6	-619	+444	-20.3	
	no	4-t-Butylpyridine	1	51.3	-2330	+1326	-45.6	
			2	33.5	-602	+431	-18.0	
			3	18.4	-436		-24.8	
	yes	"	1	80.9	-1975	+594	-24.2	
			2	53.1	-736	+590	-13.8	
			3	71.9	-619	+540	-8.6	

The presence of ash in the anthracite (PSOC #868) or bituminous coal (PSOC #213) made much difference in the heats of adsorption, especially in the repeatability of the heats of adsorption in a series of repetitive adsorption-desorption cycles. Table 2 shows trends indicating that the presence of ash caused stronger adsorption than desorption, especially in the first cycle, and that the heats of adsorption decreased in successive cycles. These findings suggest that the ash present in these powders binds the acid-base probes more strongly than the coal. In Table 2 results are compared for coal powders as received versus freshly micro-milled powders, and it appears that the molar heats of adsorption in the initial cycle are always higher with fresh-milled coal powders.

Surface Area Determination with Limited-Penetration Adsorbents

There has been some discussion in the literature (16) of discrepancies in specific areas determined by gas adsorption with nitrogen at liquid nitrogen temperatures versus carbon dioxide at 25 C. So much more carbon dioxide than nitrogen is picked up by the coal that it was proposed that hundreds of square meters per gram of surface is accessible to carbon dioxide but not to nitrogen. However, in modern studies it is becoming quite clear that carbon dioxide (like other small reactive organic molecules) dissolves into the coal, causing some swelling and allowing access to inner surfaces by a solution route. Carbon dioxide is a self-associated acid-base complex which readily dissolves into and swells any acidic or basic polymer. Coal is just one of the many polymers that picks up carbon dioxide vapors appreciably at one atmosphere and at room temperature. If one uses the Polanyi-Dubinin equation to elucidate the "specific surface areas" from such gas adsorption measurements the plots give very satisfying straight lines and high correlation coefficients, predicting over a hundred square meters of surface per gram for optically clear polymers such as polymethylmethacrylate.

The use of t-butyl derivatives to determine specific surface areas of coal powders has merit, for the t-butyl groups block penetration into the coal and no solution occurs. We have tried this approach with gas adsorption, using 2,2-dimethylbutane, which has a t-butyl group, and measured the adsorption of this vapor at 25 C, and calculated the specific surface areas with the BET method, using 0.40 nm² for the area per molecule. As can be seen in Table 3, the specific surface areas measured with 2,2-dimethylbutane agree quite well with those determined from nitrogen adsorption isotherms measured at -196 C. In Table 3 we compare specific surface areas for five lots of powdered Van-131 coal which were ground to various particle sizes. The specific surface areas determined from adsorption of nitrogen or 2,2-dimethylbutane increased upon grinding to smaller particle sizes, but the "areas" determined with carbon dioxide remained at about 100 m²/g. The specific surface area of the coarsest powder was measured to be 0.50-0.52 m²/g by nitrogen adsorption and 1.49 m²/g by 2,2-dimethylbutane. An intermediate powder was found to have 2.76-2.82 m²/g by nitrogen adsorption and 3.52 m²/g by 2,2-dimethylbutane adsorption, and the finest powder was found to have 14.0-20.5 m²/g by nitrogen adsorption and 14.7 m²/g by 2,2-dimethylbutane adsorption. It appears that the best agreement is found for the finer powders.

Specific surface areas were also estimated for the same Van-131 powders, using the amounts of adsorption determined in the flow microcalorimetric measurements with t-butyl derivatives of pyridine, phenol and cyclohexanone adsorbing from solution in iso-octane. The estimates shown in Table 3 were calculated from the assumption that the maximum surface concentrations attained in flow microcalorimetry correspond to tight-packed monolayers (4.1 micromoles/m²); however, the results with the finer powders suggest that the films are not tight-packed.

Table 3. Surface Areas (m²/g) Versus Particle Size of Ground Van-131 Coal

Coal Lot	Mesh Size	Adsorbent	Temp,C	Method	Analysis	m ² /g
Van-131C	50-100	Nitrogen	-196	Dynamic	BET	0.50
		Nitrogen	-196	Static	BET	0.52
		2,2-Dimethylbutane	25	Static	BET	1.49
		4-t-Butylphenol	40	Flow-Cal		3.8
		4-t-Butylcyclohexanone	40	Flow-Cal		2.8
		Carbon dioxide	25	Static	BET	88
		Carbon dioxide	25	Static	D-P	117
		Carbon dioxide	25	Static	D-P	117
Van-131F	<325	Nitrogen	-196	Dynamic	BET	2.82
		Nitrogen	-196	Static	BET	2.76
		2,2-Dimethylbutane	25	Static	BET	3.52
		4-t-Butylcyclohexanone	40	Flow-Cal		1.9
		3,5-di-t-Butylphenol	40	Flow-Cal		2.2
		Carbon dioxide	25	Static	BET	56.6
		Carbon dioxide	25	Static	D-P	94.6
		Carbon dioxide	25	Static	D-P	94.6
Van-131T	<<325	Nitrogen	-196	Dynamic	BET	14.0
		Nitrogen	-196	Static	BET	20.5
		2,2-Dimethylbutane	25	Static	BET	14.7
		4-t-Butylcyclohexanone	40	Flow-Cal		5.5
		4-t-Butylphenol	40	Flow-Cal		5.3
		3,5-di-t-Butylphenol	40	Flow-Cal		4.6
		Carbon dioxide	25	Static	BET	57.8
		Carbon dioxide	25	Static	D-P	99.8

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