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EQUIVALENT WEIGHT DETERMINATIONS OF BLACK ACIDS OBTAINED BY THE REDUCTIVE CARBOXYLATION WITH BITUMINOUS AND LIGNITE COALS

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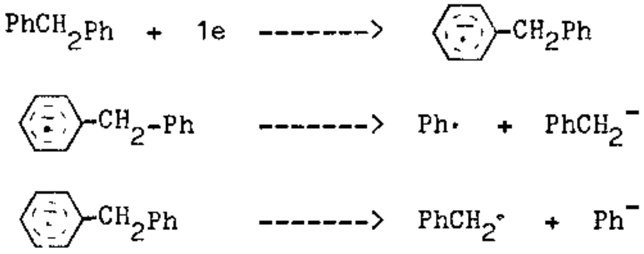
ABSTRACT

A back-titration method with standardized hydrochloric acid has been used to determine the equivalent weight of carboxylic acids generated from Illinois #6 bituminous coal and a North Dakota lignite. The carboxylic acids were produced by carboxylating the coals in aprotic solvents (toluene and triethylamine) with alkali metals (sodium and potassium) and carbon dioxide. The infrared stretching intensity of the carboxyl groups correlated well with their equivalent weights. Equivalent weights of known mono and polycarboxylic acids, including tannic acid, produced results within 0.27% to 2.6% accuracy.

INTRODUCTION

Carboxylation reactions with Illinois bituminous coal and lignite coals have been accomplished with potassium in aprotic solvents of toluene and triethylamine (Duty, 1981). These reactions were successful in solubilizing the coals to a maximum of 68% with more than half of the soluble products isolated as black acids. Recently, reactions with potassium and a Westerholt Mine coal in glyme and triglyme solvents were reported which reduced the coal into smaller fractions with an increase in hydrogen content (Hornback, 1977). This study prompted Collins *et al.* (1980) to examine if aromatic-aliphatic model compounds could be cleaved at the aliphatic linkages with the potassium-coal reactions in glyme-triglyme solvent had suggested.

Sternberg and co-workers (1968, 1971 and 1974) previously had successfully alkylated coal and their high solubility was attributed to the cleavage of ether linkages to form phenolate anions which subsequently could be O-alkylated. In addition, C-alkylation was proposed for the aromatic anions produced. Collins' study (1980) unequivocally proved that aliphatic carbon-carbon bonds were cleaved at low temperature when toluene was isolated as a reaction product from both 1, 2-diphenylethane and diphenylmethane. Collins' proposed mechanism suggests the formation of aromatic anions, aromatic radical anions as well as aliphatic and aromatic free radicals.

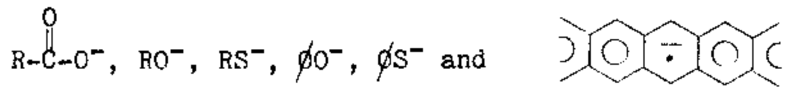


Previously, other authors (Conant, 1927; Willig, 1931; Gilman, 1936) had claimed that 1, 2-diphenylethane could not be cleaved with alkali metals, but Quest *et al.* (1977) had found that a cesium-sodium-potassium alloy could cleave bibenzyl. Collins' reactions with alloys of alkali metals does support Quest's experimental observations with the cesium-potassium alloy, and aliphatic carbon-carbon bond linkages indeed are broken. As Collins suggests, this may be an efficient low-temperature method for degrading coal by cleavage of aliphatic and aromatic-aliphatic bonds.

A study (Duty, 1981) has shown that the carboxyl group content of coal can be increased several fold by reacting coal with sodium metal and carbon dioxide. Undoubtedly, the reaction occurs via the carboxylation of the α-position of sodium phenolate sites (Lindsey, 1957) and the carboxylation of aromatic radical anions that are generated (Wawzonek, 1959) from the sodium.

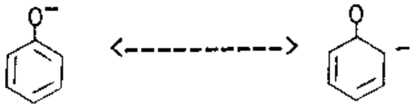
Results in this laboratory (Duty and Chiri; Duty and Lavin) indicate that potassium is a more efficient alkali metal than sodium for carboxylation reactions, and Stock's meticulous studies (Stock, 1978; Stock, 1979) with potassium in tetrahydrofuran are ample evidence to suggest this also. Stock's reactions with potassium, naphthalene and coal at ambient temperature generated 20 ± 1 anions per 100 carbon atoms. Consequently, in addition to these 20 carbanion sites, the alkali metal alloys should break the macromolecular coal structure further through cleavage of the aliphatic and aliphatic-aromatic linkages to generage additional carbanion sites (Collins, 1980).

Coal samples are known to contain the following functional groups: 1) carboxyl groups, albeit low percentages in brown coal (Tucks, 1929), lignite (Tucks, 1929), and bituminous coal (Ruberto, 1978); 2) ether linkage (Tucks, 1929; Ruberto, 1978); 3) hydroxyl groups (Heathcoat, 1932); 4) mercaptans (Lissner, 1935); and 5) thio ethers (Lissner, 1935). Consequently, when a coal sample is treated with an active alkali metal-alloy, the following basic sites would occur:



$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O^-$, RO^-, RS^-, $ØO^-$, $ØS^-$ and

The phenolate ion acts as a precursor to carboxylation reactions through a delocalized resonance hybrid.



RESULTS AND DISCUSSION

Reductive carboxylation reactions of Illinois bituminous coal were run in toluene and triethylamine with potassium, carbon dioxide and biphenyl at 100°, 200° and 300°C. North Dakota lignite was reacted under the same conditions with toluene as a solvent.

Material Balance

The material balance comparison between bituminous and lignite coal is shown in Table 1 with toluene as the solvent in each case.

One case is evident from examination of Table 1 in that a weight increase is proportional to an increase in temperature, e.g., the higher the temperature the higher the weight increase. Wachowska (1979) had reported a similar weight increase in his alkylation study where the weight increase of alkylated coal was higher than the corresponding alkyl group content. Evidence was presented to suggest the anions of the aromatic clusters in coal were reacting with the solvent and the electron transfer agent that were incorporated into the products. We ran a blank run with toluene, biphenyl, potassium and a catalytic amount of bituminous (0.2g) at 200°C in the exact manner as previously run with 10 g of bituminous coal and experienced a 47% increase in weight. A result that confirms Wachowska's observations.

Table 1. Material Balance for Reductive Carboxylation Reactions with Bituminous & Lignite Coals (Solvent-Toluene)

Reaction Temperature	Coal Type	Weight of Reactants (g)[a]	Weight of Isolated Products (g)[b]	Weight Increase (decrease)
100°C	bituminous	20	18.6	(8%)
	lignite	20	19.2 ± 0.2[c]	(3.9 ± 1.1%)
200°C	bituminous	20	20.3 ± 0.3[c]	6.0 + 2.0%
	lignite	20	19.6 ± 0.1[c]	(2.1 ± 0.2%)
300°C	bituminous	20	30.6 ± 2.1[c]	52 ± 11%
	lignite	20	25.4 ± 5.0[c]	51%

[a] Weight includes 10 g coal plus 10 g biphenyl.

[b] Weight includes the insoluble residue, the biphenyl, the black acids, the neutral compounds and the amphoteric compounds.

[c] Two determinations.

Percent Solubility and Black Acid Yields

The percent solubility and black acid yields are presented in Table 2.

The maximum solubility occurred at 200°C with a lower solubility occurring at 300°C. The ratio of the weight of the insoluble residue to that of the original coal sample was used as a measure of the solubility. An indirect way of looking at solubility would be to compare the weight ratios of the black acids to that of the insoluble residues. One could assume that if all the high molecular weight insoluble residue had broken down during carboxylation, that it would have been totally converted into the low molecular weight black acids. Consequently, as the insoluble residues weight approaches zero, the black acid's weight should approach unity, i.e.

lim (weight fraction of black acids) = 1.0
residue -------> 0

Table 2. Percent Solubility and Black Acid Yields

Reaction Temperature (°C)	Coal Type	Initial Weight of Coal (g)	Weight Insoluble Residue (g)	Weight Black Acids (g)	% Solubility
(Solvent — Toluene)					
100°	bituminous	10.0	8.9	1.70	11.1
	lignite	10.0	5.7 + 0.2[a]	4.4 ± 0.8[a]	43.4 ± 9
200°	bituminous	10.0	6.9 ± 0.6[a]	4.9 ± 0.05[a]	31.0 ± .0
	lignite	10.0	3.6 ± 0.3[a]	4.5 ± 0.50[a]	63.5 ± 3.3
300°	bituminous	10.0	15.0 ± 1.3[a]	1.8 ± 1.5[a]	(neg.)
	lignite	10.0	7.3 ± 0.9[a]	3.8 ± 0.7[a]	27.1 ± 8.1
(Solvent — Triethylamine)					
100°	bituminous	10.0	6.6 ± 0.1[a]	2.2 ± 1.0[a]	24.3 ± 9.0
200°	bituminous	10.0	3.2 ± 1.4[a]	6.6 ± 0.2[a]	68.5 ± 14.5

[a] Average & average deviation for two determinations

Table 2 exhibits this weight fraction increase very well because the 200°C reaction in every case has a maximum of carboxylic acids generated regardless of the solvent or the coal used.

Equivalent Weight Determinations

Equivalent weight determinations were measured by back titrating an excess of standardized sodium hydroxide as described further in the experimental. The equivalent weights of these black acids are shown in Table 3.

The highest equivalent weights occurred for those reactions at 300°C. This, undoubtedly, results from the fact that the higher temperature promotes decarboxylation reactions to occur.

Equivalent weights are no indication of the molecular size unless one knows the number of carboxyl groups per molecule. If one assumes these black acids are the same molecular size as those generated from Mayo's hypochlorite studies (1979) (mol. wt. 557 via vapor pressure osomometer), the number of carboxyl groups per molecule would be approximately two. This piece of evidence is very tenuous, especially so since these acids were generated under two extremely different chemical environments. It becomes even more tenuous when one compares the carbon content for reductive carboxylation reactions (72%) with those acids from the hypochlorite study (58%).

Table 3. Equivalent Weight of Black Acids

Reaction Temperature (°C)	Coal	Solvent	Equivalent[a] Weight
100°	bituminous	toluene	258 ± 8
100°	lignite	toluene	305 ± 10
100°	lignite	toluene	258 ± 3
200°	bituminous	toluene	307 ± 19
200°	lignite	toluene	324 ± 8
200°	lignite	toluene	342 ± 32[c]
300°	bituminous	toluene	335 ± 3
300°	lignite	toluene	458 ± 3
300°	lignite	toluene	500 ± 10
100°	bituminous	triethylamine	541 ± 118[b]
100°	bituminous	triethylamine	395 ± 155[c]
200°	bituminous	triethylamine	468 ± 129[b]
200°	bituminous	triethylamine	490 ± 172[c]

[a] Two determinations.
[b] Four determinations.
[c] Six determinations.

One more direct comparison we can make is to measure the strength of the carbonyl stretching frequency and compare this to the equivalent weight measurements. If the equivalent weight size is directly proportional to the number of carboxyl groups, one should be able to show a correlation between equivalent weight and strength of carboxyl peak. This correlation is shown in Table 4 for the bituminous and lignite coals run in toluene.

As the equivalent weight increases, the carbonyl stretching vibration decreases and this suggests there are fewer carboxyl groups present at the higher equivalent weights. The strength of the carbonyl peak was determined by measuring the height of the carbonyl peak and subtracting the background vibration at 2100 cm^{-1} from the carbonyl peak height.

Table 4. Carbonyl Group Strengths versus Equivalent Weights

Reaction Temperature (°C)	Coal	Carboxyl Peak Strength @1710 cm^{-1} (cm/mg)[a]	Eq. Wt. of Black Acids
100°	bituminous	0.87	258 ± 8
200°	bituminous	0.55	307 ± 19
300°	bituminous	0.40	335 ± 3
100°	lignite	11.6 ± 1.7[b]	282 ± 7
200°	lignite	10.4 ± 0.1[b]	333 ± 20
300°	lignite	5.3 ± 0.9[b]	479 ± 7

[a] Height of carbonyl peak measured from background at 2100 cm^{-1}

[b] Two determinations.

The elemental analyses for the bituminous and lignite coals are shown in Table 5.

Table 5. Elemental Analyses of Black Acids

Reaction Temperature (°C)	% C	% H	% N	% S	% Ash	% O[a]
A. Bituminous Coal — Solvent: Toluene						
100	70.71	5.26	0.87	1.83	2.26	19.07
100	70.66	5.00	0.88	1.64	1.26	20.56
200	72.93	4.54	1.66	0.92	0.97	18.98
200	72.28	4.77	1.18	1.73	0.67	19.37
300	66.99	3.66	1.71	5.89	1.66	19.96
300	69.58	3.92	1.91	1.00	1.86	21.73
B. Lignite Coal — Solvent: Toluene						
100	65.86	4.09	1.25	0.53	0.31	27.96
100	70.92	4.22	0.71	0.26	0.46	23.43
200	69.77	4.37	1.81	0.40	0.34	23.32
200	69.09	4.31	1.31	0.65	0.25	24.39
300	64.04	4.36	1.76	0.43	0.39	29.02
300	65.17	4.61	2.85	0.26	4.19	22.92

[a] Obtained by difference (%O = 100% − %C − %H − %N − %S − %ash)

The oxygen trend in this table does not correlate well with the equivalent weight, e.g., the smaller the equivalent weight, the higher the oxygen content should be. Unfortunately, Table 5 does not exhibit this trend; however, it might be due to the way the oxygen content was determined which was by difference, i.e., the oxygen was determined by subtracting the percentage sum of carbon, hydrogen, sulfur, nitrogen and ash from 100%. Therefore, all errors generated from any of these elements and other elements not reported will show up as an error in oxygen. One point Table 5 does make is that all black acids have a higher oxygen content than what was found in the raw bituminous or raw lignite coals.

EXPERIMENTAL PROCEDURE

Materials, Reactions and Autoclave

Illinois bituminous coal and North Dakota lignite were reacted as raw coals (250-325 Tyler mesh) that had been dried at 100°C. Reactions of coals were run in an Autoclave Engineers magnedrive packless, 1-liter stainless-steel autoclave equipped with a three-blade paddle wheel stainless steel stirrer that extended to the bottom of the autoclave. The autoclave was stirred at 900-1100 rpm. The temperature of these reactions was varied from 100° to a high temperature of 300°C.

The autoclave was charged with 10 g of coal, 10 g of alkali metal, and an aprotic solvent. The reactions were purged with dry nitrogen and run under nitrogen for five days, and the autoclave was pressurized with carbon dioxide for two days. After the reaction was complete, the excess alkali metal was decomposed by quenching the reaction with isopropyl alcohol.

The solvent was removed by rotary evaporation under vacuum, and the neutral compounds were extracted with an ether-benzene reflux (3/1 v/v) (Duty, Hayatsu, *et al.*, 1980). The ether-benzene layer was separated from the insoluble residue by centrifuging at 10,000 rpm with a Sorvall Model GLC-1 centrifuge and extracting with 5% potassium hydroxide to remove any solubilized acids.

The insoluble residue was refluxed with the 5% potassium hydroxide solution to extract the black acids. The potassium hydroxide solution was centrifuged, and the black acids were precipitated by acidifying the basic solutions with hydrochloric acid.

The insoluble residue from the potassium hydroxide extraction was demineralized (Duty and Liu, 1980), and a total acidity and carboxyl group analyses were determined (Duty and Chiri; Duty and Lavin).

Infrared Analysis

Potassium bromide wafers were made in a pellet die (Beckman Model K-13) under 18,000-20,000 psi for periods of 20 min. The spectral grade potassium bromide (Fischer) was dried in a drying pistol overnight under vacuum at 100°C. Approximately 6 mg. of the residue, known to the nearest mg., was weighted and mixed with 1.00 g of potassium bromide, known to 3 significant figures. This was shaken on an automatic shaker for 90 sec. From 0.150 to 0.200 g of the mixture was placed into the press, made into a wafer and run on a Perkin-Elmer 621 Grating IR.

Equivalent Weights of Black Acids

Demineralized moisture-free (dmmf) black acids were dissolved in an excess of standardized sodium hydroxide solution and stirred under nitrogen until dissolved. The excess sodium hydroxide was back titrated to pH 7, and the equivalent weight of the acids were determined from the amount of sodium hyroxide consumed. Equivalent weight of known acids were titrated to determine the accuracy of this procedure and these results are shown in Table 6.

Table 6. Equivalent Weight of Known Acids

	Eq. wt.	% Error
m-HO-Ø/COOH	138	0.27%
2, 3-Napthalene dicarboxylic acid	108 ± 3.7[a]	0.26%
1, 2, 4-Ø/$(CO_2H)_3$	68.2 ± 0.35[a]	2.60%
1, 2, 4, 5-Ø/$(CO_2H)_4$	63.5	2.00%
Tannic Acid 547 $C_{76}H_{52}O_{46}$ F. W. 1701.23		

[a] Average and average deviation for two determinations.

SUMMARY

Carboxylic acids generated via a reductive carboxylation reaction with alkali metals and carbon dioxide have produced acids with an equivalent weight varying between 258 to 500 g. Equivalent weights were determined by dissolving the acids in excess standardized sodium hydroxide and back titrating with standardized hydrochloric acid. Infrared analysis of the carbonyl stretch for the acids agreed very well with the corresponding equivalent weights. Over 60% of the coal was solubilized with this procedure with over half of the soluble material recovered as carboxylic acids

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