

ON THE SOLUBILIZATION OF COAL VIA REDUCTIVE ALKYLATION

Heinz W. Sternberg, Charles L. Delle Donne, and Peter Pantages

Pittsburgh Coal Research Center, U. S. Bureau of Mines,
4800 Forbes Avenue, Pittsburgh, Pa. 15213

INTRODUCTION

We have recently shown (1) that treatment of Pocahontas (lvb) coal with alkali metal in hexamethylphosphoramide produced a "coal anion." The latter reacts readily with methyl iodide to give a methylated coal soluble in benzene at room temperature. We now present further work on the formation and alkylation of the coal anion.

EXPERIMENTAL DATA AND RESULTS

Reagents. Metallic potassium, naphthalene, alkyl halides, and tetrahydrofuran (THF) were of the highest purity available commercially. Potassium, naphthalene, and the alkyl halides were used as received. Tetrahydrofuran was purified by refluxing over potassium metal for 72 hr. followed by distillation under a protective cover of helium.

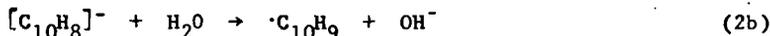
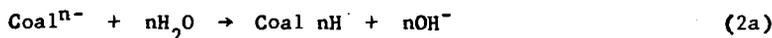
Coal. In all experiments, a hand-picked Pocahontas (lvb) vitrain sample, ground to pass 325 mesh, was used.

Petroleum Asphaltenes. The asphaltene sample was the pentane insoluble, benzene soluble (21%) fraction of a straight run residual asphalt of a California crude (85/100 penetration).

Formation and Titration of the "Coal Anion". Three anion species are produced when coal is treated with alkali metal in THF in the presence of naphthalene: naphthalene anion ($[C_{10}H_8]^-$), coal anion ($coal^{n-}$), and solvent anion ($\cdot CH_2(CH_2)_3O^-$). The latter is formed (2) by electron transfer from naphthalene anion to THF,



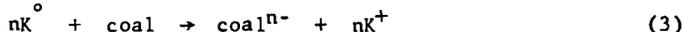
Each anion, on treatment with water, liberates an equivalent amount of hydroxyl ion:



The amount of hydroxyl ions formed can be readily determined by potentiometric titration with acid. By subtracting the equivalents of hydroxyl ions formed according to equations 2b and 2c from the total equivalents of hydroxyl ions, one obtains the equivalents of hydroxyl ions formed by the coal anion according to equation 2a. Knowing the amount and carbon content of the coal and the equivalents of hydroxyl ions formed according to (2a), one can calculate the number of negative charges associated with the coal anion in terms of negative charges per 100 carbon atoms.

In a typical experiment, under a protective cover of helium, a 250-ml Erlenmeyer flask provided with a glass enclosed stirring bar and suitable ground joint connections was charged with 120 ml of tetrahydrofuran (THF), 112 millimoles (4.4 grams) of potassium and 2.4 millimoles (0.304 gram) of naphthalene. The contents of the flask were stirred for 24 hr. A 1-ml sample of the dark green solution was withdrawn, placed in a 50-ml volumetric flask and diluted with water.

The aqueous solution was titrated with n/100 hydrochloric acid. To the dark green THF solution was added 6.17 grams of the vitrinite and stirring was continued for 72 hr. Every 24 hr. a 1-ml sample was withdrawn from the stirred reaction mixture and diluted with water to 50 ml. On addition of water, the coal anion suspension coagulates into a voluminous, brownish precipitate entirely different in appearance from the original coal. The aqueous mixture was allowed to stand for 48 hr. with occasional agitation to insure complete hydrolysis prior to titration. The results are summarized in Figure 1. Figure 1 shows that a sharp increase in the number of equivalents (43) takes place during the 24 hr. following the addition of coal. This increase is due mainly to the formation of coal anion,



The increase of 9 equivalents occurring during the final 48 hr. of stirring is caused by the formation of anions produced by electron transfer from naphthalene anion to solvent (THF) molecules according to equation (1). The value of 43 equivalents obtained for the neutralization of the coal anion, in conjunction with the amounts of coal used (6.17 grams) and the carbon content of the coal (88.3%), leads to the conclusion that the coal anion derived from Pocahontas coal contains 9.5 negative charges per 100 carbon atoms. The value of charges per 100 carbon atoms obtained in six separate titrations of freshly prepared coal anion suspensions varied from 9.5 to 12.1. The average value of these six titrations was 10.7 negative charges per 100 carbon atoms.

Alkylation of the Coal Anion. Under a protective cover of helium, the coal anion suspension described above was removed from unreacted potassium and was placed in an Erlenmeyer flask provided with a glass enclosed stirring bar. The flask was cooled in an ice bath. A solution of 10 ml of C-14 labelled ethyl iodide in 30 ml THF was added dropwise to the stirred dark red, almost black coal anion suspension in the course of 30 min. The mixture was allowed to warm to room temperature as stirring was continued for 2 hr. During this period the mixture became dark brown. The contents of the flask were poured into 600 ml of ethanol and the alkylated coal was separated by centrifugation. The supernatant ethanol solution was decanted and the residue treated with fresh ethanol. Treatment with ethanol and centrifugation was repeated until a sample of the ethanol washing was free of iodide ion. The precipitate was then repeatedly treated with water and centrifuged to remove any water soluble material. Finally, the precipitate was dried in vacuo at 100° to constant weight. The dried, treated coal weighed 6.03 grams. Taking into account the amount of coal withdrawn for titration (0.23 gram) and the amount of ethyl groups (8.8) added per 100 carbon atoms (see below), this corresponds to a recovery of 86%. The C-14 activity of the ethylated coal expressed in dpm/mg (disintegrations per minute per milligram) was 3.09×10^3 and that of the ethyl iodide (in dpm/ml) was 7.05×10^6 . The C-14 activity of the coal was determined by combustion analysis and that of the ethyl iodide by direct liquid scintillation analysis using an internal standard. On the basis of these data, the ethylated coal contained 8.8 ethyl groups per 100 carbon atoms. In similar experiments, coal was alkylated with C-14 methyl iodide and also with unlabelled normal butyl iodide. Radioactivity and combustion analysis of the methylated coal showed that the latter contained 8.1 methyl groups per 100 carbon atoms. Analyses of the original coal and alkylated coals as well as those of the benzene soluble and benzene insoluble fraction of the methylated coal are shown in Table 1. Hexane and benzene solubilities at room temperature (Table 2) were determined by tumbling 0.1 gram of alkylated coal and 15 ml of solvent in a sealed test tube for 1 hr. and centrifugation of the undissolved coal. This process was repeated two more times and then the residue was dried in vacuo at 100° to constant weight. The benzene soluble fraction of the methylated coal was practically free of ash (0.03%) while the original coal

contained 1.97% ash. In contrast to ethylated and butylated coal which were 95 and 93% soluble in benzene, methylated coal was only 48% soluble in benzene. Based on C-14 analysis and carbon content of the benzene soluble and benzene insoluble portion, the benzene soluble portion contained 8.4 methyl groups and the benzene insoluble portion 7.4 methyl groups per 100 carbon atoms. Infrared spectra (KBr pellet) of the alkylated coals showed strong bands at 3.4 μ and 7.25 μ attributable to the methyl group and the associated stretching vibration. The intensities of these bands in the original coal were only about one tenth of those found in the alkylated coal.

TABLE 1. Ultimate analyses of alkylated coal

	C	H	N	S	O ^{1/}	I	Ash
Original coal	88.25	4.55	1.19	0.57	3.47	.00	1.97
Methylated coal	87.22	6.03	1.14	.13	3.34	.00	1.54
a. Benzene soluble fraction	89.40	6.34	1.15	.06	3.02	.00	.03
b. Benzene insoluble fraction	85.71	5.43	1.09	.30	4.33	.00	3.14
Ethylated coal	87.81	6.33	.94	.37	2.52	.02	2.02
Butylated coal	87.24	7.23	.90	.31	2.17	.08	2.08

1/ By difference.

TABLE 2. Solubility of the alkylated coal

	Percent soluble	
	Hexane	Benzene
Original coal	nil	0.5
Methylated coal	3	48
Ethylated coal	11	95
Butylated coal	17	93

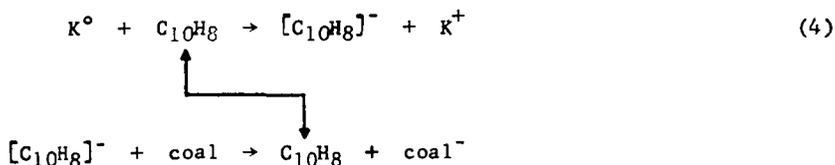
Molecular Weight Determinations. Number average molecular weights of the benzene soluble portions of alkylated coals and, for comparison, of one sample of petroleum asphaltens, were obtained by vapor pressure osmometry. Four samples, ranging in concentration from 5 to 35 grams per 1000 ml of benzene were used in each determination and the molecular weight at infinite dilution was obtained by the method of least squares. A typical plot of molecular weight vs. concentration is shown in Figure 2. The results are summarized in Table 3 along with the molecular weights calculated on an alkyl-free basis. In calculating the molecular weight of butylated coal on a butyl-free basis, it was assumed that the butylated coal contained the same number (8.8) of alkyl groups per 100 carbon atoms as the ethylated coal.

TABLE 3. Number-average molecular weights of alkylated Pocahontas vitrain and petroleum asphaltens

	Number-average molecular weight	
	Found	Calculated for alkyl-free coal
Ethylated coal	3300	2800
Butylated coal	4100	3000
Petroleum asphaltens	4200	

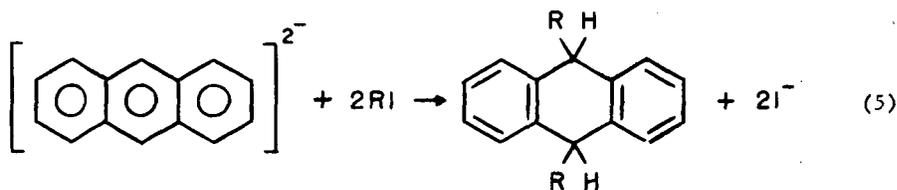
DISCUSSION

Formation of the "Coal Anion." Pocahontas vitrinite, when treated with potassium in tetrahydrofuran in the presence of a small amount of naphthalene, is converted to a coal anion. An electron transfer agent such as naphthalene is required because neither potassium nor coal are soluble in THF. Naphthalene, being soluble in THF, readily reacts with K^0 to form the anion $[C_{10}H_8]^-$. The latter is a strong electron donor and transfers its charge to the polycyclic aromatic hydrocarbons in coal as illustrated in equation (4)

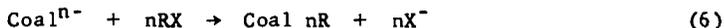


By this method, a large amount of coal can be converted to coal anion in the presence of a small amount of naphthalene. The number of charges associated with the coal anion was found to be 9.5 charges per 100 carbon atoms. When hexamethylphosphoramide (HMPA) is used as a solvent, an electron transfer agent is not required since alkali metals are soluble in HMPA and can react directly with coal (1).

Alkylation of the Coal Anion and the Effect of Alkyl Groups on the Solubility of the Alkylated Coal. Alkylation of the coal anion by alkyl halide is analogous to that of anthracene anion (equation 5)



and may be formulated according to equation (6)



where n, the number of negative charges associated with the coal anion expressed in charges per 100 carbon atoms, is about 11. These are the negative centers that are theoretically available for alkylation. The number of alkyl groups actually introduced was 8.1 and 8.8 per 100 carbon atoms in the case of methyl and ethyl, respectively.

A large portion (52%) of the methylated coal is insoluble in benzene in spite of the fact that the number of methyl groups per 100 carbon atoms is almost as high (7.4) in the benzene insoluble as in the benzene soluble portion (8.4).

Table 2 illustrates the effect of alkyl groups on solubility. Ethyl and butyl groups are about twice as effective as the methyl groups in imparting benzene

solubility to the alkylated coal. The ethyl group is almost four times as effective as the methyl group and the butyl group almost twice as effective as the ethyl group in solubilizing coal in hexane.

Molecular Weights and Structure of Alkylated Coal and Petroleum Asphaltenes. The fact that introduction of alkyl groups into lvb coal produces a benzene-soluble material points to a relationship between this type of lvb coal and petroleum asphaltenes. The latter are soluble in benzene in spite of the fact that they contain a larger number of rings (3,4) (8 to 9) per cluster than coal (4) (3 to 4 rings per cluster). However, petroleum asphaltenes, in contrast to coal, contain a considerable number of alkyl groups attached to the aromatic clusters (3). It is these alkyl groups which impart benzene solubility to the petroleum asphaltenes by preventing stacking of the aromatic clusters. The conversion of a lvb coal into a benzene-soluble product by introduction of alkyl groups indicates that the difference between this coal and petroleum asphaltenes is not one of molecular size but one of molecular structure. This view is supported by the fact that the molecular weights of alkylated coal and petroleum asphaltenes are in the same range as may be seen in Table 3. The higher molecular weight of the butylated as compared to the ethylated coal is merely a reflection of the higher molecular weight of the butyl group. On an alkyl-free basis, the difference between the molecular weights is only 7%, i.e., within the limit of experimental error. Hodek (5), who converted coal by acylation into a benzene-soluble product, reported a molecular weight (on acyl-free basis) of about 2000. The molecular weight of 4200 obtained for the petroleum asphaltenes is in good agreement with values reported in the literature (6). Petroleum asphaltenes resemble lvb coal not only with regard to molecular weight but also with regard to chemical reactivity. A petroleum "asphaltene anion," prepared in the same manner as the coal anion, contained 8 negative charges per 100 carbon atoms, i.e., about as much as the corresponding coal anion. Methylation of the asphaltene anion with C-14 labelled methyl iodide yielded a methylated asphaltene containing 5 methyl groups per 100 carbon atoms, i.e., about half as many alkyl groups as were incorporated into the coal molecule. This difference may be due to steric hindrance caused by the presence of alkyl groups in the aromatic clusters of the petroleum asphaltenes.

SUMMARY

Pocahontas (lvb) coal, when treated with alkali metal in tetrahydrofuran in the presence of a small amount of naphthalene, is converted to a "coal anion." The coal anion is formed by transfer of negative charges from the alkali metal to the aromatic clusters in coal with naphthalene acting as an electron transfer agent. The coal anion, containing about 11 charges per 100 carbon atoms is readily alkylated by alkyl halides. The alkylated coals contain about 8.5 alkyl groups per 100 carbon atoms and are soluble in benzene at room temperature. The molecular weight of the alkylated coals is in the same range as that of petroleum asphaltenes. The solubility in benzene of alkylated coal and of petroleum asphaltenes is believed to be due to the presence of alkyl groups which prevent stacking of the aromatic clusters.

REFERENCES

1. Sternberg, H. W. and Delle Donne, C. L. American Chemical Society, Division of Fuel Chemistry, Preprints, Vol. 12, No. 4, p. 13, September 1968.
2. Henrici-Olivé, G. and Olivé, S. Z. physik. Chem. Neue Folge, 1964, 43, 334.

3. Winniford, R. S. and Bersohn, M. American Chemical Society, Division of Fuel Chemistry, Preprints, September 1962, 21-32; C.A., 1964, 61, 509.
4. Friedel, R. A. and Retcofsky, H. L. Proceedings of the Fifth Carbon Conference, Vol. II, pp. 149-165, Pergamon Press, New York, 1963.
5. Hodek, W. Paper presented at the 7th International Conference on Coal Science, Prague, 1968.
6. Altgelt, K. H. American Chemical Society, Division of Petroleum Chemistry, Vol. 13, No. 3, 37, September 1968.

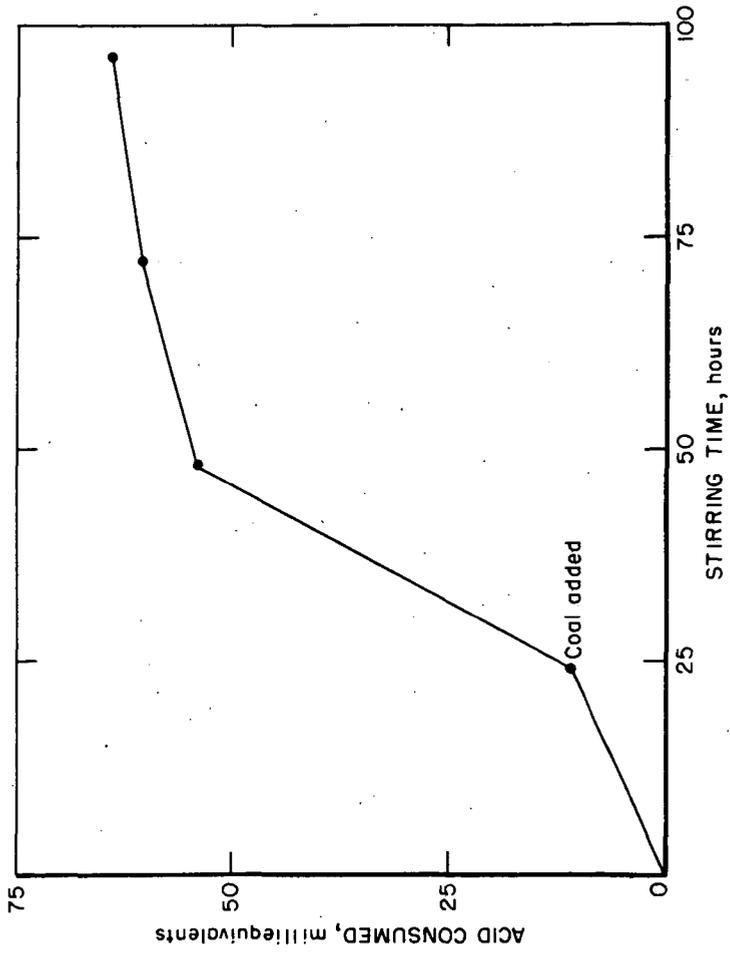


Figure 1 - Titration of the coal anion

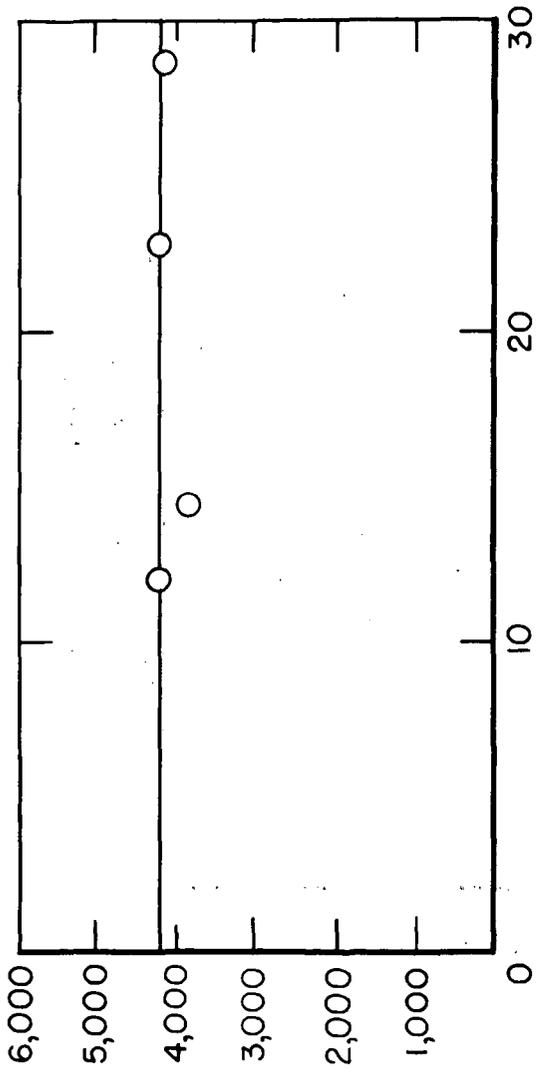


Figure 2 - Concentration dependence of apparent molecular weight by VPO of butylated coal.

L-11493