Thermochemistry of Acid-Base Interactions of Three Coal Samples of Different Ranks at Elevated Temperatures

B. Chawla[†] and E. M. Arnett*

Department of Chemistry, Duke University, Durham, North Carolina 27706

Received December 28, 1983

Heats of reaction (ΔH_{rxn}) of aqueous tetrabutylammonium hydroxide (TBAH) with three coal samples of different grades (Wyoming Rawhide subbituminous, Texas Big-Brown lignite, and Illinois No. 6 bituminous) have been measured at 80 °C with a Setaram C-80 calorimeter and the results obtained are discussed in terms of coal acidity. The temperature dependence of ΔH_{rxn} of the aqueous TBAH + Rawhide coal system has also been determined from 40 °C to 100 °C. Heats of immersion (ΔH_{imm}) of the three coal samples have been measured at 40 °C and 60 °C in 10% aqueous TBAH (1.47 M) in tetrahydrofuran (THF) and also in 10% water in THF. The exothermic interactions of these coals toward TBAH are always in the following decreasing order: ΔH(Wyoming Rawhide) > ΔH(Texas Big-Brown) > ΔH(Illinois No. 6). Heats of immersion (ΔH_{imm}) of Wyoming Rawhide coal in 31 liquid bases are reported at 80 °C and 120 °C. The ΔH_{imm} values of Wyoming Rawhide and Texas Big-Brown coals in 12 selected bases at 80 °C are correlated fairly well, the reactions of Wyoming Rawhide coal with liquid bases being slightly more exothermic than those of Texas Big-Brown coal. On the other hand, a comparison of ΔH_{imm} values of Illinois No. 6 coal with those of Wyoming Rawhide and Texas Big-Brown coals suggests that access to acidic structural units of Illinois No. 6 coal is different from that of the other two.

Calorimetry is a powerful tool for the study of acid-base interactions. Since all organic compounds are potentially acids or bases or both, the reaction is very general as well as being of great utility. However, it is not convenient, or even feasible, in many cases to obtain reliable equilibrium constants or other free-energy terms for proton transfer. In a series of previous studies[1] we have demonstrated that for many types of proton-transfer processes, in a variety of homogeneous media, extending from superacid to superbases, there is a close correlation between the standard free energies and enthalpies of protonation for many organic species. Although differential entropies of ionization may make some contribution to such processes, within a related series of compounds there is often either a constant entropy of proton transfer or one which is proportional to the enthalpy and free-energy change.

Against this background of thermochemical comparisons of acids and bases we have begun to apply the same techniques to the difficult and very important problem of comparing heterogenous acid-base systems.[2]

The present paper extends the thermochemical acid-base technique to the interactions of a variety of bases with three different well-characterized coal samples: Wyoming Rawhide subbituminous, Texas Big-Brown lignite, and Illinois No. 6 bituminous. A number of previous studies have used heats of immersion of coal and other solids in a variety of solvents.[3-10] Such measurements are relevant to the swelling of coals, the solvent refinement of coals, coal depolymerization and, within the context of this paper, are of interest in comparing fossil fuels as heterogeneous acid-base systems.

The present contribution differs from previous studies in the following ways.

1. It relates the acidic behavior of three typical but somewhat different types of metamorphosed vegetation to simpler and better defined homogeneous and heterogeneous acid systems.

2. The heats of reaction and heats of immersion presented here were conducted at considerably higher temperatures than most previous studies so that they are related more directly to industrial process conditions. At higher temperatures the time required for heat evolution is drastically reduced which allows measurements of higher precision and accuracy.

3. In heats of immersion measurements the emphasis throughout is mainly on nonaqueous, nonhydroxylic solvents in which heat capacity problems are largely eliminated. However, some aqueous basic solutions were also used for the sake of comparison.

Experimental Section

Heats of immersion were measured under various conditions with a Setaram C-80 heat flow calorimeter (Setaram Instruments, Lyon, France) which is built to operate up to 300 °C on the Tian-Calvet heat-flow principle. It consists of two identical and independent heat flow detectors which are surrounded by a heat conductive block whose temperature is controlled precisely by a temperature programmer with temperature stability better than 0.01 °C over the range of ambient to 300 °C.

Digital outputs for both the thermal power and the temprature measurements provide direct data processing through a Hewlett-Packard-85 desktop computer.

For a typical measurement, the inner cell containing 30-50 mg of coal sample was installed with the cap on in the mixing cell and then 0.8-1.8 mL of mercury was added in the cell to act as a vapor barrier to prevent mixing prior to activating the reversing mechanism. The mixing cell was then filled nearly to the top with 4-5 mL of reactant solvent in order to minimize air space. The reference cell was filled with the reactive solvent but contained no solute in the inner cell. The calorimeter was loaded with the

---

[†] On leave from Department of Chemistry, Indian Institute of Technology, New Delhi-110016, India.

(1) (a) Arnett, E. M.; Quirk, R. P.; Burke, J. J. *J. Am. Chem. Soc.* **1970**, *92*, 1260. (b) Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. *Ibid.* **1974**, *96*, 3875. (c) Arnett, E. M.; Small, L. E.; Oancea, D.; Johnston, D. E. *Ibid.* **1976**, *98*, 7346. (d) Arnett, E. M.; Johnston, D. E.; Small, L. E. *Ibid.* *97*, 5598. (e) Arnett, E. M.; Johnston, D. E.; Small, L. E.; Oancea, D. *Symp. Faraday Soc.* **1975**, *No. 10*, 20. (f) Arnett, E. M.; Small, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 808. (g) Arnett, E. M.; Bentrude, W. G.; Burke, J. J.; Duggleby, P. *Ibid.* **1965**, *87*, 1541. (h) Arnett, E. M.; Moriarity, J. C.; Small, L. E.; Rudolf, J. P.; Quirk, R. P. *Ibid.* **1973**, *95*, 1492. (i) Arnett, E. M.; Chawla, B. *Ibid.* **1978**, *100*, 217. (j) Arnett, E. M.; Chawla, B. **1979**, *101*, 7141.

(2) Arnett, E. M.; Haaksma, R. A.; Healy, M. H.; Chawla, B., manuscript in preparation.

(3) Chessick, J. J.; Zettlemoyer, A. C. *J. Phys. Chem.* **1958**, *62*, 1217.

(4) Chessick, J. J.; Zetlemoyer, A. C. *Adv. Catal.* **1959**, *9*, 263 and references cited therein.

(5) Larsen, J. W.; Kuemmerle, E. W. *Fuel* **1978**, *57*, 59.

(6) Fuller, E. L., Jr. *J. Colloid Interface Sci.* **1980**, *75*, 577.

(7) Nordon, P.; Bainbridge, N. W. *Fuel* **1983**, *62*, 619.

(8) Barton, S. S.; Boulton, G. L.; Dacey, J. R.; Evans, M. J. B.; Harrison, B. H. *J. Colloid Interface Sci.* **1973**, *44*, 50.

(9) Glanville, J. O.; Wightman, J. P. *Fuel* **1980**, *59*, 557.

(10) Widyani, E.; Wightman, J. P. *Colloids Surfaces* **1982**, *4*, 209.

0022-3263/84/1949-3054$01.50/0

Table I. Analysis of Wyoming Rawhide, Texas Big-Brown, and Illinois No. 6 Coals[a,b]

	wt %							
coal	C	H	N	S	S_{org}	O	mineral matter	volatile matter
Rawhide[a]	66.85	4.79	0.88	0.53	0.47	19.5	7.5	44
Texas[b]	64.79	5.03	1.22	1.15	1.07	19.6	8.3	c
Illinois No. 6[a]	67.85	4.78	1.23	4.22	2.96	9.2	14.0	37

[a] Reference 21. [b] Private communication from R. Liotta, Exxon Research and Engineering Company, Linden, NJ. [c] Data not available.

Table II. Heats of Reaction (ΔH_{rxn}) of Aqueous Tetrabutylammonium Hydroxide with Three Coal Samples of Different Grades at 80 °C

particle size	coal sample[b]	ΔH_{rxn}[a]
d	Wyoming Rawhide Subbituminous	−12.75 ± 0.37
d	Texas Big-Brown Lignite	−11.76 ± 0.31
e	Illinois No. 6 Bituminous	−9.55 ± 0.30
	Effect of Particle Size	
45/60 mesh	Wyoming Rawhide Subbituminous[c]	−11.83 ± 0.28
230/325 mesh	Wyoming Rawhide Subbituminous[c]	−12.32 ± 0.17

[a] ΔH_{rxn} values are in terms of kcal/mol of tetrabutylammonium hydroxide. [b] Old samples. [c] New samples. [d] Used as received, 80/400 mesh. [e] Powdered to 80/400 mesh.

Table III. Heats of Reaction (ΔH_{rxn}) of Aqueous Tetrabutylammonium Hydroxide with Old Samples of Wyoming Rawhide Subbituminous Coal at Different Temperatures

temp, °C	mixing time, min	ΔH_{rxn}[a]
40	30	−9.34 ± 0.97
60	20	−10.53 ± 0.28
80	15	−12.75 ± 0.37
90	10	−13.48 ± 0.21
100	5	−13.94 ± 0.40

[a] ΔH_{rxn} values are in terms of kcal/mol of tetrabutylammonium hydroxide.

cells and then left for 90–120 min to equilibrate. The experiment was started only when the calorimeter had reached complete thermal equilibrium.

Mixing was effected by actuating the "reversing" mechanism which completely inverts the entire calorimetric assembly every 15 s. The number of inversions depended on the ease with which the materials mixed. In the experiments reported here, the reversing mechanism was left on for 3–30 min, depending upon the coal particle size and the temperature.

Materials. Commercially available organic liquids were purified according to standard, established procedures.[11,12] The 40% aqueous solution of tetrabutylammonium hydroxide (TBAH), obtained from Aldrich, was titrated against a standard solution of HCl to obtain its concentration as 1.47 M.

Three coal samples of different grades, Wyoming Rawhide subbituminous, Texas Big Brown lignite, and Illinois No. 6 bituminous obtained from the Exxon Research group, were stored under nitrogen in a drybox. Since they had been handled previously and shipped under dry, air-free conditions, their exposure to oxygen and moisture had at least been minimized and standardized. Coal samples were ground in the drybox and screened by hand through sieves of desired mesh. Two sets of coal samples were used; one was approximately four months old and the other about ten days old when these experiments were run. We shall refer to them as the "old" and "new" samples. The proximate analyses are presented in Table I.

Results

The calorimeter was calibrated by using heats of solution of potassium chloride and barium chloride into water at 26 °C and 75 °C, respectively. Our ΔH_{soln} values for potassium chloride and barium chloride of 4.25 ± 0.04 and −6.65 ± 0.30 kcal/mol agree well with the literature values [4.20[13] and −6.76[14] kcal/mol, respectively].

Heats of reaction (ΔH_{rxn}) of aqueous tetrabutylammonium hydroxide (TBAH) with three powdered coal samples (used as received, 80/400 mesh) of different grades (old samples) were measured at 80 °C. A relatively small amount of TBAH (0.5 mL, 1.47 M) was used with the coal samples suspended in 4.5 mL of water. The amount of coal used in each case was varied from 0.4 to 0.6 g, showing that the ΔH_{rxn} values were independent of the amount of coal used. Results are given in Table II.

The temperature dependence of ΔH_{rxn} of Rawhide coal with an aqueous solution of TBAH was studied from 40 °C to 100 °C by using the old sample. In order to assure that TBAH had reacted completely at all temperatures, the mixing time was varied from 5 min at 100 °C to about 30 min at 40 °C. The ΔH_{rxn} values are given in Table III.

Heats of immersion of three new samples of coal with 10% aqueous TBAH in tetrahydrofuran (THF) and also with 10% water in THF, as control experiments, were measured at 40 °C and 60 °C. A small amount of the coal samples (30–50 mg) was reacted with 5 mL of 10% TBAH (10 mL of aqueous 1.47 M TBAH diluted to 100 mL by THF). Since we have previously had difficulty with wetting the coals (old powdered samples) with the aqueous base, this approach was tried in the hope of getting more complete interaction. It will be noted in Table IV that units are expressed in terms of calories per gram of coal (instead of kcal/mol of base) in view of the fact that base was in excess and we have not determined how much base was consumed in the process. Results are listed in Table IV.

Heats of immersion, ΔH_{imm}, of 45/60 mesh Rahwide coal were measured in various liquid bases at 80 °C and 120 °C. ΔH_{imm} values are given in Table V along with some properties of liquids at 25 °C. The comparison between the heats of immersion for all the three coals in 12 selected liquids at 80 °C are shown in Table VI.

The ΔH value for every system reported herein is the averaged value of two to four independent determinations. Times taken for the complete release of heat after bringing a solid in contact with liquid varied from 40 min to about 100 min depending upon the nature of the solid and the liquid used.

Discussion

I. Heats of Reaction of Coals with Tetrabutylammonium Hydroxide under Various Conditions. Data given in Table II indicate clearly that Wyoming Rawhide subbituminous coal is the most thermochemically acidic of the three coals investigated at 80 °C. According to these ΔH_{rxn} values, the acidity of these coals is ranked in the following decreasing order of exothermicity:

Wyoming Rawhide > Texas Big Brown > Illinois No. 6

---

(11) Perrin, D. D.; Armarego, W. L. E.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: 1966.

(12) Riddick, J. A.; Bunger, W. B. "Organic-Solvents-Physical Properties and Methods of Purification"; Weissberger, A., Ed.; Interscience: New York, 1970; Vol. 2.

(13) Gunn, S. *J. Phys. Chem.* **1965**, *69*, 2902.

(14) Criss, C. M.; Cobble, J. W. *J. Am. Chem. Soc.* **1961**, *83*, 3223.

Table IV. Heats[a] of Immersion of New Coal Samples with 10% Aqueous TBAH and 10% Water Both in THF

particle size	coal sample	temp, °C	$\Delta H_{imm}{}^{TBAH}$ (in 10% TBAH in THF)	$\Delta H_{imm}{}^{water}$ (in 10% water in THF)	$\Delta\Delta H$ ($\Delta H_{imm}{}^{TBAH} - \Delta H_{imm}{}^{water}$)
230/325 mesh	Wyoming Rawhide Subbituminous	40	−85.66 ± 5.24	−26.04 ± 2.28	−59.62 ± 5.71
45/60 mesh	Wyoming Rawhide Subbituminous	40	−84.42 ± 0.72	−24.54 ± 0.09	−59.89 ± 0.79
		60	−81.52 ± 4.93	−23.68 ± 2.64	−57.84 ± 5.62
45/60 mesh	Texas, Big Brown Lignite	40	−81.50 ± 3.92	−22.08 ± 0.52	−59.42 ± 3.95
		60	−70.86 ± 3.67	−21.92 ± 0.05	−48.94 ± 3.67
45/60 mesh	Illinois No. 6 Bituminous	40	−70.46 ± 4.73	−23.01 ± 0.75	−47.42 ± 4.79
		60	−63.00 ± 1.21	−22.60 ± 1.17	−40.40 ± 2.57

[a] ΔH_{imm} values are in terms of calories per gram of coal.

Table V. Heats of Immersion of 45/60 Mesh Wyoming Rawhide Subbituminous Coal in Some Basic Liquids at 80 °C and 120 °C

liquid	ΔH_{imm}, cal g^{-1} 80 °C	ΔH_{imm}, cal g^{-1} 120 °C	aq pK_{BH^+}	$\Delta H_{HB}{}^{d}$	$\Delta H_i{}^{d}$
1. 1,3-diaminopropane	−111.38 ± 3.02				
2. ethylenediamine	−105.50 ± 1.96				
3. *n*-hexylamine	−88.60 ± 3.27	−70.85 ± 3.42	10.6^{a,e}		
4. *n*-octylamine	−80.38 ± 0.39	−69.97 ± 1.00	10.6^{e}		
5. dimethylformamide	−35.98 ± 0.97	−29.33 ± 0.50	−0.01^{b}	−6.6	−29.5
6. dimethylsulfoxide	−41.05 ± 0.37	−41.23 ± 1.52	1.4^{b}	−6.6, −7.2	−28.6
7. methylformamide	−32.57 ± 0.84	−34.60 ± 1.79	−0.04^{a}	−5.2, −6.4	−29.6
8. 4-methylpyridine	−35.15 ± 0.10	−35.83 ± 0.68	6.0^{a}	−7.3	−39.0
9. pyridine	−32.14 ± 0.90	−34.82 ± 1.20	5.2^{a,b}	−7.1	−38.6
10. 2-methylpyridine	−31.44 ± 0.95	−31.04 ± 1.97	6.0^{a}		
11. 3,5-dimethylpyridine	−28.48 ± 0.98	−35.01 ± 0.53	6.2^{e}		
12. 2,6-dimethylpyridine	−8.70 ± 0.60	−15.75 ± 1.03	6.7^{a}	−7.8	−40.7
13. 2,6-diethylpyridine	−3.08 ± 0.20		6.7^{c}		
14. 2,4,6-trimethylpyridine	−2.47 ± 0.19	−6.17 ± 1.62	7.6^{e}	−7.9	−42.7
15. quinoline	−8.58 ± 1.23	−20.84 ± 0.86	4.9^{a,b}	−7.4	−37.0
16. isoquinoline	−8.06 ± 1.24	−22.11 ± 1.05	5.1^{a,b}		
17. piperidine	−29.14 ± 1.59		11.1^{e}		
18. aniline	−15.20 ± 0.29	−16.71 ± 3.22	4.6^{a,b,e}		
19. *N*,*N*-dimethylaniline	−1.98 ± 0.71	+4.57 ± 0.49	5.1^{b}		
20. triethylamine	−2.30 ± 1.49		10.7^{b}	−8.9	−49.1
21. *tert*-octylamine	−2.86 ± 0.39	−0.97 ± 0.49	10.6^{e}		
22. *p*-dioxane	−3.72 ± 0.37		−2.9^{b}	−5.1	−21.5
23. acetophenone	−0.29 ± 0.40		−6.2^{b}		
24. acetonitrile	−3.25 ± 0.76		−10.1^{b}	−4.2	−13.6
25. cyclohexanone	+2.08 ± 0.59	−0.41 ± 0.65	−6.8^{b}	−5.8	−18.1
26. propylene carbonate	+2.52 ± 1.20			−4.5	−17.8
27. decalin	−0.16 ± 0.80	+5.56 ± 0.82			
28. naphthalene		+5.26 ± 0.66			
29. aqueous tetrabutylammonium hydroxide (1.47 M)	−72.53 ± 1.85				
30. aqueous sodium hydroxide (1 M)	−56.74 ± 0.16				
31. water	−14.26 ± 0.62				

[a] Reference 17. [b] Reference 12. [c] In 50% alcohol in water. [d] ΔH_{HB}'s and ΔH_i's are enthalpies of hydrogen bonding and ionization of bases with *p*-fluorophenol and fluorosulfuric acid, respectively, at 25 °C, ref 19. [e] Reference 18.

Table VI. Heats of Immersion of Three Coals in Some Basic Liquids at 80 °C

liquid[a]	ΔH_{imm}, cal g^{-1} Rawhide Subbituminous	Texas Big-Brown	Illinois No. 6
2. ethylenediamine	−105.50 ± 1.96	−93.35 ± 1.42	−86.11 ± 1.98
4. *n*-octylamine	−80.38 ± 0.39	−50.04 ± 0.32	−78.20 ± 1.17
6. dimethyl sulfoxide	−41.05 ± 0.37	−36.81 ± 0.17	−35.90 ± 1.00
8. 4-methylpyridine	−35.15 ± 0.10	−21.27 ± 0.74	−43.70 ± 1.17
9. pyridine	−32.14 ± 0.90	−29.46 ± 0.17	−41.30 ± 0.40
17. piperidine	−29.14 ± 1.59	−19.98 ± 1.17	−45.13 ± 0.59
21. *tert*-octylamine	−2.86 ± 0.39	−1.46 ± 0.77	−5.56 ± 0.21
24. acetonitrile	−3.25 ± 0.76	−7.33 ± 0.48	+0.92 ± 0.55
25. cyclohexanone	+2.08 ± 0.59		−11.30 ± 0.30
29. aqueous tetrabutylammonium hydroxide (1.47 M)	−72.53 ± 1.85	−61.60 ± 0.43	−44.56 ± 2.43
30. aqueous sodium hydroxide (1 M)	−56.74 ± 0.16	−48.92 ± 2.08	−28.97 ± 0.86
31. water	−14.26 ± 0.62	−13.39 ± 1.00	−7.82 ± 0.23

[a] Liquid numbers are same as in Table V.

The ΔH_{rxn} values given in Table II suggest that Wyoming Rawhide and Texas Big Brown are considerably more acidic than Illinois No. 6, whereas Wyoming Rawhide is slightly more acidic than Texas Big-Brown litnite. Rawhide coal is reported to have about 40% more acidic hydroxyl groups (8 vs. 5 per 100 carbons) than the higher ranked Illinois No.6 coal and also has an appreciable concentration of carboxylic acid functionalities which are

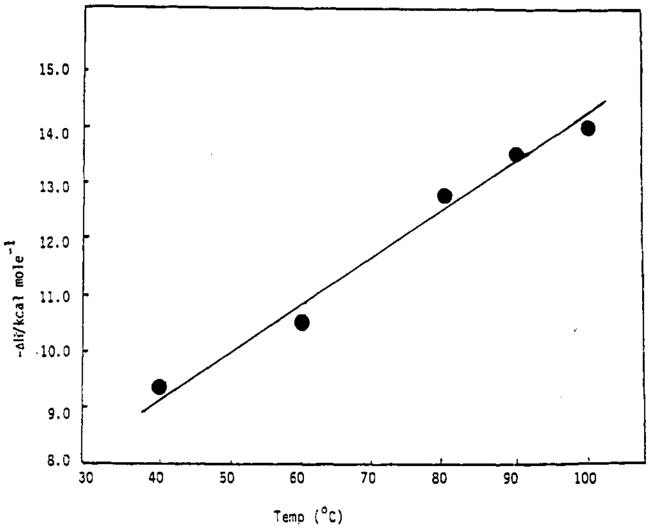


Figure 1. Temperature dependence of ΔH_{rxn} of Wyoming Rawhide coal with tetrabutylammonium hydroxide in water.

not present in Illinois No. 6 coal.[15]

Heats of interaction of TBAH with Rawhide coal samples of two different particle sizes (45/60 mesh and 230/325 mesh) were almost the same (see Table II), indicating that the effect of particle size on ΔH_{rxn} is not significant. Since these represent the practical limits of our sample particle size, no further variation was tried.

From the temperature dependence of ΔH_{rxn} values for Wyoming Rawhide coal in aqueous TBAH given in Table III and shown in Figure 1, it will be noted that the reaction becomes steadily more exothermic as the temperature is increased, corresponding to a heat capacity of reaction in the neighborhood of −77 cal/(mol deg). The heat capacities of ionization for most acids in aqueous solution are large and negative (−36 to −51 cal/(mol deg)).[16] That for phenol is about −50 cal/(mol deg), close to that reported here for coal. The actual correspondence of the values is probably fortuitous but since it is probably phenolic groups which are interacting in the coal it is interesting that these values are so close together.

Table IV shows that decreasing heats of immersion on going from Rawhide subbituminous to Illinois No. 6 bituminous for the reaction with the basic solution are followed almost exactly in their trend by the interaction with the aqueous THF solvent at almost all temperatures. As a result, the difference between them ($\Delta\Delta H$) remains essentially constant for Rawhide coal, suggesting that aqueous THF is interacting with the coal in very much the same way that the base is. However, interaction of base and water in the THF with the other two coals is different at different temperatures.

II. Heats of Immersion of 45/60 Mesh Rawhide Coal in Some Basic Liquids.

Data given in Table V suggests some effects of the shapes, sizes, and basicities of the molecules of immersion liquid on ΔH_{imm} of Rawhide coal in various liquids at 80 °C and 120 °C. The heats of immersion values at 80 °C are plotted against those at 120 °C in Figure 2. The observed scatter indicates modest differences in heat capacities of solution in the different bases.

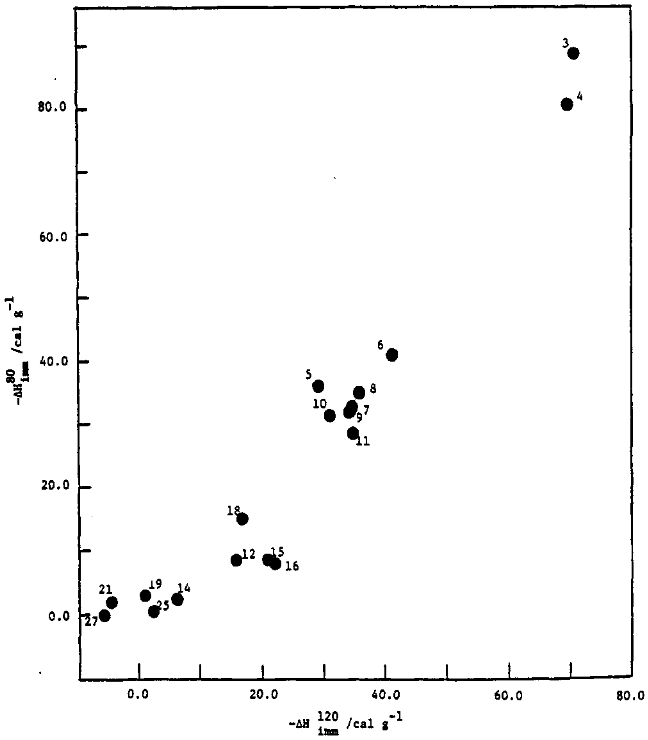


Figure 2. Heats of immersion of Rawhide coal in liquids in Table V at 80 °C vs. values at 120 °C.

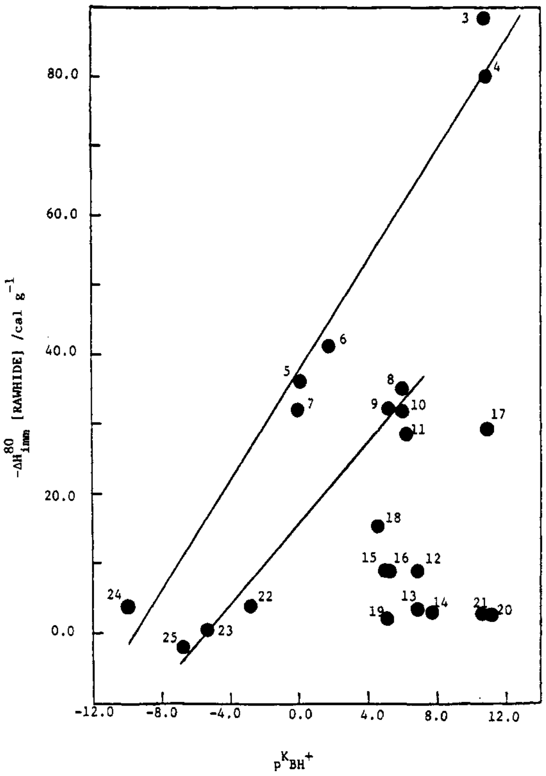


Figure 3. Comparison of heats of immersion of Rawhide Coal in basic liquids at 80 °C with pK_{BH^+} values of the same bases.

The ΔH_{imm} values at 80 °C are plotted against the aqueous pK_{BH^+} values of the immersion liquids[12,17,18] in Figure 3. For the sake of discussion we have suggested separation of these bases into three categories: the liquids having six-membered rings fall on one line and aliphatic

---

[15] (a) Liotta, R.; Rose, K.; Hippo, E. *J. Org. Chem.* **1981**, *46*, 277. (b) Liotta, R. *Fuel* **1979**, *58*, 724. (c) Liotta, R.; Brons, G. *J. Am. Chem. Soc.* **1981**, *103*, 1735.

[16] (a) Mirejovsky, D.; Arnett, E. M. *J. Am. Chem. Soc.* **1983**, *105*, 1112 and references cited therein. (b) Hughes, D. L.; Arnett, E. M. *Ibid.* **1983**, *105*, 4157 and references cited therein.

[17] Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum Press: New York, 1975; Vol. 2.

[18] Perrin, D. D.; Dempsey, B.; Serjeant, E. P. "pK_a Predictions for Organic Acids and Bases"; Chapman and Hall: New York, 1981, and references cited therein.

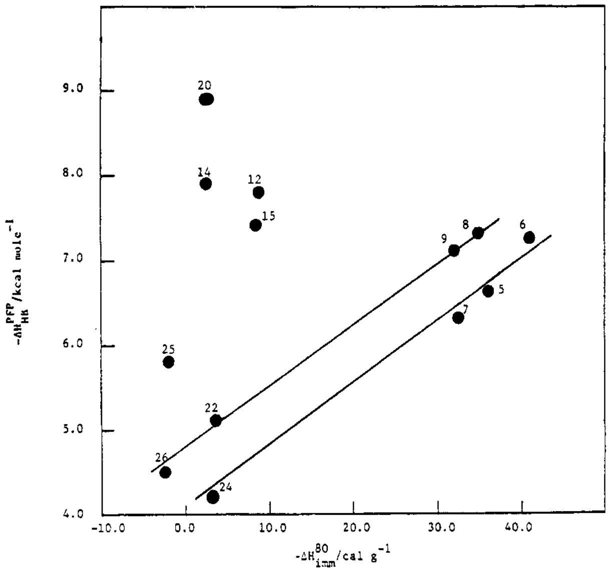


Figure 4. Comparison of heats of immersion, $\Delta H_{\text{imm}}^{80}$, of Rawhide coal in basic liquids vs. the H-bonding enthalpies of the bases with *p*-fluorophenol at 25 °C.

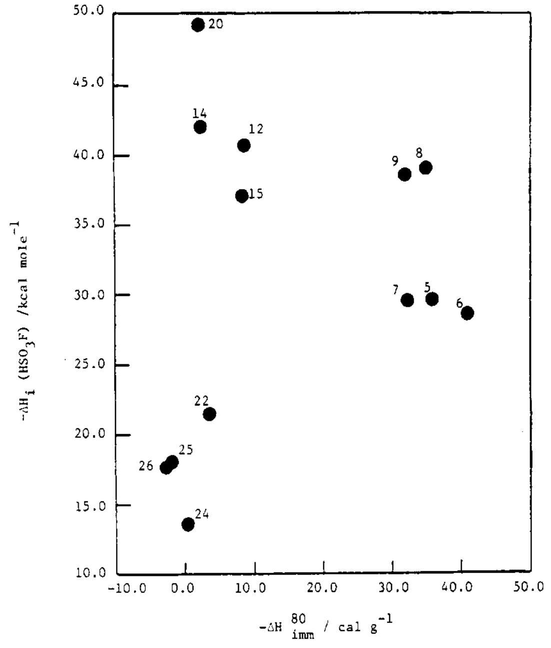


Figure 5. Comparison of heats of immersion of Rawhide Coal in basic liquids at 80 °C with heats of protonation of the same bases with fluorosulfuric acid at 25 °C.

bases fall on the other. Compounds of either class with sterically bulky functions are grouped separately with the discrepancy between their basicities in aqueous acid ($\mathrm{p}K_{\mathrm{BH}^+}$) and their interactions with Rawhide coal (ΔH_{imm}) depending rougly on the number of bulky groups and their proximity to the basic functionality. If such a steric effect is general and real, it presumably reflects different geometrical restrictions on the ability of the functional groups in the coal structure to interact with the basic liquids. Straight-chain aliphatic compounds have higher ΔH_{imm} values than the rest of the organic liquids. Similar behavior is also noticed in Figure 4 when ΔH_{imm} values are plotted against hydrogen-bonding enthalpies ΔH_{HB} which have been measured for many bases against *p*-fluorophenol[19] as a hydrogen-bonded donor. This observation is in good conformity with observations by Larsen[20] and Barton[8] regarding the effect of steric hindrance on the rates of diffusion of liquids into coal and microporous carbon, respectively. Finally, Figure 5 demonstrates that there is no significant correlation between $\Delta H_{\text{imm}}^{80}$ and the heats of protonation of the basic solvents by the superacid HSO_3F. Clearly the overall behavior is suggestive of a combination of proton transfer and hydrogen bonding with

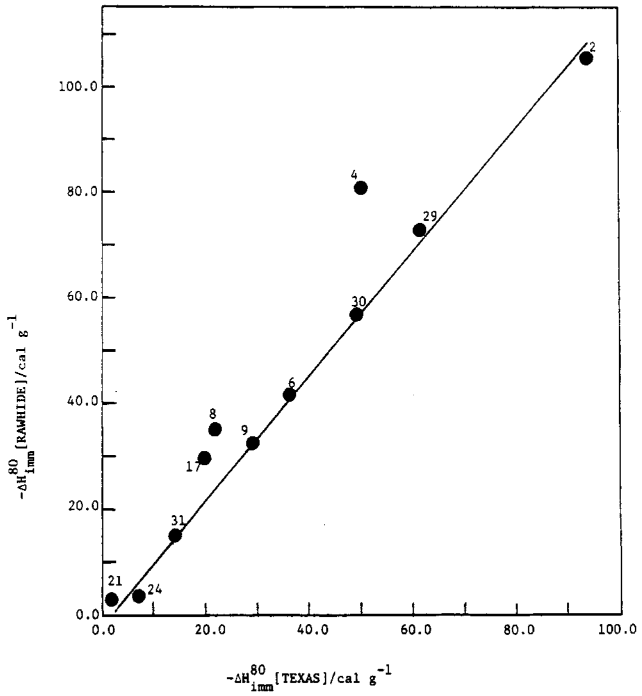


Figure 6. Correlation of heats of immersion of Rawhide Subbituminous and Texas Big-Brown Coals in eleven basic liquids at 80 °C.

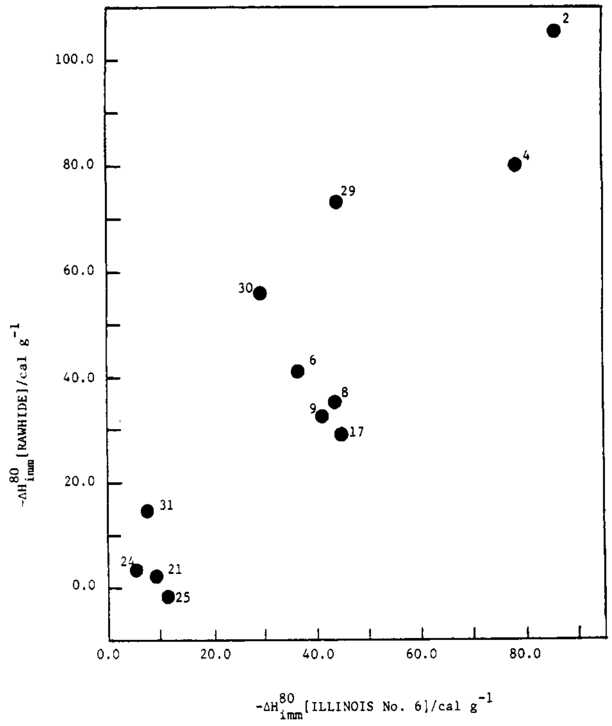


Figure 7. Comparison of heats of immersion of Rawhide Subbituminous and Illinois No. 6 Bituminous coals in 12 basic liquids at 80 °C.

---

(19) Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. *J. Am. Chem. Soc.* **1974**, *96*, 3875.

(20) Larsen, J. W.; Green, T. K.; Shawver, S., private communication.

(21) Liotta, R. *Fuel* **1981**, *60*, 453.

a strong influence from steric interactions.

III. Thermochemical Comparisons of Three Coal Samples: As Acids. Table VI presents heats of immersion, ΔH_{imm}, of three 45/60 mesh coal samples (Wyoming Rawhide, Texas Big-Brown, and Illinois No. 6) measured at 80 °C in 12 basic liquids selected from a list of 31 liquids used for ΔH_{imm} measurements for Rahwide coal as given in Table V.

A good linear correlation ($r = 0.998$) with almost zero intercept shown in Figure 6 (and only a few points removed from the correlation line) is found between the $\Delta H_{\mathrm{imm}}{}^{80}$ values of Rawhide subbituminous and Texas Big-Brown for eight liquids. These two coals have quite similar analyses (Table I), and it is interesting to see that their acid–base behavior is also similar although the slope of the line (1.16) suggests that the interactions of Rawhide coal with these eight liquids are slightly more exothermic than those of Texas Big-Brown.

Figure 7 compares the ΔH_{imm} values of Rawhide coal with those of Illinois No. 6 coal. The scatter diagram suggests that interaction of bases with acidic sites in Illinois No. 6 coal is different from that for Wyoming Rawhide and Texas lignite coals. Table I shows that the Illinois coal differs considerably from the other coals in several features of its analysis, the most important being mineral content. It is reasonable to suppose that different Lewis acid interactions with coal minerals as well as hydrogen bonding, proton transfer, and various other types of adsorption contribute to heats of immersion in basic solvents. We hope to clarify the role of these interactions in future work.

Acknowledgment. We are glad to acknowledge support for this work by Department of Energy Grant DE-FG22-82PC50807 and a grant from the Exxon Education Foundation. Also we appreciate the contribution of coal samples and advice by Dr. Ronald Liotta and help with instrumentation by Mr. Eric Johnson.

Registry No. 1,3-Diaminopropane, 109-76-2; ethylenediamine, 107-15-3; *n*-hexylamine, 111-26-2; *n*-octylamine, 111-86-4; dimethylformamide, 68-12-2; dimethyl sulfoxide, 67-68-5; methylformamide, 123-39-7; 4-methylpyridine, 108-89-4; pyridine, 110-86-1; 2-methylpyridine, 109-06-8; 3,5-dimethylpyridine, 591-22-0; 2,6-dimethylpyridine, 108-48-5; 2,6-diethylpyridine, 935-28-4; 2,4,6-trimethylpyridine, 108-75-8; quinoline, 91-22-5; isoquinoline, 119-65-3; piperidine, 110-89-4; aniline, 62-53-3; *N,N*-dimethylaniline, 121-69-7; Triethylamine, 121-44-8; *tert*-octylamine, 107-45-9; *p*-dioxane, 123-91-1; acetophenone, 98-86-2; acetonitrile, 75-05-8; cyclohexanone, 108-94-1; propylene carbonate, 108-32-7; decalin, 91-17-8; naphthalene, 91-20-3; tetrabutylammonium hydroxide, 2052-49-5; sodium hydroxide, 1310-73-2; water, 7732-18-5.

$(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$. A Useful Synthetic Equivalent of Methyl 1,3-Cyclopentadiene-5-carboxylate in Cycloaddition Reactions

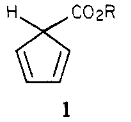
Michael E. Wright, James F. Hoover, Gregory O. Nelson,[1] Carl P. Scott, and Richard S. Glass*

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

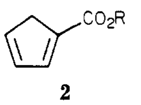
Received November 15, 1983

A variety of activated unsaturated compounds, including acrylonitrile, react with $Fp(\eta^1\text{-}C_5H_5)$, where Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$, to give cycloadducts in good yield. Diethylchloroalane facilitates these cycloadditions and even methyl acrylate cycloadds in good yield in the presence of this Lewis acid. These reactions all occur regio- and stereoselectively to afford syn-7-Fp cycloadducts exclusively. The stereochemistry at C(2) and C(3) is selective in some cases but not in others. Stereospecific replacement of the Fp moiety in these cycloadducts by a CO_2Me group with retention of configuration occurs in good yield by oxidation with ammonium cerium(IV) nitrate in carbon monoxide saturated methanol. This two-step sequence, cycloaddition followed by oxidation, renders $Fp(\eta^1\text{-}C_5H_5)$ a synthetic equivalent of methyl 1,3-cyclopentadiene-5-carboxylate in cycloaddition reactions.

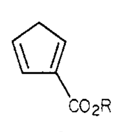
Diels–Alder reactions of cyclopentadiene are widely used in organic synthesis.[2] However, the value of such reactions with substituted cyclopentadienes is limited by their facile isomerization.[3] Thus, no Diels–Alder reactions of esters of 1,3-cyclopentadiene-5-carboxylate **1** have been reported, undoubtedly, due to their isomerization to the thermodynamically more stable 1- and 2-isomers, **2** and **3**, respectively.[4] Diels–Alder reactions of these latter isomers are known.[4,5]



1



2



3

The Diels–Alder adducts **6** and **7b**, derived in principle but not practice from methyl 1,3-cyclopentadiene-5-

---

(1) Presently located at Research Laboratories, Tennessee Eastman, Co., Kingsport, TN 37662.

(2) An especially elegant and important example is the stereocontrolled total synthesis of all of the primary prostaglandins from a single resolved precusor reported by Corey and co-workers: Corey, E. J.; Weinshenker, N. M.; Schaaf, T. K.; Huber, W. *J. Am. Chem. Soc.* **1969**, *91*, 5675. Corey, E. J.; Schaaf, T. K.; Huber, W.; Koelliker, U.; Weinshenker, N. M. *Ibid.* **1970**, *92*, 397. Corey, E. J.; Noyori, R.; Schaaf, T. K. *Ibid.* **1970**, *92*, 2586. Corey, E. J.; Shirahama, H.; Yamamoto, H.; Terashima, S.; Venkateswarlu, A.; Schaaf, T. K. *Ibid.* **1971**, *93*, 1490. Corey, E. J.; Varma, R. K. *Ibid.* **1971**, *93*, 7319. Corey, E. J. *Ann. N.Y. Acad. Sci.* **1971**, *180*, 24. Corey, E. J.; Becker, K. B.; Varma, R. K. *J. Am. Chem. Soc.* **1972**, *94*, 8616. Corey, E. J.; Schaaf, T. K. *J. Org. Chem.* **1972**, *37*, 2921. In this synthesis a 5-substituted-1,3-cyclopentadiene is selectively prepared and trapped in a Diels–Alder reaction before isomerization (see ref 3).

(3) This is particularly true of 5-alkyl-1,3-cyclopentadienes. 5-Methyl-1,3-cyclopentadiene readily isomerizes to the thermodynamically more stable 1- and 2-isomers: Mironov, V. A.; Sobolev, E. V.; Elizarova, A. N. *Tetrahedron* **1963**, *19*, 1939. McLean, S.; Haynes, P. *Tetrahedron Lett.* **1964**, 2385. McLean, S.; Haynes, P. *Tetrahedron* **1965**, *21*, 2329. McLean, S.; Webster, C. J.; Rutherford, R. J. D. *Can. J. Chem.* **1969**, *47*, 1555.

(4) Alder, K.; Flock, F. H.; Hausweiler, A.; Reeber, R. *Chem. Ber.* **1954**, *87*, 1752. Peters, D. *J. Chem. Soc.* **1959**, 1761. Franklin, W. E.; Mack, C. H.; Rowland, S. R. *J. Org. Chem.* **1968**, *33*, 626.

(5) Kresze, G.; Schulz, G.; Walz, H. *Liebigs Ann. Chem.* **1963**, *666*, 45. Wiesner, K.; Philipp, A. *Tetrahedron Lett.* **1966**, 1467. Stedman, R. J.; Miller, L. S. *J. Org. Chem.* **1967**, *32*, 3544. Mamer, O. A.; Rutherford, K. G.; Siedewand, R. J. *Can. J. Chem.* **1974**, *52*, 1983. Kyba, E. P.; Hudson, C. W. *J. Org. Chem.* **1977**, *42*, 1935. Irie, T.; Tanida, H. *Ibid.* **1978**, *43*, 3274. Nallet, J. P.; Arnaud, C.; Huet, J. *Tetrahedron Lett.* **1979**, 2583. Yates, P.; Gupta, I. *J. Chem. Soc., Chem. Commun.* **1981**, 449.

0022-3263/84/1949-3059$01.50/0 © 1984 American Chemical Society