

THERMOCHEMICAL COMPARISON OF ARGONNE PREMIUM COAL SAMPLES WITH MODEL SOLID ACIDS.

by

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Abstract

This presentation will be a summary of results acquired over the last five years using the heats of interaction of a series of bases with various solid acids as a means for classifying them. A sulfonic acid resin provides a solid model for Brønsted acidity. Silica is a model solid for hydrogen bonding interactions and several grades of graphitized carbon black are an excellent model for van der Waals/dispersion force interactions. Heats of interaction of the series of bases with several types of Argonne premium coals will be compared with those for the model solids and will serve as a means for coal classification.

INTRODUCTION

Thermochemical methods based on various types of calorimetry are a powerful tool for comparing acid-base interactions both in homogeneous and heterogeneous systems. Previous reports from this laboratory have described the thermochemical method for comparing solid acids with their homogeneous analogues in response to interactions with a variety of basic liquids. We have attempted to find appropriate solid prototypes for Brønsted acidity (1), hydrogen-bonding acidity (2), and dispersion force interactions (3). These could be used as standards for comparison in classifying more complex solid acids such as coals.

Much of the recent literature on the thermochemistry of adsorption onto coals has focused on their interactions with water or alkanols so that pre-treatment conditions could be examined with respect to their influence on the resulting heat of interaction (4-7). Some studies have examined other types of interacting compounds, such as amines, pyridines, and alkanes (8-12).

The present report compares six carefully classified coals from the Argonne National Laboratory Premium Coal bank by two calorimetric methods (heats of immersion and thermometric titration) using a series of twelve solvents chosen especially to bring out the differences between Brønsted acidity, hydrogen-bonding and dispersion force interactions (13).

RESULTS

Heats of immersion of the six premium coal samples, three coals from a previous study and two prototype solids (Dowex, silica) into twelve carefully chosen solvents at 75° are listed in Table I. Also listed in Table I are the heats of adsorption of the bases with Carboxpack F. The values reported are averages of two or three measurements, along with the standard deviation.

DISCUSSION

An important goal of this project is to see whether acid-base interactions of complex solids such as coals can be characterized thermochemically in the same manner which has been successful for characterizing acid-base interactions of homogeneous systems. A number of years ago, we demonstrated that there was a clear difference between the thermochemical order for interaction of a series of bases with the strong Brønsted acid, fluorosulfuric acid, as compared with the hydrogen-bonding acid, *p*-fluorophenol (14,15). The twelve basic solvents listed in Table I were chosen primarily to discriminate between surface sites which form hydrogen-bonds and those which are capable of Brønsted acid interactions. For example, dimethyl sulfoxide is a strong hydrogen-bond acceptor although it is a relatively weak proton acceptor from Brønsted acids in solution (15).

Comparison of Premium Coals with Each Other. Heats of immersion data for six coals listed in Table I were subjected to linear correlation analysis. By heat of immersion, the greatest similarity is between Illinois #6 and Pittsburgh #8 and between Wyodak and N. Dakota lignite. The biggest difference is between Pittsburgh #8 and Pocahontas #3.

Comparison with Earlier Work. The premium Wyodak coal sample (taken from the Gillette strip-mine) may be compared to the four year old sample of Wyoming Rawhide coal obtained from Exxon and kept dry under nitrogen. Comparison of heats of immersion in ten solvents (see Table I) gives a correlation coefficient of 0.96. A similar correlation for the Exxon sample of Illinois #6 as compared to the Argonne Premium, using only six bases, has an *r* value of 0.97. Finally, with a sample of only five bases, correlation of the old data for Texas Big Brown lignite with the Premium sample of North Dakota lignite gives an *r* value of 0.97.

Comparison with Standard Solid Acids. Heats of immersion of Dowex sulfonic acid resin, the prototype Brønsted acid, and of silica, the prototype solid hydrogen-bonding acid, can be compared with heats of immersion of the five premium coals using data for ten bases: pyridine, dimethyl sulfoxide, 4-methylpyridine, toluene, cyclohexanone, 2,6-dimethylpyridine, 2,4,6-trimethylpyridine, *n*-butylamine, propylene carbonate and *n*-hexylamine as shown by the correlations in Table II.

It is clear that by themselves neither Dowex, silica, or graphitized carbon black provide good models for the interaction of basic liquids with these coals. When two parameter equations are used to include contributions from both Brønsted acidity and hydrogen-bonding, there is considerable improvement. As might be expected, the introduction of yet another correlation parameter for dispersion forces improves things even more. Recent work in this laboratory indicates that Carbo-pack F[®], graphitized carbon black, is a better model than graphite for non-specific physical adsorption. Regression equations using heats of immersion of Dowex, silica and van't Hoff heats of adsorption determined by gas chromatography on Carbo-pack F as parameters to describe the heats of immersion of five premium coals in ten liquids are also shown in Table II.

The percentage contributions of Brønsted acidity (Dowex), hydrogen bonding (Silica), and dispersion force interactions (Carbo-pack) to the heats of immersion for each coal in ten bases were determined by the method of Swain and Lupton. It is interesting to see the variation of these contributions from one type of coal to another and the relatively large role of hydrogen-bonding. This supports the proposal of Larsen (16) for the role of this type of interaction to the swelling and solubilization of coal. This treatment has the advantage of expressing the results of three types of actions that are presumed to affect an interaction (such as that between a solid and liquid) in percentage terms. However, its shortcoming is that the results are assumed to be completely

determined by these actions, that is, they add up to 100%, which in turn implies that a perfect fit should be obtained with three parameters. This is clearly far from the case.

Table II shows that our fundamental strategy of trying to dissect the interactions of a complex solid, such as a coal, with a series of solvents into contributions that are modeled by prototype "simpler" solids has had only modest success.

Finally, it may be asked whether accessibility or acid properties are strongly affected by the surface areas of the coals. These have been determined by BET analysis and when the results are compared with heats of immersion or titrametric heats there is no indication that surface area is a significant factor. This behavior is very different from heats of immersion of silicas in the same bases where surface area plays a key role (2). In all probability the difference lies in the fact that coals are readily swollen and penetrated by the basic solvents so that eventually most acid sites are reached in the open cross-linked gel network. In contrast silica is a relatively undeformable solid.

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Table II. Regression of Premium Coal Immersion Values Against Those for Dowex and Silica and Carbopack-F for Ten Bases (see Table I).

(10 Bases as listed in Table I).

$$\Delta H_{\text{Wyodak}} = -10.833 - 0.754\Delta H_{\text{Dowex}} + 4.440\Delta H_{\text{silica}} - 7.218\Delta H_{\text{Carbopack-F}}$$
$$r = 0.962; r_{\text{Dowex}} = -.546; r_{\text{silica}} = 0.886; r_{\text{Carbopack-F}} = 0.468$$

$$\Delta H_{\text{Ill. #6}} = 61.806 - 0.312\Delta H_{\text{Dowex}} + 3.625\Delta H_{\text{silica}} + 1.126\Delta H_{\text{Carbopack-F}}$$
$$r = 0.947; r_{\text{Dowex}} = 0.662; r_{\text{silica}} = 0.942; r_{\text{Carbopack-F}} = 0.078$$

$$\Delta H_{\text{Pitts. #8}} = 29.867 - 0.366\Delta H_{\text{Dowex}} + 2.821\Delta H_{\text{silica}} - 1.197\Delta H_{\text{Carbopack-F}}$$
$$r = 0.946; r_{\text{Dowex}} = 0.618; r_{\text{silica}} = 0.934; r_{\text{Carbopack-F}} = 0.235$$

$$\Delta H_{\text{Pocah. #3}} = -5.084 - 0.085\Delta H_{\text{Dowex}} + 0.202\Delta H_{\text{silica}} - 0.519\Delta H_{\text{Carbopack-F}}$$
$$r = 0.658; r_{\text{Dowex}} = 0.156; r_{\text{silica}} = 0.466; r_{\text{Carbopack-F}} = 0.453$$

$$\Delta H_{\text{N.Dakota}} = -52.691 - 0.905\Delta H_{\text{Dowex}} + 3.481\Delta H_{\text{silica}} - 9.556\Delta H_{\text{Carbopack-F}}$$
$$r = 0.893; r_{\text{Dowex}} = 0.375; r_{\text{silica}} = 0.715; r_{\text{Carbopack-F}} = 0.596$$