

A METHOD FOR COUNTING THE HYDROGEN BOND CROSS  
LINKS IN COAL

John W. Larsen and Ilona Gurevich  
Department of Chemistry  
Lehigh University  
Bethlehem, Pennsylvania 18015

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ABSTRACT

A method has been developed which is able to count the number of hydrogen bond crosslinks in coals. The method consists of swelling the coal in non-polar solvents to which small amounts of a good hydrogen bond acceptor have been added. In an entropy controlled process, the hydrogen bond acceptor selectively interacts with those hydroxyl groups which are participating in hydrogen bond crosslinks. This results in a rapid decrease in the effective cross link density of the coals, rapid uptake of the non-polar solvent, and a rapid increase in the swelling. The resulting "titration curve" readily yields an estimate of the number of hydrogen bond crosslinks in the coal.

INTRODUCTION

We begin by discussing the interactions of a good hydrogen bond acceptor, for example pyridine, with hydroxyl groups in coals. For the sake of simplicity, we shall assume in our idealized experiment that all of the hydroxyl groups are phenolic. This is not necessary in the real system, it just makes the explanation easier to follow. We divide the hydroxyl groups in coals into three types. Free hydroxyls which are not participating in any hydrogen bond, hydroxyls which are hydrogen bonded but within the cluster or to a nearby molecule such that the hydrogen bond is not a crosslink, and hydrogen bonds between different macromolecular units such that the hydrogen bond is a non-covalent crosslink in the system.

We now inquire into the selectivity of a hydrogen bond acceptor for the three different types of hydroxyl groups. In thermodynamic terms; for which hydroxyl group is the free energy ( $\Delta G$ ) of interaction with pyridine most favorable. To do this, in a gedanken experiment we envision two extreme situations. Consider first the one in which the enthalpy dominates. That is,  $\Delta H$  for hydrogen bonding will be much larger than  $T\Delta S$  and control the situation. In this case, the pyridine will selectively hydrogen bond to the free hydroxyls. The reasons for this are straightforward. The heat of hydrogen bond formation between pyridine and phenol is  $-7.5$  kcal/mole (exothermic).<sup>1</sup> If the pyridine interacts with a hydroxyl group which is already hydrogen bonded, then the heat of its interaction will be reduced by the enthalpy of the existing hydrogen bond. A  $2.8$  kcal/mole hydrogen bond existing in the coal would lead

to a 100 to 1 preference of the pyridine for the free hydroxyls, given constant entropy. A plot of solvent swelling as a function of the pyridine concentration in the non-polar solvent would start almost flat as the free hydroxyls are saturated with pyridine while the cross-link density of the coal remains constant. Once all of the free hydroxyls have been bonded, the hydrogen bond cross links in the coal would be broken by pyridine thus reducing the cross-link density of the coal and leading to a very rapid increase in solvent swelling. The result is a curve which is initially nearly independent of pyridine concentration but which then rises sharply at some higher pyridine concentration.

The next situation to consider is that of entropy control, where the TAS term is much larger than the  $\Delta H$  term. If pyridine hydrogen bonds to a free hydroxyl or to a hydroxyl which is hydrogen bonded but not a crosslink, there will be a net loss of transnational entropy of the pyridine. The overall entropy change will be modestly unfavorable. If the pyridine breaks a hydrogen bond crosslink, the two macromolecular chain segments which were pinned together by the hydrogen bond are now free from each other and can adopt many more configurations. This provides a potentially large and favorable entropy term. It is this configurational entropy which is responsible for the elastic restoring force in rubbers.<sup>2</sup> It can be quite large. In this case, the pyridine driven by the favorable and dominant entropy change would first interact with the cross-linking hydroxyls in the coal to destroy the crosslinks, and only when these had been saturated would it interact with the other two classes of hydroxyls. The prediction here is that a plot of swelling versus pyridine concentration would show an initial very steep rise eventually almost leveling off as all of the crosslinks are broken. A further and striking prediction is that this swelling behavior will be independent of the hydrogen bond acceptor used. The driving force for the selectivity is the increase in configurational entropy of the coal which occurs when the hydrogen bond cross link is broken. This is independent of the solvent used to break the hydrogen bond. Thus, over an as yet undetermined range of hydrogen bond acceptor strengths, the selectivity for the cross-linking hydroxyls will be independent of the hydrogen bond acceptor. This would not be the case in an enthalpy controlled process.

Our data for Illinois No. 6 coal swollen with pyridine in toluene and THF in toluene are shown in Figures 1 and 2. It is clear from these figures that the predictions of an entropy controlled selective "titration" of the hydroxyl crosslinks in coal are followed. Superposition of the two plots reveals essentially identical behavior by both hydrogen bond acceptors in spite of a 1.7 kcal/mole difference in their heats of hydrogen bonding with phenol.<sup>1</sup> Extension of this technique to other materials and other interactions is underway.

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## REFERENCES

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