

A Question Concerning Coal Structure and/or Reactivity. The Reaction of Maleic Anhydride with Pittsburgh No. 8 Coal

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ABSTRACT. Maleic anhydride reacts readily with coals under Diels-Alder conditions and the coals gain 10% or more in mass. This reaction has been carried out using ^{13}C labeled maleic anhydride and Pittsburgh No. 8 coal. The results are consistent with the occurrence of the Diels-Alder reaction. There is evidence against the occurrence of all other conceivable (to us) reactions. The amount of maleic anhydride incorporated is inconsistent with all published coal structures. Either coal structures are seriously in error by omitting a significant population of reactive diene structures or coal reactivity is strongly enhanced by mechanisms not understood.

INTRODUCTION. Several groups have studied the reaction of maleic anhydride and coals and, with one exception, concluded a Diels-Alder reaction was responsible for the mass increase.¹⁻⁵ This conclusion immediately leads to a significant dilemma. The maleic anhydride uptake observed by all workers is too large to be consistent with a Diels-Alder reaction between maleic anhydride and current published coal structures. The amount of incorporation is much higher than would be predicted by the number of reactive diene structures thought to be present. Such reactive structures in coals are primarily anthracene and higher acenes. β -naphthol undergoes a Diels-Alder reaction, but only under forcing conditions much more vigorous than those used with coal.⁶ There are two possible explanations for the large maleic anhydride incorporation. One is that the coal structures are in error and contain more reactive dienes than suspected. This is a reasonable conclusion because such reactive dienes are unlikely to survive any of the degradation conditions so far used to probe coal structure and would be spectroscopically indistinguishable from the aromatics. Another possible explanation is that functional groups, for example naphthalenes, might be reactive in coals under conditions much milder than in other situations. Stated another way, coals are showing strongly enhanced reactivity. Either of these explanations raises fundamental questions about the chemistry and structure of coals and it is this which makes the study of the maleic anhydride-coal reaction important. Reported here is a thorough re-examination of this reaction.

EXPERIMENTAL METHODS. Argonne samples of Pittsburgh No. 8 coal were reacted with maleic anhydride in chlorobenzene. The coal was dried by distilling off some of the chlorobenzene-water azeotrope. Work-up followed the procedure used by Nishioka.⁵ Samples of maleic anhydride independently labeled at both carbonyl and vinyl carbons were used. Solid state NMR spectra of the coals were obtained using a General Electric GN300 solid state NMR spectrometer operating at 75.4MHz for carbon using a Doty Scientific, Inc. 7 mm or 5 mm probe and a radio frequency feedback control circuit. The spectrometer was operated with radio frequency field strengths of 50 to 63 kHz for carbon and protons while acquiring 1 K of complex data points with a dwell time of 15 μs , a receiver gate time of 15 μs , and a filter delay of 15.75 μs . The times for the recycle delays were selected after the proton and carbon spin lattice relaxation times T_1 , of 0.23-0.27 s for protons and 0.2-9.8 s for carbons were determined. Relaxation delays of 2 s for cross polarization experiments, and 60 s for Bloch decay experiments were employed. The data were processed using a baseline correction, exponential multiplication equivalent to 100Hz line broadening and one zero-fill followed by Fourier transformation. The spectra were phased using an auto phase function followed by linear baseline adjustment and another auto phase so that only minor adjustments were required. Samples were examined under magic angle spinning and high power proton decoupling. Sapphire rotors with Kel-F[®] end caps were used to minimize ^{13}C background. Bloch decay single pulse experiments were used for most of the coal spectra. A cross polarization ^{13}C - ^{13}C double quantum filter pulse sequence was also utilized.¹¹

RESULTS. Figure 1 shows solid state ^{13}C Bloch decay NMR spectra for a physical mixture of Pittsburgh No. 8 coal and maleic anhydride and Pittsburgh No. 8 coal after reactions with a mixture of 50% ^{13}C maleic anhydride labeled in the 2 and 3 (vinyl) positions or in the 1 and 4 (carbonyl) positions.

RESULTS AND DISCUSSION. The NMR spectra show that the vinyl carbons have become sp^3 hybridized carbons in the adduct and that the carbonyl carbons remain unaltered. That the carbonyl carbons have not shifted confirms earlier reports that ester formation has not occurred and rules out Nishioka's assertion that a charge transfer interaction was responsible for maleic anhydride incorporation.^{1,2,5} If charge transfer was responsible for the upfield shift of the vinyl carbons, then a large upfield shift of the carbonyl carbons must also occur due to the presence of the transferred electron in the maleic anhydride LUMO. The conversion of the vinyl carbons from sp^2 to sp^3 is consistent with the occurrence of a Diels-Alder reaction. A ^{13}C - ^{13}C double quantum experiment confirms the double bond is converted to a single bond.

There are several other reactions which might also convert the vinyl carbons to sp^3 . An ene reaction would do this, but there is no precedent in the literature for an ene reaction between maleic anhydride and either phenols or alkyl aromatics. Maleic anhydride can be homo polymerized only with difficulty and it has been demonstrated that the unshared electrons in coals are remarkably inefficient at inducing polymerizations; vitrinite radicals are not capable of initiating the polymerization of vinyl pyridine.^{7,8} The radical addition of maleic anhydride to benzylic positions is a known reaction, but adding radical initiators or using peroxide containing air-oxidized coals did not give any increase in maleic anhydride incorporation ruling out this pathway.^{7,9} Michael addition to phenols or thiols is possible.¹⁰ This reaction does not occur with phenols in coals, but does occur with coal thiol groups. The amount of thiol sulphur in this coal is much too small to explain the observed maleic anhydride incorporation.

It is clear that maleic anhydride is adding to the coals via a reaction involving the carbon-carbon double bond. The most reasonable candidate for this reaction remains the Diels-Alder. We are left with the puzzle with which we began, although this puzzle is now based on firmer ground. Either there are under characterized reactive diene structures in coals or the maleic anhydride reaction with coals is somehow enhanced. In one investigation of this latter possibility, we attempted to catalyze the Diels-Alder reaction between maleic anhydride and naphthalene by carrying it out in the presence of added coal. The added coal had no effect. It is clear from these results that major features of coal structure and/or reactivity are still not understood.

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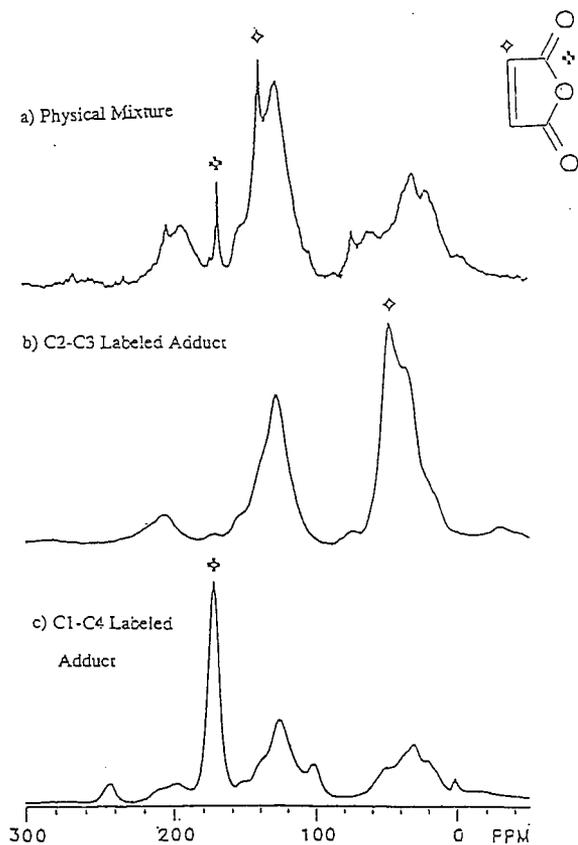


Figure 1. Solid State ^{13}C NMR spectra for a) a physical mixture of Pittsburgh 8 coal and maleic anhydride and Pittsburgh No. 8 coal reacted with b) $^{13}\text{C}_2$ $^{13}\text{C}_3$ and c) $^{13}\text{C}_1$ $^{13}\text{C}_4$ labeled maleic anhydride for 10 days in chlorobenzene at 110°C , then Soxhlet extracted with methanol for 3 days and dried.

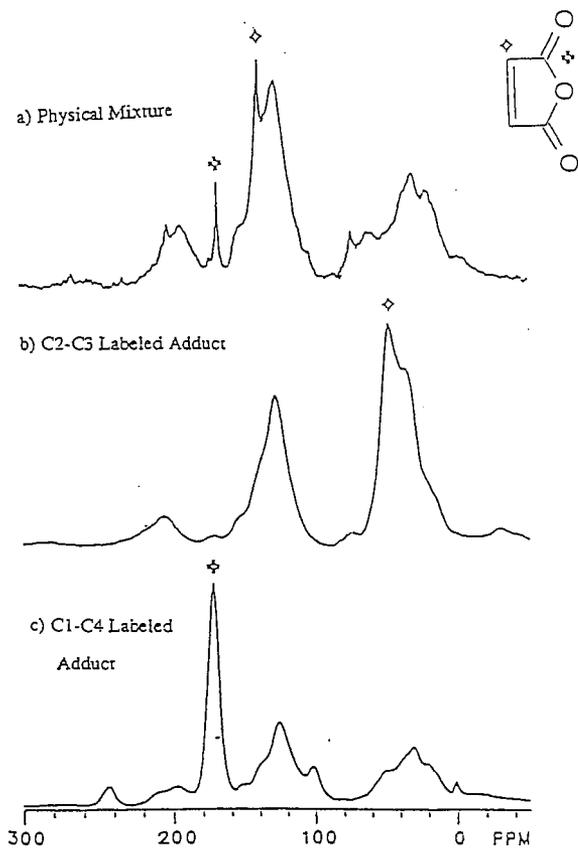


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