

BOND DISSOCIATION ENERGY CALCULATIONS FOR COAL FRAGMENTS AND MODEL COMPOUNDS

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Abstract

Anderson's modified version¹ of the extended Hückel molecular orbital method and the MNDO and AM1 methods of Dewar have been used to study bond cleavage in molecular fragments of interest to coal liquefaction. Geometric conformations, molecular orbital coefficients for the HOMO's and LUMO 's, bond dissociation energies, and heats of reaction have been computed and compared for the three methods. Qualitative agreement with experiments for bond cleavage is observed for the three methods for the neutral molecule. However, the modified Hückel method appears to best describe bond cleavage in the presence of an electron-accepting catalyst. Heats of reaction are also calculated for reaction conditions appropriate to the presence of a hydrogen donor.

Introduction

Given the complexity of coal at the molecular level, it is not clear at the outset that useful quantum chemical computations of relevance to coal chemistry can be carried out. However, there are two significant developments that are paving the way for quantum chemical calculations to play a useful role in this field. One is the steady escalation in the power of computers. The other is the synthesis of model compounds that mimic, in a controlled way, aspects of the molecular structure of coal. Careful, quantitative experimental studies on reaction pathways and catalytic action in reactions involving model compounds promise to offer new insights into coal chemistry and the possibility of developing more economical processes for direct liquefaction.

For any modeling of coal to be significant, it must first be shown that the method employed in the study gives meaningful results for model compounds for which experimental results are available. We have begun by performing quantum chemical calculations on 4-(1-naphthylmethyl)biphenyl (referred to hereafter as Model Compound I), studied recently by Farcasiu and Smith.^{2,3} In Figure 1 the skeletal structure of Model Compound I is shown. In their experiments Farcasiu and Smith demonstrated the bond breaking selectivity of a novel catalyst, carbon black (BP 2000), and measured kinetic reaction rates and bond activation energies for cleavage of the methylene and ethylene linkages of the compound. We have recently used^{4,5} several semi-empirical quantum chemical methods to calculate bond dissociation energies of model compounds and coal fragments. In this paper we describe some further calculations that are designed to elucidate the bond-selective catalytic action in the hydrogenation reaction of 4-(1-naphthylmethyl)biphenyl studied by Farcasiu and Smith.^{2,3}

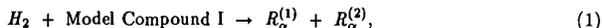
In the earlier papers^{4,5} we used Anderson's modified version of the extended Hückel molecular orbital method¹ and the MNDO and AM1 methods of Dewar, *et al.*^{6,7} to study bond cleavage in

neutral and positively charged Model Compound I. The interest in the positively charged radical ion formed from Model Compound I by removal of an electron comes from the suggestion of Farcasiu and Smith^{2,3} that the BP 2000 catalyst acts as an electron acceptor and removes an electron from the naphthyl portion of model compound I.

Geometric conformations, molecular orbital coefficients for the HOMO's and LUMO's, and bond dissociation energies were computed and compared for the three methods. Qualitative agreement with experiment for bond cleavage was observed for the three methods for the neutral molecule. Our earlier calculations suggest that the ASED-MO method appears to best describe the bond cleavage in the presence of an electron-accepting catalyst. This can be seen from the results shown in Table 1, where the product distributions with and without the catalyst (i.e., for the neutral molecule and the positive radical ion, respectively) calculated by the ASED-MO method are compared with the thermolysis results. The bond labels referred to in the Table are shown in Figure 1. The theoretical relative product distributions were calculated from the computed bond dissociation energies (shown in columns 2 and 5) using the Boltzmann distribution at the experimental temperature. The qualitative agreement between theory and experiment with regard to the bond-selectivity of the catalytic reaction is evident from the Table.

Calculation of Energies of Reaction

In our earlier papers the reactions in the presence of a hydrogen donor, which are more directly relevant to the study of coal liquefaction, were not studied. In this paper we have calculated the energy differences for the five reactions



where $\alpha = a, b, c, d, e$ denotes the bond that is cleaved in the reaction (as labeled in Figure 1), and in each instance, $R^{(1)}$ denotes the product molecule containing the naphthyl portion of the starting Model Compound I and $R^{(2)}$ the product molecule containing the remainder of Model Compound I. This is a rather simplistic model of the reaction in the presence of the hydrogen donor; clearly, the energy of reaction for hydrogen extraction from the donor (e.g., 9,10-dihydrophenanthrene) will be involved. However, our interest is in the relative product stabilities for the different bond cleavages, and the hydrogen extraction contribution should be essentially the same in all the cases. We present results for ASED-MO, MNDO, and AM1 methods. It should be noted that only the relative energies of reaction for the five paths indicated above within any given method are significant. The absolute numbers calculated by the different methods depend on the calculated dissociation energy for the hydrogen molecule. For example, the dissociation energy for the hydrogen molecule is overestimated by about 5 eV by the ASED-MO method, and by about 1 eV by the AM1 method.

In Table 2 we show the energies of reaction for the hydrogenation reactions of the neutral and charged Model Compound I calculated by the three methods. As explained above, only the relative magnitudes within each method are meaningful. For reactions involving the positive radical ion, the positive charge is kept with the product species containing the naphthyl fragment; the justification for this has been given in our earlier papers. The main conclusion from Table 2 is that the energies of reaction for the five different paths are similar; the product stabilities relative to the reactants are not greatly different, and further there is no correlation between product stability and the observed product distributions. This is true for reactions involving the neutral molecule as well as the positive radical ion.

Discussion and Conclusions

From these calculations we conclude that the driving force behind the bond-selectivity found in the reaction is not the relative thermodynamic stabilities of the products formed. Other possible factors for the bond selectivity are the differences in the activation energies for the different bond cleavages, and/or the charge distribution in the radicals formed after bond cleavage. We will consider first whether the experimentally found product distribution might be accounted for by the differences in the hydrogen affinity of the radicals formed by the bond cleavage. To test the importance of this factor, we have compared the charge localized on the terminal carbon atoms of the cleaved bond for the neutral and the charged Model Compound I in the different methods. We find no correlation between the charge build-up in the radicals and the observed product distributions.

Since the entropy changes in all the reactions are expected to be small, the bond dissociation energies, which are directly calculated by the theoretical methods, should be an upper bound to the activation energies and appears to be the most important factor in determining the product distributions. The ASED-MO method predicts the difference between the neutral molecule and the positive radical ion in qualitative agreement with experiment. The fact that this simple method succeeds where the more sophisticated semi-empirical methods fail is surprising. Of course, the MNDO and AM1 methods have not really been parameterized for charged species, and this may be the reason for their apparent failure. We are presently carrying out more calculations both to further elucidate the catalytic action, and to test the methods for other model compounds.

Acknowledgments

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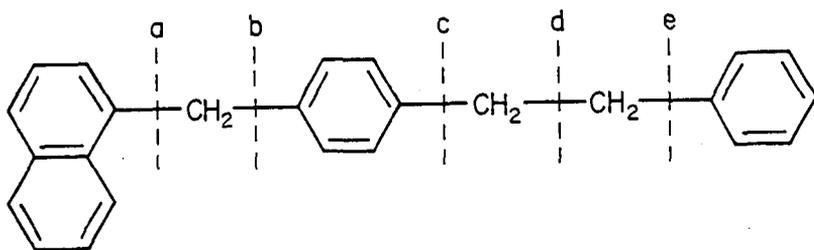


Figure 1: The skeletal structure of 4-(1-naphthylmethyl)bibenzyl. The methylene and ethylene linkages, whose cleavage is of interest here are labeled for use in the text.

| Bond | Neutral | | | Charged (+1) | | |
|------|---------|-----------|--------------------|--------------|-----------|--------------------|
| | BDE(eV) | Product % | | BDE(eV) | Product % | |
| | ASED | ASED | Expt. ^a | ASED | ASED | Expt. ^a |
| a | 4.09 | 0.4 | 17 | 2.80 | 94 | 51 |
| b | 3.89 | 11 | 3 | 3.08 | 0.7 | 7 |
| c | 4.23 | 0.0 | 16 | 3.01 | 2 | 8 |
| d | 3.77 | 88 | 64 | 3.00 | 3 | 34 |
| e | 4.18 | 0.1 | - | 3.40 | 0.0 | - |

^aFrom Farcasiu and Smith (Ref. 2)

Table 1: Bond dissociation energies (BDE) and product distributions for the thermolysis of Model Compound I. The results for the positively charged radical ion are appropriate to the presence of BP 2000 catalyst, as described in the text. From Ades, *et al.*, Ref. 5.

| Bond | ASED-MO | | MNDO | | AM1 | |
|------|---------|---------|---------|---------|---------|---------|
| | Neutral | Charged | Neutral | Charged | Neutral | Charged |
| a | 0.90 | 0.96 | -0.60 | -0.54 | -0.12 | 0.00 |
| b | 0.93 | 0.98 | -0.43 | -0.44 | -0.02 | -0.09 |
| c | 0.93 | 0.93 | -0.37 | -0.43 | 0.05 | -0.02 |
| d | 1.07 | 1.07 | -0.50 | -0.55 | -0.03 | -0.10 |
| e | 0.93 | 0.93 | -0.37 | -0.42 | 0.05 | -0.03 |

Table 2: The calculated energies of reaction (in eV) for the neutral and charged (+1) Model Compound I using three semi-empirical methods. As explained in the text the numbers are only meaningful for the comparison of the thermodynamic stability of the products relative to the reactants within a particular method.