

HETEROGENOUS CATALYSIS:
Mechanisms of Selective Cleavage of Strong Carbon-Carbon Bonds.

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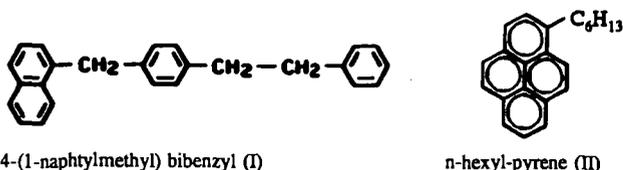
INTRODUCTION

This paper discusses the catalytic cleavage of strong carbon-carbon bonds in compounds which also contain relatively weaker carbon-carbon bonds which can be cleaved thermally by a homolytic, free radical process. The majority of the reactions described here are performed under condition where the thermal background is very small or nonexistent.

We will discuss the reactivity of two model compounds (Figure 1) relevant to fossil fuels (oil and coal) in the presence of several heterogenous catalysts: carbon black, graphite and solid acids. Previously, we have reported a very selective carbon black C-C cleavage of bonds between a polycondensed aromatic moiety and an adjacent aliphatic carbon¹⁻⁴ and on carbon black catalyzed dehydroxylation and dehalogenation of polycondensed aromatic phenols and halogenated polycondensed compounds⁵. We attributed the observed catalytic activity and selectivity in hydrocracking reactions to the formation of radical cations on the surface of carbon-based catalysts at temperatures over 320 °C² and the dehydroxylation and dehalogenation reactions to a free radical mechanism identical with that of the thermal reaction⁵. We concluded that two types of catalytic active centers are present on carbon black. In this presentation we will elaborate on the nature of carbon black catalytic activity and contrast it to that of graphite.

The ion radical mechanism for the C-C cleavage mechanism which we observe in the case of carbon black catalysts is disputed by Penn and Wang based on an extensive presentation of literature data and on their own experimental results for radical-cation generated in solution in the presence of polar solvents⁶. Under their reported conditions, no cleavage of any C-C bond is observed unless a tetraaryl-substituted ethane was used as a substrate. They conclude that the ion-radical mechanism we proposed for the carbon black catalyzed reactions is incorrect and that the solvent-assisted ipso addition of a hydrogen atom⁷ is the most likely explanation for both thermal and catalytic carbon-carbon cleavage of the type we observed. The role of the catalyst is considered to be to accelerate either the formation of the hydrogen atom or the addition of the hydrogen atom to the substrate, or both. The source of the H-atom is the solvent.

We will discuss in this paper the data that rise doubts about extending the free radicals (including ipso addition of hydrogen atoms from solvents) as the initial step in the cleavage of specific strong C-C bonds under the conditions of heterogenous catalysis on carbon catalysts.



4-(1-naphthylmethyl) biphenyl (I)

n-hexyl-pyrene (II)

Fig. 1 Model compounds used in this study

EXPERIMENTAL

The experimental conditions for testing the model compounds described in Fig. 1 and the methods used for products identification and conversion calculations have been already published^{2,3}. In this study, the catalytic reactions of I and II have been studied both in tetralin and perdeuterated tetralin, both from Aldrich Co.

RESULTS AND DISCUSSION

Carbon-catalyzed C-C cleavage reactions were performed for I and II, compounds having the general formula Aryl-CH²-R, where aryl is naphthalene (I) or pyrene (II). The selective cleavage is catalyzed by carbon black at temperatures of 320 to 420°C. The graphite does not catalyze the cleavage. Unlike the dehydroxylation and dehalogenation reactions which require the presence of a H-donor, the carbon black catalyzes the C-C cleavage both in the presence and absence of the H-donor. Another reaction observed in the presence of deuterotetralin is H-D exchange. This reaction is catalyzed both by carbon black and graphite. At 350°C and reaction time of one hour the degree of H-D exchange is 58% in the presence of BP2000 and 12% in the presence of graphite. At 400°C and one hour reaction time the H-D exchange is 93% in the presence of BP2000 and 74.6% in the presence of graphite. However, the yield of selective cracking of the bond adjacent to the naphthalene ring is 20.4% in the case of BP2000 and zero for graphite. In the presence of graphite, the cracking is less than 1% and the selectivity is typical of the thermal reaction². We conclude that it is no connection between the mechanism of H-D exchange and the selective cleavage of C-C bond described above. We believe that this result, together with the calculations of Ades et al.^{8,9} and the results of Charge Distribution Analysis reported previously² make the ipso addition unlikely as the mechanism of the carbon black catalyzed C-C cleavage.

The mechanism we propose can be described as follows: the condensed polyaromatic moiety of the compounds studied is adsorbed preferentially on the surface of the carbon black concurrent with the carbon surface becoming positively charged (at temperatures over 320 °C). Subsequently an electron is transferred from the condensed aromatic ring to the carbon catalyst. In the ion radical formed, the weakest bond becomes the C_{ar} - C_{subst} adjacent to the polyaromatic system^{8,9}. If the temperature is high enough for cleavage of this bond, the reaction will take place and the free radical formed from the substituent group will abstract a hydrogen atom from another molecule (for example the hydrogen donor present in excess). The naphthalene fragment resulting from cleavage has a higher oxidation potential than I (1.54 eV for naphthalene¹⁰ vs 1.257 eV for I¹¹ and will not transfer an electron to the carbon black. Consequently, a free naphthalene radical will desorb and abstract a hydrogen from another molecule. This initial cleavage of the ion radical could explain why cleavage reactions are obtained only at temperatures where the surface becomes positively charged and why the cleavage is observed at temperatures much below the thermal background.

The high energy, very likely more delocalized radical ions typically formed in mass spectrometers could also exhibit very different reactivity from the radical ions formed on a surface. The extrapolation, therefore, of gas-phase ion-radical reactivity to surface reactions is tenuous at best and can be misleading when interpreting results from heterogeneous catalytic reactions.

The data presented above may be useful for understanding some of the observed differences in the chemistry of radical ions in the gas phase or solution as compared with reactions on a surface. They could also be helpful for understanding why many of the heterogeneously catalyzed reactions require higher temperature than those under homogenous catalysis conditions.

CONCLUSIONS

Our data indicate that the mechanism of selective C-C cleavage in the presence of carbon black involves in the first step an electron transfer from a condensed aromatic ring to the carbon black surface when this surface become positively charged (i.e. at temperatures higher than 320° C). The result is a very different reactivity and selectivity of the ion-radicals toward C-C bond cleavage than that taking place in solution or in a mass spectrometer.

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