

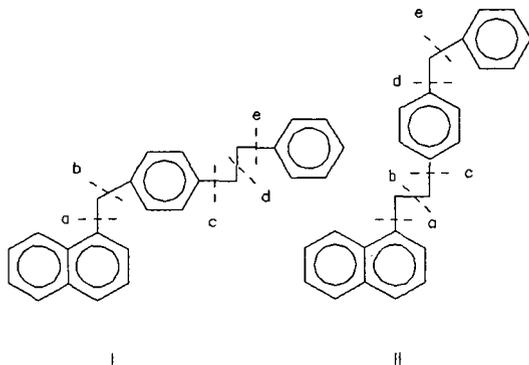
ALTERNATIVE MECHANISMS FOR RADICAL CATION BOND CLEAVAGE

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INTRODUCTION

Recently, a new set of model compounds has been advocated for understanding the reactivity occurring under processing conditions of fossil fuel substrates. These compounds possess multiple functionality and high molecular weight in order to better simulate the reactions which occur in real fuel conversion processes.¹ Chief among these compounds are 4-(naphthylmethyl)bibenzyl, hereafter referred to as Model Compound I, and 4-(2-naphthylethyl)diphenylmethane, II (see structures below). These compounds contain a dicyclic aromatic compound in addition to the monocyclic phenyl groups. Chemical reactivity can then be inferred from the position of the cleavage of the linkages between the aryl groups.



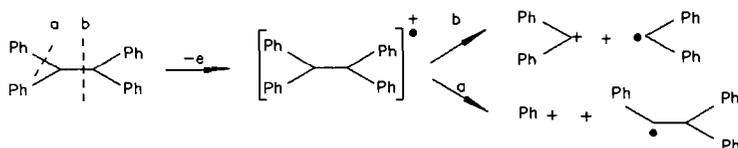
These compounds have been used to test the reactivity of various catalysts. For both compounds, these catalysts cleave bond a, i.e., the bond next to the naphthyl ring. Radical cation reactivity has been implicated in these reactions because the naphthyl group is the moiety most likely to lose an electron in these compounds and because the catalytic behavior originates at temperatures in which the surface of the catalyst becomes charged.² Theoretical calculations have also been used to support

radical cation cleavage of bond a in these compounds.³

This reactivity contrasts with the known radical cationic cleavage pathways of monocyclic arenes. For example, the radical cation of 1,1,2,2-tetraphenylethane (TPE) is known to cleave at bond b, as shown in eq (1).⁴ The radical cation of bibenzyl also cleaves at bond b, albeit at a much slower rate. The slow cleavage of the radical cation of bibenzyl presumably results from loss of resonance stabilization in the incipient radical and cation formed in this reaction.

In order to distinguish between the contrasting reactivity patterns exhibited by the polycyclic aromatic radical cations and the monocyclic aromatic compounds, we have attempted to independently generate and observe the bond cleavage of the radical cations of naphthyl-containing compounds I, di-(1-naphthyl)methane (DNM), and 1,2-di(1-naphthyl)ethane (DNE). Our strategy for these reactions was to use the photoinitiated electron transfer reactions from 9,10-dicyanoanthracene (DCA).⁵ In these reactions, DCA absorbs a photon of light to produce an excited state of DCA (i.e., DCA*) which does a one-electron oxidation of compounds with oxidation potential ≤ 2.88 V vs SCE.⁵ These reactions are usually performed in methanol or acetonitrile solutions to facilitate electron transfer and to trap the resulting cations which are expected to be produced in these reactions.

(1)



RESULTS AND DISCUSSION

Generation of the Radical Cation of I, DNM, and DNE Under Degassed Conditions: Irradiation of a freshly distilled acetonitrile solution of I (2.0 mM) and DCA (0.1 mM) using light of 350 nm from a Rayonet reactor for 96 h yielded no product when the reaction solution was degassed with N_2 for 15 min prior to the irradiation and then sealed with a latex septum. The lack of reaction was initially indicated by the lack of low molecular weight products by GC analysis of the reaction solution and was confirmed by the use of internal standards which were added prior to initiation of the reaction. The reactions of DNM and DNE were similar in that no reactions were detectable after 96 h of irradiation. Again the lack of reactivity was conclusively demonstrated by the use of internal standards.

Since the interpretation of negative results can be often ascribed to poor technique or the inability of a laboratory to reproduce other worker's results, we have generated the radical cation of TPE using this methodology. As expected, diphenylmethane and diphenylmethyl methyl ether were produced in quantitative yield in just 24 h of irradiation. These results are consistent with the results obtained in Reference 4 and demonstrate that the radical cations of these substrates are being generated under these conditions.

The significance of these results is that the radical cations of DNM and DNE do not cleave readily at room temperature. These results are analogous to those reported for bibenzyl (i.e., 1,2-diphenylethane)⁶ in which a very low quantum efficiency for cleavage has been reported using the photoinitiated electron transfer methodology for radical cation generation. While the lack of bond cleavage from the radical cation of these 1,2-diarylethanes does not rule out the bond cleavage reactions of radical cations under catalytic conditions where higher temperatures may lead to faster reactions from these intermediates, the lack of bond cleavage suggests that these intermediates have higher energy bond dissociation energies which makes their intermediacy more difficult to postulate without further characterization of their reactivity.

Generation of the Radical Cation of I, DNM, and DNE With O_2 in the Solution: Similar experiments to those above were performed after bubbling of O_2 for 15 min prior to irradiation. In contrast to the lack of reactivity observed under degassed conditions, bond cleavage is observed for I, DNM, and DNE (Note Figure 1). In all cases, bond a cleavage is noted in addition to a variety of other products.

Complete interpretation of the reaction results is not possible since the mass balances in these reactions are poor at the present time. We speculate that secondary reactions involving O_2 and the $DCA^{\bullet+}$ (formed by electron transfer from the DCA^+ and the aromatic moiety) to yield $O_2^{\bullet-}$, followed by a H^+ transfer to yield a pair of radicals which initiate a chain reaction may be responsible for the observed reactivity (Note Figure 2). However, definitive interpretation must await better mass balances and more detailed work to explore the bounds of this

reactivity.

ACKNOWLEDGEMENTS

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FIGURES

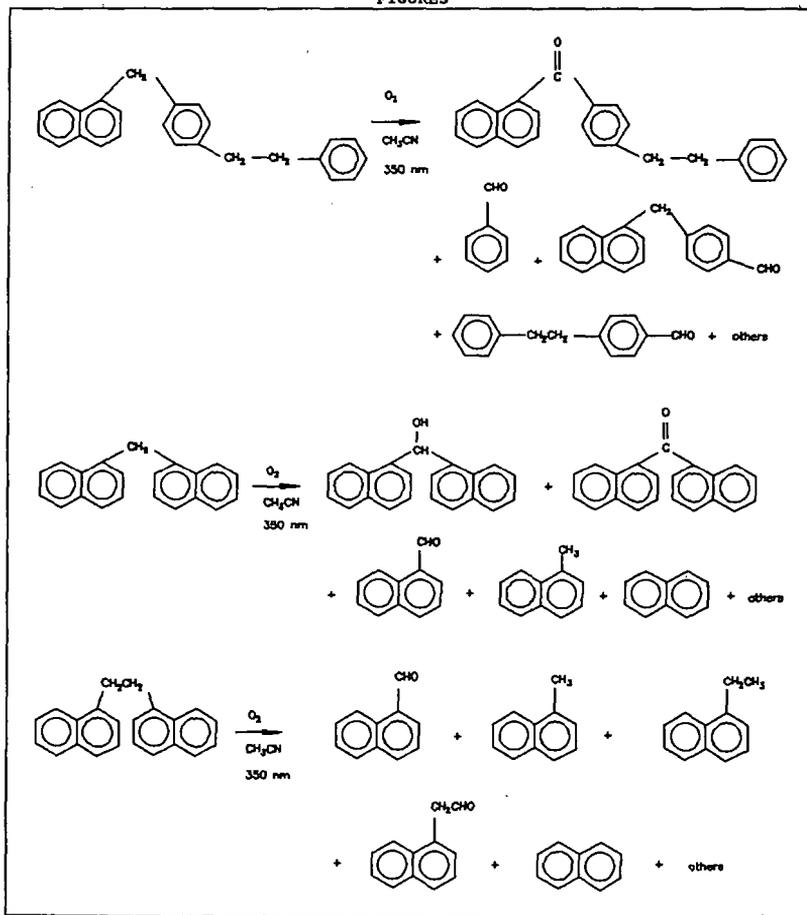


Figure 1. Change in reactivity influenced by O_2

