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FROM AN IRON-BASED CATALYST TO ALKYLARENES

S.T. Autrey T.R. Powers
J.C. Linehan E.F. McMillan
D.M. Camaioni J.A. Franz

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Pacific Northwest Laboratory
Richland, WA 99352

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CATALYTIC CONVERSION OF POLYCYCLIC AROMATIC HYDROCARBONS:
MECHANISTIC INVESTIGATIONS OF HYDROGEN TRANSFER FROM AN IRON-
BASED CATALYST TO ALKYLARENES.

Tom Autrey, John C Linehan, Donald M Camaioni, Tess R Powers,
Eric F McMillan and James A Franz.
Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352 USA

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Introduction.

The utility of iron-based nanophase catalysts in the liquefaction of coal and coal model compounds has been demonstrated to increase the efficiency of liquefaction during the early stages of catalytic coal hydrotreatment.¹ Despite numerous model compound studies, the mechanism of "liquefaction" remains controversial. Wei and coworkers²⁻⁵ proposed a hydrogen atom - ipso displacement pathway, however, this pathway alone cannot explain the observed selectivity.⁶ Farcasiu and co-workers⁷ proposed a mechanism in which the alkyl-arene moiety is activated to undergo bond scission by electron transfer to the catalyst. However, a key step in this pathway, unimolecular scission of the radical cation, has been argued to be kinetically and thermodynamically unfavorable.⁸

We recently reported a beneficial characteristic of the Fe/S catalysts, generated in situ by the reaction of sulfur with iron oxyhydroxides produced by the RTDS process: *scission of strong carbon-carbon bonds without addition of hydrogen gas and with minimum formation of light gases.*^{6,9} We investigated a series of mono-, di-, and trimethyldiphenylmethanes and found that in all cases the benzyl group is preferentially displaced. We proposed a variant of the Farcasiu mechanism⁷ in which a hydrogen atom is transferred to the ipso position of the radical cation, which then scissions a benzyl cation. Back electron transfer from the reduced catalyst surface to the benzyl cation would give the benzyl radical.⁶ We refer to this radical ion mechanism as "ET/HT". The mechanism is consistent with (1) the proposed redox properties of the catalyst,⁷ (2) the observed "dealkylation" selectivity, benzyl >> methyl, and (3) the low yield of transalkylation products.

Recent examination of the structure - reactivity relationships for the methylated diphenylmethanes shows the rate of catalytic-induced bond scission correlates not only with the ease of arene oxidation but also correlates with the stability of the ipso radical adduct.¹⁰ To accommodate the observed selectivity for benzyl scission >> methyl scission by a radical pathway, we proposed a reversible hydrogen atom transfer between the catalyst surface and the arenes, in which case, the rate of back hydrogen transfer from the ipso and nonipso adducts must be fast compared to scission of methyl radical.

In the present study, we designed and prepared model compounds to differentiate between the ET/HT radical ion pathway and the reversible hydrogen atom transfer pathway.

Experimental.

Materials. All catalytic experiments used the RTDS-prepared, 6-line ferrihydrite catalyst precursor.¹¹ 9,10- dihydrophenanthrene (DHP), xanthene, and *o*-hydroxydiphenylmethane were purchased from Aldrich. The DHP was distilled and recrystallized from methanol/dichlormethane. 1,2-ditolylethanol was available from a previous study.¹² *o*- and *p*- benzylidiphenyl ether were prepared by the same method used for our synthesis of the alkylidiphenylmethanes.¹³ The isomers were separated on a Chromatotron® eluting with pentane.

Thermolysis Studies. The model compound (15 mg), the 6-line ferrihydrite (3 mg),

the sulfur (3 mg), and the DHP solvent (100 mg) were loaded into the glass tubes and sealed under vacuum. The thermolysis was carried out in sealed 5-mm o.d. borosilicate glass tubes immersed in a fluidized sand bath regulated at 400°C for 1 h. The GC and GC/MS analysis were carried out as described previously.¹¹

Results and Discussion.

Given the parallel structure - reactivity trends for ion, radical, and radical-ion intermediates in the alkylarene series previously examined, we prepared a new series of model compounds to discriminate between the ion, radical, and radical ion hydrogen transfer pathways. A comparison of diphenyl ether analogs with our diphenylmethane model compounds was suggested as an approach to obtain insight into the proposed multi-step ET/HA transfer step or a free radical pathway.¹⁴ The cation formed by ipso addition of H-atom to the radical cation of diphenyl ether (DPE) was suggested to be more resistant to bond scission than the analogous cation obtained from diphenylmethane (DPM) because of the differences in the stability of the leaving group, $\text{PhO}(+) \ll \text{PhCH}_2(+)$, while the opposite selectivity was predicted for a radical pathway, $\text{PhO}\cdot > \text{PhCH}_2\cdot$. Unfortunately, while the β -scission of a phenoxy cation from DPE is expected to be significantly slower than the β -scission of a benzyl cation from DPM the first step, oxidation of the DPE, is faster than oxidation of DPM.¹⁵ Thus, an "external" comparison of DPM and DPE derivatives could complicate direct kinetic comparisons. To alleviate this concern, we used model compounds that had both the PhO- and PhCH₂- substituents in a single molecule -- xanthone (XA), *p*-benzyldiphenyl ether (pBDPE), and *o*-benzyldiphenyl ether (oBDPE). This approach avoids complications caused by differences in oxidation potential of diphenylmethane and diphenyl ether and takes advantage of the selectivity differences between scission of PhO* and PhCH₂*.¹⁶ Thus, the appearance of PhCH₂Ph would be consistent with a carbon-oxygen (PhCH₂Ph-OPh) free radical bond scission pathway, and the appearance of PhOPh would be consistent with an apparent carbon-carbon (PhCH₂-PhOPh) cationic bond scission pathway.

Thermolysis of pBDPE in DHP- Fe/S at 400 °C leads to ca. 70% consumption of the starting material in 60 minutes with the formation of DPM, DPE, toluene and phenol. The ratio of DPM/DPE (i.e. carbon-oxygen/carbon-carbon bond scission) is 8:1.

This result offers significant insight into the mechanism of catalytic-induced bond scission. The selectivity of the 8:1 ratio for scission of benzyl over phenoxy radical from pBDPE is significantly less than expected for β -scission of PhCH₂(+) over PhO(+).¹⁷ Therefore, we have considerably less confidence with the involvement of a cationic intermediate formed either by acidic proton transfer or multi-step ET/HA pathways for promoting bond scission. What is interesting about these results is that the selectivity is the opposite of the relative stabilities of the benzyl and phenoxy radicals. Therefore, bond cleavage must not be the rate-limiting step for reaction of this molecule. The selectivity is consistent with rate-limiting formation of the ipso adducts. The stability of the ipso adduct, (a), leading to formation of DPE and the benzyl radical is 3±2 kcal/mol¹⁸ more stable than the ipso adduct, (b), leading to formation of DPM and the phenoxy radical (Scheme 1).

Thermolysis of oBDPE under the same reaction conditions again yields DPM, DPE, toluene and phenol, however, the ratio of DPM/DPE is 1:1. The apparent lower selectivity observed from the catalytic thermolysis of oBDPE could be due to a competing neophyl-like phenyl migration, 1,5 addition, in Scheme 2. These Ar₁-5 radical rearrangements are known to occur,¹⁹ especially when heteroatom termini are involved.^{20,21} Tautomerization of the phenol, followed by unimolecular scission,²² can yield diphenylmethane by an alternative pathway. The expected side product from this radical rearrangement pathway, 9-phenylxanthene -- formed from addition of the diphenylmethyl radical to the *ortho*-position, 1,6 addition, followed by disproportionation--is detected in the thermolysis of oBDPE. This

provides further evidence for the presence of the precursor to the neophyl rearrangement pathway under the reaction conditions.²³

Thermolysis of xanthene under the same catalytic reaction conditions yields little bond scission after 60 minutes, no detectable 2-methyldiphenyl ether, and only traces of 2-bond scission products, toluene and phenol. Here, the absence of significant quantities of scission products in the xanthene thermolysis is probably due to competing reversible reactions that regenerate the starting material. Because the leaving group is "attached," little bond scission is observed.

Unimolecular Scission of Radical Ions. Early mechanistic studies demonstrated the preference for catalytic-induced scission of diarylmethane linkages over the thermally labile bibenzyl linkages in 4-(1-naphthylmethyl)bibenzyl (NMBB). Farcasiu and coworkers invoked single electron oxidation of the arene followed by a unimolecular scission to yield naphthalene and 4-methylbibenzyl (referred to as -A- bond cleavage).⁷ However, the observed selectivity is the opposite of that expected based on reactions in solution or reactions in the gas phase based upon fragmentation reactions of the NMBB radical cation in a mass spectrometer.⁸ Almost as surprising as radical cation cleavage at the diarylmethane -A- bond is the suggestion that the positive charge is carried on the naphthyl group,²⁴ not the benzyl group, given the difference between stabilization of benzyl cation and a benzyl radical. To favor -A- bond scission over -D- bond scission, the catalyst must uniquely stabilize the naphthyl cation and/or destabilize the benzyl cation. This novel unimolecular scission pathway is reported to be supported by atom superposition and electron delocalization molecular orbital (ASED-MO) methods, however, AM1 and MNDO theoretical methods indicate cleavage of the -D- bond is favored.²⁵

NMBB probably is not the best model compound to test the unimolecular radical cation dissociation mechanism. Although the bond dissociation energy (BDE) for bibenzyl radical cation, at about 30 kcal/mol, is substantially weaker than the bibenzyl bond, we expect that -D- bond scission in the NMBB radical cation will be a minimum of 40 kcal/mol, given that oxidation of 1-methylnaphthalene is ca. 10 kcal/mol more favorable than oxidation of *p*-xylene, and conservatively assuming no barrier for the ET process that generates the radical cation. A barrier of this magnitude probably cannot compete with bimolecular reactions of the radical cation or alternative free radical pathways, Scheme 3. A more judicious choice of model compounds, for example one with a much lower radical cation BDE, could provide support for the proposed electron transfer pathway if the bond were broken more rapidly than purely thermal pathways allow.

We used 1,2-*p*-ditolylethanol (DTE) as a probe for the electron transfer mechanism. Diphenylethanol radical cation has a BDE of 15 kcal/mol and therefore is expected to dissociate ca. 8 orders of magnitude faster than the NMBB radical cation at 400°C, and will be more likely to compete with other pathways. Thermolysis of DTE in DHP for 60 minutes at 400°C results in ca. 50% conversion to yield 4,4'-*p*-dimethylbibenzyl, *p*-xylene, 4-methylbenzylalcohol, 4-methylbenzaldehyde and a trace of toluene. The ratio of toluene to *p*-xylene is 1:25. The 4,4'-*p*-dimethylbibenzyl is formed by a reduction pathway that competes with unimolecular scission. Since the 4,4'-*p*-dimethylbibenzyl is thermally stable under the reaction conditions, the xylene is predominately formed from unimolecular thermal scission of the starting material.

Thermolysis of DTE in DHP containing the Fe/S catalyst for 60 minutes at 400°C results in complete conversion to yield 4,4'-*p*-dimethylbibenzyl, *p*-xylene, and toluene. The *p*-xylene is most likely formed from the thermal background and reduction of the alcohol and aldehyde since no oxygen-containing products are detected. The most significant finding is the ratio of toluene to *p*-xylene has increased to 1:1. The presence of the Fe/S catalyst pathway apparently increases the yield of toluene! Toluene is not a product

expected from single electron oxidation of the diphenylethanol.¹² The formation of toluene under the catalytic conditions is more rationally explained by an ipso hydrogen displacement pathway. Hydrogen atom addition to the phenyl ring α - to the hydroxy group leads to the β -scission of a stabilized ketyl radical. As we have previously observed efficiency of bond scission is strongly dependent on the stability leaving group.¹⁰

If the radical cation of DTE was formed under the reaction conditions, instantaneous unimolecular scission of the bibenzylic bond would have occurred to yield *p*-xylene as the major product. While we are convinced DTE is an improved probe molecule for investigating the radical ion pathway, we would like to investigate better models, e.g. the methyl ether of DTE, that are not expected to be reduced under the reaction conditions. We are confident that electron transfer from the alkylarene to the catalytic surface does not occur, otherwise we would have observed much higher yields of xylene. Admittedly, oxidation of this xylene derivative will be more endergonic than oxidation of the naphthyl moiety in NMBB, however, the selective catalytic pathways seem to operate even for single ring model compounds.^{6,9} We cannot guess what the ASED-MO methods would find for single electron transfer cleavage pathways of DTE, but experiments¹² and AM1 calculations²⁶ suggest highly efficient bibenzylic bond scission.

Summary and Conclusions.

The results of our model compound studies suggest that free radical hydrogen transfer pathways from the catalyst to the alkylarene are responsible for the scission of strong carbon-carbon bonds. There are two requisites for the observed selective bond scission. First, and most importantly is the stability of the ipso adduct precursor leading to displacement, the more stable the adduct the more probable bond scission. This explains why benzyl radical displacement > phenoxy radical displacement in benzyl diphenyl ether and explains why $\text{PhCH}_2\text{CH}_2\text{PhCH}_2$ radical > naphthylmethyl radical from NMBB. Second, given "equal" ipso adduct precursor stabilities, e.g. methyldiphenylmethane, the stability of the departing radical determines the selectivity. This explains benzyl radical > methyl radical in the methylated diphenylmethanes and explains why α -hydroxyphenethyl radical > methyl radical in 1,2-ditolylethanol.

We have assumed little physical interaction between the molecules and the catalytic surface and have been able to satisfactorily explain most of the observed selectivity. However, for NMBB we expect a higher selectivity for -A- bond scission relative to -B- bond scission, given the ca. 6 kcal/mol difference between the radical adduct formed by the hydrogen atom addition to 1-methylnaphthalene and *p*-xylene. It is possible that physical properties play a role in lowering the selectivity in NMBB bond scission. Also, we realize that catalysts prepared by other methods may contain different activity sites and operate by different mechanisms.

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Glossary of Acronyms.

BDE	bond dissociation energy
RTDS	Rapid Thermal Decomposition of Precursors in Solution
DHP	9,10-dihydrophenanthrene
pBDPE	p-benzylidiphenyl ether
oBDPE	o-benzylidiphenyl ether
DPM	diphenylmethane
DPE	diphenyl ether
DTE	1,2-ditolylethanol
NMBB	4-(1-naphthylmethyl)bibenzyl

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