

**ACID-CATALYZED CRACKING OF SURFACE-IMMOBILIZED
1,3-DIPHENYLPROPANE IN DISPERSED SOLIDS**

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ABSTRACT

We previously examined the impact of restricted mass transport on thermally induced, free-radical reaction pathways through the study of diarylalkanes covalently linked to an inert silica surface. We have now dispersed surface-attached 1,3-diphenylpropane (\approx DPP) with a low acidity SiO_2 -1% Al_2O_3 (surface area of 170 m^2/g) by solvent removal from a colloidal suspension of the components. Thermolysis studies at 310-375 $^\circ\text{C}$ under vacuum reveal a surprisingly efficient and selective acid-catalyzed cracking reaction for \approx DPP in the solid state. Even at 375 $^\circ\text{C}$, acid-catalyzed aromatic dealkylation of \approx DPP dominates over the normal free-radical decomposition path. The results indicate that significant solid-state interactions between catalyst and substrate can occur, which has significant implications for the use of dispersed catalysts in coal liquefaction and hydropyrolysis.

INTRODUCTION

There has been considerable recent interest in the development of unsupported, highly dispersed catalysts for improving the conversion and product selectivity in coal liquefaction^{1,2} and hydropyrolysis.³ This includes the study of sulfate-promoted metal oxide catalysts, which are reported to have strong surface acidity.^{2b} One potential advantage of such dispersed catalysts is the improved contact between the coal, solvent vehicle if present, hydrogen gas and the catalyst surface, particularly when catalysts with very small particle sizes can be generated. A significant mechanistic question still to be addressed is if, in the early stages of coal dissolution, significant activation of solid coal particles by solid catalyst can occur. In this paper we report initial results from model systems that begin to address this issue.

The cross-linked, network structure of coal may impose constraints on conventional reaction mechanisms as a consequence of restricted mass transport. We have examined this phenomenon for thermal reactions through the study of model compounds that are covalently anchored to an inert silica surface.⁴⁻⁷ In our current study, we employ surface-immobilized 1,3-diphenylpropane (\approx DPP) as the model compound. Thermolysis of \approx DPP has been studied in detail both by itself⁵ and in the presence of co-attached aromatics.⁶ The free-radical chain decomposition reaction that occurs for \approx DPP can be considered prototypical for

trimethylene (and longer) aliphatic groups that connect aromatic clusters in coal. In this study we examine the reactivity of solid \approx DPP dispersed in solid $\text{SiO}_2\text{-}1\% \text{ Al}_2\text{O}_3$ at 310-375 °C. Products that may be generated from potential acid-catalyzed reactions of \approx DPP will be easily distinguished from products of the thermal, free-radical reaction.

EXPERIMENTAL

Two-batches of \approx DPP were prepared with surface coverages of 0.532 and 0.320 mmol/g according to published procedures⁵ by the reaction of $p\text{-HOC}_6\text{H}_4(\text{CH}_2)_3\text{C}_6\text{H}_5$ with the surface hydroxyls of a fumed silica (Cabosil M-5, Cabot Corp., $200 \pm 25 \text{ m}^2/\text{g}$). The solid diluents, Aerosil 200 silica or Aerosil MOX 170 silica-alumina (Degussa Corp.), were dried in air at 200 °C for 4 h prior to use. The Aerosil 200 is an amorphous, fumed silica ($200 \pm 25 \text{ m}^2/\text{g}$; average primary particle size of 12 nm), while the Aerosil Mox 170 is a co-fumed oxide containing ca. 1% Al_2O_3 ($170 \pm 30 \text{ m}^2/\text{g}$; average primary particle size of 15 nm).⁸ Solid mixtures were prepared by making dilute slurries of \approx DPP and diluent in dry benzene, followed by solvent removal at 70 °C under vacuum. Analysis of aliquots of the diluted \approx DPP by standard procedures⁵ gave the expected amounts of \approx DPP within $\pm 5\%$.

Reactions were performed at 310-375 °C (± 1 °C) under vacuum (ca. 5×10^{-6} torr) in a controlled temperature tube furnace as previously described.^{4,5} Vapor-phase products migrated from the heated zone into a liquid nitrogen cold trap, and were analyzed by GC and GC-MS with the use of internal standards. Products on the surface were detached by digestion of the solid in aqueous base and, following workup, were analyzed by GC and GC-MS as phenols or the corresponding trimethylsilyl ethers.

RESULTS AND DISCUSSION

Thermolysis of \approx DPP (0.532 mmol/g) alone occurs readily at 375 °C by a free-radical chain pathway to afford the simple product mixture shown in Fig. 1a and Table 1. The origins of selectivity in product formation including the dependence on surface coverage and co-attached aromatics have been discussed.^{5,6} When \approx DPP is diluted with the Aerosil 200 silica (wt ratio of 1:2.8), the thermolysis products are the same but, as shown in Table 1, the rate of conversion of \approx DPP is reduced by a factor of four.

On the other hand, dilution of \approx DPP with the silica-alumina leads to a substantial rate acceleration as well as a remarkably different set of reaction products as shown in Table 1. Even at 375 °C, the products obtained are principally derived from aromatic dealkylation chemistry, which is characteristic of acid-catalyzed reactions over aluminosilicates involving carbocation intermediates.⁹ Another indicator of acid-catalyzed chemistry is the fact that the $\approx\text{PhCH}_3$ and $\approx\text{PhC}_2\text{H}_5$ products (isolated as the corresponding phenols) are isomerized to a mixture of ortho-, meta- and para- isomers with the meta-isomers formed in the largest amounts. Although numerous other products were detected in very small quantities, the acid-catalyzed cracking of \approx DPP is reasonably selective leading principally to surface-attached benzene ($\approx\text{PhH}$) and vapor-phase indan as the major products (Fig. 1b). Over the temperature range of 375-310 °C, these two products account for 67-74% of the total products (mass balances were $\geq 95\%$).

Large quantities of catalyst are not required to drive this reaction. Thermolysis of \approx DPP (surface coverage of 0.320 mmol/g) at 375 °C for 60 min with weight ratios of silica-alumina: \approx DPP of 0, 0.20, and 2.80 gave \approx DPP conversions of 5.5, 11.6, and 18.2%, respectively. Again, in the absence of the silica-alumina only thermally derived products are detected. However, even in the presence of the small quantity of catalyst, the product distribution is dominated by acid-catalyzed products and is similar to the distribution obtained when excess catalyst is employed.

The mechanism of acid-catalyzed cracking of liquid or vapor-phase organics over aluminosilicates is generally accepted to occur through the generation of carbocation intermediates at Brønsted and/or Lewis acid sites.⁸⁻¹¹ Although diarylalkanes have received little attention, alkylbenzenes exhibit products resulting from competition between cracking, transalkylation, and various isomerization reactions. Acid-catalyzed cracking of alkanes over aluminosilicates appears to proceed through a chain reaction involving hydride transfer from reactant molecules to chemically transformed (isomerized, cracked, etc.) carbocations.⁸⁻¹¹ For cracking of alkylbenzenes, a pathway is generally invoked involving protonation at the ipso position on the benzene ring followed by cleavage of the alkyl group as a carbocation, which generally leads to formation of an alkene.⁹ A similar path has been used to explain the hydrocracking at 350 °C of bibenzyl (to benzene and ethylbenzene) with zinc chloride supported on silica gel.¹² On the other hand, fluid-phase DPP has been shown to undergo selective acid-catalyzed cracking to benzene and indan at 100-130 °C in SbCl_5 and $\text{SbCl}_5\text{-AlCl}_3$ melts by a benzylic cation/hydride transfer chain mechanism.¹³ In the current study, cracking of \approx DPP to \approx PhH and indan (Fig. 1b) can be accommodated by either an ipso protonation path or a benzylic cation/hydride transfer chain path. Additional studies will be required to probe the involvement of these processes on the catalytic cracking of \approx DPP in dispersed solids.

It is interesting that the aluminosilicate employed in this study has a Si/Al atomic ratio of ca. 84, which indicates that a much smaller density of acidic sites is present than for typical amorphous aluminosilicate cracking catalysts whose corresponding ratio is 3-8.⁹ Furthermore, the substrate is a solid and the DPP moieties are subject to diffusional constraints as a result of surface attachment. Yet, the acid-catalyzed cracking of \approx DPP in this solid mixture is quite efficient. The small particle size of the fumed silica-alumina employed and the highly dispersed nature of the catalyst may be key factors in the observed efficiency of acid-catalyzed cracking of \approx DPP.

CONCLUSIONS

We have used surface-immobilized 1,3-diphenylpropane (\approx DPP) as a model system to investigate the potential role of acid-catalyzed cracking in dispersed solids. Initial results employing a small particle size, low aluminum content amorphous aluminosilicate demonstrate that efficient catalysis can occur in the dispersed solids at 310-375 °C. The product distribution is distinctly different from that obtained from a thermal free-radical process, and is consistent with the intermediacy of carbocations. The results indicate that significant interactions between the catalyst and substrate occur in the solid state. Hence, these results suggest that small particle size, highly dispersed catalysts may interact significantly with solid coal particles in the early stages of coal liquefaction/hydropyrolysis.

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Table 1. Effect of Dispersed Solids on Thermolysis of \approx DPP (0.532 mmol/g)

Diluent ^a	None	A	B	B	B	B
\approx DPP (mmol)	0.255	0.0692	0.0644	0.0675	0.0437	0.0413
Temp ($^{\circ}$ C)	375	375	375	375	345	310
Time (min)	60	60	60	10	10	10
\approx DPP Conversion(%) ^b	10.3	2.6	23.5	17.4	11.8	4.8
Products						
(mol/100 mol \approx DPP)						
PhCH ₃	4.45	1.26	0.27	0.13	0.06	c
\approx PhCH ₃ ^c	5.85	1.34	2.61 ^e	1.60 ^e	1.00 ^e	0.36 ^e
PhCH=CH ₂	5.85	1.28	0.18	0.09	c	c
\approx PhCH=CH ₂	4.38	1.36	c	c	c	c
PhC ₂ H ₅	c	c	1.79	1.25	0.65	0.20
\approx PhC ₂ H ₅ ^e	c	c	0.88	0.70	0.44	0.24
PhH	d	d	5.17	3.47	1.95	0.73
\approx PhH	d	d	15.13	11.07	8.07	3.21
Indan	d	d	16.24	12.76	9.17	3.70
\approx Indan ^f	d	d	0.87	1.15	0.84	0.36
Indene	d	d	2.57	1.42	0.87	0.54
PhC ₃ H ₇	d	d	0.76	0.48	0.21	c
PhCH=CHCH ₃	d	d	0.30	0.14	c	c

^aA=Aerosil 200 SiO₂; B=Aerosil MOX-170 SiO₂-1%Al₂O₃; wt diluent: \approx DPP=2.80.

^bMass balances \geq 95%.

^c<0.05.

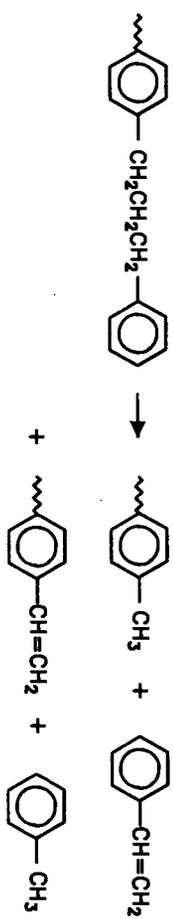
^dNot detected.

^eMixture of ortho-, meta-, and para- isomers in runs with silica-alumina.

^fMixture of two isomers.

Figure 1. Principal products from the reactions of surface-attached 1,3-diphenylpropane

(a) Thermolysis at 345–400 °C



(b) Acid-catalyzed cracking at 310–375 °C

