

NEW APPROACH TO IMMOBILIZATION OF COAL-MODEL COMPOUNDS ON SILICA USING A CALCIUM CARBOXYLATE LINKAGE

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INTRODUCTION

In an earlier report,¹ we described our efforts to study the hydrothermolysis of surface-immobilized coal model compounds by attaching 1-(4'-hydroxyphenyl)-2-phenylethane to the surface of fumed silica via a Si-OAr linkage using procedures developed by Buchanan, Poutsma and coworkers² and heating the resultant material (SIO-DPE) under D₂ pressure. These studies were complicated by the fact that phenolic compounds present in equilibrium with ether-linked materials react with thermolytically-produced radicals to form phenoxyl radicals which then react with D₂ to give DOAr compounds. These provide D for ring-deuteration via a silica-catalyzed process which is restricted to hydroxyl-substituted aromatic rings. It is believed that the free phenol present in SIO-DPE experiments is due to small amounts of water which is known to be generated continually through the formation of siloxane bonds as silica is heated. In simple thermolysis experiments carried out in vacuum,² any water produced is driven out of the reaction zone. In our experiments, however, the reaction proceeds under D₂ pressure (14 MPa) and reaction products are necessarily available for secondary processes.

Coincident with this process, the benzylic radicals produced under these conditions react with D₂ to form D atoms. The D atoms react both with gas-phase reaction products and surface-attached substrates. We found that much of the behavior of the surface-attached material was similar to that of free diphenylethane, DPE, under these conditions,³ particularly that the differences between thermolysis and hydrothermolysis were preserved. Also, the increased tendency to rearrangement and cyclization for surface-attached radicals was still observed under D₂. Because of the phenol-specific exchange process we could follow the D-atom-induced aromatic substitution only in the non-phenolic rings. We could also demonstrate that the D-atom induced part of H-D exchange is greater for gas-phase than for surface-bound materials.

Despite the successes noted, we sought to find a method for constructing links between silica and organic materials which might better survive hydroliquefaction conditions. Attachment of long-chain aliphatic carboxylic acids to silica through Mg⁺⁺ or Ca⁺⁺ ions is a patented method for silica flotation⁴ which we thought might be adapted to our purposes. This preprint is a preliminary report on the preparation, thermolysis and hydrothermolysis of materials believed to have the general structure, SiO⁻Ca⁺⁺O₂CAr.

EXPERIMENTAL

Preparation of Ca⁺⁺-Linked Arene Carboxylates. Aqueous Ca(OH)₂ (ca. 0.02 M) which had been prepared with deaerated, deionized water was mixed with sufficient fumed silica (Cab-O-Sil M5 Cabot Corporation) to provide a coverage of 0.35 to 0.50 mmoles/g. The aqueous slurry was filtered under an argon blanket and washed with deaerated deionized water. When the filter cake was partially dry, it was remixed with acetonitrile in the filter funnel and the solvent pulled through the filter. This process was repeated and the cake sucked dry under argon. The base-treated silica was then stirred with an acetonitrile

solution of the appropriate carboxylic acid and filtered. The resultant solid was stirred with additional acetonitrile and filtered. The acetonitrile washing was repeated and the coated silica dried in an oven at 110 °C. Evaporation of the combined acetonitrile washings showed that most of the acid was removed by the base-treated silica. In the case of 4-(2'-(4''-methylphenyl)ethyl)benzoic acid, the acid was not completely soluble in acetonitrile and it was necessary to add some methanol. Scanning electron microscopic studies on the DPECO₂-coated material indicated that with the 200 Å resolution of the equipment used, calcium was evenly distributed on the surface.

Synthesis of 4-(2'-Phenylethyl)benzoic Acid. A modified version of a literature procedure⁵ was used. Silver nitrate (2.62 g, 15.4 mmole) in 60 mL water was mixed with sodium hydroxide (1.25 g, 31.2 mmole) in 60 mL water. To this solution was added *trans-p*-stilbene carboxaldehyde, Aldrich Chemical Co. (2.00 g, 9.6 mmole). This was refluxed for 16 h. The reaction mixture was cooled to room temperature and neutralized with concentrated nitric acid. The resultant mixture was extracted with a solvent mixture of equal amounts of CH₂Cl₂ and ethyl acetate. The solvent was removed by rotary evaporation to give 2.11 g of product which was 92 % *trans-p*-stilbene carboxylic acid (86 %). Purification by base extraction and reacidification gave pale yellow crystals, mp 222-223 °C, ¹H NMR (CDCl₃) δ 8.10 (d, 2 H), 7.5 - 7.7 (m, 4 H), 7.1 - 7.4 (m, 5 H). This material (0.475 g, 2.12 mmole) was dissolved in a mixture of 40 mL CH₂Cl₂ and 20 mL methanol. Palladium (5 %) on carbon (200 mg) was added and the mixture shaken under 35 psi H₂ at 25 °C in a Parr apparatus for 24 h. The catalyst was removed by filtration and the solvent removed by rotary evaporation. The product was recrystallized from aqueous ethanol to give a first crop of 280 mg, 58 %, of the desired product, mp 148-150 °C. ¹H NMR (CDCl₃) δ 8.03 (d, 2 H), 7.1 - 7.3 (m, 7 H), 2.92 - 3.04 (m, 4 H). MS, 226, 91. Trimethylsilylation of this material and GC analysis showed it to be >99% pure.

Synthesis of 4-(2'-(4''-Methylphenyl)ethyl)benzoic Acid. This material was synthesized by a Wittig reaction following a literature procedure⁶ using α-bromo-*p*-xylene and 4-carboxybenzaldehyde producing a mixture of *cis*- and *trans*-4-methyl-4'-carboxystilbene which is hydrogenated using the procedure described above for stilbene carboxylic acid. This gives the desired product as white crystals, mp 201-202 °C. ¹H NMR (CDCl₃) δ 7.95 (d, 2 H), 7.1 - 7.16 (m, 4 H), 2.90 - 3.03 (m, 4 H), 2.28 (s, 3 H). Trimethylsilylation of this material and GC analysis showed it to be >99% pure.

General Procedure for Reactions. Hydrogenations of coated solids were carried out in glass tubes with capillary openings in a manner essentially identical to that described earlier¹ for SiO-Ar type materials. Volatile products were pumped out and collected in a liquid N₂ trap and materials remaining on the surface were recovered by hydrolysis of the silica and trimethylsilylation of the carboxylic acids obtained. Deuterium analysis was carried out by gas chromatography/mass spectrometry (GC/MS).

RESULTS AND DISCUSSION

Product distribution for the volatile products of the thermolysis of Ca⁺⁺-immobilized 4-(2'-phenylethyl)benzoate, SiO⁻ Ca⁺⁺ O₂CDPE, is given in Table I. The distribution of products in the residual solid is given in Table II.

Table I. Distribution^a of Volatile Products from Thermolysis of SiO⁻ Ca⁺⁺ O₂CDPE under D₂ and under N₂.

	Time(N ₂ or D ₂)			
	10 min (D ₂)	30 min (D ₂)	50 min (D ₂)	30 min (N ₂)
PhMe	<1%	2.8	5.7	1.1
PhEt	<1%	3.3	4.2	ca. 0.4
DPM	<1%	1.2	1.0	ca. 0.5
1,1-DPE	<1%	1.5	2.2	ca. 1
DPE	78.6	65.7	62.7	94.7
STB	2.6	2.8	2.4	2.3

^a Distribution is given as approximate weight % of total volatiles. The totals are less than

100 % due to the presence of an unidentified product which appears to be an oxidation product of **DPE**. Some benzene was produced in the reaction but analysis was unreliable in this set of runs. **DPM** = diphenylmethane, **STB** = stilbene.

Table II. Distribution^a of Materials Remaining on the Surface after Thermolysis of $\text{SiO}^+ \text{Ca}^{++} \text{O}_2 \text{CDPE}$ under D_2 and under N_2 .

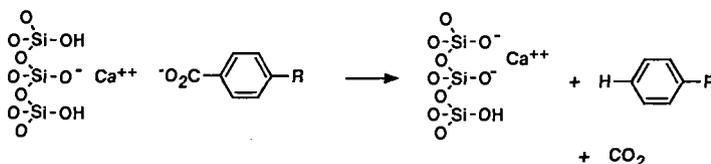
	Time(N_2 or D_2)			
	10 min (D_2)	30 min (D_2)	50 min (D_2)	30 min (N_2)
PhCO_2^-	1.1	1.4	1.3	0.7
MePhCO_2^-	1.4	3.1	4.2	1.7
EtPhCO_2^-	<0.2	0.5	0.7	<0.2
DPMCO_2^-	0.6	1.0	1.1	0.6
1,1-DPECO_2^-	1.8	3.8	5.7	2.7
DPECO_2^-	91.5	86.9	83.9	84.1
STBCO_2^-	3.3	2.5	0.4	3.1

^a Values given are approximate weight %s of materials recovered from hydrolysis of residual solids after trimethylsilylation.

It is clear from these data that the major volatile product of thermolysis, both under N_2 and under D_2 is **DPE**. This result contrasts with the thermolysis of **SiO-DPE** where **DPE** represents a relatively minor fraction of the volatile products (of the order of 10%). This suggests the possibility that the **DPE** might be arising by a decarboxylation process.

To determine whether the **DPE** formed in this reaction is the result of decarboxylation or recombination of benzyl radicals formed from fragmentation, we have also prepared 4-(2-(4'-methylphenyl)ethyl)benzoic acid, HO_2CDPEMe , and attached it to silica in the same manner to give $\text{SiO}^+ \text{Ca}^{++} \text{O}_2 \text{DPEMe}$. Thermolysis of $\text{SiO}^+ \text{Ca}^{++} \text{O}_2 \text{DPEMe}$ both in the presence and absence of D_2 gives 1-phenyl-2-(4'-methylphenyl)ethane, **DPEMe**, as the major volatile product. A small amount of 1,2-di(4'-methylphenyl)ethane was present, but this was formed in less than 10% of the amount of **DPEMe**. This clearly demonstrates that decarboxylation is a major reaction path, at least in the initial stages of the reaction. The fact that **DPE** remains the major product when $\text{SiO}^+ \text{Ca}^{++} \text{O}_2 \text{DPE}$ is subjected to thermolysis under N_2 suggests that protons rather than hydrogen atoms are involved in its production. A reasonable path is that shown in Scheme I wherein the silica surface (directly or indirectly) supplies a proton to the *ipso*-position of the attached substrate, releasing **DPE**. As this reaction proceeds, the surface should increase in basicity and, possibly, the release of **DPE** will decrease. The increase in other products relative to **DPE** supports this hypothesis.

Scheme I



The remainder of the products are analogous to those observed in the thermolysis and hydrothermolysis of **SiO-DPE**. Toluene, **PhMe**, results from thermolysis of the central bond in the **DPE** moiety to give benzyl radicals which react either with D_2 or with residual $-\text{CH}_2\text{CH}_2-$ groups to lead to $\text{PhCH}=\text{CHPh}$, stilbene (**STB**), or $^-\text{O}_2\text{CC}_6\text{H}_4\text{CH}=\text{CHPh}$, **STB-CO}_2^-. D atoms produced from the reaction $\text{R} \cdot + \text{D}_2 \rightarrow \text{RD} + \text{D} \cdot$ react to give "hydrocracking" products via $\text{D} \cdot + \text{Ar-R} \rightarrow \text{Ar-D} + \text{R} \cdot$ and also H/D exchange via $\text{D} \cdot + \text{Ar-H} \rightarrow \text{Ar-D} + \text{H} \cdot$. Compared to the **SiO-DPE** case, there is more hydrocracking**

Table III. Deuterium Distribution in Products from Thermolysis of $\text{Ca}^{++} \cdot \text{O}_2\text{CDPE}$ under D_2 at 420 °C.

Product (time - min)	d_0	d_1	d_2	d_3	d_4	d_5	d_6
PhMe (10)	76.0	23.0					
PhMe (30)	24.9	31.5	23.8	11.4	6.1	2.1	
PhMe (50)	18.6	26.6	29.3	8.1 ^a	10.5 ^a	6.9 ^a	
EtPh (10) → PhCH_2^+	44 58.1	56 33.8	8.1				
EtPh (30) → PhCH_2^+	12.8 29.9	24.1 32.8	21.8 20.8	15.7 10.2	11.7 4.4	8.8 1.6	5.0 0.3
EtPh (50) → PhCH_2^+	8.0 19.5	18.5 30.5	22.5 25.0	19.1 15.0	14.6 7.1	10.7 2.6	6.5 0.3
DPM (30)	18.1	20.5	20.0	15.9	10.6	6.6	3.8
DPM (50)	14.7	18.2	20.7	18.9	13.9	8.9	4.6
1,1-DPE (30)	13.8	14.6	26.5	24.8	16.1	7.9	4.2
1,1-DPE (50)	2.1	7.9	19.3	26.6	22.5	6.3	2.8
DPE (10) → PhCH_2^+	13.5 45.7	45.1 36.8	27.8 13.6	9.6 3.1	2.5 0.6	0.8 0.2	
DPE (30) → PhCH_2^+	5.8 26.4	16.8 31.9	27.9 24.6	24.6 12.1	14.7 3.7	6.5 0.9	2.6 0.2
DPE (50) → PhCH_2^+	3.2 17.9	8.6 25.1	20.1 23.0	26.2 15.4	21.7 6.4	12.4 1.7	5.4 0.3
PhCO₂⁻ (10)	43.1	30.2	19.5	6.2	0.9		
PhCO₂⁻ (30)	16.3	34.2	34.0	12.7	2.2	0.5	
PhCO₂⁻ (50)	9.1	27.1	41.7	18.6	3.6	0.9	
MePhCO₂⁻ (10)	44.6	34.3	14.0	1.8	1.7		
MePhCO₂⁻ (30)	12.9	32.1	32.4	15.5	4.9		
MePhCO₂⁻ (50)	7.2	22.3	34.9	24.1	8.8	2.2	0.5
EtPhCO₂⁻ (10)	41.5	33.8	15.2	6.1	3.4		
EtPhCO₂⁻ (30)	13.1	30.8	31.2	17.1	6.8	0.9	
EtPhCO₂⁻ (50)	4.4	20.4	32.4	26.0	12.5	4.2	
1,1-DPECO₂⁻ (10)	48.3	33.2	12.7	4.2	1.4		
1,1-DPECO₂⁻ (30)	15.7	30.8	31.1	16.3	6.1		
1,1-DPECO₂⁻ (50)	5.2	18.9	32.8	25.2	12.1	4.5	1.4
DPECO₂⁻ (10) → PhCH_2^+	49.5 87.3	35.0 11.3	11.9 1.0	2.7 0.8	0.6		
DPECO₂⁻ (30) → PhCH_2^+	12.8 65.1	30.2 27.9	32.2 5.9	17.0 0.8	5.6 0.2	1.6	0.4
DPECO₂⁻ (50) → PhCH_2^+	3.5 51.2	18.1 35.2	32.0 11.1	27.3 1.9	13.3 0.3	4.4 0.1	1.2

Notes for Table III: ^a Errors accumulate in calculation for toluene at high D content due to large P-1 fragment.

of this substrate and, most strikingly, a marked increase in the amount of rearrangement

of the surface-bound substrate in that 1-phenyl-1(4'carboxyphenyl)ethane, **1,1-DPECO₂H**, has become the major reaction product remaining on the surface. The tendency to increased rearrangement of surface-bound radicals has been discussed earlier.¹

For the runs carried out under D₂, the deuterium distribution of the major products is given in Table III. Many of the features of these data are similar to those noted for hydrothermolysis of **SiO-DPE**. Gas-phase products continue to undergo exchange after separation from the surface so that initially formed **PhMe** (10 min) contains 0.23 atom of D per molecule, more than present in the PhCH₂ part of surface-bound substrate, whereas after 30 min, the D content of **PhMe** averages 1.5 atoms of D per molecule while PhCH₂ in surface-bound substrate averages only 0.43 atoms. It is interesting that the PhCH₂ part of surface-bound **DPECO₂** appears to be protected from exchange relative to gas-phase molecules, showing 0.13, 0.43 and 0.65 atoms of D per molecule in the three runs. These contrast with values of 0.50, 1.32 and 1.69 in the PhCH₂ fragment from **PhEt** and 0.77, 1.38, and 1.53 in this fragment from **DPE**. Thus, PhCH₂ moieties on the surface appear to be less susceptible to D-atom attack by at least a factor of 3 compared with PhCH₂ parts of free molecules. In surface-bound **DPECO₂** exchange in the carboxy-substituted benzyl group exceeds that in the unsubstituted benzyl moiety by a factor of three to four. This could be due either to preference for D-atom attack on the carboxy-substituted ring or to some special mechanism for exchange of carboxy-substituted aromatics. We do not have sufficient evidence to distinguish these alternatives at present.

SUMMARY

A new method for surface attachment has been devised to attach arene carboxylic acids to fumed silica via a SiO⁻ Ca⁺⁺ O₂Ar linkage. This has been used to attach coal-model compounds such as **DPECO₂H** to the surface and the resultant **SiO⁻ Ca⁺⁺ O₂DPE** has been subjected to thermolysis and hydrothermolysis. Part of the material undergoes decarboxylation to give **DPE** and part reacts via the usual homolytic pathways. Radical rearrangement leads to the main surface-retained product and surface-attached molecules are partially protected from D-atom induced exchange. Exchange in carboxy-substituted rings is favored and mechanistic reasons for this are under investigation.

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