

THERMOLYSIS OF SUBSTITUTED ANISOLES

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INTRODUCTION

The possibility of using biomass as a chemical feedstock has in recent years attracted increasing interest. Lignin is one of the major components of biomass. It is produced in large amounts during wood pulping but the main part of it is simply burnt. There should, however, be some possibilities to use part of the lignin as raw material for more valuable products (1-3).

The first reaction step in any chemical conversion process of lignin is thermal rupture to smaller units (3, 4). Only the products thus formed are small enough to react with a heterogeneous catalyst to the ultimate products. This behavior corresponds to that found for coal. Thermal reactions of lignin as well as coal are usually very complicated. This makes the interpretation of experimental results from thermal reactions of lignin quite difficult though not impossible (5-7). Study of suitable lignin related model compounds can be of great use in the interpretation of the results. Application of the results of model compound studies on more complicated structures must, however, always be done with care since the reactions of macromolecular structures are not necessarily well represented by simple model compounds as has been noted in connection with coal (8).

Thermolysis of hydroxy, methoxy and methyl substituted anisoles in the presence of tetralin has earlier been studied by Bredenberg and Ceylan (9). Their results are, however, probably influenced by effects caused by the reactor walls. This paper considers the thermolysis of the guaiacyl structure of lignin by comparing the thermal reactions of different hydroxy and methoxyanisoles (and anisole) both neat and in the presence of tetralin at molar ratio 1:1 under conditions where wall effects have been minimized. Some comments about the kinetic parameters of the model compounds studied are also made though the experiments performed are insufficient for a strict kinetic analysis.

EXPERIMENTAL

All the model compounds used as well as tetralin were pure or analytical grade and they were used without further purification. Only the meta substituted compounds contained so much impurities (about 2.5 % by GC) that these had to be accounted for in the results.

The experiments were performed in 1 ml boron silicate glass ampoules (Duran 50) under argon atmosphere as described elsewhere (10). The same analytical procedures were also followed. The GC-MS analyses were needed only for the products from the experiments with meta compounds.

In addition to the thermolysis experiments some additional experiments were performed to test the effects of different kinds of materials as well as the possible wall effect on the thermolysis of hydroxyanisoles in the presence of tetralin at 638 K. The materials used for this purpose with all three hydroxyanisoles were sodium glass, AISI 304 and AISI 316 steels, molybdenum powder, and boron silicate glass. Coal ash and silicon carbide were tested only with *o*- and *p*-hydroxyanisole. The reaction time was 3.0 h for *ortho* and *para* compounds and 5.0 h for meta compound. The surface

area was approximately doubled in the experiments, except for the experiments with coal ash where the area was more than two hundred times the original. The results showed that sodium glass led to the formation of higher products with all hydroxyanisoles. Molybdenum and coal ash were found to enhance the conversion of the ortho and para compounds while there was no clear trend with the meta compound. No significant difference between the runs with plain boron silicate ampoules and those where boron silicate, silicon carbide or the aforementioned steels had been added were found. It should, however, be noted that molybdenum containing steel alloys have been reported to be activated in hydroliquefaction of coal when treated with pyrocatechol (11, 12).

RESULTS AND DISCUSSION

Table 1 summarizes the experiments performed. The results are summarized in Figures 1 and 2 which contain the conversions and the selectivities of the formation of the main products from each model compound. Formation of higher products and char is also indicated in Figures 1 and 2.

All hydroxyanisoles gave as the main primary products the correspondingly substituted dihydroxybenzenes and cresols (Figure 1). Neat *m*-hydroxyanisole showed also some formation of methyl-*m*-hydroxyanisoles but because of the low conversions as well as the content of impurities (about 0.7 % methyl-*m*-hydroxyanisoles by GC) these results are uncertain. Figure 2 shows that the *o*- and *p*-methoxyanisoles followed a reaction pattern of same type as the hydroxyanisoles while *m*-methoxyanisole showed a stronger trend than *m*-hydroxyanisole to the formation of ring methylated products with two oxygen atoms. The possible pathways for product formation will be discussed in detail in relation to the C-O bonds reacting.

The methyl C-O bond

The bond energy of the methyl C-O bond in a guaiacyl structure has been evaluated to be about 247 kJ/mol (3). It is clearly the weakest bond in *o*-hydroxyanisole (guaiacol). The results in Figures 1 and 2 also demonstrate that the majority of the main products from both hydroxy and methoxy-anisoles were formed by breaking of this bond.

Breaking of this bond in all hydroxyanisoles seemed to follow two parallel primary pathways. The formation of pyrocatechol from guaiacol has earlier been explained to take place by a free radical mechanism (13) or by a concerted mechanism (14). A concerted mechanism for the formation of the corresponding dihydroxybenzenes cannot be visualized for *m*- and *p*-hydroxyanisoles.

The question of a concerted versus a free radical mechanism has been widely discussed in the context of both biomass and coal liquefaction. Stein (15) has commented on the mechanistic possibilities of the thermal reactions of guaiacol by noting that there are under conditions of very low pressure pyrolysis where bimolecular reactions cannot occur, methyl radicals but little or no methane as a product. This would indicate a free radical reaction. The mechanism of guaiacol thermolysis is obviously more complicated under high concentration. The presence of water, which is formed during the reaction, has also been found to have a pronounced effect on the thermolysis of guaiacol (16). A combined free radical chain and concerted mechanism has recently been proposed for thermolysis of dibenzyl ether in the presence of tetralin (17).

Our results (Table 2) showed that the rate of decomposition of guaiacol was about one order of magnitude higher than that of any other model compound studied. The apparent first order activation energy found for guaiacol in the presence of tetralin (Table 3) was also unusually low which is in agreement with the values reported elsewhere (14). This

suggests that in addition to the homolytic mechanism an additional reaction mechanism, i.e. the concerted mechanism is also operating. It is in this connection important to note that o-methoxyanisole did not show any similar trend.

The formation of correspondingly substituted cresols from the hydroxyanisoles as well as the formation of correspondingly substituted cresols and methylanisoles from o- and p-methoxyanisoles was the second primary pathway of the methyl C-O bond cleavage. For the para compounds an intramolecular ipso-substitution seems to be the only reasonable explanation. For the ortho and meta compounds an intermolecular methylation is still possible though, especially for the meta compound hardly probable. For the ortho compounds there is, in addition, the possibility of an intramolecular methyl shift to the ortho position from the methoxyl group. Ceylan and Bredenberg (13) have presented an intramolecular rearrangement of guaiacol to o-cresol which takes place via an enolic form of the ortho hydroxyl. No significant interaction between the substituents in m-hydroxyanisole can be expected. Therefore the ipso-substitution requires some other mechanism. Anisole has been explained to react through a phenoxymethyl radical formed by methyl hydrogen abstraction to a benzyloxy radical via a spiranic oxiran intermediate under corresponding reaction conditions (10, 18). The primary products from a benzyloxy radical are, however, benzaldehyde and benzyl alcohol which in turn can then be reduced to toluene. There was no indication of this type of products in any GC or GC-MS analyses made of the thermolysis products of hydroxy and methoxyanisoles during the present work. It should, however, be noted that Kisilitsyn et al. (19) have found both o-hydroxybenzaldehyde and o-hydroxybenzyl alcohol among the products of short contact time pyrolysis of guaiacol at 773 K.

The results of the experiments with m-methoxyanisole (Figure 2) differed from those noted above. The cleavage of the methyl C-O bond to form m-hydroxyanisole corresponds

to the reaction of the other compounds studied. There was, however, no noticeable ipso-substitution of the methyl group despite of the greater proportion of ring methylated dihydroxy compounds. m-Hydroxyanisole also showed a similar trend. This is probably due to the ortho-para-activating effect of both hydroxyl and methoxyl groups. The meta compound has been found to give the greatest proportion of ring methylated products also in catalytic hydrodeoxygenation of hydroxyanisoles (20).

It is also interesting to note that the decomposition rate of neat m-methoxyanisole was roughly twice the decomposition rate of neat anisole (Table 2). This could be interpreted to mean that the methoxyl groups in m-methoxyanisole react fairly independently.

The aromatic C-O bond

The bond energy of the aromatic C-O bond of the methoxyl group in a guaiacyl structure has been evaluated to be about 356 kJ/mol, and of the hydroxyl group about 414 kJ/mol (3). For the corresponding homolytic bond scissions a high activation energy is hence required. This correlates well with the fact that guaiacylic model compounds have usually been found to give, under mild thermolysis conditions, only small amounts of products with one oxygen atom (6, 13, 14, 21).

Our results suggest that there was no significant direct scission of the aromatic C-O bonds in guaiacol (Figure 1). The formation of phenol takes place most probably via pyrocatechol. The results of the experiments with m- and p-hydroxyanisole are not as clear.

Anisole and aromatic hydrocarbons were found only in trace amounts in the hydroxyanisole series. The scission of the phenolic C-O bond has been suggested by Stein (15) to take place probably by an ionic mechanism. Tentative experiments

performed with the dihydroxybenzenes in the presence of tetralin gave almost exclusively phenol as a single ring aromatic product from pyrocatechol and hydroquinone whereas no phenol was found in experiments with resorcinol. These experiments also showed that higher products were formed from hydroquinone even in the presence of tetralin, a result which can also be seen in Figure 1.

The results of the methoxyanisole series (Figure 2) showed significant differences in the breaking of the aromatic C-O bonds in comparison with the hydroxyanisole series. In addition to the formation of phenol there was also significant formation of anisole from all three methoxyanisoles. The analyses made also indicated the presence of the products formed in the decomposition of anisole (10).

Anisole has earlier been reported to be formed from *o*-methoxyanisole (22). The formation of anisole from all three methoxyanisoles is not easily explained. It must take place by direct demethoxylation but the presence of a hydroxyl group seems to prevent it for reasons not known.

The overall kinetics

The decomposition rates of all the model compounds studied can be fitted into first order kinetics (Table 2) though the gross conversion include parallel reaction pathways. The apparent first order activation energies are shown in Table 3. These values are partly uncertain since in some cases they are based only on a few experiments at two temperatures (Table 1). Hence, only a few comments are made. The unusually low activation energy of guaiacol in the presence of tetralin has already been discussed. The results of neat guaiacol are too few for a proper analysis. Tables 2 and 3 also show that tetralin has, in addition to decreasing the reaction rates, some effect on the apparent activation energies. This is probably due to the quenching effect tetralin has on free radical chain reactions.

CONCLUSIONS

The main reaction in the thermolysis of all hydroxyanisoles is the breaking of the methyl C-O bond. Two reaction pathways can be distinguished, the first one leading to the formation of the correspondingly substituted dihydroxybenzenes, and the second one leading to the formation of the correspondingly substituted cresols. For guaiacol the former pathway takes partly place, in addition to a homolytic bond breaking, by a concerted mechanism. A concerted mechanism cannot, however, be visualized for *m*- and *p*-hydroxyanisole. The latter pathway is thought to take place via a spiranic oxiran intermediate. For guaiacol there is also the possibility of an intramolecular methyl shift to the ortho position from the methoxyl group. The formation of cresols via methyl-dihydroxybenzenes does not, however, seem to be very probable. Neat *m*-hydroxyanisole shows, in addition, some formation of methyl-*m*-hydroxyanisoles. Breaking of the aromatic C-O bond in the hydroxyanisoles occurs only to a minor extent under mild thermolysis conditions.

The *o*- and *p*-methoxyanisoles follow a reaction pattern of the same type as the hydroxyanisoles while *m*-methoxyanisole gives more ring methylated products with two oxygen atoms. There is, however, no indication of a concerted mechanism for *o*-methoxyanisole. The formation of anisole by direct demethoxylation is significant for all three methoxyanisoles.

The decomposition rate of all the model compounds studied is decreased by the presence of tetralin.

ACKNOWLEDGEMENTS

This work has been funded in part by grants from the Ministry of Education and Neste OY Foundation. The authors are grateful to Mrs. Eija Kinnunen and Mr. Timo Karinen for their contribution to the experimental part of this work.

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Table 1. Experimental data.

model compound	reaction temperature (K)	reaction time (h)
<i>o</i> -OH-anisole, neat	623	0.6; 1.0; (2.0)
	648	0.5; 1.0; 2.0; 3.0
	673	(1.0; 2.0)
-with tetralin	623	0.75; 1.0; 2.0; 3.0; 4.0
	648	0.5; 0.5; 1.0; 2.0; 2.0; 3.0; 4.0; 4.0
<i>m</i> -OH-anisole, neat	623	2.0; 3.0; 4.0
	648	1.0; 1.0; 2.0; 2.0; 3.0; 4.0
	673	1.0; 1.0; 2.0; 4.0; 4.0
-with tetralin	648	0.5; 1.0; 2.0; 3.0; 4.0; 4.0
	673	0.5; 1.0; 2.0; 2.0; 3.0; 4.0
<i>p</i> -OH-anisole, neat	648	1.0; 2.0; 4.0
	673	0.5; 2.0
-with tetralin	648	0.5; 1.0; 2.0; 2.0; 3.0; 4.0; 4.0
	673	0.5; 1.0; 2.0; 2.0; 3.0; 4.0
<i>o</i> -OCH ₃ -anisole, neat	648	1.0; 2.0; 4.0
	673	0.25; 0.5; 2.0
-with tetralin	623	1.33; 2.0; 4.0; 5.0; 7.0
	648	1.0; 1.0; 2.0; 3.0; 4.0
	673	0.5; 1.0; 1.0; 1.5; 2.0
<i>m</i> -OCH ₃ -anisole, neat	623	2.0; 3.0; 4.0
	648	1.0; 1.0; 2.0; 4.0
	673	1.0; 2.0; 2.0; 4.0
-with tetralin	648	1.0; 2.0; 2.0; 3.0; 4.0
	673	0.5; 1.0; 1.5; 2.0; 2.0
<i>p</i> -OCH ₃ -anisole, neat	648	1.0; 2.0; 4.0
	673	0.25; 0.5; 2.0
-with tetralin	623	1.33; 2.0; 4.0; 5.0; 7.0
	648	1.0; 1.0; 2.0; 3.0; 4.0
	673	0.5; 1.0; 1.0; 1.5; 2.0

-experiments in parentheses are not used for kinetic parameters.

Table 2. The apparent first order rate coefficients of the model compounds.

model compound	623 K		648 K		673 K	
	$10^5 k$ (1/s)	r	$10^5 k$ (1/s)	r	$10^5 k$ (1/s)	r
-neat						
anisole(10)						
o-OH	12.5 \pm 1.0	0.997	0.76 \pm 0.13	0.959	3.91 \pm 0.59	0.957
m-OH	0.43 \pm 0.02	0.998	1.34 \pm 0.11	0.983	23.7 \pm 2.6	0.977
p-OH			5.36 \pm 0.83	0.977	54.0 \pm 9.4	0.985
o-OCH ₃			7.41 \pm 1.05	0.981	70.8 \pm 14.2	0.962
m-OCH ₃	0.51 \pm 0.13	0.945	1.33 \pm 0.16	0.979	8.09 \pm 1.67	0.942
p-OCH ₃			6.84 \pm 0.75	0.988	57.0 \pm 14.4	0.942
-with tetralin						
anisole(10)						
o-OH	6.58 \pm 0.39	0.993	0.31 \pm 0.04	0.967	2.09 \pm 0.16	0.987
m-OH			23.0 \pm 1.4	0.987		
p-OH			0.48 \pm 0.11	0.897	1.93 \pm 0.14	0.986
o-OCH ₃	1.52 \pm 0.11	0.989	2.50 \pm 0.16	0.988	18.5 \pm 1.0	0.992
m-OCH ₃			8.01 \pm 0.73	0.984	45.7 \pm 2.4	0.995
p-OCH ₃	1.02 \pm 0.12	0.975	1.00 \pm 0.19	0.932	4.58 \pm 0.20	0.996
			5.82 \pm 0.54	0.983	30.3 \pm 0.4	1.000

Table 3. The apparent first order Arrhenius parameters of the model compounds.

model compound	E_A (kJ/mol)	$\log_{10} A$ (1/s)
-neat		
anisole(10)		
o-OH	237 \pm 46	14.0 \pm 3.7
m-OH	143 \pm 20	8.1 \pm 1.7
p-OH	277 \pm 11	17.8 \pm 0.9
o-OCH ₃	335 \pm 49	22.7 \pm 3.9
m-OCH ₃	327 \pm 51	22.3 \pm 4.1
p-OCH ₃	192 \pm 31	10.7 \pm 2.5
	308 \pm 57	20.6 \pm 4.6
-with tetralin		
anisole(10)		
o-OH	276 \pm 30	16.8 \pm 2.3
m-OH	168 \pm 16	9.9 \pm 1.3
p-OH	201 \pm 40	10.9 \pm 3.1
o-OCH ₃	290 \pm 17	18.8 \pm 1.4
m-OCH ₃	237 \pm 9	15.0 \pm 0.7
p-OCH ₃	221 \pm 32	12.8 \pm 2.5
	237 \pm 9	14.8 \pm 0.6

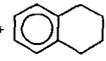
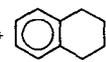
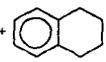
 <p>623 K, 0.6-2.0 h X = 25.8-40.8 % 648 K, 0.5-3.0 h X = 52.3-98.0 % 673 K, 1.0-2.0 h X = 99+ %</p>	<p>HIGHER, 623 K- CHAR, 648 K-</p>      <p>S (%): 14.7-15.8 4.3-6.6 2.7-3.1 1.4-1.6 1.0-1.3 S (%): 7.1-18.2 1.2-5.2 3.0-4.1 0.6-1.5 0.5-1.1 S (%): 4.4-8.5 1.0-1.6 6.5-8.8 0.4-0.6 0.4-0.6</p>
<p>+</p>  <p>623 K, 0.75-4.0 h X = 14.4-60.0 % 648 K, 0.5-4.0 h X = 25.1-96.8 %</p>	     <p>S (%): 71.7-82.0 2.4-7.7 2.7-4.9 6.0-8.1 6.0-7.0 S (%): 64.1-83.6 3.6-10.3 2.0-14.3 4.4-7.2 3.8-5.2</p>
 <p>(97.5%) 623 K, 2.0-4.0 h X = 3.4-6.1 % 648 K, 1.0-4.0 h X = 3.6-17.5 % 673 K, 1.0-4.0 h X = 41.7-97.5 %</p>	<p>HIGHER, 648 K- CHAR, 673 K-</p>      <p>S (%): 34.6-44.9 6.6-12.4 5.9-7.3 27.5-30.2 3.0-5.1 S (%): 42.7-67.1 2.8-5.1 1.3-13.4 17.7-27.9 2.5-5.2 S (%): 0.7-23.1 1.8-5.0 0.3-1.5 0.3-6.0 0.3-2.0</p>
<p>+</p>  <p>648 K, 0.5-4.0 h X = 0-8.4 % 673 K, 0.5-4.0 h X = 3.3-24.7 %</p>	     <p>S (%): 24.7-64.2 - - - 4.9-14.7 S (%): 56.7-86.6 8.5-16.3 - - 10.1-15.4</p>
 <p>648 K, OH 1-4 h X = 26.3-54.7 % 673 K, 0.5-2.0 h X = 81.0-98.3 %</p>	<p>HIGHER, 648 K- CHAR, 673 K-</p>      <p>S (%): 26.6-27.9 8.4-10.6 4.0-5.9 1.7-2.7 S (%): 5.8-24.3 4.4-7.2 7.1-8.3 0.8-2.1</p>
<p>+</p>  <p>648 K, 0.5-4.0 h X = 4.0-31.1 % 673 K, 0.5-4.0 h X = 26.4-93.7 %</p>	<p>HIGHER, 673 K-</p>      <p>S (%): 63.4-82.2 8.4-12.1 1.4-2.4 8.2-9.4 S (%): 30.7-78.5 10.7-12.2 2.1-3.6 5.3-7.2</p>

Figure 1. Main products from the experiments with hydroxy-anisoles.

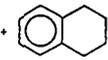
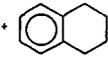
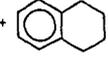
 648 K, 1.0-4.0 h X = 36.5-67.1 % 673 K, 0.25-2.0 h X = 84.7-99.7 %	CHAR, 648 K-      
	S (%) : 14.0-18.8 1.9-5.4 3.1-4.9 0.6-3.4 5.6-7.5 9.8-11.8 S (%) : 0.2-7.2 4.7-11.2 4.0-4.5 4.1-6.6 0.6-2.6 4.6-9.1
 623 K, 1.33-7.0 h X = 5.7-30.5 % 648 K, 1.0-4.0 h X = 17.2-69.8 % 673 K, 0.5-2.0 h X = 55.3-96.3 %	     
	S (%) : 34.7-63.8 10.4-22.8 2.3-8.1 7.4-15.4 1.6-4.5 5.4-15.0 S (%) : 13.7-55.8 6.3-47.0 2.8-7.3 0.7-1.7 9.5-14.4 4.6-7.9 S (%) : 2.0-19.5 46.3-58.3 2.5-6.9 1.3-4.0 8.3-11.4 4.9-9.3
 (97.5%) 623 K, 2.0-4.0 h X = 5.8-7.2 % 648 K, 1.0-4.0 h X = 5.6-17.8 % 673 K, 1.0-4.0 h X = 41.4-70.2 %	HIGHER, 673 K-     
	S (%) : 26.0-32.2 30.2-34.8 2.4-7.4 - 9.3-11.6 S (%) : 34.9-39.6 22.7-32.2 4.8-8.2 - 11.5-16.6 S (%) : 16.6-29.6 1.9-11.4 2.9-5.7 1.3-4.0 17.8-20.5
 648 K, 1.0-4.0 h X = 3.5-14.6 % 673 K, 0.5-2.0 h X = 10.9-28.9 %	    
	S (%) : 36.7-58.9 12.8-21.0 12.1-14.7 2.7-5.3 8.5-23.2 S (%) : 44.2-55.1 9.4-15.6 6.4-11.9 1.8-3.8 14.6-21.7
 648 K, 1.0-4.0 h X = 26.7-62.9 % 673 K, 0.25-2.0 h X = 87.1-99.2 %	HIGHER, 648 K- CHAR, 673 K-      
	S (%) : 16.1-23.0 0.5-0.6 0.8-1.5 0.3-0.6 8.8-10.1 10.8-14.6 S (%) : 3.3-15.4 4.6-4.8 2.3-5.1 2.5-5.8 2.9-6.1 6.6-15.8
 623 K, 1.33-7.0 h X = 3.1-21.2 % 648 K, 1.0-4.0 h X = 13.7-58.6 % 673 K, 0.5-2.0 h X = 43.7-88.9 %	     
	S (%) : 61.7-73.1 2.2-3.4 (2.0) 6.0-10.9 4.2-6.7 8.8-11.2 S (%) : 57.7-68.4 2.1-10.6 1.0-3.9 0.8-1.7 9.0-11.5 4.2-9.7 S (%) : 40.1-66.1 7.2-26.0 1.7-7.1 1.2-1.6 9.3-9.8 8.0-10.8

Figure 2. Main products from the experiments with methoxy-anisoles.