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"Catalysis and Co-catalysis of Bond Cleavages in Coal and Coal Analogs"

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Research Progress

9-Phenylthioanthracene (9-PTA) was chosen as an appropriate substrate to test the hypothesis that reductive cleavage of bonds to aromatic rings caused by heating in hydrogen donor solvents, such as tetralin, may be catalyzed by electron donating agents in the absence of hydrogen bonding or acidic reagents.

9-PTA was prepared according to literature procedures in two ways: by reaction of sodium thiophenoxide with 9-bromoanthracene and by acid catalyzed exchange of thiophenol with 9-methoxyanthracene. Both procedures required use of multiple crystallizations to yield pure 9-PTA, and gave low yields of the purified product.

In order to carry out analyses of product mixtures, several potential internal standards for vpc analysis were examined. Eicosane was chosen as the most useful standard, since vpc retention time did not coincide with that of the starting material or any of the reaction products. VPC analyses were carried out on a 0.5 meter, 1% OV101 on chromosorb W column. During analyses the temperature was kept at 170° for 3 min., then raised to 180° for an additional 3 min., and then rapidly raised to 250° for the remainder of the analysis. Under these conditions, anthracene had a retention time of ca. 2.4 min., eicosane of ca. 4.8 min., and 9-PTA of 8.0 min.

Ca. 0.02 M solutions of 9-PTA in tetralin (purified by chromatography on neutral alumina) were heated in glass ampoules.

It was observed that decomposition of 9-PTA occurs on heating at temperatures as low as 250°C, even in the absence of additives or catalysts. Reductive cleavage (measured by yields of anthracene), however, was invariably a minor process. Two major products, obtained at retention times of ca. 6.5 and

9.0 min., respectively, were observed in all runs. However, these products were obtained in rather variable yields, with an increase in the yield of one product often being accompanied by a decrease in the yield of the other. The nature of the products in unknown. GC-MS analysis is awaited.

Addition of 2,6-xylenol, 1,3,5-trimethoxybenzene, or 1,4-dimethoxynaphthalene to the thermolysis mixtures appeared to offer, at best, only slight increases in reaction rates, and little change in product compositions. The results are summarized in the Table.

TABLE

Reaction of 0.02 M 9-Phenylthioanthracene in Tetralin

Temp. (°C)	Reaction Time (hrs)	Additive (Molarity)	Fraction Unreacted 9-PTA	% Yield anthracene[3]	Unidentified Products (ratio + peak areas to initial area of 9-PTA) Product A[1]	Product B[2]
250	18	---	0.67	6.7	0.17	0.18
300	5	---	0.57	9.4	0.59	0.09
300	5	---	0.61	6.9	0.31	0.21
300	5	---	0.58	10.1	0.21	0.23
300	5	2,6-xylenol (0.15)	0.53	10.7	0.19	0.25
300	5	"	0.54	9.4	0.34	0.19
300	5	1,3,5-trimethoxy-benzene (0.18)	0.55	8.9	0.21	0.29
300	5	"	0.47	11.3	0.34	0.21
300	5	2,4-dimethoxyna-phthalene (0.15)	0.49	9.4	0.48	0.17
300	5	"	0.55	10.7	0.27	0.28
350	5	---	0.12	22.4	0.57	0.48
350	5	---	0.17	20.9	0.71	0.31
350	2	---	0.43	14.7	0.43	0.24
350	2	---	0.46	15.3	0.17	0.49
350	2	2,6-xylenol (0.16)	0.39	15.1	0.49	0.29
350	2	"	0.44	12.2	0.31	0.34
350	2	1,3,5-trimethoxy-benzene (0.15)	0.42	14.7	0.50	0.27
350	2	"	0.49	13.3	0.30	0.41
400	0.5	---	0.29	18.4	0.40	0.31

1. Retention time = 6.5 min. 2. Retention time = 9. 0 3. Based on starting quantity of 9-PTA.

END

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