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

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PRINCIPAL INVESTIGATOR:

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RESEARCH PROGRESS:

Our attempts to confirm the report by Yao and Kamiya (*Bull. Chem. Soc. Japan*, 1979, 52, 492) that quinoline catalyzes the transfer hydrogenolysis of di-2-naphthyl ether (DNE) in tetralin at 450°C were unsuccessful. As is shown in the Table, neither quinoline nor pyridine, even when present in large excess, exhibited any catalytic effects in increasing the rate of disappearance of DNE. Furthermore, addition of either quinoline or pyridine actually *decreased* the effect of added phenol on the rates of disappearance of DNE. Studies employing di-1-naphthyl sulfide (DNS) as the substrate similarly showed no evidence that either quinoline or pyridine had catalytic properties by themselves, and resulted in almost total disappearance of rate acceleration by phenol.

It seems probable that the basicities of the amines reduced the effects of hydrogen bonding of phenol to DNE or DNS in the transition states for transfer hydrogenolysis, and thereby vitiated any possible effects of electron transfer from the amines to the substrates.

In continuation of our investigation of the thermal fragmentations of 1,1-dibenzyl 1,4-dihydronaphthalenes to 1-benzyl naphthalenes and toluenes (eq. 1) we synthesized olefins 1b and 1c

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by the process previously employed to prepare **1a**. Kinetic studies of the decompositions of **1a** and **1b**, followed by ^1H NMR analysis, showed that rates were variable. Addition of free radical chain inhibitors, including 2,6-di-*t*-butylphenol, galvinoxyl, and (most effective) diphenylamine resulted in decreases in the rates of fragmentation of the alkenes, indicating that radical chain processes (eq. 2) accounted for at least part of the fragmentation processes. However, even addition of very large

amounts of diphenylamine did not completely suppress the decompositions. Residual fragmentation processes occurred in each case, and the rates of those processes were independent of inhibitor concentration (see Charts I-III). The half lives for disappearance of **1a**, **1b**, and **1c**, respectively, in the presence of ca. 30-50 mol % of diphenylamine at 150°C, were approximately 3 hours, 2 hours, and 6 hours, respectively. Thus, the rates of fragmentation follow an order paralleling the relative bond energies of the carbon-carbon bonds being cleaved in each reaction.

To determine whether the residual fragmentation reactions are due to free radical processes continuing even in the presence of large amounts of inhibitor, or whether a concerted fragmentation process remains after all free radical chains are inhibited, the deuterated olefin **1b-d** was synthesized. Thermolysis of a mixture of the deuterated alkene and **1c** in the presence of diphenylamine inhibitor has been carried out. Mass spectroscopic analysis of the resulting mixture of *p*-xylene and *p*-chlorotoluene is awaited.

TABLE
TRANSFER HYDROGENOLYSIS IN TETRALIN AT 450°C IN STAINLESS STEEL REACTORS

	Substrate ^a	No. of Runs	Catalyst (mole/mole) ^b	Reaction Time (hrs)	% Disappearance of Substrate
1)	E	2	Quinoline (14.7)	5	4.0 ± 2.1
2)	E	2	Pyridine (12.9)	5	3.2 ± 1.6
3)	E	2	Quinoline (7.4)	5	8.6 ± 2.7
			Phenol (7.1)		
4)	E	1	Quinoline (8.2)	5	10.1
			Phenol (15.2)		
5)	E	1	Pyridine (6.5)	5	7.7 ± 0.9
			Phenol (7.1)		
6)	E	2	N,N-Dimethylaniline (14.0)	5	2.7 ± 0.9
7)	E	1	Aniline (16.1)	5	4.1
8)	S	2	Quinoline (15.4)	2	12.0 ± 4.0
9)	S	2	Quinoline (7.7)	2	12.7 ± 1.2
			Phenol (7.1)		
10)	S	2	Pyridine (9.4)	2	10.0 ± 2.1
			Phenol (7.1)		

a) E = Di-2-naphthyl ether, S = Di-1-naphthyl sulfide.

b) mols catalyst/mols substrate.

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CHART I. Effects of Diphenylamine on Fragmentation of 1,1-Dibenzyl-1,4-dihydronaphthalene at 150°C.

CHART II. Effect of Diphenylamine on Rate of Fragmentation of 1,1-Di-p-tolyl-1,4-dihydronaphthalene at 150°C.

CHART III. Fragmentation of 1,1-Di-(4-chlorobenzyl)-1,4-dihydronaphthalene at 150°C.

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