DoE/PC/902

DOE/PC/90298--T11

DE93 008099

Quarterly Report: August 1, 1992 - October 31, 1992

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

DOE Grant #90PC90298

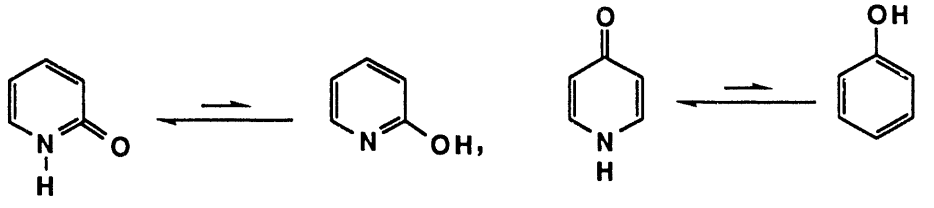
DE-FG22-90PC90298

PRINCIPAL INVESTIGATOR:

Bernard Miller, Professor of Chemistry, University of Massachusetts, Amherst, MA 01003.

RESEARCH PROGRESS:

Our last report demonstrated that 2-aminophenol and 4-aminophenol were exceptionally effective catalysts for transfer hydrogenolyses of dinaphthyl ether and dinaphthyl sulfide. We have therefore investigated the catalytic efficiency of 2-pyridone and 4-pyridone, the tautomers of 2-hydroxy and 4-hydroxypyridine.



As can be seen in the Table (entries 1 and 2) neither compound appeared to be a particularly effective catalyst for hydrogenolysis of di-2-naphthyl ether (one) under the conditions usually employed (5 hrs at 450°C). However, a comparison of the effectiveness of 2-pyridone and 2-aminophenol at shorter reaction times showed that 2-pyridone was as effective as 2-aminophenol if the reaction time were reduced to one hour. At longer reaction times, the effectiveness of 2-pyridone dropped sharply, suggesting that the catalyst is destroyed under the reaction conditions.

We previously reported that reaction of compound I with bromine in carbon tetrachloride solution yielded primarily a rearrangement product, with the cyclization product, II, a minor component. We have now discovered that if the reaction is carried out in acetonitrile solution only the

pure rearrangement product is obtained in essentially quantiative yield. The reason for this interesting solvent effect is not yet understood.

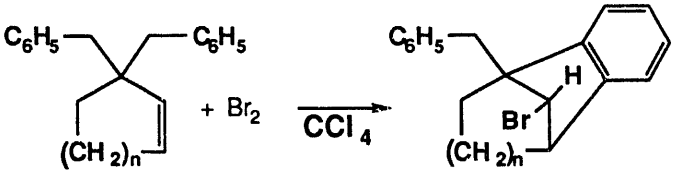
TABLE

TRANSFER HYDROGENOLYSIS OF DI-2-NAPHTHYL ETHER IN TETRALIN AT 450°C IN STAINLESS STEEL REACTORS

	No. of Runs	Catalyst (mole/mole)[a]	Reaction Time (hrs)	% Disappearance of DNE
1	2	2-Pyridone (14.6)	5.0	12.2 ± 1.1
2	2	4-Pyridone (13.9)	5.0	10.9 ± 1.6
3	1	2-Pyridone (14.6)	3.0	10.4
4	1	2-Aminophenol (13.6)	3.0	14.2
5	1	2-Pyridone (14.6)	1.1	7.2
6	1	2-Aminophenol (13.6)	1.1	6.1
7	1	2-Pyridone (14.2)	8.4	14.5
8	1	2-Aminophenol (13.6)	8.4	32.0
9	1	2-Pyridone (14.2)	22.5	19.1
10	1	2-Aminophenol (13.6)	22.5	40.5

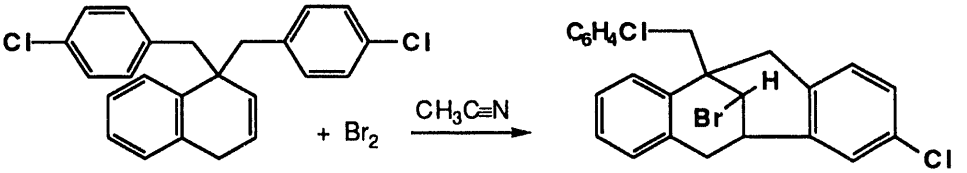
a. Moles catalyst/moles DNE.

We have observed that the novel cyclization reaction proceeds with cyclohexene and cyclopentenes as well as with dihydronaphthalene derivatives:



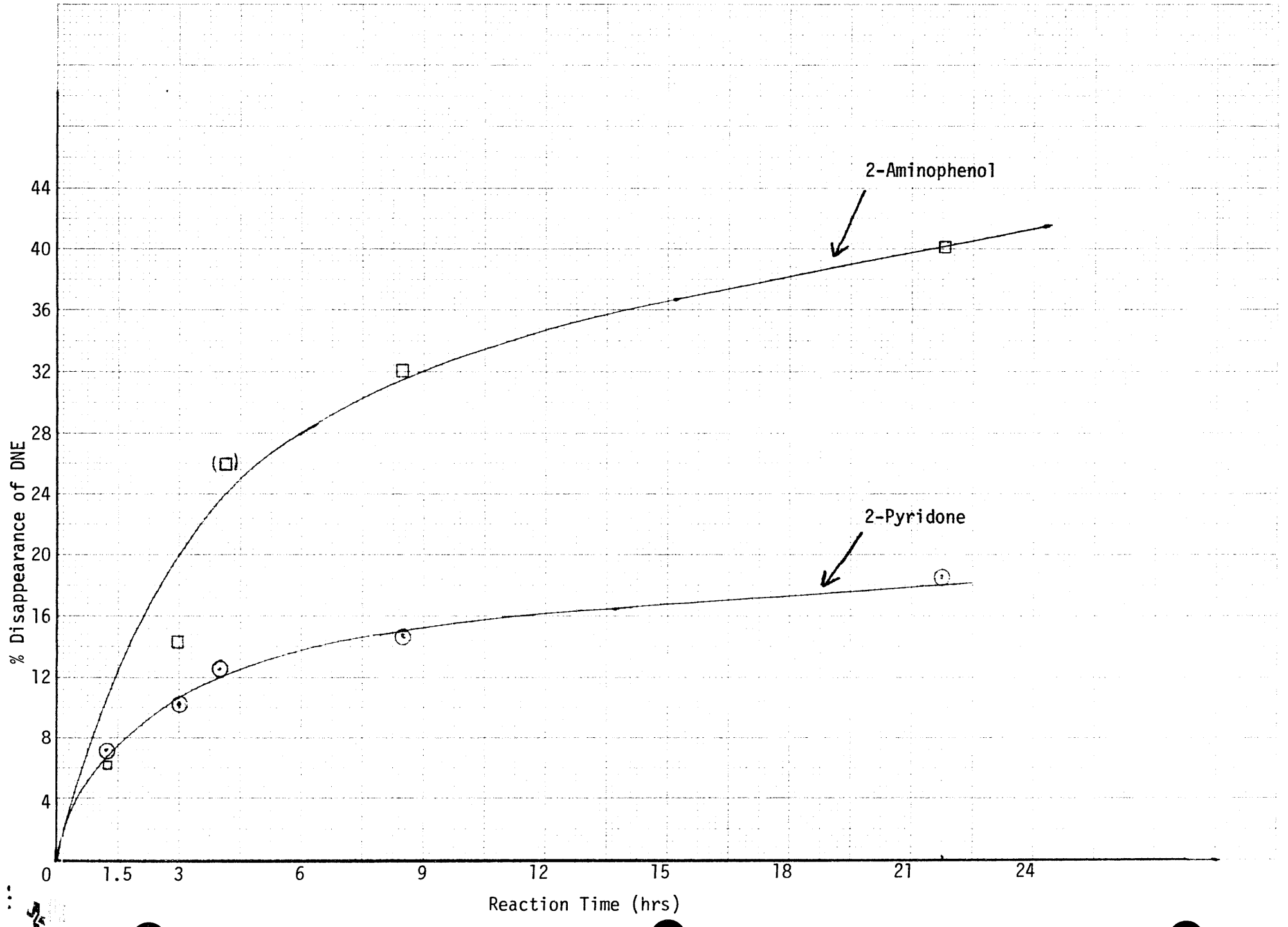
n = 1, 2

A manuscript describing this aspect of our work is in preparation.



I II

DISCLAIMER


2-Aminophenol
2-Pyridone
% Disappearance of DNE
Reaction Time (hrs)
0
1.5
3
6
9
12
15
18
21
24
4
8
12
16
20
24
28
32
36
40
44

END

DATE
FILMED
2/19/93