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MASTER

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PROJECT TITLE: Desulfurization with Transition Metal Catalysts
(Contract No.) DE-AC0179ET14879

QUARTERLY SUMMARY

OBJECTIVES: The overall objective of this research is to develop desulfurizing transition metal catalysts, which are active in homogeneous media at moderate temperatures and pressures for the purification of coal-derived fuels and chemicals. To this end, the mechanism of action is being examined whereby newly identified nickel(0) complexes desulfurize organosulfur compounds in solution at 65-70°C. The sulfur compounds under investigation are typical of those commonly encountered in coal-derived liquids and solids, such as thiophenes, sulfides and mercaptans.

WORK: During the second quarter of this two-year contract the following studies on the homogeneous, stoichiometric desulfurizing agent, bis(1,5-cyclooctadiene) nickel(0) [(COD)$_2$Ni], were continued: a) activation of the agent by means of added mono-, bi- and tri-dentate amines, either of the tertiary or primary amine type; b) labeling studies designed to reveal the source of the hydrogen that replaces the sulfur in the desulfurization of dibenzothiophene; c) comparison of the desulfurizing activity of (COD)$_2$Ni, both in the presence and in the absence of lithium aluminum hydride; and d) testing for the role of any biphenylene intermediate in these desulfurizations.

ACHIEVEMENTS: The following results have been obtained: a) the efficiency of added amine in promoting the desulfurization of dibenzothiophene by (COD)$_2$Ni decreases in the order, bipyridyl >> 4-dimethylaminopyridine >1,10-phenanthroline ∿ 1,2-diamino=ethane ∿ pyridine ∿ hexamethylphosphorus triamide >tetramethylethylenediamine ∿ 1,8-bis (dimethylamino) naphthalene ∿ N,N'-dimethylpiperazine; b) the desulfurization of dibenzothiophene, followed by treatment with O-deuterio=acetic acid gave dideuteriobiphenyl (42%), monodeuteriobiphenyl (28%) and biphenyl (29%), showing that ca. 70% of the desulfurized product retained carbon-nickel bonds until protolysis; c) the combination of (COD)$_2$Ni-bipyridyl with LiAlH$_4$ was shown to be a more efficient desulfurizing agent than (COD)$_2$Ni-bipyridyl alone; and d) with the synthesis of 2,8-dimethyldibenzothiophene the role of a biphenylene intermediate in the desulfurization mechanism can now be tested.

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QUARTERLY TECHNICAL PROGRESS REPORT

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CONTRACT NO.: DE-AC01-79ET14879

PERIOD OF PERFORMANCE: 12/28/79 - 3/28/80

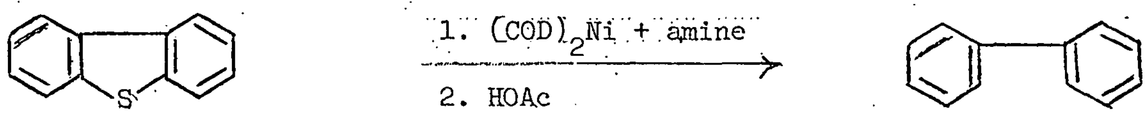
OBJECTIVE: The overall objective of this research is to develop desulfurizing transition metal catalysts, which are active in homogeneous media at moderate temperatures and pressures, for the purification of coal-derived fuels and chemicals. To this end, the mechanism of action is being examined whereby newly identified nickel(0) complexes desulfurize organosulfur compounds in solution at 65-70°C. The sulfur compounds under investigation are typical of those commonly encountered in coal-derived liquids and solids, such as thiophenes, sulfides and mercaptans.

PRESENT WORK AND ACCOMPLISHMENTS: During this second quarter, the research has concentrated on the following studies: a) activation of the homogeneous desulfurating agent, bis(1,5-cyclooctadiene) nickel(0) [$(COD)_2Ni$], by amines; b) labeling studies designed to identify the source of the hydrogen that replaces the sulfur in the desulfurization of dibenzothiophene; c) comparison of the activity of $(COD)_2Ni$ when lithium aluminum hydride is included; and d) testing for the presence of biphenylene intermediates in these desulfurizations.

a. Activation by Amines. Continuing studies of amine activation have added to our understanding of how structure influences reactivity. Further work has revealed one error in our previous results: our previous report that N,N,N',N'-tetramethylethylenediamine gave the greatest activation proved to be irreproducible. The revised table of amine activities, including several new amines, is given in Table I. The yield of biphenyl obtained from dibenzothiopene and two equivalents of a 1:1 mixture of $(COD)_2Ni$ and the amine is indicated.

TABLE I

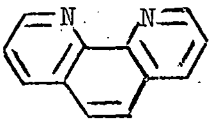
Desulfurization of Dibenzothiophene by $(COD)_2Ni$



Amine	Yield of Biphenyl (%)
Bipyripyl	45%
4-Dimethylaminopyridine	21
Ethylenediamine	17
1,10-Phenanthroline	16
Pyridine	14
Hexamethylphosphorus triamide	14
N,N,N',N'-Tetramethylethylenediamine	8
1,8-Bis(dimethylamino) naphthalene	7
N,N'-Dimethylpiperazine	4

Conditions: 55°C in THF with 2 equiv. $(COD)_2Ni$.

It is noteworthy that bipyridyl is the most effective amine, significantly superior to 1,10-phenanthroline. Since phenanthroline has a rigid planar structure (1), compared with bipyridyl (2), steric factors should be less with 1. One might have expected this lessened steric factor to make 1 a better ligand for nickel. Possibly, however, the increased back-bonding from nickel complexed with 1 causes the nickel to transfer electrons to the organosulfur substrate less readily.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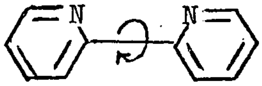
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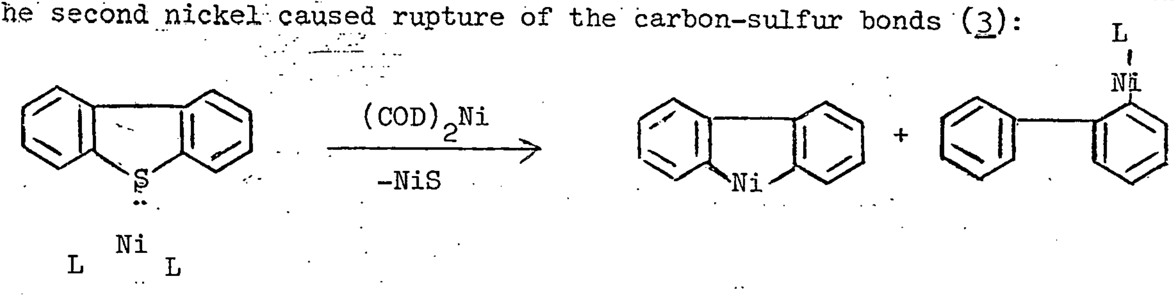
b. Labeling Studies. Since our previous studies have shown that efficient desulfurization requires two equivalents each of $(COD)_2Ni$ and the amine, this indicated that one nickel was required for coordination at the sulfur and that the second nickel caused rupture of the carbon-sulfur bonds (3):



3 4 5

In order to learn whether nickel-containing precursors (4 and 5) were present prior to hydrolytic work-up, such a desulfurization with $(COD)_2Ni$ and bipyridyl was worked up with CH_3COOD. If either 4 or 5 were present, then deuterated biphenyl should be isolated. Indeed, mass spectrometric analysis of the isolated biphenyl showed it to consist of 42% of dideuterated (from 4), 28% of monodeuterated (from 5) and 29% of undeuterated biphenyl. Thus, ca. 45%

of the biphenyl's hydrogens were acquired prior to hydrolysis, presumably from the solvent, tetrahydrofuran.

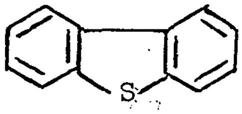
c. Effect of Lithium Aluminum Hydride. We have examined the influence of added amine on the desulfurizing action of the combination, $(COD)_2Ni$ and $LiAlH_4$. Given in Table II are the yields of biphenyl from dibenzothiophene.

TABLE II

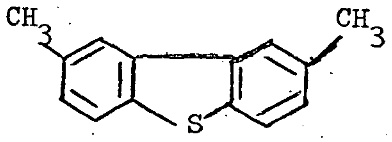
Desulfurization of Dibenzothiophene by $(COD)_2Ni + LiAlH_4$

Amine	Yield of Biphenyl (%)
Bipyridyl	93
Ethylenediamine	91
Hexamethylphosphorus triamide	86
N,N,N',N'-Tetramethylethylenediamine	79
Pyridine	75
N,N'-Dimethylpiperazine	74
1,10-Phenanthroline	67
4-Dimethylaminopyridine	51

It is clear that bidentate or tridentate amines are superior to most monodentate amines, but that the nature of the amine is not as crucial for desulfurizations with $LiAlH_4$. Moreover, the presence of $LiAlH_4$ with $(COD)_2Ni$ does produce a more efficient (i.e., higher yielding) and more potent desulfurizing agent than using $(COD)_2Ni$ alone. Consider the extent of desulfurization of dibenzothiophene and 2,8-dimethyldibenzothiophene by these desulfurizing agents under comparable conditions:



and



45%	$(COD)_2Ni$ + bipy	12%
93%	$(COD)_2Ni$ + bipy + $LiAlH_4$	85%

d. Testing for Biphenylene Intermediates. We are currently conducting desulfurization tests with 2,8-dimethyldibenzothiophene to learn whether any biphenylene intermediate may be involved in these desulfurizations.

PLANS FOR THE NEXT QUARTER

Further substantiation of the role of certain intermediates in the desulfurization of dibenzothiophene will be carried out. Studies will be begun on the role of hydrogen-donating solvents and a hydrogen gas atmosphere on the extent of desulfurization and on whether the more efficient stoichiometric reagents can function catalytically.

PUBLICATION

1. The principal investigator has presented an invited lecture on his DOE-sponsored research as part of a symposium entitled, "Novel Methods of Metal and Heteroatom Removal", organized by J. E. Sobel (Exxon) and held in the Petroleum Division at the 173rd National Meeting of the American Chemical Society in Houston, Texas, on March 24, 1980. The title of his symposial lecture was, "Transition Metal-Mediated Desulfurization of Aromatic Sulfur Compounds", co-authored by J. J. Eisch, K. R. Im and L. E. Hallenbeck.

2. He has also accepted an invitation to present a lecture on this research before the Gordon Research Conference on Organometallic Chemistry, to be held at Proctor Academy, Andover, New Hampshire, during August 11-15, 1980.