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STATUS REPORT

THERMOCHEMISTRY AND THERMOPHYSICAL PROPERTIES OF ORGANIC NITROGEN- AND  
DIHETEROATOM-CONTAINING COMPOUNDS (1988 STATUS REPORT)

by

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## I. INTRODUCTION

This status report provides a summary of research performed by the NIPER Thermodynamics Research Group as part of the Advanced Process Technology (APT) program sponsored by the U.S. Department of Energy Office of Fossil Energy. Included are summaries of data acquired, a discussion of the utility of the data, and an updated assessment for future work.

## II. SIGNIFICANCE AND OBJECTIVES OF THE PROGRAM

The report, *"Future Directions in Advanced Exploratory Research Related To Oil, Gas, Shale, & Tar Sand Resources,"*<sup>(1)</sup> prepared by the Panel on Future Directions in Fundamental Research Related to Fossil Energy for the Department of Energy (DOE) Assistant Secretary for Fossil Energy states, "Research to establish feedstock structure at the molecular level and the relationship between molecular structure and physical and chemical properties is essential. Research of this type will have an impact on not only the processing of petroleum, shale oil, and tar sand oil but also on the processing of synthetic petroleum derived from coal." Table 4.1 of the report shows the importance of nitrogen removal reactions in the conversion of each alternative feedstock. The degree of importance ranges from "important" for heavy petroleum to "very important" in the case of tar sand bitumen.

The determination of the relationship between molecular structure and the physical and chemical properties of organic nitrogen-containing and diheteroatom-containing compounds is the major goal of this research project. The results of the thermodynamic measurements made in this program can be used to derive structure-property relationships, and, when sufficient data on related structures are available, relate the influence of substituent groups to changes in the reactivity for key structural elements. The research is also crosscutting having application in the processing of the range of alternate feedstocks: heavy petroleum, shale oil, tar sand oil, and synthetic petroleum from coal. The project does not purport to measure the thermodynamic properties of all the organic nitrogen-containing and diheteroatom-containing compounds found in characterization studies of the feedstocks, but rather uses the concept of "key compounds." In the concept of "key compounds," the available characterization data are reviewed, selection of the major compound and structural types present in the feedstock is made, and a set of "key compounds" chosen such that measurements on the selected compounds will have the maximum utility. The application of the proven methodology of additivity of thermodynamic properties within a homologous series of compounds assures the maximum utility of the data. It also means

that in some cases the compounds chosen for the thermodynamic studies may not be actually present in the feedstocks themselves. However, the structural groupings are present, and the chosen compounds are more amenable to study.

The objective was summarized in the FY88 annual plan<sup>(2)</sup> as follows: To provide, interpret, and correlate with molecular structure and polarity of molecules, precise and accurate values of thermodynamic properties of organic nitrogen-containing compounds that occur in or are readily derived from heavy petroleum and oil shale. The results will enable the prediction of chemical equilibria for conceptual as well as current processes.

### III. SUMMARY OF DATA ACQUIRED

#### A. Vapor Pressure Studies

##### 1. Method

Two complementary methods of vapor-pressure measurements are used. One, the ebulliometric method, is a comparative technique that uses twin ebullimeters to reflux the compound under study and a standard of known vapor pressure under a common helium atmosphere.<sup>(3-7)</sup> The operating pressure and temperature ranges are 2.0 to 270.1 kPa and 290 to 700 K respectively. The second method, the inclined-piston method, is an absolute technique that involves exposure of one end of a piston cylinder assembly to a vacuum and the other to the vapor pressure of the compound under study through a nitrogen gas interface.<sup>(6-10)</sup> The vapor pressure of the sample is determined by the equilibrium balance angle of the piston. The pressure and temperature ranges of operation of the inclined piston are 1.3 to 3500 Pa and 210 to 500 K, respectively. The range of vapor-pressure overlap acts as a means of checking the performance of both systems. This is particularly useful for the inclined piston which is a static method, and hence, is susceptible to the presence of small quantities of low-molecular-weight impurities.

##### 2. Measurements Completed in FY87

Ebulliometric vapor-pressure studies (2 to 270 kPa pressure range) were performed this year on indoline, 2-methylaniline, 1,2,3,4-tetrahydro-N-methylcarbazole, and benzothiazole. Inclined-piston vapor-pressure measurements were determined for 7,8-benzoquinoline (0.1 to 3.5 kPa). The Cox equation was fitted to the vapor pressures, and enthalpies of vaporization were derived via the Clapeyron equation over the temperature range of the measurements. Details of the measurements

and results will be published in topical reports and journal publications scheduled for the coming year.

## **B. Enthalpy of Combustion Studies**

### **1. Method**

The basic method used in the determination of the enthalpy of combustion, and hence, the standard enthalpy of formation of an organic compound is well documented in the literature.<sup>(11)</sup> The calorimetric apparatus and procedures applied at NIPER in the combustion of organic nitrogen-containing compounds have been described.<sup>(12-14)</sup>

### **2. Measurements Completed**

Enthalpy of combustion measurements were performed on indoline, 2-methylaniline, 1,2,3,4-tetrahydro-N-methylcarbazole, and benzothiazole this year. The results have been used to derive the corresponding standard enthalpies of formation for the condensed phase at 298.15 K. The ideal gas enthalpies of formation have also been determined by combining the condensed phase values with the the enthalpies of vaporization (see above) and heat capacity data (see below). Details of the results will be published in scheduled topical reports and journal publications.

## **C. Adiabatic Heat Capacity Studies**

### **1. Method**

The essential features of the adiabatic calorimetric equipment for heat capacity studies from near 0 K to 523 K have been described.<sup>(6,15,16)</sup> The equipment has been upgraded and extensively automated. Details are described in reference 6.

### **2. Measurements Completed**

Compounds for which adiabatic heat-capacity and enthalpy studies were completed this year are; indoline, 2-methylaniline, and benzothiazole (in progress). Details of the measurements and results will be published in topical reports and journal publications scheduled for the coming year.

## **D. Summary**

The above thermodynamic property measurements, plus those determined previously in this project, have enabled the calculation of the condensed-phase and ideal-gas-phase Gibbs energies of formation for each of the above nitrogen-containing compounds.

These data plus those reported in NIPER-Topical Report 188<sup>(17)</sup> form the most comprehensive collection of thermodynamic properties for nitrogen-containing organic compounds ever produced.

#### IV. APPLICATION OF RESULTS

##### A. Overview

Results derived from the measurements described in this status report are valuable aids to the solution of problems in the refining industry both individually and in combination. Individually, these studies provide the model compound data which serve as the basis for state-of-the-art thermophysical and thermochemical correlations. The combined data are essential in the development of new processes by testing the process feasibility before costly laboratory investigations begin. The key quantity for this purpose is the Gibbs free energy of formation. The remainder of this section outlines the progress made within this project in applying the thermodynamic results obtained to problems in nitrogen removal in alternate feedstocks.

##### B. Thermodynamics of Hydrogenation of Quinoline

Hydrodenitrogenation (HDN) reaction mechanisms contain steps where the aromatic ring structures are hydrogenated. These reaction steps are all reversible within the temperature and pressure ranges of hydrogenation reactors used commercially at present. Therefore, a knowledge of the thermodynamic equilibria among the species is necessary for the proper interpretation of reaction data, for comparing different catalysts, and for accurate modelling of the overall reaction.

The HDN of quinoline has been used as model system in kinetics, catalysis, and equilibria studies designed to provide insights into the fundamental processes involved. A topical report, NIPER-301, (see publications and presentations section of this Status Report) and a separate journal article were written on the thermodynamic properties of quinoline and isoquinoline. The journal article has been accepted for publication and will appear in *The Journal of Chemical Thermodynamics* later this year (1988).

Figure 1 shows part of the most recently proposed reaction scheme for the hydrodenitrogenation of quinoline.<sup>(18)</sup> Within this project, thermodynamic data on quinoline and both tetrahydroquinolines have been obtained over the whole range of temperature of interest in processing. Data on several of the other intermediates and products of hydrogenation are available in the literature or can be estimated via group additivity. An exception is the intermediate, 2-propylaniline, for which data is not available and cannot be estimated due to the ortho-interaction. This year the completion

of measurements on 2-methylaniline (see above) will enable estimation of the thermodynamic properties of this important intermediate in the quinoline HDN reaction scheme.

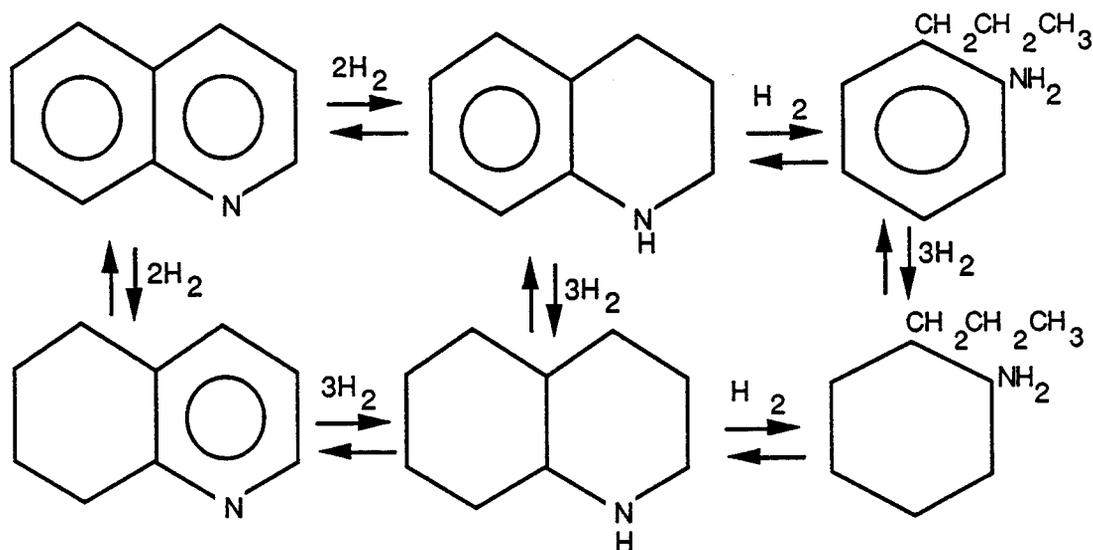


Figure 1. Partial reaction scheme for the HDN of quinoline.

### C. Thermodynamics Properties of the Benzoquinolines

A topical report (NIPER-337) and a separate journal article were written on the thermodynamic properties of the five benzoquinolines. The thermodynamic properties of three of the isomers, acridine (2,3-benzoquinoline), phenanthridine (3,4-benzoquinoline), and 7,8-benzoquinoline were measured in this laboratory using conventional calorimetry. The thermodynamic properties at 400 K of the remaining two isomers, 5,6-benzoquinoline and 6,7-benzoquinoline, were estimated using group-additivity methodology. Reaction schemes for the formation of the benzoquinolines were outlined, and insights provided by the new thermodynamic information were discussed. For example, the ring-closure (and subsequent aromatization) of 3- $\eta$ -butylquinoline could form either acridine or phenanthridine. Under thermodynamic control the reaction scheme simplifies considerably. The **only** pathway to acridine is via a 2-alkyl (butyl or longer chain) quinoline. Reaction of the 3-substituted quinoline gives **solely** phenanthridine. Similarly, 6,7-benzoquinoline is a **minor** product under thermodynamic equilibrium conditions from both the 6- and 7-substituted quinolines. In fact 6,7-benzoquinoline has never been listed as a constituent of any alternate fuel source.

The journal article has been accepted for publication and will appear in The Journal of Chemical Thermodynamics early next year (1989).

#### **D. Thermodynamics of the HDN of Indole**

A topical report (NIPER-379) was written giving a provisional thermodynamic analysis of the HDN of indole. The report shows that thermodynamic limitations exist in the reaction network. The first step in the reaction scheme (indole  $\rightarrow$  indoline) is a reversible reaction in the temperature range of interest, favored by **low** temperature. At 473 K (200° C) 21 atmospheres of hydrogen is needed to obtain a 50/50 mole percent mixture of indole and indoline: at 573 K (300° C) 136 atmospheres of hydrogen is needed.

In NIPER-379 the results of the thermodynamic analysis are shown to be in substantial agreement with the equilibrium data available in the literature. Also, the thermodynamic data are used to help elucidate another study in the literature in which several different catalysts were compared. The results show that for a given catalyst, increasing the hydrogen pressure fails to promote the hydrogenolysis reaction relative to the hydrogenation equilibrium while increasing the temperature does promote hydrogenolysis. In agreement with the conclusions in NIPER Topical Report-264,<sup>(19)</sup> the relatively large C-NH<sub>2</sub> bond dissociation energy in 2-ethylaniline compared to 2-ethylcyclohexane means that the major pathway to HDN using present technology is via ring saturation. However, if catalysts can be found to selectively cleave the C-NH<sub>2</sub> bond in 2-ethylaniline, significant hydrogen saving can result.

### **V. FUTURE WORK**

#### **A. Thermodynamic Property Measurements**

Make measurements of enthalpies of combustion, condensed-phase heat-capacities (standard entropies), vapor pressures, and densities on selected key organic nitrogen-containing and diheteroatom-containing compounds as equipment becomes available from queued experiments on these substances.

Use the recently reactivated Vapor-Flow Calorimeter to determine vapor-phase heat capacities of isoquinoline over a range of temperatures. Make measurements of the enthalpies of vaporization over a series of pressures, and hence, derive second virial coefficients for this important class of aromatic nitrogen compounds. The derived second virial coefficients will add to the meager data available on the properties of aromatic nitrogen compounds in the real-gas state, and hence, aid in future equation-of-state development.

## **B. Applications of Results in Process Design**

During FY89 the evaluations (started in FY88) of the thermodynamic equilibria possible during the removal of nitrogen by the hydrotreating/hydrocracking of heavy petroleum and shale oil will continue. In this financial year thermodynamic analyses will be performed on the model compounds isoquinoline, acridine, and phenanthridine. In addition, studies will be made on the thermodynamic conditions necessary for the formation of nitrogen aromatic heterocycles in the alternate crudes.

Experimental results from this laboratory will be compiled and interpreted in reports and journal articles. In the coming year these reports and journal articles will include ones on the thermodynamic properties of 1,2,3,4-tetrahydroquinoline, 5,6,7,8-tetrahydroquinoline, indoline, and 2-methylindole.

## **VI. PUBLICATIONS AND PRESENTATIONS**

### **Publications**

1. Messerly, J. F.; Todd, S. S.; Finke, H. L.; Good, W. D.; Gammon, B. E. *Condensed-Phase Heat-Capacity Studies and Derived Thermodynamic Properties for Six Cyclic Nitrogen Compounds*. J. Chem. Thermodynamics 1988, 20, 209.
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6. Steele, W. V.; Chirico, R. D.. *Preliminary Thermodynamic Studies on the Hydrodenitrogenation of Indole*. NIPER-379. September 1988.

## Presentations

1. Steele, W. V.; Chirico, R. D.; Hossenlopp, I. A.; Nguyen, A.; Smith, N. K. *The Thermodynamic Properties of the Five Benzoquinolines*. A paper presented at the 43rd Calorimetry Conference, Bartlesville, Oklahoma. August 9-12, 1988.
2. Steele, W. V.; Chirico, R. D. *NIPER Thermodynamic Research Group. Summary of Present Research Programs*. A seminar presented at Pittsburgh Energy Technology Center, March 15, 1988.

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