133
6/17/87 *Em*

⑤

J. 30925

DR 0255-0

MLM-3435

**DO NOT MICROFILM
COVER**

**The Separation and Characterization of
a Hydrogen Getter Product Mixture
Part 2. Measurement of Product Vapor
Pressures**

David W. Firsich and Tracy R. Shell

June 4, 1987

Monsanto

MOUND

Miamisburg, Ohio 45342

operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company

for the

U. S. DEPARTMENT OF ENERGY

Contract No. DE-AC04-76-DP00053

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes
Printed Copy: A02
Microfiche copy: A01

DO NOT MICROFILM
COVER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MLM-3435

UC-4

MLM--3435

DE87 010640

The Separation and Characterization of a Hydrogen Getter Product Mixture Part 2. Measurement of Product Vapor Pressures

David W. Firsich and Tracy R. Shell

Issued: June 4, 1987

MOUND

Miamisburg, Ohio 45342

operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company

for the

U. S. DEPARTMENT OF ENERGY

Contract No. DE-AC04-76-DP00053

zb
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

Contents

	<u>Page</u>
ABSTRACT	3
INTRODUCTION	3
RESULTS AND DISCUSSION	3
COMPONENT 1 - HCPB	4
COMPONENT 2	5
COMPONENT 3	5
COMPONENT 4	6
SUMMARY	7
ACKNOWLEDGEMENT	7
REFERENCE	7
DISTRIBUTION	8

Abstract

HCPB is the acronym of an organic hydrogen getter compound used in weapon systems. When this material scavenges hydrogen by reacting with it, a number of compounds are formed, each of which is more volatile than HCPB. It is desirable to know the vapor pressure of these products in order to assess their migration potential within the weapon. In this study, individual compounds from a reacted HCPB mixture were isolated and their vapor pressures were measured. Three of the four fractions examined with a modified capacitance manometer were found to have vapor pressures under 1 mtorr; the fourth was measured at 92 ± 15 mtorr. An attempt was made to obtain boiling point data on the two liquid components of the getter mixture, but they decomposed before reaching their boiling points.

Introduction

The organic hydrogen getter bis (1-hydroxyl cyclopentyl) butadiyne (HCPB, Figure 1) is used to protect some weapon components from the potentially negative effects of hydrogen. HCPB scavenges the available hydrogen by reacting with it, thereby forming reaction products that must be evaluated for their compatibility with the weapon system.

In an earlier report [1], it was shown how such a mixture of reaction products could be separated with thermal gradient sublimation and the components subsequently structurally analyzed with a combination of infrared (IR), chemical ionization mass spectroscopy, proton nuclear magnetic resonance (NMR) and carbon-13 NMR. The physical state of each component in the mixture was also determined; some were solids while others were viscous liquids. This was interesting from a compatibility standpoint

because of the expected increase in migration potential of a liquid relative to a solid.

The determination of the volatilities of these getter reaction products is at least as important as, if not more important than, the assignment of their chemical structures. The fact that some of these mixtures have a noticeable butanolic smell indicates that some components have a significant vapor pressure. In this study, the vapor pressures of a number of isolated getter products were measured, providing for the first time hard data relevant to the migration potential of these materials.

Results and Discussion

It is possible to isolate small quantities (approximately 0.1 g) of individual compounds within a getter product mixture through repeated thermal gradient sublimation, as described in the previous paper [1]. To measure the vapor pressure of such a small quantity, a special device was built that consists of a Baratron capacitance manometer coupled to the sample holder and vacuum system (Figure 2). The system is all metal, except for the glass sample tube, and it

FIGURE 1 - The chemical structure of HCPB.

FIGURE 2 - Diagram of the vapor pressure measurement device (not to scale).

can therefore degas quickly and hold a tight seal. The dead volume (volume of the system up to valve A) in the unit is kept low (approximately 10 cc) so that the solid or liquid sample of interest quickly reaches equilibrium with its vapor phase prior to the pressure measurement. The Baratron manometer was calibrated over the 1-1000 mtorr range.

The following procedure was utilized for vapor pressure measurement. A small quantity of compound (less than 0.1 g) was placed in the glass sample tube, which was connected to valve B with a swagelock fitting. The sample tube was then cooled with a cold ethanol bath (-20°C), and the entire system was evacuated to below 1 mtorr. Typically, three freeze/pump/thaw cycles were performed to degas the sample and ensure that it was dry. (Water will be pumped away under these conditions.) After the final freeze and pumpdown, valve A was closed, the cold ethanol bath was removed, and the sample was allowed to warm to room temperature. As warming occurred, the measured pressure gradually

increased, levelling off in about 30 s. This value was taken as the vapor pressure of the sample.

The vapor pressures in this report were obtained at room temperature. While it might be desirable to measure them as a function of temperature, the entire manometer apparatus of Figure 2 would have to be held at the temperature of interest in order to make the measurement. Since the Baratron capacitance manometer is calibrated to operate at room temperature only, it was not practical to pursue variable temperature work.

A sample of hydrogen getter reaction products (DD-31) was obtained from Dr. Dan Doughty of Sandia-Livermore. This mixture resulted from the partial hydrogenation of an HCPB sample. The product distribution in DD-31 is indicated by its gas chromatogram shown in Figure 3. Correlation of this gas chromatogram (GC) with the results from thermal gradient sublimation of DD-31 shows that the GC peaks with higher scan numbers correspond to the less volatile compounds in the mixture; i.e., those with the lowest vapor pressure. In this study, the vapor pressures of the components labelled 1, 2, 3, and 4 were measured. Repeated thermal gradient sublimations were performed to obtain pure samples of components 2, 3, and 4 for vapor pressure measurement. A sample from another source was available for component 1.

Component 1 - HCPB

Earlier work has shown that component 1 is HCPB, the unreacted getter material. A sample of this crystalline white solid

FIGURE 3 - Gas chromatogram of mixture DD-31. Peak numbers identify mixture components referred to in this report.

FIGURE 4 - Gas chromatogram of an HCPB sample.

(whose purity was confirmed with GC, Figure 4) was examined with the pressure measurement device described above, but gave no signal in repeated measurements, indicating that its vapor pressure was below one mtorr at room temperature (22°C). This result is consistent with the observation that HCPB must be heated to about 50°C before it will sublime at any appreciable rate under an applied vacuum of 3×10^{-4} torr.

Component 2

Component 2 is a crystalline white material whose structure is shown in Figure 5. A sample of this material which had been analyzed by gas chromatography for purity (Figure 5) was used for vapor pressure measurement. In repeated trials, measurements indicated that the vapor pressure was below the range of the Baratron (i.e., below 1 mtorr). The melting point of the compound was measured at 87°C, which was lower than the HCPB melting point of 132°C.

FIGURE 5 - Gas chromatogram shows the purity of a component 2 sample isolated from mixture DD-31.

Component 3

Component 3 is a colorless oil whose structure is shown in Figure 6. A sample of this material was checked for purity using GC (Figure 6) prior to the measurement of its vapor pressure. In a number of determinations, the value obtained was either at or below 1 mtorr. Since these measurements were at the lower detection

FIGURE 6 - Gas chromatogram shows the purity of a component 3 sample isolated from mixture DD-31.

limit of the Baratron, the correct value can only be estimated at somewhere in the range of 1×10^{-4} torr to 1×10^{-3} torr. This low value is consistent with the sublimation behavior of the material and with the fact that this oil has no discernible smell when it is in a pure form.

An attempt was made to measure the boiling point of component 3 using a standard microboiling point apparatus (Figure 7). In this device, an inverted capillary tube is placed in a drop of sample mounted adjacent to a thermometer in a heated oil bath. The bath is heated until bubbles of vapor stream from the capillary tube, whereupon heat is removed. The temperature at which bubbling stops is taken as the boiling point. The application of this technique to component 3 showed that it does not boil at or below 170°C ; at this temperature it began to thermally decompose.

FIGURE 7 - Diagram of a microboiling point determination apparatus.

Component 4

Component 4 consists principally of two compounds, as shown in the GC trace in Figure 8. These materials have not been unambiguously identified. Gas phase IR, ^{13}C and ^1H NMR, and GC/mass spectroscopy were run on samples of this component, but generated conflicting data which have not been helpful in assigning the structures of the two compounds. The small sample size has added to these difficulties. It may be cautiously stated that the compounds have masses 206 and 208 and that the 208 compound does not contain an alcohol. Other conclusions are less certain; some results point to a ketone or other type of unsaturation in one or both of these molecules.

The compounds are too close in volatility to isolate individually with gradient sublimation or trap-to-trap distillations. However, since their volatilities are so similar, the individual vapor

FIGURE 8 - Gas chromatogram shows the two compounds of component 4 which were isolated from mixture DD-31.

pressures of the two will be close to vapor pressure measured for component 4. The value obtained for component 4 was 92 ± 15 mtorr.

An attempt was made to measure the boiling point of component 4 using the apparatus described above. No boiling was observed up to 150°C , the point at which thermal decomposition began.

Summary

An organic hydrogen getter is included in an existing weapon component to scavenge unwanted hydrogen gas within the device. A sample of this getter was subjected to a test hydrogenation, which produced a mixture of products. It was desirable to quantify the vapor pressure of these products in order to assess their migration potential within the weapon.

An earlier report [1] on hydrogen getter analysis described how a reacted getter material could be separated into its component fractions through thermal gradient sublimation and vacuum line trapping. The repeated application of these procedures resulted in the isolation of small quantities of purified fractions whose individual vapor pressures were measured with a modified capacitance manometer. A total of four fractions were examined: two solids and two oils. The two solids had room temperature vapor pressures below 1 mtorr. One oil seemed to have a vapor pressure close to the lower limit of the manometer (1 mtorr); the second oil gave a value of 92 ± 15 mtorr.

The first solid was the parent getter compound, whose known melting point is 132°C . The previously undetermined melting point of the second solid is 87°C . Attempts were made to determine the boiling points of the two oils, but each thermally decomposed without boiling at around 160°C .

Acknowledgement

The authors would like to thank Dr. Robert Ellefson for the loan of the Baratron capacitance manometer used in this work.

Reference

1. Firsich, D. W., and R. O. Yelton, The Separation and Characterization of a Hydrogen Getter Product Mixture, Monsanto Technical Report MLM-3360, July 1986.

Distribution

EXTERNAL

TIC, UC-4 (143)

J. A. Morley, DOE/DAO

H. A. Schneiderman, St. Louis

Monsanto Reports Library, R2C, St. Louis

Bendix - Kansas City

H. M. Smith

E. W. Grotheer

Sandia National Laboratories, Albuquerque

D. H. Anderson

D. H. Doughty

P. D. Wilcox

Lawrence Livermore National Laboratory

J. E. Clarkson

R. R. McGuire

M. Finger

R. H. Sanborn

H. A. Golopol

D. Seton

D. Lidner

Sandia National Laboratories, Livermore

M. Brown

A. Riveness

D. Nissen

E. S. W. Wong

INTERNAL

P. S. Back

C. L. Fellers

P. S. Miller

G. L. Ball

R. J. Finney

J. M. Pickard

B. V. Barnhart

D. W. Firsich (25)

J. W. Reed

B. D. Barton

R. A. Fischbein

D. R. Rogers

J. D. Braun

J. D. Hastings

R. F. Salerno

J. R. Brinkman

L. D. Haws

P. W. Seabaugh

D. A. Buckner

W. B. Hogeman

T. L. Shell (10)

A. R. Burke

J. A. Holy

G. L. Silver

T. L. Buxton

C. R. Hudgens

W. H. Smith

H. S. Carden

C. W. Huntington

R. Thorpe

R. S. Carlson

D. P. Kelly

P. D. Trainer

R. J. DeSando

T. L. Koeller

R. E. Vallee

J. V. Dichairo

J. M. Lavoie

M. D. Vannet

L. R. Dosser

J. W. Leffingwell

P. S. Wang

D. G. Draper

C. M. Love

R. B. Whitaker

W. R. Fearheller

G. D. Miller

Library (15)

Publications

Lisa R. Kramer, Editor
Technical Publications