150° C. distillate, bringing to 44 the total number of this class of sulfur compounds found in Wasson, Texas, crude oil. From this study, some observations relative to the abundance of certain thiol types are presented. The perfected separation and identification techniques discussed should materially aid other researchers interested in similar studies.

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Melting Point and Vapor Pressures of 3-Hexyne

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The equilibrium vapor pressure of 3-hexyne was measured in the temperature range of −20° C. to 25° C. using a modified isotensioscope and a mercury manometer. From the slope of the Clausius-Clapeyron plot of the data, the heat of vaporization was calculated to be 7560 cal. per mole, and an equation was written to fit the data. The melting point of purified and degassed 3-hexyne was obtained with the use of a calibrated platinum resistance thermometer. The measured value of −102.5 ± 0.2° C. for the melting point falls within the wide range of scant literature values.

LITTLE INFORMATION on the physical constants of 3-hexyne is available. The most recent chemical handbooks (*4, 5*) listed no melting point, boiling point, or vapor pressure data. An extensive search of the literature yielded reliable boiling point data (*1—3*) but the melting points found ranged from −101 to −105.53° C. (*1, 3*). No vapor pressure data could be found. In view of the discrepancy in the reported melting points and for want of vapor pressure data, the authors deviated slightly in this study of the radiation chemistry of 3-hexyne to look into its physical chemistry. No special effort was made to determine accurately the boiling point since good agreement was found in the literature.

EXPERIMENTAL

Purification. The 3-hexyne was obtained from Farchan Research Laboratories and purified by distillation through a 5-foot, 5-mm. I.D., monel wire column at a 10 to 1 reflux ratio. The purification was monitored by gas-liquid chromatography. Analysis of the chromatogram of the middle third cut showed an impurity level of 0.05%.

Boiling Point. At total reflux, the middle third cut had a boiling point of 80.0-80.5° C. at 747 torr. Using the heat of vaporization obtained from the authors' vapor pressure data, the corrected boiling point for 760 torr was 81.2° C. This is in excellent agreement with the following literature

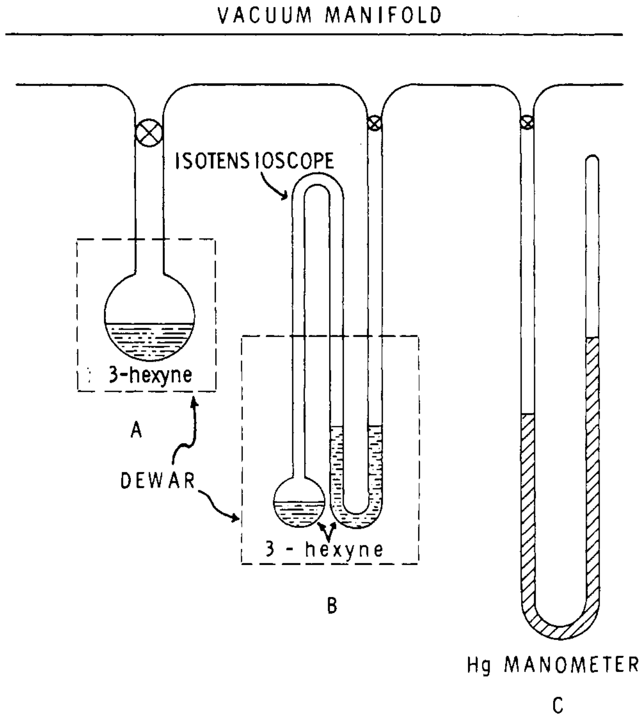

Figure 1. Vapor pressure measurement apparatus

values: 81.2–81.3° C. at 760 torr (*1*), 80.0–80.6° C. at 746 torr (*2*), and 81° C. at 760 torr (*3*).

Melting Point. The melting point of the distilled and degassed 3-hexyne was obtained with the use of a calibrated resistance thermometer and a borosilicate glass apparatus originally designed by Stock (*6*). The apparatus consists of a length of thin-walled, borosilicate glass tubing closed at one end and containing a weighted glass plunger. The plunger was made by sealing a small iron rod into 10-mm. glass tubing and drawing the glass a few inches at both ends. The bottom end was then looped into a small horizontal ring while a blue bead of cobalt glass was fused at the top end for use as a visual end point indicator. The plunger could then be lifted vertically by means of a magnet.

The apparatus and a flask containing the purified 3-hexyne were attached to a high vacuum manifold. The alkyne was thoroughly degassed by repeated freeze-pump-thaw cycles, and both the melting point apparatus and the frozen 3-hexyne were evacuated to less than 10^{-3} torr.

While the metal plunger was held up with a magnet, a solid ring of the alkyne was condensed in the thin-walled outer section of the apparatus with the use of liquid nitrogen. The plunger was carefully lowered with a magnet until the glass ring came to rest on the frozen compound. After the apparatus was removed from the vacuum system, the bulb of an N.B.S.-calibrated platinum resistance thermometer was attached to the frozen ring portion of the tube, and the combination was transferred to an ethyl bromide-liquid nitrogen slush bath (−119° C.). The temperature rise, about 0.2° per minute, was measured with a Mueller Temperature Bridge while watching the blue bead sticking up above the cooling bath. The resistance of the end point was recorded and converted to ° C.

Table I. Pressure-Temperature Data for 3-Hexyne

T, ° K.	P, Torr	T, ° K.	P, Torr
297.6 ± 0.2°	88 ± 0.5	285.4 ± 0.2°	50 ± 0.5
297.1	85	283.1	44
296.0	82	281.7	41
294.7	77	278.2	35
292.6	70	274.2	30
292.2	69	273.4	28
290.0	61	267.9	21
289.2	60	262.1	16
288.0	57	253.2	10

After five runs, the melting point of 3-hexyne was recorded at −102.5 ± 0.2° C. In each run, the plunger dropped abruptly, without any sign of sinking into the compound. The above melting point falls within the −101 to −105° C. range found in the literature.

Vapor Pressure. The vapor pressure measurements were obtained through the use of the apparatus shown in Figure 1. The apparatus consists of a flask, *A*, an isotensioscope, *B*, and a mercury manometer, *C*—all attached to a high vacuum manifold. Purified 3-hexyne was placed in flask *A* and in the bulb of the isotensioscope where it was thoroughly degassed by repeated freeze-pump-thaw cycles under vacuum. Some of the alkyne was then vacuum distilled into the U-tube of the isotensioscope and the entire assembly, *B*, was immersed in a constant temperature dewar. A zero-pressure differential was maintained in the 3-hexyne manometer by placing flask *A* into a constant temperature dewar and allowing the temperature of both baths to rise very slowly. The temperature at each equilibrium point listed in Table I was read to the nearest 0.2° C. while the corresponding pressure was read from the mercury manometer to the nearest 0.5 torr.

RESULTS AND DISCUSSIONS

The data on Table I were plotted as the log of the vapor pressure *vs.* the reciprocal of the absolute temperature. The slope of the straight line plot yielded a heat of vaporization of 7560 cal. per mole for 3-hexyne. The assumptions made in calculating the heat of transition were: The molar volume of the 3-hexyne was negligible in comparison to the molar volume of the vapor, the vapor behaved ideally, and the heat of vaporization was independent of temperature over the range in question. These assumptions permit the integration of the Clausius - Clapeyron equation and lead to the following expression which represents the data.

$$\log_{10} P_{torr} = \frac{-1650}{T} + 7.5$$

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