to another over the range of 220 to 305 mμ. In at least three cases (2-mercaptoethylamine, cysteine, and mercaptosuccinic acid), the λ_{max} varies with pH—i.e., with RS^-/RSH. This latter variation may well reflect the concomitant ionization of the ammonium ion in the first two cases, and of the β-carboxyl group in the third case.

Neither of the two methods employed appears to have any intrinsic advantage over the other, at least when the thiol is of high purity. However, if the thiol contains unknown contaminants an electrometric titration cannot be meaningfully carried out, while a spectrophotometric determination may still be successful.

Table I is arranged according to decreasing values for pK_a. This arrangement clearly displays the inductive effect of the substituent groups on the acidities of the thiols, which has been discussed by Kreevoy *et al.* (*15, 16*). Thus, it should be feasible to make reasonable estimates for the pK_a values of thiols for which experimental determinations have not yet been carried out.

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Latent Heat of Sublimation of Terephthalic Acid from Differential Thermal Analysis Data

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The latent heat of sublimation of terephthalic acid has been calculated from differential thermal analysis data. This value was 33.3 ± 0.9 kcal. per mole from 7.0 to 760 mm. of Hg. In addition, the sublimation temperature of terephthalic acid at 760 mm. of Hg and the melting point in a sealed tube have been observed. These values were 402° and 427° C., respectively.

THE latent heats of sublimation of terephthalic acid as calculated from vapor pressure data reported by Hirsbrunner (*5*), Jordan (*6*), and Kraus *et al.* (*8*) are not in agreement. The value obtained from the equation presented by Hirsbrunner is 23.6 kcal. per mole. The value obtained from a vapor pressure curve in the compilation by Jordan, who cites Hirsbrunner as the source of his data, is 20.2 kcal. per mole. More recently, Kraus *et al.* reported a value of 31.3 kcal. per mole. The work reported here was undertaken to check these values and to extend the range of the vapor pressure–temperature data.

Hirsbrunner (*5*) measured vapor pressures in a sealed tube at different temperatures. Kraus *et al.* (*8*) used a gas saturation method with nitrogen as the carrier gas. The nitrogen was saturated with terephthalic acid vapor by slow passage over the powdered acid, which was maintained at a constant temperature. The acid vapor was caught in alkali, and the vapor pressure was calculated from the amount of acid found by titration. The vapor pressure–temperature data being reported in this paper were obtained by a variable pressure differential thermal analysis (DTA) technique. In this technique, the pressure of the gaseous environment of the sample is controlled by bleeding nitrogen into the sample chamber. At each preset value of the pressure, a thermogram is recorded and the sublimation temperature is obtained from the thermogram. Markowitz and Boryta (*10*) have used this technique to study the sublimation equilibria of ammonium chloride, and Krawetz and Tovrog (*7*) used a similar method to obtain the vapor pressure of toluene. The limitations of the DTA method have been discussed by Sarasohn (*12*).

EXPERIMENTAL

Terephthalic acid produced by catalytic oxidation of *p*-xylene (*11*) was treated with potassium permanganate in ammonia solution to ensure complete oxidation of any intermediate oxidation products that may have been present. The resulting black suspension was filtered through paper to give a yellow filtrate to which was added decoloring carbon and analytical filter pulp. Filtration of this gave a colorless filtrate which was heated with excess glacial acetic acid to regenerate terephthalic acid. The washed product was heated for 3 hours at 140° C. under vacuum and then analyzed. A Kjeldahl method showed no detectable nitrogen, and gas chromatography showed only terephthalic acid. Titration in pyridine with tetrabutylammonium hydroxide showed a purity of 100.1%. The terephthalic acid used for each determination was 100-mesh powder.

The DTA experiments were performed with the commercially available duPont 900 differential thermal analyzer. The cell assembly, which makes operation at reduced pressure possible, was described by Chiu (*2*) except that in the present work the duPont "macro" sample block was used. This is an aluminum block (2.223 x 3.810 cm.) with a centered hole for a 55-watt cartridge heater (0.953 x 2.858 cm.) and symmetrically placed reference and sample wells to accommodate the macro sample tubes (4 x 30 mm.). The aluminum block also has a third well close to the heater for the temperature-programming thermocouple. The block, heater, thermocouples, and gas ports are enclosed in a glass bell jar during operation of the instrument. The thermocouples are Chromel-Alumel and are connected such that the DTA unit records the difference in the temperature between the reference and sample thermocouples *vs.* the temperature of the sample thermocouple.

Each experiment was run with 50 ± 1 mg. of terephthalic acid in the sample well and with the same amount of glass beads in the reference well. The procedure involved weighing the sample into the macro tube, placing the thermocouple into the tube, and inserting the tube into the aluminum block heater assembly. The entire assembly was covered with the bell jar and the inside of the jar was evacuated to the desired pressure. The pressure was maintained by bleeding nitrogen through the needle valve of the purge port and was measured to ±0.2 mm. with a closed-end manometer. Before each thermogram was run the system was thoroughly flushed with nitrogen.

After setting the desired pressure, the thermogram was recorded from room temperature by heating at a constant rate of 30° C. per minute and the ΔT attenuator set in the 1 position. The transition temperature was obtained by extrapolating the low temperature edge of the endotherm to the temperature axis (*13*).

RESULTS

Table I lists the DTA sublimation temperatures observed at each pressure. A Clausius-Clapeyron plot of $\log_{10}P$ *vs.* $1/T$ yields a straight line (Figure 1), and least squares treatment of the data gives the equation:

$$\log_{10}P = -7280/T + 13.6$$

Table I. Variable Pressure DTA Data for Terephthalic Acid Sublimation

Pressure, Mm.	Temperature, ° K.
760	675
142	632
100	626
76	618
27	595
18	588
9.0	575
7.0	568

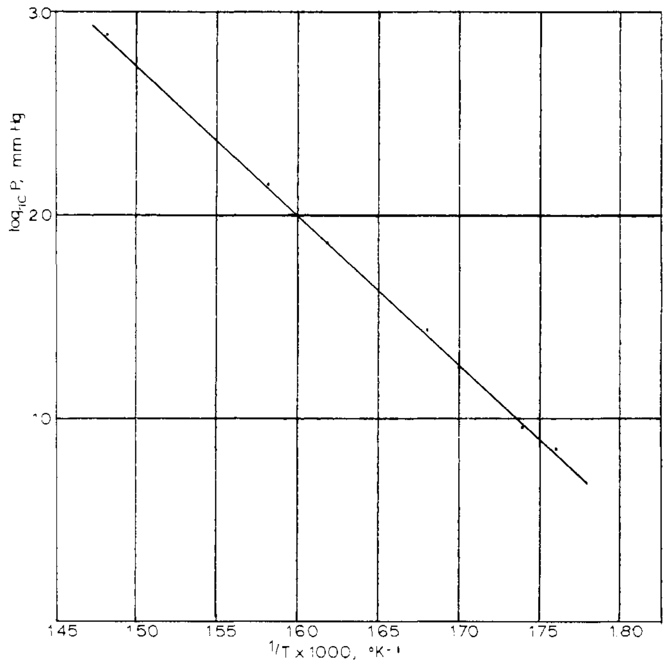

Figure 1. Clausius-Clapeyron plot for terephthalic acid

The standard deviation of the slope (*14*) was 206. Consequently, the latent heat of sublimation, ΔH_s, is equal to $-(7280 \pm 206)(2.303)(R)$ where R is taken as 1.987 cal. per °K. per mole. Computation results in the value $\Delta H_s = 33.3 \pm 0.9$ kcal. per mole over the pressure range from 7.0 to 760 mm. of mercury.

The data show that the sublimation point of terephthalic acid—i.e., the temperature at which its vapor pressure is 1 atm.—is 402° C. The value calculated for 760 mm. with the above equation is 404° C. These values are much higher than the generally accepted literature value of 300° C. (*1*).

In separate experiments in which terephthalic acid was heated in a sealed tube containing a thermocouple junction, an endotherm having a transition temperature of 427° C. was observed in addition to the sublimation endotherm at 402° C. The 427° C. endotherm must represent melting because the value is in agreement with the melting point range of 425° to 430° C. observed visually in a sealed tube (*4*).

DISCUSSION

The experimental DTA value of $\Delta H_s = 33.3$ kcal. per mole is much closer to the 31.3 reported by Kraus (*8*) than to the value of 23.6 obtained from Hirsbrunner's equation. The agreement with the Kraus data is even better when his equation [$\log P = 12{,}697 - 6150/(T - 43)$] is converted to the conventional Clausius-Clapeyron expression. The value calculated with the Kraus data and the Clausius-Clapeyron relation is 32.8, a result which does not differ significantly from the DTA value of 33.3 ± 0.9 kcal. per mole. It is difficult to explain why Hirsbrunner's value is so much lower. Possibly, Hirsbrunner's sample of terephthalic acid (for which no physical constants were given) was contaminated with more volatile materials since his data cover a temperature range (119° to 152° C.) at which the vapor pressure of terephthalic acid should be essentially zero. After the completion of the work reported in this paper, it was learned that a value of 33.3 ± 0.4 was obtained by other workers by means of a thermal gradient strip technique (*9*).

A value of $\Delta H_s = 33.1$ kcal. per mole can be calculated from data obtained for benzoic acid and benzene (*3*). The contribution to the heat of sublimation per six benzenoid carbons is taken as 10.5 kcal. per mole, and the contribution of each carboxyl group is taken as 11.3 kcal. per mole.

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Spectroscopic Identification of Basic Nitrogen Compounds in Wilmington Petroleum

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A study of the basic nitrogen compounds in Wilmington (Calif.) petroleum fractions has produced considerable information on their composition. Characterization of the classes of basic nitrogen compounds in the 130° to 350° C. distillate fractions was made by low-voltage mass spectral analyses. Two individual compounds—an alkyl-substituted cyclopentapyrindan and an alkylcycloalkyl-substituted pyridine—were separated and identified. Procedures used to separate the compounds from the oil included distillation, mineral acid extraction, and gas-liquid chromatography. The identifications were made by a combination of mass, infrared, ultraviolet, and nuclear magnetic resonance spectrometry.

NITROGEN compounds are an important, minor constituent of petroleum. Even in trace amounts, they cause serious problems in processing and in the stability of products. They cause catalyst poisoning and are involved in the formation of gums, lacquers, and precipitates.

The nitrogen present in petroleum is usually divided into two broad types: basic nitrogen, defined as that which is titratable with perchloric acid in acetic acid solution, and nonbasic nitrogen which is not titratable.

Numerous studies have been made on the nature of the basic nitrogen compounds in petroleum fractions. Bratton and Bailey (*1*) found several pyridines and quinolines in a cracked gasoline. Hackman, Wilbant, and Gitsel (*4*), studying a cracked California gasoline, identified pyridines, quinolines, isoquinolines, and a tetrahydroquinoline or pyrindan. Nixon and Thorpe (*15*) reported quinolines, pyrindines, and anilines present in catalytically cracked jet fuel. LaLau (*8*), who investigated unspecified fractions, found pyridines, quinolines, and their naphtheno-substituted homologs. Jewell and Hartung (*7*) identified quinolines, benzoquinolines, indolo- and carbazoloquinolines, hydroxybenzoquinolines, and 1,10-phenanthroline in a straight run heavy gas oil although some of these identifications have been questioned (*19*). Drushel and Sommers (*2*) studied a catalytic cycle oil and found pyridines, quinolines, pyrindines, and cyclopentaquinolines present. An American Petroleum Institute-sponsored project at the University of Texas extensively studied the composition of the basic nitrogen compounds in a California petroleum. As a result of this study, 10 pyridines, 22 quinolines, one tetrahydroquinoline, and two dihydropyrindines were identified (*9-11*).

This paper describes a characterization of the classes of basic nitrogen compounds present in distillate fractions of Wilmington crude oil (*6*) and includes the identification of two individual compounds. Distribution of the classes of compounds was determined by low-voltage mass spectral analyses. The individual compounds were identified by a combination of mass, infrared, ultraviolet, and nuclear magnetic resonance spectral techniques. The work was carried out as part of American Petroleum Institute Research Project 52, which was concerned with the study of nitrogen compounds in petroleum. The project was discontinued June 30, 1966.

EXPERIMENTAL

The separation procedure used in this study is outlined in Figure 1. The investigations reported in this paper were carried out on the fractions indicated by the solid-lined

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