pensating variance occurs in the constants of the second reaction. The entropy of activation of the reaction producing hydrogen chloride is thus thought to be about −20 e.u., and the energy of activation around 23 kcal. The more negative entropy of activation of this reaction is consistent with the view that the process is also one of internal rearrangement, involving a six-membered ring rather than a four-membered one. Examination of possible configurations by means of Fisher-Hirshfelder atomic models has suggested that the activated complex of the reaction producing hydrogen chloride is a configuration in which the chlorine atom lies between the two methyl groups of the isopropyl radical. This configuration is obviously impossible for the ethyl compound, and probably accounts for the difference in the behavior of the two chlorocarbonates.

In the case of the isopropyl compound the position of the chlorine atom allows the formation of six-membered rings, involving the methyl hydrogen and carbon atoms. The chlorine attack occurs on one of the hydrogens attached to a methyl group, and hydrogen chloride is formed. The remainder of the molecule being unstable, rearrangement occurs, forming propylene and carbon dioxide. By this mechanism no side reactions are to be expected. Furthermore, the formation of an activated complex containing a six-membered ring would freeze more degrees of freedom than the four-membered ring, and so a more negative entropy of activation is to be expected.

Acknowledgment.—The junior author wishes to express his appreciation to the Ethyl Corporation for a fellowship grant in support of part of this work.

Summary

Isopropyl chlorocarbonate has been found to decompose in the range 180–220°. The decomposition is homogeneous and first order, following the equation $k = 3.1 \times 10^9 e^{-26360/RT}$. Two simultaneous decomposition reactions occur, one producing isopropyl chloride and carbon dioxide, and the other producing propylene, hydrogen chloride and carbon dioxide. Mechanisms of internal rearrangement are proposed.

RECEIVED MARCH 29, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS OF DUKE UNIVERSITY]

Vapor Pressures of Trimethylbenzenes in the Low Pressure Region[1,2]

BY E. R. HOPKE AND G. W. SEARS

The vapor pressures of the isomeric trimethylbenzenes have been reported in the region 10–750 mm. A study of the ultraviolet absorption spectra of these compounds in the vapor, which is in progress in this Laboratory, made it desirable to have vapor pressure data available in the region 0.01–1.0 mm. The measurements were made with a Rodebush manometer.

Compounds.—These samples of API–NBS hydrocarbons have been made available through A. P. I. Research Project 44 on the "Collection analysis, and calculation of data on the properties of hydrocarbons." The samples were purified at the National Bureau of Standards by the A.P.I. Research Project 6 on the "Analysis, purification, and properties of hydrocarbons" under the direction of Frederick D. Rossini, from material supplied by the following laboratories: mesitylene and hemimellitene, by the A.P.I. Research Project 45 on the "Synthesis, and properties of hydrocarbons of low molecular weight" at the Ohio State University under the supervision of Cecil E. Boord, pseudocumene, by the A.P.I. Research Project 6 on the "Analysis, purification, and properties of hydrocarbons" at the National Bureau of Standards under the supervision of Frederick D. Rossini. The mesitylene (1,3,5-trimethylbenzene) was stated to contain 0.04 ± 0.02 mole % impurities; the pseudocumene (1,2,4-trimethylbenzene) was stated to contain 0.32 ± 0.20 mole % impurities; and the hemimellitene (1,2,3-trimethylbenzene) was stated to contain 0.010 ± 0.009 mole % impurities.

Experimental

The vapor pressure measurements were made with a Rodebush gage of the type described by Rodebush and Henry.[3] The calibration of the gage has been previously described by Sears and Hopke.[4]

A 0.5-ml. sample of the compound under investigation was vacuum distilled into an outgassed break-seal vessel. This vessel was sealed on to the vapor enclosure via a seal-off constriction. After the gage had been evacuated to 10^{-6} mm. accompanied by torching, the break-seal was broken and the compound was distilled into the vapor enclosure. The sample was frozen out with Dry Ice and the empty break-seal vessel was sealed off from the gage.

The sample was then melted and refrozen with Dry Ice with the vapor enclosure closed off from the vacuum pumps. The enclosure was then opened to the vacuum and the evolved gases were removed by a ten-minute pump-out period. The outgassing procedure was carried out four times in all.

An attempt to measure the vapor pressure of the sample following this outgassing procedure was abandoned when it was found that the sample continued to evolve a volatile substance. Since the gage contained, beside the com-

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[1] This investigation was assisted by the Office of Naval Research under contract N6Ori-107, Task Order I, with Duke University.

[2] Taken from part of a thesis submitted by E. R. Hopke in partial fulfillment of the requirements for the degree of Master of Science at Duke University.

[3] Rodebush and Henry, THIS JOURNAL, **52**, 3159 (1930).

[4] Sears and Hopke, *J. Phys. Chem.*, **52**, 1137 (1948).

pound, only outgassed glass and quartz the volatility was attributed to the sample. In order to remove the volatile constituent it was necessary to subject the sample to a high vacuum for thirty-six hours while frozen out with dry ice.

In view of the known purity of these compounds the presence of a volatile impurity was surprising. However, a calculation showed that the presence of 10 p. p. m. of a low molecular weight organic impurity would be sufficient to cause the observed effect. This represents but a small fraction of the known impurity and would be undetectable in vapor pressure measurements at a higher pressure region.

In these measurements the presence of the volatile component tended to make the measured pressures high and the slopes of the vapor pressure plots low. To avoid error from this source the measurements were repeated over a several day period. Their continued reproducibility was taken as proof of the removal of the volatile constituent.

After the vapor pressure data on a given compound were taken, the material was distilled out of a Rodebush gage into a seal-off tube. The tube was sealed off while the compound was frozen out with Dry Ice. The refrigerant was taken off all traps, and the system was pumped out with the diffusion pump for twenty-four hours. This guaranteed the complete cleanliness of the system before the admission of a new compound.

Results

The vapor pressure of mesitylene was measured over the temperature range −18 to −5°. The vapor pressures of pseudocumene and hemimellitene were measured over the temperature ranges −16 to −6°, and −14 to −3°, respectively. Each set of data was treated by the method of least squares to fit an equation of the form

$$\log_{10} P = -(A/T) + B \qquad (1)$$

where P is the pressure in mm. and T is the absolute temperature. The ice point was taken as 273.2°K.

Table I

	A	B
Mesitylene	2667.51	9.394
Pseudocumene	2432.42	8.437
Hemimellitene	2219.69	7.508

Table I gives the constants of equation 1 for the respective compounds and Fig. 1 represents the experimental data and the calculated curve for each compound. Curve (1) represents mesitylene, curve (2) psuedocumene, and curve (3) hemimellitene.

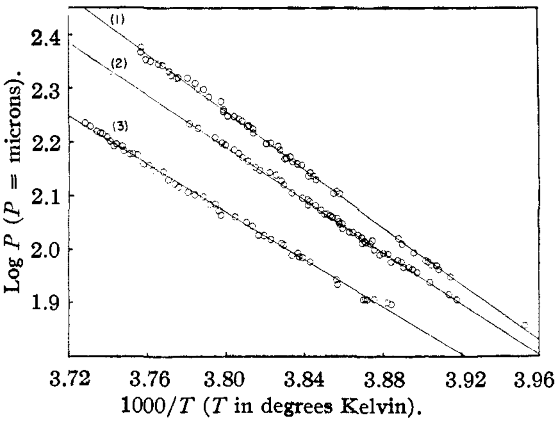

Fig. 1.—Vapor pressures: (1) mesitylene, (2) pseudocumene, (3) hemimellitene.

Discussion

A word should be said at this point concerning the accuracy of the present data. The absolute error of pressure measurements was estimated to be 4.8%. This figure included the error in vapor pressure caused by uncertainty in the temperature scale. For each compound an average deviation has been calculated. This represents the self-consistency of the data in terms of closeness of fit to the least squares equation. The average deviations were 1.08, 0.73, 1.06% for mesitylene, pseudocumene and hemimellitene, respectively.

Woringer[5] has measured the vapor pressures of mesitylene and pseudocumene by a static method. Comparison with the present data indicates that insufficient outgassing has caused his results to be in error by a factor of about ten. Consequently no consideration was taken of his data.

The vapor pressure of mesitylene has also been measured by Linder,[6] Kassel[7] and Stuckey and and Saylor.[8] The experimental technique of Stuckey and Saylor appeared to be superior to that of Kassel, whose data were judged to be more accurate than that of Linder. Since only Stuckey and Saylor used carefully purified mesitylene, their measurements were compared to the present data by extrapolation.

The average deviation in the vapor pressure of mesitylene in the present investigation was 1.08%; the average deviation in Stuckey and Saylor's data was 0.7%. When the present data are extrapolated up to 0°, a value of 0.427 mm. was obtained compared to 0.423 mm. obtained by extrapolating Stuckey and Saylor's data downward to 0°. In view of the larger absolute error in the measurements such agreement is fortuitous.

The vapor pressure of pseudocumene has been measured by Smith and Lund.[9] Their data have been fitted by API-NBS Research Project 44[10] to the Antoine equation. The measurements of the former have been made on carefully purified material. From their data on deviations we calculated an average deviation of 8.8% for five experimental points from 8 to 58 mm. While the exact value of this error was given no significance, it was taken to indicate that the self-consistency of their data was substantially less than the Stuckey and Saylor data on mesitylene.

The Antoine equation on pseudocumene extrapolated to 0° gives a vapor pressure of 0.363

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(5) Woringer, *Z. physik. Chem.*, **34**, 257 (1900).

(6) Linder, *J. Phys. Chem.*, **35**, 531 (1931).

(7) Kassel, This Journal, **58**, 670 (1936).

(8) Stuckey and Saylor, *ibid.*, **62**, 2922 (1940).

(9) Smith and Lund, *ibid.*, **52**, 4144 (1930).

(10) American Petroleum Institute Research Project 44 at the National Bureau of Standards. Selected Values of Properties of Hydrocarbons, Table No. K-5, Vapor Pressures and Boiling Points, June 30, 1944.

mm. in comparison to 0.342 mm. obtained by extrapolation of the present data upward. The agreement is considered satisfactory in view of errors in the two methods.

The vapor pressure of hemimellitene has been measured by Smith and Spillane[11] on carefully purified material. They used the method of Smith and Lund.[9] Their data have been fitted by the API–NBS Research Project 44[10] to the Antoine equation. The extrapolations of the Antoine equation downward and the present data upward to 0° give 0.255 mm. and 0.242 mm., respectively. The agreement was considered satisfactory.

It was called to the authors' attention that the heats of vaporization calculated from equation (1), Table I, are in discrepancy with calorimetrically measured values[12] in the cases of pseudocumene and hemimellitene. The short temperature range of this investigation, the recognized errors in temperature and pressure, and the difficulty of removal of the last traces of the volatile component undoubtedly account for these discrepancies.

In order to obtain the best representation of vapor pressures over the range covered, the present data and the extrapolated calorimetric heats of vaporization were combined to fit an equation of the type

$$\log p = -(A/T) - B \log T + C \qquad (2)$$

The constants of the equations are given in Table II for the three isomeric trimethylbenzenes. The average deviations of the present data from equation (2) is also tabulated for each compound.

TABLE II

	A	B	C	Av. % deviation
Mesitylene	4106.4	12.588	45.3277	1.0
Pseudocumene	4120.6	12.588	45.3311	1.6
Hemimellitene	4182.2	12.588	45.4053	4.0

As a check on the validity of the calibration the vapor pressure of water was measured from -40 to $-32°$. The results were compared with the data of Scheel and Heuse,[13] who made careful measurements over the same temperature range using the Rayleigh manometer. The present vapor pressure data were about 4% higher, but slopes of the vapor pressure curves were alike. The average deviation of Scheel and Heuse's data from their calculated vapor pressure curve was 2.2% over the temperature range in question. The agreement was thus quite satisfactory.

Acknowledgments.—The authors wish to acknowledge the continued interest of Dr. Hertha Sponer at whose suggestion this investigation was undertaken.

One of us (E.R.H.) held a research assistantship which was supported by a grant-in-aid from the Duke University Research fund.

Acknowledgment is made to the American Petroleum Institute and the National Bureau of Standards for the loan of samples measured in this investigation.

Summary

1. The vapor pressures of the three isomeric trimethylbenzenes were measured in the region 0.01–1.0 mm. by a Rodebush manometer.

2. The data were fitted to the equation

$$\log_{10} P = -(A/T) + B$$

by the method of least squares.

3. The data were compared by an extrapolation method to the data of previous workers in a higher pressure range. The agreement was satisfactory.

DURHAM, N. C.

RECEIVED APRIL 30, 1948

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[11] Smith and Spillane, THIS JOURNAL, **62**, 2639 (1940).

[12] Osborne and Ginnings, *J. Research Natl. Bur. Standards*, **39**, 453 (1947).

[13] Scheel and Heuse, *Ann. Physik*, **29**, 723 (1909).

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXXV. Conductance of Some Long Chain Salts in Methanol–Water Mixtures[1]

BY PHILIP F. GRIEGER AND CHARLES A. KRAUS

I. Introduction

In a previous paper of this series,[2] the effect of added methanol on the equivalent conductance of long chain electrolytes in aqueous solution was described. It was found that in the case of *n*-octadecyltrimethylammonium nitrate and *n*-hexadecylpyridonium bromide, the breakpoint concentration increases with increasing methanol content of the solvent, while the critical phenomenon becomes less pronounced. On the other hand, for *n*-octadecylpyridonium chloride in methanol–water mixtures, the form of the conductance curve differs strikingly from that in water. While the usual "breakpoint" phenomenon is observed in water, in mixtures containing 10 to 35% methanol, Λ passes through a maximum at concentrations in the neighborhood of the critical concentration in water. This is apparently the first observation of such an effect in solutions of simple paraffin-chain salts.[3]

Since *n*-octadecylpyridonium bromide shows the

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[1] This paper is based on a portion of a thesis presented by Philip F. Grieger in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, June, 1947.

[2] Evers and Kraus, THIS JOURNAL, **70**, 3049 (1948).

[3] Robinson and Garrett, *Trans. Faraday Soc.*, **35**, 771 (1939), found maxima in the equivalent conductance of certain dyes.