standing, yellow needles separated which were recrystallized from 70% methyl alcohol; m. p., 150–152°; $[\alpha]_D^{25} = -20.24$ in methyl alcohol. They were dried in a vacuum desiccator over sulfuric acid for analysis.

Anal. Calcd. for $C_{24}H_{32}N_4O_8.H_2O$: C, 53.50; H, 6.37; N, 10.42. Found: C, 53.29, 53.05; H, 6.46, 6.38; N, 10.64, 10.50.

The author is indebted to Dr. C. S. Hudson for helpful suggestions.

Summary

Gentiobiose has been identified through the isolation of its β-octa-acetate in pure, crystalline form, as one of the constituents of the mother liquor ("hydrol") obtained in the commercial manufacture of crystalline *d*-glucose.

It has been shown, through a comparison of physical and chemical properties, that the unfermentable part of hydrol, while closely resembling isomaltose, contains only a comparatively small amount of gentiobiose, and criticism, therefore, is made of applying the name "isomaltose," which should presumably indicate a definite sugar, to a product that apparently consists of a mixture of carbohydrates.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

STUDIES IN VAPOR PRESSURE. II
THE MONONITROTOLUENES

BY J. F. T. BERLINER AND ORVILLE E. MAY

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Many of the earlier determinations of the vapor pressures of the more important organic compounds that enter into the manufacture of dyes are unreliable owing to the lack of refined instruments for making observations and to the impurity of the materials measured. As a result of these conditions, the National Research Council has suggested that the vapor pressures and boiling points of these compounds be determined by the more accurate methods now available. This paper gives the results of a study of the vapor pressures of the three isomeric nitrotoluenes, and their latent heats of vaporization and entropies have also been derived. The method used to measure the vapor pressures and the means employed to calculate their vapor-pressure equations, latent heats of vaporization, and entropies are given in detail in a recent communication.[1]

Materials

The nitrotoluenes used in this investigation, which were the purest procurable, were further purified as follows.

The *o*-nitrotoluene was distilled, the first and last sixth of the distillate being dis-

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[1] Berliner and May, THIS JOURNAL, **47**, 2350 (1925).

carded. The collected distillate was then crystallized thrice by freezing with a mixture of ether and solid carbon dioxide, the first portion to crystallize being discarded in each case. This material was refluxed for about one hour with animal charcoal, distilled from the charcoal, and distilled two more times, the first and last sixth of the distillates being discarded each time. In the last two distillations the fraction collected was distilled within a range of 0.2°. The color of the final product was a very pale straw-yellow.

The *m*-nitrotoluene was purified by distillation as described in the case of the *o*-nitrotoluene, after which it was crystallized by freezing four times in an ice-bath, the first portion to crystallize being utilized. The final product was a shade darker than the *o*-nitrotoluene.

The *p*-nitrotoluene was distilled and crystallized four times from 95% ethyl alcohol. This fraction, having a melting point of 51.6° was then distilled under reduced pressure and recrystallized twice from pure benzene. The material crystallized in stout, white prisms and melted at 51.6°.[2]

Results

The determinations of the vapor pressures were made at approximately 2° intervals. The results of several runs on each compound were plotted. The maximum variation between the separate runs on the same compound was of the order of 1 to 4 mm. pressure.

These curves were drawn to a very large scale in order to reduce, as much as possible, any inaccuracy in reading the values of the corresponding temperatures and pressures. From this smoothed curve the equations for the vapor pressure were derived by the use of the Clapeyron-Clausius equation of state as explained in the first paper of this series.[1] The values calculated by this means agree with the smoothed curve to ±0.3 mm.

The equations derived for the vapor-pressure curves of the three nitrotoluenes and their latent heats of evaporation[1] over the temperature range studied are given in Table I. The latent heats of evaporation as calculated from the data remained practically constant over this range. The temperature (T) is expressed on the absolute scale.

TABLE I

PROPERTIES OF MONONITROTOLUENES

Nitrotoluene	L	Log p	B. p., °C. (760 mm.)
o	11,246	$7.97285 - 2513.0/T$	220.38
m	11,990	$8.06553 - 2618.2/T$	231.87
p	11,945	$7.98149 - 2608.9/T$	238.34

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[2] There appears to be a discrepancy between the various determinations of the melting point of *p*-nitrotoluene reported in the literature. Some of the values recorded are 54° (Beilstein); 52° (Mulliken); 58° (Van Nostrand's Chemical Annual, 1923); 54° (Neubeck); 51.6–51.9° (Chemist's Year Book, 1924); 51.4° (Color Index, 1924).

Dr. Ernest Anderson and Mr. Henry Eyring of the University of Arizona have very generously allowed us to use some of their unpublished data on the physical properties of *p*-nitrotoluene. They purified their *p*-nitrotoluene by recrystallizing it from absolute alcohol and ether, fractionally distilling and finally fractionally recrystallizing the solid from the molten material, using no solvent. The melting point of the material thus obtained was very accurately determined by them and found to be 51.63°, which we believe to be the correct value.

The vapor-pressure curves for the three isomeric nitrotoluenes are shown for the sake of comparison in Fig. 1.

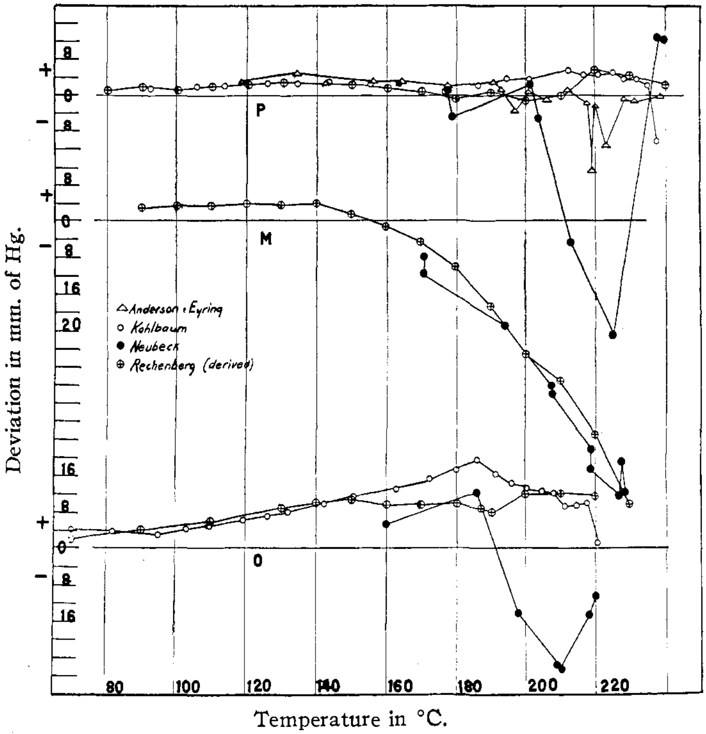

Fig. 1.

The entropies of vaporization of these compounds were calculated by the methods suggested by Hildebrand[3] in order to determine whether the nitrotoluenes form normal or associated liquids. They show (Table II) that the nitrotoluenes form normal liquids, that is, S = approximately 13.7 cal. per degree.

TABLE II

ENTROPIES OF VAPORIZATION OF THE NITROTOLUENES = $L/RT^a = S$

Nitrotoluene	T	S
o	416.30	13.6
m	427.17	14.0
p	431.46	13.9

[a] T is the temperature on the absolute scale at which the concentration of the vapor is 0.00507 mole per liter.

From a consideration of the Clapeyron-Clausius equation of state, after reduction and integration, it is evident that when the heat of vaporization remains constant over a limited temperature range, the ratio of the loga-

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[3] Hildebrand, THIS JOURNAL, **37,** 970 (1915).

rithmic value of pressure to the reciprocal of the absolute temperature is a constant. Therefore, when these two variables are plotted against each other, a straight-line relationship will appear.

Comparison with the Data of Others

Vapor-pressure determinations of *o*-nitrotoluene have been made by Neubeck[4] and by Kahlbaum.[5] Measurements on the *m*-nitrotoluene were made by Neubeck and on the *p*-nitrotoluene by Neubeck, by Kahlbaum, and by Dr. Anderson and Mr. Eyring of the University of Arizona in connection with their study of the physical properties of this substance. The boiling point of *p*-nitrotoluene determined by Anderson and Eyring at atmospheric pressure is identical with that determined by us although the materials used were purified by different methods and the vapor pressures were determined by the simple dynamic boiling-point method.

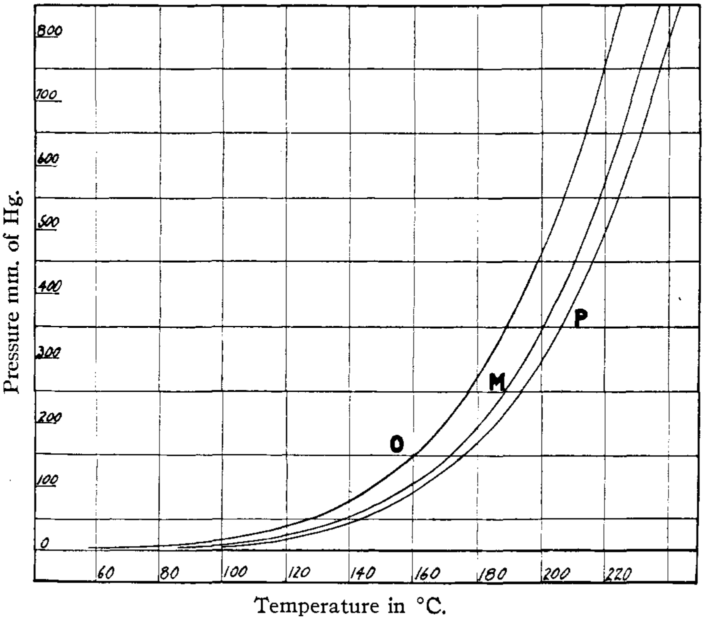

Fig. 2.

Other values for the vapor pressures of these compounds are those reported in the excellent treatise of Rechenberg.[6] These values are not independent observations but are calculated, by means of the Dühring relation (plotted against *n*-hexane) from the results of vapor-pressure determinations by Kahlbaum and by Neubeck and from the boiling-point data given by others.

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[4] Neubeck, *Z. physik. Chem.*, **1,** 649 (1887).

[5] Kahlbaum, *ibid.*, **26,** 603 (1898).

[6] Rechenberg, "Einfache und Fraktionierte Destillation in Theorie und Praxis," Schimmel and Co., Leipzig, **1923.**

The boiling points recorded in the literature for *o*-nitrotoluene are 218° (Beilstein); 218.4° (734 mm.) (Neubeck); 220.4° (Kahlbaum); 220.96° (Rechenberg).

For the *m*-nitrotoluene the following boiling points are given: 230–231° (Beilstein); 227.5° (736 mm.) (Neubeck); 228.63° (Rechenberg).

The following boiling points are reported for *p*-nitrotoluene: 238.0° (Beilstein); 239.0° (Neubeck); 237.7° (Kahlbaum); 239.0° (Rechenberg); 238.3° (Anderson and Eyring).

These data are plotted in terms of their deviation from our empirical equation in Fig. 2.

Summary

The vapor pressures of the three isomeric mononitrotoluenes have been determined from 50° to a few degrees above their respective boiling points. The boiling points at atmospheric pressure have been found to be as follows: *o*-nitrotoluene, 220.38°; *m*-nitrotoluene, 231.87°; *p*-nitrotoluene, 238.34°.

The latent-heat equations have been derived and the latent heats of vaporization calculated. The pressures calculated from these equations agree well with the observed values.

The entropies of vaporization at a concentration of 0.00507 mole per liter indicate that the molten mononitrotoluenes are normal liquids.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

COMPLEX SALTS OF QUINOLINE, MERCURIC HALIDES AND ALKYL HALIDES, AND SOME ISOMERS

BY WILLIAM M. DEHN AND HARVEY COPE

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In two earlier papers[1] it was shown that complex salts of quinoline, metallic halides and hydrohalogen acids conform to types such as Q.MXn.HX, 2Q.MXn.HX, 2Q.MXn.2HX, 2Q.3MXn.2HX and also to certain hydrated forms of these types. Other types, as found in the literature, seem of doubtful existence.

In connection with these studies it was anticipated that if HX of these types were substituted by RX, salts of analogous composition could be formed, because some types, containing quaternary derivatives of quinoline[2] and other bases,[3] though comparatively rare, are found in the literature.

It is known that compounds of the composition Q.RX are more stable toward hydrolysis than compounds of the composition Q.HX, so it was

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[1] Dehn, THIS JOURNAL, **48**, 275, 278 (1926).

[2] See $2(Q.C_2H_5Cl).PtCl_4$ of Williams [*Jahresber.*, **9**, 534 (1856)]; $2(Q.C_5H_{11}Cl).PtCl_4$ of Tosse [*Ber.*, **16**, 1279 (1882)]; $Q.CH_3Cl.AuCl_3$ of Ostermayer [*Ber.*, **18**, 593 (1884)]; $Q.CH_3I.CuI$ of Kohn [*Monatsh.*, **33**, 419 (1912)].

[3] See $(CH_3)_4NI.HgI_2$ and $(C_2H_5)_4NI.HgI_2$ of Risse [*Ann.*, **107**, 223 (1858)].