that parallel experiments be made with known alcohols, so that the identity of the esters obtained may be confirmed by the determination of the melting points of mixtures. Special tests have shown that all the pairs of mono-alkyl nitrophthalates listed which have melting points sufficiently near to one another to be readily confused, form mixtures with much lower melting points. It is accordingly believed that 3-nitrophthalic anhydride may be found generally useful for the identification of the simpler alcohols.

Summary

The use of 3-nitrophthalic anhydride as a reagent for the qualitative identification of alcohols has been studied. The results reported seem to justify a recommendation for the use of the procedure outlined.

CHICAGO, ILLINOIS

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STUDIES IN VAPOR PRESSURE. I. THE NITRO-ANILINES

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

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The vapor pressures and boiling points of numerous organic compounds have been determined by methods that have, in many cases, proved unreliable. The physical constants of a very large number of these compounds, particularly the intermediates used in the manufacture of dyes, have never been determined. As a result of these conditions the National Research Council has requested that the vapor pressures and boiling points of these compounds be determined by the more accurate methods that are in use at the present time.

This paper reports a study of the vapor pressures of the three isomeric nitro-anilines and gives their latent heats of vaporization and entropies.

A comprehensive study of the vapor pressures of the more important organic compounds that enter into the manufacture of dyes is being undertaken, and the results of these studies will appear in subsequent publications.

The method used for the measurements here recorded was devised by Smith and Menzies.[1] This method has been used in the accurate determination of the vapor pressures of a number of organic compounds, among which may be mentioned phthalic anhydride,[2] naphthalene, anthracene, phenanthrene, anthraquinone,[3] carbazole[4] and the mono- and dimethyl- and -ethylanilines.[5]

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[1] Smith and Menzies, THIS JOURNAL, **32**, 1416 (1910).

[2] Monroe, *J. Ind. Eng. Chem.*, **12**, 969 (1920).

[3] Nelson and Senseman, *ibid.*, **14**, 58 (1922).

[4] Senseman and Nelson, *ibid.*, **15**, 382 (1923).

[5] Nelson and Wales, THIS JOURNAL, **47**, 867 (1925).

The method employed was essentially that described by Nelson and Senseman, with the exception that a U-tube leveling type of isoteniscope was employed instead of the "bubbling" type.

The nitro-anilines decompose at temperatures below their boiling points. As the extent of this decomposition is a function of the time and temperature, it was necessary to devise a means whereby the temperature of the bath could be very quickly lowered. The system adopted was, essentially, one by which hot sulfuric acid in the bath was siphoned into a cooling reservoir, while cold sulfuric acid was simultaneously introduced into the bath. By this procedure a lowering of the temperature of approximately 200° could be effected in from one to two minutes.

The temperature measurements were made entirely by means of copper-constantan thermo-elements, which were calibrated according to the procedure recommended by Adams.[6] The temperatures were determined to within ±0.01°, using a d'Arsonval type galvanometer and a Type K Leeds and Northrup potentiometer. The pressures were read directly from a manometer with the aid of attached lenses, which made it possible to determine the pressures to within ±0.2 mm.

Materials

The nitro-anilines used in this investigation were the purest procurable and were purified as follows.

The *o*-nitro-aniline was converted into the hydrochloride; this was dissolved in aqueous hydrochloric acid solution and the solution concentrated. The first material to separate from the solution was discarded. The salt was hydrolyzed with dil. sodium carbonate and recrystallized thrice from 95% ethanol; m. p., 71.5° (corr.). Two further recrystallizations from pure benzene produced no change in the above melting point.

The *m*-nitro-aniline was recrystallized thrice from pure benzene; m. p., 112.5° (corr.). Two precipitations from alcoholic solution by means of distilled water did not change the melting point.

The *p*-nitro-aniline was converted into the hydrochloride, which was recrystallized several times from 1:1 hydrochloric acid solution. The salt was then hydrolyzed with dil. sodium carbonate solution and the base was recrystallized four times from 95% ethanol; m. p., 147.8° (corr.). Two further recrystallizations from ether produced no change in the melting point.

All of these materials were kept in a desiccator over anhydrous calcium chloride until used.

Results

The vapor pressures of the nitro-anilines were determined from about 160° to temperatures somewhat above their actual boiling points. As mentioned above, all the nitro-anilines decompose at temperatures below those at which they boil under atmospheric pressure. *o*-Nitro-aniline decomposes to a small extent at temperatures just below its boiling point,

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[6] Adams, *Am. Inst. Min. Met. Eng. Bull.*, **153** (1919).

while *p*-nitro-aniline is almost completely decomposed at temperatures about 50° below its calculated boiling point.

The approximate temperatures at which notable decomposition took place could be readily observed by the rapid darkening of the material under observation.

From the observed results the latent heat of vaporization was calculated by applying the well-known Clapeyron equation of state which, over short ranges of temperature, may be considered either as remaining constant or as a linear function of the absolute temperature. If the volume of the liquid, which is negligible in comparison with the volume of the vapor, be disregarded, the equation takes the form of $\mathrm{d}P/\mathrm{d}T = L/RT^2/P$ which upon integration and solving for L, the latent heat of vaporization, becomes $L = (ln\ p_2 - ln\ p_1)\ T_1T_2R/(T_2 - T_1)$.

From the calculated values of the latent heat of vaporization, the equation may be derived representing it as a function of the absolute temperature, over the ranges used in these studies. This may be expressed by $L = a + bT + cT^2 \ldots$ etc., where $a, b, c, \ldots$ etc., are constants.

In general, if the latent heats of vaporization were plotted against the temperatures, the curves would become steeper with the rise in temperature, until at the critical temperatures they would be perpendicular to the temperature axis. For this reason the equations derived for the latent heats of vaporization as functions of the absolute temperature do not hold true much above the highest temperatures recorded and cannot be used for calculating the critical temperatures and pressures.

Substituting the value of the latent heat of vaporization in the above equation and integrating, the Clapeyron equation of state becomes $ln\ p = c - a/RT + b/R\ lnT + CT/R \ldots$ etc., where c is the constant of integration, p the vapor pressure in millimeters of mercury, T the absolute temperature, R the gas constant (= 1.9885) and $a, b, c, \ldots$ etc., are the constants of the equation of the latent heat of vaporization. It will be noted that the constant b, which is the slope of the latent-heat curve, must always be a negative quantity, as the heat of vaporization is lowered as the temperature is increased.

TABLE I

o-NITRO-ANILINE

L = 15,280. Log p = 8.86842 — 3336.52/T. Calculated b. p. = 284.11°. Temperature at which decomposition becomes appreciable = 270°.

	Pressure, mm. of Hg			Pressure, mm. of Hg	
Temp. °C.	**Obs.**	**Calcd.**	Temp. °C.	Obs.	Calcd.
150	10.6	9.9	220	126.2	126.6
155	13.0		225	145.4	
160	16.2	15.4	230	172.0	172.6
165	18.4		235	198.2	
170	22.2	22.1	240	232.4	232.4
175	26.0		245	268.7	

TABLE I (*Concluded*)

	Pressure, mm. of Hg			Pressure, mm. of Hg	
Temp. °C.	Obs.	Calcd.	Temp. °C.	Obs.	Calcd.
180	32.0	32.0	250	309.8	309.2
185	38.2		255	357.8	
190	46.3	46.2	260	407.0	407.4
195	55.8		265	466.7	
200	65.6	65.5	270	538.5	531.3
205	78.7		275	627.4	
210	91.4	91.7	280	743.6	686.1
215	106.6		285	922.0	
			290	...	877.9

TABLE II

m-NITRO-ANILINE

L = 15,758. Log $p = 8.81881 - 3440.93/T$. Calcd. b. p. = 306.35°. Temperature at which decomposition becomes appreciable = 270°.

170	11.2	11.3	245	147.4	
175	13.5		250	170.4	170.3
180	16.9	16.9	255	198.8	
185	20.0		260	230.4	230.7
190	24.6	24.5	265	265.6	
195	30.0		270	304.2	304.5
200	35.4	35.3	275	356.2	
205	42.8		280	433.4	396.3
210	49.4	49.8	285	533.0	
215	57.4		290	653.2	511.1
220	69.0	69.3	295	855.0	
225	80.4		300	...	650.3
230	95.2	95.4	305	...	719.2
235	109.8		310	...	827.9
240	129.8	129.7			

TABLE III

p-NITRO-ANILINE

L = 18,500. Log $p = 9.55950 - 4039.74/T$. Calcd. b. p. = 331.73°. Temperature at which decomposition becomes appreciable = 260°.

190	8.5	8.1	255	80.5	
195	9.2		260	95.4	95.9
200	11.0	10.6	265	116.8	
205	13.4		270	155.0	132.2
210	16.1	15.8	275	210.6	
215	19.4		280	...	178.4
220	23.2	23.3	290	...	243.0
225	28.2		300	...	324.2
230	33.9	33.7	310	...	429.3
235	40.9		320	...	559.0
240	49.0	48.6	330	...	717.0
245	58.9		334	...	804.9
250	68.7	68.7			

By means of the above relations the vapor-pressure equations for the three nitro-anilines were derived from the recorded observations. The vapor pressures at 10° intervals have been calculated and these values are given in Tables I, II and III, with the observed pressures, which are given at 5° temperature intervals.

It will be noted that the calculated values for the vapor pressure are in very close agreement with the observed values for temperatures below about 270° for the *o*-nitro-aniline and the *m*-nitro-aniline and about 260° for the *p*-nitro-aniline. It was at these temperatures that the darkening and decomposition, previously referred to, were noted.

In order to determine whether appreciable decomposition occurred, the samples were rapidly cooled from various temperatures and the vapor-pressure determinations repeated. Care was taken in cooling to diminish the outside pressure at such a rate that no air or gas contained in the system was drawn back into the isoteniscope. The results of these experiments showed that the vapor pressures of the materials, when cooled from temperatures lower than those designated above, were identical with the vapor-pressure determinations of the original materials, thereby indicating that no decomposition sufficient to affect the vapor pressure of the material had taken place.

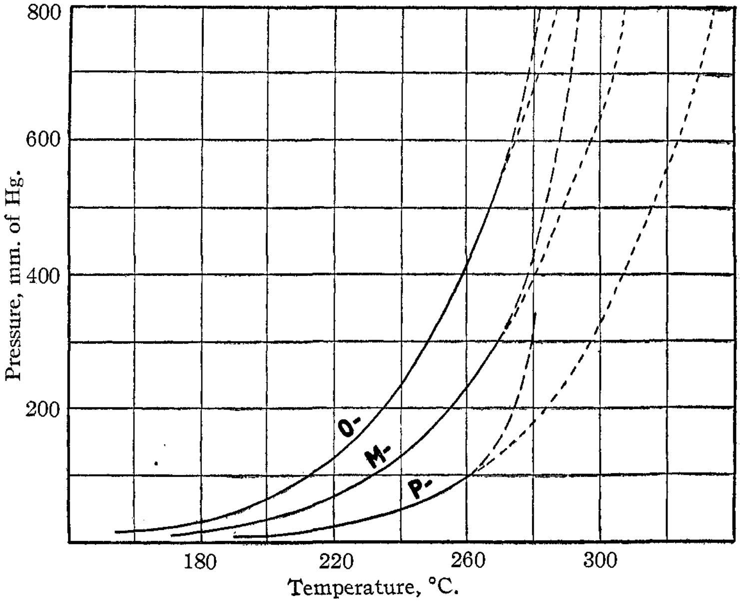

Fig. 1.—Observed and calculated ———. Observed — — —. Calculated - - - -.

A fresh sample of material was used for every run and from seven to ten runs were made on each of the nitro-anilines.

Fig. 1 shows the deviation, due to decomposition, between the observed and calculated results. Above the temperatures at which the curves cease to coincide the observed values have no true significance, as the vapor pressure above these temperatures is merely a function of the time and the rate of heating. However, for these observations the rate of heating was maintained fairly constant (approximately 1° per min.), thereby allowing the results to be in some degree comparative.

The values derived from the equations represent the theoretical vapor pressures that the nitro-anilines would exert if no decomposition occurred. This limit is very closely approached by the *o*-nitro-aniline for the rate of heating employed. No doubt a more rapid rate of heating would allow the observed and calculated values of the *o*-nitro-aniline to coincide throughout the temperature range studied.

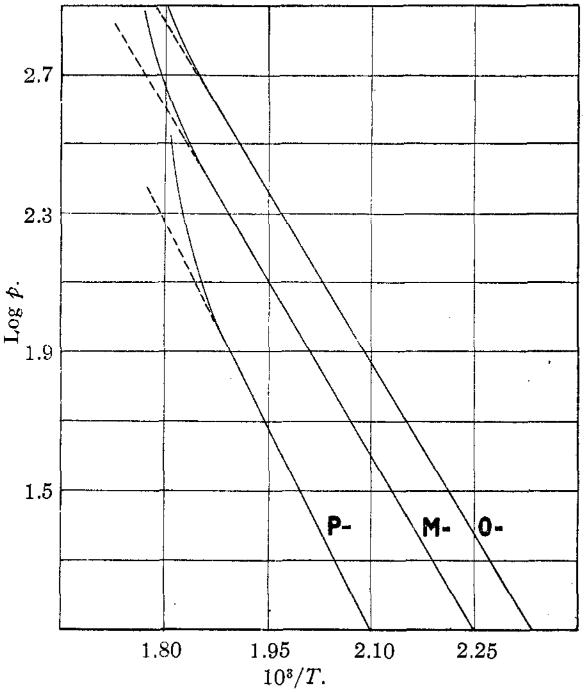

Fig. 2.

In Fig. 2 the logarithms of the pressures of the nitro-anilines are plotted against the reciprocals of the absolute temperatures. It is to be noted that a perfect straight-line relation exists up to the temperature at which decomposition ensued. When, as is the case in the three nitro-anilines throughout the temperature ranges studied, the latent heat does not, observably, vary with the temperature, the above relation must necessarily be of a straight-line type, since when $L = a$, then $\log p = C + a/T$. Above the temperatures at which decomposition occurred this relationship no longer holds and the amount of divergence is indicated in Fig. 2 by the dashed lines which are the extensions of the log $p:1/T$ relation for the undecomposed nitro-anilines.

The only boiling point for the nitro-anilines recorded in the literature is that given for the *m*-nitro-aniline. Beilstein gives its boiling point at 285°; a temperature of 286° is recorded in the Landolt-Börnstein tables. A sample of pure *m*-nitro-aniline was introduced into a distillation flask and heated very rapidly. The *m*-nitro-aniline boiled at about 305–307° for about two minutes with profound decomposition. This temperature closely approaches the calculated boiling point for this material.

The entropy of vaporization of these compounds has been calculated in order to determine whether the nitro-anilines form normal or polar liquids. The entropy of vaporization is found by dividing the product RT, where T represents the absolute temperature at which the concentration of the vapor is 0.00507 mole per liter, into the latent heat of vaporizations at this temperature. The entropy of vaporization at this concentration of vapors, according to Hildebrand,[7] should be about 13.7 cal. per degree for every normal liquid.

TABLE IV

ENTROPIES OF VAPORIZATION OF THE NITRO-ANILINES $= L/RT = S$

	Obs. temp.	S
o-Nitro-aniline	480.9	16.0
m-Nitro-aniline	500.4	15.7
p-Nitro-aniline	530.4	17.5

Table IV shows that the entropies of vaporization of the nitro-anilines, at the temperatures defined, do not approach the value of 13.7, and therefore they do not form normal liquids.

Summary

1. The vapor pressures of the three isomeric nitro-anilines have been determined. It was found that all decomposed to some extent before their boiling points at atmospheric pressure were attained, the *p*-nitro-aniline decomposing completely, while the *o*-nitro-aniline was decomposed to a small extent.
2. The latent-heat equations have been derived and these correspond very closely with the observed results up to the range where the nitro-anilines decompose.
3. The entropies of vaporization at a concentration of 0.00507 mole per liter of vapor have been determined and indicate that the molten nitro-anilines are not normal liquids.

WASHINGTON, D. C.

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