

2. A series of unsymmetrical tetra-arseno compounds, $\text{RAs}=\text{As}-\text{As}=\text{AsCH}_2\text{COOH}$, has been synthesized for the first time.

3. One member of the previously unknown series of unsymmetrical hexa-arseno compounds, $\text{RAs}=\text{As}-\text{As}=\text{As}-\text{As}=\text{AsCH}_2\text{COOH}$, has been made.

4. The properties of the three new series have been found to conform with predictions made on the basis of their relation to the previously known types of arseno compounds.

5. Similar series are being prepared in which substituted aliphatic arsonic acids other than arsono-acetic acid form the material from which the aliphatic portion of the molecule is derived.

6. More exact proof of the structure of these series is being sought in connection with a general study of the constitution of arseno compounds now in progress in this Laboratory.

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STUDIES IN VAPOR PRESSURE. III. THE TOLUIDINES

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In the previous communications¹ of this series, the method employed for the measurement of the vapor pressure and the means employed to calculate the latent heat of vaporization, the vapor-pressure equations and the entropies of vaporization are discussed in detail. This study is being pursued because of the lack of accurate vapor-pressure data for the organic compounds that enter into the manufacture of dyes and other commodities.

In this paper the measurement of the vapor pressures of the three isomeric toluidines is reported, together with some related physical properties.

In the purer toluidines that are procurable, the principal impurities, besides the isomers, are very small amounts of the nitrotoluene, aniline and complex oxidation products related to the quinones. In some commercial analyses small quantities of aminobenzylamine toluenes have been reported. An excellent separation of the *o*- and *p*-toluidines may be obtained by means of the formation of the dioxalates of these compounds.² The *o*-toluidine dioxalate is considerably more soluble in water and ether than the corresponding *para* compound. In fact, the *p*-toluidine dioxalate is so insoluble in ethyl ether that a practically complete quantitative separation may be accomplished.³ The separation of the *m*-toluidine depends

¹ (a) Berliner and May, *THIS JOURNAL*, **47**, 2350 (1925); (b) **48**, 2630 (1926).

² Rosenstiehl, *Ann. chim. phys.*, [4] **26**, 249 (1872).

³ Wülfing, *Jahresber.*, **39**, 2066 (1886); **40**, 2570 (1887).

on the fact that of the toluidine hydrochlorides, the *meta* compound is several times more soluble in water than the other two, and the *o*- and *p*-toluidine hydrochlorides are relatively insoluble in cold alcohol, while the *meta* derivative is soluble to the extent of about 55 g. per 100 cc. of ethanol at 5°.

The toluidines were purified as follows.

***o*-Toluidine.**—The *o*-toluidine was distilled twice and dissolved in four times its volume of ether. An ethereal solution of an equivalent amount of oxalic acid to form the dioxalate was added and the precipitated *p*-toluidine dioxalate removed by filtration. In this material the *p*-toluidine was present to the extent of 0.08 to 0.1%. The ether was then evaporated and the *o*-toluidine oxalate recrystallized five times from water slightly acidified with oxalic acid, to prevent the hydrolysis of the salt. This purified oxalate was then treated with dil. sodium carbonate solution, and the *o*-toluidine base separated and dried with anhydrous calcium chloride. The base was then distilled thrice under reduced pressure. This pure material was completely colorless; however, on standing exposed to sunlight for three months it took on a light vermilion coloration. This color was accentuated on heating, but was entirely lost upon distillation.

***m*-Toluidine.**—The *m*-toluidine was twice distilled and then heated with a slight excess of hydrochloric acid. This hydrochloride was fractionally crystallized five times from 95% ethyl alcohol and thrice from distilled water. In each case the first material to crystallize from the solution was discarded. This purified *m*-toluidine hydrochloride was then treated with dil. sodium carbonate solution, the base being separated and distilled thrice under reduced pressure. The color of the final product was a very slight straw-yellow.

***p*-Toluidine.**—The *p*-toluidine was distilled thrice and twice sublimed at 30°. It was then dissolved in five times its volume of ether, and an equivalent amount of oxalic acid dissolved in ether was added. The *p*-toluidine dioxalate was removed by filtration, recrystallized thrice from hot distilled water and then treated with a solution of sodium carbonate. The released base, after being crystallized thrice from distilled water, melted at 43.5° (corr.). It was then crystallized seven times from ethyl alcohol without producing any change in the melting point. The material crystallized as pure, white leaflets which, after standing for four months exposed to direct sunlight, showed no change of color.

Various melting points have been reported for this compound, a few of which are 45° by Stadelcr and Arndt,⁴ 42.77° by Mills,⁵ and 42.9° by Mulliken.⁶

Results

An average of eight complete vapor-pressure determinations from 2 to 850 mm. were made on each isomer. All the observations from the several determinations of the pressure exerted by the compound under observation were plotted to a very large scale and an average curve was drawn through these points. The temperature interval between observations was about 2°. The maximum variation of the vapor-pressure observations from the curve representing the average values was about 0.4%, that is, about 3 mm.

⁴ Arndt, *Jahresber.*, 425, 1864.

⁵ Mills, *Phil. Mag.*, [5] 14, 27 (1882).

⁶ Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, 1916.

at 800 mm. pressure. The results presented in the tables are read off these average curves and are correct to within ± 0.2 mm. pressure and $\pm 0.1^\circ$.

No evidence of decomposition was apparent and the same specimen could be used repeatedly. The material in every case assumed a darker shade on heating, but this seemed to have no effect on the vapor pressures of these substances. The vapor pressures of the three toluidines are very similar; in fact, the *o*- and *p*-toluidines apparently exert nearly identical pressures over the lower temperature range.

From the values observed, the vapor-pressure equations were calculated by the application of the expanded and integrated form of the Clausius-Clapeyron equation of state,

$$\ln p = C - (a/RT) + (b/R)\ln T + (c/R)T \dots$$

where C is the constant of integration, p the pressure in millimeters of mercury, T the absolute temperature, R the gas constant (1.9869) and a , b , c , are the constants of the separation of the latent heat of vaporization. The constant b , which in physical terms represents the slope of the heat of vaporization curve, must have a negative value, as the heat of vaporization decreases with an increased temperature.

From this equation, therefore, the equations for the latent heat of vaporization are readily derived. From the vapor-pressure equations it was found that the heats of vaporization of the three isomeric toluidines varied linearly with the absolute temperature over the temperature range investigated.

The equations for the heats of vaporization and vapor pressure of these compounds are given in Table I.

TABLE I
PROPERTIES OF THE TOLUIDINES

Compound	Heat of vaporization equation	Vapor-pressure equation		B. p., $^\circ\text{C}$., at 760 mm.
<i>o</i> -Toluidine	$L = 7670.3 - 2.557 T$	$\log P = 23.8296 - \frac{3480.3}{T} - 5.081 \log T$		199.84
<i>m</i> -Toluidine	$L = 6996.5 - 1.673 T$	$\log P = 18.5043 - \frac{3200.9}{T} - 3.323 \log T$		202.86
<i>p</i> -Toluidine	$L = 7145.8 - 1.951 T$	$\log P = 20.1569 - \frac{3269.3}{T} - 3.877 \log T$		200.35

The equations in Table I are valid only over the temperature range investigated and are not subject to extrapolation for higher or lower values of temperature or pressure.

Their vapor-pressure curves are shown in Fig. 1.⁷ Since the curves are almost coincident over certain ranges, the pressure coördinates have been staggered, so that the curves of these compounds could be distinguished on reproduction.

⁷ Copies of tables giving the actual vapor-pressure determinations at temperature intervals of 5° for the toluidines as well as for the mononitrotoluenes (Ref. 1 b) may be obtained by application to the Research Information Service of the National Research Council at Washington, D. C.

Relatively few vapor-pressure determinations have been made on the toluidines, which is somewhat unusual in consideration of the vast quantities of toluidines that are annually consumed in the industries.

The vapor pressures of the three isomeric toluidines were studied by Neubeck⁸ and Kahlbaum,⁹ Louguinine,¹⁰ in an investigation of the heats of vaporization of several organic compounds, determined the boiling temperature of *o*-toluidine at normal pressure and reported a value of 198.12°. In his excellent work on vapor pressures, Rechenberg¹¹ has derived the vapor pressures of these compounds by means of the Dühring relation, using *n*-hexane as the substance for comparison.

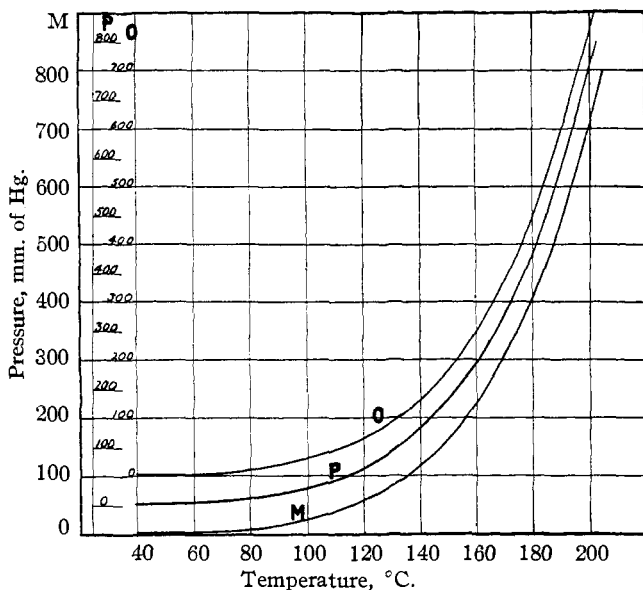


Fig. 1.

In order to determine whether or not these compounds form normal or associated liquids, their entropies of vaporization were calculated by the method suggested by Hildebrand.¹² These values, given in Table II, show that the toluidines form rather highly associated liquids and that the Dühring relation, using a non-associated substance, such as *n*-hexane, as a comparison, will not give as reliable results as if some associated substance, such as water, had been employed for comparison.

⁸ Neubeck, *Z. physik. Chem.*, 1, 649, 657 (1867).

⁹ Kahlbaum, *ibid.*, 26, 600 (1898).

¹⁰ Louguinine, *Ann. chim. phys.*, [7] 27, 105 (1902).

¹¹ Rechenberg, "Einfache und fraktionierte Distillation," Schimmel and Co. Leipzig, 1923.

¹² Hildebrand, *THIS JOURNAL*, 37, 970 (1915).

TABLE II
ENTROPIES OF VAPORIZATION OF THE TOLUIDINES ($S = L/RT$)

Compound	Temp., °C. ^a	S
<i>o</i> -Toluidine	401.6	16.4
<i>m</i> -Toluidine	405.1	15.6
<i>p</i> -Toluidine	402.4	15.8

^a Temperature on the absolute scale at which the concentration of the vapor is 0.00507 mole per liter.

Many values of the boiling points of the toluidines have been reported; however, most of the temperatures are in remarkably close agreement, considering the fact that in many cases no precautions had been taken to correct for barometric pressure, and there is little evidence that an emergent stem correction had been applied or an accurate thermometer employed. The values reported for the *o*-derivative are 197°, Beilstein; 198.45° at 735 mm., Brühl,¹³ 199.7°, Kahlbaum;⁹ 198–198.2° at 730 mm., Neubeck;⁸ and 198.12°, taken by Rechenberg from Louguinine's¹⁰ data.

The boiling points of the *m*-toluidine show a much greater variation; 197°, Beilstein; 199–202°, Buchka and Schachtebeck;¹⁴ 199.0–199.5°, Schraube and Romig;¹⁵ 200–205°, Merz and Müller;¹⁶ 203.3°, Kahlbaum;⁹ 200.5–201.0° at 731.2 mm., Neubeck;⁸ and 203.3°, given by Rechenberg¹¹ from Kahlbaum's data.

For the *para* isomer the boiling points recorded are 198°, Muspratt and Hofmann;¹⁷ 200.4°, Kahlbaum;⁹ 200.0° at 734 mm., Neubeck;⁸ and 200.54°, calculated by Rechenberg.¹¹

Summary

The vapor pressures of the three isomeric toluidines have been determined from about 40° to a few degrees above their normal boiling points. The normal boiling points found were as follows: *o*-toluidine, 199.84°; *m*-toluidine, 202.86°; *p*-toluidine, 200.35°.

The vapor-pressure equations have been calculated and the equations for the heats of vaporization derived therefrom. The calculated values from the vapor-pressure equations agree well with the observed values and the heats of vaporization vary linearly with the temperature.

The entropies of vaporization at a vapor-phase concentration of 0.00507 mole per liter indicate that the toluidines are somewhat highly associated substances.

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¹³ Brühl, *Ann.*, **200**, 189 (1880).

¹⁴ Buchka and Schachtebeck, *Ber.*, **22**, 840 (1889).

¹⁵ Schraube and Romig, *Ber.*, **26**, 579 (1893).

¹⁶ Merz and Müller, *Ber.*, **20**, 548 (1887).

¹⁷ Muspratt and Hofmann, *Ann.*, **54**, 16 (1845).