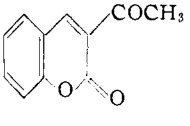
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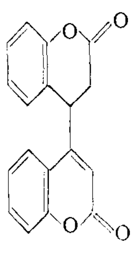
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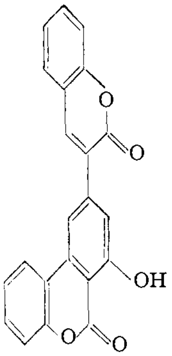
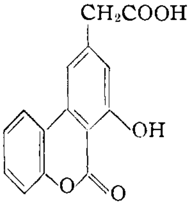

III

The presence of an hydroxyl group is indicated by the formation of an acetate with acetic anhydride. The presence of two coumarin nuclei and a phenolic ring are indicated by the formation of salicylic acid and a phenolic acid, $C_{15}H_{10}O_5$ (IV), when the substance is fused with alkali.

The formation of III involves a Michael condensation in which one molecule of 3-acetocoumarin acts as an acceptor and another as an addendum. The phenolic ring of III is then formed by spontaneous intramolecular aldolization, dehydration and dehydrogenation.

When 3-acetocoumarin is heated with piperidine in acetone, a similar initial reaction takes place, but a molecule of acetone, rather than a second molecule of 3-acetocoumarin, acts as the addendum in the Michael condensation. The product is best formulated as the lactone of a β-keto acid (V), for it loses carbon dioxide (and water) when it is boiled with sodium carbonate, forming a phenolic ketone (VI).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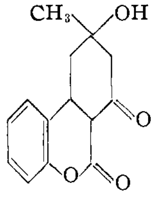
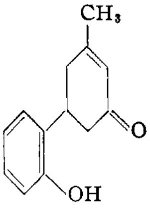

V


VI

Experimental

2-(3-Coumarinyl)-4-benzo[c]coumarinol, III.—Three 2.5-g. portions of piperidine were added at intervals during twenty-one hours to a boiling solution of 100 g. of 3-acetocoumarin in 300 ml. of absolute alcohol. The crystalline product (16.7 g.) was removed from the hot mixture, washed with alcohol and crystallized from pyridine; m. p. 298°.

Anal. Calcd. for $C_{22}H_{12}O_5$: C, 74.1; H, 3.4. Found: C, 74.1; H, 3.5.

No pure substance other than unchanged acetocoumarin (11 g.) could be isolated from the dark oil comprising the rest of the reaction product.

The acetate of III, faintly yellow crystals from benzene, m. p. 234–236°, was obtained by boiling III with acetic anhydride containing a little sulfuric acid for twenty-five minutes.

Anal. Calcd. for $C_{24}H_{14}O_6$: C, 72.4; H, 3.5. Found: C, 72.1; H, 3.9.

One gram of III was heated at 200–225° for thirty minutes with 10 g. of sodium hydroxide and 1 ml. of water. The acidic products were separated by extraction with hot water into 0.1 g. of salicylic acid and 0.23 g. of an insoluble acid. The latter, **4-hydroxybenzo[c]coumarin-2-acetic acid (IV)** formed colorless needles from acetone, m. p. 209–210°. It gave a red ferric chloride test.

Anal. Calcd. for $C_{15}H_{10}O_5$: C, 66.7; H, 3.7. Found: C, 66.4; H, 3.9.

1,2,3,4,4a,10b-Hexahydro-2-hydroxy-2-methyl-4-benzo[c]coumarinone, V.—A solution of 8.8 g. of 3-acetocoumarin and 2 ml. of piperidine in 250 ml. of acetone was boiled for ten hours. The excess acetone was then distilled, and the residue was crystallized from alcohol, giving 2.5 g. of unchanged 3-acetocoumarin and 2.5 g. of V. The latter formed colorless needles from acetone, m. p. 231–231.5°.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.3; H, 5.7. Found: C, 68.2; H, 6.1.

One gram of V dissolved rapidly when it was boiled with 10 g. of sodium carbonate in 100 ml. of water, but during ninety minutes of continued boiling, the solution deposited 0.9 g. of **5-(*o*-hydroxyphenyl)-3-methyl-2-cyclohexen-1-one, VI,** colorless needles from dilute alcohol, m. p. 132.5°.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.3; H, 6.9. Found: C, 77.6; H, 7.3.

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Vapor Density of Bromine Near 100°

By James A. Lasater, Stone D. Cooley and Robbin C. Anderson

In order to calibrate a flowmeter for use with bromine vapor, it became necessary to have data on the density of bromine vapor at temperatures close to 100°, and on its deviation from the perfect gas laws. Perman[1] measured the density at several temperatures including 78.4 and 132.2° but his results were such that values could not well be determined for 100° by interpolation (*cf.* Fig. 1). Accordingly experimental determinations have been made of the bromine vapor density in the region from 87 to 112°.

Experimental

The density of bromine vapor was determined by weighing a bulb of known volume filled with vapor at atmospheric pressure and at constant temperature. A mineral oil-bath was used as the heating medium for the gas bulb. To minimize any effect of residual gases, the bulb was evacuated with an oil pump and refilled with helium several times before it was finally evacuated and weighed. A small amount of liquid bromine was introduced into the bulb. It was then placed in the oil-bath and brought to the desired temperature. Excess bromine vapor was permitted to escape until the pressure in the bulb was equal to that of the atmosphere. When the bulb had reached bath temperature and the pressure was equalized, the stopcock on the bulb was closed and it was removed from the bath. The bulb was washed with benzene and rinsed with acetone and allowed to reach atmospheric temperature before each weighing.

The volume of the bulb was determined by calibration with distilled water at room temperature. Correction for the buoyancy of air and for the expansion of the bulb and stem corrections for the thermometer were applied. Temperatures were measured with a thermometer calibrated against a U. S. Bureau of Standards thermometer. Pressures were measured with a mercury barometer corrected

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(1) Perman, *Proc. Roy. Soc.* (*London*), **48**, 45 (1890); **66**, 10 (1900).

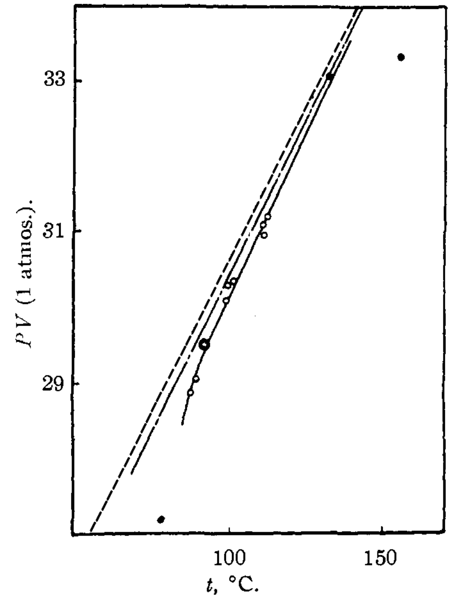

Fig. 1.—*PV* data: ●, data of Perman; O, data of Lasater, Cooley and Anderson; – – –, $PV = nRT$; —·—, van der Waals equation.

for elevation, and weights were determined with an analytical balance having a sensitivity of 0.0002 g. per scale division. A blank test made to determine the possible error in weighing which might result from the washing procedures gave weights before and after washing differing only by 0.009 g. No correction has been made for the wall adsorption, but the measurements of Perman indicated that this is within the limit of other experimental errors for pressure close to atmospheric.

Results

The data obtained are summarized in Table I. For comparison, density values were also calculated from the molecular weight, assuming the bromine vapor to be a perfect gas of formula Br_2.

TABLE I

BROMINE VAPOR DENSITY

Br_2, g.	Bulb, ml.	Bath temp., °C.	Barometric pressure, mm.	Density at bar. press., g./l.	Density calcd. from mol. wt., g./l.
1.567	285.95	87.7	751.9	5.480	5.347
1.525	285.96	91.7	747.9	5.333	5.260
1.486	285.98	99.6	747.8	5.196	5.148
1.454	286.01	111.4	747.8	5.084	4.990
1.546	285.96	89.2	746.2	5.406	5.284
1.492	285.98	98.8	746.1	5.217	5.147
1.443	286.01	110.9	745.8	5.045	4.983
1.522	285.96	91.4	746.1	5.322	5.252
1.478	285.98	101.2	745.0	5.168	5.107
1.441	286.01	112.4	745.3	5.038	4.960

Discussion

It is notable from these results and those of Perman at temperatures close to 100° (which are summarized in Table II) that at temperatures above 100° the deviations from ideal gas behavior are quite small.

TABLE II

DATA OF PERMAN

Temp., °C.	Pressure, mm.	Dens. Br_2/Dens. H_2
78.4	764.3	81.0
132.2	761.4	80.3
155.5	749.0	80.8

This was shown further by calculations of pressure–volume products at various temperatures, using van der Waals equation. *a* and *b* were evaluated from the critical constants. T_c = 575.1°K. and d_c = 1.18 g./cc. for bromine are reported in the International Critical Tables.[2] V_c = 0.1355 l. was calculated from d_c, and P_c = 130.56 atm. from the relation

$$R = 0.08205 = 8P_cV_c/3T_c$$

Results of these calculations are shown in Table III. It may be noted that the van der Waals corrections show only a small deviation from the perfect gas law.

TABLE III

PV VALUES FOR 1 MOLE Br_2

Temp., °C.	Present observations, l. atm.	Observed by Perman, l. atm.	Calcd. using perfect gas law, l. atm.	Calcd. using the van der Waals Equation, l. atm.
78.4		27.19	28.86	28.6
87.7	28.85		29.61	
89.2	29.03		29.73	
91.4	29.48		29.91	29.71
91.7	29.49		29.94	
98.8	30.08		30.52	
99.6	30.27		30.59	30.39
101.2	30.32		30.72	
110.9	31.09		31.51	
111.4	30.94		31.56	31.36
112.4	31.11		31.64	
132.2		33.07	33.26	33.06
155.5		33.33	35.18	35.00

The "compressibility factor" was estimated using the Hougen and Watson chart[3] and the reduced pressure (P/P_c) and reduced temperature (T/T_c). This gives a correction factor to be applied to *PV* values from the perfect gas law equation of only 0.992–0.993 for the range of temperatures and pressures in these experiments. A graphical comparison of theoretical and observed values is shown in Fig. 1.

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[2] "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1933, Vol. 3, p. 435.

[3] Hougen and Watson, "Chemical Process Principles Charts," J. Wiley and Sons, Inc., New York, N. Y., 1946, p. 103.