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The Vapor Pressures and Some Other Properties of Di-*i*-butyl Ketone and Di-*i*-butylcarbinol

BY F. H. STROSS, C. M. GABLE AND G. C. ROUNDS

Di-*i*-butyl ketone (2,6-dimethyl-4-heptanone) and di-*i*-butylcarbinol (2,6-dimethyl-4-heptanol) present some technical interest as solvents and plasticizers. Several properties of carefully purified samples of both compounds have been determined. While a few of these properties have been determined previously, it is believed that the present results are appreciably more accurate.

Experimental

Purification.—Di-*i*-butyl ketone (96%) was distilled in an 80-plate Oldershaw column[1] at 200 mm. Heart-cuts of constant refractive index 1.4123 were composited and passed through an adsorption column containing silica gel to remove alcohols, unsaturated ketones and water. Flash distillation over solid sodium hydroxide of the middle cut derived from the adsorption removed peroxides and diketones. The water content of the resulting material, stored over freshly calcined calcium sulfate, was less than the uncertainty of determination by Fischer's method (<0.002%w.). Ultraviolet absorption indicated the absence of unsaturated conjugated ketones and mesitylene within experimental error (<0.006%w.).

Di-*i*-butylcarbinol (98%) was distilled in a 70-plate column and the material of constant refractive index (1.4230) stored over calcined calcium sulfate. No ketones were detected by chemical methods and no impurities detectable by infrared analysis were found.

Samples for the measurements were distilled from the calcium sulfate under reduced pressure.

Results

The vapor pressures were determined as described previously[2] and gave the following Antoine equations

Di-*i*-butyl ketone:

$$\log_{10} P_{mm.} = 6.94539 - 1476.40/(t + 195.0) \quad (1)$$

Di-*i*-butylcarbinol:

$$\log_{10} P_{mm.} = 6.53806 - 1144.81/(t + 135.0) \quad (2)$$

Deviations of the observed data from these equations are plotted in Figs. 1 and 2.

The normal boiling points calculated from these equations are: di-*i*-butyl ketone, 168.24°; di-*i*-butylcarbinol, 178.02°. Previous values given for the boiling points are, for di-*i*-butyl ketone: 164–168°,[3] 165–166°,[4] 162–164°,[5] 168°,[6] 166–172°[7]; for di-*i*-butylcarbinol: 172–174° (750 mm.),[8] 174–175°,[9] 171.4–173.4°.[10] The heats of vaporization (Table I) were calculated from the Clausius–Clapeyron equation, correction being made for the imperfection of the gas by means of Berthelot's equation of state. The correction amounts to about 4% at atmospheric pressure, and the uncertainty of the estimate of the critical constants produces an error believed to be ±1% or less in the final result. The critical constants were estimated from atomic and constitutive constants derived from known values of related

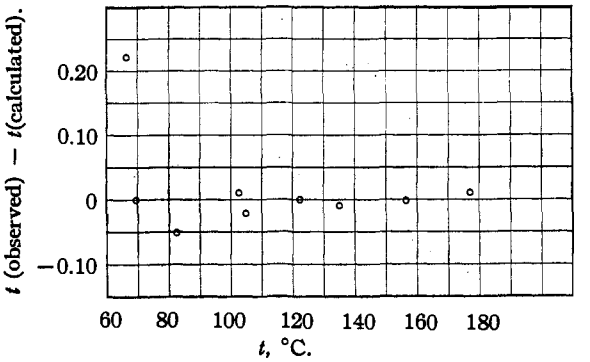

Fig. 1.—Temperature deviations from Antoine equation for vapor pressure of di-*i*-butyl ketone.

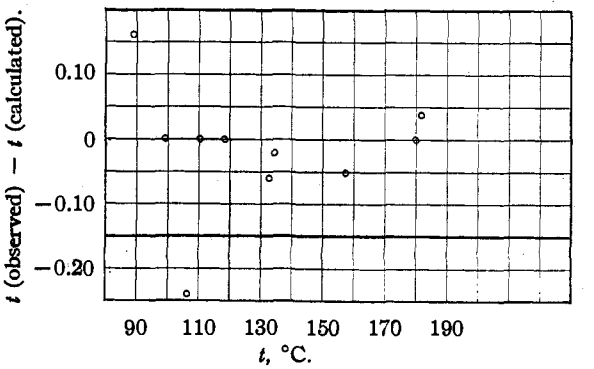

Fig. 2.—Temperature deviations from Antoine equation for vapor pressure of di-*i*-butylcarbinol.

TABLE I

THE MOLAL HEATS OF VAPORIZATION

	Di-*i*-butyl ketone				Di-*i*-butylcarbinol	
P, mm.	*t*, °C.	dP/dt, mm./°C.	ΔH, g. cal./mole	*t*, °C.	dP/dt, mm./°C.	ΔH, g. cal./mole
50	86.41	2.16	11020	101.57	2.36	13090
100	103.54	3.83	10700	117.27	4.14	12460
760	168.24	19.6	9540	178.02	20.5	10500

(1) Oldershaw, *Ind. Eng. Chem., Anal. Ed.*, **13**, 265 (1941).
(2) Stross, Monger and Finch, THIS JOURNAL, **69**, 1627 (1947).
(3) Leroide, *Ann. chim. phys.*, (9) **16**, 391 (1921).
(4) Kubota and Yoshikawa, *Chem. Zentr.*, **96**, II, 1582 (1925).
(5) Hara, *ibid.*, **97**, II, 2658 (1926).
(6) Cowan, Jeffery and Vogel, *J. Chem. Soc.*, 171 (1940).
(7) Ipatieff and Haensel, *J. Org. Chem.*, **7**, 189 (1942).
(8) Grignard, *Chem. Zentr.*, **72**, II, 622 (1901).
(9) Vavon, *Ann. chim. phys.*, [9] **1**, 196 (1914).
(10) Willcox and Brunel, THIS JOURNAL, **38**, 1838 (1916).

compounds, and were as follows: For di-*i*-butyl ketone, t_c = 340°, P_c = 30 atm.; for di-*i*-butylcarbinol, t_c = 310°, P_c = 35 atm.

Table II records other properties measured.

TABLE II

VARIOUS PHYSICAL PROPERTIES

Property	Temp., °C.	Di-*i*-butyl ketone	Di-*i*-butylcarbinol
Density, g./ml.	20.00 ± 0.01	0.80600	0.80969
(vac.)	40.00 ± .02	.78995	.79522
	60.00 ± .02	.77379	.77990
Refractive index, n_D	20.00 ± .01	1.41225	1.42314
n_F	20.00 ± .01	1.41751	1.42836
n_C	20.00 ± .01	1.41012	1.42096
Specific dispersion, $\frac{n_F - n_C}{d} \times 10^4$	20.00 ± .01	91.7	91.4
Viscosity, centipoises	0	1.320	54.7
	20	0.903	13.9
	30	.765	7.87
	40	.665	4.76
Sol., water in cpd., %w.	23	.4	1.0
Solubility in water, %w.	25	.043	0.03
Freezing point, °C.		−46.04 ± 0.01	

The densities of the liquids are the averages of determinations which did not differ more than 1.5×10^{-5} from the mean. They were measured by means of 15 ml. Bingham pycnometers. Special care was taken in all manipulations to avoid contamination of the samples. The accuracy is estimated to be $\pm 3 \times 10^{-5}$.

The refractive indices are the averages of determinations carried out with a Bausch and Lomb precision refractometer and a Pulfrich refractometer. The instruments were checked by means of standard liquids of the Bureau of Standards and the deviations from the mean did not exceed 2×10^{-5}. The accuracy is estimated to be $\pm 4 \times 10^{-5}$.

The viscosities were determined by means of a Zeitfuchs viscosimeter, with an estimated accuracy of 2×10^{-3} centipoises.

The saturation equilibria di-*i*-butyl ketone–water (Table II) were established by ultraviolet analysis and the Fischer method.

The freezing point of di-*i*-butyl ketone (Table II) was obtained by means of a platinum resistance thermometer according to the procedure described by Glasgow.[11] The value given is that calculated for zero impurity.

Summary

The following properties of di-*i*-butyl ketone (2,6-dimethyl-4-heptanone) and di-*i*-butylcarbinol (2,6-dimethyl-4-heptanol) have been determined: vapor pressure, heat of vaporization, density of the liquid, refractive index, specific dispersion, viscosity, and the saturation equilibria with water. The freezing point of di-*i*-butyl ketone has also been measured.

(11) Glasgow, Streiff and Rossini, *J. Res. Natl. Bur. Standards*, **35**, 355 (1945).

EMERYVILLE, CALIF. RECEIVED FEBRUARY 3, 1947

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The Infrared and Ultraviolet Absorption Spectra of Two Isomers of Mesityl Oxide

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The infrared absorption bands from 2 to 15μ of the low- and high-boiling isomers of mesityl oxide[1] as determined on the pure liquids in 0.02 mm. cells, are as follows.

TABLE I

B. p., 121.5°		B. p., 130°	
3.25	(50)	3.00	(5)
3.37	(70)	3.37	(70)
5.83	(90)	5.36	(5)
6.06	(60)	5.57	(5)
6.95	(70)	5.91	(90)
7.02	(70)	6.14	(100)
ca. 7.1	(60)	6.91	(90)
ca. 7.25	(60)	*ca.* 7.0	(80)
7.36	(80)	7.23	(90)
7.54	(60)	7.35	(90)
7.88	(40)	7.90	(20)
8.20	(80)	8.20	(90)
8.62	(90)	8.56	(90)
9.53	(20)	9.33	(30)
10.39	(10)	9.82	(40)
11.16	(100)	10.35	(90)
11.79	(5)	12.16	(70)
12.58	(10)		

Wave lengths are in μ; intensities are indicated as per cent. absorption at the maximum.

The prevalent isomer, which has the commonly accepted conjugated structure and according to the results of the preceding article is the high-boiling one, exhibits the strong C=O band at 6.14μ, greatly shifted from the normal unconjugated position at 5.83μ.[2] Also, the arrangement

(1) F. H. Stross, J. M. Monger and H. de V. Finch, paper I, THIS JOURNAL, **67**, 1627 (1947).

(2) *E. g.*, see spectra given by R. B. Barnes, R. C. Gore, U. Liddel and V. Z. Williams, "Infra-red Spectroscopy," Reinhold Publishing Co., New York, N. Y., 1944; H. W. Thompson and P. Torkington, *J. Chem. Soc.*, 640 (1945).