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,	0	1.320	54.7
centipoises	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

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

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

BY H. F. GRAY, JR., R. S. RASMUSSEN AND D. D. TUNNICLIFF

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

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(1) F. H. Stross, J. M. Monger and H. de V. Finch, paper I, THIS JOURNAL, **69**, 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).

of substituents about the double-bonded carbons ($R_2C{=}CHR$) is reflected in the strong 12.16μ band.[3] The structure of the low boiling isomer is clearly indicated to be the unconjugated form, 4-methyl-4-penten-2-one, by the fact that the C=O band appears at the normal unconjugated ketone position, 5.83μ, and that the strong band in the 10 to 15μ region occurs at 11.16μ, the position associated with the $R_2C{=}CH_2$ configuration.[3] This result is in agreement with the Raman work of Dupont and Menut[4] on a mixture of the isomers, the presence of a 1716 $cm.^{-1}$ line associated with unconjugated C=O indicating an unconjugated form.

In agreement with chemical evidence referred to in the preceding article, no appreciable concentration of enol form was present as indicated by the weakness of hydroxyl group absorption near 3.0μ.

The ultraviolet absorption spectra (2100 to 5000 Å.) independently lead to the same conclusion. The high-boiling isomer exhibits bands at 2310 and 3290 Å. (molar extinction coefficients 1.20×10^4 and 40.5 liters/mole cm. respectively; spectra of *i*-octane solutions). These bands are closely similar in position and intensity to those of other compounds containing the conjugated system C=C—C=O. The low-boiling isomer shows only the single band near 2900 Å. (molar extinction coefficient *ca.* 77 liters/mole cm., spectrum of *i*-octane solution) characteristic of simple unconjugated ketones.

The intensity of the 2310 Å. band made it a logical choice for quantitative analyses for the conjugated isomer, and it was so used in the work described in the preceding article.[1] The infrared spectra, which as obtained for this work were not suitable for use in precise quantitative analyses, were nevertheless used analytically to get approximate ratios of conjugated to unconjugated isomers, and to check for the presence of extraneous compounds (water, acetone, hydration products, etc.).

Summary

1. The infrared (2 to 15μ) and ultraviolet (5000 to 2100 Å.) absorption spectra of two isomers of mesityl oxide are reported.

2. The spectra of the high-boiling isomer show it to have the commonly accepted conjugated structure, 4-methyl-3-penten-2-one. Those of the low-boiling isomer clearly indicate it to be 4-methyl-4-penten-2-one.

EMERYVILLE, CALIF. RECEIVED FEBRUARY 3, 1947

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[3] R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 120 (1947).

[4] G. Dupont and M. L. Menut, *Bull. soc. chim.*, **6**, 1215 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Temperature Dependence of the Osmotic Pressure of Polyvinyl Chloride Solutions[1]

BY PAUL DOTY[2] AND ELI MISHUCK[3]

Statistical thermodynamic theories[4,5] of polymer solutions give for the free energy of dilution ΔF_1, the following expression

$$\Delta \bar{F}_1 = RT[\ln (1 - v_2) + v_2(1 - 1/x) + \mu v_2] \quad (1)$$

The volume fraction of polymer is denoted by v_2 and the ratio of the volume of the polymer molecule to the solvent molecule by x. The quantity μ is of critical importance. Huggins[4] suggested that it be considered as the sum of a temperature independent term, β, corresponding to the entropy contribution and a temperature dependent term α/RT, corresponding to the heat contribution.

To a first approximation β is equal to the reciprocal of the coördination number of the hypothetical lattice used in deriving equation (1). More detailed considerations,[4,6,7] however, show that β depends in a complicated manner on the concentration of polymer segments in the immediate vicinity of a given polymer segment; this in turn depends on the flexibility of the polymer, the amount of branching and on the concentration. Estimates from experimental measurements on rubber–benzene[8] and rubber–toluene[9] and from the theory place the value of β in dilute solutions in the range 0.3 to 0.4 for non-polar polymers.

The quantity α is approximately equal to the heat of dilution, $\Delta \bar{H}_1$, divided by v_2^2. (This approximation would be an exact equality if v_2 were independent of temperature.) For non-polar polymers in dilute solution the value of α should be in the range of 0 to about 100 cal./mole. For

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[1] Presented at the Polymer Forum, 109th meeting of the American Chemical Society, Atlantic City, N. J., April 9, 1946.

[2] Present address: Department of Colloid Science, The University, Cambridge, England.

[3] Taken in part from a thesis presented in partial fulfilment for the degree of Master of Science, Polytechnic Institute of Brooklyn, June, 1946.

[4] Huggins, *J. Chem. Phys.*, **9**, 440 (1941); *Phys. Chem.*, **46**, 151 (1942); *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942); **44**, 431 (1943).

[5] Flory, *J. Chem. Phys.*, **9**, 666 (1941); **10**, 51 (1942).

[6] Flory, *ibid.*, **13**, 453 (1945). In this paper there is a review of all measurements which allow an estimation of the values of β and α in dilute solution.

[7] Zimm, *ibid.*, **14**, 164 (1946).

[8] Gee and Treloar, *Trans. Faraday Soc.*, **38**, 147 (1942).

[9] Meyer, Wolff and Boissonnas, *Helv. Chim. Acta*, **23**, 430 (1940).