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The Isolation and Purification of Two Isomers of Mesityl Oxide

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Mesityl oxide has long been known to exist in two isomeric forms,[1] and more recent literature indicates that the mesityl oxide as usually prepared consists of a mixture of 4-methyl-3-penten-2-one ($(CH_3)_2C{=}CHCOCH_3$, conjugated mesityl oxide) and 4-methyl-4-penten-2-one ($CH_2{=}C(CH_3)CH_2COCH_3$, isomesityl oxide). Estimates of the concentration of the isomesityl oxide in the mixture range from 5[2] to 20%,[3] based on investigations of derivatives and on Raman spectra of the mixture. However, previous attempts to isolate the pure isomers have not been successful. This paper confirms the existence of these isomers, describes a method for their isolation and reports a number of their properties. A value for the equilibrium between the two forms at room temperature has been found by approaching it from both isomers in their pure states.

Experimental

Purification of 4-Methyl-4-penten-2-one.—It has been found in these laboratories that the rate of isomerization is increased by addition of hydrogen ion or alkali. This principle was used to obtain a good yield of the unconjugated isomer in the following purification procedure. To remove products of oxidation usually present,[4] including acids, commercial mesityl oxide was washed several times with 0.5 *N* sodium hydroxide, the temperature being held below 10° in order to avoid condensation and oxidation. After washing with water and drying with calcium sulfate, the material was distilled at atmospheric pressure in a column having 85 actual plates, in the presence of 0.2% *p*-toluenesulfonic acid monohydrate. The acid maintained the isomerization equilibrium while the lower boiling isomesityl oxide distilled off in high concentration from the equilibrium mixture. Distillate cuts with a refractive index of 1.4210 to 1.4230 were redistilled at 50 mm. pressure (85 plates, 40:1 reflux ratio). The colorless distillate of constant refractivity was transferred into evacuated ampoules and stored at −20°. Under these conditions the purest samples showed a constant content of less than 0.05% of conjugated mesityl oxide by ultraviolet analyses carried out one week apart. Absence of compounds containing the hydroxyl group, including enolic tautomers, was shown by chemical and infrared analyses within the sensitivity of the methods, that is, 0.02 and 1 per cent., respectively. The freezing curve indicated less than 0.06 mole per cent. of impurities insoluble in the solid phase.

The orange crystals of the 2,4-dinitrophenylhydrazone melted at 70°. *Anal.* Calcd. for $C_{12}H_{14}N_4O_4$: C, 51.9; H, 5.04; N, 20.1. Found: C, 52.0; H, 5.0; N, 20.1.

Purification of 4-Methyl-3-penten-2-one.—Commercial mesityl oxide, washed as before, was distilled (20-plate, atm. pressure) to free it from higher boiling contaminants. The heart-cut of highest purity entered the fiftieth plate of a 60-plate still, operated continuously under 200 mm. pressure. In this way any isomesityl oxide present in the feed or formed during distillation is distilled off while the conjugated mesityl oxide is collected in the reboiler. This product was then flash distilled at 0.1 mm. pressure. The virtually colorless distillate was transferred and stored as described above. It contained 0.007% water by weight and the freezing curve indicated about 0.15 mole per cent. impurities insoluble in the solid phase.

The 2,4-dinitrophenylhydrazone consists of crimson crystals melting at 203°. It is much less soluble in ethyl alcohol and other common solvents than the corresponding derivative from isomesityl oxide; hence as would be expected, the 2,4-dinitrophenylhydrazone prepared from mesityl oxide as usually obtained yields on recrystallization from ethyl alcohol a 2,4-dinitrophenylhydrazone which is identical with this one (m. p. 203°, mixed 203°).

Results

The vapor pressures were determined by means of a mercury manometer connected to a Cottrell boiler with nitrogen as a buffer gas. The boiling points were measured with a five-ohm platinum resistance thermometer. Pressures were determined by comparing the mercury height in the manometer with a standard meter scale with the aid of a cathetometer. The meter scale was calibrated by the National Bureau of Standards. Estimated accuracy of pressure and temperature readings was ±0.03 mm. and ±0.02°, respectively.

The pressure readings were reduced to 0° and standard gravity. The data were fitted to the Antoine equation[5] by an exact least squares treatment giving the equations

Isomesityl oxide:

$$\log_{10} P_{\text{mm.}} = 7.01301 - 1361.50/(t + 208.0) \quad (1)$$

Conjugated mesityl oxide:

$$\log_{10} P_{\text{mm.}} = 7.01266 - 1399.09/(t + 208.85) \quad (2)$$

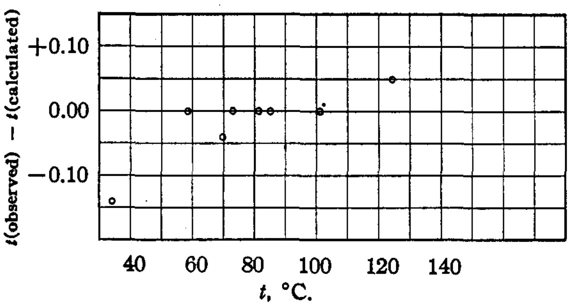

Fig. 1.—Temperature deviations from Antoine equation for vapor pressure of isomesityl oxide.

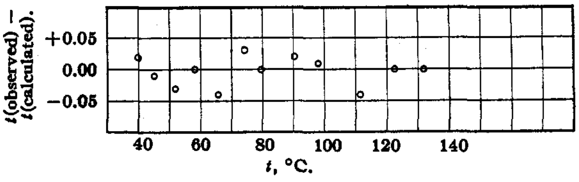

Fig. 2.—Temperature deviations from Antoine equation for vapor pressure of conjugated mesityl oxide.

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[1] Harries, *Ber.*, **32**, 1326 (1899); *Ann.*, **330**, 185 (1904).

[2] Dounevre, *Bull. soc. chim.*, **39**, 1594 (1926).

[3] Dupont and Menut, *ibid.*, **6**, 1215 (1939); Kenyon and Young, *J. Chem. Soc.*, 1547 (1940).

[4] Weitz and Scheffer, *Ber.*, **54**, 2327 (1921).

[5] Thomson, *Chem. Rev.*, **38**, 1 (1946).

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

Good reproducibility of low pressure measurements before and after observations at higher temperature indicated absence of appreciable isomerization or decomposition of the sample. Ultraviolet analysis showed 0.4 weight per cent. conjugated mesityl oxide at the end of the observations on isomesityl oxide; this would introduce an error of about 0.05° in the boiling point. The conjugated mesityl oxide remained unchanged during the vapor pressure measurements within the limits of error of these and the refractive index measurements (Pulfrich).

The normal boiling points, and the heats of vaporization (Table I) are calculated from equations (1) and (2). The heats of vaporization were calculated from the Clausius–Clapeyron equation; the gas volumes were corrected for imperfection by means of the Berthelot equation of state. The critical constants were estimated from atomic and constitutive constants to be as follows: For isomesityl oxide, $t_c = 280°$, $P_c = 35$ atm.; for conjugated mesityl oxide, $t_c = 330°$, $P_c = 35$ atm.

Table I

The Heats of Vaporization

P, mm.	*t*, °C.	d*P*/d*t*, mm./°C.	Δ*H*, kcal./mole
	Isomesityl oxide		
2.9	0	0.21	10.73
50.0	48.21	2.39	9.75
100.0	63.59	4.25	9.50
760.0	121.49	21.95	8.62
	Conjugated mesityl oxide		
2.06	0	0.15	10.95
50.0	54.45	2.32	9.86
100.0	70.26	4.14	9.63
760.0	129.76	21.36	8.63

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

Table II

Physical Constants of Mesityl Oxide

Property		Temp., °C.	Isomesityl oxide	Conjugated mesityl oxide
Density (vac.), g./ml.		20.00 ± 0.01	0.84111	0.85482
		40.00 ± .02		.83663
		60.00 ± .02		.81834
Refractive index	n_D	20.00 ± .01	1.42130	1.44575
	n_F	20.00 ± .01	1.42802	1.45562
	n_C	20.00 ± .01	1.41852	1.44195
Specific dispersion $\frac{n_F - n_C}{d} \times 10^4$		20.00	113	160
Freezing point, °C.			−72.60	−52.85
Viscosity, centipoises		0.0		0.839
		20.0	0.634	.639
		30.0		.569
		40.0		.512
Surface tension, dynes/cm.		20	23.0	22.9

The refractive indices were determined with a Pulfrich refractometer and a Bausch and Lomb precision refractometer. The measurements differed by not more than 3×10^{-5}. They are believed to be accurate to $\pm 4 \times 10^{-5}$ unit.

The freezing points were measured according to the procedure described by Rossini and coworkers.[6] They are probably accurate to ±0.05°. They are the values calculated for zero impurity.

The viscosities were measured by means of a Zeitfuchs viscometer, with an accuracy of about $\pm 2 \times 10^{-3}$ centipoise.

The surface tension determinations were made by the ring method, with an accuracy of about one dyne per cm.

The Isomerization Equilibrium.—Experiments with small concentrations of acid showed the rate of isomerization to be a direct function of the acid concentration. To obtain the equilibrium at room temperature a sample of each of the pure materials was placed in contact with 10% of its weight of solid sodium hydroxide, and another, similarly, with *p*-toluenesulfonic acid monohydrate. Both samples of the unconjugated isomer attained a constant composition in twenty-four hours, while the conjugated form required weeks. The samples were flash distilled at reduced pressure and room temperature and analyzed spectrographically for the two isomers and water. Acetone, a possible decomposition product, was absent. Within a fraction of 1%, the ratio of the two isomers was 91 of the conjugated to 9 of the unconjugated form in all four samples. The error is probably not more than ±½%. Under similar conditions *p*-hydroxybenzoic acid was quite ineffective as isomerization catalyst. The fact that several compositions of commercial mesityl oxide are reported in the literature probably results from the establishment of equilibrium at other temperatures, from possible changes in composition during distillation from a catalyst and from the slow rate of non-catalyzed isomerization at room temperature.

Summary

Two isomers of mesityl oxide have been prepared in a pure state. The vapor pressures, heats of vaporization, densities of the liquids, refractive indices, specific dispersions, freezing points, viscosities and surface tensions of the two forms have been determined. The composition of the equilibrium mixture at room temperature has been found to be 91% conjugated and 9% unconjugated isomer.

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