[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Thermodynamic Properties of the Hexyl Alcohols. VI. 2,3-Dimethylbutanol-2 and 3-Methylpentanol-2[1]

BY FRANK HOVORKA, HERMAN P. LANKELMA AND JOHN W. BISHOP

2,3-Dimethylbutanol-2 and 3-methylpentanol-2 were prepared by the Grignard synthesis, from methyl isopropyl ketone and methylmagnesium bromide, and from acetaldehyde and *s*-butylmagnesium chloride, respectively. Both alcohols were distilled through a column of 25 theoretical plates, 2,3-dimethylbutanol-2 being distilled under diminished pressure since it tended to dehydrate, and middle fractions with a boiling point range of 0.04° were used.

The apparatus, procedure and limits of accuracy were the same as described by Stanford[2] except that in determining the viscosity of 3-methylpentanol-2 the automatic control of the pressure was discarded for manual control. The results obtained are listed in Table I.

TABLE I

Temp., °C.	Vapor press., mm.	Abs. viscosity, poises	Abs. density, d^t_4	Surface tension, dynes	Refract. index, n_D	Parachor, P	Eötvös const., k_E	Total surface energy, ergs
			A. 2,3-Dimethylbutanol-2					
5	...	0.1256	0.83513	25.46	....	274.8	1.89	...
15	...	.07194	.82678	24.53	1.4198	275.0	1.95	51.32
25	9.0	.04392	.81861	23.59	1.4151	275.1	1.95	51.61
35	17.5	.02867	.80953	22.64	1.4101	275.3	2.00	51.91
45	30.5	.01977	.79986	21.67	1.4047	275.7	1.82	52.53
55	54.0	.01473	.79058	20.79		276.1	2.10	49.66
65	88.0	.01099	.78072	19.80		276.2	1.92	53.27
75	142.5	.00845	.77004	18.88		276.8	2.11	50.91
85	222.5	.00680	.75969	17.89		276.9	2.09	53.34
95	329.0	.00561	.74894	16.95		277.3	2.12	51.55
105	475.0	.00474	.73806	15.98		277.5	2.09	52.66
115	674.0	.00407	.72638	15.04		278.1	..	51.52
120	789.5	.....	.....	...		...	..	....
			B. 3-Methylpentanol-2					
5	...	0.1357	0.84153	26.44	....	275.3	1.78	...
15	...	.07408	.83328	25.55	1.4211	275.7	1.72	51.19
25	5.0	.04426	.82475	24.68	1.4175	276.1	1.81	50.61
35	7.0	.02914	.81633	23.79	1.4128	276.4	1.77	51.21
45	12.5	.02048	.80752	22.92	1.4077	276.8	1.70	50.59
55	24.0	.01431	.79855	22.08		277.4	1.89	49.64
65	42.5	.01144	.78934	21.17		277.7	1.78	51.94
75	70.0	.00894	.77988	20.31		278.2	1.79	50.94
85	116.0	.00722	.77030	19.45		278.7	2.04	50.25
95	183.0	.00593	.76035	18.51		279.0	1.80	53.11
105	271.5	.00498	.75019	17.66		279.6	1.95	49.80
115	398.5	.00424	.73965	16.77		280.1	2.09	51.70
125	564.0	.00368	.72888	15.83		280.5	..	53.25
130	662.5	.....	.....	...		...	..	...
135	775.0	.....	.....	...		...	..	...

Discussion.—The vapor pressure data agree closely with Rankine equations whose constants for 2,3-dimethylbutanol-2 and 3-methylpentanol-2 are, respectively, $A = -2876.66$ and -5096.50, $B = -3.7728$ and -16.2405, $C = 20.0097$ and 57.7781, the average deviations being 0.74 and 0.12% and the maximum deviations 1.8 and 0.4%, respectively.

The heats of vaporization of 2,3-dimethylbutanol-2 and 3-methylpentanol-2 were derived from the slopes of the curves obtained by plotting log P against $1/T$. The boiling points were obtained graphically from the vapor pressure curves. The resulting data are, for 2,3-dimethylbutanol-2

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[1] See Hovorka, Lankelma and Smith, THIS JOURNAL, **62**, 2372 (1940).

[2] Hovorka, Lankelma and Stanford, *ibid.*, **60**, 820 (1938).

and 3-methylpentanol-2, respectively: heats of vaporization, 9901 and 10,014 cal.; boiling points, 118.70 ± 0.02 and 134.32 ± 0.02°; Trouton constants, 25.3 and 24.6. These last values are considerably greater than the normal value of 21. This characterization is typical of all the hexanols thus far studied.

The viscosity data were found to be in very poor agreement with the values calculated from the equations of Andrade[3] and Raman.[4]

From the surface tension data the Eötvös constants were calculated and it can be seen that as the temperature is raised, they approach the normal value of 2.12, indicating decreasing association with increasing temperature. It can also be seen that the values of the parachor approach, although somewhat less closely, the normal value of 288.2.

The data for the refractive indices, substituted in the Lorenz–Lorentz formula, give for the molecular refractive power of the two alcohols, 31.26 and 31.19, respectively, which is in close agreement with the molecular refractive power as calculated from the atomic refractive constants of carbon, hydrogen and oxygen as given by Eisenlohr,[5] namely, 31.44 and 31.44, respectively.

Summary

The various thermodynamic properties of 2,3-dimethylbutanol-2 and 3-methylpentanol-2 have been measured carefully. The vapor pressures follow the Rankine equation accurately. The values of Trouton's constant derived from these data are considerably greater than the normal value of 21, a behavior which is typical of all the hexanols thus far studied. The measured viscosities are in poor agreement with the values calculated from the equations of Andrade and Raman. The molecular refractions agree closely with the values calculated from the recognized atomic refractive constants. The values of the parachor and the Eötvös constants suggest that both alcohols are associated and that the degree of association decreases with increasing temperature.

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(3) Andrade, *Phil. Mag.*, **17**, 497 (1934).

(4) Raman, *Nature*, **111**, 532 (1923).

(5) Eisenlohr, *Z. physik. Chem.*, **75**, 585 (1911).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF FURMAN UNIVERSITY]

Photochemical Bromination of Aryl Methyl Ketones

BY JOHN R. SAMPEY AND ELIJAH M. HICKS

While sunlight and artificial irradiation have been employed in the preparation of individual ω-bromo ketones,[1] little quantitative study has been made of the photochemical bromination of aryl methyl ketones in spite of much current interest in the mechanism of ketone bromination.[2] Altschul and Bartlett[3] record a few results on the rate of bromination of diphenylacetophenone in acetic acid in "daylight" and "dark" but no data are given on the intensity of the illumination during the experiments which ranged in time from forty-six hours to twenty-eight days. In the present investigation a study has been made of the photochemical bromination of several aryl methyl ketones under varying intensities of irradiation and in the presence of different concentrations of water, sulfur and acid, three catalysts which profoundly influence the rates of bromination. Interesting observations are made also on the rates of formation and disappearance of the intermediate addition compounds between the ketones and the bromine.

Negative Catalytic Effect of Water

The marked negative catalytic effect of water on the photochemical bromination in carbon tetrachloride became apparent when acetophenone was found so hygroscopic that it was not possible to weigh samples in the air; the rates of bromination were found to vary as much as 15%, and when one sample was exposed to the air for several hours there was actually no bromination within the five-minute period that gave 100% bromination on a dry sample.

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(1) (a) Lazennec, *Bull. soc. chim.*, [4] **5**, 501–508 (1909); (b) Evans, THIS JOURNAL, **35**, 1770–1774 (1913); (c) Ruggli and Reichwein, *Helv. Chim. Acta.*, **20**, 913–918 (1937).

(2) (a) Nathan and Watson, *J. Chem. Soc.*, 217–220 (1933); (b) Morgan and Watson, *ibid.*, 1173–1174 (1935); (c) Evans, *et al.*, *ibid.*, 1167–1173 (1935); 785–789 (1936); 1434–1439 (1938); (d) Paul and Hammett, THIS JOURNAL, **58**, 2182–2187 (1936); (e) Kröhnke, *Ber.*, **69B**, 614–621 (1936); 921–935 (1936); (f) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, Chapter 8.

(3) Altschul and Bartlett, *J. Org. Chem.*, **5**, 623–636 (1940).