Summary

The neutralization of trinitrotriphenylmethide ion is interpreted as an acid-catalyzed reaction. The interpretation is in accord with the kinetic experiments.

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

Thermodynamic Properties of the Hexyl Alcohols. IV. 3-Methylpentanol-1 and 2-Methylpentanol-5

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This paper represents the fourth[2,3,4] of a series of investigations being carried out in this Laboratory concerned with the relation between physical properties and chemical constitution of the hexyl alcohols, and deals with the preparation, purification and determination of the vapor pressure, viscosity, density, surface tension and refractive index of 3-methylpentanol-1 and 2-methylpentanol-5 (4-methylpentanol-1).

Experimental

Preparation of Materials.—Both alcohols were prepared in a manner similar to that described by Dreger[5] for the preparation of hexanol-1. 3-Methylpentanol-1 was made by the Grignard reaction using secondary butyl bromide and ethylene oxide. Similarly, 2-methylpentanol-5 was prepared from isobutyl bromide and ethylene oxide.

Purification.—The alcohols were allowed to stand over "Drierite"[6] for a period of two months, filtered from the drying agent and fractionally distilled. The fractionating columns used have been described previously.[3]

The alcohols were considered pure when the boiling point range did not exceed 0.02°.

Apparatus.—A complete description of the apparatus and technique used for the determination of the physical constants can be found in the paper by Hovorka, Lankelma and Stanford.[3]

All the instruments used in the surface tension, density, and viscosity measurements were recalibrated before determinations were made.

Discussion of Results

Vapor Pressure.—The vapor pressure data are tabulated in Table I, column 5.

The summary of the values calculated from the vapor pressure data is given in Table II. The temperature variation of the vapor pressure was found to be given very closely by the Rankine equation, whose constants A, B and C are listed.

The values of the Trouton constant are considerably higher than the normal value of 21. These high values correspond with those found for the hexanols previously reported.[2,3,4]

Viscosity.—The viscosity data are tabulated in Table I, column 3. The viscosity *vs.* temperature curves for the two hexanols cross at 65° although the values from 65–150° do not vary by more than 0.6%. This peculiar behavior has been noticed previously. Like hexanol-1, reported by Hovorka, *et al.*, these two alcohols have a small temperature coefficient of viscosity.

Plots of Raman's equation[7] and Andrade's equation[8] yielded perfectly symmetrical curves instead of the required straight lines. The constants of the two equations and the deviations of the calculated from the observed viscosities are listed in Table III. It is very interesting to note here that of all the hexyl alcohols so far studied, hexanol-1 gives the least deviation from Andrade's equation, and that it is closely followed by 2-methylpentanol-5 and 3-methylpentanol-1.

Values of the degree of association have been calculated from the fluidity using a formula proposed by Bingham, *et al.*[9,10] The association factor as determined by the fluidity method is the ratio of the temperature required to give a certain fluidity to the temperature calculated from the "atomic temperature" constants. The values obtained are listed in Table IV. Calculation of the association factor for hexanol-1 gave values of 1.59, 1.48 and 1.41.

Bingham further calculates the degree of association by application of the formula, $n =$

(1) Abstracted from a Thesis by I. Schneider, submitted to the Graduate School of Western Reserve University, in partial fulfillment of the requirements for the Degree of Master of Arts, May, 1937.

(2) Hovorka, Lankelma and Naujoks, THIS JOURNAL, **55**, 4820 (1933).

(3) Hovorka, Lankelma and Stanford, *ibid.*, **60**, 820 (1938).

(4) Hovorka, Lankelma and Axelrod, *ibid.*, **62**, 187 (1940).

(5) "Organic Syntheses," Coll. Vol. I, p. 299.

(6) Hammond and Withrow, *Ind. Eng. Chem.*, **25**, 1112 (1933).

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

(8) Andrade, *Phil. Mag.*, **17**, 698 (1934).

(9) Bingham and Darrall, *J. Rheol.*, **1–2**, 174 (1929–31).

(10) Bingham and Spooner, *ibid.*, **3**, 228 (1932).

TABLE I

SURFACE TENSION, VISCOSITY, DENSITY, VAPOR PRESSURE AND REFRACTIVE INDEX

Temp., °C.	Surface tension, dynes	Absolute viscosity	Absolute density	Vapor press., mm.	Index of refraction	Parachor	Eötvös constant
			A. 3-Methylpentanol-1				
5.0	26.28	0.09615	0.83328	...	....	277.2	1.63
15.0	25.35	.06714	.82602	...	1.4208	277.2	1.61
25.0	24.65	.04755	.81870	1.3	1.4169	277.6	1.63
35.0	24.01	.03447	.81160	2.2	1.4136	278.2	1.66
45.0	23.21	.02574	.80484	4.4	1.4096	278.2	1.66
55.0	22.51	.01968	.79740	9.1		278.6	1.69
65.0	21.83	.01538	.78964	18.0		279.2	1.72
75.0	21.18	.01218	.78173	31.5		280.0	1.78
85.0	20.47	.00992	.77352	52.0		280.5	1.83
95.0	19.67	.00812	.76520	85.5		280.9	1.85
105.0	18.85	.00679	.75666	133.0		281.1	1.88
115.0	18.04	.00577	.74784	201.0		281.5	1.91
125.0	17.22	.00495	.73728	294.5		282.5	1.97
135.0	16.35	.00428	.72725	427.0		282.6	1.95
145.0	15.43	.00374	.71750	599.5		282.6	1.76
150.0	15.05	.....	.71260	702.5		282.9	..
154.0	...	.....	.....	797.5		...	..
			B. 2-Methylpentanol-5				
5.0	25.19	0.09091	0.82376	...	....	277.4	1.55
15.0	24.50	.06293	.81647	...	1.4172	277.9	1.56
25.0	23.84	.04604	.80940	1.3	1.4135	278.5	1.58
35.0	23.32	.03376	.80246	1.8	1.4092	279.3	1.65
45.0	22.58	.02547	.79493	4.0	1.4055	279.7	1.66
55.0	21.80	.01959	.78742	8.4		279.9	1.65
65.0	21.14	.01538	.77968	16.5		280.5	1.69
75.0	20.45	.01220	.77180	31.2		281.5	1.73
85.0	19.78	.00998	.76378	52.8		281.7	1.77
95.0	18.99	.00815	.75526	85.8		282.0	1.79
105.0	18.28	.00683	.74683	134.2		282.5	1.85
115.0	17.49	.00578	.73780	205.0		283.0	1.89
125.0	16.69	.00497	.72850	302.5		283.5	1.95
135.0	15.88	.00428	.71880	435.8		283.7	1.96
145.0	15.00	.00374	.70900	611.5		284.1	2.10
150.0	14.55	.....	.70392	721.5		284.1	..
154.0	...	.....	.....	816.5		...	..

TABLE II

SUMMARY OF VALUES CALCULATED FROM VAPOR PRESSURE DATA

$$\log P = A/T + B \log T + C$$

Substance					Deviation Maximum +	Deviation Average −
		A	B	C		
3-Methylpentanol-1	−4209.8	− 9.3605	37.3838	0.3	2.8	−0.43
2-Methylpentanol-5	−4778.8	−12.617	47.2894	.1	3.0	− .20

	Boiling point °C.[a]	Heat of vaporization[b]	Trouton's constant
3-Methylpentanol-1	152.44° ± 0.02	11,278	26.5
2-Methylpentanol-5	151.63° ± 0.02	11,124	26.2

[a] Boiling point values were obtained by interpolation from the vapor pressure curves.

[b] These values were calculated from the slope of the curve obtained by plotting log P against $1/T$.

$2.139 - 0.097\ N_c$, where N_c is the number of carbon atoms. This gives a value of 1.56 for the degree of association of the hexyl alcohols.

Refractive Index.—Using the values given by Eisenlohr[11] for the atomic refractive constants of carbon, hydrogen, and oxygen, the molecular refractive powers of 3-methylpentanol-1 and 2-methylpentanol-5 have been calculated. These values are compared with those calculated from the Lorenz–Lorentz equation in Table V.

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

TABLE III

CONSTANTS FOR RAMAN'S EQUATION $n = Ae^{B/T}$

	$A \times 10^6$	B	Maximum deviation +	Maximum deviation −
3-Methylpentanol-1	5.909	2675	5.8	7.4
2-Methylpentanol-5	6.759	2626	4.5	6.4

CONSTANTS FOR ANDRADE'S EQUATION $nv^{1/3} = Ae^{c/vT}$

	$A \times 10^6$	c	Maximum deviation +	Maximum deviation −
3-Methylpentanol-1	51.14	2503	6.9	10.5
2-Methylpentanol-5	56.13	2491	5.1	8.7

TABLE IV

CALCULATION OF ASSOCIATION FROM FLUIDITY

	3-Methylpentanol-1			2-Methylpentanol-5	
Rhes.	Calcd. temp., °A.	Obsd. temp., °A.	X	Obsd. temp., °A.	X
100	226.2	357.8	1.58	358.2	1.58
200	271.1	396.6	1.46	396.6	1.46
300	305.5	425.5	1.39	425.0	1.39

TABLE V

MOLECULAR REFRACTIVE POWER

	Lorenz–Lorentz equation	Summation of atomic constants
3-Methylpentanol-1	31.35	31.44
2-Methylpentanol-5	31.44	31.44

Surface Tension.—The surface tension data are listed in Table I, column 2.

The values of the Eötvös constant and the parachor were calculated over the entire temperature range and also are tabulated in Table I. The values listed are very similar to those calculated for the other hexanols. In all cases the values are those of associated substances.

The critical temperatures have been calculated from the Ramsay–Shields equation and are given in Table VI. A comparison of the surface tension of the two alcohols at equal distances from the critical point, so as to put the alcohols in corresponding states, showed that the values of the surface tension at one-third the critical temperature were identical, namely, 17.43 dynes. This may be ascribed to the fact that both alcohols seem to possess the same molecular aggregation at the higher temperatures.

TABLE VI

CRITICAL TEMPERATURES

Alcohol	T_c °C.	T_c °C.
3-Methylpentanol-1	403.9 (25–35)[a]	366.6 (145–150)
2-Methylpentanol-5	398.3 (25–35)	346.9 (145–150)

[a] The values in parentheses show the two temperatures used to calculate the critical temperature in question.

Summary

1. The preparation and purification of two hexyl alcohols, 3-methylpentanol-1 and 2-methylpentanol-5, have been described.

2. The surface tension, viscosity, density and vapor pressure have been determined over the temperature range from 5° to the boiling point. The refractive index has been determined from 15–45°.

3. The heat of vaporization, boiling point and the constants for Rankine's equation have been determined from the vapor pressure data. The vapor pressure values agreed very well with those calculated by the Rankine equation.

4. The viscosity values calculated from Raman's and Andrade's equation gave poor agreement with the experimental values. The two alcohols gave almost the same values for Andrade's constants and for degrees of association as obtained for hexanol-1.

5. The parachor, Eötvös constant and critical constants have been calculated from the surface tension data.

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