For tetrafunctionally branched polymers composed of long chains randomly distributed in length,[14] the critical condition, according to results of a preceding paper,[7,15] is given by

$$\alpha_c = \frac{4\text{ (no. of cross links)}}{4\text{(no. of cross links)} + \text{(unreacted terminal groups)}} = 1/3$$

Since there are two unreacted terminal groups per chain, the number of cross linkages at the gel point is *one-fourth* of the number of chains. This result is one-half of the critical degree of cross-linking derived above for chains of uniform length. The number average molecular weight of the polymer at the gel point, therefore, is only three-halves the number average molecular weight of the non-uniform chains.

In principle, the theory presented here should be applicable to vinyl–divinyl copolymers,[2,3,4] *e. g.*, styrene–divinylbenzene copolymers. However, it is necessary to know the ratio in which the two co-reactants enter the polymer chains (on the average) and not merely their ratio in the initial mixture. Staudinger and co-workers[2,3] have shown that divinylbenzene is more reactive than styrene. Until the ratio of divinylbenzene to styrene in the polymer chains is known, quantitative application of statistical theory to these co-polymers would be futile.

Although the principles which have been deduced from statistical consideration should be of widespread assistance toward an understanding of the composition and behavior of three dimensional polymers and high polymer gels, few experimental data suitable for a quantitative test of the theory are available. Application of the theory to rubber and to protein gels will be discussed in another paper.

The author desires to acknowledge his indebtedness to Professor William C. Taylor, of the Mathematics Department of the University of Cincinnati, with whom he had the opportunity to discuss various phases of the theory presented in the three papers of this series.

Summary

The distribution of species in three dimensional polymers composed of randomly cross-linked chains of uniform length has been discussed. The results parallel those of the preceding paper for trifunctionally branched polymers. Gelation occurs when the cross-linking index γ (equal to the number of structural units which are cross-linked per chain) is equal to unity, and the number average molecular weight is twice that of the chains.

The effect of non-uniformity in the lengths of the chains has been discussed. When the chains are randomly distributed in length, $\gamma = {}^1/_2$ at the gel point.

Elizabeth, New Jersey Received June 18, 1941

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(14) The distribution given by eq. (1) of ref. (7) is referred to here as the "random" distribution; it seems to prevail frequently in linear polymers.

(15) See in particular equations (2) and (8) of ref. (7).

[Contribution from the Chemical Laboratory of the Johns Hopkins University]

Structure–Property Relationships in Some Isomeric Octanols

By G. L. Dorough,[1] H. B. Glass,[1] Thos. L. Gresham,[1] G. B. Malone[1] and E. Emmet Reid

Introduction

In most previous studies of the relations between structures and properties of isomeric organic compounds, the number of isomers has been small or only a few properties have been measured. The work of Edgar and co-workers[2] on the isomeric heptanes stands out for its completeness. Clarke's summary for the octanes[3] includes a larger number of compounds but fewer properties. Other outstanding studies are represented by the work of Sherrill and Errera[4] on the straight chain heptanols and certain of their derivatives, and by the work of Hovorka, Lankelma, and co-workers[5] on the isomeric hexanols. It does not appear, however, that any comprehensive study of a large number of properties of a large number of isomers ever has been made. We have accordingly undertaken an investigation of this type.

The following considerations governed the selection of the compounds to be studied and the manner of study: a large but not excessive number of isomers; a functional variant to give wide

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(1) Taken in part from Dissertations submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1929 and 1930.

(2) Edgar and co-workers, This Journal, **51**, 1483 (1929).

(3) Clarke, *ibid.*, **33**, 520 (1911).

(4) Sherrill and Errera, *ibid.*, **52**, 1982, 1993 (1930).

(5) Hovorka, Lankelma, *et al.*, *ibid.*, **62**, 2372 (1940), and earlier papers there referred to.

differences in properties, to permit preparation and comparison of derivatives, and to allow measurements of reaction velocities; an additional but non-functional variant to give sub-series and to permit a study of secondary effects; compounds of unquestionable authenticity and purity; preparation of relatively large amounts to allow many measurements with the same lot; the measurement of a large number and variety of properties; and the measurement of each particular property for all the isomers within a relatively short time by a single observer using the same apparatus and technique.

Certain of the octyl alcohols, *viz.*, the four straight chain octanols and the eighteen methyl heptanols, presented themselves as logical candidates for a study of this type. By fixing the methyl group in the four possible positions, beginning at the right-hand end of the heptane chain, and then in each instance moving the hydroxyl along the chain from left to right, four sub-series are obtained, as follows:

Series	Members	References[6]
7-Methylheptanols	4	71, 72, 73, 74
6-Methylheptanols	7	61, 62, 63, 64, 65, 66, 67
5-Methylheptanols	7	51, 52, 53, 54, 55, 56, 57
4-Methylheptanols	4	41, 42, 43, 44

Other types of sub-series, *e. g.*, that obtained by moving the methyl group while keeping the hydroxyl fixed, can be set up with the same 22 compounds, but only the above four, which are more significant, will be considered at present.

All these octanols, both new and old, were prepared in quantities of at least 200–300 g. in this Laboratory by the authors, who collaborated closely on methods of synthesis and purification. Unusual precautions were taken to ensure purity, precision stills being used with intermediates as well as with final products. About twenty properties have been measured, some of them in this Laboratory and others in friendly coöperation by specialists in laboratories elsewhere. From these measured properties, still other values were calculated. Both measured and derived data appear in Tables I and II.[7] Footnote acknowledgments and literature references appear with these tables when a particular measurement was not made by one of the authors of this paper. The properties most commonly determined appear in Table I, and in both Tables I and II properties ordinarily associated or derived one from the other (*e. g.*, $n^{25}\text{D}$ and $M\text{D}$) are placed adjacent or close to each other. The maximum and minimum values, and the difference, have been entered just under each column of figures in order to show the remarkably great variation for many of the properties.

Included in Tables I and II are the final average figures arrived at for most of the measurements in this Laboratory, but none of the many individual determinations, intermediate values, or calculations. The derived properties are only a representative and important few. Repetition of measurements already published by our collaborators has been carefully restricted to data which are necessary for the purposes of this paper, and those which are here included represent only a minor part of the measured and calculated values in the various papers referred to in the tables.

In Fig. 1 a number of the properties are plotted. For purposes of comparison they have all been brought to a common denominator by taking the highest as 100 and the lowest as 0 and calculating the others on this scale. In several cases data not in Tables I and II are included. The skeletons of the parent hydrocarbons are at the top and the hydroxyl is considered as moving from one carbon to another. Properties which show similar patterns are grouped together as far as practicable.

Discussion of Results

General.—The first object of the presentation is to show the relations of individual properties to structure; the second, but more important, is to bring to light correspondences between different properties. We hope other investigators will find reasons for some of the correspondences which are not now obvious.

Variations in the Individual Constants.—Variations of a given constant with changes in structure of these 22 octanols can be broken down

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(6) The first digit of the reference number locates the methyl group and the second digit the hydroxyl group; thus, "72" is 7-methylheptanol-2, *i. e.*, octanol-2, and "53" is 5-methylheptanol-3. In some instances, the reference numbers depart for convenience from the official nomenclature.

(7) In addition to the measurements in Tables I and II, Edith Wilson has determined in this Laboratory the second order velocity constants for esterifications with *p*-nitrobenzoyl chloride, and F. K. Bell, also in this Laboratory, has examined infrared absorptions. At the present time, these data are not in form for publication. The Raman spectra of 19 of our octanols have been obtained in the Physical Laboratory of this University by G. Collins and are published in *Phys. Rev.*, **40**, 829–834 (1932). Professor P. W. Bridgman of Harvard University studied the pressure–volume–temperature relations of five of these octanols and found no significant variations; see *Proc. Am. Acad. Arts Sci.*, **68**, 1–25 (1933).

TABLE I

Key no.	Structure	Boiling point, °C., at mm. 20	100	300	760	B. p. elev.[a]	Lat. ht. of vap.	d^0_4	d^{25}_4	Dens. elev.[b]
71	C 1 OH	100.7	135.0	164.0	195.0	70.3	267.9	0.8394	0.8224	0.1238
72	C 2 ↓	87.6	120.5	149.3	180.0	55.3	240.2	.8353	.8170	.1184
73	C 3	75.9	110.2	140.5	173.0	48.3	230.4	.8361	.8169	.1182
74	C 4	81.3	114.7	144.2	176.3	51.6	237.7	.8346	.8159	.1173
61	C 1 OH	95.8	128.5	157.9	187.6	71.6	270.0	.8347	.8176	.1223
62	C 2 ↓	81.0	114.3	143.0	171.8	55.8	259.9	.8219	.8034	.1081
63	C 3	60.2	95.1	125.5	158.5	42.5	224.9	.7960	.7766	.0813
64	C 4	75.9	108.8	136.8	166.3	50.3	249.0	.8281	.8098	.1145
65	C 5	76.1	109.2	137.2	167.2	51.2	245.6	.8400	.8210	.1257
66	C—C 6	70.4	103.1	129.6	156.1[d]	(40.1)	...	.8245	.8050	.1097
67	C 7	77.6	111.5	143.0	175.4	59.4	236.1	.8168	.7987	.1034
51	C 1 OH	91.1	124.9	155.2	186.5	68.9	257.2	.8329	.8152	.1067
52	C 2 ↓	75.9	110.8	140.7	171.9	54.3	244.1	.8290	.8100	.1015
53	C 3	57.0	91.5	122.5	153.4	35.8	225.1	.8367	.8162	.1077
54	C 4	67.3	103.2	133.6	164.7	47.1	234.7	.8537	.8335	.1250
55	C—C 5	71.3	103.0	131.8	159.4	41.8	254.9	.8471	.8271	.1186
56	C 6	68.1	104.2	134.8	166.1	48.5	233.5	.8375	.8177	.1092
57	C 7	87.7	123.5	155.0	185.8	68.2	258.7	.8027	.7845	.0760
41	C 1 OH	84.6	116.6	150.3	182.7	64.7	243.3	.8246	.8065	.0930
42	C 2 ↓	78.3	112.1	141.0	171.7	53.7	238.4	.8173	.7990	.0855
43	C 3	57.7	94.7	125.5	155.4	37.4	236.2	.8145	.7946	.0810
44	C—C 4	71.6	103.1	132.6	160.8	42.8	256.7	.8397	.8202	.1067
	High	100.7	135.0	164.0	195.0	71.6	270.0	.8537	.8335	.1257
	Low	57.0	91.5	122.5	153.4	41.8	224.9	.7960	.7766	.0760
	Difference	43.7	43.5	41.5	41.6	29.8	45.1	.0577	.0569	.0497

Key no.	Structure	Expansion × 10^6 0–25°	80–100°	Exp. ratio $\frac{80\text{–}100°}{0\text{–}25°}$	n^{25}_D	M_D	M. p.,[c] °C.	Molal ht. cap.[d]	Soly. g./kg. H_2O	Surface tension[e]
71	C 1 OH	828	1044	1.164	1.4275	40.68	− 15.0	68.0	0.538	24.58
72	C 2 ↓	897	1229	1.307	1.4238	40.64	− 31.6	74.9	0.955	22.97
73	C 3	940	1274	1.355	1.4209	40.41	− 45.0	78.0	1.252	25.05
74	C 4	918	1214	1.322	1.4227	40.61	− 40.7	76.7	1.206	25.43
61	C 1 OH	839	1065	1.269	1.4251	40.72	−106.0G	..	0.647	21.40
62	C 2 ↓	921	1241	1.347	1.4209	41.08	−105.0G	72.9	1.178	24.93
63	C 3	1000	1295	1.295	1.4113	41.65	− 58.5	71.5	1.540	23.74
64	C 4	906	1250	1.381	1.4196	40.65	− 81.0G	75.0	1.610	...
65	C 5	925	1276	1.379	1.4246	40.51	− 85.0G	...	2.007	25.51
66	C—C 6	969	1348	1.391	1.4201	40.93	− 50.4	76.9	2.612	25.24
67	C 7	908	1190	1.309	1.4219	41.41	−112.0	70.5	0.721	23.32
51	C 1 OH	866	1130	1.305	1.4272	41.01	−104.0G	69.8	0.712	25.95
52	C 2 ↓	939	1211	1.290	1.4218	40.82	−120.0G	69.3	1.638	25.48
53	C 3	1005	1207	1.180	1.4156	39.99	− 91.2	..	1.797	24.76
54	C 4	968	1186	1.225	1.4211	39.61	.....	..	1.880	25.94
55	C—C 5	970	1226	1.264	1.4263	40.35	− 83.0G	..	2.394	25.71
56	C 6	970	1163	1.199	1.4199	40.28	−114.0G	70.9	1.140	25.82
57	C 7	931	1113	1.196	1.4225	42.21	− 90.0	..	0.806	25.74
41	C 1 OH	899	1119	1.244	1.4253	41.30	.....	..	0.685	...
42	C 2 ↓	918	1288	1.403	1.4225	41.43	−102.0G	72.3	1.725	24.53
43	C 3	1005	1252	1.245	1.4179	41.28	−123.0G	70.7	1.416	24.67
44	C—C 4	954	1288	1.351	1.4240	40.50	− 82.0G	81.8	3.373	25.00
	High	1005	1348	1.403	1.4275	42.21	− 15.0	81.8	3.373	25.95
	Low	828	1044	1.164	1.4113	39.61	−123.0	68.0	0.538	21.40
	Difference	177	304	0.239	0.0162	2.60	108.0	13.8	2.835	4.55

[a] Compared with corresponding hydrocarbon at 760 mm.: *n*-octane, 124.7°; 2-methylheptane, 116.0°; 3-methylheptane, 117.6°; 4-methylheptane, 118.0°. [b] Compared with corresponding hydrocarbon at 25°: *n*-octane, 0.6985; 2-methylheptane, 0.6953; 3-methylheptane, 0.7085; 4-methylheptane, 0.7135. [c] "G" indicates formation of a glass. Determined in this Laboratory by Teets and Andrews. For apparatus and method, see THIS JOURNAL, **56**, 1143 (1934).

[d] These values are for 13°, one of the temperatures where variations were largest. Measured in this Laboratory by Cline and Andrews, *ibid.*, **53**, 3669 (1931). [e] Measured by Professor O. Maass and H. R. Wyman, McGill University; see M.Sc. Thesis of Wyman, 1930. Values given in dynes/sq. cm. at 20°. Method used was that of Richards and Carver, THIS JOURNAL, **43**, 827 (1921).

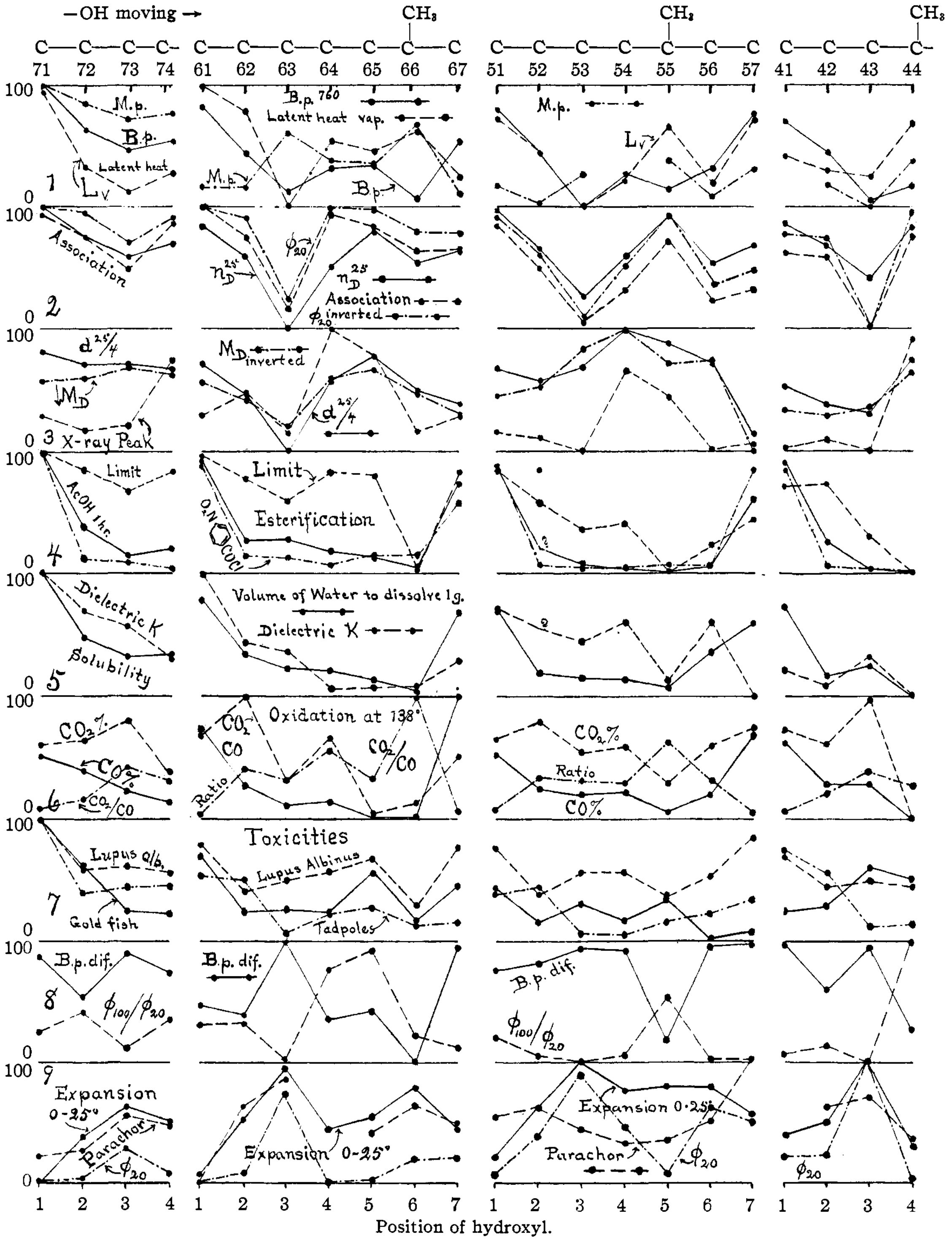

Fig. 1.—Numerical values of properties plotted against position of hydroxyl group, the highest and lowest values of each being taken as 100 and 0.

TABLE II

Key no.	Structure	$E^{f,g}$	$P^{f,h}$	$C^{f,i}$	Diel. const.[j]	$\phi 20°$[k]	$\phi 20°$[k] / $\phi 100°$	Assoc. 15°[l]	X-ray sec. peak[m]	Odors[n] FABC
71	C 1 OH	58.6	348.5	3.10	9.8	11.03	19.48	1.51	11.0	5425
72	C 2 ↓	40.8	350.2	1.34	7.7	12.49	28.11	1.47	6.0	5325
73	C 3	50.8	358.3	2.01	6.7	31.82	12.23	1.32	7.5	5426
74	C 4	49.8	356.4	2.13	5.0	17.20	24.95	1.48	27.2	5526
61	C 1 OH	35.0	342.1	1.02	9.8	10.45	21.80	1.53	11.0	5326
62	C 2 ↓	48.3	360.8	1.93	5.9	17.00	22.26	1.43	17.8	5426
63	C 3	49.5	368.2	2.21	5.4	65.25	6.40	1.19	6.0	5425
64	C 4	..	...	..	3.36	10.60	46.96	1.50	36.2	5626
65	C 5	49.9	354.6	1.96	3.44	11.07	55.59	1.46	28.0	4526
66	C—C 6	52.0	361.1	1.99	3.46	25.38	16.92	1.38	6.0	6524
67	C 7	46.0	356.6	1.84	4.95	25.52	12.86	1.38	11.0	5425
51	C 1 OH	50.6	358.6	2.07	7.1	16.20	16.65	1.47	6.0	5424
52	C 2 ↓	48.9	360.7	1.91	7.5	39.86	8.89	1.32	4.0	5526
53	C 3	53.2	355.4	2.40	6.0	76.95	5.14	1.14	0	5747
54	C 4	51.8	352.1	2.11	7.18	45.59	8.87	1.25	24.6	5626
55	C—C 5	51.2	352.9	2.07	3.76	16.17	34.91	1.42	16.5	5526
56	C 6	50.1	357.2	1.96	7.16	56.17	6.71	1.21	0	5526
57	C 7	52.6	371.7	2.32	2.85	47.89	6.77	1.25	2.7	5435
41	C 1 OH	..	...	..	4.37	25.98	10.21	1.37	1.0	5335
42	C 2 ↓	46.9	361.0	1.86	3.58	27.50	13.49	1.36	4.0	5325
43	C 3	51.8	363.4	2.30	5.15	83.30	5.07	1.12	0	4627
44	C—C 4	49.2	353.1	2.00	2.92	12.34	59.58	1.44	33.8	4526
	High	58.6	371.7	3.10	9.8	83.30	59.58	1.53	36.2	6747
	Low	35.0	342.1	1.02	2.85	10.45	5.07	1.12	0	4324
	Difference	23.6	29.6	2.08	6.95	72.85	54.51	0.41	36.2	2423

Key no.	Structure	Ester. with HOAc[o]		Ester. with acet. anhyd.[p]	Low temp. oxidations[q]		Toxicities[r]			
		One hr.	Limit.		% C oxidized	CO_2/CO	Lup. Albus[s]	Goldfish[t]	Newts[u]	Tadpoles[v]
71	C 1 OH	38.55	69.38	40	1.56	0.54	56	11	2	9
72	C 2 ↓	15.90	59.02	8	1.42	0.70	33	18	6	23
73	C 3	7.36	47.77	4	1.25	1.47	34	44	7	31
74	C 4	9.24	58.54	4	0.74	1.20	32	50	8	20
61	C 1 OH	36.47	68.11	40	2.18	0.41	45	16	2	17
62	C 2 ↓	12.03	54.78	6	1.53	1.46	23	30	20	18
63	C 3	12.31	42.39	3	0.58	1.26	28	28	55	120
64	C 4	8.99	58.55	2.5	0.95	1.89	32	30	57	44
65	C 5	7.08	57.41	0	0.13	1.25	38	13	25	32
66	C—C 6	3.20	4.18[d]	2	0.21	3.14	17	20	9	70
67	C 7	29.21	59.59	37	2.52	0.24	44	24	3	54
51	C 1 OH	34.60	60.28	39	1.72	0.56	43	25	2.5	23
52	C 2 ↓	34.00	41.85[d]	1	1.31	1.31	22	45	27	20
53	C 3	4.87	27.47[d]	0	0.97	1.20	32	23	50	125
54	C 4	3.26	30.87[d]	0	1.10	1.17	32	40	60	130
55	C—C 5	1.76	2.91[d]	1	0.45	2.10	21	11	8	65
56	C 6	4.97	18.16[d]	2	1.03	1.24	30	240	120	40
57	C 7	24.22	32.80	36	2.12	0.49	48	120	4	26
41	C 1 OH	36.13	50.13	39	2.00	0.51	39	42	4	12
42	C 2 ↓	11.56	51.65	0	1.23	0.91	25	37	17	16
43	C 3	2.70	23.00	0	1.54	1.43	28	11	21.5	73
44	C—C 4	1.45	2.53[d]	0	0.09	1.40	25	6	5	60
	High	38.55	69.38	40	2.52	3.14	56	6	2	9
	Low	1.45	2.53	0	0.09	0.24	17	240	120	130
	Difference	37.10	66.85	40	2.43	2.90	39	234	118	121

[f] Surface energy relations derived by Maass, *et al.*, from surface tension data. [g] Total surface energy in ergs/sq. cm. as calcd. by $E = S + T\,dS/dT$. [h] Parachors (mean of values in range 0–50°) as calcd. by $P = M/DS^{1/4}$. [i] Ramsey and Shields const. [j] Based on data of Prof. C. P. Smyth, Princeton Univ., THIS JOURNAL, **51**, 3330 (1929). Values at 25° except 52 at 5°. [k,l] ϕ = Fluidity. From Prof. E. C. Bingham, Lafayette College. Bingham and Darrall, *J.*

Rheol., **1,** 174 (1930). [m] From Prof. G. W. Stewart, Ia. St. Univ.; Stewart, *Phys. Rev.*, **35,** 726 (1930); Stewart and Edwards, *ibid.*, **38,** 1575 (1931). [n] Determined by Crocker and Henderson, Arthur D. Little, Inc., for method, see *Am. Perf. Essent. Oil Rev.*, 22, 3 (1927). [o] Dissertation, H. C. Tidwell, J. H. U., 1930. [p] Values are for 125 hr. [q] Dissertation, Thos. Cross, Jr., J. H. U., 1933. [r] Toxicities to these and other organisms determined by Macht and coworkers of Hynson, Westcott and Dunning. See Macht and Leach, *J. Pharmacol. Exp. Ther.*, **39,** 71 (1930); Macht, *Am. J. Bot.*, **17,** 572 (1930); Macht, *Physiol. Zoöl.*, **3,** 412 (1930); Macht and Schroeder, *Archiv. exp. Path. Pharmakol.*, **158,** 53 (1930). [s] Retardation of seedlings. [t] Paralysis of respiration (min.). [u] Anesthesia of tails (min.). [v] Paralysis of movement (min.).

into changes associated with (a) variations in position of hydroxyl, methyl being fixed, (b) the primary, secondary or tertiary character of the alcohol, (c) the proximity of the hydroxyl to the center of the carbon chain. The tables and figure are designed to show the effect of introducing hydroxyl in different positions into the four hydrocarbons. They can be arranged also on the basis of placing of a methyl group at different positions in the four heptanols.

A glance at the figure indicates that many of the properties show much greater variations in the methylheptanols than in the octanols. In the several groups most of the properties have the highest values when the hydroxyl is farthest from the methyl group. They are lower when it is on the next carbon atom and still lower when it is on the third but higher for the fourth position.

In Table III the average values of several properties are given for the three classes of alcohols.

TABLE III

AVERAGE VALUES OF SOME PROPERTIES FOR THE THREE CLASSES OF ALCOHOLS

	Primary	Secondary	Tertiary
Boiling point, °C.	185.5	167.4	158.8
Density 25/4	0.8075	0.8101	0.8174
Index of ref.	1.4249	1.4202	1.4235
Solubility	0.685	1.565	2.793
Fluidity	22.84	38.04	17.96
Est. 1 hr., %	33.0	8.36	2.14
Est. limit, %	56.7	44.0	3.21
Oxidation, %	2.01	1.06	0.25

The boiling points and oxidations are like esterification velocities and limits in being highest for primary and lowest for tertiary; the solubilities and densities are the reverse.

Boiling Points.—The vapor pressure curves for 11 representative octanols—as many as could be plotted without confusion—are in Fig. 2. Those for the primaries fall in the order of the distance of the hydroxyl group from the side methyl group except that 57 (not plotted) is close to 51. Of the secondaries which are not plotted, 74 is practically identical with 62; 73, 65, 52 and 42 are very close to 64; 43 is near 53, while 54 and 56 form a pair between 63 and 53. The curves for the other two tertiaries, 55 and 66, would fall almost exactly on that for 44. The curves for the tertiaries are steeper than those for the secondaries which are steeper than those for the primaries. In the several groups the boiling points, except 65, go down as the hydroxyl moves from either end to the third carbon and then go up at the center even when it is tertiary as 44. As expected, the primaries boil highest (except that 74 is above 67), but except 66, the low boiling points are associated with the hydroxyl on the third carbon from either end rather than with the tertiary character of the octanol. The boiling point differences, plotted in sec. 8, are the differences between the boiling points at 760 and at 20 mm. They always are high when the hydroxyl is on the third carbon from the long end and always low for tertiaries. Except for 65–67, it is almost the reverse of the boiling point difference; the steeper the vapor pressure curve the greater the change in fluidity with temperature.

Latent Heats of Vaporization.—As shown in sec. 1 of Fig. 1 the L_{v} values follow the boiling points from which they are derived except at the tertiaries 65, 55 and 44.

Boiling Point Elevations.—In each group these follow the boiling points from which they are obtained by subtracting the boiling points of the hydrocarbons.

Melting Points.—The four octanols of the 7 group melt higher than any of the methylheptanols. They give a pattern similar to that of the boiling points in that group as shown in sec. 1 of Fig. 1. The methyl side chain, regardless of its position, lowers the melting point greatly and favors the formation of glasses of which the melting points are unsatisfactory. In each group the tertiary has the highest melting point. The variation of the molal heat capacity is not great in any series.

Densities and Derived Properties.—The densities in the 7 series alternate but the variation is small. In the other series the variations are large, each series showing an individual pattern.

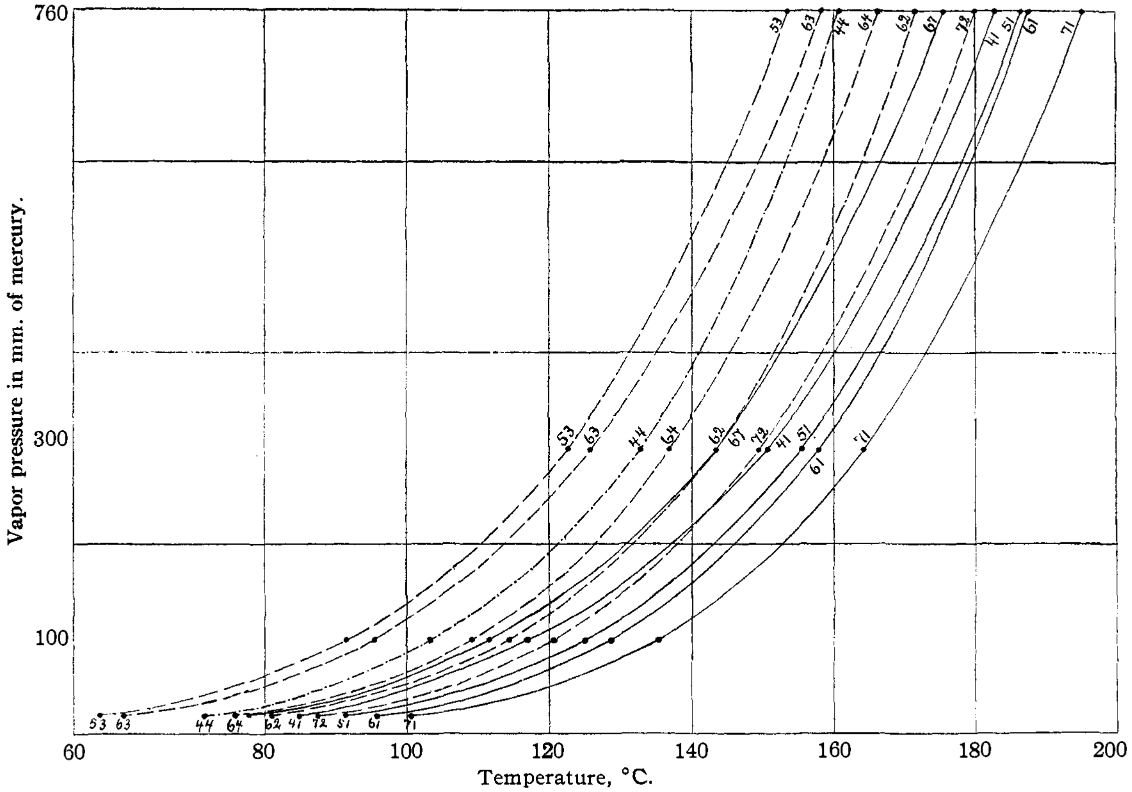

Fig. 2.—Vapor pressures of some of the octanols: primary, ————; secondary, — — —; tertiary, — · — · —.

The densities in the 6 and 4 series resemble the boiling points and refractive indexes but not so in the 5. The molecular refraction inverted, *i. e.*, plotted downward, gives a pattern similar to that of the densities. The heights of the secondary X-ray peaks seems to follow the densities but not closely.

The coefficient of expansion 0–25°, plotted in sec. 9, is almost the mirror image of the b. p. curve in 1. This is reasonable; the further the octanols are from their boiling points the less they expand.

Indexes of Refraction.—The shifting of the methyl group has relatively little effect when the hydroxyl is on the first, second or fourth carbon, but causes sharp minima when it is on the third. The primaries tend to be high when the methyl is not near the hydroxyl. The 6 and 5 series show remarkably similar patterns. The association follows the same pattern.

Solubilities.—In sec. 5 of Fig. 1 the volume of water to dissolve 1 g. of an alcohol has been plotted instead of the data in Table I. This makes a pattern very like that of the dielectric constants except in the 5 series and even more like the esterification for one hour except 43. The dielectric constant usually goes up instead of down in the fourth position. On the average, the tertiary octanols are about twice as soluble as the secondary and four times as soluble as the primary.

Esterification.—The figures for one hour with acetic acid at high temperature are the initial velocities. For determining the limits the heating was continued at the same temperature for one hundred and twenty-five hours. The primaries have high initial velocities, 36–38% when the hydroxyl is far from the methyl group and 24–29% when it is near. The secondaries show a wide variation from 12–15% when the hydroxyl is near the end of a long carbon chain down to 2.7%, which is lower than the tertiary 66. The velocities are very low when the hydroxyl and methyl are near the middle of the carbon chain as in 54 and 43. The tertiaries, which are all low, arrange themselves in the order of the distance of the hydroxyl from the end of the chain, 66, 55 and 44. With acetanhydride as well as with *p*-nitrobenzoyl chloride the secondaries and tertiaries are very slow. Esterification limits for the secondaries are comparatively high. Attention is called

TABLE IV

PREPARATION AND ANALYSES OF NEW OCTANOLS

Ref. no.	Methyl-heptanols	Bromide used	Other reagent	Analyses, %	
				Calcd. C 73.76	H 13.94
67	2-Methyl-ol-1	2-Bromoheptane	Formaldehyde	73.71	14.06
51	5-Methyl-ol-1	1-Bromo-3-methylpentane	Ethylene oxide	73.92	14.18
52	5-Methyl-ol-2	1-Bromo-3-methylpentane	Acetaldehyde	73.73	13.59
54	3-Methyl-ol-4	2-Bromobutane	*n*-Butyraldehyde	73.80	13.93
56	3-Methyl-ol-2	2-Bromohexane	Acetaldehyde	73.83	13.82
41	4-Methyl-ol-1	1-Bromo-2-methylpentane	Ethylene oxide	73.58	14.38

to the close resemblance between the groups 71–74 and 61–64. The four 51–54 give a similar pattern except that it is tilted by the methyl group at 5. The limits for the tertiaries are not significant as they suffered more or less dehydration during the long heating, there being less than twice as much ester in one hundred and twenty-five hours as in one.

Fluidity.—The fluidities at 20°, sec. 9 of Fig. 1, vary widely, the highest being 8 times the lowest. In each group the fluidity is highest when the hydroxyl is on the third carbon from the long end. In 73, 63, 53 and 43 it increases as the methyl moves in. The fluidity of a primary is low when the hydroxyl is far from the methyl. The more symmetrical a tertiary is the lower its fluidity. In sec. 2 the fluidities are inverted, *i. e.*, plotted downward. This makes them follow the associations; the greater the association the less the fluidity. The ratio of the fluidity at 100° to that at 20° is plotted in sec. 8 and compared to b. p. differences.

Low Temperature Oxidations.—The carbon monoxide pattern, sec. 6 in Fig. 1, is curiously like that for the reciprocal solubility and much like that for esterification velocity except that the primaries in which the hydroxyl is near the methyl group, go faster than those in which it is further away, 67 > 61 and 57 > 51. The carbon dioxide shows alternation. The average ratios of carbon dioxide to monoxide are 0.46 for primary, 1.27 for secondary and 2.21 for tertiary. The total oxidation averages 2% for primary, 1% for secondary and only 0.25% for tertiary.

Toxicity.—The toxicities plotted in sec. 7 agree only roughly among themselves. The primaries tend to be high. There is some resemblance in the patterns to that of the solubilities in sec. 5. The amounts of the alcohols which actually get into the living cells depend on the partition coefficients between water and cell substance.

Variations in Properties.—Attention is called to the wide variation in some of the properties: no. 44 is six times as soluble as 71, no. 28 resists oxidation 28 times as well as 67 while no. 61 is 8 times as fluid as 43. The toxicity of 44 is 40 times that of 56 and 71 stops a newt's tail in two minutes while 56 takes two hours.

Experimental

A. Synthesis of Octanols.—Octanol-1 and octanol-2 were obtained from Eastman Kodak Co. and purified carefully. The remaining 20 octanols were prepared in this Laboratory by the Grignard reaction, generally standard procedure being followed. Runs varied in size from 1–12 moles, but were usually 5 moles. The apparatus consisted of a 3-neck flask fitted with a mechanical stirrer, high-capacity circulating ice water reflux, and dropping funnel. The total amount of absolute ether was 200–300 cc./mole, a small part of it usually being employed to dilute the bromide. Some reactions were initiated with a crystal of iodine. The magnesium was a C. P. product in the form of bright turnings. The aldehyde or other oxygen compound was added until there was no further test for free RMgX with Michler ketone.[8] Ethylene oxide was vaporized into the mixture through a wide-mouth tube, placed a few cm. above the liquid in the flask.[9] Monomeric formaldehyde was obtained by depolymerization of paraformaldehyde previously dried over phosphorus pentoxide for seventy-two hours at 90° and 3 mm. It was vaporized directly into the Grignard reagent[10a,b] or added as a previously prepared 50% ethereal solution cooled to below −21°,[11] approximately equal yields being obtained by both methods. The basic magnesium halide was usually decomposed with dilute sulfuric acid, and the ethereal solution dried over anhydrous potassium carbonate before distillation.

Table IV shows the 6 new octanols prepared, reagents used, and analytical data.

In a few instances check preparations were made as follows: (1) *n*-octanol (71) was prepared by the Bouveault–Blanc reduction of ethyl caprylate, density, b. p., and other common properties being identical with those of the purified Eastman product; (2) 41 was prepared by the Grignard reaction from 1-bromo-3-methylhexane and formaldehyde (yield, 52%), n^{25}D being 1.4280 as compared to 1.4253 for the product in the table; (3) 67 was prepared by reduction of 2-methylheptanoic acid, n^{25}D being 1.4213

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(8) Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

(9) "Organic Syntheses," Vol. VI, John Wiley & Sons, N. Y., 1926, p. 54.

(10) (a) Auerbach and Plüddemann, *J. Chem. Soc.*, **106**, 488A (1914); (b) Wood and Scarf, *J. Soc. Chem. Ind.*, **42**, 13T (1923).

(11) Kekulé, *Ber.*, **25**, 2435 (1892).

TABLE V

INTERMEDIATES

Compound	Prepared from	B. p., °C.	Mm.
Pentanol-1	n-BuBr + HCHO	137.8	760
Pentanol-2	n-PrBr + CH_3CHO	119.5	760
3-Methylbutanol-1	i-BuBr + HCHO	130.5	760
2-Methylbutanol-1	s-BuBr + HCHO	128.0	752
4-Methylpentanol-1	i-BuBr + $(CH_2)_2O$	151.7	758
2-Methylpentanol-1	n-PrOH + n-PrOH	148.9	760
Hexanol-2	n-BuBr + CH_3CHO	139.7	759
Heptanol-2	n-AmBr + CH_3CHO	158.5	754
3-Methylhexanol-1	3-Methylhexanoic acid + H	94.6	40
*n-Amyl bromide	n-Amyl alcohol	127.8	745
*n-Butyl bromide	n-Butyl alcohol	101.3	760
*1-Bromo-4-methylpentane	4-Methylpentanol-1	147.6	760
*1-Bromo-3-methylbutane	3-Methylbutanol-1	121.0	760
*i-Butyl bromide	i-Butyl alcohol	91.2	760
*2-Bromoheptane	Heptanol-2	81.7	45
*1-Bromo-3-methylpentane	3-Methylpentanol-1	146.5	760
*1-Bromo-3-methylbutane	2-Methylbutanol-1	117.5	760
*2-Bromobutane	s-Butyl alcohol	91.2	750
*2-Bromohexane	Hexanol-2	143.9	750
*1-Bromo-2-methylpentane	2-Methylpentanol-1	83.8	100
*2-Bromopentane	Pentanol-2	118.4	760
*1-Bromo-3-methylhexane	3-Methylhexanol-1	87.5	50
* Propionaldehyde	n-Propanol	48.8	760
*n-Butyraldehyde	n-Butanol	74.9	760
*Isobutyraldehyde	i-Butanol	63.5	760
*Methyl ethyl ketone	s-Butyl alcohol	80.6	760
*2-Methylheptanoic acid	n-AmBr + methylmalonic ester	...	
*3-Methylheptanoic acid	2-Bromohexane + malonic ester	...	
3-Methylhexanoic acid	2-Bromopentane + malonic ester	...	

as compared to 1.4219 for the product in the table; (4) 57 was prepared by reduction of 3-methylheptanoic acid, $n^{25}D$ being identical with that of the product in the table. Most of the measurements were made with the lots whose preparation is given in the table.

B. **Intermediate Alcohols.**—n-PrOH, n-BuOH, i-BuOH, and s-BuOH were the best available commercial grades, each carefully purified before use. 2-Methylpentanol-1 was obtained by the Guerbert reaction by condensation of 2 moles of n-PrOH[12] in the presence of potassium propionate as a catalyst. All others were synthesized by the Grignard reaction following the procedure given above.

C. **Higher Aldehyde and Ketone Intermediates.**—These were obtained by catalytic dehydrogenation of the corresponding alcohols over a copper alloy catalyst by the method of Bouveault[13] except that the superheated vapors were passed downward over the catalyst. Temperatures were generally in the range 250–300° and yields per pass ranged from 20 to 35%.

D. **Other Oxygen-Containing Intermediates.**—Ethyl acetate, ethylene oxide, acetone, paraformaldehyde, and acetaldehyde were the best obtainable commercial grades, each purified before use. The malonic ester was a commercial but authentic product, and ethyl caprylate was obtained by fractionation of the ethyl esters of coconut oil acids.

E. **Intermediate Bromides.**—Bromides were prepared from the corresponding alcohols and HBr–H_2SO_4 mixture (from reduction of Br_2 with SO_2) by the general method of Kamm and Marvel,[14] with minor variations for different bromides. Thus, for the secondary bromides, *e. g.*, 2-bromohexane, very little additional sulfuric acid was added to the 48% hydrobromic acid, and conditions of heating were in general more mild, *e. g.*, ten to fifteen hours on a water-bath with stirring. If the reaction is sluggish but the alcohol and bromide relatively more stable (as is the case with most of the higher primary compounds), somewhat higher yields are obtained by adding larger amounts of sulfuric acid (up to 2–3 moles extra), heating and stirring on the water-bath for ten to twelve hours, steam-distilling, and heating the resulting mixture of alcohol and bromide with a fresh lot of hydrobromic acid–sulfuric acid mixture.

Table V shows the intermediates prepared, their principal source, and their boiling points. The octanol intermediates are marked by an asterisk.

F. **Methods of Purification.**—All intermediates and all octanols were purified by distillation through high precision stills,[15] one designed for operation at atmospheric pressure, and another at reduced pressure. Both had

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[12] Guerbert, *Compt. rend.*, **146**, 298 (1908).

[13] Bouveault, *Bull. soc. chim.*, (4) **3**, 50, 119 (1908).

[14] "Organic Syntheses," Vol. I, John Wiley & Sons, N. Y., pp. 1–13.

[15] Essentially like that of Peters and Baker, *Ind. Eng. Chem.*, **18**, 69 (1926).

glass-packed columns 152 cm. high. The vacuum still was fitted with the pressure regulator described by Ellis.[16]

The intermediates used were fractions boiling over a range of 0.5° and usually 0.2–0.3°. The octanols were collected over a range of 0.1–0.2°.

Properties and Derivatives.—The measurements in this Laboratory on the octanols were carried out as follows. Those conducted in other Laboratories are referred to in footnotes to Tables I and II.

A. **Determination of Boiling Points.**—Boiling points were determined at three reduced pressures and at atmospheric pressure, and from the data vapor pressure curves were constructed. A modification of the Cottrell boiling point apparatus[17] was used, the lower end of the tube being narrowed to give it a capacity of 10 cc. The thermometers used were graduated in half-degrees and carried a U. S. Bureau of Standards calibration and certificate. Suitable stem corrections were applied. Pressure was maintained constant by the Ellis regulator previously mentioned.[16]

Boiling points at 760 mm. are interpolated values. The latent heats of vaporization were calculated by means of the Clausius–Clapeyron equation.

B. **Determination of Refractive Indices.**—An Abbe refractometer was used giving duplicate readings to within ±0.0002, which is the accuracy of the values given. By means of the compensating prism, the dispersions were calculated and found to be practically identical for all alcohols, 0.0077. The Lorentz–Lorenz formula was used to calculate molecular refractions.

C. **Densities and Coefficients of Expansion.**—Densities were taken in triplicate at two temperatures, 0/4 and 25/4, by means of carefully calibrated pycnometers, temperatures being held to within 0.02° in each case. The maximum variation was 0.00008 between the three measurements, and the average value is therefore considered correct to 0.0001.

Expansions were assumed to be a linear function of the temperature between 0 and 25°. The coefficient of thermal expansion α was calculated by the formula

$$\alpha = (d_1/d_2) - 1/t_2 - t_1$$

D. **α-Naphthylurethans.**—The α-naphthylurethans of all the octanols were prepared, but in only nine cases was it possible to obtain crystalline solids. These were recrystallized from dilute alcohol to constant melting points; a change of solvent to petroleum ether (heptane fraction) caused no change in melting point. Corrected melting points of those obtained are: octanol-1, 67.0°; octanol-3, 54.0°; octanol-4, 65.5°; 4-methylheptanol-4, 90.0°; 3-methylheptanol-3, 52.0°; 2-methylheptanol-2, 57.5°; 2-methylheptanol-3, 73.0°; 2-methylheptanol-4, 70.0°; 6-methylheptanol-1, 68.5°.

E. **3,5-Dinitrobenzoates.**—Attempts were made to prepare the 3,5-dinitrobenzoates of all of the octanols according to the method of Mulliken[18] with the apparatus, thermometers, and variations in procedure given by Malone and Reid.[19] No esters of the tertiary alcohols could be obtained. The esters of 2-methylheptanol-3, 4-methylheptanol-3, 5-methylheptanol-3, and 3-methylheptanol-4 underwent alcoholysis, as shown by the gradual changing to the ethyl ester, and could be crystallized only from the ether mixture. The esters of 2-methylheptanol-1, 3-methylheptanol-1, and 2-methylheptanol-3 were unstable and were prepared by heating at 65° for six hours. Of the nineteen esters obtained, twelve were crystalline and the others oils at room temperature. The corrected melting points of the solid esters are: octanol-1, 60.8°; octanol-2, 32.3°; octanol-3, 69.4°; octanol-4, 53.9°; 6-methylheptanol-1, 58.3°; 2-methylheptanol-1, 50.6°; 2-methylheptanol-3, 38.5°; 2-methylheptanol-4, 71.7°; 6-methylheptanol-2, 34.4°; 3-methylheptanol-4, 91.8°; 5-methylheptanol-3, 89.8°; 4-methylheptanol-3, 92.4°.

F. **Measurements of Solubility in Water.**—For these measurements it was necessary to employ a method capable of showing up small differences in solubility as well as one which would permit accurate measurements on limited amounts of material. The interferometer method of Adams,[20] with the adaptations of Gross and Saylor[21] was used. Samples were weighed out in ground-glass-stoppered vials. The stoppered vial then was dropped into the water, and the flask stoppered and the vial opened under water by shaking. Saturated solutions were made up by shaking for twelve hours in a thermostat kept at 25 ± 0.01°.

G. **Relative Reaction Rates with Acetanhydride.**—The comparative values for the reaction rates of the isomers were obtained as follows. Into a 15-cc. flask was weighed 0.932 g. ± 1 mg. of one of the alcohols, and 10 cc. of a 1 molal solution of acetanhydride in acetone was added. The flask, along with others similarly charged, was kept in a bath at 35 ± 0.01°; 2-cc. portions were pipetted out at the desired intervals and titrated with standard barium hydroxide solution. The results were compared with a like portion taken out at the start of the run. The accuracy of the results is estimated at about 2%. Runs were made at 50, 125 and 175 hours for the more reactive alcohols and at 100, 125 and 250 hours for the others. Table II shows actual or interpolated values for the per cent. esterification after 125 hours.

H. **Esterification Rates and Limits with Acetic Acid.**—These measurements were carried out in this Laboratory by H. C. Tidwell. Equivalent amounts of octanol and acetic acid were sealed in small glass tubes, several for each octanol, which were heated for periods ranging from one to two hundred hours at 136 ± 0.5°. The tubes were broken under water after various periods of heating, the free acid titrated, and the per cent. esterification calculated. Some of the octanols decomposed to a certain extent.

I. **Low Temperature Oxidations.**—These measurements were carried out in this Laboratory by Thomas Cross, Jr. Five grams of each octanol was heated to 137° and oxygen bubbled through for nine hours. The carbon monoxide and carbon dioxide were determined after 3 periods of three hours each. The per cent. oxidation shown in Table II is the percentage of the carbon appearing as carbon monoxide and carbon dioxide, the total carbon in 5 g. octanol being 3.7 g.

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(16) Ellis, *Ind. Eng. Chem., Anal. Ed.*, **4**, 318–319 (1932).

(17) Cottrell, THIS JOURNAL, **41**, 721 (1919).

(18) "Identification of Pure Organic Compounds," Vol. I, 1st Ed. by S. P. Mulliken, John Wiley and Sons, New York, N. Y., 1905, p. 168.

(19) Malone and Reid, THIS JOURNAL, **51**, 3424 (1929).

(20) Adams, *ibid.*, **37**, 1181 (1915).

(21) Gross and Saylor, *ibid.*, **51**, 2362 (1929); **53**, 1745 (1931).

Acknowledgment

We acknowledge gratefully the coöperation in this work of Professor C. P. Smyth of Princeton University, Professor P. L. Bridgman of Harvard University, Professor E. C. Bingham of Lafayette College, Messrs. E. C. Crocker and Henderson of Arthur D. Little, Inc., Professor O. Maass of McGill University, Dr. D. I. Macht of Hynson, Westcott and Dunning, and Professor G. W. Stewart of Iowa State University; also of Professor D. H. Andrews, Dr. J. B. Tidwell, Dr. F. K. Bell, Dr. Thomas Cross, Jr., Dr. D. E. Teets, Dr. Edith Wilson, Professor R. W. Wood and Dr. G. Collins of the Chemical and Physical Laboratories of this University. It was only through their assistance and special abilities that an investigation of this magnitude could be brought to fruition.

Summary

1. The four straight chain octanols and the eighteen methylheptanols have been prepared in large experimental quantities by well-characterized synthetic methods. Six of the methylheptanols had not previously been made.

2. These 22 alcohols have been carefully purified by distillation through high-precision stills.

3. We and our collaborators in this Laboratory and other laboratories have determined, by actual measurement and mathematical derivation, a large number of physical and chemical properties of these alcohols. In general, each measured property was obtained for all the octanols by a single investigator over a short period of time using the same apparatus and technique.

4. Most of the data obtained in this Laboratory and some of those obtained elsewhere are brought together in tables arranged according to different positions of the hydroxyl group. As a rule, this variation causes the greatest change in properties.

5. The data have been plotted so as to show the variation in properties with changes of structure. The graphs have been grouped so as to show which properties change in the same direction and which inversely when the hydroxyl is moved.

6. The relations of the values obtained in this Laboratory to molecular structure have been discussed.

BALTIMORE, MD. RECEIVED APRIL 16, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Rate and Equilibrium Studies of Carbinol Formation in the Triphenylmethane and Sulfonphthalein Dyes

BY SEYMORE HOCHBERG AND VICTOR K. LAMER

The determination of the effects of substituents and of molecular structure upon the rates of chemical reactions is a problem of interest and importance. The necessary measurements can be made most accurately and conveniently in aqueous media. Reactions involving dyestuffs are particularly well suited for such investigations but as is the case for most reactions in aqueous solution, the reactant species are frequently of an ionic nature. To analyze accurately the effects of substitution it is imperative that all disturbing influences arising from the presence of the net charges of the reactant molecules be eliminated or adequately corrected.

Even if the comparisons of different substituents are restricted to ionic reactions of the same electric charge type and ionic strength, it is possible that the comparisons may still be complicated by specific electrostatic effects which depend on the size of the reactant ions and the location of the charges in these molecules. These specific effects can be eliminated if a satisfactory method can be developed for correcting the rates of ionic reactions to the hypothetical rate for the corresponding uncharged reactants.

A well-recognized procedure is to determine the functional dependence of the free energy of activation ($-RT \ln k/\nu$) upon the dielectric constant of the medium at a given temperature and to extrapolate the results to infinite dielectric constant where all electrostatic effects vanish.

An alternate method has been presented by one of us.[1-3] It consists essentially in determining the rate of reaction in mixed solvents so chosen that the temperature coefficients of the rate may be evaluated not only under the customary re-

(1) LaMer, *J. Franklin Inst.*, **225**, 709 (1938).

(2) Amis and LaMer, THIS JOURNAL, **61**, 905 (1939).

(3) Warner, *Ann. N. Y. Acad. Sci.*, **39**, 345 (1940).