TABLE II

REARRANGEMENTS OF SILICON CHLORO(ISO)CYANATES

Run	Initial Mixture	Atom % Cl Initial	Atom % Cl Final	$SiCl_4$	$SiCl_3(NCO)$	$SiCl_2(NCO)_2$	$SiCl(NCO)_3$	$Si(NCO)_4$
1	$^1/_2$ $SiCl_4$ + $^1/_2$ $Si(NCO)_4$	0.50	0.50	found 8	25	34	25.0	8.0
				calcd. 6.25	25.0	37.5	25.0	6.25
2	pure $SiCl_2(NCO)_2$	.50	.50	found 8	25	34	26	7
				calcd. 6.25	25.0	37.5	25.0	6.25
3	pure $SiCl_3(NCO)$	.75	.75	found 33	38	24	5	(0)
				calcd. 31.6	42.2	21.1	4.7	0.4
4	pure $SiCl(NCO)_3$	.25	.26	found (0)[a]	5.0	26	36	33
				calcd. 0.4	4.7	21.1	42.2	31.6

[a] Too small for satisfactory measurement, although $SiCl_3(NCO)$ started to distill at 80°, instead of 87°.

react together; all five possible compounds are produced in amounts predictable by assuming random distribution of groups. Previous work on redistribution in the lead alkyl series[7] indicated random distribution of groups, and included a method of calculating the percentage occurrence of each compound. Thermal rearrangement of individual compounds ($SiCl_3(NCO)$, $SiCl_2(NCO)$, and $SiCl(NCO)_3$) was studied carefully; vapor was passed through a hot tube at 600°, at a slow rate, with later determination of products by fractional distillation. Table II summarizes the results.

Experimental Work on Rearrangements.—The redistribution between $SiCl_4$ and $Si(NCO)_4$ was done on a large scale and produced large amounts of the compounds desired, as explained at the beginning of the section on preparation. By adjusting the amounts found according to molecular volumes (Table I), the correct molecular ratios were obtained. Rearrangements of $SiCl_3(NCO)$, $SiCl_2(NCO)_2$, and $SiCl(NCO)_3$ were obtained by the passage of 5 ml. of each pure compound through a small Pyrex tube at 600°, over a period of thirty minutes. Values in Table II have been rounded off to the nearest per cent. More precise and therefore slower distillation would have led to secondary rearrangements of considerable magnitude. Amounts of less than 2% are difficult to determine, notably if the least volatile compound is involved. Volumes were measured to 0.05 ml. in calibrated receivers of the same bore and with nearly flat bottoms.

The percentages indicate random distribution within a few per cent. Secondary rearrangements are too close for attainment of theoretical ratios. Values of the chief component are a little low in all cases, but this is within experimental error, and without significance.

A sample of $SiCl_2(NCO)_2$ rearranged to the extent of several per cent. after standing four months at room temperature. Mixtures of $Si(NCO)_4$ and $SiCl_4$, as well as the three chloro(iso)cyanates, are being set aside at room temperature with the intention of determining the distribution of products after considerable time intervals.

The author is much indebted to Professor George S. Forbes of this Laboratory for many helpful suggestions. Other work on rearrangement of mixed halides and on cyanates and thiocyanates is in progress and will be reported soon.

Summary

1. $SiCl_3(NCO)$, $SiCl_2(NCO)_2$, and $SiCl(NCO)_3$ have been prepared. The progression of several physical properties in the series $SiCl_4$ through $Si(NCO)_4$ has been tabulated. $SiCl_4$ and $Si(NCO)_4$ react rapidly at 600° to give all three chloro(iso)cyanates. Interaction is moderate in rate at 135°, and extremely slow at room temperature. Gradual addition of AgNCO to a large excess of $SiCl_4$ in solution yields $SiCl_3(NCO)$ and $SiCl_2(NCO)_2$, but no $SiCl(NCO)_3$.

2. Random distribution, such as previously found by Calingaert, Beatty and Soroos in the lead alkyl series, also applies to the rearrangement of any mixture or pure compound in the series $SiCl_4$ through $Si(NCO)_4$. No catalyst is needed.

CAMBRIDGE, MASSACHUSETTS RECEIVED JANUARY 15, 1944

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[7] Calingaert, Beatty and Soroos, THIS JOURNAL, **62**, 1100 (1940).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

A Study of Organic Parachors. VI. A Supplementary Series of Tertiary Alcohols[1]

BY OSBORNE R. QUAYLE AND KATHERINE O. SMART

The parachor values for a series of tertiary alcohols[2] have been previously reported from this Laboratory and values for the CH_2 group in various positions have been determined and suggested as a means of calculating the parachors of other tertiary alcohols. Nine additional supplementary tertiary alcohols have been prepared and their refractive indices, densities, surface tensions and parachors have been determined. The alcohols were prepared by standard methods and were purified by successive vacuum distillations.[3] To minimize decomposition the temperatures of distillation were kept below 75°. Refractive indices were determined at 20, 25 and 35°. Densities and surface tensions were measured at 25, 45 and 55°, and the parachors were calculated for the same temperatures, using the standard formula $P = M\gamma^{1/4}/(D - d)$. The data obtained are shown in Table I. The varia-

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[1] The authors wish to express their gratitude to Professor E. Emmet Reid, Research Consultant to the department, for his continued interest and suggestions in connection with this investigation.

[2] K. Owen, O. R. Quayle and E. M. Beavers, THIS JOURNAL, **61**, 900 (1939).

[3] Prepared by Harry M. Stubbs of this Laboratory.

TABLE I

PHYSICAL PROPERTIES DETERMINED FOR NINE TERTIARY ALCOHOLS

Carbinol	T	n^{20}_D[a]	T	D	γ	P exp.	P calcd.[b]	Dev. %
Methylethylbutyl	20	1.4284	25	0.8252	25.22	353.6	353.8	0.1
	25	1.4263	45	.8083	23.33	354.1		
	35	1.4214	55	.7999	22.41	354.3		
Methylpropylbutyl	20	1.4325	25	.8268	25.60	392.4	392.4	.0
	25	1.4301	45	.8104	23.65	392.5		
	35	1.4256	55	.8022	22.66	392.3		
Methylbutylbutyl	20	1.4350	25	.8258	26.20	430.9	430.9	.0
	25	1.4326	45	.8095	24.23	431.1		
	35	1.4280	55	.8013	23.23	430.9		
Methylmethylamyl	20	1.4238	25	.8133	24.74	357.1	357.3	.1
	25	1.4218	45	.7969	22.86	357.3		
	35	1.4172	55	.7889	21.93	357.3		
Methylethylamyl	20	1.4324	25	.8275	26.06	393.8	393.8	.0
	25	1.4301	45	.8111	24.19	394.4		
	35	1.4256	55	.8029	23.23	394.4		
Methylpropylamyl	20	1.4350	25	.8271	25.73	431.0	432.4	.3
	25	1.4332	45	.8108	24.04	432.2		
	35	1.4287	55	.8026	23.17	432.7		
Ethylbutylamyl	20	1.4424	25	.8357	26.58	506.2	506.8	.1
	25	1.4401	45	.8191	24.80	507.6		
	35	1.4356	55	.8108	23.95	508.4		
Propylbutylamyl	20	1.4420	25	.8320	26.25	545.1	545.6	.1
	25	1.4397	45	.8160	24.64	547.0		
	35	1.4354	55	.8081	23.80	547.7		
Butylbutylamyl	20	1.4458	25	.8348	26.82	584.4	584.1	.1
	25	1.4434	45	.8189	25.04	585.6		
	35	1.4390	55	.8109	24.18	586.2		

[a] Refractive indices by J. P. Sutton, Jr. [b] Calcd. P based upon values of Owen, Quayle and Beavers.[3]

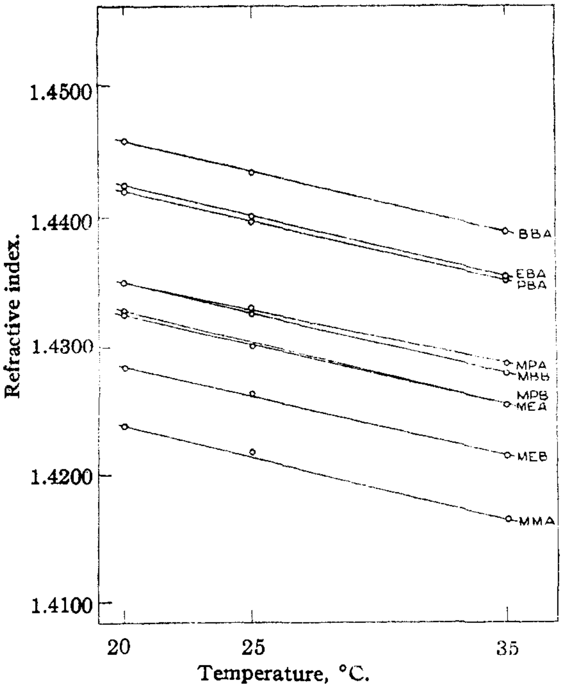


Fig. 1.—Refractive indices of tertiary carbinols.

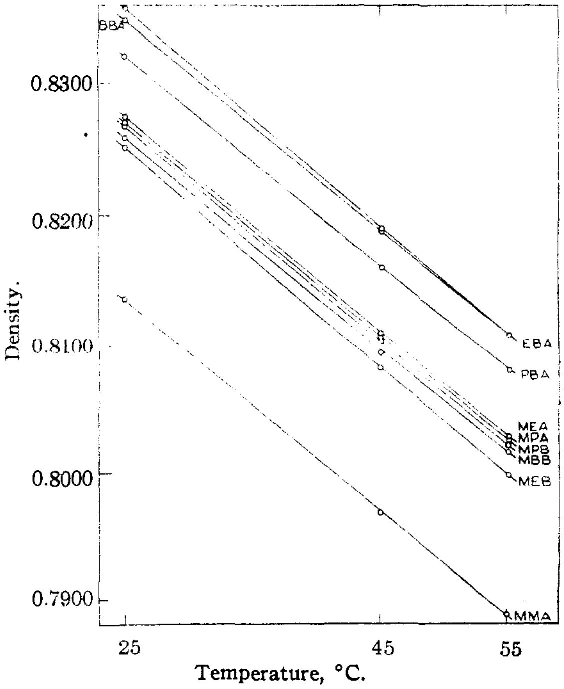


Fig. 2.—Densities of tertiary carbinols.

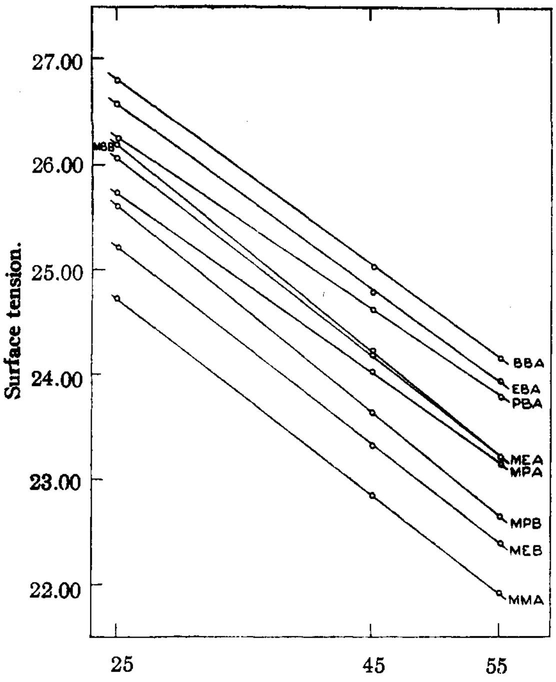


Fig. 3.—Surface tensions of tertiary carbinols.

tions of refractive indices, densities, surface tensions, and parachors with temperature are shown in Figs. 1, 2, 3, 4, respectively.

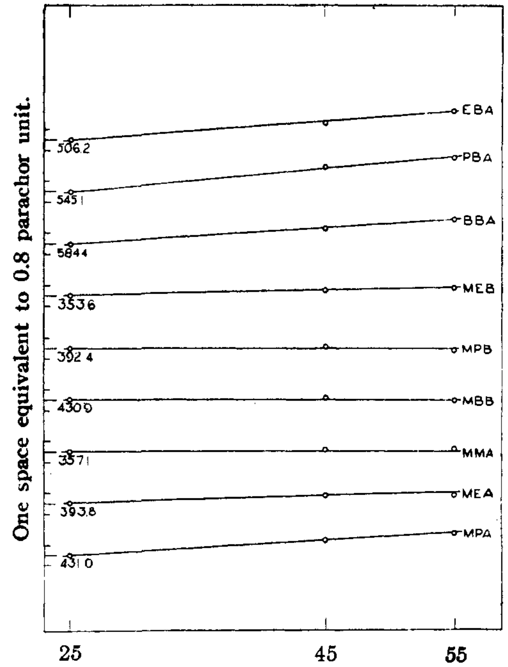


Fig. 4.—Parachors of tertiary carbinols.

Surface tensions were determined by the maximum bubble pressure method. Certain modifications were made in the design of the bubbler to ensure greater accuracy and reproducibility of readings, as well as to decrease the time necessary for measurement. It has long been recognized that it is essential that the bubbler tubes be vertical. In order to check this the tubes were attached to a cap, with an externally ground glass joint, so that they might be conveniently rotated. After a reading was completed the tubes were rotated 180° and a second reading made. If the same value, within experimental error, was obtained the tubes were considered vertical and the readings were accepted as a measurement. Each measurement was independently checked by a second observer. To avoid loss of time in readjusting the tubes to the vertical position after a change in sample, the bubbler was equipped with a heavy ground-glass flange fitting into a heavy ground collar. If the collar is securely clamped, the bubbler after being removed and replaced will seat itself in the same vertical position. In order to permit the use of samples as small as three cubic centimeters the bubbler may be slightly smaller in diameter below the flange. The design of the bubbler is shown in Fig. 5. While the modifications described may appear to be minor, the changes greatly facilitate more accurate and more rapid measurement.

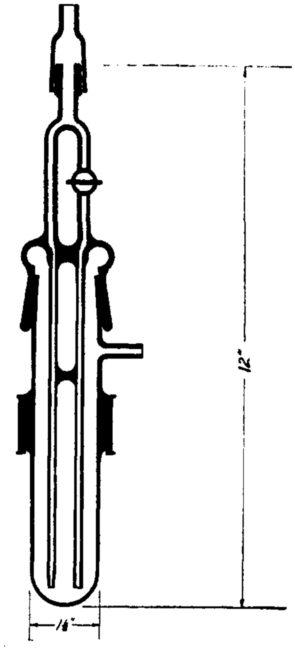
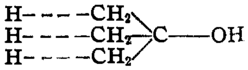


Fig. 5.—Bubbler for surface tension.

The results obtained offer an opportunity to test the values on the parachor in tertiary alcohols previously reported.[2] Using the previously reported position values for the CH_2 increments in obtaining calculated parachors, the maximum deviation between an experimental value and the corresponding calculated value was found to be 0.3% in the case of methylpropylamylcarbinol. In no other case did the deviation exceed 0.1%. The experimental error has been considered to be 0.1%. These values are given in Table I.

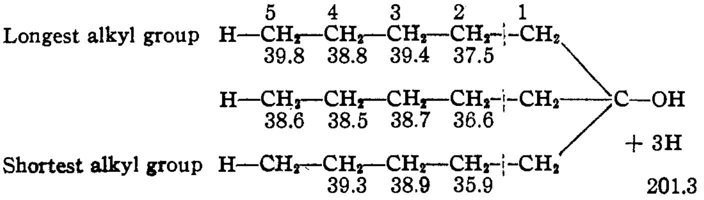
From the newly-determined tertiary alcohols several additional CH_2 values for various positions in tertiary alcohols may be calculated. Combining these values with those previously reported a table may be constructed for the estimation of the parachor of any tertiary alcohol having unbranched alkyl groups. Assuming the parachor value for



to be the determined value 201.3 of *t*-butyl alcohol, the parachor of any tertiary alcohol may be estimated by adding the CH_2 values for the various positions as given in Table II.

TABLE II

POSITION VALUES OF CH_2 IN PARACHORS OF TERTIARY ALCOHOLS



For example, the parachor for methylethyl butylcarbinol would be calculated by adding the values shown below.

t-butyl alcohol	201.3
butyl group	
1st CH_2 included in *t*-butyl linkage	——
2nd CH_2	37.5
3rd CH_2	39.4
4th CH_2	38.8
ethyl group	
1st CH_2 included in *t*-butyl linkage	——
2nd CH	36.6
methyl group included in *t*-butyl linkage	——
	353.6

Values for CH_2 units further removed from the —OH group than the amyl position may be considered constant at 40.0. It should be remembered in the use of this table that the actual value of the CH_2 is, in all cases, considered to be essentially a constant, 40.0. The values in the table to be added in calculation represent the sum of two factors; the increase of the added CH_2 minus the effect of increasing the carbon chain upon the $>$C——OH group. Also, each position value is only an average of values which (by the fundamental assumption of variation with different attached groups) would not be expected to be identical.

Summary

1. The refractive indices, densities, surface tensions, and parachors of nine additional tertiary alcohols have been reported for three temperatures.

2. The experimental values for the parachor have been shown to be in close agreement with the calculated values.

3. A table for the estimation of parachors for tertiary alcohols has been given.

4. Modifications in the bubbler for determining surface tension more accurately and rapidly have been described.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

A Study of Organic Parachors. VII. A Series of Saturated Hydrocarbons[1]

BY OSBORNE R. QUAYLE, R. A. DAY AND GEORGE M. BROWN[2]

The parachor is one of the more useful constants in the correlation of the physical properties of organic compounds and their structures. The parachor, first considered an additive property, has been found to be susceptible to minor as well as to gross variations in structure. It is particularly so to any variations in the degree of unsaturation of the molecule. The parachor values in normal saturated hydrocarbons have been found to be almost unique in being additive in nature.[3] In calculating the values of other groups the alkyl residues are, therefore, considered to be of known value and are subtracted from the observed parachors determined for the whole compound. It is essential, therefore, that the validity of the accepted parachor value for the CH_2 increment in the saturated hydrocarbons be reëxamined from time to time as compounds of higher purity become available and as the techniques of measurement are improved.

Sugden,[4] the original worker in the field, upon examination of several series of various types obtained the values of 39.0 for CH_2, 17.1 for H, and 4.8 for C. Mumford and Phillips,[5] limiting their calculations to series of the same type, established the values: $CH_2 = 40.0$, $H = 15.4$, $C = 9.2$. Vogel,[6] studying esters and alkyl halides arrived at the values: $CH_2 = 40.3$, $H = 14.4$, and $C = 11.5$. Gibling[7] asserts that the CH_2 value seems to show progressively higher values throughout any homologous series due to decreasing "interference"

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(1) The authors wish to express their gratitude to Prof. E. Emmet Reid, research consultant to the department, for his continued interest and suggestions in connection with the problem; to the American Petroleum Institute for samples of hydrocarbons; and to the University Center in Georgia for a grant for the purchase of a constant temperature bath.

(2) New York Community Trust Fellow, Emory University 1942–43; present address Princeton University, Princeton, N. J.

(3) Even the values for the saturated chains are not considered to be strictly additive by some observers. However, they are at least essentially so. If variations exist they appear to be of a distinctly lower order of magnitude for chains of short or moderate length.

(4) Sugden, *J. Chem. Soc.*, **125**, 1177 (1924).

(5) Munford and Phillips, *ibid.*, 2113 (1929).

(6) Vogel, *ibid.*, 333 (1934).

(7) Gibling, *ibid.*, 299 (1941).