

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

A Study of Organic Parachors. IV. Constitutive Variations of the Parachors of a Series of Tertiary Chlorides¹

BY OSBORNE R. QUAYLE, KATHERINE OWEN AND ELLINGTON M. BEAVERS²

The concept of the highly constitutive nature of parachor has grown out of the fact that it has been shown that many irregularities between observed and calculated values are due, not to experimental error as first believed, but to differences in molecular volume arising from the variations within the molecule. Isomeric compounds show that the additive nature of this constant is modified by constitutive effects. The branching of the chain in hydrocarbons^{3,4} causes a lowering of the parachor from that of the value for the straight chain.

Any explanation of the difference in chemical behavior of two carbon atoms in the same general type of structure ultimately must be resolved to a postulation of differences in the extent of consumption of the valence forces of the two, caused by the influences of spatial arrangement and minor differences in adjacent groups. Since the effective volume of an atom is dependent upon its electrical forces, an accurate atomic and molecular volume property should vary slightly from compound to compound because of constitutive influences. On the assumption that the parachor is such a property, most observed deviations are explainable. The validity of this assumption has been tested by comparing the parachors of regular series of compounds.

Beck, Macbeth and Pennycuik⁵ measured the parachors of a series of malonic esters, noting the effect of lengthening the ester chain and that of alkyl substitution in the malonic residue. The differences between the observed and calculated parachors showed a regular, depressive constitutive effect, the depression increasing with the length of the alkyl ester chain and apparently reaching a limiting value with the butyl group.

In a study of a series of alkylbenzenes, Buehler,

Gardner and Clemens⁶ found that the CH₂ parachor value decreased in a very regular manner through the butyl substitution, the amyl rising to the normal value.

In a previous paper,⁷ the authors pointed out the influence of varying the length of normal straight chains attached to a tertiary carbon atom jointed to an hydroxyl group. Using trimethylcarbinol as a standard, the effect of substitution in the alcohol was most constitutive with the first CH₂ units added and approached the CH₂ constant of Mumford and Phillips⁸ as the length of the chains approached five. These values gave a closer agreement between calculated and observed parachors than those of previous determinations.

This paper is concerned with the measurement of the parachors of the corresponding tertiary chlorides⁹ and the resulting extension of the knowledge of the constitutive constants of the compounds containing branching of the tertiary type. As with the alcohols, the chain branching of the chlorides used is limited to the tertiary carbon atom. The values obtained from these compounds afford a second series of position values in tertiary branching. Since chlorides are generally non-associated these values also would indicate any large effect of association that had distorted the values previously recorded for the alcohols.

For the lower molecular weight chlorides densities (Table I) were determined at 15, 25, 50 and 65° with the exception of trimethylchloromethane which boils at 51°. The densities of the higher molecular weight chlorides were determined at 25, 50 and 75°. Extrapolation from the curves shown in Fig. 1 was used to obtain all values at 0°. The surface tensions (Table II) were measured at 0, 25 and 50° for the lower molecular weight compounds and at 25, 50 and 75° for those of higher weight. The estimated experimental precision of the surface tension determinations by

(1) The authors wish to express their gratitude to Prof. E. Emmet Reid, research consultant to the department, for his continued interest in the problem and for his kindness in supplying the chlorides studied.

(2) Abstracted from material presented by Ellington M. Beavers to the graduate faculty of Emory University in partial fulfillment of the requirements for the degree of Master of Science, June, 1939.

(3) G. Edgar and G. Calingaert, *THIS JOURNAL*, **51**, 1540 (1929).

(4) T. W. Richards, C. L. Speyers and E. K. Carver, *ibid.*, **46**, 1196 (1924).

(5) A. B. Beck, A. K. Macbeth and S. W. Pennycuik, *J. Chem. Soc.*, 2258 (1932).

(6) C. A. Buehler, T. S. Gardner and M. L. Clemens, *J. Org. Chem.*, **2**, 167 (1937).

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

(8) S. A. Mumford and J. W. C. Phillips, *J. Chem. Soc.*, 2112 (1929).

(9) The chlorides used were those prepared and described by J. D. Pollard, Johns Hopkins University, Thesis, 1934.

TABLE I
THE DENSITIES OF SIXTEEN TERTIARY CHLORIDES AT VARIOUS TEMPERATURES

Chloromethane	Temperature for densities					
	0°	15°	25°	50°	65°	75°
Methylmethylmethyl	0.8619	0.8457	0.8347			
Methylmethylethyl	.8876	.8702	.8589	0.8327		
Methylethylethyl	.8949	.8811	.8720	.8488	0.8365	
Ethylethylethyl	.9065	.8946	.8862	.8645	.8527	
Ethylethylpropyl	.9018	.8894	.8813	.8604	.8480	
Ethylpropylpropyl	.8963	.8843	.8765		.8441	
Propylpropylpropyl	.8897	.8780	.8703	.8507		0.8308
Methylmethylpropyl	.8766	.8608	.8523	.8288	.8145	
Methylpropylpropyl		.8741	.8658	.8447	.8322	
Methylethylpropyl	.8915	.8783	.8698	.8477	.8346	
Methylmethylbutyl			.8566	.8342		.8104
Methylmethylhexyl			.8538	.8334		.8124
Methylethylhexyl			.8638	.8442		.8241
Methylpropylhexyl			.8621	.8431		.8236
Methylbutylhexyl			.8612	.8426		.8237
Methylamylhexyl			.8578	.8395		.8206

the maximum bubble pressure method employed is 0.2%. In the case of these chlorides, the surface tensions are evidently a linear function of temperature (Fig. 2).

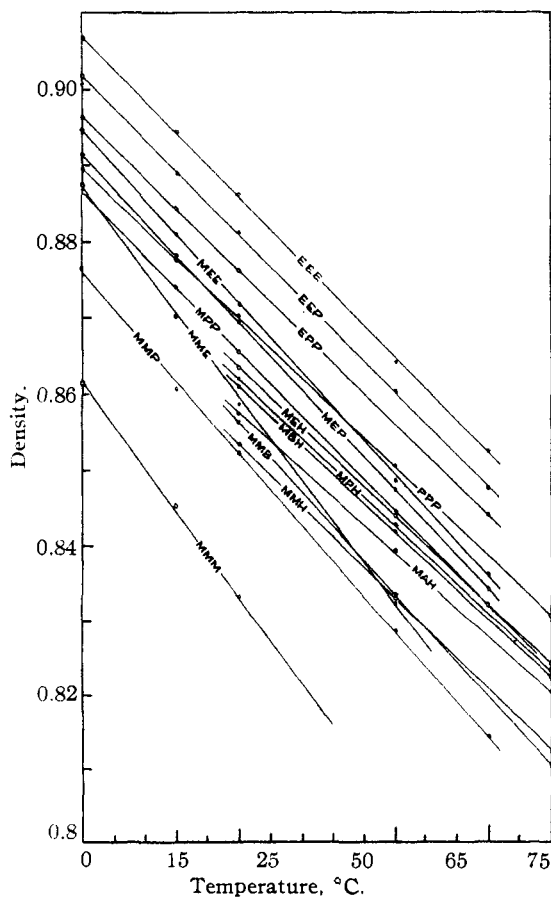


Fig. 1.—Variation of density with temperature for sixteen tertiary chlorides.

TABLE II
THE SURFACE TENSIONS OF SIXTEEN TERTIARY CHLORIDES

Chloromethane	Temperature for surface tensions			
	0°	25°	50°	75°
MMM	21.35	18.30		
MME	25.39	21.38	18.67	
MEE	26.55	23.46	20.93	
EEE	27.76	25.46	22.82	
EEP	28.06	25.43	23.03	
EPP	28.17	25.76	23.52	
PPP		25.94	23.58	21.25
MMP	25.00	22.37	19.80	17.31
MPP		24.75	22.41	
MEP	26.88	24.32	21.90	
MMB		23.69	21.15	18.80
MMH		25.38	23.00	20.60
MEH		26.37	24.03	21.67
MPH		26.50	24.20	21.97
MBH		27.05	24.83	22.53
MAH		27.01	24.94	22.72

The parachors of the chlorides (Table III) decrease with the exception of ethylpropylpropylchloromethane, in a linear manner with temperature (Fig. 3). The rate of this decrease is less than 0.2% per 10° rise in temperature. The experimental precision of measurement was approximately 0.1%. The parachors were calculated from the mathematical expression¹⁰ $P = \gamma^{1/4} M/D$ where M is the molecular weight, γ is the surface tension, and D is the density of the liquid.

Since the parachor values for the series vary in an essentially regular manner with temperature, comparisons would be essentially the same at any temperature within the range studied. The com-

(10) The more exact expression $P = \gamma^{1/4} M/(D - d)$ includes the value of d the density of the vapor at same temperature. The omission of d introduces an error of less than 0.05% and the shorter expression has been used throughout.

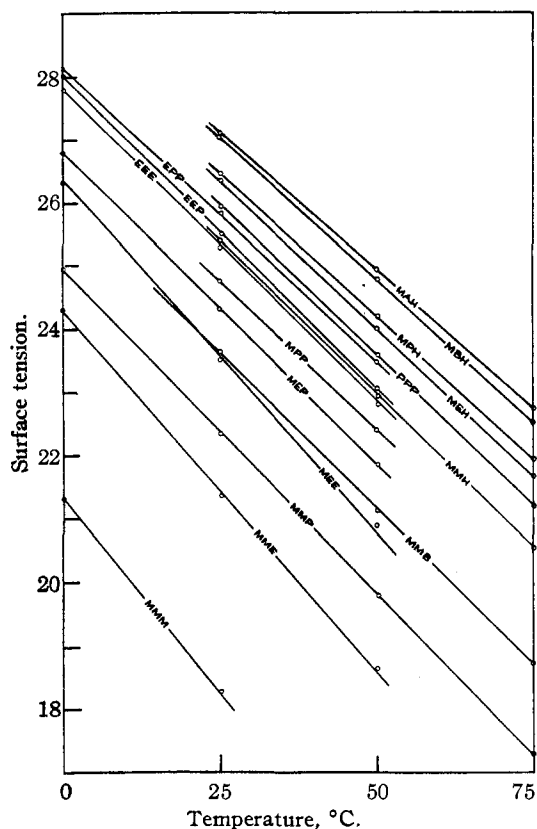


Fig. 2.—Variation of surface tension with temperature for sixteen tertiary chlorides.

TABLE III
THE PARACHORS OF SIXTEEN TERTIARY CHLORIDES

Chloromethane	Temperature for parachors			
	0°	25°	50°	75°
MMM	230.9	229.4		
MME	269.6	266.9	265.4	
MEE	306.0	304.4	303.9	
EEE	341.0	341.3	340.6	
EPP	379.4	378.8	378.5	
EPP	418.2	418.2	418.6	
PPP		458.3	457.8	456.8
MMP	307.7	307.6	307.0	305.6
MPP		383.0	382.9	
MEP	343.9	343.8	343.6	
MMB		346.8	346.2	346.0
MMH		427.7	427.5	426.7
MEH		463.6	463.5	462.7
MPH		502.0	501.8	501.4
MBH		542.3	542.5	541.7
MAH		581.5	582.5	582.1

parisons recorded are for convenience made at 25°. Trimethylchloromethane was taken as an observed base for the purpose of making comparisons. The value of the >C-Cl group was obtained by subtracting the value of the three methyl groups from the total value. By assum-

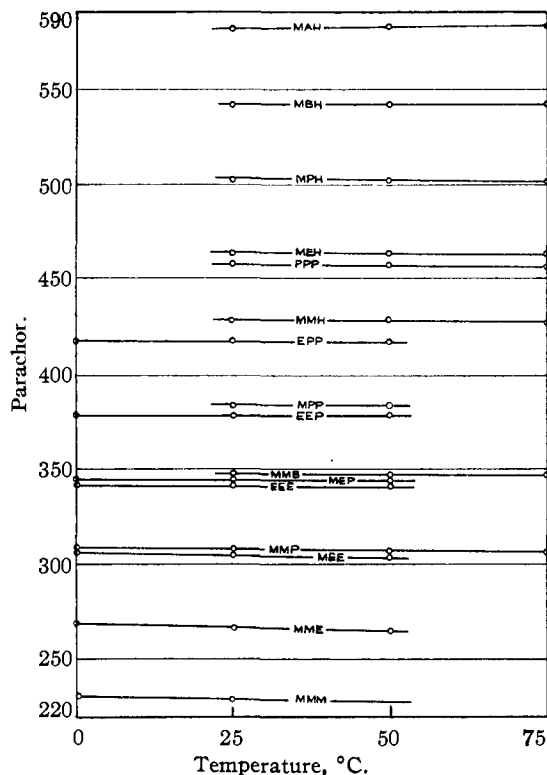


Fig. 3.—Parachors of sixteen tertiary chlorides at various temperatures.

ing this basic value, the effect of uniformly lengthening the chains on the value of the >C-Cl group may be observed (Table IV).

The effect is of the same order of magnitude as that obtained for the tertiary carbinols. The first several additions to the chains cause the greatest crowding and adsorption of any residual forces on the tertiary carbon.

The effect of substitution at different distances from the tertiary carbon atom has been calculated for the CH_2 values (Table V), and is quite comparable to those obtained in a similar manner for the tertiary carbon in the carbinol series.⁸

The curves of Fig. 4 showing the results of the study of the chlorides, while in no sense identical with those obtained with the corresponding carbinols, are unmistakably of the same general shape.

While by the very nature of the postulate of the extreme constitutive nature of the parachor, the values for the various CH_2 units would not be expected to be identical in the two series, the main structural feature of both series is the same, the varying tertiary carbon atom, and it is of interest to substitute in the chloride series the average

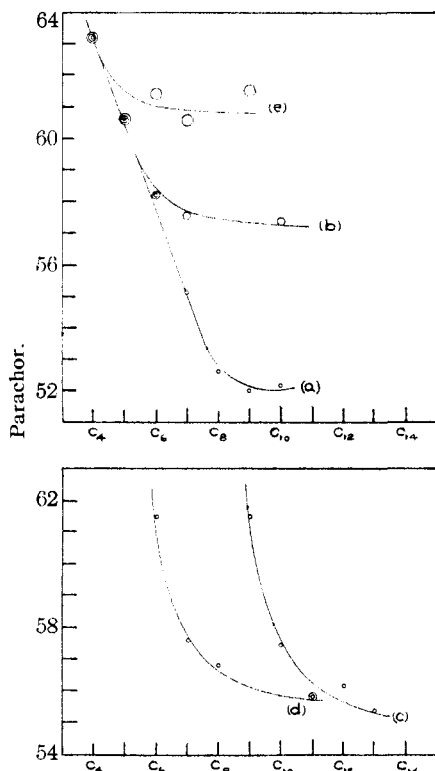


Fig. 4.—Variation of parachor value of C-Cl groups in series.

CH₂ values as obtained from the two series (Table VI).

TABLE IV
VARIATION OF C-Cl GROUP IN SERIES
(Basic value C-Cl assumed 63.2)

Chloromethane	Parachor C-Cl group	Parachor decrease	% decrease from basic C-Cl
Series a			
MMM	63.2	0.0	0
MME	60.7	2.5	4
MEE	58.2	5.0	8
EEE	55.1	8.1	13
EPP	52.6	10.6	17
EPP	52.0	11.2	18
PPP	52.1	11.1	18
Series b			
MEM	60.7	2.5	4
MEE	58.2	5.0	8
MEP	57.6	5.6	9
MEB	No determination		
MEA	No determination		
MEH	57.4	5.8	9
Series c			
MHM	61.5	1.7	3
MHE	57.4	5.8	9
MHP	55.8	7.4	12
MHB	56.1	7.1	11
MHA	55.3	7.9	13

Series d			
MPM	61.4	1.8	3
MPE	57.6	5.6	9
MPP	56.8	6.4	10
MPB	No determination		
MPA	No determination		
MPH	55.8	7.4	12
Series e			
MMM	63.2	0.0	0
MME	60.7	2.5	4
MMP	61.4	1.8	3
MMB	60.6	2.6	4
MMA	No determination		
MMH	61.5	1.7	3

TABLE V
VALUE OF THE CH₂ GROUP

In first ethyl position	37.5
second ethyl position	36.5
third ethyl position	35.7
In first propyl position	39.2
second propyl position	39.0
third propyl position	39.9
In first butyl position	39.2
second butyl position	40.3
third butyl position	40 +
In first amyl position	40.7
second amyl position	40 +
third amyl position	40 +
In first hexyl position	40.7
second hexyl position	40 +

TABLE VI
COMPARISON OF OBSERVED AND CALCULATED VALUES FOR THE PARACHORS

M and P values are obtained from the constants as given by Mumford and Phillips. BOQ' values are obtained from the study of the tertiary chlorides. Average values are obtained from the average value of the CH₂ position of the alcohols and chlorides.

Chloro-methane	Obsd. P 25°	Calcd. P M and P	% diff.	Calcd. P BOQ'	% diff.	Calcd. P average	% diff.
MME	266.9	270.4	1.4	266.9	0.0	266.9	0.0
MEE	304.4	310.4	2.0	303.4	.3	303.4	.3
EEE	341.3	350.4	2.6	339.1	.6	339.2	.6
EPP	378.8	390.4	3.0	378.3	.1	378.5	.1
EPP	418.2	430.4	2.8	417.3	.2	417.3	.2
PPP	458.3	470.4	2.6	457.2	.2	456.6	.4
MMP	307.6	310.4	0.9	306.1	.5	306.2	.5
MPP	383.0	390.4	1.9	381.6	.4	381.5	.4
MEP	343.8	350.4	1.9	342.6	.4	342.7	.4
MEH	463.6	470.4	1.4	463.2	.1	462.6	.3
MMH	427.7	430.4	0.6	426.7	.2	426.1	.4
MPH	502.0	510.4	1.6	502.2	.0	501.4	.2
MBH	542.3	550.4	1.5	542.5	.0	540.8	.3
MAH	581.5	590.4	1.5	582.5	.2	580.1	.3
MMB	346.8	350.4	1.0	354.3	.4	354.3	.4
Average % diff.			1.8		0.2		0.3

The average error using the previous most satisfactory values is approximately three times the maximum error of that using these newer values. Still more exact values for the various CH₂ positions of this series as indicated in Table V may be calculated from the chloride values here reported

and when applied show an average error of 0.2%. If averages be found between these two sets of values, the new set would describe both the alcohols and the chlorides with an average error of 0.3% when applied to the chlorides.

The constitutive effect is strikingly brought out by comparing homologs. The maximum CH₂ value from methylethylhexylchloromethane to ethylpropylpropylchloromethane would be 14.8 units or 45% higher than the minimum value in comparing propylpropylpropylchloromethane and methylmethylhexylchloromethane.

Summary

1. The densities, surface tensions and parachors of sixteen tertiary chlorides have been determined.

2. The parachors show a decrease with tem-

perature of approximately 0.2% per 10° rise in temperature.

3. The effect of substitution in trimethylchloromethane has been found to be of the same order as that with trimethylcarbinol.

4. Values for the individual CH₂ groups in the tertiary chlorides have been determined and found to be of approximately the same value as those obtained for the corresponding CH₂ groups in the tertiary carbinols.

5. The similarity of the values obtained for the chlorides and alcohols indicates that association is not an important factor in the parachor values of the alcohol series.

6. The values for the tertiary branching give closer agreement between the calculated and observed values than the values previously used.

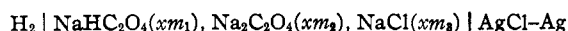
EMORY UNIVERSITY, GA. RECEIVED AUGUST 18, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Second Ionization Constant of Oxalic Acid from 0 to 50°

BY HERBERT S. HARNED AND LESLIE D. FALLON

From the electromotive forces of the cells



the ionization constant of HC₂O₄⁻ has been determined at 5° intervals from 0 to 50°.

The observed electromotive forces are given in Table I. The concentrations of the most concentrated solution, m_1 , m_2 and m_3 , are given. The concentrations of all other solutions are given by xm_1 , xm_2 and xm_3 where x is less than unity. The concentrations were known with an accuracy greater than 0.1%. The reproducibility of the measurements was of the order of ± 0.05 mv.

The Determination of the Ionization Constant.

—By applying the method of Harned and Ehlers¹ in the manner used by Nims² for the second ionization constant of phosphoric acid, the electromotive force of the cell may be expressed by

$$\frac{(E - E_0)F}{RT} + \log \frac{m_{\text{Cl}} m_{\text{HC}_2\text{O}_4}}{m_{\text{C}_2\text{O}_4}} + \frac{2u \sqrt{\mu}}{1 + A \sqrt{2\mu}} = -\log K_2 + f(\mu) = -\log K_2' \quad (1)$$

where the symbols have their usual significance. This differs from the equation of Nims by including the Debye and Hückel factor containing A which allows for the effect of the mean distance of

TABLE I
ELECTROMOTIVE FORCES OF THE CELLS

$$\text{H}_2 \mid \text{NaHC}_2\text{O}_4(xm_1), \text{Na}_2\text{C}_2\text{O}_4(xm_2), \text{NaCl}(xm_3) \mid \text{AgCl}-\text{Ag}$$

$m_1 = 0.04945; m_2 = 0.02600; m_3 = 0.03782$

t	$x \dots 1$	0.8546	0.7263	0.5617
0	0.51317	0.51736	0.52217	0.52939
5	.51595	.52029	.52510	.53245
10	.51860	.52319	.52806	.53551
15	.52147	.52609	.53110	.53869
20	.52410	.52903	.53416	.54135
25	.52723	.53207	.53724	.54510
30	.53014	.53511	.54035	.54840
35	.53302	.53814	.54353	.55162
40	.53594	.54126	.54664	.55486
45	.53909	.54446	.54999	.55833
50	.54201	.54753	.55330	.56159
t	$x \dots 0.4684$	0.4050	0.3210	0.1737
0	0.53459	0.53851	0.54465	0.56180
5	.53767	.54187	.54823	.56570
10	.54096	.54504	.55167	.56935
15	.54416	.54836	.55504	.57308
20	.54739	.55172	.55849	.57691
25	.55073	.55509	.56206	.58066
30	.55412	.55856	.56570	.58461
35	.55741	.56202	.56925	.58850
40	.56090	.56554	.57285	.59244
45	.56431	.56915	.57662	.59654
50		.57275	.58016	.60054

approach of the ions. In order to determine the ionization constant, K_2 , it is necessary to evaluate

(1) Harned and Ehlers, *THIS JOURNAL*, **54**, 1350 (1932).

(2) Nims, *ibid.*, **55**, 1946 (1933).