

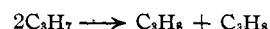
ether to give an ether peroxide. This ether peroxide has been shown by Clover<sup>7</sup> to decompose to give carbon dioxide, ethyl alcohol, methane and acetaldehyde. The oxidation of the ether in this manner is usually a slow one, but it has been reported<sup>8</sup> that the oxidation may be catalyzed by the Grignard compound.

Thus the carbon dioxide and the ethyl alcohol are easily explained. The secondary alcohol would be the product of the reaction between the acetaldehyde and the Grignard compound. This seems to be a very complex mechanism, but it must be remembered that this is by no means the major course of the reaction but merely offers an explanation for the products that appear practically as traces. A Podbielniak distillation was run on the gas liberated from the isopropyl run to see if it would be possible to find any of the methane that this newer theory predicts. None was found. This does not prove the theory in error, because the amount of methane formed would be so small that it might easily be missed on a distillation. From the distillation, however, a considerable amount of hydrogen was obtained, proving without a doubt that it is a product of the electrolysis. The presence of the hydrogen is most likely explained on the basis of the disproportionation of the isopropyl radical. Table III

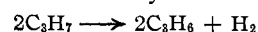
(7) Clover, *THIS JOURNAL*, **44**, 1107 (1922).

(8) Gilman and Wood, *ibid.*, **48**, 806 (1926).

indicates that the propylene is always in excess of the propane by a few per cent. This means that although most of the reaction was of the type



there was a small tendency toward



All of the propylene formed by the latter reaction would be in excess of the amount necessary to balance the propane. Also the amount of hydrogen should correspond to one-half the difference of the propylene and the propane. On reference to the tables it is found that within experimental error this is the case.

### Summary

1. The formation of the liquid products in the electrolysis of *n*-propyl- and isopropylmagnesium halides is explained.

2. As the length of the straight chain increases, the tendency of the free radical formed to couple increases.

3. If a branched chain compound is electrolyzed, the tendency for the free radical to couple is much less than that of the corresponding straight chain compound.

4. The current density has no effect on the composition of the gaseous products in the electrolysis of *n*-propyl- and isopropyl-magnesium bromides.

EVANSTON, ILL.

RECEIVED DECEMBER 19, 1938

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

## A Study of Organic Parachors. II. Temperature, and (III) Constitutive Variations of Parachors of a Series of Tertiary Alcohols<sup>1</sup>

BY KATHERINE OWEN, OSBORNE R. QUAYLE AND ELLINGTON M. BEAVERS<sup>2</sup>

It has been noted that irregularities between observed and calculated parachors are encountered when the normal, straight chain is departed from. In the case of the compounds containing branched chains the observed parachors are consistently lower than the calculated. With the establishment of this observation, Mumford and Phillips<sup>3</sup> in 1929 reevaluated the parachor con-

stants to give better agreement with the observed parachors of compounds of high molecular weight. Among these reevaluated constants were two new "strain constants": -3 units for a branched chain of the secondary type; -6 units for the tertiary branching.

Each "strain constant" was evaluated as the mean of many observations on secondary and tertiary compounds, and there are many cases of large deviations from these values.

The present program of research was begun in an endeavor to examine the apparent irregularities in parachor values and to discover, where possible, any existing consistencies caused by con-

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

(2) Abstracted from material to be 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.

(3) S. A. Mumford and J. W. C. Phillips, *J. Chem. Soc.*, 2112-2158 (1929).

TABLE I  
THE DENSITIES OF SIXTEEN TERTIARY ALCOHOLS AT VARIOUS TEMPERATURES  
Density values in heavy type are those determined experimentally.

Carbinol	0°	25°	35°	45°	55°	65°
Methylethylpropyl	<b>0.8415</b>	<b>0.8198</b>	0.8107	0.8016	0.7925	<b>0.7835</b>
Ethylethylpropyl	<b>.8546</b>	<b>.8333</b>	.8246	.8156	.8067	<b>.7980</b>
Methylpropylpropyl	<b>.8393</b>	<b>.8183</b>	.8096	.8010	.7925	<b>.7839</b>
Ethylpropylpropyl	<b>.8505</b>	<b>.8299</b>	.8210	.8126	<b>.8043</b>	.7963
Propylpropylpropyl	<b>.8485</b>	<b>.8268</b>	.8185	.8102	.8020	<b>.7935</b>
Methylmethylethyl	<b>.8262</b>	<b>.8018</b>	.7923	.7827	<b>.7731</b>	.7624
Methylmethylpropyl	<b>.8240</b>	<b>.8019</b>	.7938	.7852	<b>.7766</b>	.7680
Methylmethylbutyl	<b>.8311</b>	<b>.8097</b>	.8014	.7929	<b>.7842</b>	.7760
Methylethylethyl	<b>.8445</b>	<b>.8215</b>	.8122	.8031	.7940	<b>.7848</b>
Ethylethylethyl	<b>.8603</b>	<b>.8367</b>	.8273	.8175	.8080	<b>.7982</b>
Methylmethylhexyl	<b>.8336</b>	<b>.8134</b>	<b>.8055</b>	.7977	.7897	<b>.7816</b>
Methylethylhexyl	<b>.8455</b>	<b>.8251</b>	.8173	.8092	.8010	<b>.7927</b>
Methylpropylhexyl	<b>.8437</b>	<b>.8236</b>	.8158	.8080	.8000	<b>.7923</b>
Methylbutylhexyl	<b>.8447</b>	<b>.8247</b>	.8170	.8097	<b>.8024</b>	<b>.7945</b>
Methylamylhexyl	<b>.8452</b>	<b>.8274</b>	.8190	.8110	<b>.8035</b>	<b>.7955</b>
Methylmethylmethyl		<b>.7785</b>	<b>.7682</b>	<b>.7582</b>	<b>.7473</b>	<b>.7357</b>

stitutive differences, and to enhance thereby the value of the parachor as a structural property and tool.

In 1938, Quayle, Owen and Estes<sup>4</sup> compared the parachors of a series of fifteen isomeric esters, and showed that the deviations from the calculated values are in themselves regular. The lowest parachors of the esters were obtained when R and R' of R—COOR' are of intermediate size, the highest values either when R is largest and R' small or when R' largest and R small. This is compatible with the concept of the greatest decrease in the parachor of a series of isomers in the most highly saturated members of the series.

This paper is concerned with (1) the determination of the parachors of a series of tertiary alcohols<sup>5</sup> together with a consideration of (2) the change of the parachor values with temperature and (3) the variation of the values for these alcohols with variation of constitution. In order to simplify the comparison, the alcohols measured are of strictly comparable type, there being no branched chains other than the branching of the tertiary carbon atom joined to the hydroxyl group. Thus, the influence may be studied of varying the length of normal straight chains attached to this atom.

As the parachor is not entirely independent of temperature the necessary data (densities and surface tensions) to calculate these values were determined for five temperatures (25, 35, 45, 55 and 65°). The densities were available at 0

TABLE II  
THE SURFACE TENSIONS OF SIXTEEN TERTIARY ALCOHOLS AT VARIOUS TEMPERATURES

Carbinol	25°	35°	45°	55°	65°
MEP	24.35	23.62	22.60	21.71	20.80
EEP	25.58	24.66	23.73	22.83	22.05
MPP	24.49	23.68	22.77	21.79	20.90
EPP	25.18	24.43	23.72	22.66	22.05
PPP	25.04	24.28	23.44	22.62	21.87
MME	22.27	21.31	20.36	19.44	18.51
MMP	22.58	21.68	20.79	19.95	19.03
MMB	23.78	22.80	22.01	21.02	20.24
MEE	24.12	23.24	22.31	21.34	20.37
EEE	25.20	24.39	23.47	22.60	21.67
MMH	25.45	24.57	23.67	22.87	22.05
MEH	26.15	25.27	24.39	23.56	22.69
MPH	26.08	25.21	24.32	23.49	22.79
MBH	26.22	25.25	24.43	23.70	22.92
MAH	25.69	25.82	25.06	24.22	23.40
MMM	19.98	19.06	18.11	17.26	16.38

and 25°<sup>6</sup> and were determined at higher temperatures to give curves shown by Fig. 1. From the densities (Table I) the surface tensions (Table II) were obtained with an estimated experimental precision of 0.2%, using the method of maximum bubble pressure.

In 1924, Sugden<sup>7</sup> showed that for many normal liquids, a straight-line relation exists between  $\gamma$  and  $T^{1.2}$ . The exponent was chosen as a mean of values which had been shown by Ferguson<sup>8</sup> to vary between the limits of 1.192 and 1.248 from series to series. In the case of these alcohols, the best linear relationship is obtained when  $\gamma$  is taken as a direct function of  $T^{1.5}$  (Fig. 2).

The parachors of the alcohols increase slightly,

(4) O. R. Quayle, K. Owen and R. R. Estes, *THIS JOURNAL*, **60**, 2716-2719 (1938).

(5) The alcohols used were those described in the dissertation of J. D. Pollard, Johns Hopkins University, 1934.

(6) Determined by Dr. Pollard with the assistance of B. Hadley.<sup>6</sup>

(7) S. Sugden, *J. Chem. Soc.*, **125**, 32-41 (1924).

(8) Ferguson, *Phil. Mag.*, [vi] **31**, 37 (1916).

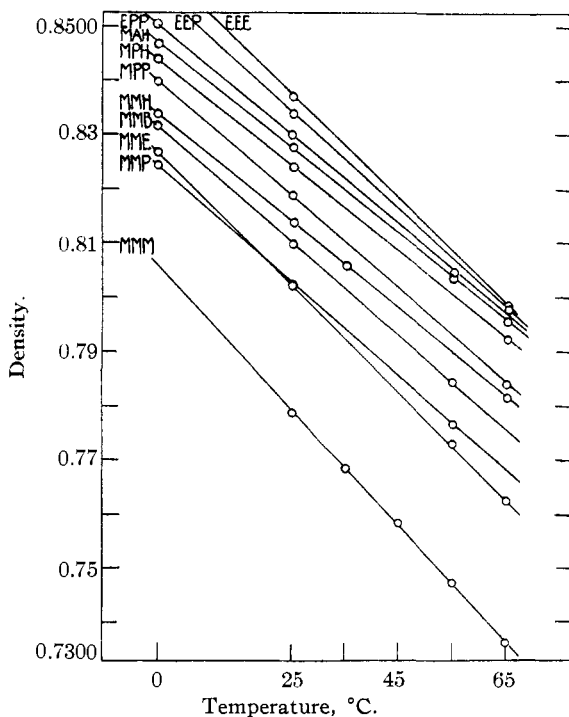


Fig. 1a.—Variation of density with temperature.

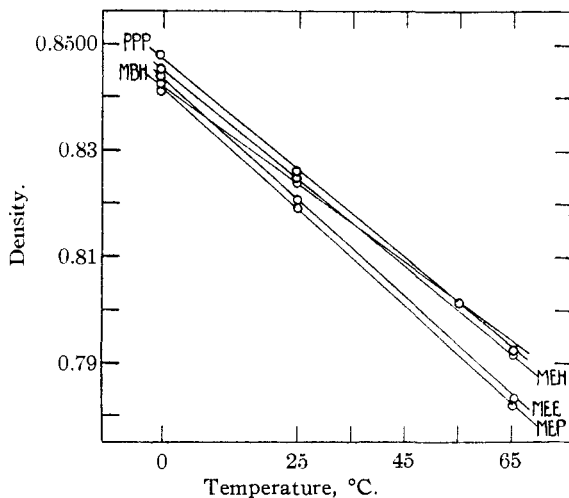


Fig. 1b.—Variation of density with temperature.

but regularly, with rise in temperature (Fig. 3). The change is in the order of 0.2% per 10° rise in temperature (Table III).<sup>9</sup>

The parachor values have been calculated from the experimentally determined surface tensions using the parachor equation  $P = \gamma^{1/4}M/(D - d)$ . The density of the vapor,  $d$ , is relatively negligible and has in no case been included in the calculations. The error thus introduced is greatest

(9) The approximate experimental error in parachor is 0.1%.

TABLE III  
THE PARACHORS OF SIXTEEN TERTIARY ALCOHOLS AT  
VARIOUS TEMPERATURES

Carbinol	25°	35°	45°	55°	65°
MEP	314.9	316.0	316.1	316.5	316.7
EPP	351.2	351.7	352.2	352.6	353.4
MPP	353.8	354.6	354.9	354.8	355.0
EPP	389.1	390.4	391.5	391.1	392.3
PPP	427.9	429.0	429.6	430.1	431.1
MME	238.8	239.0	239.2	239.4	239.8
MMP	277.7	277.7	277.8	278.0	277.8
MMB	316.9	316.8	317.4	317.3	317.6
MEE	275.6	276.2	276.5	276.6	276.6
EEE	311.2	312.1	312.9	313.6	314.1
MMH	398.3	398.7	398.9	399.5	399.9
MEH	433.8	434.2	434.7	435.3	435.8
MPH	472.8	473.3	473.6	474.2	475.2
MBH	511.3	511.2	511.6	512.4	513.1
MAH	549.9	551.4	552.7	553.2	553.9
MMM	201.3	201.6	201.7	202.2	202.7

at 65° and at that temperature is in the order of 0.05%, at lower temperatures 0.02% or less.

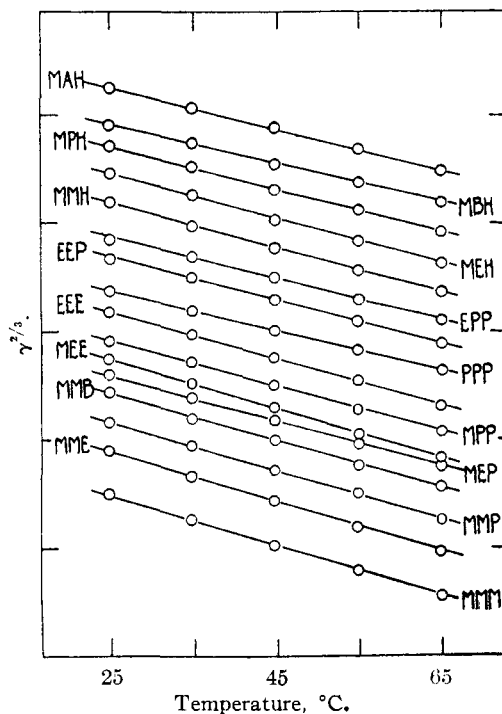


Fig. 2.—Variation of  $\gamma^{2/3}$  with temperature. Each division on  $\gamma^{2/3}$  scale represents one (dyne/cm.)<sup>2/3</sup>.

A study of the constitutive differences at any arbitrarily chosen temperature would result in essentially the same conclusions. For this reason the comparisons here reported are all based upon the determinations at the most generally used temperature, 25°.

Since it has been observed by Mumford and

Phillips, Desreux<sup>10</sup> and other workers that the parachors for normal, straight-chain hydrocarbons are almost unique in the constancy of the CH<sub>2</sub> value, it is then legitimate to attribute any deviations from the calculated values, of parachors here observed, largely to the tertiary carbon atom and the hydroxyl group. That this should

be the locus of variation is particularly reasonable because of the oxygen atom's unpaired electrons and "unsaturation" due to the resulting valence forces.

TABLE IV  
VARIATION OF PARACHOR VALUE OF COH GROUP IN SERIES  
(Basic Value COH assumed 35.1)

Carbinol	Parachor COH group	Parachor decrease	% Decrease from basic COH
Series (a)			
MMM	35.1	0.0	0
MME	32.6	2.5	7
MEE	29.4	5.7	16
EEE	25.0	10.1	29
EEP	25.0	10.1	29
EPP	22.9	12.2	35
PPP	21.7	13.4	38
Series (b)			
MEM	32.6	2.5	7
MEE	29.4	5.7	16
MEP	28.7	6.4	18
MEB	No determination		
MEA	No determination		
MEH	27.6	7.5	21
Series (c)			
MHM	32.1	3.0	9
MHE	27.6	7.5	21
MHP	26.6	8.5	24
MHB	25.1	10.0	28
MHA	23.6	11.5	33
Series (d)			
MPM	31.6	3.5	10
MPE	28.7	6.4	18
MPP	27.6	7.5	21
MPB	No determination		
MPA	No determination		
MPH	26.6	8.5	24
Series (e)			
MMM	35.1	0.0	0
MME	32.6	2.5	7
MMP	31.6	3.5	10
MMB	30.7	4.4	13
MMA	No determination		
MMH	32.1	2.2	9

Early work was considered check if within 2%. Two per cent. error in parachor of MMM is 4.0 units; for MAH, 11.0 units. Present experimental error is approximately 0.1%. This for MMM is 0.2 unit; for MAH, 0.5 unit. It is contemplated that additional measurements to eliminate the vacancies in these series will be made in this Laboratory. The value for MMH appears to be somewhat irregular.

(10) V. Desreux, *Bull. soc. chim. Belg.*, **44**, 249-287 (1935).

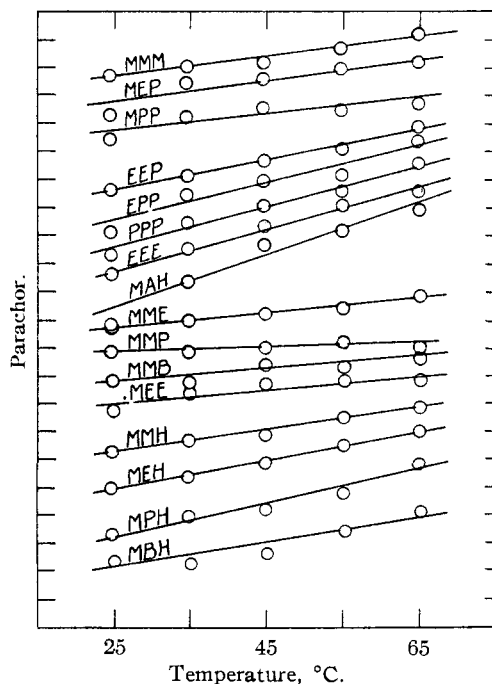


Fig. 3.—Variation of parachor with temperature. Each division on parachor scale represents one parachor unit.

For purposes of comparison, trimethylcarbinol may be taken as an observed base, and the parachor value calculated for three methyl groups deducted to give a basic value (35.1) for the tertiary carbon-hydroxyl group residue. (The value for this residue by Mumford and Phillips' constants is 33.2.) By uniformly lengthening the chains on the tertiary carbon, values for the COH residues may be regularly compared (Table IV). The decrease of parachor with increasing substitution is apparently greatest at the beginning of the series, and as the chains become longer the influence of an added CH<sub>2</sub> group becomes smaller (Fig. 4). It might be expected that a point would be reached eventually at which the free valence force of the COH residue is almost or entirely utilized by the hydrocarbon chains, and that further lengthening would have a constant effect on its parachor value. Furthermore, if the region of influence of the molecule be considered an approximate sphere, whose volume increases as the cube of the radius, the first several additions to the chains might be expected to cause greatest crowd-

ing and to have an appreciable effect on the total volume, and this effect would diminish as the molecule becomes larger in respect to the unit added. Thus, the effect of substituting ethyl

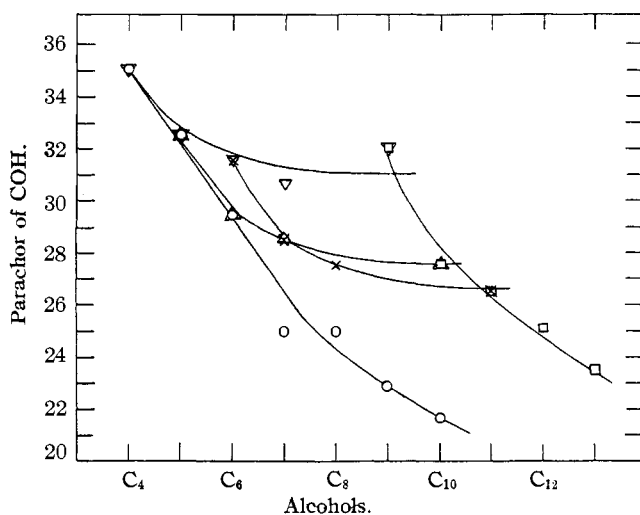


Fig. 4.—Variation of parachor value of COH group in series.  $\circ$ , series a;  $\Delta$ , series b;  $\square$ , series c;  $\times$ , series d;  $\nabla$ , series e.

groups for the methyls in trimethylcarbinol would be expected to be large, and that of substituting further to propyl groups greater but not as much so, this effect diminishing to the point of saturation.

By substituting from the first ethyl to the second ethyl, a further decrease of the total molecular parachor from the calculated would be expected, but not twice the lowering caused by substituting to the first ethyl, and this is borne out experimentally. Using the absolute value of trimethylcarbinol as a base for calculations, the effect of substitution may be derived from the experimental data by reference to the other carbinols. The values for the substituted  $\text{CH}_2$  groups should be expected to differ as they do, since, to obtain as many as three values for one

TABLE V  
VALUE OF THE  $\text{CH}_2$  GROUP

$\text{CH}_2$ in first ethyl position	37.5
in second ethyl position	36.5
in third ethyl position	35.9
$\text{CH}_2$ in first propyl position	39.4
in second propyl position	38.6
in third propyl position	38.8
$\text{CH}_2$ in first butyl position	39.1
in second butyl position	38.5
$\text{CH}_2$ in first amyl position	40.0
in second amyl position	38.6
$\text{CH}_2$ in first hexyl position	40.0

group, three different carbinols, of different degrees of saturation, must be used in the calculations. Obtaining average values in all cases, the data may be tabulated in the form shown in Table V, where some values are more significant than others because of the greater number of determinations possible in some cases than in others.<sup>11</sup>

Using the values thus obtained and the experimental value of trimethylcarbinol as a base, the parachors of the alcohols are calculated in much better agreement with the observed than those calculated from the constants of Mumford and Phillips alone (Table VI).

By comparing the parachors of alcohols differing by a  $\text{CH}_2$  (Table VII) the same regularities are noted. In each case, where the smaller  $\text{CH}_2$  values occur, one of the longer chains has been shortened to fill in the lower levels, making the chains more symmetrical. In each case where the  $\text{CH}_2$  value is greater than the average value, the difference in the length of the chains has been increased by deducting  $\text{CH}_2$  from a lower level and adding two  $\text{CH}_2$  to the longer chains.

TABLE VI  
Observed  $P$  at  $25^\circ$ . Rise of approximately 0.2% per  $10^\circ$  rise in temperature.

Carbinols	Obsd. P.	M. and P. calcd.	Diff.	% error	BOQ calcd.	Diff.	% error
MME	238.8	239.4	0.6	0.3	238.3	0.0	0.0
MEE	275.6	279.4	3.8	1.3	275.3	-.3	.1
MMP	277.8	279.4	1.6	0.6	278.2	-.4	.2
EEE	311.2	319.4	8.2	2.7	311.2	.0	.0
MMB	316.9	319.4	2.5	0.8	317.3	.4	.1
MEP	314.9	319.4	4.5	1.4	314.7	-.2	.1
EEP	351.2	359.4	8.2	2.3	350.6	-.6	.2
MPP	353.8	359.4	5.6	1.6	353.3	-.5	.1
EPP	389.1	399.4	10.2	2.6	389.2	.1	.0
MMH	398.3	399.4	1.1	0.3	397.3	-1.0	.3
PPP	428.0	439.4	11.5	2.7	428.0	0.0	.0
MEH	433.8	439.4	5.6	1.3	433.8	.0	.0
MPH	472.8	479.4	6.6	1.4	472.4	-.4	.1
MBH	511.3	519.4	8.2	1.6	510.9	-.4	.1
MAH	549.8	559.4	9.6	1.7	549.5	-.3	.1

Homo-logs	$\text{CH}_2$ value	Homo-logs	$\text{CH}_2$ value	Homo-logs	$\text{CH}_2$ value
MMB	41.3	EEE	33.4	MPP	42.6
MEE		MMP		EEE	
EEP	34.3	MMH	44.5	MMB	36.9
MMB		MPP		MPP	
MEH	44.7	MPH	44.8	PPP	29.7
EPP		PPP		MMH	

(11) Other alcohols are being prepared in this Laboratory, and will be used for additional determinations.

The maximum  $\text{CH}_2$  value is 17.4 units, or 59%, greater than the minimum. The average  $\text{CH}_2$  value is 38.5 units. It is interesting to note that in no case below amyl in the regular symmetrical increase of the chains is the  $\text{CH}_2$  value equal to that given by Mumford and Phillips.

### Summary

1. The surface tensions and parachors of sixteen tertiary alcohols have been determined.
2. The parachors are found to increase with

temperature in the order of approximately 0.2% per  $10^\circ$  rise in temperature.

3. The effect of substitution in trimethylcarbinol has been found to be most constitutive with the first  $\text{CH}_2$  units added to the molecule, and to become more regular as the length of the carbon chains becomes greater.

4. Values for the  $\text{CH}_2$  groups in tertiary alcohols have been determined which yield closer agreement between the calculated and observed parachors than the values previously used.

EMORY UNIVERSITY, GA. RECEIVED JANUARY 9, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

## The Entropies and Energies of Activation of Ionic Reactions. The Kinetics of the Alkaline Fading of Brom Phenol Blue in Isodielectric Media

BY EDWARD S. AMIS AND VICTOR K. LA MER

The rates of many reactions between ionic species can be measured with a precision and ease exceeding that of non-ionic reactions. The interpretation of the data, however, is complicated by the profound effect of the electric charges upon the rate. The modern theory of electrolytes predicts that the presence of electric charges will affect the number of rate determining collisions in two ways: (a) through the electrical repulsion (or attraction) between reactants and (b) through the ionic atmosphere (Brönsted primary salt effect) which disturbs the statistical distribution of the reactant ions as a function of the concentration of all ions in the system.

The objective of this paper is to employ procedures which correct the thermodynamic factors determining the rate of reaction, namely, the energy and entropy of activation for electrostatic contributions so that the rate calculated for uncharged molecules of the same chemical characteristics as the reactant ions may be compared with the predictions of the collision theory.

The frequency factor,  $B$ , in the integrated form of the Arrhenius equation

$$\log k = B - \frac{\Delta E^*}{2.3RT} \quad (1)$$

determines the rate at which molecules endowed with the energy of activation  $\Delta E^*$  react.  $B$  is related to  $\Delta E^*$  through the relation<sup>1</sup>

$$2.3RB = \int_0^T \frac{\partial \Delta E^*}{\partial T} \frac{dT}{T} + 2.3R \log \nu \quad (2)$$

where  $\nu$  is a frequency.

(1) La Mer, *J. Chem. Phys.*, **1**, 289 (1933).

Setting<sup>2</sup>  $\nu = kT/h$  then the integral term in eq. (2), designated hereafter as  $\Delta S^*$ , becomes the entropy of activation for all degrees of freedom. For ionic reactions it will be expedient to decompose  $\Delta S^*$  into a non-electrical and an electrical part

$$\Delta S^* = \Delta S_0^* + (\Delta S_D^* + \Delta S_{in}^*) \quad (3)$$

Thus  $\Delta S_0^*$  refers to the entropy contribution for the reactants as uncharged molecules.  $\Delta S_D^*$  arises from the presence of electric charges upon the reactant ions alone, whereas  $\Delta S_{in}^*$  is the interaction contribution of the ionic atmosphere.

By combining eq. (1) with the Brönsted-Debye-Hückel limiting equation

$$\log k = \frac{2z_A z_B \beta \sqrt{\mu}}{(DT)^{3/2}} + \log k \sqrt{\mu} = 0 \quad (4)$$

La Mer and Kamner<sup>3</sup> derived the following expressions for the contributions of the ionic atmosphere to  $B$  and  $\Delta E^*$  valid for small values of the ionic strength,  $\mu$

$$\frac{\Delta E_{in}^*}{2.3RT} = -\frac{2z_A z_B \beta \sqrt{\mu}}{(DT)^{3/2}} \left[ \frac{3}{2} \frac{\partial \ln D}{\partial \ln T} + \frac{1}{2} \frac{\partial \ln V}{\partial \ln T} + 3/2 \right] \quad (5)$$

$$\frac{\Delta S_{in}^*}{2.3R} = -\frac{2z_A z_B \beta \sqrt{\mu}}{(DT)^{3/2}} \left[ 3/2 \frac{\partial \ln D}{\partial \ln T} + 1/2 \frac{\partial \ln V}{\partial \ln T} + 1/2 \right] \quad (6)$$

In these equations  $\beta$  equals  $1.816 \times 10^6$  and is a constant independent of the temperature,  $z$  is the

(2) Eyring, *ibid.*, **3**, 107 (1935); *Chem. Rev.*, **17**, 65 (1935).

(3) La Mer and Kamner, *THIS JOURNAL*, **67**, 2662 (1935). See also Moelwyn-Hughes, *Proc. Roy. Soc. (London)*, **155**, 308 (1936); **A157**, 667 (1936), for substantially identical equations, derived more explicitly by means of the collision theory.