cides with literature data on such binary mixtures as benzene–nitrobenzene and toluene–nitrobenzene.[6,7]

In the above equation, S is spreading coefficient in dynes per centimeter, S. $T._A$ surface tension at the water–air interface, S. $T._B$ surface tension at the organic mixture–air interface, and S. $T._{AB}$ surface tension at the organic mixture–water interface. Using our measured values for S and data due to other experimenters for S. $T._A$ and S. $T._B$, good agreement is obtained between our values of S. $T._{AB}$ and those due to Bartell and Mack.[6]

In all the mixtures studied this general condition exists. If, when the mixture–air and mixture–water surface tension values are plotted against composition, the curves intersect, the composition–spreading pressure curve reaches a maximum, but if the surface tension–composition curves do not intersect the composition–spreading pressure curve does not reach a maximum. Also, when the spreading pressure–composition curves show a maximum, the composition at this maximum is practically the same as the composition where the respective surface tension curves intersect. Surface tension data for mixtures are limited and further conclusions will require information on surface tensions and spreading pressures for mixtures at various compositions.

Attempts were made to correlate the spreading pressures of mixtures with other physical properties, such as viscosity and vapor pressure. It might be expected that the curves resulting from plotting spreading pressure, viscosity, or vapor pressure against composition might be similar. However, no similarities were found. One reason for this might be in the fact that, in addition to the binary mixture, a third component, water, is always introduced in spreading pressure measurements by means of the surface film balance and a surface film on water.

Summary

1. Spreading pressures at various compositions of toluene–benzene, nitrobenzene–benzene, bromobenzene–benzene, cyclohexane–benzene, and toluene–nitrobenzene were measured by means of a stearic acid film and a film pressure balance.

2. For the mixtures studied the spreading pressure–composition curves show that the mixture–air surface tension–composition curve and the mixture–water surface tension–composition curve cannot be straight lines.

3. For benzene–nitrobenzene and toluene–nitrobenzene mixtures there is a close agreement between the composition at the intersection of the mixture–air surface tension–composition and the mixture–water surface tension–composition curves with the composition at the maximum spreading pressure on the spreading pressure–composition curve.

LINCOLN, NEBRASKA RECEIVED JUNE 17, 1940

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[6] Bartell and Mack, *J. Phys. Chem.*, **36**, 65 (1932).

[7] "Int. Crit. Tables," Vol. IV, 1928, p. 473.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DUKE UNIVERSITY]

The Electric Moments of Morpholine and Some Halogenated Toluenes[1]

BY ARTHUR A. MARYOTT, MARCUS E. HOBBS AND PAUL M. GROSS

In order to test further the validity of the vector bond moment addition method[1a] for determining the electric moment of molecules and to learn something of the possible influences of induction and resonance effects on the observed moment, six halogenated toluenes including 3,5-dichlorotoluene, 3,5-dibromotoluene, 2,4,6-trichlorotoluene, 2,4,6-tribromotoluene, 3,5-dibromobenzyl bromide, and *p*-chlorobenzotrichloride have been measured. The moment of morpholine also has been determined. For the data on *p*-chlorobenzotrichloride we are indebted to Dr. J. W. Jacokes.[2] All measurements were carried out as described previously[3] using essentially the same apparatus. A slight modification was made by changing the oscillating circuit to a grid-tuned type and by replacing each of the RCA 01 radio tubes with a type 37.

Materials

Benzene.—Kahlbaum best grade benzene was washed with concd. sulfuric acid, dried over phosphorus pent-

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[1] Part of thesis of Arthur A. Maryott submitted in partial fulfilment of the requirements of the Ph.D. degree in Chemistry at Duke University, June, 1940.

[1a] Eucken and Meyer, *Physik. Z.*, **30**, 397 (1929).

[2] Jacokes, Ph.D. Thesis, Duke University (1936).

[3] De Bruyne, Davis and Gross, THIS JOURNAL, **55**, 3936 (1933).

oxide, then distilled in a 180-cm. Dufton column after refluxing over sodium for several hours. Fractions boiling over 0.02° range were used in the measurements, b. p. 80.06–80.08° (corrected); d^{30}_4 0.86825 (average).

3,5-Dichlorotoluene.—*o*-Acetotoluidide was chlorinated with calcium hypochlorite (HTH). Hydrolysis of the acetyl group was effected by dissolving the 3,5-dichloroacetotoluidide in 75% sulfuric acid and heating at 130–140° for several hours. Elimination of the amino group was accomplished by the method of Chattaway and Evans.[4] The product was purified by distillation through a Podbielniak column under reduced pressure; f. p. 24.8–25.0°.[5]

3,5-Dibromotoluene.—*o*-Toluidine was treated in a manner analogous to the preparation of *sym*-tribromobenzene as described by Coleman and Talbot.[6] The product was recrystallized from alcohol and distilled under vacuum through the Podbielniak column, f. p. 36.8–37.0°.

2,4,6-Trichlorotoluene.—*m*-Acetotoluidide was chlorinated using calcium hypochlorite (HTH) and the trichloroacetotoluidide hydrolyzed with 50% sulfuric acid. Diazotization removed the amino group. The compound was purified by recrystallizations from alcohol and finally by a vacuum distillation in the Podbielniak still, f. p. 31.9–32.0°.

2,4,6-Tribromotoluene.—This compound was prepared from *m*-toluidine in a manner analogous to the preparation of 3,5-dibromotoluene. It was recrystallized several times from alcohol and then distilled under vacuum in a Claisen flask which was equipped with a fractionating column, f. p. 65.3–65.4°.

3,5-Dibromobenzyl Bromide.—3,5-Dibromotoluene was brominated[7] directly. It was recrystallized several times from alcohol and finally from ligroin, f. p. 92.2–92.4°.

_p_-Chlorobenzotrichloride.—The compound was made from *p*-chlorotoluene by direct chlorination at high temperature under ultraviolet light. Upon distillation the middle fraction boiling at 244–251° was collected and redistilled under reduced pressure, b. p. at 4.9 mm., 99–100° C. Analysis of side-chain chlorine: found, 42.23%; calcd., 42.28%.

Morpholine.—Morpholine (Carbide and Carbon Chemical Corp.) was refluxed over sodium and distilled in a 60-cm. Widmer column. The middle fraction was redistilled over sodium and the portion boiling at 128.39–128.46° (cor.) was used.

Results

The apparatus was checked by measuring chlorobenzene in benzene. A value of 1.57 *D* was obtained for the moment if no account was taken of the atomic polarization. All measurements were made at 30.0° with benzene as the solvent. Calculation of the moments has been made in the usual manner. No account has been taken of possible atomic polarization terms. The molar refraction R_D was obtained from the atomic refractivities as listed in "Landolt-Börnstein Tabellen" except in the case of *p*-chlorobenzotrichloride.

TABLE I

f_2	d	ϵ	P_2
3,5-Dichlorotoluene			
0.0000	0.8683	2.2627	...
.01055	.8742	2.3176	112.5
.01875	.8777	2.3564	112.0
.02281	.8796	2.3767	112.6
.03154	.8835	2.4206	112.4
$P_2^\infty = 112.6$	$R_D = 40.6$	$\mu = 1.88\ D$	
3,5-Dibromotoluene			
0.0000	0.8683	2.2627	...
.002485	.8718	2.2758	113.9
.004297	.8744	2.2849	117.7
.006582	.8776	2.2958	116.1
.01090	.8837	2.3180	116.2
$P_2^\infty = 116.0$	$R_D = 46.5$	$\mu = 1.84\ D$	
2,4,6-Trichlorotoluene			
0.0000	0.8683	2.2627	...
.04304	.8997	2.2960	51.9
.05632	.9089	2.3051	51.8
.07495	.9227	2.3184	51.6
.09164	.9338	2.3311	51.7
$P_2^\infty = 52.0$	$R_D = 45.5$	$\mu = 0.57\ D$	
2,4,6-Tribromotoluene			
0.0000	0.8683	2.2627	...
.03093	.9343	2.3040	65.3
.03602	.9461	2.3093	63.8
.04019	.9537	2.3142	64.4
.05467	.9841	2.3295	63.3
$P_2^\infty = 65.0$	$R_D = 54.2$	$\mu = 0.73\ D$	
3,5-Dibromobenzyl Bromide			
0.0000	0.8682	2.2627	...
.005418	.8796	2.2860	111.0
.008210	.8862	2.2988	110.6
.01097	.8920	2.3096	108.0
.01522	.9016	2.3287	108.3
$P_2^\infty = 110.6$	$R_D = 54.2$	$\mu = 1.66\ D$	
p-Chlorobenzotrichloride			
0.0000	0.8673	2.2627	...
.008240	.8759	2.2727	64.0
.01524	.8831	2.2804	63.5
.01967	.8877	2.2841	62.3
.03096	.8989	2.2963	62.7
$P_2^\infty = 64.0$	$R_D = 51.4$	$\mu = 0.78\ D$	
Morpholine			
0.0000	0.8683	2.2627	...
.009956	.8700	2.2937	71.3
.01951	.8758	2.3228	70.6
.03054	.8723	2.3575	70.6
.04439	.8740	2.4027	71.0
.05741	.8753	2.4465	71.4
$P_2^\infty = 70.4$	$R_D = 23.7$	$\mu = 1.51\ D$	

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(4) Chattaway and Evans, *J. Chem. Soc.*, **69**, 850 (1896).

(5) Melting points were determined by the cooling curve method and the range indicated is the observed change from the time of first appearance of crystals until so much solid had formed that it became impossible, because of stirring difficulties, to maintain equilibrium.

(6) Coleman and Talbot, "Organic Syntheses," Vol. XIII, p. 96.

(7) Wheeler and Clapp, *Am. Chem. J.*, **40**, 340 (1908).

In this latter case the refractivity was determined experimentally using the Na D line. All results are shown in Table I in which the symbols have their usual significance.

Discussion of Results

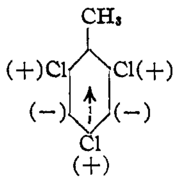
The values predicted on the basis of a vector addition of the individual bond moments[8] are shown together with the observed values in Table II. The bond moment values used were as follows: C_{ar}–CH_3, 0.40; C_{ar}–Cl, 1.56; C_{ar}–Br, 1.52; C_{al}–O, 0.86; C_{al}–N, 0.40; N–H, 1.30 and C_{ar}–CH_2Cl, 1.85.

TABLE II

Substance	μ (calcd.)	μ (obsd.)
3,5-Dichlorotoluene	1.96	1.88
3,5-Dibromotoluene	1.92	1.84
2,4,6-Trichlorotoluene	0.40	0.57
2,4,6-Tribromotoluene	0.40	0.73
3,5-Dibromobenzyl bromide	2.16	1.66
p-Chlorobenzotrichloride	0.55	0.78
Morpholine	1.68	1.51

Agreement between the calculated and observed moments for 3,5-dichlorotoluene and 3,5-dibromotoluene is quite good. It has been observed[9] that the *m*-dihalogenated benzenes have moments slightly smaller than the corresponding monohalogenated benzenes. If the moments of *m*-dichlorobenzene and *m*-dibromobenzene are used in the calculations the agreement is almost perfect. The calculated value for the chloro compound is now identical with the observed value and that for the bromo compound is 1.86 compared with the observed moment of 1.84 *D*.

In the case of the 2,4,6-trihalogenated toluenes, the observed moments are somewhat larger than the moment of toluene. Smyth[10] has recently measured 2,4,6-trichlorotoluene and found a moment of 0.56 *D* which value agrees with that reported here. If an attempt is made to eliminate the atomic polarization by using the total polarization found by Tiganik[9] for *sym*-trichlorobenzene and *sym*-tribromotoluene in place of the molar refractivity, the calculated moments are reduced to 0.46 *D* and 0.64 *D*, respectively. The difference in the moments of these two compounds is then about 0.2 *D* and, although small, it appears to be real. It is improbable that simple dipole induction could account for this difference for the distance between polarizable groups and dipoles is essentially the same in both cases, and the polarizability of Br is only about 1.5 times that of Cl. It also seems unlikely that any solvent effect of the type postulated by Higasi[11] could account for the difference since the shape of both molecules is quite similar. Resonance effects between the halogen atoms and the benzene ring might, however, account for the observed anomalies. In chlorobenzene, for example, resonance occurs, leading to some double bond character in the carbon–chlorine bond. This has the effect of conferring a negative formal charge on the carbon atoms in the ortho and para positions. In symmetrical trichlorobenzene the charge distribution accompanying this resonance would be perfectly symmetrical and thus would lead to no permanent electric moment. However, when a methyl group is attached to one of the other carbon atoms, the aromatic carbon atom acquires a slight negative charge as is indicated by the direction of the C_{ar}–CH_3 moment in toluene. It might be expected that this negative charge would inhibit resonance structures which would place an additional negative charge on this carbon atom. Consequently in 2,4,6-trichlorotoluene those resonance structures placing a negative charge on the carbon atoms in the 3 and 5 positions would be favored. As indicated in the accompanying diagram, this partially inhibited resonance would tend to produce an unsymmetrical charge distribution in the ring which would increase the observed moment. The difference in moments between the chlorine and bromine compounds may lie in the following facts. First the directive influence to the ortho and para positions is stronger for bromine than for chlorine and second the ratio of ortho to para rate of substitution for bromobenzene is greater than that for chlorobenzene. This would indicate that there is a greater accumulation of negative charge in the ortho and para positions in bromine compounds than in chlorine compounds, and consequently one would expect the unsymmetrical charge distribution to be more pronounced and the moment larger in 2,4,6-tribromotoluene than in 2,4,6-trichlorotoluene. In this connection it is interesting to note that the calculated moments for *o*-chloro-,



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(8) Sidgwick, "The Covalent Link in Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1933, p. 153; Smyth, *J. Phys. Chem.*, **41**, 210 (1937).

(9) Tiganik, *Z. physik. Chem.*, **B13**, 425 (1931).

(10) Smyth and Lewis, THIS JOURNAL, **62**, 721 (1940).

(11) Higasi, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo) **28**, 284 (1936).

o-bromo- and *o*-iodotoluene are all smaller than the observed values. The difference has been attributed to dipole induction between the adjacent groups; however, resonance effects might explain the observed deviations. The carbon atom attached to the methyl group, having a negative charge, would inhibit the resonance structure leading to a negative charge on this atom. The other two resonance structures would lead to an unsymmetrical charge distribution which would increase the total moment. The difference between the observed and calculated moments increases from chlorine to iodine. This trend would be expected from the fact that the ortho-para orienting power increases from chlorine to iodine.

The discrepancy between the observed and calculated moments in 3,5-dibromobenzyl bromide is quite marked and a deviation of the same order has previously been noted in *p*-chlorobenzyl chloride. Therefore, the indication is that the C_{ar}–CH_2–Br group is the source of the discrepancy as it is not dependent upon the position of the ring substituents. The calculated moment for benzyl bromide using 0.4 and 1.9 for the C_{ar}–CH and the C_{al}–Br bond moments, respectively, is 1.81 *D* and makes an angle of 98° with the C_{ar}–C_{al} axis. This calculated value is in good agreement with the observed moment of benzyl bromide in benzene, which is 1.86 *D*. However, the agreement is somewhat misleading, as is shown by the following. Assuming that the moment of 3,5-dibromobenzyl bromide is the resultant of two vector moments, one the moment of *m*-dibromobenzene (1.46 *D*) and the other that of benzyl bromide (1.86 *D*), with an angle of 98° between them, the calculated value is 2.16 *D*. It is necessary to assume an angle of approximately 121° between the two vectors to obtain the experimental value of 1.66 *D*. Contributions from a resonance structure such as that suggested by Sutton[12] may be sufficient to account for the apparent discrepancy, as this structure does give a contribution in the right direction.

The calculated moment for *p*-chlorobenzotrichloride was obtained from the difference between the moments of benzotrichloride and of chlorobenzene. An average value of 2.11 *D* was taken as the moment of benzotrichloride. The difference between the observed and calculated values is a little more than 0.2 *D* and is considered to be beyond experimental error. The —CCl_3 group, in contrast to the methyl group, orients substituents principally to the meta position. This fact indicates that induction and resonance effects on the ring are such as to give all the carbon atoms in the ring a positive formal charge. Resonance leading to double bond character between the C_{ar}–Cl bond would be favored somewhat more than in chlorobenzene and the C_{ar}–Cl bond moment would be somewhat less than in the latter compound. The net effect would thus be an increase in the observed moment of *p*-chlorobenzotrichloride over the calculated value.

For morpholine the calculated value for only the symmetrical Sachse Z-form of the molecule is given. The U-form gives 2.02 *D* if the N–H bond moment aids the other bond moments. The tetrahedral angle has been assumed in all cases not specifically excepted. Partington[13] reports a value for morpholine of 1.48 measured and 1.52 *D* calculated on the basis of the Z-form. Smyth[14] has recently found a value of 1.58 *D*. Partington's calculations were made using values of the moment of diethyl ether and diethyl amine with an angle of 80° for the N–H moment with respect to the C–N–C plane. Although Partington's agreement is excellent, one must not overlook the possibility of a contribution from a low moment form of morpholine with an internal M---H–O bond. The distances between the atoms in this molecule are approximately the same as those usually found in such bonds,[15] and a small amount of this form would readily account for the discrepancy between the calculated and the observed values in Table II.

Summary

The electric moments of morpholine, 3,5-dichlorotoluene, 3,5-dibromotoluene, 2,4,6-trichlorotoluene, 2,4,6-tribromotoluene, 3,5-dibromobenzyl bromide, and *p*-chlorobenzotrichloride have been determined in benzene solutions at 30°. Dipole induction effects between the different groups within the molecules seem to be small. The suggestion is made that the resonance affecting the halogen atoms might be altered upon the addition of other substituents in the rings so as to account for the observed discrepancies in the *sym*-trihalogenated toluenes and in *p*-chlorobenzotri-

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[12] L. E. Sutton, *J. Chem. Soc.*, 544 (1940).

[13] Coomber and Partington, *Nature*, **144**, 918 (1938).

[14] Lewis and Smyth, THIS JOURNAL, **61**, 3067 (1939).

[15] Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, New York, 1939, p. 314.

chloride. The moment for morpholine is found to be in rough agreement with the Sachse Z-form with the possibility of a small contribution from a less polar form such as the configuration allowing an internal N---H–O bond.

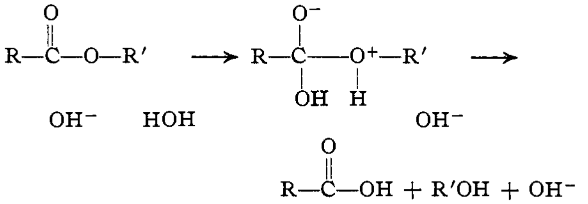
DURHAM, NORTH CAROLINA RECEIVED JUNE 18, 1940

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

Kinetics of the Saponification of the Ethyl Esters of Several Phenyl Substituted Aliphatic Acids[1]

BY H. S. LEVENSON AND HILTON A. SMITH

The Lowry mechanism for saponification[2] proposes that the rate-determining step is the addition of hydroxyl to the carbonyl carbon atom of the ester to form an intermediate complex, decomposition of which leads to completion of reaction.



$$\mathrm{R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}R'} \;\xrightarrow[\mathrm{OH^-}\quad\mathrm{HOH}]{}\; \mathrm{R{-}\underset{\displaystyle OH}{\overset{\displaystyle O^-}{C}}{-}\underset{\displaystyle H}{O^+}{-}R'} \;\xrightarrow[\mathrm{OH^-}]{}\; \mathrm{R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH + R'OH + OH^-}$$

Electron sinks which tend to make the carbon atom more positive facilitate addition of the negative hydroxyl, thereby lowering the activation energy, most of which, probably, is required for addition of the hydroxyl.[3] The opposite is produced by electron release. Substituents in the ester molecule, then, affect the reaction velocity through their polarization and polarizability as well as steric effects.

When not part of a conjugated system the phenyl group acts as an electron sink, and this effect (negative inductive, $-I$) has been observed by Dippy and Lewis[4] in the dissociation constants of phenyl substituted monocarboxylic acids. Random data in the literature[5] indicate that this same effect operates in the saponification of esters, the effect of a phenyl substituent being to increase the reaction rate over that for the unsubstituted analog. In continuation of work on the kinetics of saponification there are reported here results obtained in a systematic study of several ethyl esters of phenyl substituted aliphatic acids.

Experimental

All the esters were prepared by esterification of absolute ethanol with the corresponding acid, using sulfuric acid as a catalyst. They were purified by distillation under reduced pressure in a 5 ft. (1.5 meter) Vigreux column, with the exception of ethyl diphenylacetate which was vacuum distilled in a 2 ft. (0.6 meter) Vigreux column. Each ester distilled at constant head temperature, and each sample used was shown, by the method of analysis previously employed,[6] to be, within the precision of the method, 100% pure.

Phenylacetic acid, hydrocinnamic acid, phenylethylacetic acid and **diphenylacetic acid** were obtained from Eastman Kodak Co. **γ-Phenylbutyric acid** was prepared by carbonation of the Grignard reagent of γ-phenylpropyl bromide by the method previously described.[7]

δ-Phenylvaleric acid and **cyclohexylacetic acid** were prepared from γ-phenylpropyl bromide and cyclohexyl bromide, respectively, by malonic ester syntheses carried out in the usual manner.[8]

Hydratropic acid (phenylmethylacetic acid) was prepared from hydratropic aldehyde[9] by oxidation with silver oxide in alkaline medium using the method described by Delépine and Bonnet.[10]

The reaction medium for the saponification experiments was 85% aqueous ethanol prepared in the manner already described.[11] The method of making velocity determinations was similar to that previously employed.[6,11]

Experimental Calculations and Results

The values of k were calculated from the second order reaction rate equation

$$k = x/at(a - x)$$

where a is the initial concentration of each reactant, and x is the concentration of each reactant at the time t. All the saponifications here reported were fast enough so as to make correction for reaction of the reagents with the Pyrex reaction bottles negligible. Table I gives the results

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[1] Most of the material in this paper was presented before the Boston meeting of the American Chemical Society, September 11, 1939.

[2] *Cf.* Waters and Lowry, "Physical Aspects of Organic Chemistry," D. Van Nostrand Co., New York, N. Y., 1937, Chap. XII.

[3] Newling and Hinshelwood, *J. Chem. Soc.*, 1360 (1936).

[4] Dippy and Lewis, *ibid.*, 1008 (1937).

[5] *Cf.*, for example, Kindler, *Ann.*, **452**, 90 (1927).

[6] Levenson and Smith, THIS JOURNAL, **62**, 1556 (1940).

[7] Smith, *ibid.*, **61**, 1176 (1939).

[8] The authors are greatly indebted to Mr. T. E. Ricketts for his aid in the preparation of the cyclohexylacetic acid.

[9] This aldehyde was purchased from Paragon Testing Laboratories, Orange, New Jersey.

[10] Delépine and Bonnet, *Compt. rend.*, **149**, 39 (1909).

[11] Smith and Levenson, THIS JOURNAL, **61**, 1172 (1939).