[CONTRIBUTION NO. 66 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Dipole Moments of the Isomeric Dichloropropenes[1]

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Introduction

Considerable interest has been shown recently in connection with the configuration of some of the dichloropropenes. Included in the seven possible isomers are two pairs of geometric isomers, the 1,2- and 1,3-compounds. Huntress and Sanchez-Nieva[2] report the preparation of the 76° isomer of 1,2-dichloropropene with the statement that the assignment of *cis* or *trans* structure to the 76° and 93° isomers has not been made. Hatch and Roberts[3] assigned the *trans* configuration to the alpha or low-boiling 1,3-isomer on the basis of the fact that, in the presence of cuprous chloride, it was more slowly hydrolyzed than was the beta or high-boiling isomer. This assignment was subsequently questioned by Andrews and Kepner.[4]

It appears that investigation of the dipole moments of the dichloropropenes might aid in the determination of the structure of some of these compounds. Accordingly measurements were made on all of the dichloropropenes. In addition, the dipole moment of *trans*-1-chloropropene was determined, similar measurements for the *cis* isomer having been made by Rogers.[5] Vapor phase measurements for all of the monochloropropenes have been made by Hannay and Smyth.[6]

Experimental

Benzene.—Merck Reagent Grade (Thiophene-free) benzene was fractionated through a five-foot helix-packed column before use as a solvent for the dielectric constant measurements.

The Dichloropropenes.—1,1-Dichloropropene, 2,3-dichloropropene, and the two isomeric 1,2-dichloropropenes were obtained as individual isomers from Halogen Chemicals, Incorporated, of Columbia, South Carolina.[7] Each was carefully fractionated in an eight-foot Vigreux column before use, and constant boiling cuts obtained. The 1,3-dichloropropenes were procured from the same company as a mixture of the two isomers. They were separated by fractionation in the eight-foot column, and cuts of each isomer refractionated before use. The fractionation curves are shown in Fig. 1.

3,3-Dichloropropene was made by the reaction of acrolein with phosphorus pentachloride. After considerable preliminary investigation of the best procedure, the following one was adopted.[8]

In a three-necked round-bottom flask equipped with an efficient mechanical stirrer, reflux condenser, and dropping funnel was placed 160 g. of phosphorus pentachloride. This was then completely covered with *m*-xylene and subsequently dispersed in the liquid by stirring; 42 g. of acrolein was then dissolved in an equal volume of the xylene, and added slowly to the suspended halide, the addition taking about one hour. The temperature was maintained at 45° during the addition, after which the mixture was allowed to stand overnight at room temperature.

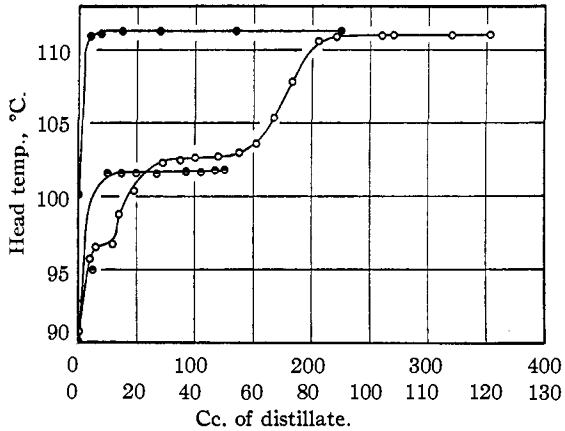

Fig. 1.—(a) Fractionation curves for isomeric 1,3-dichloropropenes: (a) first distillation (○), upper abscissa scale; (b) refractionation of 102–103° cut (◓), lower abscissa scale; (c) refractionation of 111° cut (●), lower abscissa scale.

Subsequently the flask and contents were cooled to −5° and the phosphorus salts hydrolyzed by the dropwise addition of ice water, care being taken not to allow the temperature of the reaction mixture to rise above 0°. The mixture was transferred to a separatory funnel, the lower layer immediately discarded, and the xylene layer washed with aqueous sodium carbonate solution, steam distilled, washed with saturated sodium bisulfite and finally with aqueous sodium carbonate until no acidic constituents remained. It was dried over anhydrous potassium carbonate and the dichloropropene fractions removed by distillation in the Vigreux column. By this method the yield was primarily 3,3-dichloropropene, with a small fraction of the 112° isomer of 1,3-dichloropropene. The over-all yield of dichloropropenes was 50% of the theoretical. The 3,3-dichloropropene cut was refractionated. The results are shown in Fig. 2.

1-Chloropropene was obtained as a mixture of isomers from Columbia Organic Chemicals Company, Inc. of Columbia, South Carolina.[9] These were fractionated in the eight-foot Vigreux column, with the results shown in Figure 3. A constant boiling cut of the 37° isomer was used without further fractionation.

Immediately before use, each purified chloropropene was washed three times with aqueous potassium carbonate, dried for at least twenty-four hours over anhydrous potassium carbonate, and distilled at reduced pressure (with the exception of the 1-chloropropene for which atmospheric pressure was used) from a Claisen flask. The physical properties of these isomers as well as those of the solvent are given in Table I.

The dielectric constants of dilute solutions of each chloropropene in benzene were measured at 30°. The method

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(1) See THIS JOURNAL, **70**, 3528 (1948), for a preliminary communication dealing with the 1,2- and 1,3-dichloropropenes.

(2) Huntress and Sanchez-Nieva, *ibid.*, **70**, 2813 (1948).

(3) Hatch and Roberts, *ibid.*, **68**, 1196 (1946).

(4) Andrews and Kepner, *ibid.*, **69**, 2230 (1947).

(5) Rogers, *ibid.*, **69**, 1243 (1947).

(6) Hannay and Smyth, *ibid.*, **68**, 1005 (1946).

(7) According to information received from this company, these products were, in general, prepared by dehydrohalogenation of trichloropropanes; *cf.* Huntress and Sanchez-Nieva, ref. 2.

(8) The authors are indebted to Mrs. Jack Galbraith, who did the preliminary work on this preparation.

(9) According to information received from this company, the 1-chloropropenes were prepared by dehydrohalogenation of propylene dichloride with sodium hydroxide.

TABLE I

PHYSICAL PROPERTIES OF CHLOROPROPENES AND BENZENE

Compound	Distillation temperature °C.	Mm.	°C.	Mm.	$\eta^{30}D$	$\eta^{20}D$	d^{30}_4
1-Chloropropene	37.0	741			1.3982	1.4058	0.9073
1,1-Dichloropropene	76.3	738	38.0	245	1.4397		1.1629
1,2-Dichloropropene	92.5	742	55.0	222	1.4462		1.1752
1,2-Dichloropropene	74.2	732	56.0	445	1.4431		1.1659
1,3-Dichloropropene	110.8	743	49.5	81	1.4691	1.4734	1.1973
1,3-Dichloropropene	101.7	726	41.0	81	1.4634	1.4680	1.2108
2,3-Dichloropropene	92.7	739			1.4535		1.1925
3,3-Dichloropropene	82.2	733	46.6	205	1.4430		1.1530
Benzene	79.2	737			1.4964		0.8680

was similar to that used by Rogers and Roberts.[10] The apparatus was of the heterodyne-best type, and the brass cell contained a 50 $\mu\mu$f. condenser which had been split, and by means of an external control could be used either as a whole or in part. The cell was immersed in a water bath at 30 ± 0.1° when measurements were made.[11]

Densities were determined using Sprengel pycnometers and a water-bath at 30 ± 0.01°. All dielectric constant and density measurements were made in duplicate. The density and dielectric constant of the benzene solvent were determined independently for each series of measurements; no variation in the density was found. Slight changes in the dielectric constant of benzene were eliminated from the final measurements by using for each series the value of ϵ obtained for the benzene used in making these solutions. Dielectric constants were measured as soon as possible after preparation of each series.

Experimental Calculations and Results

The dipole moments were calculated from the solute mole fractions (f_2), the dielectric constants (ϵ), and the solution densities (d) using the standard equations.[12] The experimental results are given in Table II. The values for the molar refraction (MR_D), the molar polarization (P_∞), and the dipole moment (μ), for each compound, are listed in Table III.

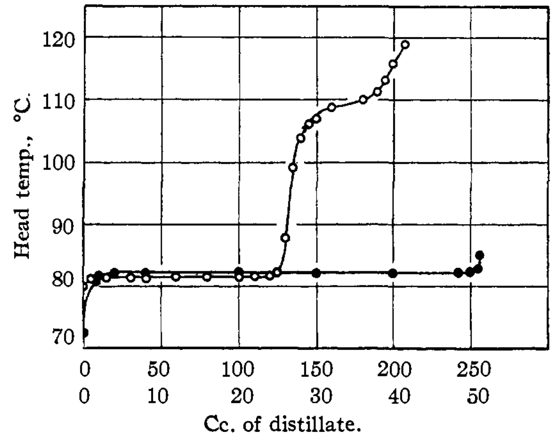
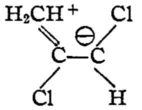


Fig. 2.—(a) Typical fractionation curve for preparation of 3,3-dichloropropene (O) lower abscissa scale, P 738 mm.; (b) refractionation of combined cuts of 3,3-dichloropropene from several preparations (●) upper abscissa scale, P 740 mm.

Discussion

The dipole moments of the 1,2-dichloropropenes allow a definite assignment of geometric configuration. The 93° isomer, with a dipole moment of 2.20, must be the *cis* isomer, while the 76° isomer must possess the *trans* configuration. It is perhaps a little surprising that the dipole moment of the latter should be as great as 0.84, when the moment for *trans*-dichloroethylene is zero.[13] This may be explained on the basis of resonating structures such as



which are not possible in the latter compound. The dipole moment of such a charge-separated isomer would increase the moment of propylene, (0.35). The moment for *cis*-12-dichloropropene, is also greater than that of *cis*-dichloroethylene (1.8).

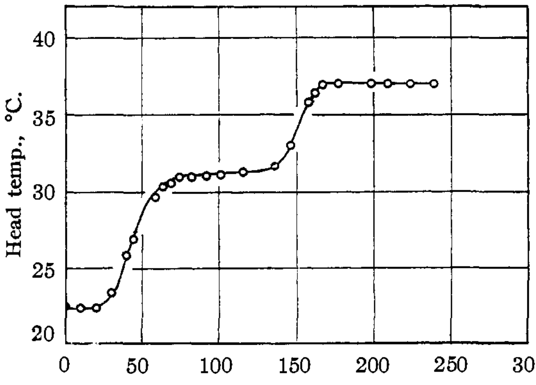


Fig. 3.—Fractionation of *cis* and *trans*-1-chloropropenes, P, 741 mm.

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[10] Rogers and Roberts, THIS JOURNAL, 68, 843 (1946).

[11] The apparatus was designed and built by Mr. Ross Hahn and Dr. A. D. Melaven, who plan to publish details of the circuit. A General Radio, Model 722-D Precision Condenser was used. With the apparatus employing a split condenser in the cell, no calibration against a substance of known dielectric constant is required. Dielectric constants are obtained directly as the ratio of capacitance differences in the medium and in air, and any cell and lead capacitances are eliminated; see Smyth, ref. 12, p. 59.

[12] Smyth, "Dielectric Constants and Molecular Structure," Chemical Catalog Company, Reinhold Publishing Corp., New York, N. Y., 1931.

[13] Errera, *Physik. Z.*, 33, 719 (1932).

TABLE II

DIELECTRIC CONSTANTS, DENSITIES AND MOLAR POLARIZATIONS OF BENZENE SOLUTIONS AT 30°

f_2	ϵ	d^{30}_4	P_2 (cc.)
1,2-Dichloropropene (93° isomer)			
0.05143	2.583	0.8844	117.8
.03819	2.497	.8801	119.8
.02566	2.411	.8762	118.3
.01281	2.333	.8721	122.8
1,2-Dichloropropene (76° isomer)			
0.07293	2.326	0.8898	43.5
.05024	2.310	.8836	44.4
.03637	2.288	.8789	43.2
.02506	2.280	.8756	43.2
.01816	2.267	.8732	41.2
.01251	2.269	.8718	45.1
1,3-Dichloropropene (112° isomer)			
0.06999	2.531	0.8910	83.6
.05340	2.459	.8856	82.9
.03498	2.392	.8793	85.7
.02666	2.355	.8766	84.2
.01332	2.304	.8721	85.9
1,3-Dichloropropene (104° isomer)			
0.07090	2.578	0.8920	91.4
.05270	2.504	.8858	95.3
.03541	2.417	.8798	94.9
.02636	2.382	.8767	99.6
.01770	2.334	.8736	96.7
.01318	2.311	.8721	95.2
1,1-Dichloropropene			
0.07242	2.545	0.8893	85.8
.05078	2.457	.8828	87.0
.03612	2.399	.8785	88.5
.02535	2.353	.8754	88.1
.01805	2.322	.8731	87.7
.01268	2.305	.8714	92.4
3,3-Dichloropropene			
0.06929	2.599	0.8885	96.3
.04763	2.489	.8820	96.6
.03454	2.425	.8780	97.1
.02376	2.376	.8749	99.1
.01725	2.349	.8729	103.5
.01191	2.318	.8713	99.6
2,3-Dichloropropene			
0.07250	2.626	0.8914	97.4
.05151	2.522	.8844	99.8
.03632	2.444	.8793	101.1
.02572	2.387	.8758	100.5
.01820	2.354	.8732	105.1
.01285	2.324	.8716	103.4
1-Chloropropene (37° isomer)			
0.08009	2.574	0.8703	78.8
.05695	2.480	.8692	78.7
.04013	2.411	.8686	78.5
.02851	2.377	.8683	82.6
.02008	2.334	.8681	77.6

TABLE III

MOLAR POLARIZATIONS, MOLAR REFRACTIONS AND DIPOLE MOMENTS MEASURED AT 30° IN BENZENE SOLUTION

Substance	MR_D, cc.	P_∞, cc.	$\mu \times 10^{18}$, e. s. u. × cm.
1,2-Dichloropropene (93° isomer)	25.2	123.0	2.20
1,2-Dichloropropene (76° isomer)	25.2	43.4	0.84
1,3-Dichloropropene (112° isomer)	25.8	86.0	1.73
1,3-Dichloropropene (104° isomer)	25.3	99.5	1.92
1,1-Dichloropropene	25.1	89.5	1.79
3,3-Dichloropropene	25.5	99.7	1.92
2,3-Dichloropropene	25.2	104.9	1.99
1-Chloropropene (37° isomer)	20.4	80.5	1.73

Assuming the value of 109° 28′ for the C–Cl bond angle to the 3-carbon and 125° 16′ for the C–Cl bond angle to the 1-carbon, the angle between the Cl vectors is constant at 109° 28′ for all configurations of the *trans*-1,3-dichloropropene. The angle between the Cl vectors for the *cis*-1,3-isomer may vary between 0 and 141° 4′ if rotation around the bond joining the 2 and 3 carbon atoms is unrestricted. However, it would appear that steric hindrance will prevent the smaller extreme from being realized; if the chloromethyl group is otherwise free to rotate it seems improbable that the average angle between the vectors is greater than the corresponding tetrahedral angle in the *trans* compound, which would indicate the probability of a greater dipole moment for the *cis* than for the *trans* isomer. If, on the other hand, the molecule were always in the extended form as assumed by Hatch, Gordon and Russ,[14] the *trans* isomer would have the greater moment.

Hatch and Perry have now been able to show that the low-boiling isomer is the *cis* form,[15] and this is the isomer which has the higher dipole moment. It would thus appear probable that the *cis* isomer is not primarily in the extended configuration. The Shell Chemical Corporation gives values of 1.66 and 1.77 Debye units for the moments of the 112 and 104° isomers, respectively,[16] while Oriani and Smyth[17] working with the vapor phase, give values of 1.81 and 1.78 for the moments of the corresponding isomers.

The dipole moment of *cis*-1-chloropropene was determined by Rogers to be 1.65 Debye units.[5] The value found for the *trans*-1-chloropropene in this research is 1.73 Debye units. The corresponding values for vapor measurements are 1.71 and 1.97.[6] In both cases, the *trans* isomer has the greater moment, although the difference is not as great for the solution measurements. The reasons for the greater moment of the *trans* isomer are discussed by Hannay and Smyth.[6]

Of the dichloropropenes other than the 1,2

[14] Hatch, Gordon and Russ, THIS JOURNAL, **70**, 1003 (1948).

[15] Hatch and Perry, *ibid.*, **71**, 3262 (1949).

[16] "Data Sheet 1,3-Dichloropropene-1," Shell Chemical Corporation, San Francisco, California, Date 8/4/47.

[17] Oriani and Smyth, *J. Chem. Phys.*, **16**, 930 (1948); **17**, 1174 (1949).

and 1,3 isomers, the 1,1-dichloropropene has been measured in benzene solution by two other investigators.[5,18] The values obtained, 1.69 and 1.73, are in reasonable agreement with the figure reported here (1.79).

The moment observed for the 3,3-dichloropropene (1.92) is in reasonable agreement with the value of 1.86 obtained by vectoral addition of the moment for dichloromethane to that for propylene.

The moment observed for the 2,3-dichloropropene is 1.99. This may be calculated by vectoral addition of the moments for methyl chloride (1.85) and vinyl chloride (1.44) provided the angle between the two vectors is known. Free rotation about the carbon–carbon single bond in this molecule is prevented by steric hindrance. The average angle between the vectors given above as calculated from the experimental moment is 105°.

Summary

The electric moments of all seven of the isomeric dichloropropenes and of *trans*-1-chloropropene (37° isomer) have been measured in benzene solution at 30°.

The dipole moments of the 1,2 isomers indicate beyond question that the 93° isomer has the *cis* configuration, while the 76° isomer is the *trans* form. The moments for the other dichloropropenes are compared with literature or calculated values.

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[18] deBruyne, Davis and Gross, *Physik. Z.*, **33**, 719 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Intramolecular Displacement of Carboxylate Ion. I. Formation of 1-Phenyl-1,2-dihydronaphtho(2,1-b)furan

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Displacement of the carboxylate ion from an alkyl ester of a carboxylic acid with consequent alkylation of the entering group is sometimes possible to accomplish when a hydrolytic medium is avoided. However, the most characteristic reaction of esters in aqueous alkali is hydrolysis with cleavage at the carbonyl carbon–alkoxy oxygen bond. We wish to describe an unusual instance in which intramolecular displacement of a carboxylate ion predominates under conditions normally expected to lead to hydrolysis.

Alkyl esters of carboxylic acids do serve as alkylating agents, but not to an extent comparable with alkyl halides, sulfates and sulfonates. Tertiary amines displace the carboxylate ion from methyl esters,[2] the ease of displacement being dependent, in part at least, on the strength of the acid from which the ester is derived. Inversion on the carbon atom bearing the acyloxy group is postulated. Dialkyl phthalates[3] react with potassium phenoxides at 190–200° to produce the alkyl ethers of the phenols. The use of a phenoxide derived from an aminophenol, *e. g.*, N-methyl-*p*-aminophenol, not only results in O-alkylation but also more or less N-alkylation. Methyl benzoate and sodium methoxide at 175° give a 55% yield of dimethyl ether,[4] but other esters of benzoic acid do not behave similarly. Grignard reagents are alkylated by esters of carboxylic acids provided the attack at the carbonyl group is sufficiently hindered by the steric effect of adjacent groups, and, apparently, provided the group attached to the alkoxy oxygen is capable of resonance stabilization as a carbonium ion.[5]

Intramolecular displacement of a carboxylate ion from an ester of a carboxylic acid, with inversion, is postulated by Fieser and Huang-Minlon[6] in their interpretation of the course of the Serini reaction. The present paper reports an intramolecular displacement of carboxylate ion that by contrast is unique with respect to the reaction conditions used.

During the course of another investigation, 2-(2-hydroxy-1-naphthyl)-2-phenylethanol (I) was obtained. When this phenol-alcohol was treated with phthalic anhydride, the ester (II) was formed. By heating in a dilute sodium bicarbonate solution the ester (II) was slowly converted into the cyclized product, 1-phenyl-1,2-dihydronaphtho-(2,1-b)furan (III). Addition of dilute sodium hydroxide to the bicarbonate solution of the ester also produced the furan, slowly at room temperature and very rapidly with gentle heating. As the concentration of added sodium hydroxide was increased, the hydrolysis to give the phenol-alcohol (I) became appreciable, but it did not appear possible to cause the ester to undergo hydrolysis to the exclusion of cyclization. The phenol-alcohol was not cyclized by dilute alkali, showing that hydrolysis did not precede cyclization.

[1] Based on a portion of a thesis submitted by Mr. Leonard H. Jules in partial fulfillment of the requirements for the degree of Master of Science.

[2] Willstätter and Kahn, *Ber.*, **35**, 584 (1902); Hammett and Pfluger, THIS JOURNAL, **55**, 4079 (1933).

[3] King and Wright, *J. Chem. Soc.*, **155**, 1168 (1939).

[4] Adickes, Müllenheim and Simson, *Ber.*, **66**, 1904 (1933); Magnani and McElvain, THIS JOURNAL, **60**, 813 (1938).

[5] Fieser and Heymann, *ibid.*, **64**, 376 (1942); Wilson, Roberts and Young, *ibid.*, **71**, 2019 (1949); Arnold and Searles, *ibid.*, **71**, 2021 (1949).

[6] Fieser and Huang-Minlon, *ibid.*, **71**, 1840 (1949).