[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE, AND THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Electric Moments of Some Unsaturated Aldehydes, Ethers and Halogen Compounds

BY MAX T. ROGERS

Considerable information concerning the nature and importance of resonance and hyperconjugation in unsaturated compounds may be obtained from their electric moments,[1] *e. g.*, values of the amount of double bond character in the carbon-halogen bonds of the vinyl halides have been derived[2] which agree well with predictions from interatomic distances. To extend existing data a series of ten simple unsaturated halogen compounds, aldehydes and ethers have been prepared and the electric moments measured in benzene solution at 25°. Vinylidene chloride and 1,1-dichloropropene-1 have been reported in earlier investigations.[3,4] Since the present work was begun, vapor measurements of four of these compounds have appeared[5]; the solution values are included here since, in any case, they are useful for comparison with other solution values.

Experimental

Preparation of Materials

Benzene.—J. T. Baker C. P. benzene was dried over sodium and filtered before use, $n^{25}\mathrm{D}$ 1.49785, d^{25}_4 0.87345.

1-Bromopropene-1.—A sample from Columbia Chemicals Co. was dried and fractionated twice through an efficient packed column. The fraction of boiling point 58–58.8° (752 mm.) was taken as *cis*-1-bromopropene-1, $n^{25}\mathrm{D}$ 1.4508, d^{25}_4 1.4157.

1-Chloropropene-1 and 2-Chloropropene.—Chloropropene from Columbia Chemicals Co. was fractionated through an efficient packed column. A low boiling fraction b. p. 24.0° (750 mm.), $n^{20}\mathrm{D}$ 1.3969, d^{20}_4 0.8988 was taken as 2-chloropropene-2; a fraction b. p. 33.5–34.5° (750 mm.) was *cis*-1-chloropropene-1, $n^{20}\mathrm{D}$ 1.4061, d^{20}_4 0.9346. The *trans* isomers were present in too small amount to make it possible to obtain pure samples of *trans*-1-chloro, or *trans*-1-bromopropene, with the small amount of material at hand.

2-Bromopropene.—Material from Columbia Chemicals was dried and fractionated, b. p. 50.5° (750 mm.), $n^{25}\mathrm{D}$ 1.4421, d^{25}_4 1.3803.

Vinylidene Chloride (1,1-Dichloroethylene).—This was prepared by dehydrohalogenation of 1,1,2-trichloroethane by aqueous calcium hydroxide solution.[6,7] It was fractionated through a packed column, b. p. 31.0° (750 mm.), $n^{10}\mathrm{D}$ 1.4286, d^{10}_4 1.2149.

1,1-Dichloropropene-1.—Material from Columbia Chemicals Co. was dried and fractionated, b. p. 75.5° (750 mm.), $n^{25}\mathrm{D}$ 1.4430, d^{25}_4 1.1864.

Tiglaldehyde (α,β-Dimethylacrolein) and α-Methacrolein.—Eastman Kodak Co. White Label chemicals were dried and fractionated; tiglaldehyde, b. p. 116.2° (752 mm.), $n^{25}\mathrm{D}$ 1.4452, d^{25}_4 0.8622; α-methacrolein, b. p. 66.5° (752 mm.), $n^{25}\mathrm{D}$ 1.4098, d^{25}_4 0.8138.

Vinyl *n*-Butyl Ether and Vinyl *i*-Butyl Ether.—Samples from General Aniline and Film Co. were dried and fractionated; vinyl *n*-butyl ether, b. p. 92.8° (752 mm.), $n^{25}\mathrm{D}$ 1.3984, d^{25}_4 0.7742; vinyl *i*-butyl ether, b. p. 82.0° (752 mm.), $n^{25}\mathrm{D}$ 1.3938, d^{25}_4 0.7645.

Apparatus and Method

The dielectric constants of dilute solutions of each substance in benzene were measured at 25° with a heterodyne-beat apparatus previously described,[8] and densities were measured with a modified Ostwald pycnometer.[9] The dipole moments were calculated from the dielectric constants (ε) and densities (*d*) of solutions of solute mole fraction f_2 with the usual equations.[10]

TABLE I

DIELECTRIC CONSTANTS, DENSITIES AND MOLAR POLARIZATIONS OF BENZENE SOLUTIONS AT 25°

f_2	ε	d	P_2
	cis-1-Bromopropene-1		
0.00483	2.288	0.87603	71.4
.00568	2.291	.87642	72.4
.00864	2.301	.87785	72.8
.01647	2.325	.88200	72.0
.01736	2.329	.88228	72.8
.02946	2.368	.88860	72.0
	cis-1-Chloropropene-1		
0.00437	2.288	0.87360	75.6
.00820	2.301	.87390	74.8
.00950	2.306	.87390	75.3
.01255	2.316	.87460	73.9
.01904	2.339	.87440	74.8
.03286	2.380	.87501	71.4
	2-Chloropropene		
0.00494	2.287	0.87364	67.3
.00549	2.289	.87373	68.0
.00813	2.296	.87376	67.7
.01509	2.317	.87399	67.6
.01669	2.322	.87396	68.0
.02674	2.350	.87444	66.6
	2-Bromopropene		
0.00514	2.288	0.87600	70.2
.00683	2.294	.87695	70.4
.01004	2.304	.87838	72.2
.01279	2.313	.87980	72.4
.01769	2.331	.88214	73.8
.02189	2.345	.88415	73.8

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[1] See, for example, Wheland, "The Theory of Resonance," John Wiley and Sons, New York, N. Y., 1944.

[2] J. A. C. Hugill, I. E. Coop and L. E. Sutton, *Trans. Faraday Soc.*, **34**, 1518 (1938).

[3] J. Errera, *Physik. Z.*, **27**, 764 (1926).

[4] J. M. A. de Bruyne, R. M. Davis and P. M. Gross, *Physik. Z.*, **33**, 719 (1932).

[5] N. B. Hannay and C. P. Smyth, THIS JOURNAL, **68**, 1005 and 1367 (1946).

[6] R. C. Reinhardt, *Ind. Eng. Chem.*, **35**, 422 (1943).

[7] I am indebted to Mr. Harold Lischner and Miss Dorothy Niedrich for carrying out this preparation and measuring the electric moment.

[8] Max T. Rogers and John D. Roberts, THIS JOURNAL, **68**, 843 (1946).

[9] G. R. Robertson, *Ind. Eng. Chem.*, **11**, 464 (1939).

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

TABLE I (*Concluded*)

	ϵ	d	P_2
	1,1-Dichloroethylene		
0.00369	2.280	0.87467	53.6
.00982	2.292	.87596	54.4
.01545	2.306	.87817	55.4
.02252	2.321	.87978	55.4
.5291	2.384	.88630	55.8
	1,1-Dichloropropene-1		
0.00435	2.289	0.87480	82.9
.00840	2.305	.87602	85.1
.00967	2.309	.87648	82.9
.01789	2.339	.87910	81.8
.02916	2.384	.88260	83.1
.03212	2.395	.88339	82.8
	α-Methacrolein		
0.00485	2.322	0.87326	171.5
.00640	2.338	.87331	172.6
.00810	2.355	.87315	171.0
.01277	2.400	.87301	167.5
.01643	2.439	.87270	168.3
.02034	2.480	.87262	168.0
	Tiglaldehyde		
0.00221	2.307	0.87349	257.6
.00375	2.331	.87344	254.7
.00538	2.356	.87337	251.4
.00601	2.364	.87344	247.3
.00950	2.418	.87334	246.5
.01289	2.468	.87328	242.7
	Vinyl *n*-Butyl Ether		
0.00955	2.288	0.87209	62.4
.01236	2.293	.87157	63.0
.01999	2.304	.87052	62.1
.02168	2.310	.87020	64.2
.02955	2.321	.86897	62.8
.04191	2.340	.86741	62.4
	Vinyl *i*-Butyl Ether		
0.01152	2.290	0.87168	60.5
.01716	2.296	.87071	59.1
.02036	2.289	.87156	60.5
.03025	2.316	.86864	60.0
.03886	2.327	.86732	59.8
.4746	2.338	.86603	59.4

TABLE II

MOLAR POLARIZATIONS, MOLE REFRACTIONS AND DIPOLE MOMENTS

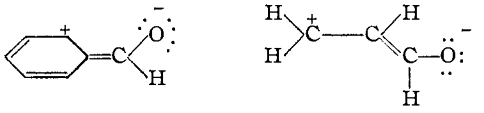
Substance	MR_D	P_∞	μ (Debye)
cis-1-Bromopropene-1	23.0	73.2	1.57
cis-1-Chloropropene-1	20.1	76.0	1.65
2-Bromopropene	23.2	70.0	1.51
2-Chloropropene	20.5	68.5	1.53
1,1-Dichloroethylene	20.5	55.0	1.30
1,1-Dichloropropene-1	24.8	83.0	1.69
Tiglaldehyde	26.0	261.0	3.39
α-Methacrolein	21.3	173.0	2.72
Vinyl *n*-butyl ether	31.3	63.5	1.25
Vinyl *i*-butyl ether	31.3	60.5	1.20

The experimental data are given in Table I and the values of the molar polarization at infinite dilution P_2^{∞}, the mole refraction MR_D, and the dipole moment μ, for each compound, are listed in Table II.

Discussion of Results

The dipole moments of acrolein and crotonaldehyde in benzene solution are 2.88[11] and 3.54,[12] respectively, and the value found for α-methacrolein in solution is 2.72 (the vapor value[5] is 2.68) and for tiglaldehyde is 3.39. Where possible, solution measurements will be used throughout the discussion since they are comparable among themselves but may differ appreciably from the corresponding vapor values.

The magnitude and direction of the $C_{aromatic}$-CHO group may be calculated simultaneously from the dipole moment of any two substituted benzaldehydes; assuming standard values of the moments of the substituents, an average group moment of 2.63, making an angle of 45° with the carbon–carbon link, was calculated from several pairs of compounds. The observed moment of acrolein is close to the value 2.93 calculated using this bond moment and angle. The contribution of structures of Type I to the ground state of the molecule apparently increases the bond moment from a value of about 2.26 in aliphatic aldehydes to 2.63, and at the same time decreases the moment angle below the expected 55–60°; a similar contribution (about 3%) of structures of Type II in acrolein accounts for the observed dipole moments.



I II

The moment of α-methacrolein is 0.20 less than acrolein although it should be nearly the same or slightly greater if there were free rotation of the aldehyde group about the C–C bond since the propylene moment (0.35*D*) makes an angle of about 80° with the C–CHO direction. If, however, the carbonyl group is restricted to a position essentially *cis* to the α-methyl group (see ref. 5), then the vector addition of moments gives a value 2.68 for α-methacrolein in excellent agreement with the observed value, 2.72. In making this calculation, it is assumed that the moment of the α-methyl group arises from structures of Type III and not from a difference in electronegativity of the methyl and ethylenic carbon atoms.

The moments of crotonaldehyde and tiglaldehyde[13] (IV, the methyl groups are *cis* to one another) are also consistent with the assumption of an essentially *cis* planar configuration of the carbonyl and α-methyl groups. The large increase (0.66) observed when a methyl group on the β-

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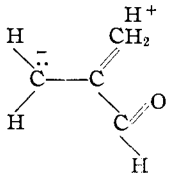
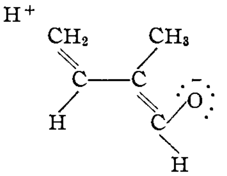
[11] D. I. Coomber and J. R. Partington, *J. Chem. Soc.*, 1444 (1938).

[12] Bentley, *Trans. Faraday Soc.*, **30**, Appendix (1934).

[13] E. C. Hurdis and C. P. Smyth, THIS JOURNAL, **65**, 89 (1943).



III



IV

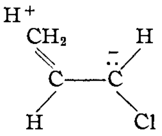
carbon atom (here, in both cases, *trans* to the aldehyde group) is observed both in going from acrolein to crotonaldehyde, and in going from α-methacrolein to tiglaldehyde. It is probably due to the contribution of structures of Type IV in which there is a large separation of charge,[5] these structures being stabilized relative to those with a negative charge on an ethylenic carbon atom by the presence of the electronegative oxygen atom. The carbonyl group must again be assumed to be principally in the position closest to the α-methyl group.

The values observed for vinyl n-butyl ether and vinyl i-butyl ether are equal within experimental error; both are close to anisole, the only aromatic analog for which a reliable value is available. They might be expected to be intermediate between diethyl ether (1.12) and divinyl ether (1.06), if the angles are not too different in these compounds, but are actually considerably higher than either.

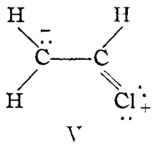
Vinyl bromide has not been studied in solution, but by analogy with compounds measured in both states, should have a moment of about 1.29 (the vapor value is 1.44). We may consider the moments of vinyl bromide and the bromopropenes to be the resultant of the C–H (or C–CH$_3$) moment, the C$_{\text{aliphatic}}$–Br moment, and a mesomeric moment m due to structures of Types II, III and IV. Then we find $m \cong 0.70$, corresponding to about 5% double bond character of the carbon–bromine bond, and the resultant moment makes an angle of about 109° with the double bond (about 13° from the C–Br direction). The aliphatic C–Br moment used in this calculation is, in each case, the solution moment of the saturated halide corresponding to the unsaturated one under consideration; some allowance is made in this way for purely inductive effects.

Combining the mesomeric moment, $m \cong 0.70$, obtained above, with the propylene moment, we predict moments of 1.29 and 1.55 for *cis*-1-bromopropene and 2-bromopropene, respectively. The angles between the various bond moments were estimated from the angles and distances found by the electron diffraction method in analogous compounds.[14] The observed moment of 2-bromopropene, 1.51, is equal to that predicted, within the limits of error, but the experimental value of *cis*-1-bromopropene-1 is 0.28 larger than predicted. This increase has been attributed[5] to a decreased contribution of structures of Type V since the propylene moment places a negative charge on the carbon atom to which the chlorine is bonded. If the mesomeric moment were reduced to 0.35, one-half its value in vinyl halides, the calculated moment of *cis*-1-bromopropene-1 would be 1.57 as observed.

The *chloro* compounds show the same behavior in that the value of 2-chloropropene, 1.53, calculated by vector addition, is equal to the observed moment but the value (1.30) calculated in the same way for *cis*-1-chloropropene-1 is 0.35 less than observed. If, as before, we assume that resonance involving positive halogen (structures of Type V) is reduced to about half the extent calculated for vinyl chloride, then the moment predicted for *cis*-1-chloropropene-1 is 1.57 in fair agreement with the value 1.65 observed. Where both are available, the relative values obtained in solution are in excellent agreement with those observed in vapor measurements.



VI



V

The dipole moment found here for vinylidene chloride in benzene solution (1.30) is higher than that reported previously[3] while that for 1,1-dichloropropene-1 agrees well with the value reported by Gross.[4] The moment predicted for vinylidene chloride by vector addition of vinyl chloride moments is 0.85, but if the contribution of structures of Type V is assumed to be reduced to about one-half when two chlorines are bonded to the same carbon atom, then the moment predicted would be 1.43. This is not unreasonable since inductive effects would be expected to lower the moment to about the observed value, 1.30 (just as ethylidene chloride, 1.98, is lower than the vector sum, 2.18, of two ethyl chloride moments). The observed dipole moment of 1,1-dichloropropene-1 (1.69) is close to the value 1.62 calculated by vector addition of the propylene moment to the observed value of vinylidene chloride.

Summary

The electric moments of ten unsaturated halides, aldehydes and ethers have been measured in benzene solution at 25°.

It has been found that an α-methyl group introduced into acrolein or crotonaldehyde increases the electric moment by the amount calculated by adding the propylene moment vectorially to the respective aldehyde. On the other hand, a β-methyl group introduced into acrolein or α-methacrolein gives an increase in moment about double that predicted. Good agreement between observed and calculated moments of the aldehydes may be obtained only if it is assumed that the carbonyl group is restricted fairly closely to a position *cis* to the substituent on the α-carbon atom, *i. e.*, the two double bonds are *trans*.

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(14) See, for example, L. R. Maxwell, *J. Opt. Soc. Am.*, **30**, 374 (1940).

Introducing an α-methyl group into vinyl chloride or bromide increases the moment by the predicted amount but a β-methyl group produces only about one-half the expected decrease in moment. Also, two chlorine atoms on the same carbon atom as in vinylidene chloride or 1,1-dichloropropene-1 fail to decrease the moment by the expected amount. These results have been interpreted in terms of resonance and hyperconjugation.

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[CONTRIBUTION FROM THE CHEMICAL RESEARCH DIVISION, CHEMICAL ENGINEERING DEPARTMENT, TENNESSEE VALLEY AUTHORITY]

Activity of Orthophosphoric Acid in Aqueous Solutions at 25° from E.m.f. Measurements with the Lead Amalgam–Lead Phosphate Electrode

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In thermodynamic studies of phosphate systems involved in industrial and physiological processes, an electrode reversible with respect to phosphate ion would have many applications.

Several investigators[1,2,3] have studied galvanic cells involving the lead amalgam electrode. Bates, Edelstein and Acree[1] have shown that the lead and lead amalgam electrodes are reproducible within 0.02 mv. Fairhall[4] has shown that, of the possible lead phosphates, the secondary salt, $PbHPO_4$, is the only stable phase in equilibrium with phosphoric acid solutions containing up to 48% phosphorus pentoxide at 25°. Fairhall and Shaw[5] have found the solubility of secondary lead phosphate in water at 25° to be 0.000043 mole per liter.

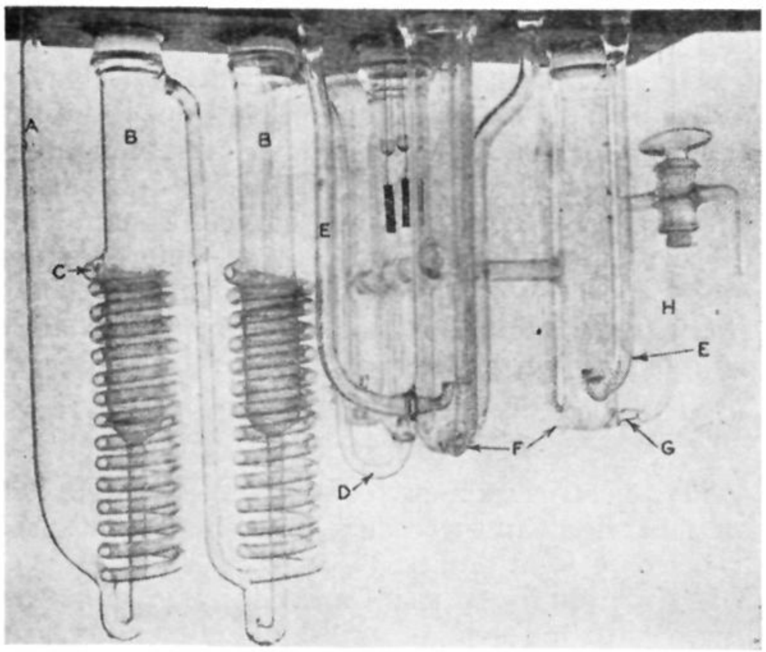

Fig. 1.—Cell.

The practicability of the lead amalgam electrode and the slight solubility of secondary lead phosphate indicated that the half-cell, Pb(2-phase amalgam), $PbHPO_4$, $H_2PO_4^-$, should be suitable for measurement of phosphate-ion activity.

The present paper describes an experimental study of the lead amalgam–lead phosphate electrode and the application of the electrode in measurement of the activity of aqueous orthophosphoric acid in concentrations up to 10 molal at 25°.

Experimental Methods

LaMer and Parks,[3] as well as Bray,[2] have reported that lead amalgam electrodes yield reproducible results only in the absence of oxygen. In the present work, therefore, care was taken to exclude oxygen from the system.

The cell, shown in Fig. 1, was so arranged that either of two hydrogen half-cells could be measured against any of three lead amalgam–lead phosphate half-cells. Oxygen-free hydrogen entered at A and passed through two saturators, B, before entering the bottom of the hydrogen electrode chamber at D. The saturators, B, contained air-free solution of the same concentration as that in the cell and were adapted from the conductivity cells described by Brown and Felger.[6]

To prevent fouling of the surface of the amalgam electrodes, the amalgam half-cells were filled in an atmosphere of oxygen-free nitrogen. Lead amalgam at 90° was run from a pipet down tube F against a stream of nitrogen. The pool of amalgam thus formed from underneath exhibited a bright surface for contact with the solution. Any scum resulting from the transfer remained in tube F. When enough amalgam had been added to cover the opening of tube F into the cell chamber, the amalgam was allowed to solidify. Nitrogen was then passed in through side tube E, and enough dried secondary lead phosphate was added through the top of the cell to make a 1-mm. layer on the amalgam.

Phosphoric acid solution, previously degassed by boiling under reduced pressure and saturated with secondary lead phosphate, was introduced, by nitrogen pressure, through tube E to fill the cell to the center of the hydrogen electrodes.

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[1] R. G. Bates, M. Edelstein and S. F. Acree, *J. Research Natl. Bur. Standards*, **36**, 159–170 (1946).

[2] U. B. Bray, THIS JOURNAL, **49**, 2372–2380 (1927).

[3] V. K. LaMer and W. G. Parks, *ibid.*, **53**, 2040–2061 (1931).

[4] L. T. Fairhall, *ibid.*, **46**, 1593–1598 (1924).

[5] L. T. Fairhall and C. P. Shaw, *J. Ind. Hyg.*, **6**, 159–168 (1924).

[6] E. H. Brown and M. M. Felger, *Ind. Eng. Chem., Anal. Ed.*, **17**, 277–280 (1945).