[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS OF PRINCETON UNIVERSITY]

THE DIELECTRIC CONSTANTS OF ETHANE, ETHYLENE, ACETYLENE AND BUTYLENE, AND THE SYMMETRY OF UNSATURATED BONDS

BY CHARLES P. SMYTH AND CHARLES T. ZAHN[1]

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In a recent paper[2] the electric moments of the molecules of a number of liquid hydrocarbons were calculated from the dielectric constants and other data. The moments of methane, the value for which had been determined by Riegger,[3] hexane, octane and decane were found to be approximately zero, while the following values were found for unsaturated compounds: amylene, 0.49×10^{-18}; hexylene,[4] 0.28×10^{-18}; octylene, 0.50×10^{-18}; decylene, 0.55×10^{-18}. These moments, calculated from the dielectric constants obtained by Landolt and Jahn,[5] as were those for hexane, octane and decane, were small, but not negligible, appearing too large to arise from inexactness in the method of calculation or from error in the measurements, unless impurities were present in considerable amounts. This indicated that a double bond in a hydrocarbon chain gave rise to a moment in the molecule. On the other hand, tetrachloro-ethylene was found to have a moment of 0.45×10^{-18}, almost identical with that of 0.48×10^{-18} for carbon tetrachloride, the double bond apparently not contributing to the moment of the molecule in this case. In view of the frequent discussion of the structure of unsaturated bonds, it was deemed advisable to study the simplest substances available for a comparison of a single, a double and a triple bond between two carbon atoms. For this purpose, the dielectric constants of ethane, ethylene and acetylene have been determined; and in order to observe the effect of a double bond unsymmetrically located in a hydrocarbon chain, the dielectric constant of α-butylene was measured.

The method of measurement has been described in a previous paper.[6]

An improved heterodyne null method is used in which the beats between the oscillations from two separate electron-tube generators operating at frequencies of about 1,000,000 and 1,001,000 cycles per second are adjusted to the frequency of an electrically driven tuning fork, the small change of capacity due to the introduction of the gas into the measuring condenser being compensated by a large change in a large capacity in series with this condenser. The effect of any alteration occurring in the apparatus

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[1] National Research Fellow.

[2] Smyth, THIS JOURNAL, **46**, 2151 (1924).

[3] Riegger, *Ann. Physik*, **59**, 753 (1919).

[4] This value is the average of results upon two different samples which showed poor agreement.

[5] Landolt and Jahn, *Z. physik. Chem.*, **10**, 289 (1892).

[6] Zahn, *Phys. Rev.*, **24**, 400 (1924).

during the course of a measurement was eliminated by repeating the measurements several times alternately at atmospheric pressure and at a carefully noted pressure of about 60 mm. The gas to be measured was condensed in a trap surrounded by liquid air and the entire apparatus evacuated by means of a mercury-vapor pump in order to eliminate any air that might be present in the gas. The liquid air was then removed from about the trap and the substance permitted to evaporate and flow, except in the case of butylene, through a spiral coil immersed in a mush of solid carbon dioxide in alcohol until the measuring condenser was filled with gas at the desired pressure, when the measuring condenser was cut off by means of a stopcock and liquid air replaced about the trap. After the capacity measurement had been made, the stopcock was opened and the gas allowed to condense again in the liquid-air trap. As repeated measurements were made at each temperature, the apparatus was evacuated many times, a small amount of the gas being removed each time. Each measurement was thus made upon a sample slightly different from that used in the preceding measurement. If the substance in the liquid-air trap had contained impurities of different boiling points, the first measurements would have been made upon a material rich in the more volatile components of the mixture and the later measurements upon a mixture containing more of the less volatile components. The complete absence of variation in the results as the, measurements progressed was taken as an indication of the purity of the substances.

The ethylene used in these experiments was obtained from cylinders of the commercial product analyzing about 99% pure. The gas was first passed through a spiral coil of glass tubing surrounded by a mush of solid carbon dioxide in alcohol to remove easily condensable impurities and then into the trap surrounded by liquid air. A considerable fraction of the material thus condensed in the trap was allowed to evaporate and the apparatus evacuated to remove the more volatile impurities before any measurements were made. The ethane was prepared by passing a mixture of dried commercial hydrogen and ethylene over a specially prepared catalyst of copper at a temperature of 150°. The gas was passed through bromine water to absorb uncombined ethylene, through a concentrated potassium hydroxide solution, over solid potassium hydroxide, over phosphorus pentoxide, into a trap surrounded by liquid air. From this trap it was fractionated into a second liquid-air trap, from which it could be admitted to the apparatus in the usual manner. Treatment of two samples of this gas with bromine water showed that it contained less than 1%, if any, of ethylene, which was regarded as the most probable impurity. The acetylene was prepared by the action of water on calcium carbide and passed successively through bottles containing calcium hypochlorite mixed with soda lime, diatomaceous earth saturated with a concentrated acid solution of cupric chloride and ferric chloride, concd. potassium hydroxide solution, soda lime, phosphorus pentoxide, a trap surrounded by carbon dioxide mush and into the liquid-air trap. The butylene was prepared by dropping *n*-butyl bromide into boiling alcoholic potassium hydroxide, and purified by passage through a trap surrounded by ice, bubbling through ice water, passage over calcium chloride and then phosphorus pentoxide, and through another trap surrounded by ice, into the liquid-air trap. From this trap it was repeatedly fractionated by evaporation into a reservoir. The first fraction then gave results agreeing with those obtained from the last, well within the limit of experimental error.

According to the theory of Debye,[7] the dielectric constant of a gas is given by the equation, $(\epsilon - 1)vT = AT + B$, in which ϵ is the dielectric constant, T is the absolute temperature, and v is the specific volume. He referred to the volume occupied by n molecules of the gas, where n is the

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[7] Debye, *Physik. Z.*, **13**, 97 (1912).

number of molecules contained in 1 cc. of an ideal gas at 0° and 760 mm. For an ideal gas $v = T/273$, but for the gases under consideration this quantity is corrected by means of the van der Waals equation. A and B are constants, the latter of which is given by the equation, $B = 4\pi n\mu^2/3k$, in which k is the Boltzmann gas constant and μ is the electric moment of the molecule. The plotting of the values of $(\epsilon - 1)vT$ as ordinates against those of T as abscissas should give a straight line, from which the values of A, the slope, and B, the intercept, may be obtained and the value of the moment then calculated from B. The constancy of $(\epsilon - 1)v$ is proof that $\mu = 0$; for, when $\mu = 0$, $B = 0$, and $(\epsilon - 1)v = A$.

TABLE I

DIELECTRIC-CONSTANT DATA

T °K.	$T/273$	v	$(\epsilon-1)_{760}$	$(\epsilon-1)v$	$(\epsilon-1)vT$
			ETHANE		
200.1	0.733	0.721	0.002058	0.001485	0.2972
294.3	1.078	1.071	.001396	.001496	.4400
364.7	1.336	1.331	.001124	.001497	.5455
470.1	1.722	1.719	.000874	.001510	.7095
			ETHYLENE		
237.4	0.870	0.863	.001682	.001450	.3442
295.6	1.083	1.078	.001336	.001439	.4252
295.6	1.083	1.078	.001345	.001448	.4277
296.2	1.084	1.079	.001333	.001438	.4257
296.4	1.085	1.080	.001342	.001449	.4295
366.5	1.343	1.339	.001081	.001447	.5300
460.9	1.688	1.685	.000853	.001437	.6624
			ACETYLENE		
196.3	0.7188	0.7089	.001891	.001339	.2630
198.5	.7262	.7163	.001854	.001329	.2639
295.7	1.083	1.078	.001236	.001333	.3938
365.6	1.339	1.335	.001000	.001335	.4881
460.5	1.687	1.684	.000792	.001333	.6140
			BUTYLENE		
273.5	1.001	0.979	.003189	.003122	.8540
293.9	1.076	1.056	.002912	.003078	.9040
298.6	1.094	1.074	.002875	.003090	.9222
373.0	1.366	1.352	.002216	.002993	1.1165
465.7	1.706	1.695	.001739	.002948	1.373

TABLE II

CALCULATED VALUES OF THE CONSTANTS OF DEBYE'S EQUATION

	A	B	$\mu \times 10^{18}$
Ethane	0.001501	0	0
Ethylene	.001444	0	0
Acetylene	.001334	0	0
Butylene	.002694	0.115	0.37

In Table I are the results of the measurements upon ethane, ethylene, acetylene and butylene. The first column gives the absolute temperature at which the dielectric constant was measured, the second column the value of $T/273$, which would be the specific volume if the gas were ideal, the third column the corrected value of v, the fourth the value of $(\epsilon-1)$ corrected to 760 mm., and the fifth and sixth columns the values calculated for $(\epsilon-1)v$ and $(\epsilon-1)vT$. In Fig. 1, the values of $(\epsilon-1)vT$ are plotted against T. The values of A and B obtained from these curves are given in the second and third columns of Table II and the moments calculated from B are given in the fourth column.

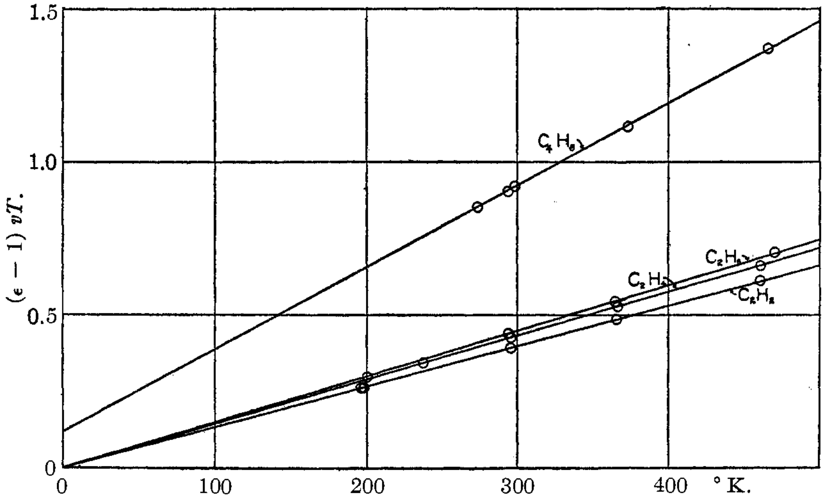
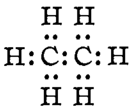
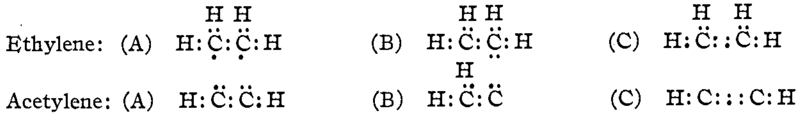


Fig. 1.

The constancy of $(\epsilon-1)v$ for ethane, ethylene and acetylene proves the absence of any measurable electric moment in these molecules, but the positive value of the intercept B for α-butylene shows the existence of a small moment.

The electronic structure of the ethane molecule may be represented in the conventional way by the formula  $H:\underset{\underset{H}{\cdot\cdot}}{\overset{\overset{H}{\cdot\cdot}}{C}}:\underset{\underset{H}{\cdot\cdot}}{\overset{\overset{H}{\cdot\cdot}}{C}}:H$, while the properties of the ethylene and acetylene molecules may be indicated by one or more of the following formulas.



Ethylene: (A) $H:\overset{H}{\underset{\cdot}{\ddot{C}}}:\overset{H}{\underset{\cdot}{\ddot{C}}}:H$ (B) $H:\overset{H}{\ddot{C}}:\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}:H$ (C) $H:\overset{H}{\ddot{C}}::\overset{H}{\ddot{C}}:H$

Acetylene: (A) $H:\ddot{C}:\ddot{C}:H$ (B) $H:\overset{H}{\ddot{C}}:\ddot{C}$ (C) $H:C:::C:H$

Structure C could be best represented spatially by two tetrahedra sharing an edge in the case of ethylene and a face in that of acetylene. It has been recognized[8] that this structure for ethylene explains the fact that the electrons in the double bond are more mobile than those in the single bond, while the structure for acetylene fails to explain the fact that the electrons in the triple bond are, if anything, slightly less mobile than those in the double bond. Lewis[9] points out that no one of these structures adequately represents the properties of either compound and suggests that the structure may, in each case, partake somewhat of the character of all three forms or that there may be a tautomeric equilibrium among the three forms.

Structure B for both substances is obviously unsymmetrical and would have a large electric moment. The absence of any measurable moment in ethylene and acetylene shows that any possible tendency toward Structure B is extremely small and that any such tautomeric form, if existing at all, must be present in an exceedingly small proportion. Structure A is more nearly symmetrical than B, but would still have a considerable moment. The paramagnetism of ethylene, to which Lewis calls attention, is suggestive of a tendency toward Structure A because of its unpaired electrons, but its lack of the symmetry needed to give zero moment makes this structure highly improbable. The most adequate explanation of the properties of ethylene appears to be provided by a structure approximating to that of C, in which two pairs of loosely conjugated electrons are shared equally between the two carbon atoms. This structure might be treated as resolved into two electric doublets, their axes lying in the same straight line, opposing and canceling each other, so that the moment of the molecule is zero. It has been shown[2] that a hydrogen atom in a molecule may be replaced by a methyl radical without changing the moment of the molecule except by the small amounts sometimes caused by altered repulsion and induction in the molecule. Thus, the moments of methane, ethane, hexane, octane and decane are practically zero. When one of the hydrogen atoms of ethylene is replaced by an ethyl radical to form α-butylene, the hydrocarbon chain may be regarded as acted upon by the two doublets into which the ethylene molecule may be resolved. The effect of the doublet adjacent to the chain overbalances the opposing effect of the more distant doublet, so that small electronic shifts are induced in the chain, equivalent to the formation of small doublets. The resultant of these small doublets gives a moment to the whole molecule as shown by the experimental value 0.37×10^{-18}. The effect of induction increases with increasing length of the hydrocarbon chain, which would explain the slightly higher values previously calculated for the moments of the homol-

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[8] Smyth, *Phil. Mag.*, **50**, 370 (1925).

[9] Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Company, **1923**, p. 124.

ogous higher hydrocarbons, which probably consisted largely of the unsymmetrical isomers.

The production of a moment by substitution on one side of the symmetrical ethylene molecule finds an analogy in the fact that, while the symmetrical benzene molecule has a moment of 0.20×10^{-18} or less, toluene has a moment of 0.40×10^{-18}, and the moment is slightly greater when the side chain is longer. The unsymmetrical molecule of *o*-xylene has a moment of 0.58×10^{-18}, and the moments of other hydrocarbon molecules formed by substitution on the benzene ring vary according to the symmetry of the locations of these substituent groups.

The results which have been considered do not eliminate the possibility of a highly unsymmetrical structure for the unsaturated bond in a very small proportion of the molecules of a substance, but it is evident that, in general, the electrons are symmetrically located in the neighborhood of the bond when the position of the bond in the molecule is symmetrical. Although the electrons in an unsaturated bond are more mobile than those in a saturated, as shown by refractivity, the external field of force near them is stronger, so that small electronic shifts are induced in the rest of the molecule and, if the unsaturated bond is unsymmetrically located, the induced doublets will not balance one another and the molecule will have an electric moment.

Summary

The dielectric constants of ethane, ethylene, acetylene and α-butylene, measured over a considerable range of temperature, are in accord with Debye's theory of dielectrics as applied to gases.

The molecules of ethane, ethylene and acetylene have no electric moments, but that of α-butylene has a small moment. The electronic structure of an unsaturated bond is symmetrical, but the field of force around it is stronger than that around a saturated bond, so that, if the unsaturated bond is unsymmetrically located in the molecule, the induced electronic shifts will give a moment to the molecule as a whole.

PRINCETON, NEW JERSEY