tive with 12 D.F. The initial rates estimated from the p–t values (method 1) were significantly low (by about 8%), but the values estimated by the other three methods were the same within the experimental error. Because of simplicity of computation and for the sake of uniformity, the initial rates discussed in this paper are all based on method 4, the analytical method described below.

Analytical Method for Determining Initial Rates.—An approximate equation for the rate of a reaction is given by the expression $dp/dt = k(p_\infty - p)^b$. This expression allows two parameters, a rate constant k and a reaction order b. The logarithmic expression is $\log (dp/dt) = \log k + b \log (p_\infty - p)$, from which b and $\log k$ are the slope and intercept of the linear relationship. The initial value of dp/dt is obtained by substituting the value $(p_\infty - p_0)$. The problem of obtaining suitable values of dp/dt was easy to solve. Since $dp/dt = (1/\Delta t)[\Delta^1 p - (^1/_2)\Delta^2 p + \ldots]$,[10] a table was prepared giving p as a function of t at even time intervals Δt. (The data had been taken at even time intervals in order to facilitate such computations.) From the appropriate column of first differences of p ($\Delta^1 p$) and of second differences of p ($\Delta^2 p$) it was possible to calculate values of dp/dt corresponding to several values of $(p_\infty - p)$. Parameters for a suitable straight line were obtained by the averaging method in which the points were divided into two equal groups. The calculation is illustrated in Table III. The range of values used was from about 5–50% of reaction. This analytical calculation is much faster than a graphical procedure of comparable accuracy.

[10] E. Whittaker and G. Robinson, "The Calculus of Observation," 4th Ed., Blackie and Son Limited, London, 1944.

COLUMBIA, S. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH]

The Inductive Effect and Chemical Reactivity. IV. Dipole Moments of Halogen Derivatives of Aliphatic Hydrocarbons[1]

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Electric dipole moments are calculated for halogen substituted aliphatic hydrocarbons (except in cases where the moment is dependent upon internal rotation) by the theory of Smith, Ree, Magee and Eyring. The polarizability parameter for the C–C bond is changed; all other parameters retain their original values. Excellent agreement with observed moments is obtained in almost every case. The relationship of this theory to other theories for correlating dipole moment and structure is discussed.

Introduction

A simple model for the calculation of inductive charge shifts in organic molecules was proposed in the first paper of this series[2] (hereafter referred to as Part I) and dipole moments were calculated for halogen-substituted methanes and for ethyl halides. The application of the method to molecules containing carbon–carbon bonds was discussed and illustrated in a subsequent paper[3] (part II).

The calculated moments for halogen-substituted methanes obtained in Part I were in good agreement with experiment. In addition it was successfully predicted that, while a decreased moment results in going from CH_3X to CH_2X_2 for X = Cl, Br or I, an increased moment should result in going from CH_3F to CH_2F_2. For in part I, methylene fluoride was predicted to have a moment of 1.91 D; an experimental value of 1.96 ± 0.02 D was subsequently observed by Lide,[4] this being appreciably higher than the moment of methyl fluoride.

However, the good agreement obtained in the Part I calculation of substituted-methane moments did not extend to the ethyl halides. It was suggested that these results did not warrant calculation of dipole moments of higher aliphatic derivatives, where the dipole moments would be even more sensitive to the charge distributions. It was pointed out that calculated charge shifts, on the other hand, were relatively insensitive to the parameters used. Hence the justification for discussing relative rates in terms of charge shifts, as was done in the second and third[5] papers of this series.

We now find that it is indeed possible to calculate moments of most halogen-substituted saturated hydrocarbons in good agreement with experiment. It is only necessary to revise the value of one parameter, the longitudinal polarizability of the carbon–carbon bond. This revision is independently demanded by the polarizability data.

In this paper, our considerations will be limited to halogenated saturated hydrocarbons having moments which are not dependent upon configuration, *i.e.*, molecules where potential barriers hindering rotation need not be considered in a discussion of dipole moments. In addition to presenting the numerical calculations, it will be pointed out that a number of trends in the moments of higher aliphatic halides are satisfactorily accounted for, though they have previously caused difficulty. For example, isopropylidene chloride has a higher moment than does isopropyl chloride, while methylene chloride has a lower moment than methyl chloride.[6] Our charge-shift model of Part I gives satisfactory qualitative and quantitative interpretations of such trends.

Calculations

The generally-high values found for moments of ethyl halides in Part I seem to indicate that the calculations allow too much C–C bond polarization, *i.e.*, β_{CC} (notation of Part I) is too high. According to Part I

$$\beta_{CC} = \frac{S_C(b_1)^{C-C}}{R_{CC}R_C^2} \qquad (1)$$

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[1] This work was supported by the National Science Foundation, Contract NSF-G1098.

[2] R. P. Smith, T. Ree, J. L. Magee and H. Eyring, THIS JOURNAL, **73**, 2263 (1951).

[3] R. P. Smith and H. Eyring, *ibid.*, **74**, 229 (1952).

[4] D. R. Lide, Jr., *ibid.*, **74**, 3548 (1952).

[5] R. P. Smith and H. Eyring, *ibid.*, **75**, 5183 (1953).

[6] M. T. Rogers and J. D. Roberts, *ibid.*, **68**, 843 (1946).

where S_C is a screening constant, $(b_l)^{C-C}$ is the longitudinal polarizability of the C–C bond, R_{CC} is the internuclear distance of the C–C bond, and R_C is the carbon covalent radius. The value for $(b_l)^{C-C}$ was taken from Denbigh.[7] According to both Wang[8] and Denbigh, the ratio of the transverse bond polarizability $(b_t)^{C-C}$ to the longitudinal bond polarizability $(b_l)^{C-C}$ is 0.01. This ratio seems unreasonably low. The ratios for other bonds are between 0.4 and 1.4. Recently Bunn and Daubeny[9] have discussed the polarizability of the C–C bond. They estimated for the ratio $(b_t)^{C-C}/(b_l)^{C-C}$ a value of 0.27. Bolton[10] obtained a ratio of 0.54 by a theoretical treatment. Evidently the longitudinal bond polarizability $(b_l)^{C-C}$ must lie between zero and 1.54×10^{-24} cm.^{3}, *i.e.*, $(b_l)^{C-C}$ cannot be less than zero nor greater than three times the mean bond polarizability (value taken from Vickery and Denbigh[11]). Denbigh[7] gives a value for $(b_l)^{C-C}$ of 1.88×10^{-24} cm.^{3}. Recently the schemes for determining bond polarizability components used by Wang and Denbigh have been analyzed, and it has been shown that the value assigned to $(b_l)^{C-C}$ is not meaningful.[12] Since the dipole moments of ethyl halides, as given by the theory of Part I, involve $(b_l)^{C-C}$ (through $\beta_C{}^C$) and Denbigh's value was used, we expect this to be the main source of error in our calculations.

We have, consequently, plotted the dipole moments of thirteen halogenated hydrocarbons as a function of $\beta_C{}^C$ (Fig. 1). Since there are no clear indications that any of the other parameters need to be changed, we have retained the original values for β_{HC}, β_{XC} (X = halogen), and γ_{XC} (notation of Part I), except that γ_{IC} has been changed from -1.37×10^{-10} e.s.u.[13] to -1.42×10^{-10} e.s.u., in accordance with recent microwave measurements of the dipole moment of methyl iodide.[14] We have taken $\gamma_{HC} = 0$ in this set of calculations, since this parameter is small and uncertain, and a zero value gave satisfactory agreement for halogenated methanes.[2] The C–H longitudinal polarizability is in doubt[12]; but β_{HC} is rather insensitive to this quantity; also, β_{HC} being relatively small, the dipole moments are insensitive to β_{HC}. Denbigh's C–X polarizabilities probably are not much in error.[12]

In the calculations of these moments, as well as all others reported in this paper, all bond angles are assumed to be tetrahedral, except for the C–C–C angles in cyclopropanes and cyclopentanes, which are taken to be 60 and 108°, respectively. (It is probable that cyclopentane and its derivatives are not planar[15]; we are assuming that such deviation from planarity as exists in these molecules has a negligible effect on the moments.) The C–C, C–H, C–F, C–Cl, C–Br and C–I distances are everywhere taken to be 1.54, 1.09, 1.38, 1.78, 1.94 and 2.14 Å., respectively, little variation from these values ever being found in saturated molecules.[16]

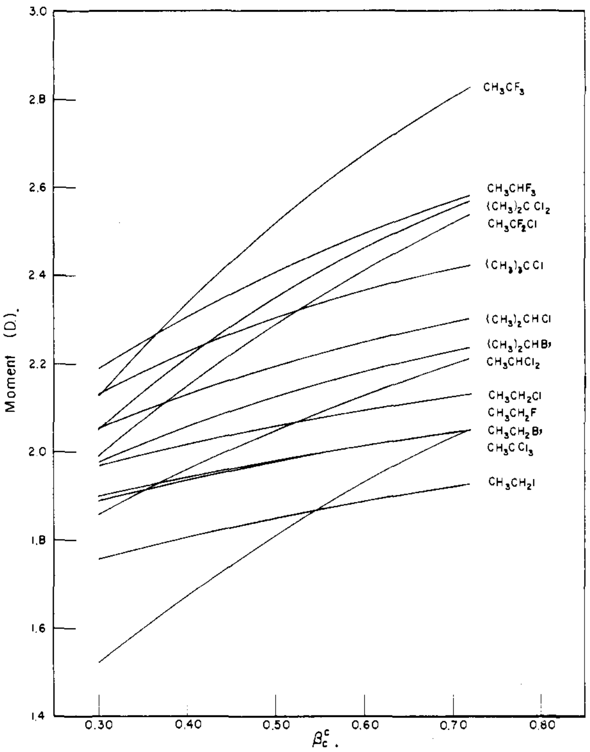

Fig. 1.—Dipole moments of selected halogenated hydrocarbons plotted as a function of β_C^C.

If one uses Denbigh's value of $(b_l)^{C-C}$ in eq. 1, together with appropriate values for the other quantities involved, one obtains[2] $\beta_C{}^C = 0.72$, corresponding to the right ends of the curves of Fig. 1. It is seen that some of the dipole moments are sensitive to $\beta_C{}^C$, while others are relatively insensitive. As $\beta_C{}^C$ is decreased (corresponding to smaller $(b_l)^{C-C}$ values) the moments all decrease, as expected. The curves in Fig. 1 were compared with the experimental values of the dipole moments. (See Table I; where more than one experimental value is given for a molecule, the first one was used.) The smallest over-all deviation between theory and experiment (average deviation 0.06 *D*) was obtained if a value of 0.43 was chosen for $\beta_C{}^C$. With eq. 1, this value leads to a longitudinal bond polarizability for the carbon–carbon bond of 1.12×10^{-24} cm.^{3}, retaining the original values[2] of S_C, etc. If the mean carbon–carbon bond polarizability α is taken as 0.5135×10^{-24} cm.^{3} (Vickery and Denbigh[11]) then by means of the relationship

$$(b_l)^{C-C} + 2(b_t)^{C-C} = 3\alpha$$

we obtain $(b_t)^{C-C} = 0.209 \times 10^{-24}$ cm.^{3}. This gives a ratio $(b_t)^{C-C}/(b_l)^{C-C} = 0.19$, which is more reasonable than the ratio given by Wang[8] and Denbigh,[7] and which is not ruled out by the experimental data on molecular anisotropies.[12]

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[7] K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

[8] S.-N. Wang, *J. Chem. Phys.*, **7**, 1012 (1939).

[9] C. W. Bunn and R. de P. Daubeny, *Trans. Faraday Soc.*, **50**, 1173 (1954).

[10] H. C. Bolton, *ibid.*, **50**, 1261 (1954).

[11] B. C. Vickery and K. G. Denbigh, *ibid.*, **45**, 61 (1949).

[12] R. P. Smith and E. M. Mortensen, to be published; C. G. Le Fevre and R. J. W. Le Fevre, *J. Chem. Soc.*, 1577 (1954).

[13] In ref. 2 a typographical error occurs in reporting this value, 1.73 being given instead of 1.37.

[14] R. G. Shulman, B. P. Dailey and C. H. Townes, *Phys. Rev.*, **78**, 145 (1950).

[15] S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954, p. 76.

[16] W. Gordy, W. V. Smith and R. F. Trambarulo, "Microwave Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1953, Appendix.

The method of calculation of the moments may be made clear by recalling the calculation for ethyl chloride, which was discussed as an example in Part I. With the present choice of parameters, eq. 22 through 26 of Part I, which determine the charge distribution for this molecule, remain unchanged, except that the value of β_{CC} is changed to 0.43. Upon solving these equations simultaneously, we find the following charges (all in units of 10^{-10} e.s.u.): $\epsilon_{Cl} = -1.030$, $\epsilon_1 = 0.648$, $\epsilon_2 = 0.153$, $\epsilon_a = 0.084$, $\epsilon_b = 0.020$. (These are, respectively, the charges on the chlorine, the attached carbon, the second carbon, the hydrogen attached to the first carbon, and the hydrogen attached to the second carbon.) Using these charges, together with the bond lengths given in the preceding section, we can calculate the magnitudes of bond moment vectors directed along the bonds. In this way the C–Cl moment is found to be 1.83 *D*, with the Cl negative; the C–H moments for C_1–H_a and C_2–H_b are 0.09 and 0.02 *D*, respectively, with the H atoms positive; the remaining moment, along the C–C bond, is $(\epsilon_2 + 3\epsilon_b)R_{CC} = 0.33\ D$, with the positive end on carbon "2." Adding these moments vectorially, with tetrahedral angles, we get 2.02 *D* for the resultant moment. The vectors add in such a way that the moment is independent of the orientation of the CH_3 group with respect to the CH_2Cl group, so that our uncertainty of the form of the barrier to rotation about the C–C bond need not concern us.

In Table I we list calculated and observed moments for the halogenated aliphatic and alicyclic hydrocarbons for which dipole moment data are available, except for those molecules which have moments that are dependent upon internal rotations (such as 1,2-dichloroethane and the cyclohexane derivatives). A number of predicted moments are included. It is of course possible to calculate, in a straightforward way, the moment of any other molecule in the class considered. Moments which depend upon rotations will be the topic of a later paper. With a more accurate induction picture than the usual constant-bond-vector model, it should be possible to draw more accurate conclusions about barriers from dipole moment data than previously.

By microwave analysis Kraitchman and Dailey[17] measured the dipole moment of ethyl fluoride, their value agreeing within experimental error with our calculated value (Table I). They also were able to measure the dipole moment components along the principal axes. The moment has components μ_A and μ_B along the two principal axes of inertia A and B in the C–C–F plane. Axis A is at an angle of 32°42′ with the C–C bond, and axis B is perpendicular to axis A. The experimental values of μ_A and μ_B were, respectively, 1.69 and 1.00 *D*. We calculate 1.70 and 0.95 *D*, respectively, for these moment components. Experimentally the resultant dipole vector is inclined at an angle of 64° with the C–C bond axis; we calculate 62°.

Table I

Dipole Moments of Aliphatic Halides

Molecule	Electric dipole moment, *D* Calcd.	Obsd.[a]
C_2H_5F	1.95	1.96,[b] 1.92[c]
C_2H_5Cl	2.02	2.02,[d,e] 2.05,[f] 2.00[g]
C_2H_5Br	1.95	2.02,[c] 1.99,[g] 2.01[h]
C_2H_5I	1.82	1.90,[c] 1.87,[h] 1.93[g]
CH_3CHF_2	2.33	2.24[i]
CH_3CHCl_2	1.99	2.07[j]
CH_3CHBr_2	1.80	2.12B[k]
CH_3CHI_2	1.56	2.30B[k]
CH_3CF_3	2.39	2.32,[l] 2.35,[m] 2.27[o]
CH_3CCl_3	1.71	1.79,[j] 1.77[r]
CH_3CBr_3	1.49	
CH_3CI_3	1.22	
CH_3CF_2Cl	2.19	2.14,[n] 2.13[o]
CF_3CF_2Cl	1.25	0.14,[o] 0.52[aa]
CF_3CHF_2	1.66	1.54[n,aa]
CCl_3CHCl_2	1.27	0.92[x]
CCl_3CH_2Cl	1.78	1.39[z]
i-C_3H_7F	2.05	
i-C_3H_7Cl	2.15	2.15,[h] 2.04[d,p]
i-C_3H_7Br	2.08	2.19,[h] 2.09B[y]
i-C_3H_7I	2.01	1.99B,[y] 1.95B[q]
$(CH_3)_2CCl_2$	2.25	2.25[j]
t-C_4H_9F	2.11	
t-C_4H_9Cl	2.25	2.13,[r] 2.15B[s]
t-C_4H_9Br	2.18	2.21B,[s] 2.17CT[t]
t-C_4H_9I	2.07	2.13B,[s] 2.20CT[u]
cyclo-C_3H_5Cl	2.25	1.76B[v,w]
cyclo-C_5H_9F	2.07	1.86B[v]
cyclo-C_5H_9Cl	2.17	2.08B[v]
cyclo-C_5H_9Br	2.10	2.20B[v]
cyclo-C_5H_9I	1.98	2.06B[v]
cyclo-1,1-$C_3H_4Cl_2$	2.51	2.04B[v]
cyclo-*dl*-(*trans*)-$C_3H_4Cl_2$	1.49	1.18B[w]
cyclo-1,1-$C_5H_8Cl_2$	2.31	2.35B[v]

[a] Observed moments are gas moments except where noted by B or CT, indicating moments in benzene or carbon tetrachloride solution, respectively. Where more than three or four measurements have been made, only three or four are listed. We have concentrated on listing gas values, where these are available. [b] J. Kraitchman and B. P. Dailey, ref. 17. [c] C. P. Smyth and K. B. McAlpine, *J. Chem. Phys.*, **2**, 499 (1934). [d] R. Sänger, *Helv. Phys. Acta*, **3**, 162 (1930). [e] R. Sänger, O. Steiger and K. Gächter, *ibid.*, **5**, 200 (1932). [f] O. Fuchs, *Z. Physik*, **63**, 824 (1930). [g] P. C. Mahanti, *Phil. Mag.*, [7], **20**, 274 (1935). [h] L. G. Groves and S. Sugden, *J. Chem. Soc.*, 158 (1937). [i] J. H. Gibbs and C. P. Smyth, This Journal, **73**, 5115 (1951). [j] A. A. Maryott, M. E. Hobbs and P. M. Gross, ref. 22. [k] P. C. Mahanti and R. N. Das-Gupta, *J. Indian Chem. Soc.*, **6**, 411 (1929). [l] R. G. Shulman, B. P. Dailey and C. H. Townes, ref. 14. [m] C. H. Townes, R. G. Shulman and B. P. Dailey, *Phys. Rev.*, **76**, 472 (1949). [n] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955. [o] R. M. Fuoss, This Journal, **60**, 1633 (1938). [p] R. Sänger, *Physik. Z.*, **32**, 21 (1931). [q] E. G. Cowley and J. R. Partington, *J. Chem. Soc.*, 977 (1938). [r] R. H. Wiswall, Jr., and C. P. Smyth, *J. Chem. Phys.*, **9**, 356 (1941). [s] A. Parts, *Z. physik. Chem.*, B**7**, 327 (1930). [t] A. Audsley and F. R. Goss, *J. Chem. Soc.*, 497 (1942). [u] A. Audsley and F. R. Goss, *ibid.*, 358 (1942). [v] M. T. Rogers and J. D. Roberts, ref. 6. [w] B. I. Spinrad, This Journal, **68**, 617 (1946). [x] J. R. Thomas and W. D. Gwinn, *ibid.*, **71**, 2785 (1949). [y] A. Parts, *Z. physik. Chem.*, B**12**, 312 (1931). [z] Ref. *w*, quoting J. E. Roberts, unpublished data. [aa] A. Di Giacomo and C. P. Smyth, This Journal, **77**, 774 (1955).

The first moments in Table I which do not seem to be in agreement are those for ethylidene bromide and iodide. However, the experimental values were measured in benzene solution, and surely the gas values for these molecules are not higher than that for ethylidene chloride. Thus the experimen-

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[17] J. Kraitchman and B. P. Dailey, *J. Chem. Phys.*, **23**, 184 (1955).

tal values indicated are surely too high for the gas moments.

In chloropentafluoroethane, C–F double bonding[18] may change our simple induction picture. As C–F bonds are expected to have more double-bond character than C–Cl bonds, this effect will make the chlorine more negative and the fluorines more positive than they would be on the basis of induction alone. Thus a moment should be set up in opposition to the calculated induction moment, tending to reduce the resultant moment to a lower value than that expected on an induction basis. These considerations are in accord with the low experimental value for the moment of chloropentafluoroethane. Similar considerations would lead us to expect the moment of CH_3CF_2Cl to be lowered, though not so much, as the C–C and C–H moments will not be changed by C–F double bonding. Unfortunately, methods for making quantitative estimates of double-bonding effects are lacking.

The calculated moments for substituted cyclopropanes are too high, though this is not surprising, in view of the large degree of strain. Rogers and Roberts[6] invoked C–Cl double bonding to explain the unexpectedly low moments; such an extra factor seems necessary on any induction basis.

Discussion of Aliphatic Halide Moments

Most of the calculated moments in Table I agree quite well with the observed values; no other scheme reported in the literature has proved so satisfactory. We emphasize that we have introduced no new parameters, except for a β_{CC} value; the other parameters are all taken from ref. 2. We also wish to point out that some freedom is permissible in choosing the parameters used; there are no critical adjustments to be made. The β parameters, the only ones calculated *a priori* from our model, may be varied widely with similar results, although the values calculated in ref. 2 do seem quite satisfactory (except for β_{CC}), so there would seem to be some truth in our model. Many investigators have treated bond dipoles as "mathematical" (*i.e.*, infinitesimal) dipoles located in bonds. Our charged sphere treatment is more tractable and, we believe, a more accurate model, in view of the results obtained. It has the further advantage that the atomic charges calculated are useful in discussing rates and equilibria.

Our theory is essentially a method in which charges on atoms are linear functions of charges on adjacent atoms (as seems a reasonable approximation for the small charges involved), in accordance with eq. 11 of ref. 2; the linear relationships for the various bonds are all made to hold simultaneously in a particular molecule, subject to the condition that the over-all charge must vanish. There are only two parameters per bond, one of which we calculate (except β_{CC}). We have specified $\alpha_{CC} = \alpha_{CH} = 0$ and calculated β_{XC} (X = H or halogen), so with an empirical γ_{XC} we can calculate, not only moments, but atomic charges, for all halogenated aliphatic and alicyclic hydrocarbons where X is the halogen. The γ_{XC} can be looked upon as "standard halogen charges," since eq. 15 of ref. 2 shows it to be the charge which a halogen can acquire in a hypothetical molecule where the electron availability would be just sufficient to keep the carbon of the C–X bond neutral as charge is withdrawn by the halogen. In our theory, this parameter replaces the standard C–X bond moment of the usual models, which also is empirical. It is interesting to note that our γ_{XC} values for the four halogens are all nearly equal. At present this appears fortuitous.

The inductive effect was first discussed in 1923 by J. J. Thomson[19] and by G. N. Lewis.[20] Thomson, in commenting on the dielectric data on some aliphatic alcohols, said "the intense electric field due to the moment [of the O–H group] will give rise by induction on the rest of the molecule to moments of the same sign as the original moment." Lewis, in discussing strengths of acids in terms of the octet theory, clearly spoke of a displacement of electron pairs throughout a molecule toward a substituent which exerts a strong pull upon its bonding pair. Our more detailed ideas are in complete accord with these early discussions. They also are in complete accord with the more fully developed ideas of Eucken and Meyer.[21] These authors discussed the series CH_3Cl, CH_2Cl_2, $CHCl_3$, among others, and commented on the probable trends in the individual C–H and C–Cl moments. The molecule CH_3Cl, with its moment of about 1.9 *D*, was assigned a C–Cl moment of 1.5 *D* and a C–H moment of 0.4 *D*; $CHCl_3$ was assigned a C–Cl moment of 0.4 *D* and a C–H moment of 0.6 *D*, making a total moment of 1.0 *D*, as observed. The idea that in $CHCl_3$ we have three chlorine atoms competing for the charge of the carbon atom, and that as charge is removed, the effective nuclear charge of the carbon increases, making further removal of charge increasingly difficult, with a smaller resulting C–Cl moment than in CH_3Cl, is clearly stated. It is further explained that in $CHCl_3$ the carbon ends up with a higher effective nuclear charge, so that the hydrogen atom gets more electronic charge removed, as reflected in the increase in C–H moment. These ideas are in harmony with our discussion of these moments in Part I.

This idea of induction, that the major effect is transmitted from atom to atom through a molecule, has been clearly discussed by many workers, *e.g.*, Sutton,[22] and Maryott, Hobbs and Gross.[23] But in various calculations, for example those of Smallwood and Herzfeld,[24] Groves and Sugden,[25] and others, bond moments have been taken to be point (mathematical) dipoles located within bonds, *e.g.*, at the surface of the carbon atom of a C–Cl bond: estimations are then made of the polarization of neighboring atoms by these dipoles. We believe the point of Eucken and Meyer and of Lewis to be more satisfactory, *i.e.*, that one should consider

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[18] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 2nd Ed., 1940, p. 235.

[19] J. J. Thomson, *Phil. Mag.*, [6] **46**, 497 (1923).

[20] G. N. Lewis, "Valence and The Structure of Atoms and Molecules," Chemical Catalog Co., Inc., New York, N. Y., 1923, p. 138.

[21] A. Eucken and L. Meyer, *Physik. Z.*, **30**, 397 (1929).

[22] L. E. Sutton, *Proc. Roy. Soc.* (*London*), **A133**, 668 (1931).

[23] A. A. Maryott, M. E. Hobbs and P. M. Gross, THIS JOURNAL, **63**, 659 (1941).

[24] H. M. Smallwood and K. F. Herzfeld, *ibid.*, **52**, 1919 (1930).

[25] L. G. Groves and S. Sugden, *J. Chem. Soc.*, 1992 (1937).

induction to be a polarization of bonds transmitted from atom to atom through altered screenings, and the across-space polarizations of bonds by dipoles to be negligible, or at least small in comparison.

Our model is in complete agreement with the points of view of Maryott, Hobbs and Gross.[23] These workers proposed that, in the case of $CHCl_3$, "as additional chlorine atoms are added [to a single carbon atom] the availability of the electrons of the carbon becomes smaller and there results a net decrease of moment per bond. This essentially involves diminished bond moment values but the decrease is now to be associated with the changing availability of the carbon atom electrons." This is in harmony with the ideas of Eucken and Meyer and Lewis. In applying this viewpoint to CH_3CCl_3, it is considered that, "The substitution of a methyl group for an H atom may be looked on as a means of increasing the availability of the electrons and so results in an increase in the net observed moment. On the basis we are proposing the detailed reasons for the increase in moment are: first, the transfer of charge that takes place from the methyl carbon to the other carbon atom and, second, the transfer of some of this new charge from the chloroform carbon to the chlorine atoms. . ." This is in accord with our model. Specifically, we calculate the chlorine net charges in chloroform and methyl chloroform, respectively, to be -0.517 and -0.572 (units of 10^{-10} e.s.u.), and the charges on the attached carbons have values 1.371 and 1.293. The methyl carbon in methylchloroform has a calculated charge of 0.305. Thus in methylchloroform we have a C–C bond moment which is not present in chloroform, plus a larger C–Cl moment. In addition to being in qualitative accord with the ideas of Lewis, Eucken and Meyer, Maryott, Hobbs and Gross, and others, our model is able to quantitatively explain the actual numerical dipole moments of these and other molecules.

In view of the agreement indicated in Table I, it is evident that our model explains certain trends which have been puzzling. For example, Rogers and Roberts[6] noted that "the moments of cyclopropylidene, cyclopentylidene and isopropylidene chlorides are larger than the respective monochlorides although one might expect the reverse to be true from the relative magnitudes of the moments of the methylene and methyl halides." This reversal is easily explained. In methylene chloride, we have two chlorines competing for charge from one carbon atom. As the carbon atom has charge withdrawn, its effective nuclear charge increases, and further removal of charge becomes more difficult. Hence in methylene chloride each chlorine is less negative than the chlorine in methyl chloride, and we have a decrease of dipole moment with increasing substitution. But in the other molecules mentioned above, the chlorines do not have to compete for the charge of one carbon atom; the carbon atom from which charge is being withdrawn has a large reservoir on which to draw, so that if there are two chlorines, each chlorine can get almost the amount of charge available to a single chlorine, and hence an increase in dipole moment results from increasing substitution. These ideas are automatically taken care of by solution of the appropriate simultaneous equations, as the reader can verify for representative molecules.

Maryott, Hobbs and Gross,[23] in studying trends in moments of a number of halides (which are included in our Table I), found "anomalous if not inexplicable" the following sequence of dipole moment increments

$$\underset{\Delta = 0.8}{CHCl_3 \longrightarrow CH_3CCl_3} \quad \underset{\Delta = 0.5}{CH_2Cl_2 \longrightarrow CH_3CHCl_2}$$

$$\underset{\Delta = 0.2}{CH_3Cl \longrightarrow C_2H_5Cl}$$

But this sequence, too, is readily explained. The first increment is relatively large, because $CHCl_3$ is under considerable constraint, and the addition of a methyl group "reservoir" considerably relieves this tension. The CCl_3 group produces a large polarization (compared with the effect of the CH_2Cl group) of the C–C bond; in addition, in the first of the above changes, the Cl atoms evidently become relatively more negative through the substitution process than in the third change. Calculations will bear out these statements. Our calculated moments for the molecules in the above series are in particularly good agreement with experiment.

It is further urged by Maryott, Hobbs and Gross that the increments in the following two cases should be approximately the same

$$\underset{\Delta = 0.3}{CH_3Cl \longrightarrow (CH_3)_3CCl} \quad \underset{\Delta = 0.8}{CHCl_3 \longrightarrow CH_3CCl_3}$$

But calculations, from our model, will show the relieving of the CCl_3 tension by adding a single methyl group reservoir to result in greater increase in moment than the addition of a large reservoir (*t*-butyl group) to a single chlorine atom. In CH_3Cl the chlorine atom already has practically the maximum amount of net negative charge which it ever can obtain. Hence the increment in the first case is small.

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